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Chapterwise Previous Years' Solved Papers

2015-2000

GATE Chemistry

Containing 3 Practice Sets

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Inside the Pages...

GATE

Graduate Aptitude Test in Engineering

Graduate Aptitude Test in Engineering is an all India level examination, conducted and controlled by the Indian Institute of Science in cooperation with seven Indian Institutes of Technology on behalf of the National Coordination Board – GATE, Department of Higher Education, Ministry of Human Resource Development (MHRD), and Government of India. The GATE committee which consists of representatives from the governing institutes is the sole authority for conducting the examination and declaring the results.

GATE Eligibility Criteria

The following categories of candidates are eligible to appear in GATE

- Candidates with Bachelor Degree in Engineering/Technology/Architecture (4 years after 10+2) and those who are in the final of such programme.
- Candidates with Master Degree in any branch of Science/Mathematics/Statistics/ Computer Applications or its equivalent and those who are in the final year of such programme.
- Candidates in the second/third/higher year of the Four-year Integrated Master Degree Programme (Post B.Sc.) in Engineering/Technology, or 4th/5th year of Five-year Integrated Master Degree Programme and Dual Degree Programme in Engineering/ Technology
- Candidates with qualifications obtained through examinations conducted by professional societies recognized by UPSC/AICTE (e.g., AMIE by IE (I), AMICE (I) by the Institute of Civil Engineers (India) - ICE (I)) as equivalent to B.E. / B.Tech. The students who have completed his/ her bachelor degree in Engineering (4 years after 10+2) or equivalent of such professional courses are also eligible.

Examination Pattern

The GATE consists of a single paper of 3 hours duration, which contains 65 questions carrying maximum of 100 marks. The question paper is divided into three sections.

First section consists of 25 questions of ONE MARK each.

Second section consists of 30 questions (26 to 55) of TWO MARKS each.

Third section consists of 10 questions (56 to 65) of ONE MARK (56 to 60) and TWO MARKS (61 to 65) each.

Multiple Choice and Numerical Answer Type Questions

The question paper consist of multiple choice and numerical answer type questions. In multiple choice type question, each question has four choices for the answer. In numerical answer type questions, there will be no responses to mark at all. To enter a number as your answer, use the virtual numerical keyboard displayed on the monitor.

Zones and Institutes *for* **GATE**

The GATE is conducted and controlled through eight zones which are as follow

Zone 1	IISC, Bangalore
Zone 2	IIT, Bombay
Zone 3	IIT, Delhi
Zone 4	IIT, Guwahati
Zone 5	IIT, Kanpur
Zone 6	IIT, Kharagpur
Zone 7	IIT, Madras
Zone 8	IIT, Roorkee

GATE 2014 exam was conducted by IIT, Kharagpur.

Common Data and Linked Answer Questions

The 2 marks questions also include two pairs of common data questions and two pairs of linked answer questions. The answer to the second question of the linked answer questions depends on the answer to the first question of the pair. If the first question in the linked pair is wrongly answered or is not attempted, then the answer to the second question in the pair will not be evaluated. Although, there were no any question of common data and linked answer in GATE 2014.

Negative Marking in GATE Exam

Incorrect answer carry negative marks i.e., 0.33 for one mark questions and 0.66 for two marks questions. However, in the case of the linked answer question pair, there will be negative marks only for wrong answer to the first question and no negative marks for wrong answer to the second question. There is no negative marking for questions of numerical answer type.

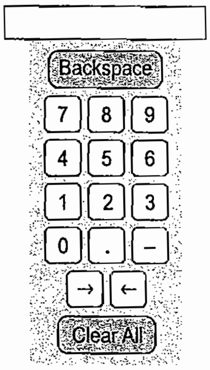
Answering a Question in Online Test

Procedure for answering a multiple choice type questions are as follows

- To select your answer, click on the button of one of the options.
- To deselect your chosen answer, click on the button of the chosen option again or click on the Clear Response button.
- To change your chosen answer, click on the button of another option, and to save your answer, you must click on the Save and Next button.
- To mark the question for review, click on the Mark for Review and Next button.

Procedure for answering a numerical answer type questions are as follows

- To enter a number as your answer, use the virtual numerical keypad displayed on the monitor.
- A fraction (*e.g.*,-0.3 or -.3) can be entered as an answer with or without '0' before the decimal point.
- To clear your answer, click on the Clear Response button and to save your answer, you MUST click on the Save and Next button.
- To mark the question for review, click on the Mark for Review and Next button.



Virtual Numerical Keypad

If an answer is entered for a question that is Marked for Review, that answer will be considered in the evaluation.

Formula for GATE Score of CE, CS, EC, EE and ME Papers

After the evaluation of the answer normalised marks based on the formula given below was calculated corresponding to the raw marks obtained by a candidate for CE, CS, EC, EE and ME papers. Normalised mark of j^{th} candidate in i^{th} session $\overline{M}_{ij}$ in given by

$$\hat{M}_{ij} = \frac{\overline{M}_t^g - M_q^g}{\overline{M}_{ti} - M_{iq}}(M_{ij} - M_{iq}) + M_q^g$$

where,

M_{ij} = the actual marks obtained by the j^{th} candidate in i^{th} session

$\overline{M}_t^g$ = the average marks of the top 0.1% of the candidates considering all sessions

M_q^g = the sum of mean and standard deviation marks of the candidates in the paper considering all sessions

$\overline{M}_{ti}$ = the average marks of the top 0.1% of the candidates in the i^{th} session

M_{iq} = the sum of mean marks and standard deviation i^{th} session

Formula for GATE Score of all Papers

The formula for GATE score of all papers is given below

$$S = S_q + (S_t - S_q)\frac{M - M_q}{\overline{M}_t - M_q}$$

where,

S = the GATE Score of the candidate,

M = the marks obtained by the candidate in the paper appeared by the candidate in GATE 2013,

M_q = the qualifying mark for general category candidates in the paper,

$\overline{M}_t$ = the mean of marks of top 0.1% or top 10 (whichever is larger) of the candidates who appeared in the paper,

S_t = 900 is the Score assigned to $\overline{M}_t$,

S_q = 350 is the Score assigned to M_q.

M_q is usually 25 marks (out of 100) or $\mu+\sigma$, whichever is larger. Here μ is the mean and s is the standard deviation of marks of all the candidates who appeared in the paper.

GATE 2014 Cut-off Marks for Some Branches & Category wise

BRANCH	GENERAL	SC/ST/PD	OBC (Non-Creamy)	Total Appeared
Computer Science & IT	25.0	16.67	22.50	1,55,190
Chemical Engineering	35.14	23.43	31.62	15,844
Civil Engineering	26.57	17.71	23.91	90,872
Electronics & Communication Engineering	25.56	17.04	23.01	2,16,367
Electrical Engineering	25.0	16.67	22.50	1,41,799
Instrumentation Engineering	25.0	16.67	22.50	22,367
Mechanical Engineering	28.86	19.24	25.97	1,85,578

Paper Codes *for* GATE

- Aeronautical/Aerospace Engineering (AE)
- Agricultural Engineering (AG)
- Architecture and Planning (AR)
- Biotechnology (BT)
- Civil Engineering (CE)
- Chemical Engineering (CH)
- Computer Science and Information Technology (CS)
- Chemistry (CY)
- Electronics and Communication Engineering (EC)
- Electrical Engineering (EE)
- Geology and Geophysics (GG)
- Instrumentation Engineering (IN)
- Mathematics (MA)
- Mechanical Engineering (ME)
- Mining Engineering (MN)
- Metallurgical Engineering (MT)
- Physics (PH)
- Production and Industrial Engineering (PI)
- Textile Engineering and Fibre Science (TF)
- Engineering Science (XE)
- Life Science (XL)
- Ecology and Evolution (EY)

Recent Changes *in* GATE

2014

- A new paper **Ecology and Evolution** is introduced in GATE 2014.
- Examinations for all the 22 papers will be conducted by an ONLINE Computer Based Test (CBT).
- GATE 2014 examination was held during forenoon and afternoon session on alternate weekends (Saturday and Sunday) between 1st February 2014 and 2nd March 2014. Examination for some of the papers in GATE 2014 was held in multiple sessions.
- Application Fee has been revised again. It is ₹1500 for Male Candidates (General/OBC), ₹ 750 for Women Candidates of any category, ₹ 1500 for Other Candidates (General/OBC) and ₹ 750 SC/ST/PwD* Category Candidates

2013

- Female candidates are exempted from paying the application fee.
- Candidates are required to upload scanned copy of Photograph and Signature.
- The Application fee was increased from ₹1000 to ₹1200.

2012

- Only final year students and passout students were eligible to write GATE exam.
- The application process was made completely online, candidates could view their responses of the ORS and also GATE Office released official solutions for GATE papers.

2011

- From 2011 onwards, four of the GATE papers can be attempted using computers through online mode. The four papers are Aerospace Engineering (paper code AE), Geology and Geophysics (paper code GG), Mining Engineering (paper code MN) and Textile Engineering (paper code TF) and Fibre Science.
- From 2011 onwards, the GATE will be held in the morning (9 - 12) and afternoon (2 - 5) session. Also the computer based tests will be held on different dates.

GATE 2015 Syllabus *for*

Chemistry

Physical Chemistry

Structure

Quantum theory: principles and techniques; applications to a particle in a box, harmonic oscillator, rigid rotor and hydrogen atom; valence bond and molecular orbital theories, Hückel approximation; approximate techniques: variation and perturbation; symmetry, point groups; rotational, vibrational, electronic, NMR, and ESR spectroscopy

Equilibrium

Kinetic theory of gases; First law of thermodynamics, heat, energy, and work; second law of thermodynamics and entropy; third law and absolute entropy; free energy; partial molar quantities; ideal and non-ideal solutions; phase transformation: phase rule and phase diagrams – one, two, and three component systems; activity, activity coefficient, fugacity, and fugacity coefficient; chemical equilibrium, response of chemical equilibrium to temperature and pressure; colligative properties; Debye-Hückel theory; thermodynamics of electrochemical cells; standard electrode potentials: applications – corrosion and energy conversion; molecular partition function (translational, rotational, vibrational, and electronic).

Kinetics

Rates of chemical reactions, temperature dependence of chemical reactions; elementary, consecutive, and parallel reactions; steady state approximation; theories of reaction rates – collision and transition state theory, relaxation kinetics, kinetics of photochemical reactions and free radical polymerization, homogeneous catalysis, adsorption isotherms and heterogeneous catalysis.

Inorganic Chemistry

Main group elements

General characteristics, allotropes, structure and reactions of simple and industrially important compounds: boranes, carboranes, silicones, silicates, boron nitride, borazines and phosphazenes. Hydrides, oxides and oxoacids of pnictogens (N, P), chalcogens (S, Se & Te) and halogens, xenon compounds, pseudo halogens and interhalogen compounds. Shapes of molecules and hard- soft acid base concept. Structure and Bonding (VBT) of B, Al, Si, N, P, S, Cl compounds. Allotropes of carbon: graphite, diamond, C60. Synthesis and reactivity of inorganic polymers of Si and P.

Fluid Mechanics and Mechanical Operations

Fluid statics, Newtonian and non-Newtonian fluids, Bernoulli equation, Macroscopic friction factors, energy balance, dimensional analysis, shell balances, flow through pipeline systems, flow meters, pumps and compressors, packed and fluidized beds, elementary boundary layer theory, size reduction and size separation, free and hindered settling, centrifuge and cyclones, thickening and classification, filtration, mixing and agitation, conveying of solids.

Transition Elements

General characteristics of d and f block elements; coordination chemistry: structure and isomerism, stability, theories of metal- ligand bonding (CFT and LFT), mechanisms of substitution and electron transfer reactions of coordination complexes. Electronic spectra and magnetic properties of transition metal complexes, lanthanides and actinides. Metal carbonyls, metal- metal bonds and metal atom clusters, metallocenes; transition metal complexes with bonds to hydrogen, alkyls, alkenes and arenes; metal carbenes; use of organometallic compounds as catalysts in organic synthesis. Bioinorganic chemistry of Na, K. Mg, Ca, Fe, Co, Zn, Cu and Mo.

Solids

Crystal systems and lattices, miller planes, crystal packing, crystal defects; Bragg's Law, ionic crystals, band theory, metals and semiconductors, Different structures of AX, AX2, ABX3 compounds, spinels.

Instrumental methods of analysis

Atomic absorption and emission spectroscopy including ICP-AES, UV- visible spectrophotometry, NMR, mass, Mossbauer spectroscopy (Fe and Sn), ESR spectroscopy, chromatography including GC and HPLC and electro-analytical methods (Coulometry, cyclic voltammetry, polarography – amperometry, and ion selective electrodes).

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Atomic absorption and emission spectroscopy including ICP-AES, UV- visible spectrophotometry, NMR, mass, Mossbauer spectroscopy (Fe and Sn), ESR spectroscopy, chromatography including GC and HPLC and electro-analytical methods (Coulometry, cyclic voltammetry, polarography – amperometry, and ion selective electrodes).

Organic Chemistry

Stereochemistry

Chirality of organic molecules with or without chiral centres. Specification of configuration in compounds having one or more stereogeniccentres. Enantiotopic and diastereotopic atoms, groups and faces. Stereoselective and stereospecific synthesis. Conformational analysis of acyclic and cyclic compounds. Geometrical isomerism. Configurational and conformational effects on reactivity and selectivity/specificity.

Reaction mechanism

Methods of determining reaction mechanisms. Nucleophilic and electrophilic substitutions and additions to multiple bonds. Elimination reactions. Reactive intermediates- carbocations, carbanions, carbenes, nitrenes, arynes, free radicals. Molecular rearrangements involving electron deficient atoms.

Organic synthesis

Synthesis, reactions, mechanisms and selectivity involving the following- alkenes, alkynes, arenes, alcohols, phenols, aldehydes, ketones, carboxylic acids and their derivatives, halides, nitro compounds and amines. Use of compounds of Mg, Li, Cu, B and Si in organic synthesis. Concepts in multistep synthesis- retrosynthetic analysis, disconnections, synthons, synthetic equivalents, reactivity umpolung, selectivity, protection and deprotection of functional groups.

Pericyclic reactions

Electrocyclic, cycloaddition and sigmatropic reactions. Orbital correlation, FMO and PMO treatments.

Photochemistry

Basic principles. Photochemistry of alkenes, carbonyl compounds, and arenes. Photooxidation and photoreduction. Di-π- methane rearrangement, Barton reaction.

Heterocyclic compounds

Structure, preparation, properties and reactions of furan, pyrrole, thiophene, pyridine, indole and their derivatives.

Biomolecules

Structure, properties and reactions of mono- and di-saccharides, physicochemical properties of amino acids, chemical synthesis of peptides, structural features of proteins, nucleic acids, steroids, terpenoids, carotenoids, and alkaloids.

Spectroscopy

Principles and applications of UV-visible, IR, NMR and Mass spectrometry in the determination of structures of organic molecules.

Solved Paper 2014

GATE Chemistry

Online
Set

Time : 3 hrs **MM :** 100

Read the following instructions carefully

1. There is a total of 65 questions carrying 100 marks of 3 hrs duration.
2. Questions 1 to 25 will carry 1 mark each and questions 26 to 55 will carry 2 marks each.
3. Questions 56 to 65 belong to General Aptitude (GA) type. Questions 56 to 60 will carry 1 mark each and questions 61 to 65 will carry 2 marks each.
4. The subject specific GATE paper section consists of 55 questions.
5. Unattempted questions will carry zero marks.
6. Wrong answers will carry negative marks. For questions 1 to 25 and 56 to 60, 1/3 mark will be deducted for each wrong answer. For questions 26 to 55 and 61 to 65, 2/3 marks will be deducted for each wrong answer.
7. There is no negative marking for questions of numerical answer type.
8. Non-programmable type calculator is allowed. Charts, graph sheets, and mathematical tables are not allowed in the examination hall.

(1 *Mark Questions*)

1. The maximum non-pV work that a system can perform at constant p is

(a) ΔH (b) ΔG
(c) ΔS (d) ΔA

2. Consider the reaction,

$$A + B \rightleftharpoons C$$

The unit of the thermodynamic equilibrium constant for the reaction is

(a) mol L^{-1} (b) L mol^{-1}
(c) mol^2 L^{-2} (d) dimensionless

3. The number of IR active vibrational normal modes of CO_2 is______

4. The number of C_2 axes in CCl_4 is ____.

5. The value of the magnetic quantum number of a p_x-orbital is

(a) −1 (b) 0
(c) +1 (d) undefined

6. The molecular partition function for a system in which the energy levels are equispaced by ε, is

(a) $\frac{1}{1+e^{\beta\varepsilon}}$ (b) $\frac{1}{1-e^{\beta\varepsilon}}$
(c) $\frac{1}{1+e^{-\beta\varepsilon}}$ (d) $\frac{1}{1-e^{-\beta\varepsilon}}$

7. A monoatomic gas, X, adsorbed on a surface, follows Langmuir adsorption isotherm. A plot of the fraction of surface coverage, θ, against the concentration of the gas $[X]$, for very low concentration of the gas, is described by the equation

(a) $\theta = K[X]$ (b) $1-\theta = \frac{1}{K[X]}$
(c) $\theta = K^{1/2}[X]^{1/2}$ (d) $\theta = \frac{K[X]}{1-K[X]}$

8. At a given temperature and pressure, the ratio of the average speed of hydrogen gas to that of helium gas is approximately______.

9. An example of *nido*-borane from the following is

(a) B_4H_{10} (b) B_6H_{10}
(c) B_6H_{12} (d) B_8H_{14}

10. The geometries of $Ni(CO)_4$ and $[NiCl_4]^{2-}$ respectively are

(a) tetrahedral and square planar
(b) square planar and tetrahedral
(c) tetrahedral and tetrahedral
(d) square planar and square planar

11. The number of S—S bonds in $H_2S_5O_6$ is____.

12. In atomic absorption spectroscopy, the atomisation process utilises

(a) flame (b) electric field
(c) magnetic field (d) electron beam

13. At room temperature, the number of singlet resonances observed in the ^1H NMR spectrum of $Me_3CC(O)NMe_2$ (N, N-dimethyl pivalamide) is______.

14. Amongst the following, the metal that does not form homoleptic polynuclear metal carbonyl is

(a) Mn (b) Fe
(c) Cr (d) Co

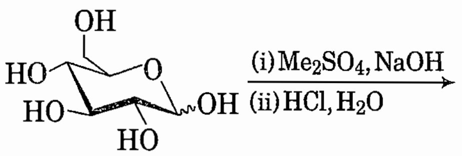
15. The reaction of $[Cp_2TaMe_2]I\,(Cp = C_5H_5^-)$ with NaOMe yields

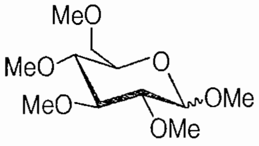
(a) $[Cp_2Ta(OMe)_2]I$ (b) $[Cp_2Ta(Me)OMe]I$
(c) $Cp_2Ta(Me){=}CH_2$ (d) $Cp_2Ta(OMe){=}CH_2$

16. The complexes $[Co(H_2O)_4Cl_2]NO_2$ and $[Co(H_2O)_4Cl(NO_2)]Cl$ are

(a) linkage isomers (b) positional isomers
(c) ionisation isomers (d) optical isomers

17. The major product of the following reaction is



(a)


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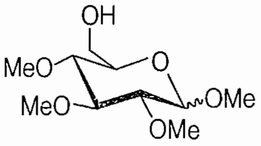
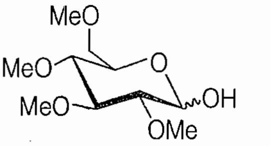
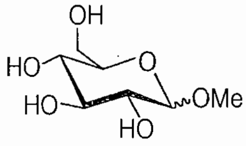
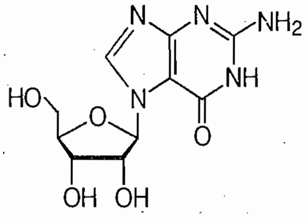
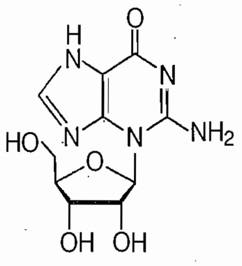


(c)


(d)


18. Amongst the following, the structure of guanosine is

(a)


(b)


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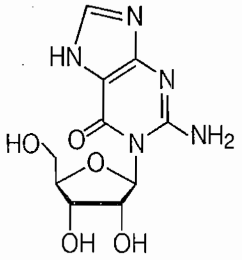

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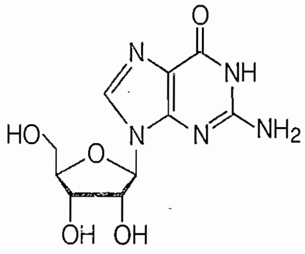
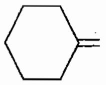
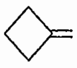


19. The correct order of IR stretching frequency of the C=C in the following olefins is

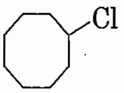

I


II

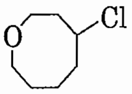

III

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

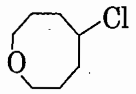
20. The correct order of the rate of solvolysis for the following chlorides in acetic acid is



I



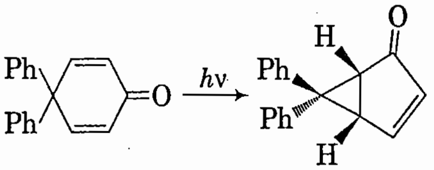
II



III

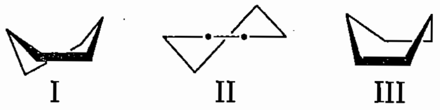
(a) II>I>III (b) III>II>I
(c) III>I>II (d) I>III>II

21. Formation of the product in the following photochemical reaction involves



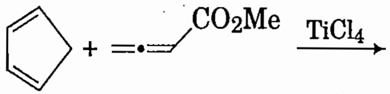
(a) di-π methane rearrangement
(b) Paterno-Buchi reaction
(c) [2,3]- sigmatropic rearrangement
(d) Norrish type I reaction

22. The correct order of stability for the following conformations of cyclohexane is

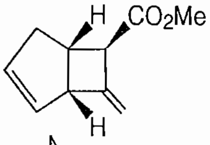


(a) I>II>III (b) I>III>II (c) II>I>III (d) III>I>II

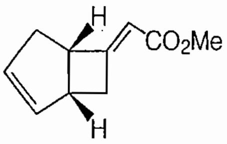
23. The major product formed in the following reaction is



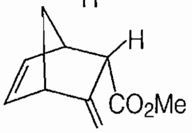
(a)



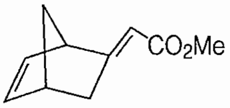
(b)



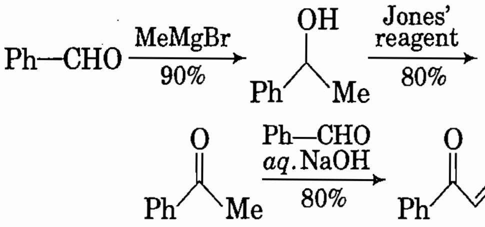
(c)



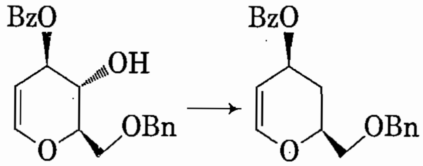
(d)



24. The overall yield (in %) for the following reaction sequence is___.



25. The most suitable reagent combination to effect the following conversion is



(a) i. NaH, CS_2, then MeI; ii. Bu_3SnH, AIBN, C_6H_6, reflux
(b) i. I_2,PPh_3, imidazole; ii. H_2, 10% Pd-C, AcOH, high pressure
(c) i. Me_3SiCl, pyridine, DMAP; ii. Bu_3SnH, AIBN, C_6H_6, reflux
(d) i. MsCl, pyridine , DMAP; ii. $LiAlH_4$, THF, reflux

(2 Marks Questions)

26. $\psi = Nr(6 - Zr)e^{-Zr/3}\cos\theta$, is a proposed hydrogenic wavefunction, where Z = atomic number, r = radial distance from the nucleus, θ = azimuthal angle, N is a constant. The incorrect statement about ψ is

(a) $\psi = 0$ in the xy - plane
(b) two radial nodes are present in ψ
(c) one angular node is present in ψ
(d) the size of the orbital decreases with increase in atomic number

27. The van der Waals' constants a and b of CO_2 are 3.64 L^2 bar mol^{-2} and 0.04 $Lmol^{-1}$, respectively. The value of R is 0.083 bar $dm^3mol^{-1}K^{-1}$. If one mole of CO_2 is confined to a volume of 0.15 L at 300 K, then the pressure (in bar) exerted by the gas, is______.

28. A plot of osmotic pressure against concentration (gL^{-1}) of a polymer is constructed. The slope of the plot

(a) increases with increase in temperature
(b) increases with increase in molar mass of the polymer
(c) decreases with decrease in concentration of the polymer
(d) decreases with increase in temperature

29. A platinum electrode is immersed in a solution containing 0.1 M Fe^{2+} and 0.1 M Fe^{3+}. Its potential is found to be 0.77 V against SHE.

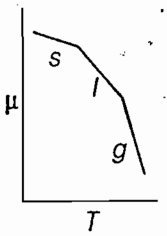
Under standard conditions and considering activity coefficients to be equal to unity, the potential of electrode, when the concentration of Fe^{3+} is increased to 1 M, is______.

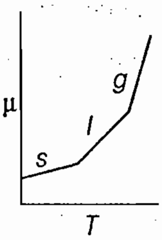
30. Molybdenum crytallises in a bcc structure with unit cell dimensions of 0.314 nm. Considering the atomic mass of molybdenum to be 96, its density (in kgm^{-3}) is______.

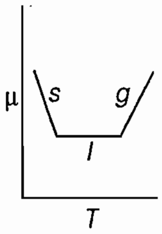
31. The ratio of molecules distributed between two states is 9.22×10^6 at 300 K. The difference in energy (in $kJmol^{-1}$) of the two states is____.

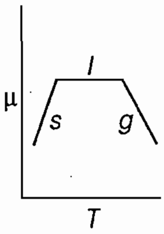
32. A Carnot engine operates at 55% efficiency. If the temperature of reject steam is 105°C, then the absolute temperature of input steam is____.

33. Of the following plots, the correct representation of chemical potential (μ) against absolute temperature (T) for a pure substance is (s, l and g denote solid, liquid and gas phases, respectively)

(a) 

(b) 

(c) 

(d) 

34. The enthalpy of fusion of ice at 273 K is 6.01 $kJmol^{-1}$ and the enthalpy of vaporisation of water at 273 K is 44.83 $kJmol^{-1}$. The enthalpy of sublimation (in $kJmol^{-1}$) of ice at 273 K, is____.

35. Suppose ψ_1 and ψ_2 are two hybrid orbitals

$$\psi_1 = 0.12\psi_{3s} + 0.63\psi_{3p_x} + 0.77\psi_{3p_y}$$

and $\psi_2 = 0.12\psi_{3s} - 0.63\psi_{3p_x} - 0.77\psi_{3p_y}$

The angle (in degrees) between them is_____.

36. BCl_3 and NH_4Cl were heated at 140°C to give compound X, which when treated with $NaBH_4$ gave another compound Y. Compounds X and Y are

(a) $X = B_3N_3H_3Cl_3$ and $Y = B_3N_3H_6$
(b) $X = B_3N_3H_9Cl_3$ and $Y = B_3N_3H_6$
(c) $X = B_3N_3H_3Cl_3$ and $Y = B_3N_3H_{12}$
(d) $X = B_3N_3Cl_6$ and $Y = B_3N_3H_6$

37. The number of microstates in ^1G is_____.

38. The set of protons (underlined) in $CH_3CH_2CH_2OCH_3$ that would exhibit different splitting patterns in high (500 MHz) and low (60 MHz) field ^1H NMR, is

(a) $C\underline{H}_3CH_2CH_2OCH_3$
(b) $CH_3C\underline{H}_2CH_2OCH_3$
(c) $CH_3CH_2C\underline{H}_2OCH_3$
(d) $CH_3CH_2CH_2OC\underline{H}_3$

39. Amongst the following, the complex ion that would show strong Jahn-Tellar distortion is

(a) $[Cr(H_2O)_6]^{2+}$
(b) $[Ti(H_2O)_6]^{3+}$
(c) $[Co(H_2O)_6]^{2+}$
(d) $[Fe(H_2O)_6]^{2+}$

40. Amongst the following, the metal carbonyl species having the highest ν_{CO} stretching frequency is

(a) $[Mn(CO)_6]^+$
(b) $Cr(CO)_6$
(c) $[V(CO)_6]^-$
(d) $[Fe(CO)_4]^{2-}$

41. The correct order of thermal stability for the given compounds is

(a) $TiMe_4 > Ti(CH_2CMe_3)_4 > TiEt_4$
(b) $TiEt_4 > Ti(CH_2CMe_3)_4 > TiMe_4$
(c) $TiMe_4 > TiEt_4 > Ti(CH_2CMe_3)_4$
(d) $Ti(CH_2CMe_3)_4 > TiMe_4 > TiEt_4$

42. Amongst the following, the complex ion that is expected to show the highest magnetic moment at room temperature is

(a) $[Ni(CN)_4]^{2-}$
(b) $[Fe(CN)_6]^{3-}$
(c) $[Cu(H_2O)_6]^{2+}$
(d) $[Co(CN)_6]^{3-}$

43. $MnCr_2O_4$ is

(a) normal spinel with total CFSE of −15.5 Dq
(b) inverse spinel with total CFSE of −15.5 Dq
(c) normal spinel with total CFSE of −24 Dq
(d) inverse spinel with total CFSE of −24 Dq

44. Mg^{2+} is preferred in photosynthesis by chlorophyll because

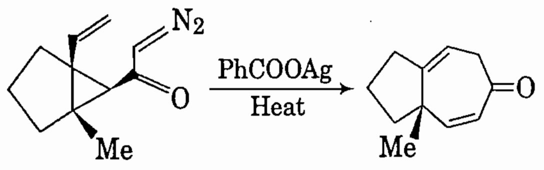
(a) it has strong spin-orbit coupling
(b) it has weak spin-orbit coupling
(c) it is a heavy metal
(d) it binds strongly with chlorophyll

45. In Monsanto acetic acid process shown below, the role of HI is

$$CH_3OH + CO \xrightarrow[180°C,\ 30\ bar]{Rh(I)\ catalyst/HI} CH_3CO_2H$$

(a) to convert CH_3OH to a stronger nucleophile (CH_3O^-)
(b) to reduce the Rh(I) catalyst to a Rh(0) species
(c) to reduce a Rh (III) active species to a Rh(I) species in the catalytic cycle
(d) to convert CH_3OH to CH_3I

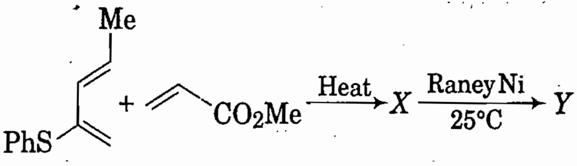
46. Formation of the ketone II from the diazoketone I involves



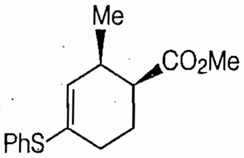
I II

(a) generation of carbene and a [2,3]-sigmatropic rearrangement
(b) generation of carbene and an electrocyclic ring closing reaction
(c) generation of ketene and a [2 + 2] cycloaddition
(d) generation of ketene and a [3,3]-sigmatropic rearrangement

47. The major products X and Y formed in the following reaction sequence are



(a) X=



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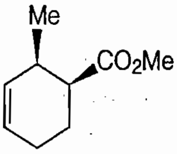
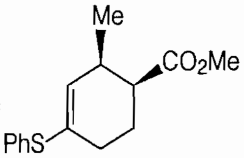


(b) X=



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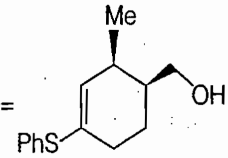
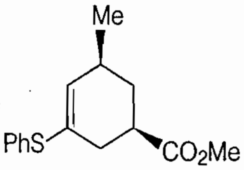


(c) X=



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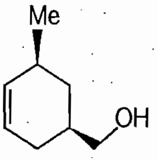

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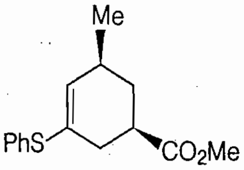

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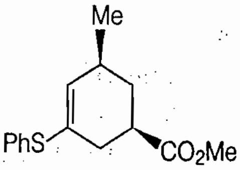
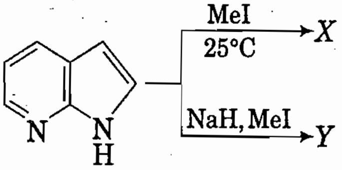


48. The major products X and Y formed in the following reactions are



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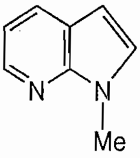

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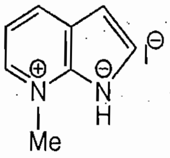
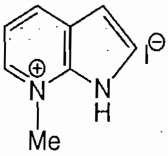


(b) X=



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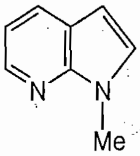
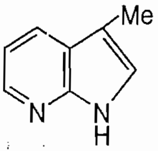


(c) X=



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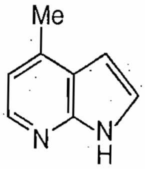
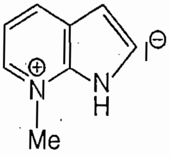


(d) X=



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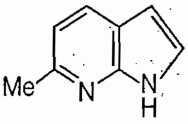
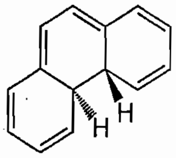


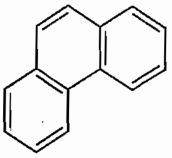
49. The major products X and Y formed in the following reaction sequence are

cis-stilbene $\xrightarrow[C_6H_{12}]{h\nu} X \xrightarrow[\text{air}]{I_2} Y$

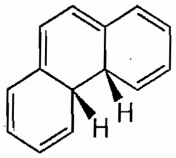
(a) X=



Y=



(b) X=



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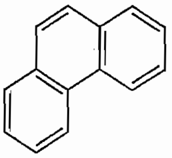
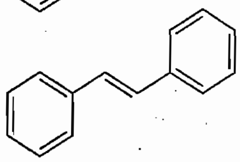


(c) X=



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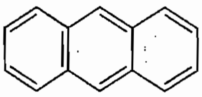

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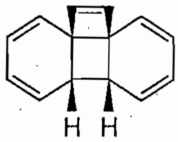

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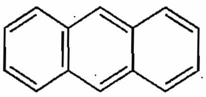
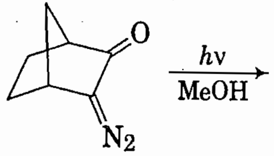
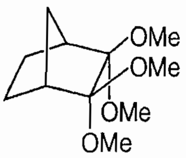


50. The product of the following reaction gave 6 line in ^{13}C NMR spectrum with peaks at δ 175, 52, 50, 46, 37, 33 ppm. The structure of the product is



(a)



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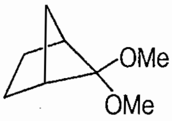

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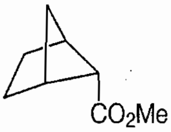

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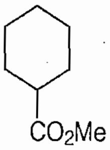
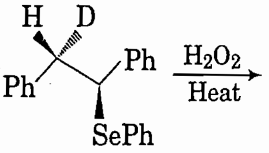
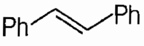


51. The major product formed in the following reaction is



(a)



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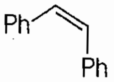

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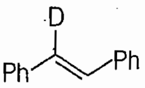

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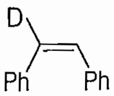
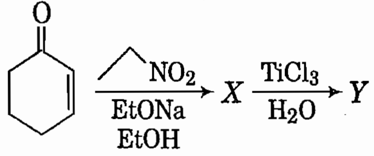
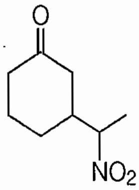
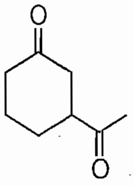
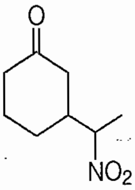
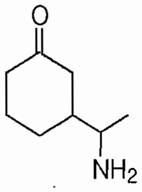
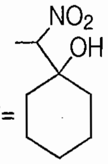
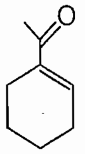


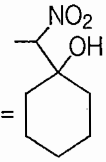
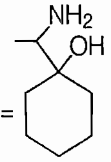
52. The major products X and Y formed in the following reaction sequence are



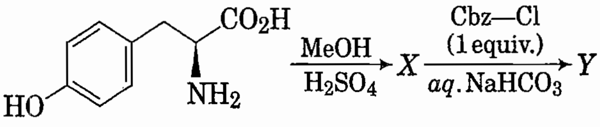
(a) $X=$  $Y=$ 

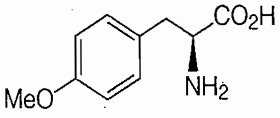
(b) $X=$  $Y=$ 

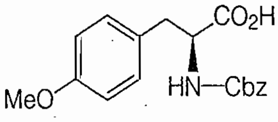
(c) $X=$  $Y=$ 

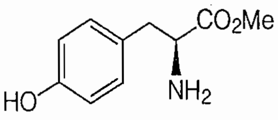
(d) $X=$  $Y=$ 

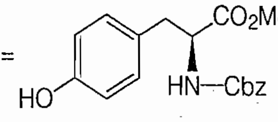
53. The major products X and Y formed in the following reaction sequence are

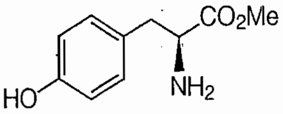


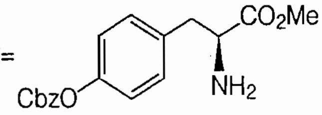
(a) $X=$ 

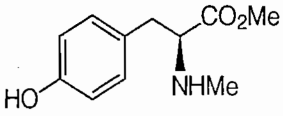
$Y=$ 

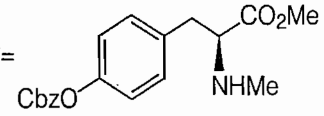
(b) $X=$ 

$Y=$ 

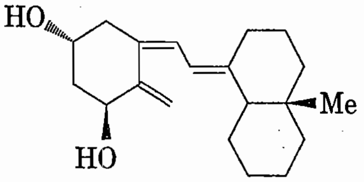
(c) $X=$ 

$Y=$ 

(d) $X=$ 

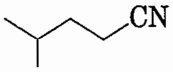
$Y=$ 

54. Given the fact that 1,3-butadiene has a UV absorption of 217 nm, the absorption wavelength (in nm) for the conjugated system shown below is_____.



(Use these absorption values for auxochromic groups alkyl: +5, exocyclic double bond: +5, every additional conjugated C ═ C: +30)

55. The m/e value of the detectable fragment formed by Mc Lafferty like rearrangement of the following compound in mass spectrometer is____



General Aptitude (GA) Questions

(1 *Mark Questions*)

56. A student is required to demonstrate a high level of comprehension of the subject, especially in the social sciences.

The word closest in meaning to comprehension is

(a) understanding (b) meaning
(c) concentration (d) stability

57. Choose the most appropriate word from the options given below to complete the following sentence.

One of his biggest _____ was his ability to forgive.

(a) vice (b) virtues (c) choices (d) strength

58. Rajan was not happy that Sajan decided to do the project on his own. On observing his unhappiness, Sajan explained to Rajan that he preferred to work independently.

Which one of the statements below is logically valid and can be inferred from the above sentences?

(a) Rajan has decided to work only in a group
(b) Rajan and Sajan were formed into a group against their wishes
(c) Sajan had decided to give into Rajan's request to work with him
(d) Rajan had believed that Sajan and he would be working together

59. If $y = 5x^2 + 3$, then the tangent at $x = 0$, $y = 3$

(a) passes through $x = 0, y = 0$
(b) has a slope of +1
(c) is parallel to the x-axis
(d) has a slope of −1

60. A foundry has a fixed daily cost of Rs 50000 whenever it operates and a variable cost of Rs 800 Q, where, Q is the daily production in tonnes. What is the cost of production in Rs per tonne for a daily production of 100 tonnes?

(2 *Marks Questions*)

61. Find the odd one in the following group: ALRVX, EPVZB, ITZDF, OYEIK

(a) ALRVX (b) EPVZB
(c) ITZDF (d) OYEIK

62. Anuj, Bhola, Chandan, Dilip, Eswar and Faisal live on different floors in a six-storeyed building (the ground floor is numbered 1, the floor above it 2, and so on). Anuj lives on an even numbered floor. Bhola does not live on an odd numbered floor. Chandan does not live on any of the floors below Faisal's floor. Dilip does not live on floor number 2. Eswar does not live on a floor immediately above or immediately below Bhola. Faisal lives three floors above Dilip. Which of the following floor-person combinations is correct?

	Anuj	Bhola	Chandan	Dilip	Eswar	Faisal
A	6	2	5	1	3	4
B	2	6	5	1	3	4
C	4	2	6	3	1	5
D	2	4	6	1	3	5

63. The smallest angle of a triangle is equal to two thirds of the smallest angle of a quadrilateral. The ratio between the angles of the quadrilateral is 3:4:5:6.

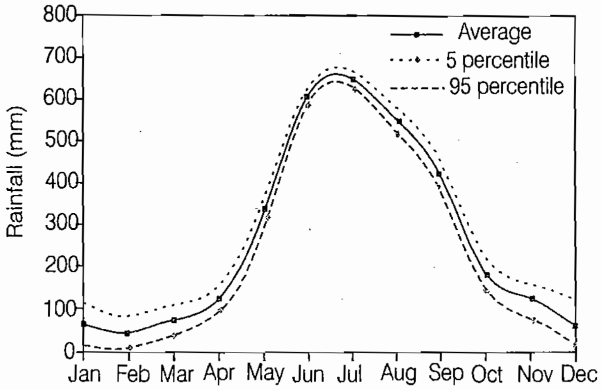
The largest angle of the triangle is twice its smallest angle. What is the sum, in degrees, of the second largest angle of the triangle and the largest angle of the quadrilateral?

64. One per cent of the people of country X are taller than 6 ft. Two per cent of the people of country Y are taller than 6 ft.

There are thrice as many people in country X as in country Y. Taking both countries together, what is the percentage of people taller than 6 ft?

(a) 3.0
(b) 2.5
(c) 1.5
(d) 1.25

65. The monthly rainfall chart based on 50 years of rainfall in Agra is shown in the following figure. Which of the following are true? (k percentile is the value such that k per cent of the data fall below that value)



(I) On average, it rains more in July than in December.
(II) Every year, the amount of rainfall in August is more than that in January.
(III) July rainfall can be estimated with better confidence than February rainfall.
(IV) In August, there is at least 500 mm of rainfall.

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

Answer *with* Solutions

1. (*b*) From first law of thermodynamics,

$$\Delta E = q + W$$

The work done W may be expansion work or non-expansion work. So,

$$\Delta E = q + W_{\text{expansion}} + W_{\text{non-expansion}}$$

$$= q - p\Delta V + W_{\text{non-expansion}} \quad (\because W_{\text{expansion}} = -p\Delta V)$$

$$\text{or} \quad q = \Delta E + p\Delta V - W_{\text{non-expansion}}$$

$$q = \Delta H - W_{\text{non-expansion}} \quad (\because \Delta E + p\Delta V = \Delta H)$$

Further, $\Delta S = \frac{q_{\text{rev}}}{T}$

$$\text{or} \quad q_{\text{rev}} = \Delta ST$$

$$\therefore \quad T\Delta S = \Delta H - W_{\text{non-expansion}}$$

$$\text{or} \quad W_{\text{non-expansion}} = \Delta H - T\Delta S$$

$$W_{\text{non-expansion}} = \Delta G \quad (\because \Delta G = \Delta H - T\Delta S)$$

The non-expansion work is also called non-pV work or useful work.

Thus, the maximum non-pV work that a system can perform at constant p is ΔG.

2. (*d*) For the given reaction,

Thermodynamic equilibrium constant

$$K^{\ominus} = \frac{\{C\}}{\{A\}\{B\}}$$

where, { } indicates thermodynamic activities of chemical species and activities have no dimensions. Thus, $K^{\ominus}$ is a dimensionless quantity.

Note Equilibrium constant, which is equal to thermodynamic equilibrium constant divided by a quotient of activity coefficient has some units for the given reaction.

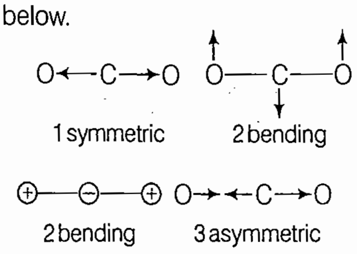
3. For a linear triatomic molecule,

The number of vibrational normal modes $= 3n - 5$

where, $n =$ number of atoms.

$$= 3 \times 3 - 5 = 4$$

But this molecule has only 3 IR active vibrational normal modes due to degeneration of two modes as shown below.



4. CCl_4 is a tetrahedral molecule and hence have T_d point group, *i.e.*, it contains four C_3 axes, $3C_2$ axes and $6\sigma_d$ mirror planes.

5. (*d*) The value of magnetic quantum number (m) depends upon the value of l. For p-orbital $l = 1$ so, value of m for a p_x-orbital may be +1, 0 or −1, depending upon the internuclear axis *e.g.*, if z axis is considered as the internuclear axis, value of m for p_x is −1.

But if x or y axis is considered as internuclear axis, the value of m for p_x may be 0 or +1. Thus, we can say for a p_x-orbital the value of magnetic quantum number is undefined.

6. (*d*) The molecular partition function, if energy levels of a system are equispaced by ε is given as

$$\text{Molecular partition function} = \frac{1}{1 - e^{-\beta\varepsilon}}$$

$$\left(\text{where, } \beta = \frac{1}{kT}\right)$$

7. (*a*) The general form of Langmuir adsorption isotherm is

$$\theta = \frac{K[X]}{1 + K[X]}$$

For very low concentration of the gas, $1 >>> K[X]$ and hence, $1 + K(X) \approx 1$

$$\therefore \quad \theta = \frac{K[X]}{1} = K[X]$$

8. We know that average speed, $\bar{v} = \sqrt{\frac{8RT}{\pi M}}$

Since, T, R and π are constant.

$$\therefore \quad \frac{\bar{v}_{H_2}}{\bar{v}_{He}} = \sqrt{\frac{M_{He}}{M_{H_2}}} = \sqrt{\frac{4}{2}} = \sqrt{2} = 1.414$$

9. (*b*) General formula for *nido*-borane is B_nH_{n+4}.

If $n = 4$, formula of borane is B_4H_8.

If $n = 6$, formula of borane is B_6H_{10}.

Thus, B_6H_{10} is a *nido*-borane.

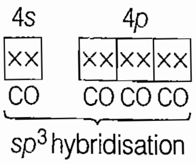
10. (*c*) In $Ni(CO)_4$, Ni is present as Ni^0.

$Ni^0 = [Ar]3d^8, 4s^2, 4p^0$

CO being strong field ligand pair up the s-electrons with d-electrons making the s-orbital empty for hybridisation. *i.e.*, Ni in the presence of CO $= [Ar]3d^{10}, 4s^0, 4p^0$

Thus,

$Ni(CO)_4 = [Ar]3d^{10}$

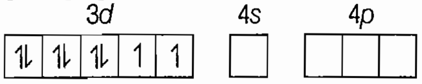


Thus, the geometry of $Ni(CO)_4$ is tetrahedral and it is a diamagnetic complex.

Further,

in $[NiCl_4]^{2-}$, Ni is present as Ni^{2+}.

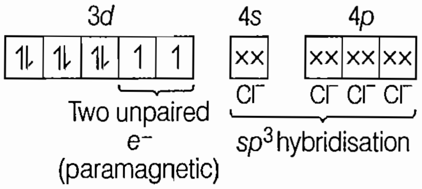
$[Ni]^{2+} = [Ar]\,3d^8, 4s^0, 4p^0$



Cl^- being a weak field ligand is not capable to pair up the unpaired *d*-electrons. So, the available orbitals for it are only 4*s* and 4*p*-orbitals.

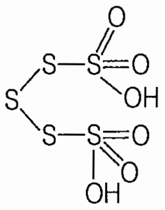
Ni in the presence of $Cl^- = [Ar]\,3d^8 4s^0 4p^0$

$[NiCl_4]^{2-} = [Ar]$



Thus, it is also a tetrahedral complex.

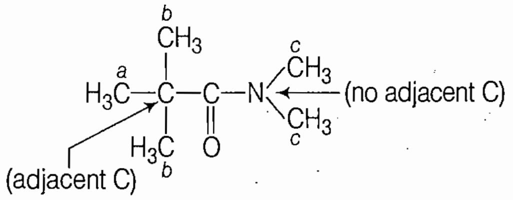
11. The structure of $H_2S_5O_6$ is as



Thus, in the above molecule, there are 4 S — S bonds.

12. (*a*) To analyse a sample for its atomic constituents, it has to be atomised which is usually done by flame or electrothermal (graphite tube) atomiser. Other atomiser such as glow discharge atomisation, hydride atomisation or cold vapour atomisation might be used for special purposes.

13. The condensed structure of N, N-dimethyl pivalamide is

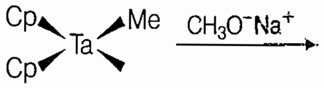


Number of singlet signals = Number of protons having no another set of proton attached with the adjacent carbon atom. In the above molecule, the number of such protons is 3.

Thus, number of singlet signals = 3.

14. (c) Among the given transition elements Cr is the metal that does not form homoleptic polynuclear metal carbonyls. This is because of large M — M and M — C bond length or weak M — M and M — C bond strength, (where, *M* = transition metal and C = carbon).

15. (*c*) CH_3O^- being a strong nucleophile eliminates a proton.



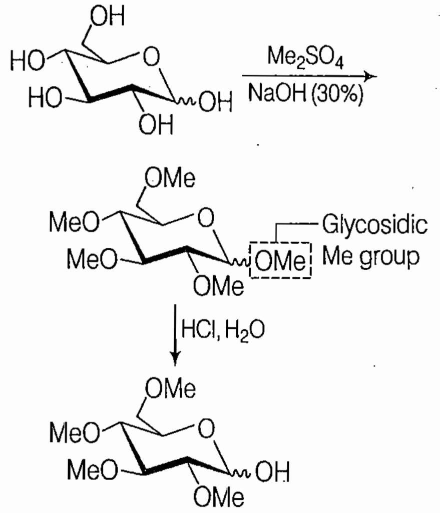
16. (*c*) The given two complexes give different ions when subjected to ionisation.

$$[Co(H_2O)_4Cl_2]NO_2 \xrightleftharpoons{\text{Ionisation}} [Co(H_2O)_4Cl_2]^+ + NO_2^-$$

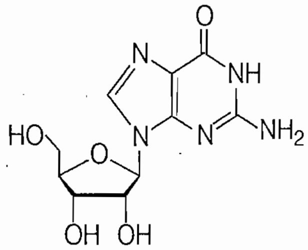
$$[Co(H_2O)_4Cl(NO_2)]Cl \xrightleftharpoons{\text{Ionisation}} [Co(H_2O)_4Cl(NO_2)]^+ + Cl^-$$

Thus, these are called ionisation isomers.

17. (*c*) Monosaccharides like glucose when treated with dimethyl sulphate (Me_2SO_4) and 30% NaOH, form methylated methyl glycoside. When the obtained glycoside is treated with acid, the glycosidic methyl group is hydrolysed to give free methylated sugar.

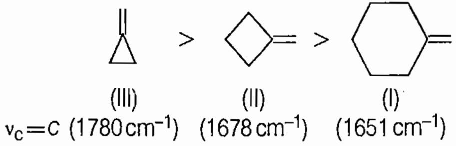


18. (*d*) The molecular formula of guanosine is $C_{10}H_{13}N_5O_5$. Thus, its structure can be represented as



19. (*c*) Exocyclic double bond have higher IR stretching frequency in highly strained rings because of increased *s*-character of C ═ C bond.

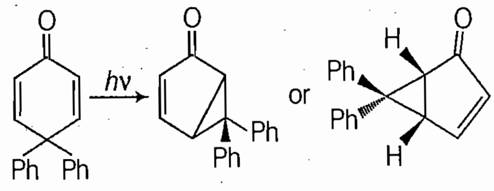
Thus, the correct order of IR stretching frequency of the bond is



20. (b) In the solvolysis process, the solvent behaves like a nucleophile. Since, CH_3COOH (acetic acid) is a polar protic solvent, but is a weak nucleophile, so it favours S_N1 process. Further, presence of an electron releasing atom like O stabilises the carbocation intermediate of S_N1 reaction. Thus, the correct order of rate of solvolysis is

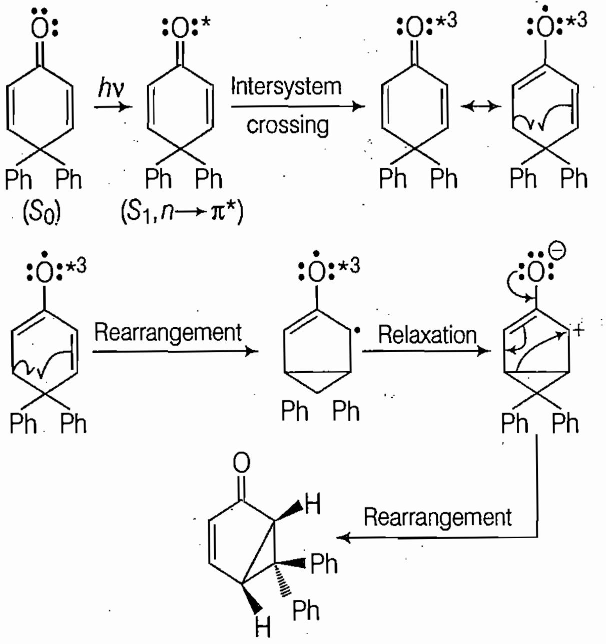
III > II > I

21. (a)



4, 4-diphenyl-2, 5-cyclohexadienone

This reaction involves di-π methane rearrangement. Its mechanism can be represented as



22. (b) III is the boat conformation of cyclohexane, in which the hydrogen of C_2 and C_3, C_5 and C_6 carbons are eclipsed. Thus, in this molecule there is a lot of torsional strain but no angle strain (due to tetrahedral angles). Hence, it is an unstable form.

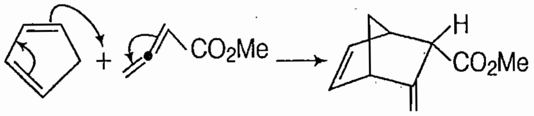
I is twist boat conformation. The non-bonded interactions between the two flag pole hydrogens are minimum and also the torsional strain due to eclipsing interactions on $C_2 - C_3$ and $C_5 - C_6$ are partly releived. Thus, it is somewhat more stable than boat conformation.

II is half chair conformation which have both angle strain and torsional strain. So, it is the least stable conformation of cyclohexane.

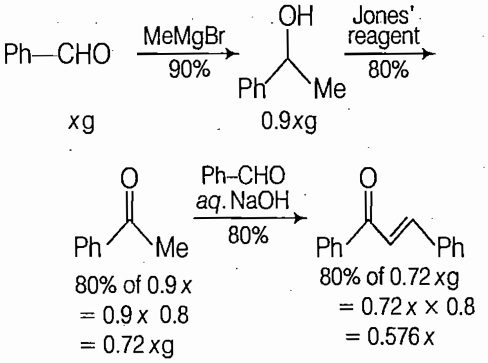
Thus, the correct order of stability of the given conformations of cyclohexane is

I > III > II

23. (c) The given reaction is a Diel's Alder type reaction. Here, $TiCl_4$ acts as a Lewis acid and catalyse the reaction by more activating the dienophile. Thus, endo: exo ratio increases, i.e., endo is the major product.



24.

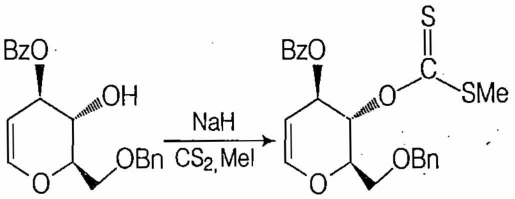


(Let the amount of PhCHO taken is xg)

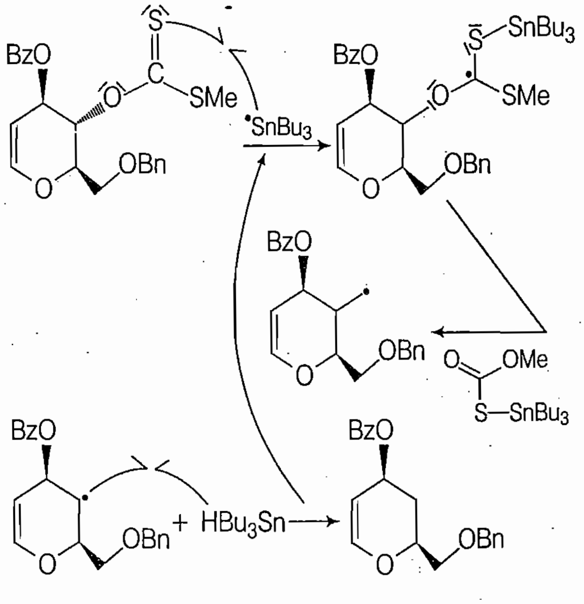
∴ Overall yield (in %) of reaction

$$= \frac{0.576x}{x} \times 100 = 57.6\,\%$$

25. (a)



$$Bu_3Sn - H \xrightarrow{AIBN} Bu_3Sn^{\bullet} + {}^{\bullet}H$$



The reaction of —OH group containing compound with AIBN, HBu_3Sn, C_6H_6, reflux to convert it into —H is called Barton McCombie reaction or Barton deoxygenation.

Thus, the correct set of reagents for the given reaction is (i) NaH, CS_2 then MeI and (ii) Bu_3SnH, AIBN, C_6H_6, reflux.

26. (*b*) For the given hydrogenic wavefunction.

$n = 3$ and $l = 1$

$\therefore$ Number of angular nodes $= l = 1$

and number of radial nodes $= n - l - 1$

$$= 3 - 1 - 1 = 1$$

$\psi = 0$ in *xy*-plane and as the atomic number (Z) increases size of orbital decreases.

27. We know that van der Waals' equation for 1 mole of a gas is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

On substituting values, we get

$$\left[p + \frac{3.64}{(0.15)^2}\right](0.15 - 0.04) = 0.083 \times 300$$

$$\left(p + \frac{3.64}{0.0225}\right)(0.11) = 24.9$$

$$\left(p + \frac{3.64}{0.0225}\right) = \frac{24.9}{0.11} = 226.36$$

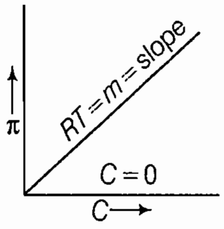
$$p + 161.78 = 226.36$$

or $p = 226.36 - 161.78 = 64.58$ bar

28. (*a*) The expression for the osmotic pressure is

$$\pi = CRT$$

When we plot π against C, a straight line is originated from the origin, slope of which is equal to RT.



Thus, as the value of T increases, slope increases (here, R = gas constant or solution constant).

29. For the Fe^{3+}/Fe^{2+} electrode, $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77$ V

$[Fe^{2+}] = 0.1$ M, $[Fe^{3+}] = 1$ M

From Nernst equation,

$$E_{Fe^{3+}/Fe^{2+}} = E^\circ_{Fe^{3+}/Fe^{2+}} - \frac{0.059}{n}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

[Here, $n = 1$, $Fe^{3+} + e^- \longrightarrow Fe^{2+}$]

$$\therefore \quad E_{Fe^{3+}/Fe^{2+}} = 0.77 - \frac{0.059}{1}\log\frac{(0.1)}{(1)}$$

$$E_{Fe^{3+}/Fe^{2+}} = 0.77 + 0.059$$

$$= 0.829 \text{ V}$$

30. (10322.5) Given, atomic mass = 96 gmol^{-1}

Lattice type = bcc for which $Z = 2$

Edge length, $a = 0.314$ nm

$$= 0.314 \times 10^{-9} \text{ m}$$

We know density, $d = \dfrac{Z \cdot M}{a^3 \cdot N_0}$

(where, N_0 = Avogadro's number)

$$= \frac{2 \times 96}{(0.314 \times 10^{-9})^3 (6.022 \times 10^{23})}$$

$$= \frac{192}{1.86 \times 10^{-5}} = 10322580 \text{ g cm}^{-3}$$

$$= 10322.5 \text{ kgm}^{-3}$$

31. Molecular distribution between two states

$$\frac{N_i}{N_j} = \exp^{-(E_i - E_j)/kT}$$

$$\ln\frac{N_i}{N_j} = \frac{\Delta E}{kT}$$

$$\ln(9.22 \times 10^6) = \frac{\Delta E}{1.38 \times 10^{-26} \times 6.023 \times 10^{23} \times 300}$$

$$\Delta E = 16.036 \times 1.38 \times 6.023 \times 10^{-3} \times 300$$

$$= 39.9 \approx 40 \text{ kJ mol}^{-1}$$

32. We know that efficiency of Carnot engine, $\eta = 1 - \dfrac{T_2}{T_1}$

(Given, $\eta = 0.55\% = 0.55$ and $T_2 = 105 + 273 = 378$ K)

$$0.55 = 1 - \frac{378}{T_1}$$

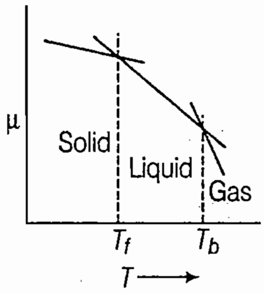
$$0.55 - 1 = \frac{-378}{T_1}$$

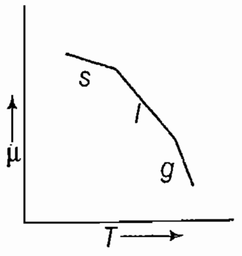
$$-0.45 = \frac{-378}{T_1}$$

$$T_1 = \frac{378}{0.45} = 840 \text{ K}$$

33. (*a*) We know that $\left(\dfrac{\partial \mu}{\partial T}\right)_p = -\bar{S}$

Thus, the plot between chemical potential (μ) and temperature (T) for a pure substance can be represented as





34. Given,

$$H_2O(s) \longrightarrow H_2O(l);\ \Delta H_1 = 6.01\ \text{kJmol}^{-1} \qquad \ldots(i)$$

$$H_2O(l) \longrightarrow H_2O(g),\ \Delta H_2 = 44.83\ \text{kJmol}^{-1} \qquad \ldots(ii)$$

Enthalpy of sublimation of ice, *i.e.*,

$$H_2O(s) \longrightarrow H_2O(g);\ \Delta H = ?$$

On adding Eqs. (i) and (ii), we get the required equation.

$$\Delta H = \Delta H_1 + \Delta H_2$$
$$= (6.01 + 44.83)\ \text{kJmol}^{-1}$$
$$= 50.84\ \text{kJmol}^{-1}$$

35. s-character $= (0.12)^2 \times 100 = 1.44\%$

p-character $= 100 - 1.44 = 98.56$

First only the wavefunction of atoms are combined to give sp^2 hybrid orbitals with bond angle 120°. But s-character (1.44) is much less and p-character is much higher as compared to that present in sp^2 hybrid orbitals, so bond order must lies in between 175 to 180°.

36. (*a*) When BCl_3 and NH_4Cl are heated at 140°C, they give substituted borazines which on reduction with $NaBH_4$ gives borazine.

$$3BCl_3 + 3NH_4Cl \xrightarrow[-HCl]{140^\circ C} \underset{\text{Substituted borazine}}{\underset{(X)}{B_3N_3H_3Cl_3}}$$

$$\underset{(X)}{B_3H_3N_3Cl_3} \xrightarrow{NaBH_4} \underset{\text{Borazine}}{\underset{(Y)}{B_3N_3H_6}}$$

37. (9) For the term ^1G, $L = 4$

Possible $m_l = \pm 4, \pm 3, \pm 2, \pm 1, 0$

If $(2s+1) = 1$, then $s = 0$

Thus, total number of microstates = total values of m_l

$= 9$

38. (*b*) In the molecule $\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2OCH_3$, C^2 is the carbon that is in direct contact of a group having e^- donating tendency CH_3- and also of a group having e^- withdrawing tendency $(-CH_2OCH_3)$, that's why proton attached to it behave differently in high (500 MHz) and low (60 MHz) field ^1H NMR.

39. (*a*) The distortion in the geometry of the non-linear molecular system is called Jahn-Tellar distortion. Among the given, $[Ti(H_2O)_6]^{3+}$ because of $3d^1$ configuration (or $t_{2g}{}^1$ configuration, a symmetrical configuration) does not exhibit this effect. But $[Cr(H_2O)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ because of their unsymmetric configuration *i.e.*, $t_{2g}{}^3e_g^1$ in Cr^{2+}, $t_{2g}^5e_g^2$ in Co^{2+} and $t_{2g}^4e_g^2$ in Fe^{2+}, exhibit Jahn-Tellar distortion.

Since, this distortion in case of t_{2g} orbitals is much weaker as compared to e_g orbitals (as the former lies in between x, y and z axes) so, $[Cr(H_2O)_6]^{2+}$ will exhibit strong Jahn-Teller distortion among the given.

40. (*a*) The ν_{co} stretching frequency is highest in case of $[Mn(CO)_6]^+$ because it possesses minimum electron density. As the electron density on the metal increases, it results in more π-back bonding to the CO ligand, which weakens the C—O bond by pumping more electron density into the formally empty carbonyl π^* orbital. This increases the M—CO bond strength making it more double bond like. Thus, results in decreased stretching frequency.

41. (*d*) An easily available β–H atom makes the TiR_4 type compound less stable.

Thus, among the given, $TiEt_4$ is highly unstable because of the availability of β–H atom and readily decomposes at – 80°C. $TiMe_4$ have no β–H atom, so it is quite stable and undergoes α–H substitution at –40°C.

$Ti(CH_2CMe_3)_4$ has no β–H atom and also it is a sterically hindered compound, so loss of β–H is much more difficult. Thus, it is most stable among the given and decomposes above 100°C.

Thus, the order of thermal stability is

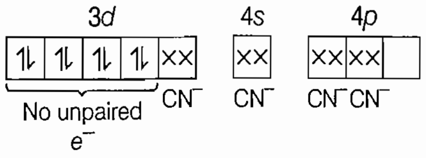
$Ti(CH_2CMe_3)_4 > TiMe_4 > TiEt_4$

42. (*b*, *c*) Magnetic moment, $\mu = \sqrt{n(n+2)}$ BM

where, n = number of unpaired electrons.

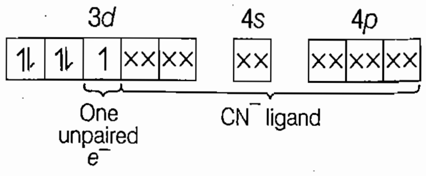
Thus, the species having maximum number of unpaired electrons, show highest magnetic moment at room temperature.

In $[Ni(CN)_4]^{2-}$, $Ni^{2+} = [Ar]$



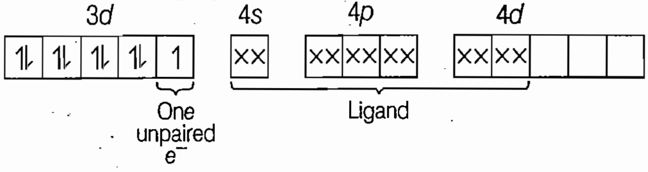
$n = 0$

In $[Fe(CN)_6]^{3-}$, $Fe^{3+} = [Ar]$



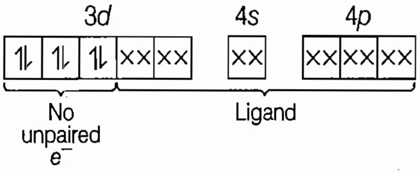
$n = 1$

In $[Cu(H_2O)_6]^{2+}$, $Cu^{2+} = [Ar]$



$n = 1$

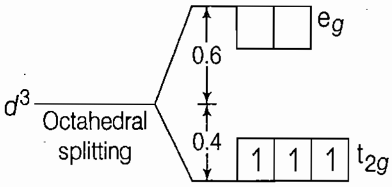
In $[Co(CN)_6]^{3-}$, $Co^{3+} = [Ar]$



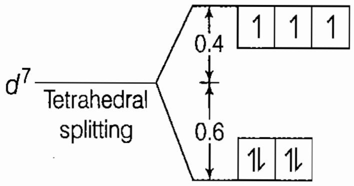
$n = 0$

43. (*c*) In $MnCr_2O_4$, Mn is present as Mn^{2+} (d^7-configuration) and Cr as Cr^{3+} (d^3 configuration). Since d^3 and d^8 ions have strong preference for octahedral geometry and d^7 has more preference for tetrahedral geometry, thus the divalent Mn^{2+} ion will occupy the tetrahedral voids and the trivalent Cr^{3+} will occupy the octahedral void in the close packed structure of oxide ion.

Thus, $MnCr_2O_4$ is a normal spinel (in which divalent ion occupy tetrahedral voids and trivalent ion occupy the octahedral voids).



$$\text{CFSE} = (-0.4 \times 3) + 0$$
$$= -1.2 = 12\ \text{Dq}$$

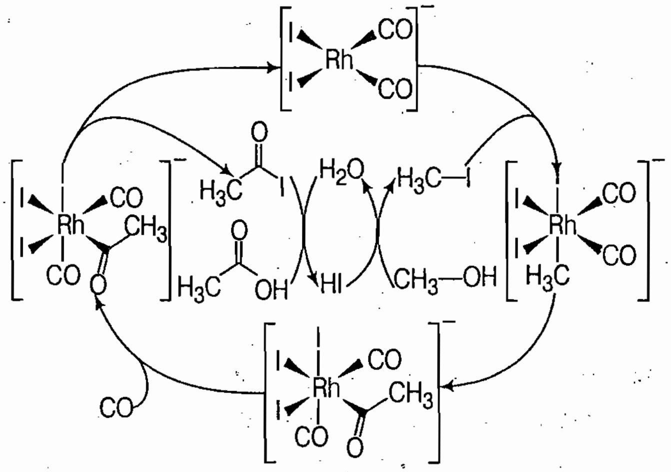


$$\text{CFSE} = (-0.6 \times 4) + (0.4 \times 3)$$
$$= -2.4 + 1.2 = -1.2 = 12\ \text{Dq}$$
$$\text{Net CFSE} = (-12\ \text{Dq}) + (-12\ \text{Dq}) = -24\ \text{Dq}$$

44. (*b*) In photosynthesis, Mg^{2+} is preferred by chlorophyll as it is a light atom with a small spin orbit coupling constant, so inter system crossing is inhibited which favours the energy transfer from the excited singlet state.

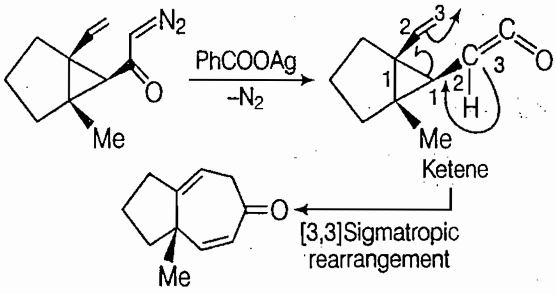
Further, it is not a redox metal and does not interfere in the charge separation step.

45. (*d*) The cyclic representation of the process is as follows.

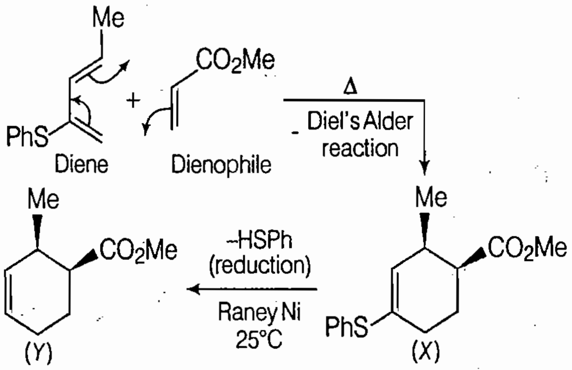


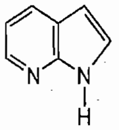
From the cycle, it is clear that HI is used to convert CH_3OH into CH_3I.

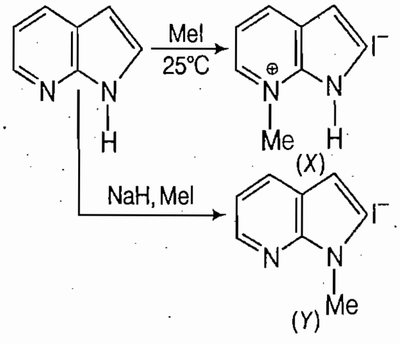
46. (*d*)



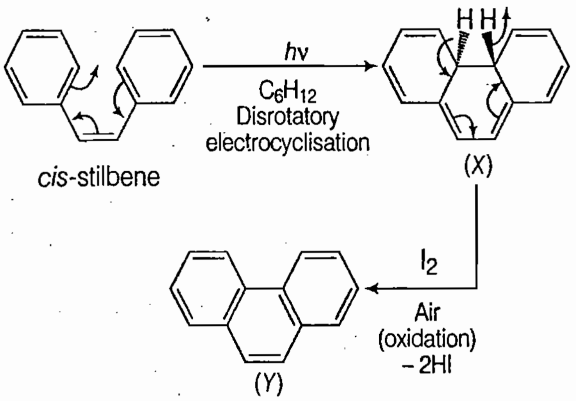
47. (*a*)



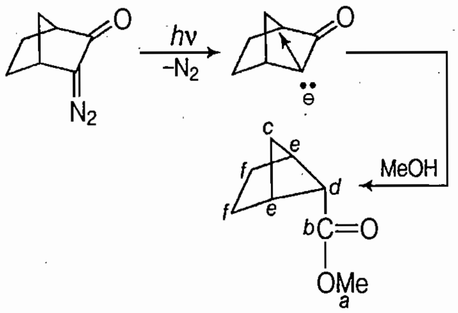
48. (*b*) When  is treated with MeI at 25°C, the substitution occurs at the pyridine ring but in the presence of NaH substitution occurs mainly at pyrrole ring.



49. (*a*)



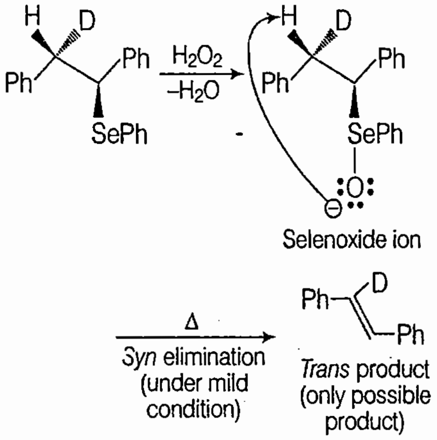
50. (*c*)



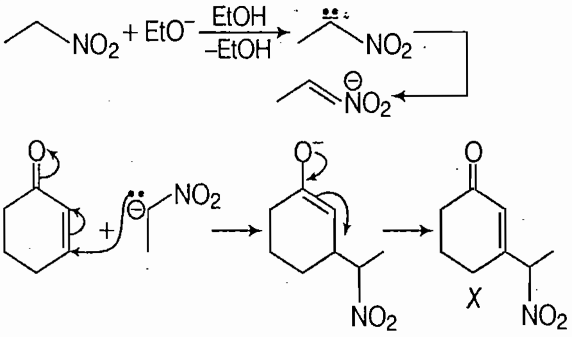
Because of the presence of six carbons in different environments

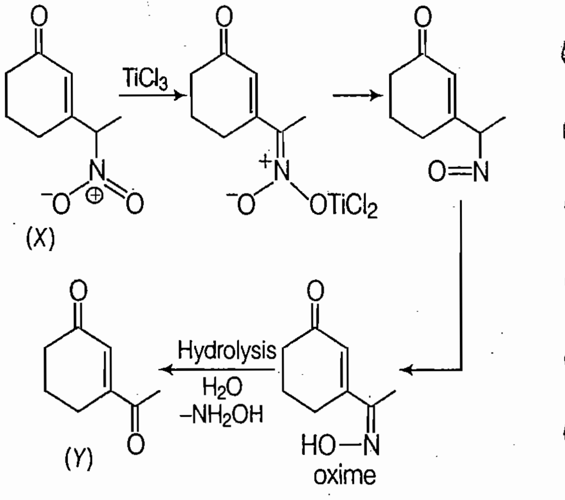
(*i.e.*, six types of carbons as represented by *a*, *b*, *c*, *d*,......) the obtained product gave six peaks in ^{13}C NMR spectrum.

51. (*c*)



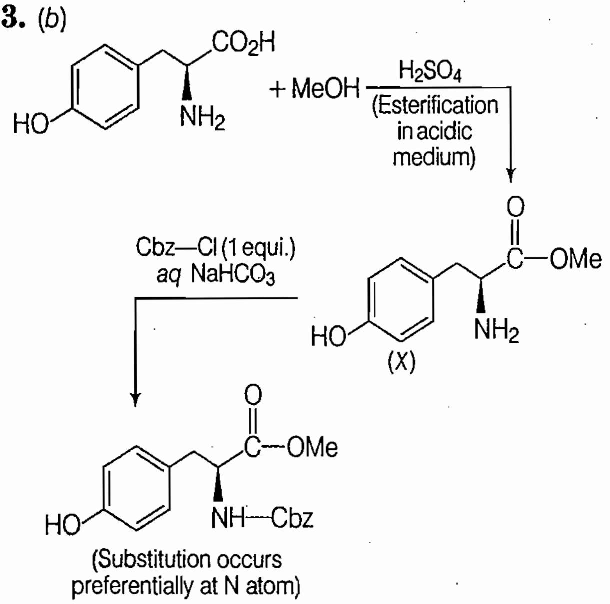
52. (*a*)



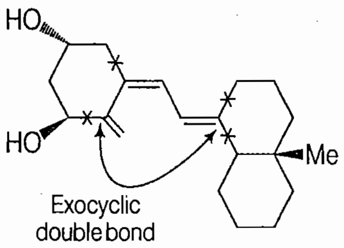


Conversion of *X* into *Y* by using $TiCl_3/H_2O$ is called nef reaction.

53. (*b*)

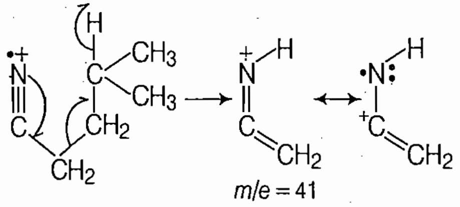


54.



Base value of 1, 3-butadiene = 217 nm
Additional conjugation = $30 \times 1 = 30$
Exocyclic double bond = $2 \times 5 = 10$
Alkyl substituent = $1 \times 5 = 5$
Ring residue = $\underline{4 \times 5 = 20}$
Total = 282 nm

55. Straight chain cyanides undergo hydrogen rearrangement in a six membered transition state and give a base peak at *m/e* 41.



56. (*a*) The word closest in meaning to comprehension is the act or fact of grasping the meaning *i.e.*, understanding.

57. (*b*) Virtues means moral excellence and righteousness.

58. (*d*) As we know, Rajan was not happy that Sajan decided to do the project on his own. It means that Rajan had believed that Sajan would be working together.

59. (c) If $y = 5x^2 + 3$

Then, $\frac{dy}{dx} = \frac{d}{dx}(5x^2 + 3)$

$\frac{dy}{dx} = 10x + 3$ at $x = 0$, then

$\left.\frac{dy}{dx}\right|_{x=0} = 3$

So, tangent at $x = 0$, then it is parallel along the x-axis.

60. Fixed cost = 50000

Variable cost = $800Q = 800 \times 100 = 80000$

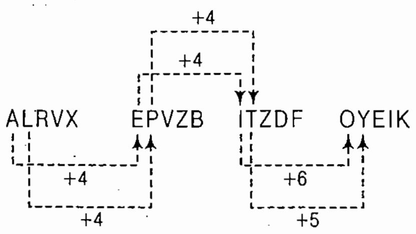
So, production cost of 100 tonne

= Fixed cost + variable cost

= 50000 + 80000 = 130000

Cost of 1 ton = $\frac{130000}{100}$ = ₹ 1300

61. (*d*)



62. (*b*)

63. Let the angle of the quadrilateral be x.

So, 3:4:5:6

i.e., $3x + 4x + 5x + 6x = 360°$

$18x = 360°$

$x = \frac{360°}{18} = 20°$

$\therefore$ Angle of the quadrilateral = $3 \times 20° = 60°$, $4 \times 20° = 80°$, $5 \times 20° = 180°$, $6 \times 20° = 120°$

The smallest angle of a Δ is equal to two third of the smallest angle of a quadrilateral.

i.e., $x_1 = \frac{2}{3} \times 60° = 40°$

The largest angle of the Δ is twice the smallest angle.

i.e., $x_2 = 2 \times 60° = 120°$

Then, third angle of a Δ = 180°–(120° + 40°)

= 180° – 160° = 20°

$\therefore$ Sum of second largest angle of a Δ and the largest angle of the quadrilateral = 120° + 40°

= 160°

64. (*d*) 1 % of the people of country X are taller than 6 ft *i.e.*, $\frac{X}{100}$.

2 % of the people of country Y are taller than 6 ft *i.e.*, $\frac{2Y}{100} = \frac{Y}{50}$.

Then, there are thrice as many people in country as in country Y *i.e.*, $X = 3Y$.

Taking both countries together

$$= \frac{X}{100} + \frac{Y}{50}$$

$$= \frac{3Y}{100} + \frac{Y}{50} \qquad [\because X = 3Y]$$

$$= \frac{5Y}{100}$$

According to the given problem, we get

$$\frac{\frac{5Y}{100}}{4Y} \times 100 = \frac{5Y}{100 \times 4Y}$$

$$= \frac{5}{400} \times 100 = 1.25$$

Hence, the percentage of people taller than 6 ft is 1.25.

65. (*b*) (i) After analysing the graph, we see that on average rainfall *i.e.*, 650 mm, the rain more in July than in December.

(ii) In July, approx 650 mm rainfall, while in February, 50 mm approx, which can be estimated with confidence in July as compared to February rainfall.

GATE
Chemistry
Solved Paper 2013

Time : 3 hrs **MM : 100**

Read the following instructions carefully

1. There is a total of 65 questions carrying 100 marks.
2. Questions 1 to 25 will **carry 1 mark** each and questions 26 to 55 will **carry 2 marks** each.
3. Questions 48 to 51 (2 pairs) are **common data** questions and questions pairs 52- 53—54- 55 are linked answer type questions. The **answer** to the second question of the linked answer type questions depend on the answer to the first question of the pair. If the first question in the linked pair is wrongly answered or is unattempted, then the answer to the second question in the pair will not be evaluated.
4. Questions 56 to 65 belong to **General Aptitude** (GA) type. Questions 56 to 60 will carry 1 mark each and questions 61 to 65 will carry 2 marks each.
5. Unattempted questions will carry **zero marks.**
6. Wrong answers will carry **negative marks.** For questions 1 to 25 and 56 to 60, 1/3 mark will be deducted for each wrong answer. For questions 26 to 51 and 61 to 65, 2/3 mark will be deducted for each wrong answer. The question pairs (questions 52 and 53) and (questions 54 and 55) are questions with linked answer. There will be negative marks only for wrong answer to the first question of the linked answer type question pair *i.e.,* for questions 52 and 54, 2/3 mark will be deducted for each wrong answer. There is no negative marking for questions 53 and 55.
7. In **numerical answer type** questions, to enter a number as your answer, use the **virtual numerical keypad.**

(1 *Mark Questions*)

1. The point group symmetry of $H_2C{=}C{=}CH_2$ is

(a) D_{2h} (b) C_{2h} (c) C_{2v} (d) D_{2d}

2. Two trial wave functions $\phi_1 = c_1x(a-x)$ and $\phi_2 = c_1x(a-x) + c_2x^2(a-x)^2$ give ground state energies E_1 and E_2 respectively, for the microscopic particle in a 1-*D* box by using the variation method. If the exact ground state energy is E_0, the correct relationship between E_0, E_1 and E_2 is

(a) $E_0 = E_1 = E_2$ (b) $E_0 < E_1 < E_2$
(c) $E_0 < E_2 < E_1$ (d) $E_0 > E_2 = E_1$

3. The ground state energies of H atom and H_2 molecule are -13.6 eV and -31.7 eV, respectively. The dissociation energy of H_2 is ________ eV.

4. A 2 L vessel containing 2 g of H_2 gas at 27°C is connected to a 2 L vessel containing 176 g of CO_2 gas at 27°C. Assuming ideal behaviour of H_2 and CO_2 , the partial pressure of H_2 at equilibrium is ________ bar.

5. Consider the reaction,

$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ at equilibrium.

The equilibrium can be shifted towards the forward direction by

(a) increasing the amount of carbon in the system
(b) decreasing the volume of the system
(c) decreasing the pressure of the system
(d) increasing the temperature of the system

6. A sparingly soluble electrolyte M_2X ionises as

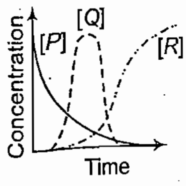
$$M_2X \rightleftharpoons 2M^+ + X^{2-}$$

The solubility product (K_{sp}), molal solubility (S) and mean molal activity coefficient ($\gamma_\pm$) are related by

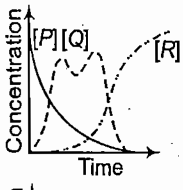
(a) $K_{sp} = S^2\gamma_\pm^2$
(b) $K_{sp} = S^3\gamma_\pm^3$
(c) $K_{sp} = 4S^3\gamma_\pm^2$
(d) $K_{sp} = 4S^3\gamma_\pm^3$

7. For the first order consecutive reaction $P \to O \to R$, under steady state approximation to $[Q]$, the variations of $[P]$, $[Q]$ and $[R]$ with time are best represented by

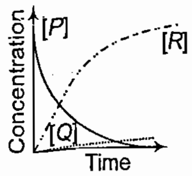
(a)



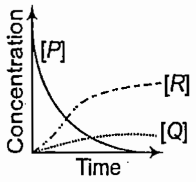
(b)



(c)



(d)



8. At 273 K and 10 bar, the Langmuir adsorption of a gas on a solid surface gave the fraction of surface coverage as 0.01. The Langmuir adsorption isotherm constant is __________ bar^{-1}. (Give the answer to the third decimal place)

9. Conversion of boron trifluoride to tetrafluorobo- rate accompanies

(a) increase in symmetry and bond elongation
(b) increase in symmetry and bond contraction
(c) decrease in symmetry and bond contraction
(d) decrease in symmetry and bond elongation

10. The correct statement with respect to the bonding of the ligands, Me_3N and Me_3P with the metal ions Be^{2+} and Pd^{2+} is,

(a) the ligands bind equally strong with both the metal ions as they are dicatonic
(b) the ligands bind equally strong with both the metal ions as both the ligands are pyramidal
(c) the binding is stronger for Me_3N with Be^{2+} and Me_3P with Pd^{2+}
(d) the binding is stronger for Me_3N with Pd^{2+} and Me_3P with Be^{2+}

11. A crystal has the lattice parameters $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$. The crystal system is

(a) tetragonal (b) monoclinic
(c) cubic (d) orthorhombic

12. The by-product formed in the characteristic reaction of $(CO)_5Cr{=}C(OMe)Me$ with $MeNH_2$ is

(a) CO (b) MeOH
(c) MeCHO (d) $MeCONH_2$

13. The catalyst and co-catalyst used in the Wacker process, respectively, are

(a) $PdCl_2$ and Cu (b) $CuCl_2$ and $[PdCl_4]^{2-}$
(c) Pd and CuCl (d) $[PdCl_4]^{2-}$ and $CuCl_2$

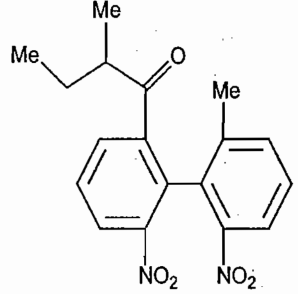
14. Oxymyoglobin $Mb(O_2)$ and oxyhaemoglobin $Hb(O_2)_4$ respectively, are

(a) paramagnetic and paramagnetic
(b) diamagnetic and diamagnetic
(c) paramagnetic and diamagnetic
(d) diamagnetic and paramagnetic

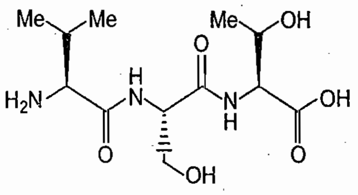
15. Hapticity of cycloheptatrienein $Mo(C_7H_8)(CO)_3$ is __________.

16. The number of oxygen molecule(s) that a molecule of hemerythrin can transport is __________.

17. The maximum number of stereo isomers possible for the compound given below is __________.



18. The correct sequence of the amino acids present in the tripeptide given below is

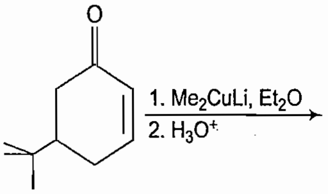


(a) Val-Ser-Thr (b) Val-Thr-Ser
(c) Leu-Ser-Thr (d) Leu-Thr-Ser

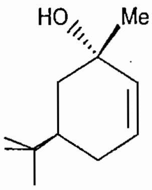
19. Among the compounds given in the options, the one that can be used as a formyl anion equivalent (in the presence of a strong base) is

(a) ethylene (b) nitroethane
(c) 1, 3-dithiane (d) 1, 4-dithiane

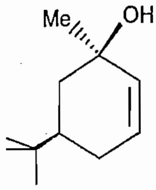
20. The major product formed in the reaction given below is

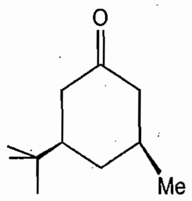


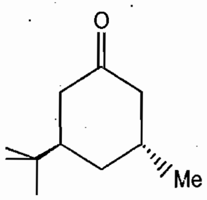
(a)



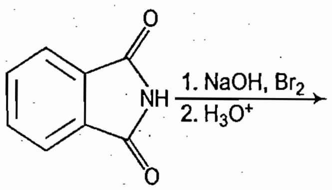
(b)

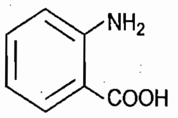


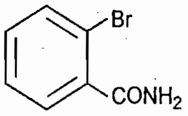
(c) 

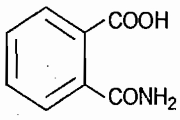
(d) 

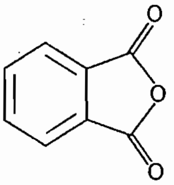
21. The major product formed in the reaction given below is



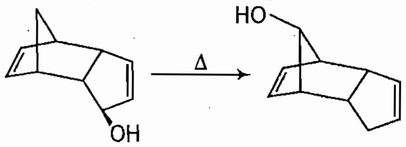
(a) 

(b) 

(c) 

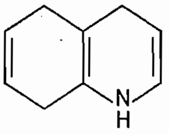
(d) 

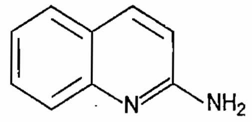
22. The pericyclic reaction given below is an example of

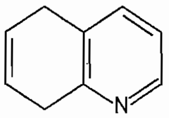


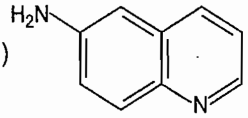
(a) [1, 3]-sigmatropic shift (b) [1, 5]-sigmatropic shift
(c) [3, 5]-sigmatropic shift (d) [3, 3]-sigmatropic shift

23. The major product formed in the reaction of quinoline with potassium amide (KNH_2) in liquid ammonia is

(a) 

(b) 

(c) 

(d) 

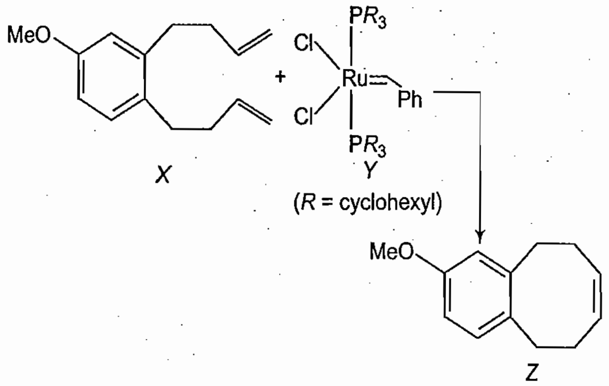
24. The number of signals that appear in the proton decoupled ^{13}CNMR spectrum of benzonitrile (C_7H_5N) is ________.

25. Among the compounds given in the options, the one that exhibits a sharp band at around 3300 cm^{-1} in the IR spectrum is

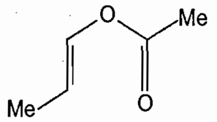
(a) 1, 2-butadiene (b) 1, 3-butadiene
(c) 1-butyne (d) 2-butyne

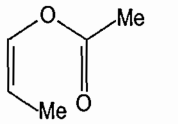
(2 *Marks Questions*)

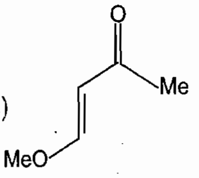
26. In the metathesis reaction given below, 4.32 g of the compound *X* was treated with 822 mg of the catalyst *Y* to yield 2.63 g of the product *Z*. The mol% of the catalyst *Y* used in this reaction is ________.
[Atomic weights of Ru = 101: P = 31; Cl = 35.5].

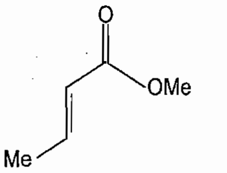


27. An organic compound *Q* exhibited the following spectral data.
IR: 1760 cm^{-1}
^{1}HNMR: δ (ppm) : 7.2 (1H, *d*, *J* = 16.0 Hz), 5.1 (1H, m), 2.1 (3H, s), 1.8 (3H, *d*, *J* = 7.0 Hz) ^{13}CNMR : δ (ppm): 170 (carbonyl carbon).
Compound *Q* is

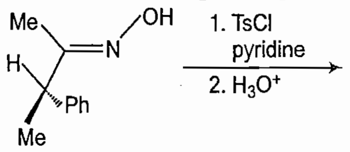
(a) 

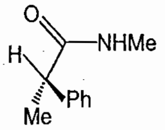
(b) 

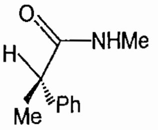
(c) 

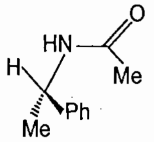
(d) 

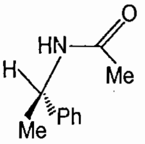
28. The major product formed in the Beckmann rearrangement of the compound given below is



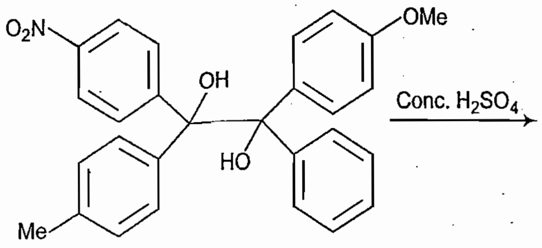
(a) 

(b) 

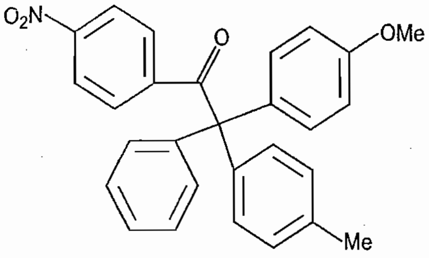
(c) 

(d) 

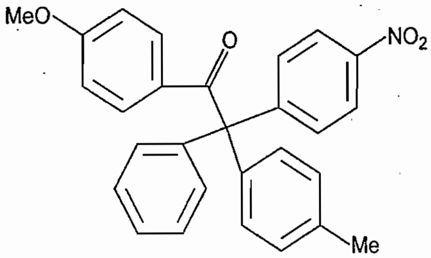
29. The major product formed in the reaction given below is



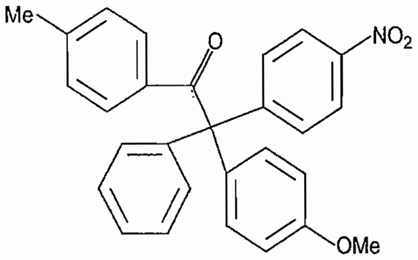
(a)



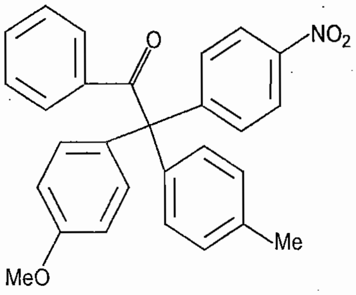
(b)



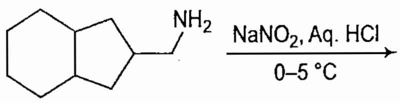
(c)



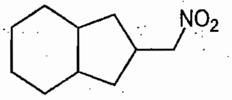
(d)



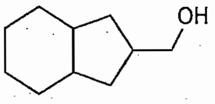
30. The major product formed in the reaction given below is



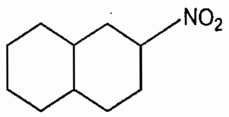
(a)



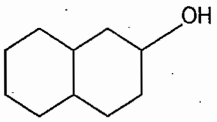
(b)



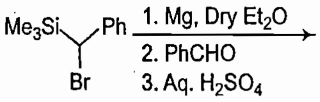
(c)



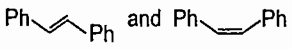
(d)



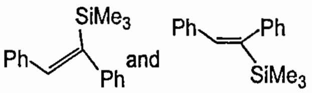
31. The major product(s) formed in the reaction sequence given below is (are)



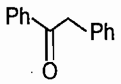
(a)



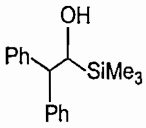
(b)



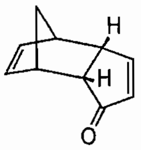
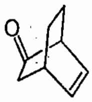
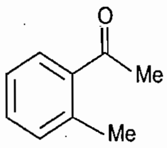
(c)



(d)



32. Match the compounds in the Column I with the photochemical reactions that they can undergo given in the Column II.

Column I	Column II
(i) 	(p) oxa-di-π-methane rearrangement
(ii) 	(q) Paterno-Buchi reaction
(iii) 	(r) Intramolecular [2 + 2] cycloaddition
	(s) Photoenolisation

(a) (i)-(q); (ii)-(s); (iii)-(p)
(b) (i)-(r); (ii)-(p); (iii)-(s)
(c) (i)-(p); (ii)-(r); (iii)-(q)
(d) (i)-(r); (ii)-(q); (iii)-(s)

33. e^{-2x^2} is an eigen function of the operator $\left(\frac{d^2}{dx^2}-16x^2\right)$.

The corresponding eigen value is

(a) + 4 (b) − 4 (c) + 2 (d) − 2

34. The infrared spectrum of HCl gas shows an absorption band centered at 2885 cm^{-1}. The zero point energy of HCl molecule under harmonic oscillator approximation is

(a) 2.8665×10^{-22} J (b) 2.8665×10^{-20} J
(c) 5.7330×10^{-22} J (d) 5.7330×10^{-20} J

35. For the reaction $X_2O_4(l) \longrightarrow 2XO_2(g)$ at 298 K, given the values, $\Delta U = 9$ kJ and $\Delta S = 84$ JK^{-1}, ΔG is

(a) −11.08 kJ (b) +11.08 kJ
(c) −13.55 kJ (d) + 3.55 kJ

36. The change in enthalpy when 3 mol of liquid benzene transforms to the vapour state at its boiling temperature (80°C) and at 1 bar pressure is ____________ kJ.

37. The moment of inertia of a homonuclear diatomic molecule is 7.5×10^{-45} kg m^2. Its rotational partition function at 500 K is ____________.

38. For a reaction of the type $X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Y$, the correct rate expression is ($[X]_0$ and $[X]$ correspond to the concentrations of X at time $t = 0$ and $t = t$, respectively)

(a) $-\frac{d[X]}{dt} = k_1[X]_0 - (k_1 + k_2)[X]$

(b) $-\frac{d[X]}{dt} = (k_1 + k_2)[X] - k_2[X]_0$

(c) $-\frac{d[X]}{dt} = (k_1 + k_2)[X]_0 - k_1[X]$

(d) $-\frac{d[X]}{dt} = (k_1 - k_2)[X] - k_1[X]_0$

39. The temperature dependence of partition functions are as follows

$q_{\text{translation}} \propto T^{3/2}$, $q_{\text{vibration}} \propto T^0$
$q_{\text{rotation}} \propto T$ (linear molecule)
$q_{\text{rotation}} \propto T^{3/2}$ (non-linear molecule)

According to the conventional transition state theory (CTST), the temperature dependence of the Arrhenius pre-exponetial factor for a reaction of the type given below is
linear molecule + linear molecule $\rightleftharpoons$ non-linear transition state → products

(a) T^{-1} (b) T^0 (c) T^1 (d) T^2

40. According to polyhedral electron count rule, the structure of $Rh_6(CO)_{16}$ is

(a) closo (b) nido
(c) arachno (d) hypho

41. Decarbonylation reaction of [*cis*-$(CH_3CO)Mn(^{13}CO)(CO)_4$] yield X, Y and Z, where

$X = [(CH_3)Mn(CO)_5]$; $Y = [cis\text{-}(CH_3)Mn(^{13}CO)(CO)_4]$;

$Z = [trans\text{-}(CH_3)Mn(^{13}CO)(CO)_4]$

The molar ratio of the products $(X:Y:Z)$ in this reaction is

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

42. The increasing order of melting points of the halides NaCl, CuCl and NaF is

(a) CuCl < NaCl < NaF (b) NaF < NaCl < CuCl
(c) NaF < CuCl < NaCl (d) CuCl < NaF < NaCl

43. The correct electronic configuration and spin only magnetic moment of Gd^{3+} (at. no. 64) are

(a) [Xe] $4f^7$ and 7.9 BM
(b) [Xe] $4f^7$ and 8.9 BM
(c) [Xe] $4f^6 5d^1$ and 7.9 BM
(d) [Rn] $5f^7$ and 7.9 BM

44. Among the following octahedral complexes, the one that has the highest enthalpy of hydration is

(a) $[Ca(H_2O)_6]^{2+}$ (b) $[Mn(H_2O)_6]^{2+}$
(c) $[V(H_2O)_6]^{2+}$ (d) $[Cr(H_2O)_6]^{2+}$

45. A metal crystallises in face-centered cubic lattice with a lattice parameter of 4.20 Å. The shortest atom to atom contact distance in the lattice is

(a) 4.20 Å (b) 2.97 Å (c) 2.42 Å (d) 2.10 Å

46. Polarographic method of analysis to obtain individual amounts of Cu^{2+} and Cd^{2+} in a given mixture of the two ions (Cu^{2+} and Cd^{2+}) is achieved by measuring their

(a) half-wave potentials
(b) migration currents
(c) decomposition potentials
(d) diffusion currents

47. The ground state term of $[Ni(H_2O)_6]^{2+}$ is

(a) $^3T_{1g}$ (b) $^3T_{2g}$
(c) $^3A_{2g}$ (d) $^4T_{1g}$

Common Data Questions

Common Data for Questions 48 and 49

N, N-dimethylformamide (DMF) gives different patterns of signals for the methyl protons when its ^{1}HNMR spectrum is recorded at different temperatures.

48. Match the patterns of the NMR signals given in Column I with temperatures given in the Column II.

(i)	Two singlets, for three protons each, at δ 2.87 and 2.97 ppm	(x)	25°C
(ii)	One sharp singlet for six protons at δ 2.92 ppm	(y)	120°C
(iii)	One broad signal for six protons	(z)	150°C

(a) (i)-(x); (ii)-(y); (iii)-(z) (b) (i)-(x); (ii)-(z); (iii)-(y)
(c) (i)-(z); (ii)-(x); (iii)-(y) (d) (i)-(z); (ii)-(y); (iii)-(x)

49. Based on the above data, the calculated difference in the frequencies of the two methyl singlets, if the spectrum is recorded on a 300 MHz spectrometer, is ________ Hz.

Common Data for Questions 50 and 51

Heating a mixture of ammonium chloride and sodium tetrahydridoborate gives one liquid product (X), along with other products, under ambient conditions.

50. Compound X is

(a) $NH_4[BH_4]$

(b) $[(NH_3)_2BH_2][BH_4]$

(c) $N_3B_3H_6$

(d) $N_3B_3H_{12}$

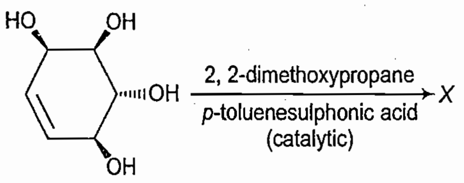
51. Compound X is an example of

(a) ionic liquid
(b) saturated heterocycle
(c) molecular cage
(d) unsaturated heterocycle

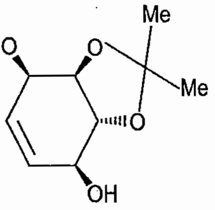
Linked Answer Questions

Linked Answer Questions 52 and 53

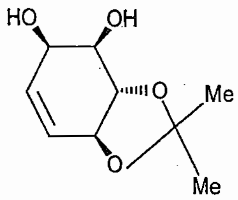
52. The major product X formed in the reaction given below is



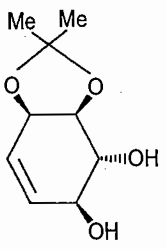
(a)



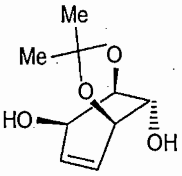
(b)



(c)

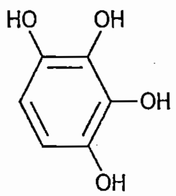


(d)

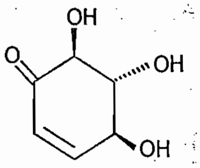


53. Oxidation of the product X obtained in the above reaction, with active manganese dioxide, followed by acidic hydrolysis gives

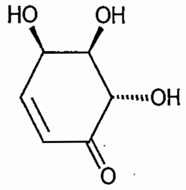
(a)



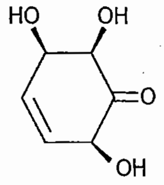
(b)



(c)



(d)



Statement for Linked Answer Questions 54 & 55

The standard half-cell reduction potential of Fe^{3+} (aq) | Fe is − 0.036 V and that of OH^- (aq) | Fe $(OH)_3$ (s) | Fe is −0.786 V.

54. For the determination of solubility product (K_{SP}) of Fe $(OH)_3$, the appropriate cell representation and its emf are, respectively,

(a) $\langle Fe\,|\,Fe(OH)_3\,(s)\,|\,OH^-\,(aq)\,Fe^{3+}\,(aq)\,|\,Fe\rangle$, − 0.750V

(b) $\langle Fe\,|\,Fe^{3+}\,(aq)\,|\,OH^-\,(aq)\,|\,Fe(OH)_3\,(s)\,|\,Fe\rangle$, − 0.750V

(c) $\langle Fe\,|\,Fe(OH)_3\,(s)\,|\,OH^-\,(aq)\,Fe^{3+}\,(aq)\,|\,Fe\rangle$, + 0.750V

(d) $\langle Fe\,|\,Fe^{3+}\,(aq)\,|\,OH^-\,(aq)\,|\,Fe(OH)_3\,(s)\,|\,Fe\rangle$, − 0.822 V

55. The value of $\log_e(K_{sp})$ for Fe $(OH)_3$ at 298 K is

(a) − 38.2
(b) + 87.6
(c) − 96.0
(d) − 87.6

General Aptitude (GA) Questions

(1 *Mark Questions*)

56. If $3 \le X \le 5$ and $8 \le Y \le 11$ then which of the following options is true ?

(a) $\frac{3}{5} \le \frac{X}{Y} \le \frac{8}{5}$
(b) $\frac{3}{11} \le \frac{X}{Y} \le \frac{5}{8}$
(c) $\frac{3}{11} \le \frac{X}{Y} \le \frac{8}{5}$
(d) $\frac{3}{5} \le \frac{X}{Y} \le \frac{8}{11}$

57. The headmaster ________ to speak to you. Which of the following options is incorrect to complete the above sentence?

(a) is wanting
(b) wants
(c) want
(d) was wanting

58. Mahatama Gandhi was known for his humility as

(a) he played an important role in humiliating exit of British from India
(b) he worked for humanitarian causes
(c) he displayed modesty in his interactions
(d) he was a fine human being

59. $\underset{\text{I}}{\underline{\text{All engineering students}}}$ $\underset{\text{II}}{\underline{\text{should learn mechanics}}}$, $\underset{\text{III}}{\underline{\text{mathematics and}}}$, $\underset{\text{IV}}{\underline{\text{how to do computation}}}$.

Which of the above underlined parts of the sentence is not appropriate ?

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

60. Select the pair that best expresses a relationship similar to that expressed in the pair.
Water: Pipe

(a) Cart : Road
(b) Electricity : Wire
(c) Sea : Beach
(d) Music : Instrument

(2 *Marks Questions*)

61. Velocity of an object fired directly in upward direction is given by $V = 80 - 32\,t$, where t (time) is in seconds. When will the velocity be between 32 m/s and 64 m/s?

(a) (1, 3/2) (b) (1/2, 1)
(c) (1/2, 3/2) (d) (1, 3)

62. In a factory, two machines M1 and M2 manufacture 60% and 40% of the autocomponents respectively. Out of the total production, 2% of M1 and 3% of M2 are found to be defective. If a randomly drawn autocomponent from the combined lot is found defective, what is the probability that it was manufactured by M2?

(a) 0.35 (b) 0.45
(c) 0.5 (d) 0.4

63. Following table gives data on tourists from different countries visiting India in the year 2011.

Country	Number of Tourists
USA	2000
England	3500
Germany	1200
Italy	1100
Japan	2400
Australia	2300
France	1000

Which two countries contributed to the one third of the total number of tourists who visited India in 2011 ?

(a) USA and Japan
(b) USA and Australia
(c) England and France
(d) Japan and Australia

64. If $|-2x+9| = 3$ then the possible value of $|-x| - x^2$ would be

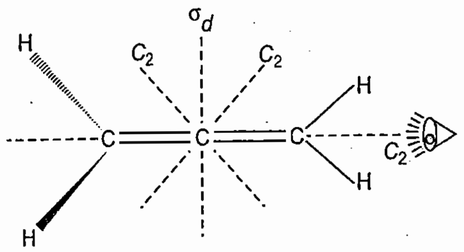
(a) 30 (b) −30
(c) −42 (d) 42

65. All professors are researchers.
Some scientists are professors.
Which of the given conclusions is logically valid and is inferred from the above arguments.

(a) All scientists are researchers
(b) All professors are scientists
(c) Some researchers are scientists
(d) No conclusion follows

Answer *with* Explanations

1. (*d*) Point group of $H_2C=C=CH_2$ is determined as



Symmetry elements $\quad E, C_2, 2C_2 \perp C_2, 2\sigma v, \sigma d$

$\uparrow$

$2C_2$'s are subsidiary axis which are perpendicular to principal C_2 axis passing through all three carbon atoms.

Hence the point group is D_{2d}.

2. (*c*) Given that

$$\phi_1 = c_1 x(a-x) \qquad \text{g.s.} = E_1$$
$$\phi_2 = c_1 x(a-x) + c_2 x^2 (a-x)^2 \qquad \text{g.s.} = E_2$$

Exact ground state energy $= E_0$

For microscopic particle in 1-D box we know that

$$\psi_1 = c_1 x(a-x)$$
$$\psi_2 = c_2 x^2 (a-x)^2$$

and % error calculated for both these trial wave functions by using variation method are 0.125% and 0.5%.

As given in question

	% error
$\phi_1 = \psi_1$	0.125%
$\phi_2 = \psi_1 + \psi_2$	0.125 + 0.5 = 0.625

$\therefore$ True ground state energy of ϕ_2 is less than true ground state energy of ϕ_1

$$\therefore \qquad E_0 < E_2 < E_1$$

3. $$H_2 \longrightarrow 2H$$

Dissociation energy = energy possessed by two H-atom − energy possessed by H_2 molecule

$$= 2 \times (-13.6\ V) - (-31.7\ V)$$
$$= -27.2\ V + 31.7\ V$$
$$= +4.5\ V$$

4.

	H_2	CO_2
Volume	$V_{H_2} = 2L$	$V_{CO_2} = 2L$ Total volume = 4 L
Number of moles	$n_{H_2} = \frac{2}{2} = 1$	$n_{CO_2} = \frac{176}{44} = 4$

Pressure $P_1 = \dfrac{n_{H_2} RT}{V} = 24.6$

$$P_2 = \frac{n_{CO_2}\ RT}{V} = \frac{4 \times 0.0821 \times 300}{4} = 6.15$$

According to dalton law of partial pressure

$$P = P_1 + P_2 = 6.5 + 24.6 \ \Rightarrow\ P = 31.1$$

$P^{\circ}_{H_2}$ (Partial pressure of H_2)

$$= \text{Mole fraction} \times \text{Total pressure}$$
$$= \frac{1}{5} \times 31.1 = 6.22 \text{ bar}$$

5. (*c*) Given equation is

$$2C\,(s) + O_2\,(g) \rightleftharpoons 2CO_2\,(g) \text{ at equilibrium}$$
$$n_R = 1 \qquad n_P = 2$$

Since number of gaseous molecule in product is greater than the number of gaseous molecules in reactant $\Rightarrow n_P = 2 > n_R = 1$

and according to Le-Chatelier principle the equilibrium shift in the direction where number of gaseous particles is minimised which can be done by decreasing pressure of system only.

6. (*d*) $$M_2X \rightleftharpoons 2M^+ + X^{2-}$$
$$2S \qquad S$$
$$K_{sp} = [2S\,\gamma_\pm]^2\,[S\gamma_\pm]$$
$$K_{sp} = 4S^3\,\gamma_\pm^3$$

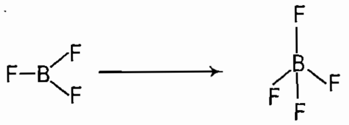
7. (*c*) According to steady state approximation, the concentration of intermediate remains constant throughout the reaction but reactant concentration decreases and concentration of product increases as the reaction proceeds hence the graph showing concentration of P, Q and R are better represented in option (c).

8. Rate of adsorption = rate of desorption (at equilibrium)

$$Ka\,(1-\theta)\,P = Kd\,\theta$$
$$\frac{Ka}{Kd} = \left(\frac{\theta}{1-\theta}\right) \times \frac{1}{P}$$
$$= \left(\frac{0.01}{1-0.01}\right) \times \frac{1}{10} \text{ bar} = 0.0010 \text{ bar}^{-1}$$

Langmuir adsorption constant $(K) = 0.0010 \text{ bar}^{-1}$

9. (*a*)



Trifluoroborane
Number of symmetry operations = 4 × 3 = 12
[For D_3h point group number of symmetry operation = $4n$]

Tetrafluoroborate
Number of symmetry operations = 24

Here number of symmetry operations increases, hence, increase in symmetry occurs.

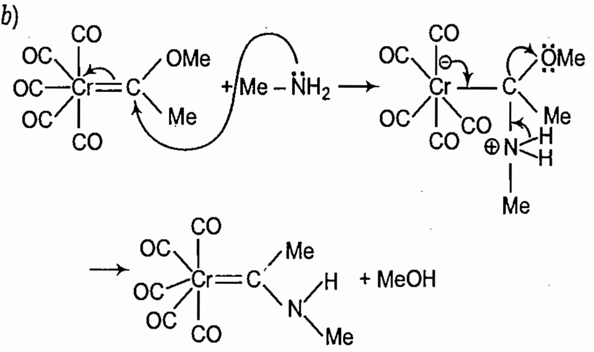
10. (*c*) According to HSAB concept (Pearson theory)
Hard acid has a tendency to combine with hard base and soft acid has a tendency to combine with soft base in order to give the stable product, hence bond is stronger.

$\ddot{N}Me_3 + Be^{2+} \longrightarrow$ Stable product
Hard base Hard acid

$\ddot{P}Me_3 + Pd^{2+} \longrightarrow$ Stable product
Soft base Hard base

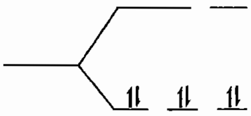
11. (*d*) $\alpha = \beta = \gamma = 90$
$a \neq b \neq c$
These parameters denotes the orthorhombic crystal system.

12. (*b*)



13. (*d*) $[PdCl_4]^{2-}$ is used as catalyst during the reaction which transforms to Pd (0). Co-catalyst $CuCl_2$ is used to convert Pd (0) to Pd (II).

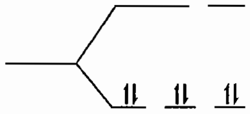
14. (*b*) Oxymyoglobin $Mb(O_2)$ contains Fe (II) present as low spin



$n = 0$

No unpaired electron, hence diamagnetic.

Oxyhaemoglobin Hb $(O_2)_4$ contains Fe (II) as low spin.



$n = 0$

No unpaired electron, hence diamagnetic.

15. According to 18 $e^{\ominus}$ rule, any molecule will be stable if and only if it contain the 18 $e^{\ominus}$ to its outermost orbitals.

Let us consider hapticity of $C_7H_8 = x$ and it follows $18e^{\ominus}$ rule

$Mo\ (C_7H_8)\ (CO)_3$

Contribution of Mo = 6

Contribution of (CO) = 2

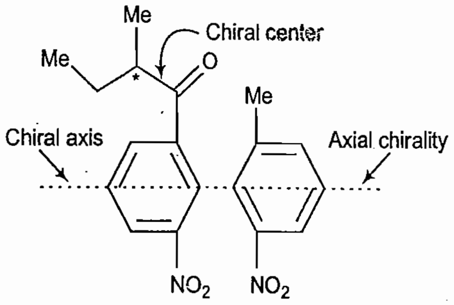
$\therefore$ For Mo $(C_7H_8)\ (CO)_3$

$$6 + x + 2 \times 3 = 18$$
$$x = 18 - 12 = 6$$

$\therefore$ Hapticity of $C_7H_8 = 6$

16. It is a non haem protein used for oxygen storage and contain two Fe (III) atoms. It transfer one oxygen molecule.

17.



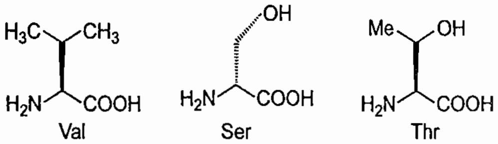
There are 2 types of chirality present in this molecule

(i) Axial chirality due to chiral axis

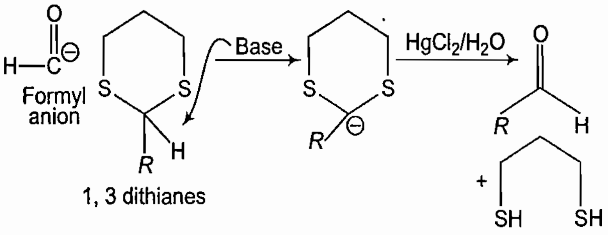
(ii) Chirality due to centre (*)

Hence total number of stereo isomers $= 2^2 = 4$

18. (*a*) Given tripeptide are made up by combination of three amino acid valine, serine and threonine sequentially.

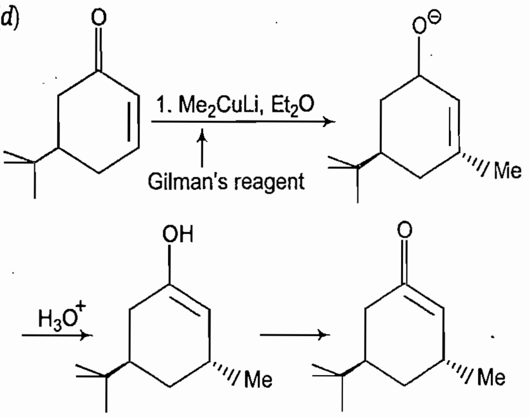


19. (*c*)



This is why 1, 3 dithiane may be used as a formyl anion equivalent in presence of strong base.

20. (*d*)



(i) Gilman's reagent causes 1, 4 addition due to HSAB concept.

(ii) It attacks from back side due to steric hinderance offered from top face by *t*-butyl group.

21. (*a*) This reaction is an example of Hoffmann bromamide reaction which convert amide to amine having one carbon atom lesser than amide.

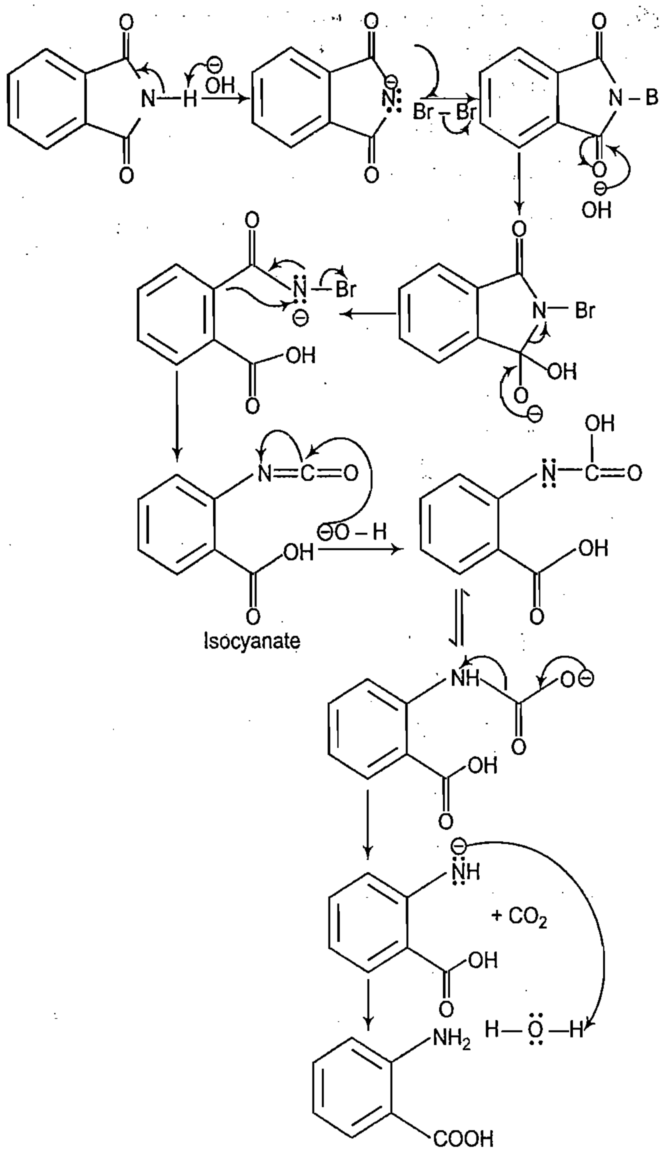
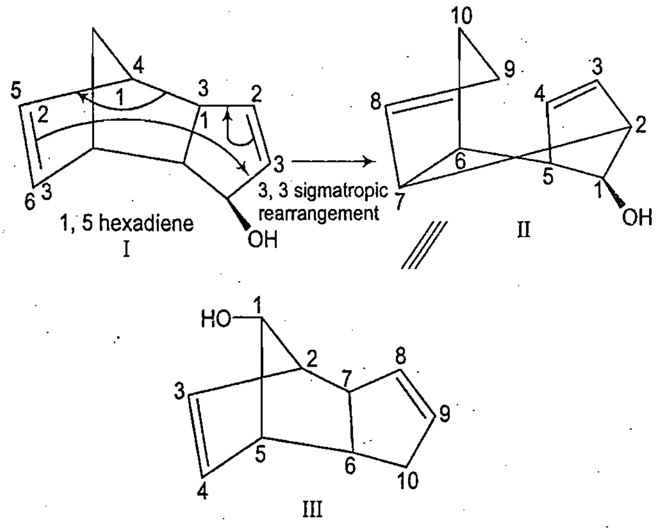
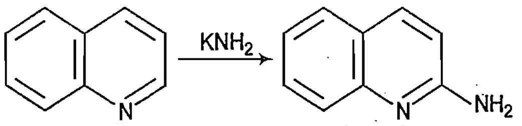


Fig. Hoffman bromamide Reaction

22. (*d*) 3,3 sigmatropic rearrangement is a characteristic property of 1, 5 hexadiene. It occurs by breaking of 1–1 bond as shown below. II and III are the same structure.

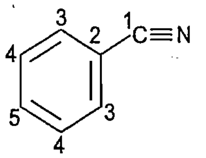


23. (*b*) This is an example of chichibabin reaction and major product is 2 amino quinaoline. This is a nucleophilic substitution reaction occurs at 2nd position of quinoline.



2 amino quinoline

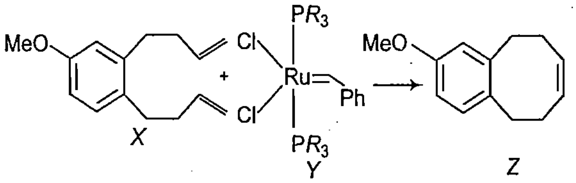
24.



There are 5 different kind of carbon, hence it gives five ^{13}CNMR signals.

25. (*c*) Sharp band at around 3300 cm^{-1} is given by terminal alkyne due to $C \equiv C \overset{\downarrow}{—} H$ streaching. 2 butyne has no C—H bond adjacent to tripple bond, hence 2 butyne does not give sharp band at 3300 cm^{-1} in IR spectrum.

26.



(R = cyclohexyl)

$C_{15}H_{17}O$ $\quad$ $RuP_2Cl_2C_{43}H_{72}$

$$M_X = 15\times12 + 17\times1 + 16$$
$$= 180 + 17 + 16$$
$$= 180 + 33 = 213$$
$$M_Y = 101 + 35.5\times2 + 43\times12 + 72\times1 + 31\times2$$
$$= 101 + 71 + 62 + 43\times12 + 72\times1 = 822$$

Number of moles of $X = \frac{4.32}{213} = 0.021$

Number of moles of $Y = \frac{822}{822}\times10^{-3}\,g = 0.001$ mol

$$\text{Mol \% of } Y = \frac{0.001}{0.001 + 0.021} = \frac{0.001}{0.021}\times100$$
$$= \frac{100}{21} = 4.99$$

27. (*a*) Analysis of IR data = 1760 cm^{-1}

Indicates presence of carbonyl group

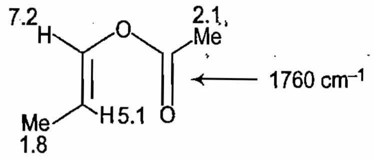
^{1}HNMR : δ (ppm) : 7.2 (1 H.*d*, $J = 16.0$ Hz) ⟵ This value of J is due to *trans* Hydrogen coupling

5.1 (1H, m)

2.1 (3H, S) ← due to 3H of CH_3

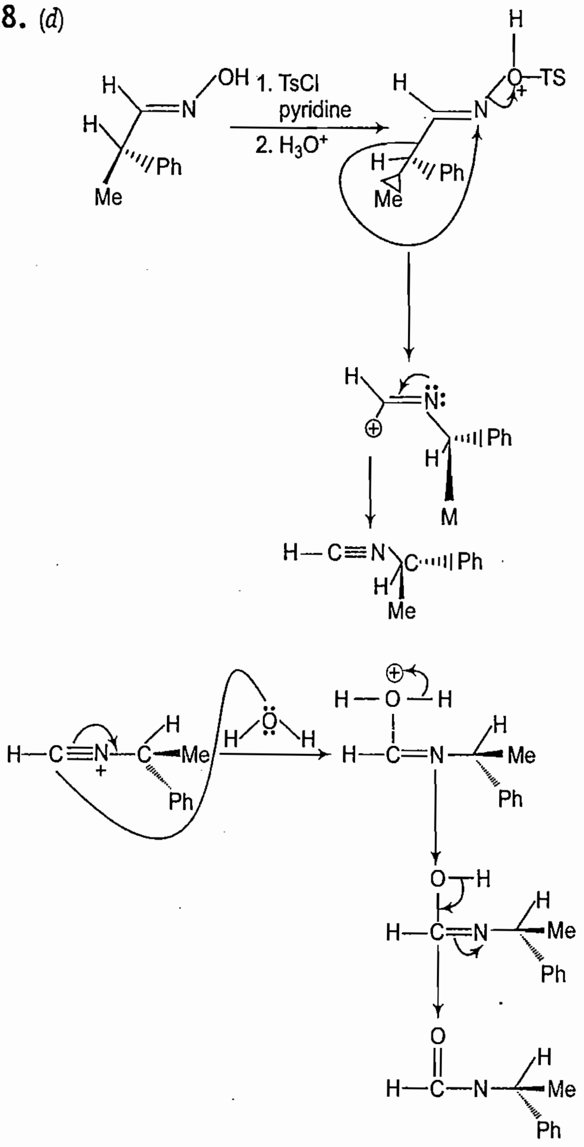
1.8 (*d*, $J = 7.0 H_2$)

^{13}CNMR δ = 170 ppm due to carbonyl carbon.



Value of $J = 16.0\ H_z$ is characteristic value to identify the desired structure.

28. (*d*)



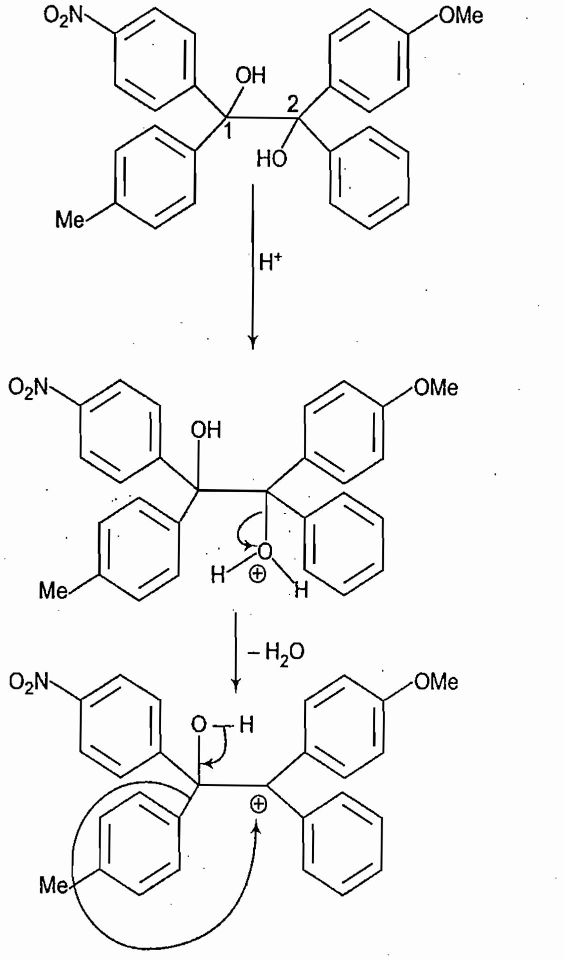
Stereochemistry is preserved

Stereochemistry of Beckmann rearrangement Beckmann rearrangement is a kind of intramolecular reaction in which the group anti to OH migrates with retension in configuration.

29. (*a*) The two fact should be kept in mind before writting the mechanism, of reaction Pinacol-Pinacolone rearrangement

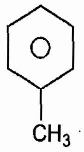
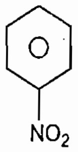
(i) Stability of carbocation

(ii) Group *anti* to OH will migrate intramolecularly

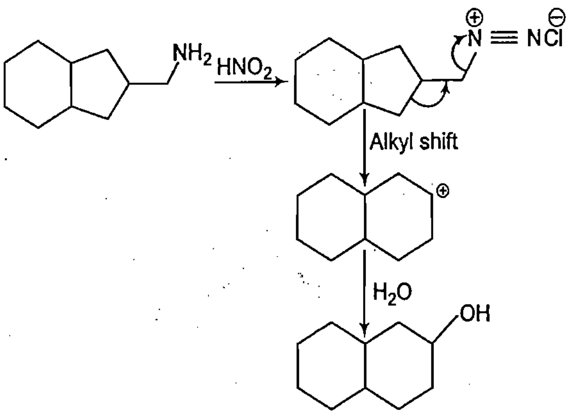


Intramolecular migration of p-methyl phenyl occurs.

Firstly we see more stability of carbocation. So OH of C-2 undergoes dehydration, not OH of C-3 because dehydration of OH from C-3 destabilises carbocation.

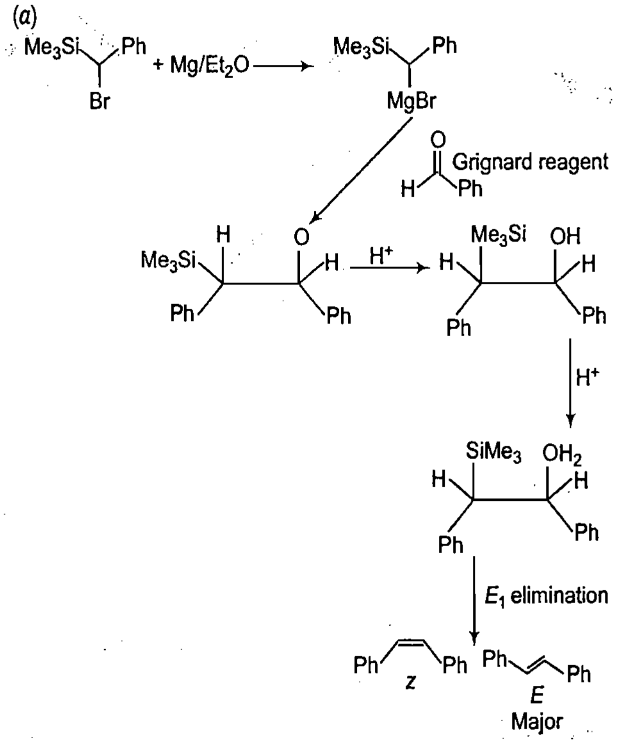
Secondly  undergoes migration due to more migrating aptitude than  and *anti* to removal OH groups.

30. (*d*) $NaNO_2 + HCl \longrightarrow HNO_2$



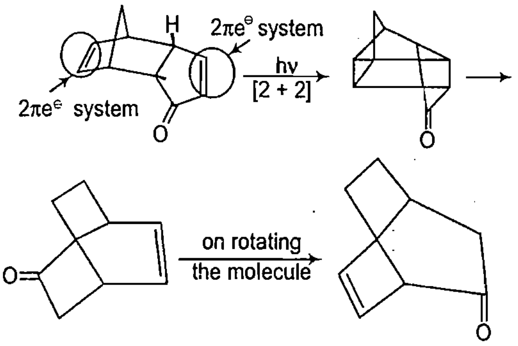
Reaction proceeds *via* diazotization leading to formation of diazonium salt followed by alkyl shift and hydrolysis to give the desired product.

31. (*a*)



E alkene occurs as major product because the bulkier phenyl group are *trans* to each other.

32. (*b*) (i) – (r), (ii) – (p), (iii) – (s)



33. (*b*) $\psi = e^{-2x^2}$ and $\text{Å} = \left(\frac{d^2}{dx^2} - 16x^2\right)$

$$\text{Å}\,(e^{-2x^2}) = a\,(e^{-2x^2})$$

↑ eigen value

$$\left(\frac{d^2}{dx^2} - 16x^2\right)e^{-2x^2} = \frac{d^2}{dx^2}e^{-2x^2} - 16x^2e^{-2x^2}$$

$$= \frac{d}{dx}\cdot\left(\frac{d}{dx}e^{-2x^2}\right) - 16x^2e^{-2x^2}$$

$$= \frac{d}{dx}(-4x\cdot e^{-2x^2}) - 16x^2e^{-2x^2}$$

$$= -\left[4x\frac{d}{dx}e^{-2x^2} + e^{-2x^2}\frac{d}{dx}(4x)\right] - 16x^2e^{-2x^2}$$

$$= -[4x \times (-4x) \times e^{-2x^2} + 4 \times e^{-2x^2}] - 16x^2e^{-2x^2}$$

$$= 16x^2e^{-2x^2} - 4e^{-2x^2} - 16x^2e^{-2x^2}$$

$$= -4 \times e^{-2x^2} = -4\psi$$

Here $a = 4$, $\therefore$ eigen value $= -4$

34. (*b*) Given $\bar{\nu} = 2885\ \text{cm}^{-1}$

We know that, zero point energy of molecule $= \frac{1}{2}h\nu$

$\because\ \nu = \frac{c}{\lambda} = c \times \frac{1}{\lambda} = c\bar{\nu}$ $\qquad \therefore\ \text{ZPE} = \frac{1}{2}hc\bar{\nu}$

$$\Delta E = \frac{1}{2} \times 6.625 \times 10^{-34}\ \text{J.s} \times 3 \times 10^{10}\ \text{cm s}^{-1} \times 2885\ \text{cm}^{-1}$$

$$= \frac{6.625 \times 3 \times 2885}{2} \times 10^{-34+10}\ \text{J} = \frac{57339.375}{2} \times 10^{-24}\ \text{J}$$

$$= 28669.6875 \times 10^{-24} = 2.8669 \times 10^4 \times 10^{-24}$$

$$= 2.86 \times 10^{-20}\ \text{J}$$

35. (*a*) Given reaction is $X_2O_4\,(l) \longrightarrow 2XO_2\,(g)$, $T = 298\,\text{K}$

$\Delta U = 9\,\text{KJ}$ and $\Delta s = 84\ \text{Jk}^{-1}$, $\Delta H = ?$

$\Delta ng = 2 - 0 = 2$

$\Delta H = \Delta U + \Delta ng\,RT$

$= 9\,\text{kJ} + 2 \times 8.314 \times 298 = (9000\ \text{J} + 4955.144)\ \text{J}$

$= 13955.144\ \text{J}$

$\Delta G = \Delta H - T\Delta S$

$= 13955\cdot144\ \text{J} - 298\ \text{k} \times 84\ \text{Jk}^{-1}$

$= 13955\cdot144\ \text{J} - 25032\ \text{J}$

$= -11076.856 = -11.08\ \text{kJ}$

36. According to Troutons rule, entropy of non associated solid is 87 J mol^{-1}, $n = 3$, $T = 80 + 273 = 353$ K

$n\Delta s = \frac{\Delta H_{\text{sub}}}{T_b} \Rightarrow \Delta H_{\text{sub}} = n\Delta s \times T_b = 3 \times 87 \times 353$

$= 92133\ \text{J mol}^{-1}\ \text{k}^{-1}$

$= 92.133\ \text{kJ mole}^{-1}\ \text{k}^{-1}$

37. Rotational partition function may be calculated by using following formula.

$$E_{\text{rot}} = \frac{KT}{\sigma B} = \frac{KT}{\sigma \frac{h^2}{8\pi^2 I}} = \frac{8\pi^2 IKT}{\sigma h^2} \left[\because \bar{B} = \frac{h^2}{8\pi^2 I}\right]$$

where σ = atomicity. Here H_2 is diatomic.

$\therefore \quad \sigma = 2$

Given $I = 7.5 \times 10^{-45}$ kg m^2. Now, we can calculate E_{rot} as

$$E_{\text{rot}} = \frac{8 \times (3.14)^2 \times 7.5 \times 10^{-45} \times 1.38 \times 10^{-23} \times 500}{2 \times (6.626 \times 10^{-34})^2}$$

$$= \frac{8 \times 9.85 \times 7.5 \times 1.38 \times 5 \times 10^{-68} \times 10^2}{2 \times (6.626)^2 \times 10^{-68}}$$

$$= \frac{8 \times 9.85 \times 7.5 \times 1.38 \times 10^2}{2 \times (6.626)^2} = \frac{4077.9 \times 10^2}{87.1828}$$

$$= 46.77 \times 10^2 = 4677 \text{ J}$$

38. (*b*) Rate of reaction = rate of forward reaction − rate of backward reaction

$$-\frac{dx}{dt} = +K_1[X] - [k_2\{[X]_0 - [X]\}]$$

$$= +k_1[X] + k_2[X] - k_2[X]_0$$

$$-\frac{dx}{dt} = [X][k_1 + k_2] - k_2[X]_0$$

$$\frac{dx}{dt} = (k_1 + k_2)[X]_0 - k_2[X]_0$$

39. (*a*) We know that $K = A \cdot e^{-\frac{E_a}{RT}}$

Taking log on both sides $\log K = \log A - \frac{E_a}{RT}$

$$\log A = \log k + \frac{E_a}{RT}$$

$$\log A = \log k + \frac{E_a}{RT}$$

Here we can analyse that A has the inverse relation to T

So $A \propto T^{-1}$ in the correct choice.

40. (*a*) According to polyhedral electron count rule, number of electrons present in

$$Rh_6(CO)_{16} = 6 \times 9 + 16 \times 2$$

$$A = 54 + 32 = 86$$

$$B = \frac{86 - 12 \times 6}{2}$$

$$= \frac{14}{2} = 7$$

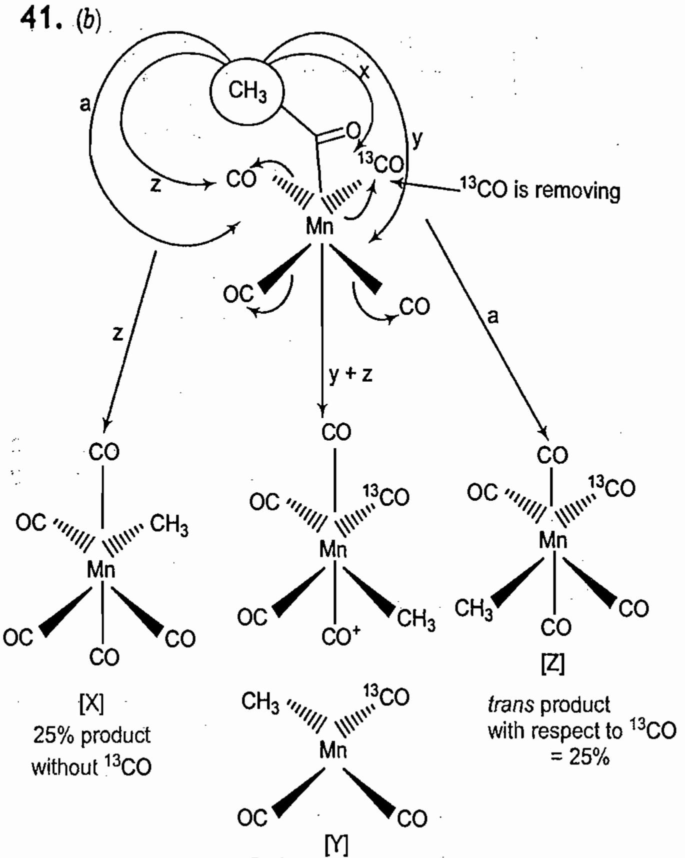
Electron count

$$= \frac{\text{Total number of valence electrons present on compound} - 12 \times \text{number of metals}}{2}$$

Since $7 = n + 1$ where $n = 6$ (6 Rh atom)

$\therefore$ The compound belongs to closo structure.

41. (*b*)



Both are same product obtained by Y and Z pathway.
Hence % of Y (in product)
= 25% + 25% = 50%

42. (*a*) As we know, more ionic crystal have more melting point and we also know that more is the electronegativity difference more is the ionic character. Among the following we can observe that

CuCl ← Covalent
NaCl ← Ionic
NaF ← More ionic

Melting point increases ↓

43. (*a*) Electronic configuration of $_{64}Gd^{3+}$ is = $[_{54}Xe]\,4f^7$

This electronic configuration is only due to extra stable half filled electronic configuration

1	1	1	1	1	1	1

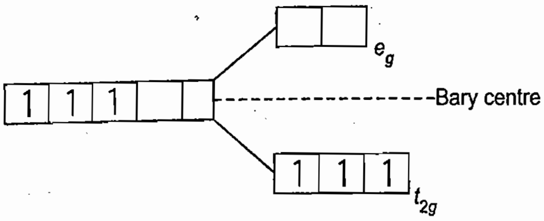
$$L = 0,\ s = 7/2,\ n = 7$$

No $L - S$ coupling because $L = 0$

$$\therefore \quad \mu = \sqrt{n(n+2)} = \sqrt{7(7+2)} = \sqrt{63}$$

$$= 7.9 \text{ BM}$$

44. (*c*) $[V(H_2O_6)]^{2+}$ has V^{2+} metal having $3d^3$ electronic configuration due to which it has maximum negative value of CFSE out of all. Hence has maximum enthalpy of hydration.



$\text{CFSE} = 3x - 0.4 = -1.2\,\Delta_0$

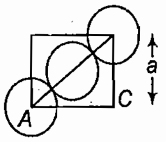
$\text{Mn}^{2+} = d^5$, CFSE = 0

$\text{Cr}^{2+} = d^4 + t_{2g}{}^3 e_g{}'$

$\text{CFSE} = 3x - 0.4 + 0.6 = -1.2 + 0.6 = -0.6\Delta_0$

Greater the negative value of CFSE greater will be its hydration energy.

45. (*b*) Shortest distance $= \frac{AB}{2}$

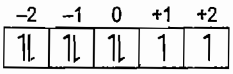


$$\sqrt{2}a = r$$

$$\Rightarrow \quad r = \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}} = \frac{4.20}{1.414}\text{ Å} = 2.97\text{ Å}$$

46. (*d*) **Polarographic method** is based on the voltametric measurement by combined diffusion mass transport using concept of diffusion current. Both metal ions have different standard electrode potential hence they will produce different extent of diffusion current and causes different diffusion mass transport hence they can be analyses using diffusion current.

47. (*c*) $Ni^{2+} = 3d^8$



$L = +1 + 2 = 3$ Term = F

$J = L + S = 3 + 1 = 4$

$S = 1/2 + 1/2 = 1$

$2S + 1 = 3$

$\text{Term} = {}^{2S+1}L_J = {}^3F$

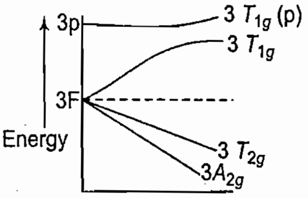
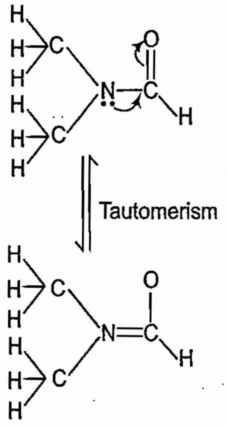


Fig. Orgel diagram of d^8-Oh compound

48. (*b*) According to exclusion principle

$\Delta V \times \Delta T = \text{constant}$



$$\Delta V = \frac{\text{constant}}{\Delta t}$$

where ΔV = bandwidth

ΔT = temperature

As temperature increases width decreases hence at 150°C width is lowest.

These two form occurs in dynamic equilibrium at high temperature, and the difference between these 6H of two methyl cannot be identified hence at high temperature sharp signal will be obtained for the 6H.

49. Chemical shift of two CH_3 hydrogen are at 2.87 and 2.97

∴ Difference in frequency = ΔV

ΔV = (Chemical shift difference between 2 singlet) × frequency of machine

$= (2.97 - 2.87)\text{ppm} \times 300\text{ MHz}$

$= 0.10 \times 300\text{ MHz} \times \text{ppm}$

$= 0.10 \times 300 \times 10^5 \times 10^{-5}$

$\Delta V = 30\text{ Hz}$

50. (*c*) This is a common method of preparation of borazine also known as inorganic benzene.

$$NH_4\,Cl + NaBH_4 \longrightarrow \underset{[X]}{N_3B_3H_6}$$

Ammonium chloride on heating with sodium borohydride gives $N_3B_3H_6$.

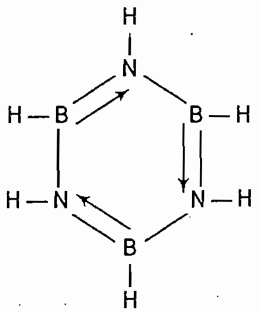
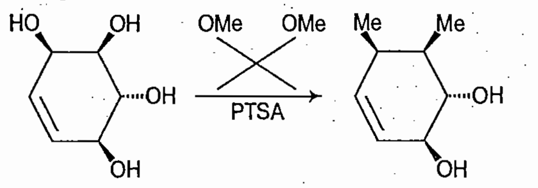


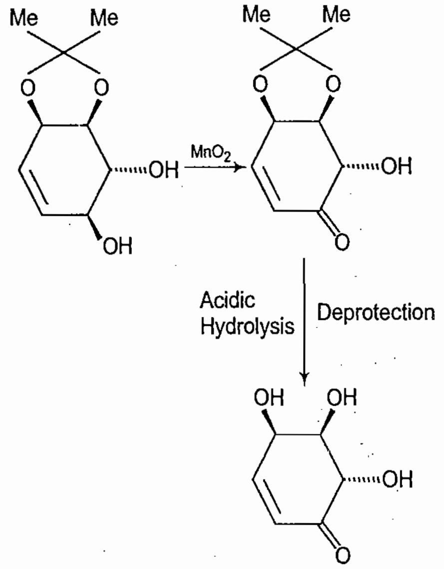
Fig. Structure of Borazine

51. (*d*) Because the compound contain *N* and *B* as cyclic member of heterocycles and have 6π electron cloud. Compound is known as borazines.

52. (*c*) Formation of cyclic acetal occurs from the same face only. Because of steric hindrance *trans* diol cannot undergo cyclic acetal formation.



53. (*c*) MnO_2 causes allylic oxidation and acidic hydrogen causes deprotection of cyclic acetal.



54. (*b*) Half-cell reactions are given below

1. $Fe \longrightarrow Fe^{3+} + 3e^{\ominus}$

$$E^{\circ}_{Fe/Fe^{3+}} = +\,0.036$$

2. $Fe(OH)_3 + 3e^{\ominus} \longrightarrow Fe + 3OH^{\ominus}$

$$E^{\circ}_{Fe(OH)_3/Fe} = -\,0.786$$

On $(1) + (2) \Rightarrow Fe(OH)_3 \longrightarrow Fe^{3+} + 3OH^{\ominus}$

$$E^{\circ} = -\,0.786 + 0.036 = (-0.750\text{ V})$$

This can be represented as

$$\underbrace{\langle Fe\,|\,Fe^{3+}(aq)|}_{\text{Oxidation half cell}}\ \underbrace{OH^{\ominus}(aq)\,|\,Fe(OH)_3(s)\,|\,Fe\rangle}_{\text{Reduction half cell}}$$

55. (*d*) Nernst equation for above reaction may be written as

$$E_{cell} = \frac{RT}{nF}\log_e K_{sp}$$

$$\log_e K_{sp} = \frac{E_{cell}\times nF}{RT} = \frac{-\,0.750\times 3\times 96500}{8.314\times 298}$$

$$= -\frac{217125}{2477.52} = -\,87.63$$

56. (*b*) $\frac{3}{11} \le \frac{x}{y} \le \frac{5}{8}$ ∵ $\frac{\text{lower numerator}}{\text{higher denominator}} = \text{lower value}$

57. (*c*) Because the Head master is 3rd person hence it is necessary to use plural verb with it but want is a singular verb so option (c) is incorrect.

58. (*c*) He displayed modesty in his interaction because Gandhi is a person when he meet with any one his behaviour attract the person.

59. (*d*) How to do computation is not appropriate it should be the computation only. Because subject should be use after should.

60. (*b*) Electricity-Wire as water flow through pipe, electricity flow through wire.

61. (*c*) By putting the given value in options, we get only option (c) is correct.

$$V = 80 - 32\times\frac{1}{2} = 80 - 16 = 64\text{ m/s} \leftarrow \text{maximum value.}$$

$$V = 80 - 32\times\frac{3}{2} = 80 - 48 = 32\text{ m/s} \leftarrow \text{minimum value.}$$

Range will be from 32 m/s to 64 m/s.

62. (*c*)

	M_1	M_2
Total manufacture or production	60%	40%
Defective	$\frac{60\times 2}{100}$ $=1.2$	$\frac{40\times 3}{100}$ 1.2

Probability of M_2 selection for defective piece

$$= \frac{\text{Defective piece manufactured by } M_2}{\text{Total defective piece}}$$

$$= \frac{1.2}{1.2 + 1.2} = 0.5$$

63. (*c*) England and France contribution = 3500 + 1000

= 4500 tourists

Total tourists = 13500

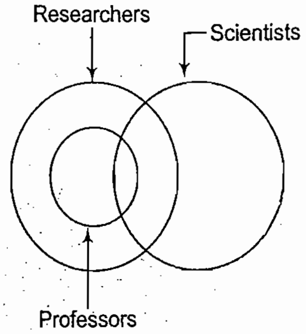
Contribution of England and France combinely

$$= \frac{4500}{13500} = \frac{1}{3}$$

64. (*b*) Given $-2x + 9 = 3 - 2x = 12$; $x = -6$

Now $|-x| - x^2 = |-(-6)| - 6^2 = 6 - 36 = -30$

65. (*c*) Some researchers are scientists.



GATE

Chemistry

Solved Paper 2012

Time : 3 hrs] **[MM : 100**

Read the following instructions carefully.

1. All questions in this paper are of objective type.
2. There is a total of 65 questions carrying 100 marks.
3. Questions 1 to 25 will carry 1 mark each and questions 26 to 55 will carry 2 marks each.
4. Questions 48 to 51 (2 pairs) are common data questions and questions pairs 52 and 53 and 54 and 55 are linked answer questions. The answer to the second question of the linked answer questions depends on the answer to the first question of the pair. If the first question in the linked pair is wrongly answered or is unattempted, then the answer to the second question in the pair will not be evaluated.
5. Questions 56 to 65 belong to General Aptitude (GA). Questions 56 to 60 will carry 1 mark each and questions 61 to 65 will carry 2 marks each.
6. Unattempted questions will carry zero marks.
7. Wrong answers will carry negatie marks. For questions 1 to 25 and 56 to 60, $\frac{1}{3}$ mark will be deducted for each wrong answer. For questions 26 to 51 and 61 to 65, $\frac{2}{3}$ mark will be deducted for each wrong answer. The question pairs (questions 52 and 53) and (questions 54 and 55) are questions with linked answer. There will be negative marks only for wrong answer to the first question of the linked answer question pair *i.e.,* for questions 52 and 54, $\frac{2}{3}$ mark will be deducted for each wrong answer. There is no negative marking for questions 53 and 55.

Atomic Structure

1. If Δy and Δp_y are the uncertainties in the y-coordinate and the y component of the momentum of a particle respectively then according to uncertainty principle $\Delta y \Delta p_y$ is ($\hbar = \frac{h}{2\pi}$ and h is Planck's constant) **[1 Mark]**

(a) $\geq \hbar$ (b) $> \frac{\hbar}{2}$ (c) $> \hbar$ (d) $\geq \frac{\hbar}{2}$

2. The angular part of the wave function for the electron in a hydrogen atom is proportional to $\sin^2\theta\cos\theta e^{2i\phi}$. The values of the azimuthal quantum number (l) and the magnetic quantum number (m) are, respectively

(a) 2 and 2 (b) 2 and −2 **[1 Mark]**
(c) 3 and 2 (d) 3 and −2

3. The wave function of a 1-D harmonic oscillator between $x = +\infty$ and $x = -\infty$ is given by $\psi(x) = N(2x^2 - 1)e^{-x^2/2}$. The value of N that normalizes the function $\psi(x)$ is

[Given, $\int_{-\infty}^{+\infty} x^{2n} e^{-x^2} dx = \frac{1 \cdot 3 \cdot 5 \ldots (2n-1)}{2^n}\sqrt{\pi}$] **[2 Marks]**

(a) $\left(\frac{1}{8\sqrt{\pi}}\right)^{1/2}$ (b) $\left(\frac{1}{3\sqrt{\pi}}\right)^{1/2}$

(c) $\left(\frac{1}{2\sqrt{\pi}}\right)^{1/2}$ (d) $\left(\frac{1}{4\sqrt{\pi}}\right)^{1/2}$

Chemical Bonding and Molecular Structures

4. Let ϕ_x^C and ϕ_z^C denote the wave functions of the $2p_x$ and $2p_z$ orbitals of carbon, respectively, and ϕ_x^O and ϕ_z^O represent the wave functions of the $2p_x$ and $2p_z$ orbitals of oxygen, respectively. If c_1 and c_2 are constants used in linear combinations and the CO molecule is oriented along the z axis, then according to molecular orbital theory, the π-bonding molecular orbital has a wave function given by **[1 Mark]**

(a) $c_1\phi_z^C + c_2\phi_x^O$ (b) $c_1\phi_z^C + c_2\phi_z^O$

(c) $c_1\phi_x^C + c_2\phi_z^O$ (d) $c_1\phi_x^C + c_2\phi_x^O$

5. The complex with *inverse*-spinel structure is **[1 Mark]**

(a) Co_3O_4 (b) Fe_3O_4

(c) $MgAlO_4$ (d) Mn_3O_4

6. The order of polarity of NH_3, NF_3 and BF_3 is **[1 Mark]**

(a) $NH_3 < NF_3 < BF_3$ (b) $BF_3 < NF_3 < NH_3$

(c) $BF_3 < NH_3 < NF_3$ (d) $NF_3 < BF_3 < NH_3$

7. Symmetry operations of the four C_2 axes perpendicular to the principal axis belong to the same class in the point group(s) **[2 Marks]**

(a) D_4 (b) D_{4d}

(c) D_{4h} (d) D_{4h} and D_{4d}

8. For a face centred cubic lattice, the Miller indices for the first Bragg's peak (smallest Bragg angle) are **[2 Marks]**

(a) 0 0 2 (b) 1 1 1

(c) 0 0 1 (d) 1 1 0

Statement for Linked Answer Questions 9 and 10

Huckel molecular orbital theory can be applied to the allene radical

$$CH_2{=}CH{-}\dot{C}H_2$$

9. The secular determinant (where α, β and E have their usual meanings) is given by **[2 Marks]**

(a) $\begin{vmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix}$

(b) $\begin{vmatrix} \alpha-E & 0 & 0 \\ 0 & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix}$

(c) $\begin{vmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & 0 \\ 0 & 0 & \alpha-E \end{vmatrix}$

(d) $\begin{vmatrix} \alpha-E & -\beta & 0 \\ -\beta & \alpha-E & -\beta \\ 0 & -\beta & \alpha-E \end{vmatrix}$

10. The possible values of E are **[2 Marks]**

(a) $\alpha + \sqrt{2}\beta, \alpha, \alpha - \sqrt{2}\beta$ (b) $\alpha + 2\sqrt{2}\beta, \alpha\ \alpha - 2\sqrt{2}\beta$

(c) $\alpha + \beta, \alpha, \alpha - \beta$ (d) $\alpha + 2\beta, \alpha, \alpha - 2\beta$

s-Block and *p*-Block Elements

11. Among the following substituted silanes, the one that gives cross-linked silicone polymer upon hydrolysis is **[1 Mark]**

(a) $(CH_3)_4Si$ (b) CH_3SiCl_3

(c) $(CH_3)_2SiCl_2$ (d) $(CH_3)_3SiCl$

12. If a mixture of NaCl, conc. H_2SO_4 and $K_2Cr_2O_7$ is heated in a dry test tube, a red vapour (P) is formed. This vapour (P) dissolves in aqueous NaOH to form a yellow solution, which upon treatment with $AgNO_3$ forms a red solid (Q). P and Q are, respectively **[2 Marks]**

(a) CrO_2Cl_2 and $Ag_2Cr_2O_7$

(b) $Na_2[CrOCl_5]$ and Ag_2CrO_4

(c) $Na[CrOCl_5]$ and $Ag_2Cr_2O_7$

(d) CrO_2Cl_2 and Ag_2CrO_4

Transition Elements

13. A metal chelate that can be used for separation and quantitative analysis of aluminium ions by gas chromatography is **[1 Mark]**

(a) EDTA (b) ethylene glycol

(c) dinonyl phthalate (d) trifluoroacetylacetone

14. The enthalpies of hydration of Ca^{2+}, Mn^{2+} and Zn^{2+} follow the order **[1 Mark]**

(a) $Mn^{2+} > Ca^{2+} > Zn^{2+}$ (b) $Zn^{2+} > Ca^{2+} > Mn^{2+}$

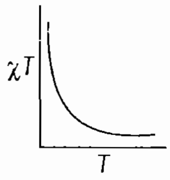
(c) $Mn^{2+} > Zn^{2+} > Ca^{2+}$ (d) $Zn^{2+} > Mn^{2+} > Ca^{2+}$

15. The number of terminal carbonyl groups present in $Fe_2(CO)_9$ is **[1 Mark]**

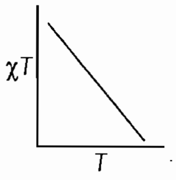
(a) 2 (b) 5 (c) 6 (d) 3

16. The plot of χT *versus* T (where, χ is molar magnetic susceptibility and T is the temperature) for a paramagnetic complex which strictly follows Curie equation is **[1 Mark]**

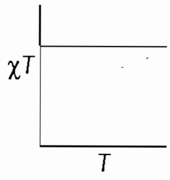
(a)



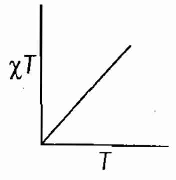
(b)



(c)



(d)



17. The IUPAC nomenclature of $Na[PCl_6]$ is **[1 Mark]**

(a) sodium hexachlorophosphine (V)
(b) sodium hexachlorophosphate (V)
(c) sodium hexachlorophosphine
(d) sodium hexachlorophosphite (V)

18. Consider the following pairs of complexes

$[CoF(NH_3)_5]^{2+}$ and $[Cr(OH_2)_6]^{2+}$
$[Co(NH_3)_5(OH_2)]^{3+}$ and $[Cr(OH_2)_6]^{2+}$
$[Co(NH_3)_6]^{3+}$ and $[Cr(OH_2)_6]^{2+}$
$[CoI(NH_3)_5]^{2+}$ and $[Cr(OH_2)_6]^{2+}$

The electron transfer rate will be fastest in the pair **[2 Marks]**

(a) $[CoF(NH_3)_5]^{2+}$ and $[Cr(OH_2)_6]^{2+}$
(b) $[Co(NH_3)_5(OH_2)]^{3+}$ and $[Cr(OH_2)_6]^{2+}$
(c) $[Co(NH_3)_6]^{3+}$ and $[Cr(OH_2)_6]^{2+}$
(d) $[CoI(NH_3)_5]^{2+}$ and $[Cr(OH_2)_6]^{2+}$

19. The extent of Mossbauer quadrupole splitting of iron follows the order **[2 Marks]**

(a) $FeCl_2 \cdot 4H_2O > K_2[Fe(CN)_5(NO)] > FeCl_3 \cdot 6H_2O$
(b) $K_2[Fe(CN)_5(NO)] > FeCl_2 \cdot 4H_2O > FeCl_3 \cdot 6H_2O$
(c) $FeCl_3 \cdot 6H_2O > K_2[Fe(CN)_5(NO)] > FeCl_2 \cdot 4H_2O$
(d) $FeCl_2 \cdot 4H_2O > FeCl_3 \cdot 6H_2O > K_2[Fe(CN)_5(NO)]$

20. Haemoglobin is an oxygen carrying protein. The correct statement about oxy-haemoglobin is that **[2 Marks]**

(a) the metal is low-spin in +3 oxidation state while dioxygen is in O_2^- form
(b) the metal is high-spin in +3 oxidation state while dioxygen is in O_2^- form
(c) the metal is low-spin in +3 oxidation state while dioxygen is in neutral form
(d) the metal is high-spin in +3 oxidation state while dioxygen is in neutral form

21. The ground states of high-spin octahedral and tetrahedral Co(II) complexes are, respectively **[2 Marks]**

(a) $^4T_{2g}$ and $^4A_2$
(b) $^4T_{1g}$ and $^4A_2$
(c) $^3T_{1g}$ and $^4A_2$
(d) $^4T_{1g}$ and $^3T_1$

22. The incorrect statement about Zeise's salt is **[2 Marks]**

(a) Zeise's salt is diamagnetic
(b) The oxidation state of Pt in Zeise's salt is +2
(c) All the Pt—Cl bond lengths in Zeise's salt are equal
(d) C—C bond length of ethylene moiety in Zeise's salt is longer than that of free ethylene molecule

23. The number of possible isomers for the square planar mononuclear complex $[(NH_3)_2M(CN)_2]$ of a metal M is **[2 Marks]**

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

Chemical and Ionic Equilibrium

24. If x_A and x_B are the respective mole fractions for A and B in an ideal solution of the two and T_A, T_B, T are the fusion temperatures of pure A, pure B and the ideal solution respectively, then **[1 Mark]**

(a) $$1 - x_B = \exp\left[\frac{-\Delta H^\circ_{fus(B)}}{R}\left(\frac{1}{T} - \frac{1}{T_B}\right)\right]$$

(b) $$1 - x_B = \exp\left[\frac{\Delta H^\circ_{fus(A)}}{R}\left(\frac{1}{T} - \frac{1}{T_A}\right)\right]$$

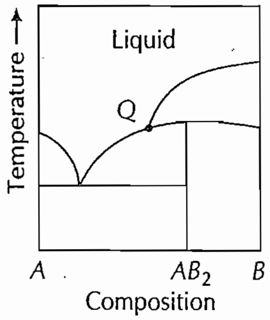
(c) $$1 - x_B = \exp\left[\frac{\Delta H^\circ_{fus(B)}}{R}\left(\frac{1}{T} - \frac{1}{T_B}\right)\right]$$

(d) $$1 - x_B = \exp\left[\frac{-\Delta H^\circ_{fus(A)}}{R}\left(\frac{1}{T} - \frac{1}{T_A}\right)\right]$$

25. Among the following donors, the one that forms most stable adduct with the Lewis acid $B(CH_3)_3$ is **[1 Mark]**

(a) 4-methylpyridine
(b) 2, 6-dimethylpyridine
(c) 4-nitropyridine
(d) 2, 6-di-*tert*-butylpyridine

26. Consider the phase diagram given below



At the intersection point Q the phases that are in equilibrium are **[2 Marks]**

(a) solid A, solid B and solid AB_2
(b) solid A, solid AB_2 and liquid
(c) solid B, solid AB_2 and liquid
(d) solid A, solid B, solid AB_2 and liquid

27. For the titration of a 10 mL (aq) solution of $CaCO_3$, 2 mL of 0.001 M Na_2EDTA is required to reach the end point. The concentration of $CaCO_3$ (assume molecular weight of $CaCO_3 = 100$) is **[2 Marks]**

(a) 5×10^{-4} g/mL
(b) 2×10^{-4} g/mL
(c) 5×10^{-5} g/mL
(d) 2×10^{-5} g/mL

Electrochemistry

28. At 298 K, the EMF of the cell,

$\text{Pt}\,|H_2(1\text{ bar})|\,H^+(\text{solution})\,||\,Cl^-\,|Hg_2Cl_2\,|Hg$

is 0.7530 V. The standard potential of the calomel electrode is 0.2802 V. If the liquid junction potential is zero, the pH of the solution is **[2 Marks]**

(a) 4.7 (b) 7.4 (c) 8.0 (d) 12.7

29. For the following reaction,

$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

$E^\circ(MnO_4^- / Mn^{2+}) = +1.51\text{V}$

and $E^\circ(CO_2 / H_2C_2O_4) = -0.49$ V. At 298 K, the equilibrium constant is **[2 Marks]**

(a) 10^{500} (b) 10^{338} (c) 10^{38} (d) 10^{833}

Chemical Kinetics

30. For a reaction involving two steps given below

First step $G \rightleftharpoons 2H$

Second step $G + H \longrightarrow P$

Assume that the first step attains equilibrium rapidly. The rate of formation of P is proportional to **[1 Mark]**

(a) $[G]^{1/2}$ (b) $[G]$ (c) $[G]^2$ (d) $[G]^{3/2}$

31. Consider the reaction, $H_2 + C_2H_2 \longrightarrow C_2H_6$

The molecular diameters of H_2 and C_2H_4 are 1.8 Å and 3.6 Å respectively. The pre-exponential factor in the rate constant calculated using collision theory in $m^3(mol)^{-1}\,s^{-1}$ is approximately (For this reaction at 300K, $\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} N_A = 1.11\times10^{27}\,\text{m (mol)}^{-1}\text{s}^{-1}$, where the symbols have their usual meanings) **[2 Marks]**

(a) 2.5×10^{8} (b) 2.5×10^{14}

(c) 9.4×10^{7} (d) 9.4×10^{23}

Chemical Thermodynamics

32. The molecular partition function of a system is given by

$$q(T) = \left(\frac{k_BT}{hc}\right)^{3/2}\left(\frac{8\pi^3mk_BT}{h^2}\right)^{3/2},$$ where the symbols have their usual meanings. The heat capacity at constant volume for this system is **[2 Marks]**

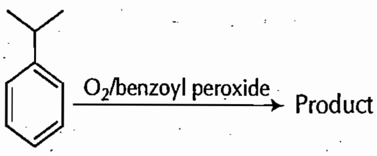
(a) $3R$ (b) $6R$ (c) $9R/2$ (d) $3R/2$

Basics of Organic Reaction Mechanism

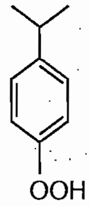
33. In the proton decoupled ^{13}C NMR spectrum of 7-norbornanone, the number of signals obtained is **[1 Mark]**

(a) 7 (b) 3 (c) 4 (d) 5

34. Identify the most probable product in the given reaction.



[1 Mark]

(a)


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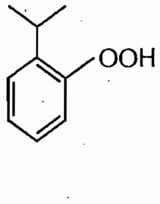

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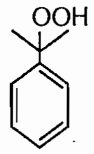
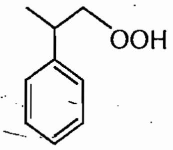
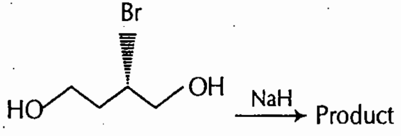
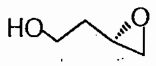
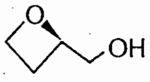


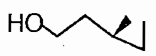
(d)


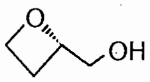
35. In the cyclization reaction given below, the most probable product formed is **[1 Mark]**



(a)


(b)


(c)


(d)


36. The average length of a typical α-helix comprised of 10 amino acids is **[1 Mark]**

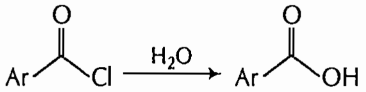
(a) 10 Å (b) 15 Å (c) 36 Å (d) 54 Å

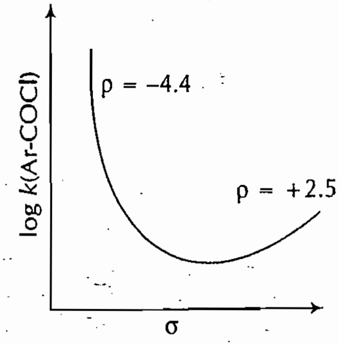
37. Number of thymine residues in a 5000 kb DNA containing 23% guanine residues is **[1 Mark]**

(a) 2.70×10^{6} (b) 2.70×10^{7}

(c) 1.35×10^{6} (d) 1.35×10^{7}

38. Shown below is a Hammett plot obtained for the reaction





The change in slope of the plot indicates that **[1 Mark]**

(a) the reaction does not follow linear free energy relationship
(b) electrons are being withdrawn from the transition state in the mechanism
(c) electrons are being donated to the transition state in the mechanism
(d) the mechanism of the reaction is changing

39. The ratio of relative intensities of the two molecular ion peaks of methyl bromide (CH_3Br) in the mass spectrum is **[1 Mark]**
(a) $M^+ : (M+2)^+ = 1:3$ (b) $M^+ : (M+2)^+ = 3:1$
(c) $M^+ : (M+2)^+ = 1:1$ (d) $M^+ : (M+2)^+ = 1:2$

40. A disaccharide that will not give Benedict's test and will not form osazone is **[1 Mark]**
(a) maltose (b) lactose
(c) cellobiose (d) sucrose

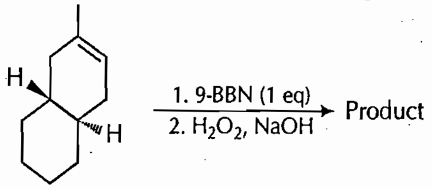
41. Choose the allowed transition **[1 Mark]**
(a) $^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ (b) $^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^-$
(c) $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ (d) $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^-$

42. The bond that gives the most intense band in the infrared spectrum for its stretching vibration is **[1 Mark]**
(a) C—H (b) N—H
(c) O—H (d) S—H

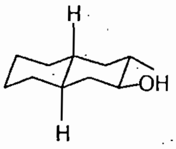
43. An intermediate formed during the hydroformylation of olefins using $Co_2(CO)_8$ as catalyst is **[1 Mark]**
(a) $HCo(CO)_6$ (b) $H_4Co(CO)_3$
(c) $H_2Co(CO)_4$ (d) $HCo(CO)_4$

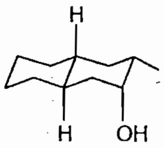
44. From a carboxymethyl-cellulose column at pH 6.0, arginine, valine and glutamic acid will elute in the order **[2 Marks]**
(a) arginine, valine, glutamic acid
(b) arginine, glutamic acid, valine
(c) glutamic acid, arginine, valine
(d) glutamic acid, valine, arginine

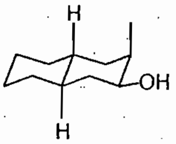
45. Identify the product from the following reaction.

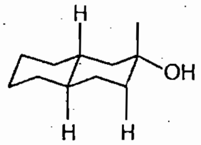


(9-BBN = 9-Borabicyclo [3·3·1] nonane) **[2 Marks]**

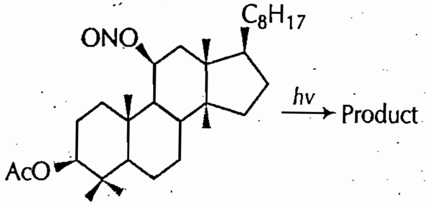
(a)


(b)


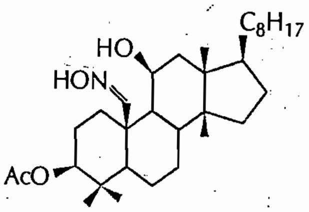
(c)


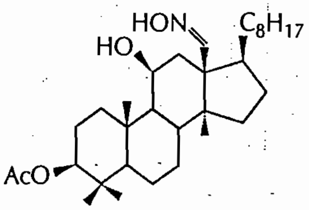
(d)


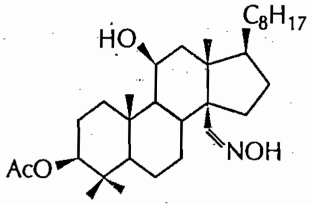
46. The product from the following reaction is

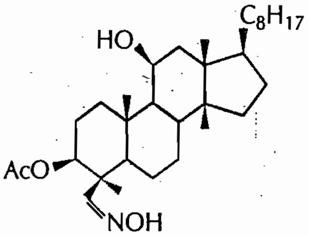


[2 Marks]

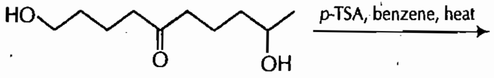
(a)


(b)


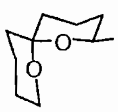
(c)


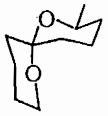
(d)


47. The acid catalyzed cyclization of 5-ketodecan-1, 9-diol is given below

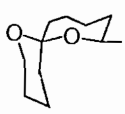


Spiroketal (*p*-TSA = *p*-toluenesulphonic acid)
The most predominant spiroketal is **[2 Marks]**

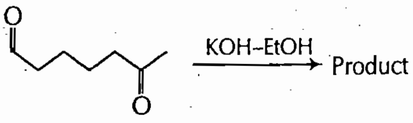
(a)


(b)


(c)

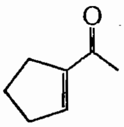

(d)


48. In the reaction

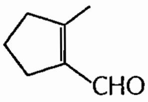


the product formed is **[2 Marks]**

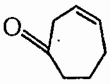
(a)



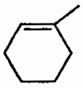
(b)



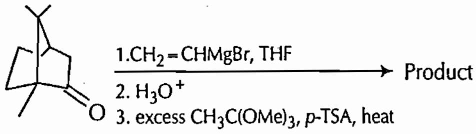
(c)



(d)

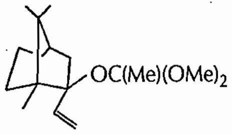


49. In the reaction given below, identify the product

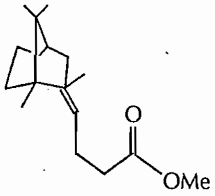


(p-TSA = p-toluenesulphonic acid;
THF = tetrahydrofuran) **[2 Marks]**

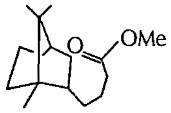
(a)



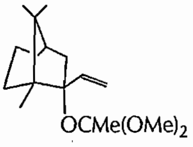
(b)



(c)

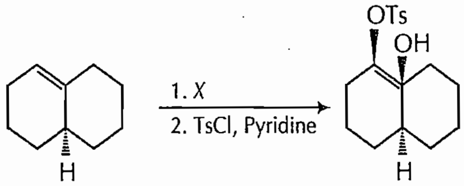


(d)



Common Data for Questions 50 and 51

Consider the reaction shown below

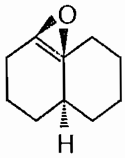


TsCl = p-toluenesulphonyl chloride

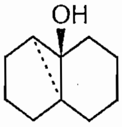
50. The oxidant X used in step 1 is **[2 Marks]**
(a) CrO_3
(b) OsO_4
(c) $NaIO_4$
(d) m-CPBA followed by NaOH

51. The product is **[2 Marks]**

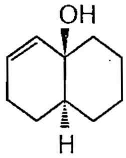
(a)



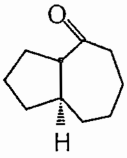
(b)



(c)

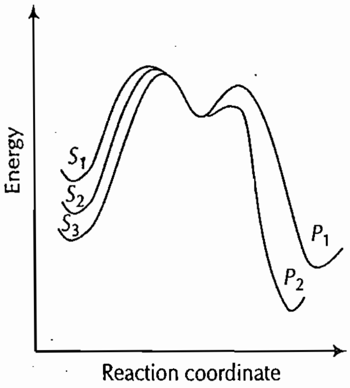


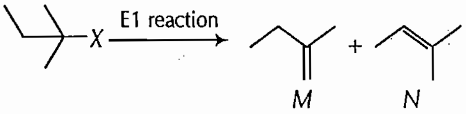
(d)



Common Data for Questions 52 and 53

Consider the E1 reaction of *tert*-amyl halides from the energy profile given below:





52. In the above reaction, X = Cl, Br or I. Based on the graph, identify the alkyl halides (R-X) as S1, S2 and S3 **[2 Marks]**
(a) S1 = R—Cl, S2 = R—Br and S3 = R—I
(b) S1 = R—I, S2 = R—Br and S3 = R—Cl
(c) S1 = R—Cl, S2 = R—I and S3 = R—Br
(d) S1 = R—I, S2 = R—Cl and S3 = R—Br

53. Identify product P_1 and its yield relative to P_2 **[2 Marks]**
(a) P_1 is M and is the major product
(b) P_1 is N and is the minor product
(c) P_1 is N and is the major product
(d) P_1 is M and is the minor product

Statement for Linked Answer Questions 54 and 55

A 20491 cm^{-1} laser line was used to excite oxygen molecules (made of ^{16}O only) to obtain the rotational Raman spectrum. The resulting rotational Raman spectrum of oxygen molecule has the first Stokes line at 20479 cm^{-1}.

54. The rotational constant (usually denoted as B) for the oxygen molecule is **[2 Marks]**
(a) 1.2 cm^{-1} (b) 2.0 cm^{-1}
(c) 3.0 cm^{-1} (d) 6.0 cm^{-1}

55. The next rotational Stokes line is expected at **[2 Marks]**
(a) 20467 cm^{-1} (b) 20469 cm^{-1}
(c) 20471 cm^{-1} (d) 20475 cm^{-1}

General Aptitude

56. If $(1.001)^{1259} = 3.52$ and $(1.001)^{2062} = 7.85$, then $(1.001)^{3321} =$ **[1 Mark]**
(a) 2.23 (b) 4.33
(c) 11.37 (d) 27.64

57. One of the parts (a, b, c, d) in the sentence given below contains an error. Which one of the following is incorrect? **[1 Mark]**

I requested that he should be given the driving test today instead of tomorrow.

(a) requested that (b) should be given
(c) the driving test (d) instead of tomorrow

58. Which one of the following options is the closest in meaning to the word given below? **[1 Mark]**

Latitude

(a) Eligibility (b) Freedom
(c) Coercion (d) Meticulousness

59. Choose the most appropriate word from the options given below to complete the following sentence:

Given the seriousness of the situation that he had to face, his ____ was impressive. **[1 Mark]**

(a) beggary (b) nomenclature
(c) jealousy (d) nonchalance

60. Choose the most appropriate alternative from the options given below to complete the following sentence.

If the tired soldier wanted to lie down, he ____ the mattress out on the balcony. **[1 Mark]**

(a) should take (b) shall take
(c) should have taken (d) will have taken

61. One of the legacies of the Roman legions was discipline. In the legions, military law prevailed and discipline was brutal. Discipline on the battlefield kept units obedient, intact and fighting, even when the odds and conditions were against them. **[2 Marks]**

Which one of the following statements best sums up the meaning of the above passage?

(a) Through regimentation was the main reason for the efficiency of the Roman legions even in adverse circumstances
(b) The legions were treated inhumanly as if the men were animals
(c) Discipline was the armies' inheritance from their seniors
(d) The harsh discipline to which the legions were subjected to led to the odds and conditions being against them

62. A and B are friends. They decide to meet between 1 pm and 2 pm on a given day. There is a condition that whoever arrives first will not wait for the other for more than 15 minutes. The probability that they will meet on that day is **[2 Marks]**

(a) $\frac{1}{4}$ (b) $\frac{1}{16}$
(c) $\frac{7}{16}$ (d) $\frac{9}{16}$

63. The data given in the following table summarizes the monthly budget of an average household. **[2 Marks]**

Category	Amount (₹)
Food	4000
Clothing	1200
Rent	2000
Savings	1500
Other expenses	1800

The approximate percentage of the monthly budget not spent on savings is

(a) 10% (b) 14%
(c) 81% (d) 86%

64. There are eight bags of rice looking alike, seven of which have equal weight and one is slightly heavier. The weighing balance is of unlimited capacity. Using this balance, the minimum number of weighings required to identify the heavier bag is **[2 Marks]**

(a) 2 (b) 3
(c) 4 (d) 8

65. Raju has 14 currency notes in his pocket consisting of only ₹ 20 notes and ₹ 10 notes. The total money value of the notes is ₹ 230. The number of ₹ 10 notes that Raju has is **[2 Marks]**

(a) 5 (b) 6
(c) 9 (d) 10

Answers with Explanations

1. (d) According to Heisenberg's uncertainty principle,

$$\Delta y \cdot \Delta p_y \geq \frac{h}{4\pi}$$

where, Δy = uncertainty in position

and Δp_y = uncertainty in momentum

or $$\Delta y \cdot \Delta p_y \geq \frac{\hbar}{2} \qquad \left(\because \hbar = \frac{h}{2\pi}\right)$$

2. (c) Angular part of wave function, *i.e.*,

$$y_{l,m}(\theta, \phi) \propto \sin^2\theta \cos\theta e^{2i\phi} \qquad \text{(given)}$$

We know that,

$$\theta_{l,m}, \text{ i.e., } \theta_{3,\pm 2} = \frac{1}{\sqrt{2\pi}} e^{+2i\phi}$$
$$\propto e^{+2i\phi}$$

$\therefore \ l = 3$ and $m = +2$

3. (c) Given, $\psi(x) = N(2x^2 - 1)e^{-x^2/2}$

For normalizable function,

$$\psi = \int \psi \cdot \psi dx = 1$$
$$= \int_{-\infty}^{+\infty} \psi^2 dx = 1$$
$$\Rightarrow \quad N^2 \int_{-\infty}^{+\infty} (2x^2 - 1)^2 e^{-x^2} dx = 1$$
$$\Rightarrow \quad N^2 \int_{-\infty}^{+\infty} (4x^4 e^{-x^2} + e^{-x^2} - 4x^2 e^{-x^2}) dx = 1$$
$$\Rightarrow N^2(3\sqrt{\pi} + \sqrt{\pi} - 2\sqrt{\pi}) = 1 \quad \left[\because \int_{-\infty}^{+\infty} e^{-x^2} dx = \sqrt{\pi}\right]$$
$$\therefore \quad N = \left(\frac{1}{2\sqrt{\pi}}\right)^{1/2}$$

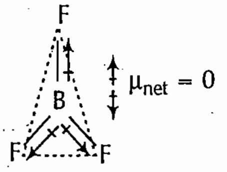
4. (d) Since, the CO molecule is oriented along the *z*-axis, combination of ϕ_z and ϕ_z results in the formation of σ bonding orbitals while combination of either ϕ_x and ϕ_x or ϕ_y and ϕ_y results in the formation of π bonding orbital.

$\therefore$ The wave function for π-bonding molecular orbital

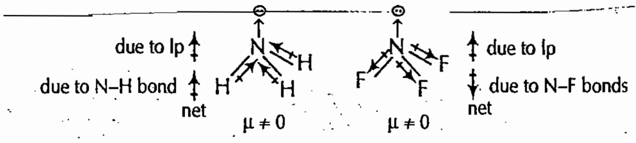
$$= c_1\phi_x^C + c_2\phi_x^O$$

5. (b) General formula of spinel and inverse spinel is $A^{2+}B_2^{3+}O_4^{2-}$. The main point of difference is that A^{2+} ions have a strong preference for the octahedral site and B^{3+} adopt the tetrahedral sites in inverse spinel structure. Such an arrangement is found in Fe_3O_4($Fe^{2+} \cdot Fe_2^{3+}O_4$) *i.e.*, Fe_3O_4 has inverse spinel structure.

6. (b) BF_3 has symmetrical structure (trigonal planar). That's why its net dipole moment is zero.



NH_3 and NF_3 has the pyramidal geometry as



Since, the direction of dipoles due to lone pair and due to bond is opposite in case of NF_3, its dipole moment is less than that of NH_3.

So, the order of polarity is

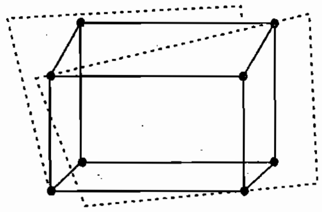
$$BF_3 < NF_3 < NH_3$$

7. (a) If no symmetry elements except for C_n and nC_2 axes which are perpendicular to the principal (C_n) axis, are present, the molecule belongs to D_n symmetry point group.

Given, $4C_2$ axes $\perp C_n$ axis

So, the point group is D_4.

8. (b) For a face centred cubic lattice, the Miller indices for the first Bragg's peak (smallest Bragg angle) are 111.



9. (a) $CH_2{=}CH{-}\dot{C}H_2$

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} \end{bmatrix}$$

$$H_{11} = S_{22} = H_{33} = \alpha$$
$$H_{12} = S_{21} = H_{23} = H_{32} = \beta$$
$$H_{13} = H_{31} = 0$$
$$S_{11} = S_{22} = S_{33} = 1$$

and $S_{12} = S_{21} = S_{23} = S_{23} = S_{13} = S_{31} = 0$

On putting values in the above matrix, we get

$$\begin{bmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{bmatrix}$$

Note In a secular determinant,

(i) all diagonal elements αE

(ii) off-diagonal elements between neighbouring atoms β

(iii) all other elements = 0.

10. (a) $\begin{bmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{bmatrix}$

or $\begin{bmatrix} \frac{\alpha - E}{\beta} & \frac{\beta}{\beta} & \frac{0}{\beta} \\ \frac{\beta}{\beta} & \frac{\alpha - E}{\beta} & \frac{\beta}{\beta} \\ \frac{0}{\beta} & \frac{\beta}{\beta} & \frac{\alpha - E}{\beta} \end{bmatrix}$

$$= \begin{bmatrix} \frac{\alpha - E}{\beta} & 1 & 0 \\ 1 & \frac{\alpha - E}{\beta} & 1 \\ 0 & 1 & \frac{\alpha - E}{\beta} \end{bmatrix} = 0$$

Let $\frac{\alpha - E}{\beta} = x$ or $E = \alpha - x\beta$ ...(i)

$\therefore \quad \begin{bmatrix} x & 1 & 0 \\ 1 & x & 0 \\ 0 & 1 & x \end{bmatrix} = 0$

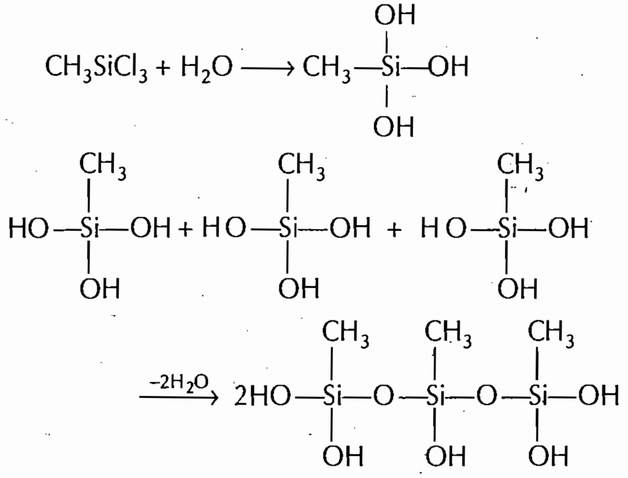
On solving we get,

$$x^2 = 0; x = 0$$
$$x^2 = 2; x = \pm\sqrt{2}$$

On putting the value of x in eq. (i), we get

$$E = \alpha + \sqrt{2}\beta, \alpha, \alpha - \sqrt{2}\beta$$

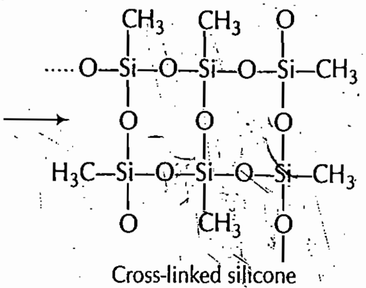
11. (b) Monoalkyl trichlorosilane on hydrolysis gives complex cross-linked silicone polymer.



$$CH_3SiCl_3 + H_2O \longrightarrow CH_3\text{—}\underset{OH}{\overset{OH}{Si}}\text{—}OH$$

$$HO\text{—}\underset{OH}{\overset{CH_3}{Si}}\text{—}OH + HO\text{—}\underset{OH}{\overset{CH_3}{Si}}\text{—}OH + HO\text{—}\underset{OH}{\overset{CH_3}{Si}}\text{—}OH$$

$$\xrightarrow{-2H_2O} 2HO\text{—}\underset{OH}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{OH}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{OH}{\overset{CH_3}{Si}}\text{—}OH$$



Cross-linked silicone

12. (d) $K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow \underset{\substack{\text{red vapours} \\ 'P'}}{2CrO_2Cl_2} + 2KHSO_4 + 4NaHSO_4 + 3H_2O$

$$CrO_2Cl_2 + 2NaOH \longrightarrow \underset{\text{yellow solution}}{Na_2CrO_4} + HCl$$

$$Na_2CrO_4 + 2AgNO_3 \longrightarrow \underset{\substack{\text{red solid} \\ 'Q'}}{Ag_2CrO_4} + NaNO_3$$

13. (d) Al^{3+} form chelate with trifluoroacetylacetone which is used for the separation and quantitative analysis of aluminium ion by gas chromatography.

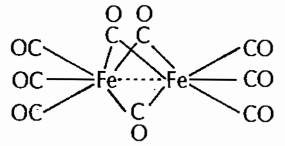
14. (d) The electronic configuration of the given ions is as

$$Ca^{2+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6$$
$$Mn^{2+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5$$
$$Zn^{2+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}$$

Thus, the size of Zn^{2+} ion is smallest and of Ca^{2+} is largest among the three due to increase in effective nuclear charge with increase in atomic number. Smaller the size of ion, higher is the hydration enthalpy. Thus, the order of hydration enthalpy is

$$\underset{(2047\,\text{kJmol}^{-1})}{Zn^{2+}} > \underset{(1841\,\text{kJmol}^{-1})}{Mn^{2+}} > \underset{(1577\,\text{kJmol}^{-1})}{Ca^{2+}}$$

15. (c) The structure of $Fe_2(CO)_9$ is as



Thus, it contains 6 terminal and 3 bridging carbonyl groups.

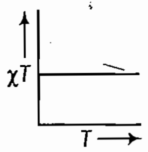
16. (c) The magnetic susceptibility of a paramagnetic substance χ_{para}, would decrease with increase in temperature. The variation of χ_{para} with temperature is given as

$$\chi_{para} = \frac{C}{T}$$

$$\chi_{para} T = C$$

(where, C = Curie constant)

Thus, the plot of χT *versus* T is



17. (b) In $Na[PCl_6]$, let the oxidation state of P is x.

$$+1 + x + (-1)6 = 0$$
$$x - 5 = 0$$
$$\therefore \quad x = +5$$

$\therefore$ The IUPAC name of $Na[PCl_6]$ is sodium hexachlorophosphate(V).

18. (d) In all the reaction, one of the reactant is $[Cr(H_2O)_6]^{2+}$ which is a very labile complex ion and can easily lose a water molecule. It acts as a reducing agent.

Among the other reactants, $[CoI(NH_3)_5]^{2+}$ is the most reactive as I is capable of forming a bridge with the reductant leading to the formation of the intermediate bridge complex.

$$[CoI(NH_3)_5]^{2+} + [Cr(H_2O)_6]^{2+} \xrightarrow[-H_2O]{\text{Slow}} [(H_2O)_5Cr{-}I{-}Co(NH_3)_5]^{4+}$$

$$[(H_2O)_5Cr{-}I{-}Co(NH_3)_5]^{4+} \xrightarrow[\text{Fast}]{\text{Hydrolysis}} [Cr(H_2O)_5I]^{2+} + [Co(NH_3)_5(H_2O)]^{2+}$$

Note The above reaction involves inner sphere mechanism.

19. (b) The extent of Mossbauer quadrupole splitting varies inversely with the number of unpaired electrons, so the order of splitting is

	$K_2[Fe(CN)_5(NO)]$ >	$FeCl_2 \cdot 4H_2O$ >	$FeCl_3 \cdot 6H_2O$
Unpaired e⁻	0	4	5
ΔE_a	1.76 mm/s	0.300 mm/s	0.02 mm/s

20. (a) Oxygenated haemoglobin $[Hb(O_2)_4]$ is diamagnetic in nature, so there are following three posibilities about the nature of Fe and O_2.

(i) Low spin $\underset{\text{(diamagnetic)}}{Fe^{2+}} + \underset{\text{(diamagnetic)}}{\text{Singlet O}} \longrightarrow$ diamagnetic

(ii) Low spin $\underset{\text{1(unpaired electron)}}{Fe^{3+}}$

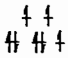
$+ \underset{\text{(1unpaired e}^-)}{O_2^-} \rightarrow$ Antiferromagnetic ally diamagnetic

(iii) Low spin $\underset{\text{(diamagnetic)}}{Fe^{4+}} + \underset{\text{(diamagnetic)}}{O_2^{2-}} \longrightarrow$ diamagnetic

Out of these (ii) resembles to be option (a).

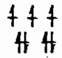
21. (b) $Co^{2+} = [Ar]3d^7$

In octahedral field



$4T_{1g}$ (from Orgel dig)

In tetrahedral field



$4A_2$ (from Orgel dig)

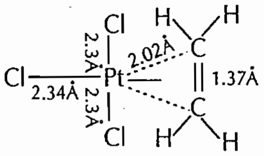
22. (c) The formula of Zeise's salt is $K[PtCl_3(C_2H_4)] \cdot H_2O$.

Let the oxidation state of Pt is x.

$$K[PtCl_3(C_2H_4)]H_2O$$
$$+1 + x + (-1) \times 3 + 0 + 0 = 0$$
$$+1 + x - 3 = 0$$
$$x = +2$$

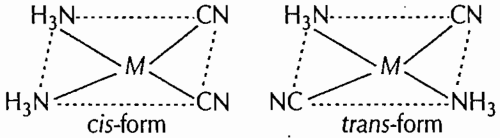
Pt = + 2

The structure of Zeise's salt is



(Normal C=C length = 1.34 Å)

23. (a) The possible isomers of $[(NH_3)_2M(CN)_2]$ are



cis-form *trans*-form

Thus, the number of possible isomers is 2.

24. (b) Chemical potentials of A in two phases are given as,

$$\mu_A^*(s) = \mu_A^*(l) + RT\ln x_A$$
$$\ln x_A = \frac{\mu_A^*(s) - \mu_A^*(l)}{RT}$$
$$\ln x_A = \frac{\Delta_{\text{fus}}G}{RT}$$

On differentiating both sides with respect to T, we get

$$\frac{d\ln x_A}{dT} = \frac{1}{R}\frac{d(\Delta_{\text{fus}}G/T)}{dT} = -\frac{\Delta_{\text{fus}}H}{RT^2}$$

On multiplying both sides by dT and integrating from $x_A = 1(\ln x_A = 0)$ to x_A, we get

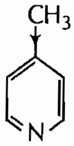
$$\int_0^{\ln x_A} d\ln x_A = -\frac{1}{R}\int_{T_A}^{T} \frac{\Delta_{\text{fus}}H}{T^2}dT$$

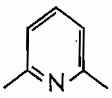
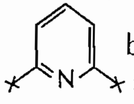
$$\ln x_A = \frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T_A}\right) \qquad (\because x_A + x_B = 1)$$

$$\text{or} \quad \ln(1 - x_B) = \frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T_A}\right)$$

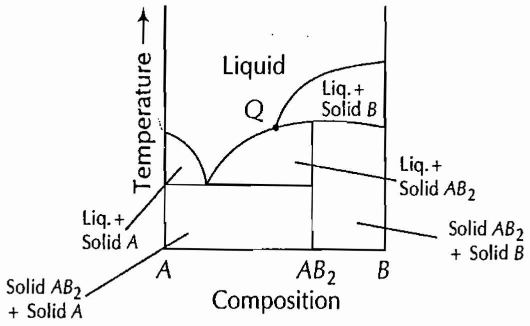
25. (a) The base in which lone pairs are more available for donation, forms most stable adduct with the Lewis acid, $B(CH_3)_3$.

Presence of electron releasing groups like Me, makes the e^- more available for donation, whereas an electron withdrawing group decreases the electron releasing tendency of the base.

Thus,  forms the most stable adduct with $B(CH_3)_3$.

 and  both are crowded molecules so do not form adduct with Lewis acids.

26. (c) At point Q, solid AB_2, solid B and liquid are in equilibrium.



27. (d) $Na_2\text{ EDTA} + CaCO_3 \longrightarrow \text{CaEDTA} + 2Na^+$

$$N_1V_1(CaCO_3) = N_2V_2(Na_2\text{ EDTA})$$

$$N_1 \times 10 = 2 \times 0.002\text{N}$$

($\because$ For Na_2EDTA, 1N = 2M)

$$N_1 = \frac{4\times10^{-3}}{10} = 4\times10^{-4}$$

$$\text{Molarity} = \frac{\text{Normality}}{2} \qquad (\text{For } CaCO_3)$$

$$= \frac{4\times10^{-4}}{2}$$

$$= 2\times10^{-4}\text{ mol/L}$$

$$= \frac{2\times10^{-4}\times100}{1000}\text{ g/mL}$$

$$= 2\times10^{-5}\text{ g/mL}$$

28. (c) $E_{cell} = 0.7530$ V

$$E^\circ_{Hg_2^{2+}/Hg} = 0.2802\text{ V}$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= 0.2802 - 0 = 0.2802\text{ V}$$

The half-cell reactions are

$$H_2 \longrightarrow 2H^+ + 2e^-$$

$$Hg_2^{2+} + 2e^- \longrightarrow Hg$$

$$H_2 + Hg_2^{2+} \longrightarrow 2H^+ + Hg$$

Net cell reaction

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[H^+]^2}{[Hg_2^{2+}]p_{H_2}}$$

Since, the liquid junction potential is zero,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log[H^+]^2$$

$$0.7530 = 0.2802 - \frac{0.0591}{2}2\log[H^+]$$

$$0.7530 - 0.2802 = \frac{0.0591\times2}{2}[-\log[H^+]]$$

$$0.4728 = 0.0591\text{pH}$$

$$\text{pH} = \frac{0.4728}{0.0591} = 8$$

29. (b) $2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + + 8H_2O + 10CO_2$

Given, $E^\circ_{MnO_4^-/Mn^{2+}} = 1.51\text{V}$

and $E^\circ_{CO_2/H_2C_2O_4} = -0.49$ V

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= 1.51 - (-0.49)$$

$$= 2\text{V}$$

The half-cell reactions are:

$$[MnO_4^- + 5e^- \longrightarrow Mn^{2+}]\times2$$

$$[2CO_2 + 2e^- \longrightarrow C_2O_4^{2-}]\times5$$

So, the balanced equation is

$$2MnO_4^- + 5C_2O_4^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

and number of electrons involved, $n = 10$

At 298 K,

$$E^\circ_{cell} = \frac{0.0591\text{V}}{n}\log K_c$$

$$2 = \frac{0.0591\text{V}}{10}\log K_c$$

$$\log K_c = \frac{2\times10}{0.0591}$$

$$= \frac{20}{0.0591} \approx 338$$

$$K_c = \text{antilog } 338 = 10^{338}$$

30. (d) For first step,

$$K_c = \frac{[H]^2}{[G]}$$

$$[H]^2 = K_c\cdot[G]$$

$$\text{or} \qquad [H] = K_c^{1/2}[G]^{1/2} \qquad \ldots\text{(i)}$$

For second step,

Rate of formation of $P = \frac{d[P]}{dt} = k_1[G][H]$

On putting the value of $[H]$ from eq. (i), we get

$$\frac{d[P]}{dt} = K_c^{1/2}\cdot K_1[G][G]^{1/2}$$

$$= K'[G]^{3/2} \qquad [\because K' = K_c^{1/2}\cdot K_1]$$

$$\frac{d[P]}{dt} \propto [G]^{3/2}$$

31. (a) Pre-exponential factor (from collision theory),

$$A = \sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A$$

where, σ = collision cross-section = πd^2

and $d = \frac{1}{2}(d_A + d_B)$

$$d = \frac{1}{2}(1.8 + 3.6) = \frac{1}{2}(5.4) = 2.7$$

$$\sigma = \pi d^2 = 3.14 \times (2.7)^2 (A^\circ)^2 = 22.9\ (A^\circ)^2$$

$$= 22.9 \times 10^{-20}\ \text{m}^2$$

$$\therefore \quad A = \sigma\left(\frac{8k_bT}{\pi\mu}\right)^{1/2} N_A$$

$$= 22.9 \times 1.11 \times 10^{27} \times 10^{-20}$$

$\text{m}^3(\text{mol}^{-1})\text{s}^{-1}$

$$= 2.5 \times 10^8\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

32. (a) $C_v = N\left(\frac{\partial <\varepsilon^M>}{\partial T}\right)_v$

$$= N\cdot k_B\,\beta^2\left(\frac{\partial <\varepsilon^M>}{\partial \beta}\right)_v \qquad \left(\because \beta = \frac{1}{K_BT}\right)$$

$$= \frac{1}{k_BT^2}\left(\frac{\partial^2 \ln q}{\partial \beta^2}\right)N$$

$$q = \left(\frac{k_BT}{hc}\right)^{3/2}\left(\frac{8\pi^3 mk_BT}{h^2}\right)^{3/2}$$

$$= \left(\frac{1}{hc\beta}\right)^{3/2}\left(\frac{8\pi^3 m}{h^2\beta}\right)^{3/2}$$

$$= \left(\frac{1}{hc}\cdot\frac{8\pi^3 m}{h^2}\right)^{3/2}\frac{1}{\beta^3}$$

$$\ln q = \frac{3}{2}\ln\left(\frac{1}{hc}\cdot\frac{8\pi^3 m}{h^2}\right) - 3\ln\beta$$

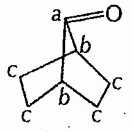
Differentiating w.r.t. β,

$$\frac{\partial \ln q}{\partial \beta} = -\frac{3}{\beta}$$

$$\frac{\partial^2 \ln q}{\partial \beta^2} = +\frac{3}{\beta^2}$$

$$\therefore \quad C_V = \frac{1}{k_BT^2}\cdot 3 \times k_B^2T^2 \times N = 3R$$

33. (b) The structure of 7-norbornanone is as



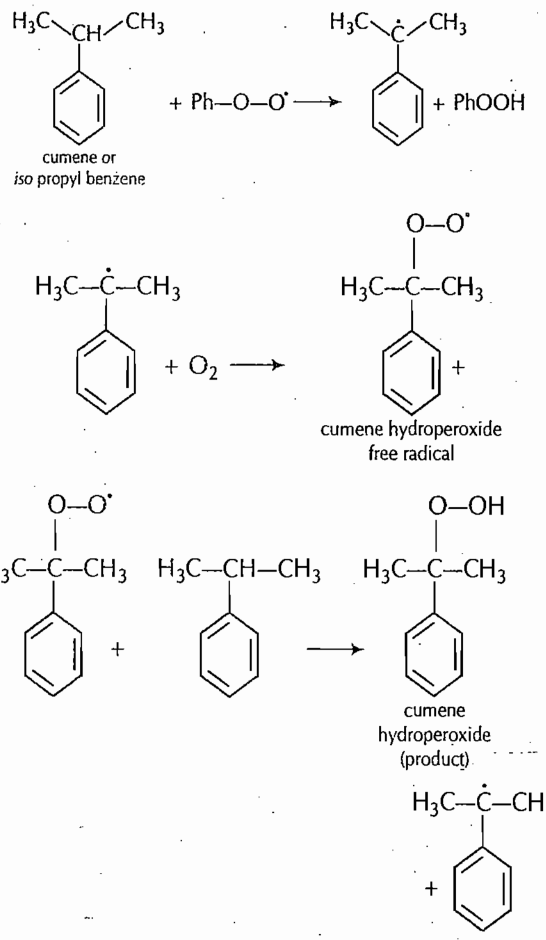
It contains carbons of three types, which are designated by *a*, *b* and *c*.

Thus, it will give 3 signals in proton decoupled ^{13}C NMR spectrum.

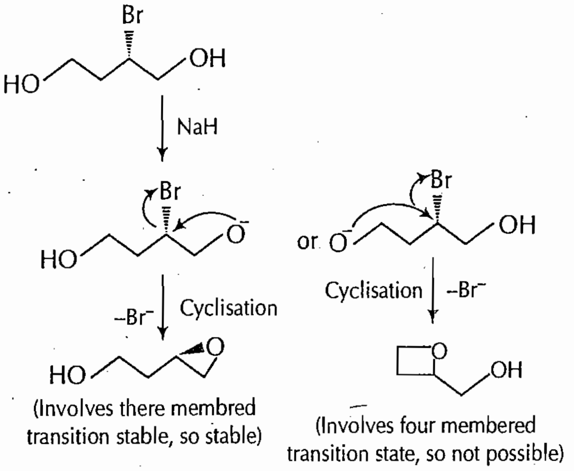
34. (c) Benzoyl peroxide, $(\text{PhCOO})_2$ generates benzoyloxyl radical $\text{PhCOO}^\bullet$ which gives $\text{Ph}^\bullet$ and CO_2. The generated $\text{Ph}^\bullet$ reacts with O_2 to give $\text{PhOO}^\bullet$, which abstract a proton from hydrocarbon and generates a new free radical.

$$\underset{\text{Benzoyl peroxide}}{\text{Ph(COO)}_2} \longrightarrow \text{PhCOO}^\bullet \longrightarrow \text{Ph}^\bullet + CO_2$$

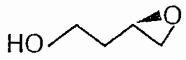
$$\text{Ph} + O_2 \longrightarrow \text{Ph—O—O}^\bullet$$



35. (c)



Thus, the product of the reaction is



36. (b) In α-helix structure, 3.6 amino acids are present in one turn, covering a distance of 5.4Å.

$\therefore$ 10 amino acids will be present in $= \dfrac{1 \times 10}{3.6}$ turns and the average length of α-helix containing 10 amino acids

$$= \frac{1 \times 10 \times 5.4}{3.6}$$
$$= 15 \text{ Å}$$

37. (c) In DNA, A always binds with T and C always binds with G (where, A = adenine, T = thymine, C = cytosine and G = Guanine), *i.e.*,

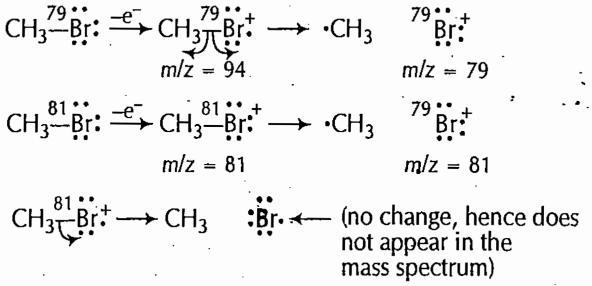
$$A = T \text{ and } C \equiv G$$
$$\text{and } A\% + T\% + C\% + G\% = 100$$
$$\text{Given, } G\% = 23\% = C\% \text{ and } A\% = T\% = x$$
$$\therefore \quad x\% + x\% + 23\% + 23\% = 100\%$$
$$2x = 100 - 46$$
$$2x = 54\%$$
$$x = 27\%$$

Thus, number of thymine residue = 27% of 5000 kb

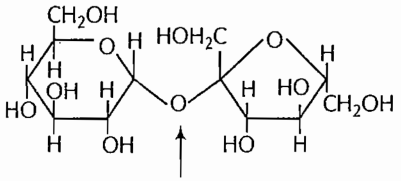
$$= \frac{27}{100} \times 5000 \times 10^3 \text{ b}$$
$$= 2.7 \times 5 \times 10^5$$
$$= 13.5 \times 10^5 = 1.35 \times 10^6$$

38. (d) Hammett plot is typically linear with either a positive or negative slop. Non-linearity in the Hammett plot shows that a substituent affects the rate of reaction or changes the rate determining step or reaction mechanism of the reaction.

39. (c) The abundance of the two isotopes of bromine is almost equal *i.e.*, ^{79}Br(50.69%) and ^{81}Br(49.31%). Hence, the mass spectrum of methyl bromide shows two very intense peaks of roughly equal intensity at *m*/*z* 94 and 96 which are the $M^{+\bullet}$ and M^{+2} peaks.



40. (d) The monomer units of sucrose are glucose and fructose, which are joined together at the hemiacetal of glucose unit and hemiketal of fructose. The bond formed (ether bond) is called glycosidic linkage. Since, there is no hemiacetals remaining in the sucrose, it is a non-reducing sugar, *i.e.*, does not reduce Benedict's solution. Moreover, it does not form osazone due to the absence of free aldehyde or keto group, which are necessary to form osazone.



glycosidic linkage
sucrose

41. (c) For the electronic transition, the selection rule are

1. Multiplicity remains the same, *i.e.*, $\Delta S = 0$
2. Components of total orbital angular momentum along internuclear axis, $\Delta \wedge = 0, \pm 1$.
3. For equal nuclear charges, $\Sigma_g^+ \longleftrightarrow \Sigma_u^+$ or $\Sigma_g^- \longleftrightarrow \Sigma_u^-$ transitions are allowed.

Thus, $^1\Sigma_g^+ \longleftrightarrow {}^1\Sigma_u^+$ transition is allowed as

$$\Delta S = 0$$
$$\Delta \wedge = 0$$
$$\Sigma_g^+ \rightarrow \Sigma_u^+$$

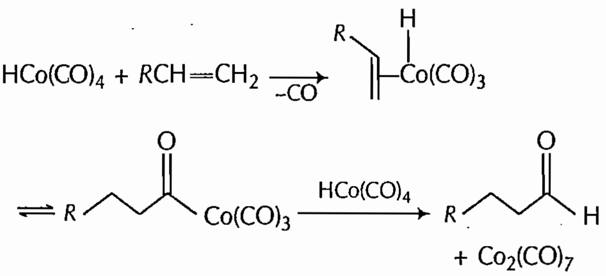
42. (c) In IR spectrum,

polarity of a bond ∝ intensity.

Among the given bonds, O—H bond being most polar gives the most intense band in the infrared spectrum for its stretching vibration.

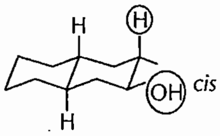
43. (d) In hydroformylation reaction, first of all catalyst $Co_2(CO)_8$ undergoes hydrogenation to give the acidic hydride $HCo(CO)_4$, which can also be prepared directly.

$Co_2(CO)_8 + H_2 \longrightarrow \underset{\text{intermediate}}{2HCo(CO)_4}$

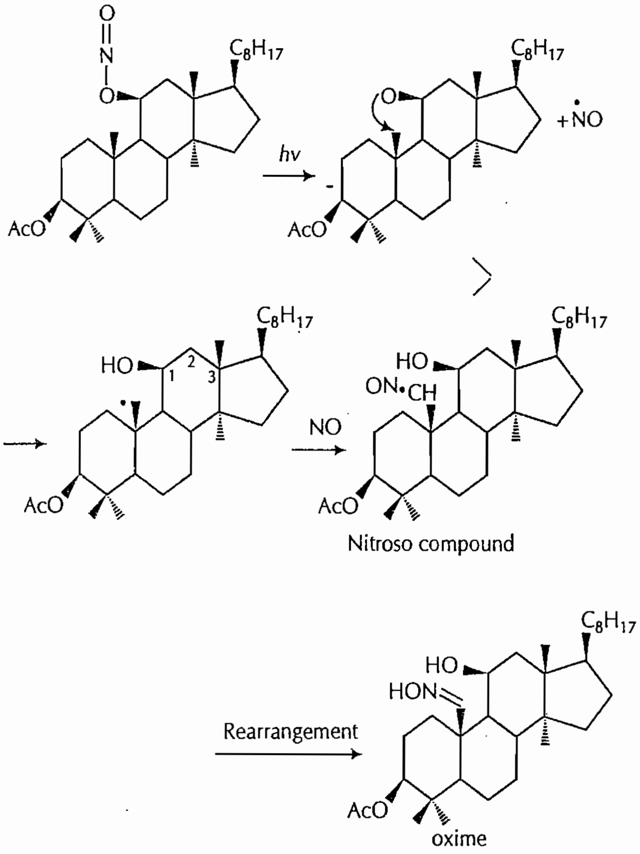


44. (d) The iso-electric point of arginine, glutamic acid and valine is 11.15, 3.22 and 5.96 respectively. Thus, the order of elution of these is (from a carboxymethyl-cellulose column at pH 6.0)
glutamic acid, valine, arginine.

45. (a) 9-BBN adds to the less substituted site and H atom occupy a position *cis* to —OH. So, the product of the reaction is

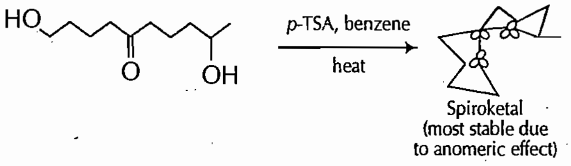


46. (a)

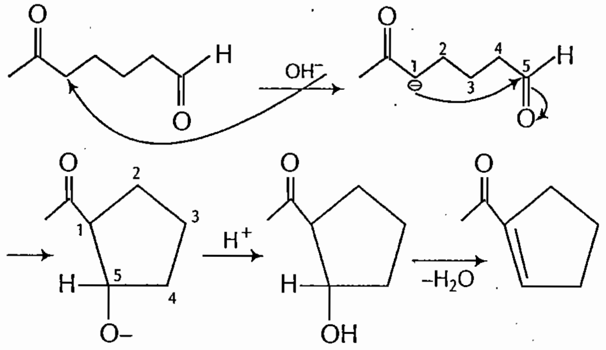


The above reaction is an example of Barton reaction, a photochemical rearrangement.

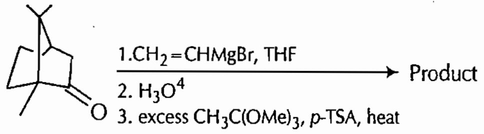
47. (a)

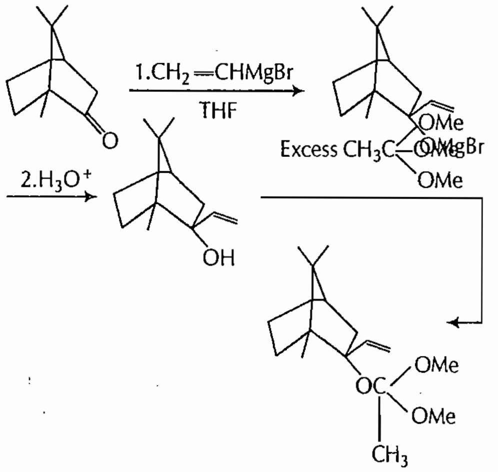


48. (a) —CHO group is more reactive than C═O.

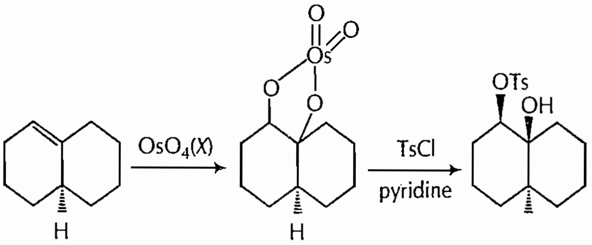


49. (d)

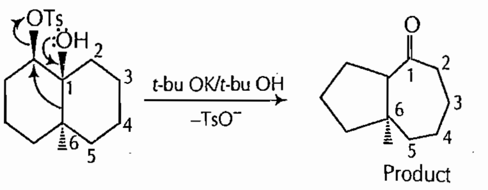




50. (b) Since, the syn addition takes place, the reagent must be OsO_4.



51. (d)



52. (b) We know that the order of reactivity alkyl halide is

$$R—I > R—Br > R—Cl$$

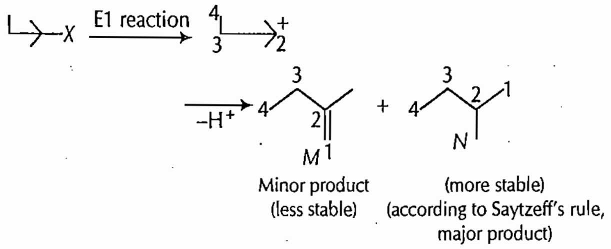
and Reactivity $\propto$ energy $\propto \dfrac{1}{\text{stability}}$

The order of energy is

$$S_1 > S_2 > S_3$$

Thus, $S_1 = R—I$, $S_2 = R—Br$ and $S_3 = R—Cl$

53. (d)



The order of energy is $P_1 > P_2$

So, P_1 is M (less stable, so has more energy) and is the minor product.

54. (b) For rotational Raman spectrum,

$$\Delta E = B(4\hat{j} + 6)$$

For the first line,

$$\hat{j} = 0 \Rightarrow \Delta E = 6B$$

$$\Delta E = 20491 - 20479$$

$$6B = 12$$

$$B = 2\,\text{cm}^{-1}$$

55. (c) For second line, $\hat{j} = 1$

$$\Delta E = B(4 \times 1 + 6)$$

$$= 10B = 10 \times 2.0 = 20\,\text{cm}^{-1}$$

$\therefore$ Second rotational line is at $20491 - 20$

$$= 20471\,\text{cm}^{-1}$$

56. (d) Let $1.001 = x$

$$x^{1259} = 3.52, \quad x^{2062} = 7.85$$

$$x^{3321} = x^{1259}x^{2062}$$

$$= 3.52 \times 7.85$$

$$= 27.64$$

57. (b)

58. (b) The meaning of Latitude is Freedom.

59. (d) Given the seriousness of the situation that he had to face, his nonchalance was impressive.

60. (c) If the tired soldier wanted to lie down, he should have taken the mattress out on the balcony.

61. (a)

62. (c) OB is the line when both A and B arrive at same time.

Total sample space $= 60 \times 60 = 3600$

Favourable cases = Area of $OABC$ − 2(Area of SRC)

$$= 3600 - 2 \times \left(\frac{1}{2} \times 45 \times 45\right) = 1575$$

Hence, required probability $= \dfrac{1575}{3600} = \dfrac{7}{16}$

63. (d) Total budget amount

$$= 4000 + 1200 + 2000 + 1500 + 1800 = ₹10500$$

Except savings, other expenditure = ₹ (10500 − 1500)

$$= ₹\,9000$$

Hence, required percentage $= \dfrac{9000 \times 100}{10500} = 86\%$

64. (a) Suppose category of bags are as follows

$$A_1A_2A_3\ B_1B_2B_3\ C_1C_2$$

1st weighting A vs B

Case I $A_1A_2A_3 = B_1B_2B_3$

Case II $A_1A_2A_3 \neq B_1B_2B_3$

$\therefore$ Either C_1 or C_2 is heavier.

Either A or B would be heavier (say $A > B$)

2nd weighting

C_1 vs C_2; If $C_1 > C_2$, then C_1

If $C_1 < C_2$, then C_2

If $A_1 < A_2$, then A_2

A_1 vs A_2; If $A_1 = A_2$, then A_3

If $A_1 > A_2$, then A_1

65. (a) Suppose the number of ₹ 20 notes = x

and the number of ₹ 10 notes = y

According to the question,

$$20x + 19y = 230 \qquad \ldots\text{(i)}$$

and $$x + y = 14 \qquad \ldots\text{(ii)}$$

From Eqs. (i) and (ii). we get

$$x = 9 \quad \text{and} \quad y = 5$$

$\therefore$ Number of ₹ 10 notes = 5

1

Atomic Structure

Syllabus

Atomic Structure Quantum Theory : Principles and techniques, applications to a particle in a box, harmonic oscillator, rigid rotor and hydrogen atom. Approximate technique : Variation and perturbation. Rotational, vibrational, electronic, NMR and ESR spectroscopy.

GATE 2011

(1 Mark Questions)

▼ *Solution Points*

1. The region of electromagnetic spectrum employed in the electron spin resonance (ESR) spectroscopy is

(a) radiowave (b) microwave (c) infrared (d) visible

GATE 2010

2. The wave function for a harmonic oscillator described by $Nx\exp\left(-\frac{ax^2}{2}\right)$ has

(a) one maximum only
(b) one maximum, one minimum only
(c) two maxima, one minimum only
(d) two maxima, two minima only

3. An electron of mass m is confined to a one-dimensional box of length b. If it makes a radiative transition from second excited state to the ground state, the frequency of the photon emitted is

(a) $\frac{9h}{8mb^2}$ (b) $\frac{3h}{8mb^2}$
(c) $\frac{h}{mb^2}$ (d) $\frac{2h}{8mb^2}$

GATE 2009

4. The de-Broglie wavelength for a He atom travelling at 1000 m/s (typical speed at room temperature) is

(a) 99.7×10^{-12} m (b) 199.4×10^{-12} m
(c) 199.4×10^{-18} m (d) 99×10^{-6} m

GATE 2005

▾ *Solution Points*

5. The vibrational partition function for a molecule which can be described as a simple harmonic oscillator with fundamental frequency ν is given by

(a) $\exp\left(-\frac{h\nu}{K_BT}\right)$

(b) $\left[1-\exp\left(-\frac{h\nu}{K_BT}\right)\right]^{-1}$

(c) $\exp\left(-\frac{h\nu}{K_BT}\right)\left[1-\exp\left(-\frac{h\nu}{K_BT}\right)\right]^{-1}$

(d) $\exp\left(-\frac{h\nu}{2K_BT}\right)\left[1-\exp\left(-\frac{h\nu}{K_BT}\right)\right]^{-1}$

6. The $2s$-orbital of H-atom has a radial node at $2a_0$ because ψ_{2s} is proportional to

(a) $\left(\frac{1}{2}+\frac{r}{a_0}\right)$ (b) $\left(2+\frac{r}{a_0}\right)$

(c) $\left(2-\frac{r}{a_0}\right)$ (d) $\left(2-\frac{r}{2a_0}\right)$

7. The function e^{ax^2} $(a > 0)$ is not an acceptable wave function for bound system because

(a) it is not continuous (b) it is multi-valued

(c) it is not normalizable (d) All of these

8. The set of eigen functions $\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$ $(0 \le x \le a, n = 1, 2, 3, \ldots)$ is

(a) orthogonal (b) normalized

(c) both orthogonal and normalized (d) unnormalized

GATE 2004

9. Which one of the following is not a photodetector?

(a) Bolometer (b) Charge-transfer device

(c) Photomultiplier tube (d) Silicon diode

10. In units of $\frac{h^2}{8ml^2}$, the energy difference between levels corresponding to 3 and 2 node eigen functions for a particle of mass m in a one-dimensional box of length l is

(a) 1 (b) 3 (c) 5 (d) 7

GATE 2002

11. The velocity of the electron in the hydrogen atom

(a) increases with increasing principal quantum number

(b) decreases with increasing principal quantum number

(c) is uniform for any value of the principal quantum number

(d) first increases and then decreases with principal quantum number

GATE 2001

12. As per the uncertainty principle, $\Delta x \cdot \Delta p$ equals to

(a) $\frac{h}{2\pi}$ (b) $\frac{h}{2}$

(c) λ (d) zero

GATE 2011

(2 Marks Questions)

13. The wave function for a quantum mechanical particle in a one-dimensional box of length a is given by $\psi = A \sin\frac{\pi x}{a}$. The value of A for a box of length 200 nm is

(a) $4 \times 10^4 (\text{nm})^2$ (b) $10\sqrt{2}\ (\text{nm})^{1/2}$

(c) $\sqrt{2}/10\ (\text{nm})^{-1/2}$ (d) $0.1 (\text{nm})^{-1/2}$

Common Data for Questions 14 and 15

A hypothetical molecule XY has the following properties:

Reduced mass $= 2 \times 10^{-26}$ kg

X—Y bond length = 100 pm

Force constant of the bond $= 8 \times 10^2$ N/m

14. The frequency of radiation (in cm^{-1} units) required to vibrationally excite the molecule from $v = 0$ to $v = 1$ state is

(a) 3184.8 (b) 2123.2

(c) 1061.6 (d) 840.0

15. The frequency of radiation (in cm^{-1} units) required to rotationally excite the molecule from $J = 0$ to $J = 1$ state is

(a) 1.4 (b) 2.8 (c) 3.2 (d) 3.6

GATE 2008

Common Data for Questions 16 to 18

An electron accelerated through a potential difference of ϕ volt impinges on a nickel surface, whose (100) planes have a spacing $d = 351.5 \times 10^{-12}$ m (351.8 pm).

16. The de-Broglie wavelength of the electron is $\lambda/\text{pm} = (a/\phi)^{1/2}$. The value of a in volt is

(a) 1.5×10^{-18} (b) 1.5×10^{-6}

(c) 6.63×10^{-5} (d) 2.5×10^{-18}

17. The condition for observing diffraction from the nickel surface is

(a) $\lambda >> 2d$ (b) $\lambda \leq 2d$

(c) $\lambda \leq ad$ (d) $\lambda \geq ad$

18. The minimum value of ϕ(volt) for the electron to diffract from the (100) planes is

(a) 3000 (b) 300

(c) 30 (d) 3

▾ ***Solution Points***

19. A particle is confined to a one-dimensional box of length 1 mm. If the length is changed by 10^{-9} m, the % change in the ground state energy is

(a) 2×10^{-4} (b) 2×10^{-7} (c) 2×10^{-2} (d) 0

ATE 2007

20. Consider a particle of mass m moving in a one-dimensional box under the potential $V = 0$ for $0 \le x \le a$ and $V = \infty$ outside the box. When the particle is in its lowest energy state, the average momentum ($< p_x >$) of the particle is

(a) $< p_x > = 0$ (b) $< p_x > = \frac{h}{a}$

(c) $< p_x > = \frac{h}{2a}$ (d) $< p_x > = \frac{h}{2\pi a}$

21. The uncertainty in the momentum (Δp_x) of the particle in its lowest energy state is

(a) $\Delta p_x = 0$ (b) $\Delta p_x = \frac{h}{a}$

(c) $\Delta p_x = \frac{h}{2a}$ (d) $\Delta p_x = \frac{h}{2\pi a}$

GATE 2006

22. The zero-point energy of the vibration of $^{35}Cl_2$ mimicking a harmonic oscillator with a force constant $k = 2293.8$ N/m is

(a) 10.5×10^{-21} J (b) 14.8×10^{-21} J

(c) 20.9×10^{-21} J (d) 20.6×10^{-21} J

23. Which of the following pairs of operators commute?

(a) x and $\frac{d}{dx}$ (b) $\frac{d}{dx}$ and $\frac{d^2}{dx^2}+\frac{2d}{dx}$

(c) $x^2\frac{d}{dx}$ and $\frac{d^2}{dx^2}$ (d) x^3 and $\frac{d}{dx}$

GATE 2005

24. First order perturbation correction $\Delta \epsilon_n^{(1)}$ to energy level ϵ_n of a simple harmonic oscillator due to the anharmonicity perturbation γx^3 is given by

(a) $\Delta \epsilon_n^{(1)} = \gamma$ (b) $\Delta \epsilon_n^{(1)} = \gamma^2$

(c) $\Delta \epsilon_n^{(1)} = \gamma^{-1}$ (d) $\Delta \epsilon_n^{(1)} = 0$

GATE 2000

25. The system for which energy (E) increases quadratically with the quantum number (n) is

(a) particle in a one-dimensional box
(b) hydrogen atom
(c) one-dimensional harmonic oscillator
(d) rigid rotor

Solution Points

Answers with Explanations

1. (b) Electron Spin Resonance (ESR) is a type of magnetic resonance. In it, the sample is loaded into a high frequency resonant cavity in a slowly varying uniform magnetic field. Unpaired electrons irradiated with microwave radiation at a fixed frequency will undergo resonant transition between the spin up and spin down state at a characteristic magnetic field.

2. (b) $\psi = Nx \exp \frac{-ax^2}{2}$

On differentiating, we get

$$\frac{\partial \psi}{\partial x} = N \exp\left(-\frac{ax^2}{2}\right) + Nx \cdot \exp\left(-\frac{ax^2}{2}\right)\left(-2\frac{ax}{2}\right)$$

$$= N \exp\left(-\frac{ax^2}{2}\right)(1 - ax^2)$$

Putting $\frac{\partial \psi}{\partial x} = 0$

$$0 = N \exp\left(-\frac{ax^2}{2}\right)(1 - ax^2)$$

$$(1 - ax^2) = 0$$

$$ax^2 = 1$$

$$x = \pm \frac{1}{\sqrt{a}}$$

On further differentiating,

$$\frac{\partial^2 \psi}{\partial x^2} = N \exp\left(-\frac{ax^2}{2}\right)(-2ax) + (1 - ax^2)$$

$$\left[N \exp\left(-\frac{ax^2}{2}\right) \cdot \frac{-2ax}{2}\right]$$

$$= N \exp\left(-\frac{ax^2}{2}\right)[-2ax + (1 - ax^2)(-ax)]$$

$$= N \exp\left(-\frac{ax^2}{2}\right)[-2ax - ax + a^2x^3]$$

$$= N \exp\left(-\frac{ax^2}{2}\right)[-3ax + a^2x^3]$$

At $x = -\frac{1}{\sqrt{a}}$,

$$\frac{\partial^2 \psi}{\partial x^2} = N \exp\left(-\frac{ax^2}{2}\right)\left[-3a\left(-\frac{1}{\sqrt{a}}\right) + a^2\left(-\frac{1}{\sqrt{a}}\right)^3\right]$$

$$= N \exp \frac{-a\left(-\frac{1}{\sqrt{a}}\right)^2}{2} [3\sqrt{a} - \sqrt{a}]$$

$$= N \exp^{-\frac{1}{2}} [2\sqrt{a}] > 0 \text{ (minima)}$$

At $x = +\frac{1}{\sqrt{a}}$,

$$\frac{\partial^2 \psi}{\partial x^2} = N \exp\left[\frac{-a\left(\frac{1}{\sqrt{a}}\right)^2}{2}\right]$$

$$\left[-3a\left(+\frac{1}{\sqrt{a}}\right) + a^2\left(+\frac{1}{\sqrt{a}}\right)^3\right]$$

$$= N \exp^{-\frac{1}{2}} [-3\sqrt{a} + \sqrt{a}]$$

$$= -N \exp^{-\frac{1}{2}} [2\sqrt{a}] < 0 \text{ (maxima)}$$

Hence, the given wave function has one maxima and one minima only.

3. (c) $E = \frac{n^2h^2}{8ml^2}$

Since, $E = h\nu$, length is b,

and for ground state $n_1 = 1$ and for second excited state $n_2 = 3$

On putting these values, we get

$$h\nu = \frac{[(3)^2 - (1)^2]\, h^2}{8mb^2}$$

$$\nu = \frac{(9 - 1)\, h}{8mb^2} = \frac{8h}{8mb^2}$$

$$= \frac{h}{mb^2}$$

4. (a) $\lambda = \frac{h}{mv}$

$$= \frac{6.63 \times 10^{-34}}{4 \times 1.66 \times 10^{-27} \times 1000}$$

$$= 99.8 \times 10^{-12} \text{ m}$$

5. (b) Vibrational partition function

$$= \left[1 - \exp\left(-\frac{h\nu}{K_BT}\right)\right]^{-1}$$

6. (c) $\psi_{2s} = \frac{1}{4\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{3/2}\left(2-\frac{zr}{a_0}\right)e^{-zr/a_0}$

At node, $\psi_{2s} = 0$

$$\therefore \quad \left[2-\frac{zr}{a_0}\right] = 0 \quad \text{or} \quad \frac{zr}{a_0} = 2$$

$$r = 2a_0 \qquad (\because z = 1 \text{ for H-atom})$$

Thus, $\psi_{2s} \propto \left[2 - \frac{r}{a_0}\right]$

7. (d) e^{ax^2}

$$\frac{d}{dx} = \frac{d}{dx}e^{ax^2} = 2ax \cdot e^{ax^2}$$

Thus, it is a multi-valued function.

$$\psi = e^{ax^2}$$

For normalizable function,

$$\psi = \int \psi \cdot \psi \, dx = 1$$

$$= \int e^{ax^2} \cdot e^{ax^2} \, dx = \int e^{2ax^2} dx$$

$$= \left[\frac{e^2 ax^2}{4ax}\right]_{-\infty}^{+\infty} = e^{\infty} - e^{\infty} = 0 \neq 1$$

Thus, it is not a normalizable function.

Further, the given function is non-continuous.

8. (c) $\psi(x) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$

For orthonormal function,

$$\int \psi_i \, \psi_i \, d\tau = 1$$

$$\psi(x) = \int_0^a \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a} \cdot \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\, dx$$

$$= \frac{1}{a}\int_0^a 2\sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{1}{a}\int_0^a \left[1 - \cos\frac{2n\pi x}{a}\right] dx$$

$$= \frac{1}{a}\left[x - \frac{\sin\frac{2n\pi x}{a}}{\frac{2n\pi}{a}}\right]_0^a$$

$$= \frac{1}{a}\left[a - \frac{\sin\frac{2n\pi a}{a}}{\frac{2n\pi}{a}}\right]$$

$$= \frac{1}{a}\left[a - \frac{a\sin 2n\pi}{2n\pi}\right] = \frac{a}{a} = 1$$

Thus, the function is orthonormal, *i.e.*, orthogonal as well as normalized.

Alternate method

Conditions for orthonormality are

$$\psi(s) = \int \psi_i \, \psi_j \, d\tau = 0 \text{ if } i \neq j$$

$$= 1 \text{ if } i = j$$

In the given function, $i = j$ and $\psi(s) = 1$

Thus, the given function is orthonormal.

9. (a) Photodetectors are used primarily as an optical receiver to convert light into electricity. They work on the principle of photoelectric effect. Photodiodes (Ge-As diode, Si diode), photomultiplier tube and charge transfer device (mainly charge coupled device). Bolometer, on the other hand, is a device used for measuring the power of incident EMR *via* the heating of material with a temperature-dependent electrical resistance.

10. (c) The energy difference is in between $n = 3$ and $n = 2$ node be the particle losing energy.

For particle in one-dimensional box,

$$E = \frac{h^2 (n_2^2 - n_1^2)}{8ml^2}$$

$$E = \frac{h^2 [(3)^2 - (2)^2]}{8ml^2}$$

$$E = \frac{5h^2}{8ml^2}$$

$\therefore$ Energy difference is 5 in units of $\frac{h^2}{8ml^2}$.

11. (b) Velocity decreases with increase in principal quantum number as

Velocity of electron $v = \frac{2\pi e^2}{nh}$

12. (b) According to Heisenberg's uncertainty principle,

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \qquad \left(\because \hbar = \frac{h}{2\pi}\right)$$

$$\therefore \qquad \geq \frac{\hbar}{2}$$

13. (d) Given,

Wave function $\psi = A\sin\frac{\pi x}{a}$

In order for the functions to be normalized,

We must have

$$\int_0^a \psi^2 dx = A^2 \int_0^a \sin^2\left(\frac{\pi x}{a}\right) dx \equiv 1$$

Let $\frac{\pi x}{a} = C, \ \frac{\pi}{a}dx = dC$

Then, $\int_0^a \psi^2 dx = \frac{A^2 a}{\pi}\int_0^\pi \sin^2 C\, dC$

$$= \frac{A^2 a}{\pi}\cdot\frac{\pi}{2} = 1$$

∴ $A = \pm\sqrt{\frac{2}{a}}$

$$= \pm\sqrt{\frac{2}{200}}$$

$$= \pm\sqrt{0.01}\ \text{nm}$$

$$= 0.1\,(\text{nm})^{-1/2}$$

14. (c) The frequency of the molecule *XY* in wave number units is

$$\omega = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$= \frac{1}{2\times 3.14\times 3\times 10^{8}}\sqrt{\frac{8\times 10^{2}}{2\times 10^{-26}}}$$

$$= 106157.11\,\text{m}^{-1}$$

$$= 1061.6\ \text{cm}^{-1}$$

$$\omega_0 \text{ to } \omega_1 = 1061.6 - 0$$

$$= 1061.6\ \text{cm}^{-1}$$

15. (b) $E_0 = \frac{j(j+1)\hbar^2}{2I}$

When $j = 0$,

$$E_0 = 0$$

$$E_1 = \frac{j(j+1)\hbar^2}{2I}$$

$$= \frac{1(1+1)\hbar^2}{2\mu r^2}$$

$$= \frac{2\hbar^2}{2\mu r^2} = \frac{\hbar^2}{\mu r^2}$$

$$= \frac{h^2}{4\pi^2\mu r^2}$$

We know that

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

$$hc\bar{\nu} = \frac{h^2}{4\pi^2\mu r^2}$$

$$\bar{\nu} = \frac{h}{4\pi^2\mu r^2\cdot c}$$

$$= \frac{6.6\times 10^{-34}}{4\times(3.14)^2\times 2\times 10^{-26}\times(100\times 10^{-12})^2\times 3\times 10^{8}}\ \text{m}^{-1}$$

$$= \frac{6.6\times 10^{-34}}{4\times 9.86\times 6\times 10^{4}\times 10^{-42}}\ \text{m}^{-1}$$

$$= \frac{6.6\times 10^{-34}}{2.4\times 10^{-36}}\ \text{m}^{-1}$$

$$= 278.9\ \text{m}^{-1}$$

$$= 2.8\ \text{cm}^{-1}$$

16. (a) $\lambda = \frac{h}{mv}$

$$E \text{ or KE} = \frac{1}{2}mv^2$$

or $v = \sqrt{\frac{2E}{m}}$

∴ $\lambda = \frac{h}{\sqrt{2mE}}$

$$= \frac{h}{\sqrt{2m\cdot eV}} \qquad [\because E = eV]$$

Given, $\lambda = \left(\frac{a}{\phi}\right)^{1/2}$

On putting values, we get

$$\sqrt{\frac{a}{\phi}} = \frac{h}{\sqrt{2\times 9.1\times 10^{-31}\times 1.6\times 10^{-19}\times\phi}}$$

$$a = \frac{h^2}{2\times 9.1\times 10^{-31}\times 1.6\times 10^{-19}}$$

$$= \frac{(6.6\times 10^{-34})^2}{2\times 9.1\times 10^{-31}\times 1.6\times 10^{-19}}$$

$$= \frac{4.356\times 10^{-67}}{3.2\times 9.1\times 10^{-50}}$$

$$= 1.49\times 10^{-18} \approx 1.5\times 10^{-18}\,\text{V}$$

17. (b) Bragg's equation is

$$n\lambda = 2d\sin\theta \quad\text{or}\quad \sin\theta = \frac{n\lambda}{2d}$$

For diffraction, $\sin\theta < 1$

For first order diffraction, $n = 1$

∴ $\frac{\lambda}{2d} \le 1$

$$\lambda \le 2d$$

18. (d) For minimum value of ϕ, λ must be maximum.

λ is maximum, when $\sin\theta = \sin 90° = 1$

i.e.,
$$n\lambda = 2d\sin\theta = 2d$$
$$n\lambda = 2d$$
$$\lambda = \frac{2d}{n}$$

For first order diffraction, $n = 1$

$$\therefore \quad \lambda = 2d$$

Given,
$$\lambda = \sqrt{\frac{a}{\phi}}$$
$$(2d)^2 = \frac{a}{\phi}$$
$$\phi = \frac{a}{4d^2}$$
$$= \frac{1.5 \times 10^{-18}}{4 \times (351.8 \times 10^{-12})^2}$$
$$= 3.0\,\text{V}$$

19. (a) $E = \dfrac{n^2h^2}{8ml^2}$

i.e.,
$$E \propto \frac{1}{l^2}$$

Per cent change in energy $\left(\dfrac{\Delta E}{E} \times 100\right)$
$$= 2 \times \frac{\Delta l}{l} \times 100$$
$$= \frac{2 \times 10^{-9}}{10^{-3}} \times 100$$
$$= 2 \times 10^{-9} \times 10^{5}$$
$$= 2 \times 10^{-4}$$

20. (a) The average value of the linear momentum along the x-axis is
$$< p_x > = \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)\frac{\hbar}{i}\frac{d}{dx}\sin\left(\frac{\pi x}{a}\right)dx$$
$$= \frac{2\pi\hbar}{a^2 i}\int_0^a \sin\left(\frac{\pi x}{a}\right)\cos\left(\frac{\pi x}{a}\right)dx$$

The integral on the right is zero (as sine function is symmetric and cosine function is antisymmetric around the centre of the range). So, we conclude that the average linear momentum is zero.

21. (b) The momentum of the particle can be in the positive and negative directions and certainty is from 0 to a.

Thus, uncertainty in momentum.
$$\Delta p_x = \frac{nh}{2a} - \left(-\frac{nh}{2a}\right) = \frac{nh}{a}$$

If $n = 1$,
$$\Delta p_x = \frac{h}{a}$$

22. (b) Reduced mass
$$\mu = \frac{35 \times 10^{-3} \times 35 \times 10^{-3}\,(\text{kg/mol})^2}{(35 \times 10^{-3} + 35 \times 10^{-3})\,\text{kg/mol}\;(6.023 \times 10^{23}\,\text{mol}^{-1})}$$
$$= \frac{1.225 \times 10^{-3}}{70 \times 10^{-3} \times 6.023 \times 10^{23}}\,\text{kg}$$
$$= 2.9 \times 10^{-26}\,\text{kg}$$

Zero point energy
$$E_0 = \frac{1}{2}\hbar\omega$$
$$= \frac{1}{2}\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$
$$= \frac{1}{2} \times \frac{6.6 \times 10^{-34}}{2 \times 3.14}\sqrt{\frac{2293.8}{2.9 \times 10^{-26}}}$$
$$= \frac{1}{2} \times \frac{6.6 \times 10^{-34} \times 2.81 \times 10^{14}}{6.28}$$
$$= 1.4766 \times 10^{-20} = 14.76 \times 10^{-21}\,\text{J}$$

23. (b) Two operators commute if the following equation is true
$$[\hat{A}, \hat{E}] = \hat{A}\hat{E} - \hat{E}\hat{A} = 0$$

(a) x and $\dfrac{d}{dx}$
$$\hat{A} = x \text{ and } \hat{E} = \frac{d}{dx}$$
$$\hat{A}\hat{E}f(x) = x \cdot \frac{d}{dx}f(x) = x \cdot f'(x)$$
$$\hat{E}\hat{A}\,f(x) = \frac{d}{dx} \cdot x f(x) = f(x) + x f'(x)$$

$\because [\hat{A}, \hat{E}] \neq [\hat{E}, \hat{A}]$, so these operators do not commute.

(b) $\hat{A} = \dfrac{d}{dx}$ and $\hat{E} = \dfrac{d^2}{dx^2} + \dfrac{2d}{dx}$
$$\hat{A}\hat{E}f(x) = \frac{d}{dx}\left[\frac{d^2}{dx^2} + \frac{2d}{dx}\right]f(x)$$
$$= \frac{d^3}{dx^3}f(x) + \frac{2d^2}{dx^2}f(x)$$
$$= f'''(x) + 2f''(x)$$

$$\hat{E}\hat{A}\,f(x) = \left[\frac{d^2}{dx^2} + \frac{2d}{dx}\right]\cdot\frac{d}{dx}\,f(x)$$

$$= \left[\frac{d^2}{dx^2} + \frac{2d}{dx}\right]\cdot f'(x)$$

$$= \frac{d^2}{dx^2}\cdot f'(x) + \frac{2d}{dx}f'(x)$$

$$= f'''(x) + 2f''(x)$$

$$[\hat{E}, \hat{A}] = [\hat{A}, \hat{E}]$$

$\therefore$ These operators commute.

Similarly, $x^2\frac{d}{dx}$ and $\frac{d^2}{dx^2}$; x^3 and $\frac{d}{dx}$ do not commute.

24. (d) First order correction to the ground state energy is

$$E_0' = \sqrt{\frac{\alpha}{\pi}}\int_{-\infty}^{+\infty}\frac{1}{6}\gamma^{x^3}e^{-ax^2}dx \qquad [\because H' = \gamma x^3]$$

Since, H' is odd *i.e.*, x^3, the E' will be zero.

25. (a) The lowest possible energy for particle in one-dimensional box $= \frac{h^2}{8\,ma^2}$

For $n = 2$, it is

$$E = \frac{2^2\,h^2}{8ma^2}$$

i.e.,

$$= \frac{4h^2}{8ma^2}$$

Thus, it increases quadratically.

The energy levels of the quantum harmonic oscillator is

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

If $n = 1$,

$$E_1 = \frac{3}{2}\hbar\omega \Rightarrow E_2 = \frac{5}{2}\hbar\omega$$

Here, energy does not increase quadratically with the quantum number.

2

Chemical Bonding and Molecular Structures

Syllabus

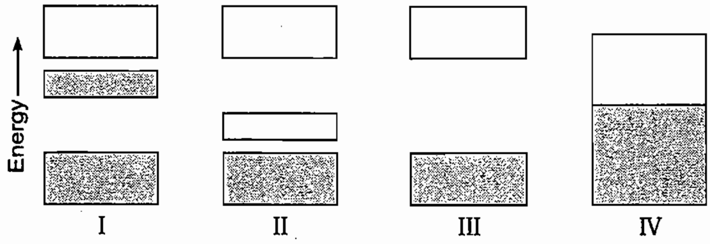
Chemical Bonding and Molecular Structures Valence band and molecular orbital theories. Huckel approximation ; symmetry, point groups. Crystal systems and lattices, Miller planes, crystal packing,crystal defects, Bragg's law, ionic crystals, band theory, metals and semiconductors, different structure of AX, AX_2, ABX_3 compounds, spinels.

GATE 2011

(1 Mark Questions)

▾ *Solution Points*

1. The band structure in an n-type semiconductor is



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

GATE 2010

2. Band theory predicts that magnesium is an insulator. However, in practice it acts as a conductor due to
   (a) presence of filled $3s$ - orbital
   (b) overlap of filled $2p$ and filled $3s$ - orbital
   (c) overlap of filled $3s$ and empty $3p$ - orbital
   (d) presence of unfilled $3p$ - orbital

GATE 2009

3. The geometry around the central atom in ClF_4^+ is
   (a) square planar (b) square pyramidal
   (c) octahedral (d) trigonal bipyramidal

4. The coordination number of the Ba^{2+} ions in barium fluoride is 8. The coordination number of the fluoride ion is

(a) 8 (b) 4 (c) 1 (d) 2

5. Among the following, the isoelectronic and isostructural pair is

(a) CO_2 and SO_2 (b) SO_3 and SeO_3

(c) NO_2^+ and TeO_2 (d) SiO_4^{4-} and PO_4^{3-}

GATE 2008

6. The highest occupied molecular orbital of HF is

(a) bonding (b) anti-bonding

(c) ionic (d) non-bonding

7. The point group of NSF_3 is

(a) D_{3d} (b) C_{3h} (c) D_{3h} (d) C_{3v}

8. Among the compounds Fe_3O_4, $NiFe_2O_4$ and Mn_3O_4

(a) $NiFe_2O_4$ and Mn_3O_4 are normal spinels

(b) Fe_3O_4 and Mn_3O_4 are normal spinels

(c) Fe_3O_4 and Mn_3O_4 are inverse spinels

(d) Fe_3O_4 and $NiFe_2O_4$ are inverse spinels

9. NaCl is crystallized by slow evaporation of its aqueous solution at room temperature. The correct statement is

(a) the crystals will be non-stoichiometric

(b) the crystals should have Frenkel defects

(c) the percentage of defects in the crystals will depend on the concentration of the solution and its rate of evaporation

(d) the nature of defects will depend upon the concentration of the solution and its rate of evaporation

10. $CaTiO_3$ has a perovskite crystal structure. The coordination number of titanium in $CaTiO_3$ is

(a) 9 (b) 6

(c) 3 (d) 12

GATE 2007

11. The ground state term for V^{3+} ion is

(a) ^3F (b) ^2F

(c) ^3P (d) ^2D

GATE 2006

12. The symmetry elements that are present in BF_3 are

(a) $C_3, \sigma_v, \sigma_h, 3C_2$ (b) $C_3, 3C_2, S_2, \sigma_v$

(c) $C_3, 3C_2, \sigma_h, S_2$ (d) $C_3, \sigma_h, \sigma_v, i$

GATE 2005

13. The shape of the molecule XeO_2F_2 is

(a) distorted tetrahedral (b) square planar

(c) trigonal bipyramidal (d) tetrahedral

▾ ***Solution Points***

GATE 2004

14. The structure of SF_4 is
(a) octahedral (b) tetrahedral
(c) trigonal bipyramidal (d) square planar

15. The bond angle of Cl_2O is
(a) smaller than of F_2O (b) greater than that of H_2O
(c) smaller than that of H_2O (d) same as that of F_2O

16. On the basis of LCAO-MO theory, the magnetic characteristics of N_2 and N_2^+ are
(a) both diamagnetic
(b) both paramagnetic
(c) N_2 diamagnetic and N_2^+ paramagnetic
(d) N_2 paramagnetic and N_2^+ diamagnetic

GATE 2003

17. According to MO theory for the atomic species C_2
(a) bond order is zero and it is paramagnetic
(b) bond order is zero and it is diamagnetic
(c) bond order is two and it is paramagnetic
(d) bond order is two and it is diamagnetic

GATE 2002

18. Which of the following species has two non-bonded electron pairs on the central atom?
(a) $TeCl_4$ (b) ClF_3 (c) ICl_2^- (d) PCl_3

19. The species which has a square planar structure is
(a) BF_4^- (b) $FeCl_4^-$
(c) SF_4 (d) XeF_4

GATE 2001

20. Icosahedral structure is generally exhibited by
(a) C (b) Si (c) Ge (d) B

21. The hybrid orbitals used by bromine atom in BrF_3 are
(a) sp^2 (b) sp^3 (c) sp^3d (d) sp^3d^2

22. The symmetry point group of the BF_3 molecule is
(a) C_{3v} (b) D_{3h} (c) C_{2v} (d) D_{2h}

GATE 2000

23. Which of the following statements about the molecule NOCl is correct?
(a) It has a linear structure
(b) It belongs to the point group C_s
(c) It does not have a dipole moment
(d) It is a chiral molecule

▾ *Solution Points*

▾ ***Solution Points***

24. Among the following molecules, the shortest bond length is to be found in

(a) C_2
(b) N_2
(c) O_2
(d) F_2

GATE 2011

(2 Marks Questions)

25. According to VSEPR theory, the shapes of $[SF_2Cl]^+$ and $[S_2O_4]^{2-}$ should be

(a) trigonal planar for $[S_2O_4]^{2-}$ and trigonal pyramidal for $[SF_2Cl]^+$
(b) both trigonal planar
(c) trigonal pyramidal for $[S_2O_4]^{2-}$ and trigonal planar for $[SF_2Cl]^+$
(d) both trigonal pyramidal

GATE 2010

26. According to VSEPR model, the shape of $[XeOF_5]^-$ is

(a) octahedral
(b) trigonal bipyramidal
(c) square pyramidal
(d) pentagonal monopyramidal

27. The point group of ClF_3 molecule and its corresponding number of irreducible representations are respectively

(a) C_{3v} and 4
(b) C_{2v} and 4
(c) C_{3v} and 3
(d) C_{2v} and 3

28. Fe_3O_4 and Co_3O_4 are metal oxides having spinel structure. Considering their CFSFs, the correct statement regarding their structure is

(a) both have normal spinel structure
(b) both have inverse spinel structure
(c) Fe_3O_4 has normal and Co_3O_4 has inverse spinel structure
(d) Fe_3O_4 has inverse and Co_3O_4 has normal spinel structure

GATE 2007

29. The pair of compounds having the same hybridization for the central atom is

(a) XeF_4 and $[SiF_6]^{2-}$
(b) $[NiCl_4]^{2-}$ and $[PtCl_4]^{2-}$
(c) $Ni(CO)_4$ and XeO_2F_2
(d) $[Co(NH_3)_6]^{3+}$ and $[Co(H_2O)_6]^{3+}$

Common Data for Questions 30 to 32

trans, 1, 2 difluoro ethylene molecule has a 2-fold rotational axis and an inversion centre.

30. The number of distinct symmetry operations that can be performed on the molecule is

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

31. The number of irreducible representations of the point group of the molecule is

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

32. If two H atoms of the above molecule are also replaced by F atoms, the point group of the resultant molecule will be

(a) C_i
(b) C_{2h}
(c) C_{2v}
(d) D_{2h}

GATE 2006

▾ *Solution Points*

33. The atomic radius (in cm) of an element with a body centred cubic unit cell of volume 75.8 cm^3 mol^{-1}, molecular weight 137.3 and density 3.62 g cm^{-3} is

(a) 1.5×10^{-8} (b) 1.6×10^{-8}
(c) 2.0×10^{-8} (d) 2.2×10^{-8}

34. $[XeO_6]^{4-}$ is octahedral whereas XeF_6 is a disordered one, because

(a) fluorine is more electronegative than oxygen
(b) Xe has a lone pair in XeF_6
(c) XeF_6 is neutral whereas $[XeO_6]^{4-}$ is anionic
(d) Xe—F bond has more ionic characters

35. The arrangement of sulphur in zinc blende and wurtzite structures, respectively are

(a) hexagonal close packing and cubic close packing
(b) cubic close packing and hexagonal close packing
(c) simple cubic packing in both the structures
(d) hexagonal close packing in both the structures

36. The crystal structure of Pb_3O_4 contains

(a) octahedral and tetrahedral units
(b) only octahedral units
(c) octahedral and pyramidal units
(d) octahedral and square planar units

37. If the dipole moment of HCl is 1.08 D and the bond distance is 1.27 Å, the partial charge on hydrogen and chlorine, respectively are

(a) +1.0 and −1.0 (b) +0.85 and −0.85
(c) +0.356 and −0.356 (d) +0.178 and −0.178

GATE 2005

38. The incorrect statement for solid sodium chloride is that

(a) both sodium and chloride ions adopt inert gas configuration
(b) the conduction band is full
(c) the conduction band is empty
(d) the valence band is full

GATE 2004

39. The structures of $N(CH_3)_3$ and $N(SiH_3)_3$ respectively are

(a) trigonal planar and pyramidal
(b) pyramidal and trigonal planar
(c) pyramidal and pyramidal
(d) trigonal planar and trigonal planar

40. The ground state term symbols for high spin d^5s^1 and d^5 configurations, respectively are

(a) ^3S and ^6S (b) ^6P and ^3S
(c) ^7S and ^6S (d) ^7P and ^6S

41. The spinels $CoFe_2O_4$ and $FeFe_2O_4$ respectively are
    (a) inverse and inverse
    (b) inverse and normal
    (c) normal and normal
    (d) normal and inverse

▾ ***Solution Points***

GATE 2003

42. The number of manganese ions in tetrahedral and octahedral sites, respectively in Mn_3O_4 are
    (a) one Mn^{2+} and two Mn^{3+}
    (b) one Mn^{3+} and two Mn^{2+}
    (c) two Mn^{3+} and one Mn^{2+}
    (d) two Mn^{2+} and one Mn^{3+}

43. The xenon compounds that are isostructural with IBr_2^- and BrO_3^- respectively are
    (a) linear XeF_2 and pyramidal XeO_3
    (b) bent XeF_2 and pyramidal XeO_3
    (c) bent XeF_2 and planar XeO_3
    (d) linear XeF_2 and tetrahedral XeO_3

GATE 2002

44. The structures of O_3 and N_3^- are
    (a) linear and bent respectively
    (b) both linear
    (c) both bent
    (d) bent and linear respectively

45. Sodium metal crystallizes in the body centred cubic lattice with cell edge a. The radius of the sodium atom is
    (a) $a/\sqrt{2}$
    (b) $a\sqrt{3}/2$
    (c) $a\sqrt{3}/4$
    (d) $a/2\sqrt{2}$

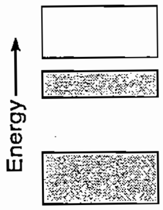
46. The bond order for N_2, O_2, N_2^-, O_2^- varies as
    (a) $N_2 > N_2^- > O_2 > O_2^-$
    (b) $N_2 > O_2 > N_2^- > O_2^-$
    (c) $O_2 > N_2 > O_2^- > N_2^-$
    (d) $N_2^- > N_2 > O_2^- > O_2$

GATE 2000

47. The compound $(SiH_3)_3N$ is expected to be
    (a) pyramidal and more basic than $(CH_3)_3N$
    (b) planar and less basic than $(CH_3)_3N$
    (c) pyramidal and less basic than $(CH_3)_3N$
    (d) planar and more basic than $(CH_3)_3N$

Answers with Explanations

1. (a) The band structure in an n-type semiconductor is as

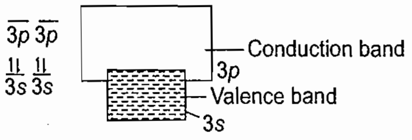


This is because a large energy difference (gap) exist between valence band and conduction band in case of a semiconductor and addition of an impurity (having higher valency) results in the n-type semiconductor. Thus, I represents the n-type semiconductor.

2. (c) The electronic configuration of Mg is

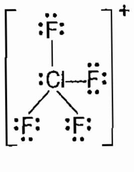
$$1s^2, 2s^2, 2p^6, 3s^2, 3p^0$$

In it $3s$-orbital is completely filled and $3p$-orbital is empty. There is very small energy difference between $3s$ and $3p$-orbitals. Thus, they overlap and make the Mg a conductor.



Band model of Mg

3. (d) ClF_4^+ has 34 valence electrons. Cl has 4 bonding pairs around it and 1 non-bonding pair is also present. If all 5 groups of electrons were involved in bonding, the shape would be trigonal bipyramidal. With one non-bonding pair, the shape becomes see-saw.



4. (b) BaF_2 is a AX_2 type salt. In its crystal, Ba^{2+} ions are arranged in ccp arrangement. Since there are two tetrahedral sites for each Ba^{2+} ion and F^- ions occupy all the tetrahedral sites, there will be two F^- ions for each Ba^{2+} ion. Thus, each F^- is surrounded by four Ba^{2+}, *i.e.*, the coordination number of F^- is 4.

5. (d) SiO_4^{4-} and PO_4^{3-} both have tetrahedral structure.

In SiO_4^{4-}, no.of electrons $= 14 + (8 \times 4) + 4 = 50$

In PO_4^{3-}, no. of electrons $= 15 + (8 \times 4) + 3 = 50$

Because of the presence of same number of electrons, SiO_4^{4-} and PO_4^{3-} are isoelectronic.

6. (a) Total number of valence electrons in HF

$$= 1 + 9 = 10$$

The electronic configuration is

$$\sigma\, 1s^2, \overset{*}{\sigma}\, 1s^2, \sigma\, 2s^2, \overset{*}{\sigma}\, 2s^2, \pi 2px^1 \approx \pi 2py^1$$

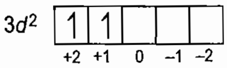
7. (d) The point group of NSF_3 is C_{3v}.

8. (d) If M^{3+} ion has a higher CFSE in an octahedral field compared to M^{2+} ion, normal spinel will result. If M^{2+} ion have a higher CFSE in a octahedral field compared to M^{3+} ion, inverse spinel will result. The general formula of spinel is $A^{2+}B_2^{3+}O_4^{2-}$. Among the compounds Fe_3O_4 (*i.e.*, $Fe\,Fe_2O_4$) and $NiFe_2O_4$ have inverse spinel structure.

9. (c) In NaCl, per cent of defect depends upon the concentration of solution and its rate of evaporation.

10. (b) $CaTiO_3$ has perovskite type structure. In it, Ti has a coordination number 6.

11. (a) $V^{3+} = [Ar]3d^2$



$$S = n \times \frac{1}{2}$$

where, n = number of unpaired electrons

$$\therefore \quad S = 2 \times \frac{1}{2} = 1$$

Multiplicity $= 2S + 1 = (2 \times 1) + 1 = 3$

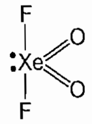
$$L = \Sigma m_2 = +2 + 1 = 3$$

when $L = 3$, orbital is F.

Thus, the ground state term symbol for V^{3+} ion is ^3F.

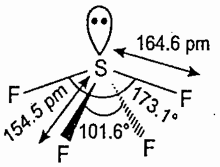
12. (a) The symmetry elements that are present in BF_3 are $C_3, \sigma_v, \sigma_h, 3C_2$.

13. (c) In XeO_2F_2 there are 4 bond pairs and 1 lone pair. Its shape should be trigonal bipyramidal but there is a lone pair, and bond pair-bond pair repulsion is lesser than lone pair-lone pair repulsion, so to attain maximum stability and to reduce repulsion, it has see-saw shape.

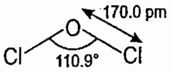


XeO_2F_2

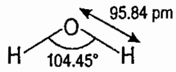
14. (c) Sulphur in SF_4 is in + 4 oxidation state. Out of total of six valence electrons of sulphur, two form a lone pair. The structure of SF_4 should be trigonal bipyramidal but due to the presence of one lone pair it has see-saw shape (according to VSEPR theory).



15. (b) The bond angle of Cl_2O is 110.10° and that of water is 104.45°.



Structure of Cl_2O



Structure of H_2O

16. (c) $N_2\ (7+7=14) = \sigma 1s^2, \overset{*}{\sigma}\ 1s^2, \sigma 2s^2, \overset{*}{\sigma}\ 2s^2, \pi 2p_x^2$

$$\approx \pi 2p_y^2, \sigma 2p_z^2$$

$N_2^+\ (7+7-1=13) = \sigma 1s^2, \overset{*}{\sigma}\ 1s^2, \sigma 2s^2, \overset{*}{\sigma}\ 2s^2, \pi 2p_x^2$

$$\approx \pi 2p_y^2, \sigma 2p_z^1$$

Nitrogen has no unpaired electron, so it is diamagnetic while N_2^+ has one unpaired electron, so it is paramagnetic in nature.

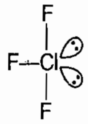
17. (d) Electronic configuration of C_2 is

$$\sigma 1s^2, \overset{*}{\sigma}\ 1s^2, \sigma 2s^2, \overset{*}{\sigma}\ 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2$$

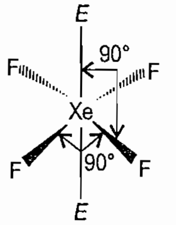
$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{8-4}{2} = 2$$

Since, all the electrons are paired, it is diamagnetic.

18. (b) ClF_3 has two lone pairs of electrons on the central atom.



19. (d) $XeF_4 \Rightarrow 4bp + 2lp = 6$ hybrid orbitals.
Thus, the geometry of XeF_4 is square planar because of the presence of two lone pairs of electrons.

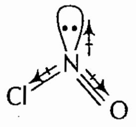


20. (d) Icosahedral structure is shown by boron compounds.

21. (c) Bromine utilized three out of the five sp^3d hybridized orbital in BrF_3.

22. (b) In BF_3 the symmetry point group is D_{3h}.

23. (b) NOCl has the following structure because of the presence of two bond pairs and one lone pair of electrons.



$\mu \neq 0$

i.e., it has some dipole moment and is not chiral. NOCl belongs to the point group C_s.

24. (b) Bond order is reciprocal to bond length. So, the molecule with higher bond order will have shorter bond length.

$$\text{Bond order of } C_2 = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[6-2] = 2$$

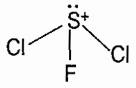
$$\text{Bond order of } N_2 = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[8-2] = 3$$

$$\text{Bond order of } O_2 = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[8-4] = 2$$

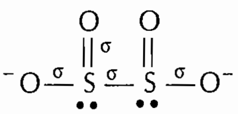
$$\text{Bond order of } F_2 = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[8-6] = 1$$

N_2 has highest value of bond order, so it will have shorter bond length.

25. (a) In $[SFCl_2]^+$, S is the central atom.
$[SFCl_2]^+ = 3bp + 1lp = 4 \Rightarrow sp^3$ hybridization and thus, $[SFCl_2]^+$ has trigonal pyramidal geometry.



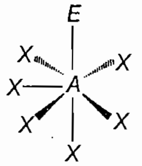
$[S_2O_4]^{2-}$ has the following structure



$$^{-}O \overset{\sigma}{-} \underset{\bullet\bullet}{\overset{\overset{\displaystyle O}{\|\,\sigma}}{S}} \overset{\sigma}{-} \underset{\bullet\bullet}{\overset{\overset{\displaystyle O}{\|}}{S}} \overset{\sigma}{-} O^{-}$$

In it the lone pair does not repel the SO_2^- group as S—S bond length is very large. Thus, its structure is trigonal planar.

26. (d) Shape of $[XeOF_5]^-$ is as



Pentagonal monopyramidal

A represents the central metal, *i.e.*, Xe the *X* represents the number of sigma bonds between the central atoms and outside atoms, *i.e.*, between Xe and F or Xe and O. The *E* represents the number of lone pair of electrons surrounding the central atom.

27. (d) The point group of ClF_3 molecule is C_{2v}. Thus, the corresponding number of irreducible representations is 3.

28. (d) If M^{3+} ion has a higher CFSE in an octahedral field compared to M^{2+} ion, normal spinel will result. If M^{2+} ion has a higher CFSE in an octahedral field compared to M^{3+} ion, inverse spinel will result.

Fe_3O_4 is composed of Fe(II) (ous) and Fe(III) (ic) ions with d^6 and d^5 configuration, respectively. Since, d^5 has no CFSE, hence the structure is inverse. Co_3O_4 has a similar structure with d^7 and d^6 configurations for +2 and +3 states respectively. Co^{3+}, *i.e.*, d^6 ion is low spin because of its (a) high charge (even with weak ligands like oxo) and (b) maximum gain in CFSE. So, the structure is normal.

29. (a) In XeF_4 and $[SiF_6]^{2-}$ both, the hybridization of central atom is sp^3d^2 as the former contains 4 bond pairs and 2 lone pairs while latter has 6 bond pairs *i.e.*, total six hybrid orbitals.

30. (a) Since, the compound have 2-fold rotational axis and an inversion centre, two distinct symmetry operations can be performed.

31. (c) The number of irreducible representations of the point group of the molecule is three (C_2, Sz, σ_h).

32. (b) The point group of the resultant molecule will be C_{2h}.

33. (b) Density of a unit cell, $d = \dfrac{Z \times M}{a^3 \times N_A}$

$$3.62 = \frac{2 \times 137.3}{a^3 \times 6.023 \times 10^{23}}$$

$$a^3 = \frac{2 \times 137.3}{3.62 \times 6.023 \times 10^{23}}$$

$$= 12.59 \times 10^{-23}$$

$$a = 2.30 \times 10^{-7.66}$$

$$= 2.30 \times 10^{-8}$$

Diagonal of any face $= a\sqrt{2}$

$$= 2.3 \times 10^{-8}\sqrt{2}$$

$$= 2.3 \times 10^{-8} \times 1.414$$

$$2n = 2.3 \times 10^{-8} \times 1.414$$

$$n = 1.6 \times 10^{-8}$$

34. (b) Due to the presence of six fluoride ligands and one lone pair of electrons in XeF_6, the structure lacks perfect octahedral symmetry and is disordered. In $[XeO_6]^{4-}$ all the valence shell electrons of xenon are involved in the bonding with oxygen and hence, no lone pair of electrons is present. So, it has perfect octahedral geometry.

35. (b) In zinc blende structure cubic closed packing is found. While in wurtzite structure hexagonal closed packing is found.

36. (a) In Pb_3O_4, the chains of $\overset{IV}{Pb}O_6$ octahedra aligned along (001) plane. The space between $[\overset{IV}{Pb}O_6]$ chains is occupied by loose pairs of Pb^{2+} ions forming tetrahedron. Thus, the crystal structure of Pb_3O_4 contains both octahedral and tetrahedral units.

37. (b) Dipole moment = Charge × Bond distance

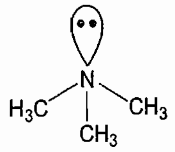
$$1.08 = \text{Charge} \times 1.27$$

$$\text{Charge} = 1.08/1.27 = 0.85$$

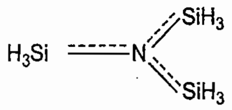
Since, HCl is electrically neutral, H^+ and Cl^- will carry the same charge with opposite sign.

38. (c) In solid sodium chloride conduction band is not empty.

39. (b) The structure of $N(CH_3)_3$ is pyramidal and structure of $N(SiH_3)_3$ is trigonal planar. This is because Si contains empty *d*-orbitals and utilised them in back bonding with N.



Structure of $N(CH_3)_3$
pyramidal

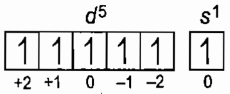


Structure of $N(SiH_3)_3$
trigonal planar

40. (c) In d^5s^1 configuration, there are 6 unpaired electrons.

So, $\quad S = n \times \dfrac{1}{2} = 6 \times \dfrac{1}{2} = 3$

Multiplicity = 2S + 1 = (2 × 3) + 1 = 7



$$L = \Sigma m_2 = +2 + 1 + 0 - 1 - 2 + 0 = 0$$

when $L = 0$, orbital is S. So, the ground state term symbol is ^7S. Similarly, for d^5, $S = \dfrac{5}{2}$ and multiplicity $= \left(2 \times \dfrac{5}{2} + 1\right) = 6$. Thus, the term symbol is ^6S.

41. (a) Both $CoFe_2O_4$ and $FeFe_2O_4$ have inverse spinel structure.

42. (a) Mn_3O_4 has normal spinel structure, so the dipositive Mn^{2+} occupy tetrahadral holes while tripositive Mn^{3+} occupy octahedral holes. Thus, two Mn^{3+} ions are present in octahedral and one Mn^{2+} ion is found at tetrahedral site.

43. (a) In IBr_2^-,

number of hybrid orbitals, $H = \frac{1}{2}[V + m + A - C]$

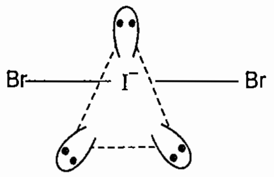
[where, V = no. of valence electrons, M = no. of monovalent atoms, A and C = negative and positive charge respectively]

$$H = \frac{1}{2}[7 + 2 + 1 - 0]$$

$$= \frac{1}{2}[10] = 5$$

So, its hybridization is sp^3d, and thus structure should be trigonal bipyramidal.

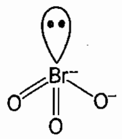
But because of the presence of three lone pairs of electrons its actual geometry is linear.



Linear geometry

In BrO_3^-, $H = \frac{1}{2}[7 + 0 + 1 - 0] = 4 \Rightarrow sp^3$ hybridization.

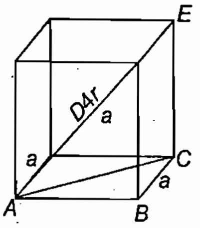
Thus, the structure should be tetrahedral.



But its actual geometry is pyramidal due to the presence of a lone pair of electrons.

44. (d) O_3 has bent and N_3^- has linear structure.

45. (c) In $\Delta\, ACD$,



$$AC^2 = a^2 + a^2 = 2a^2$$

$$\therefore \quad AC = \sqrt{2}a$$

$$AE^2 = AC^2 + EC^2$$

$$= (\sqrt{2}a)^2 + a^2 = 3a^2$$

$$AE = \sqrt{3}a$$

$$\Rightarrow \quad 4r = \sqrt{3}a$$

$$r = \frac{\sqrt{3}}{4}a$$

46. (a) Bond order of $N_2 = \frac{1}{2}(10 - 4) = 3$

Bond order of $O_2 = \frac{1}{2}(10 - 6) = 2$

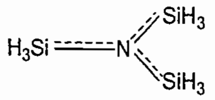
Bond order of $N_2^- = \frac{1}{2}(10 - 5) = 2.5$

Bond order of $O_2^- = \frac{1}{2}(10 - 7) = 1.5$

Thus, the order is

$$N_2 > N_2^- > O_2 > O_2^-$$

47. (b) Si because of the presence of empty d-orbital forms back bonds with lone pair of nitrogen. Thus, the lone pair is no longer available for donation or protonation. While such a condition is not found in $(CH_3)_3N$. So, $(CH_3)_3N$ is more basic than $(SiH_3)_3N$ and $(SiH_3)_3N$ has trigonal planar structure.



Trigonal planar structure of $(SiH_3)_3N$

3

s-Block and *p*-Block Elements

Syllabus

s-Block and p-Block Elements Main group elements : General characteristics, allotropes, structure and reactions of simple and industrially important compounds : boranes, carboranes, silicones, silicates, boron nitride, borazines and phosphazenes. Hydrides, oxides and oxoacids of pnicogens (N, P), chalcogens (S, Se and Te) and halogens, xenon compounds, pseudo halogens and interhalogen compounds. Shapes of molecules and hard-soft acid base concept. Structure and bonding (VBT) of B, Al, Si, N, P, S, Cl compounds. Allotropes of carbon : graphite, diamond, C_{60}. Synthesis and reactivity of inorganic polymers of Si and P.

GATE 2011

(1 Mark Questions)

1. Among the following, the group of molecules that undergoes rapid hydrolysis is

(a) SF_6, Al_2Cl_6, $SiMe_4$
(b) BCl_3, SF_6, $SiCl_4$
(c) BCl_3, $SiCl_4$, PCl_5
(d) SF_6, Al_2Cl_6, $SiCl_4$

2. The reaction of solid XeF_2 with AsF_5 in 1 : 1 ratio affords

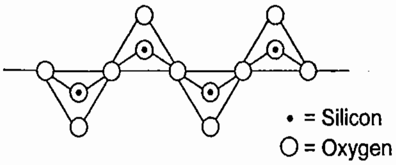
(a) XeF_4 and AsF_3
(b) XeF_6 and AsF_3
(c) $[XeF]^+ [AsF_6]^-$
(d) $[Xe_2F_3]^+[AsF_6]^-$

GATE 2010

3. The Lewis acidity of BF_3 is less than BCl_3 even though fluorine is more electronegative than chlorine. It is due to

(a) stronger $2p$ (B) – $2p$ (F) σ-bonding
(b) stronger $2p$ (B) – $2p$ (F) π-bonding
(c) stronger $2p$ (B) – $3p$ (Cl) σ-bonding
(d) stronger $2p$ (B) – $3p$ (Cl) π-bonding

4. Pyroxenes are class of silicate minerals, which exhibit a polymeric chain structure, as shown below



▾ *Solution Points*

Its simplest repeating unit is

(a) $[SiO_4]^{4-}$ (b) $[SiO_3]^{2-}$

(c) $[Si_2O_7]^{6-}$ (d) $[Si_4O_{11}]^{6-}$

5. The number of 'framework electron pairs' present in the borane cluster $[B_{12}H_{12}]^{2-}$ is

(a) 10 (b) 11 (c) 12 (d) 13

GATE 2008

6. White phosphorus, P_4 belongs to the

(a) closo system (b) nido system

(c) arachno system (d) hypho system

GATE 2007

7. The Lewis acid character of BF_3, BCl_3 and BBr_3 follows the order

(a) $BF_3 < BBr_3 < BCl_3$ (b) $BCl_3 < BBr_3 < BF_3$

(c) $BF_3 < BCl_3 < BBr_3$ (d) $BBr_3 < BCl_3 < BF_3$

8. $BaTi[Si_3O_9]$ is a class of

(a) orthosilicate (b) cyclic silicate

(c) chain silicate (d) sheet silicate

GATE 2006

9. $Mg_6Si_4O_{10}(OH)_8$ is commercially known as

(a) asbestos (b) water-glass

(c) soda-glass (d) zeolite

GATE 2005

10. Triple superphosphate is made by treating phosphate rock with

(a) conc. H_2SO_4 (b) conc. HNO_3

(c) conc. HCl (d) conc. H_3PO_4

11. The number of hydroxyl (OH) groups present in phosphorus acid is

(a) one (b) two

(c) three (d) four

GATE 2003

12. $BH_3 \cdot CO$ is more stable than $BF_3 \cdot CO$ because

(a) CO is a soft base and BH_3 and BF_3 are soft and hard acids respectively

(b) CO is a hard base and BH_3 and BF_3 are hard and soft acids respectively

(c) CO is a soft base and BH_3 and BF_3 are hard and soft acids respectively

(d) CO is a soft acid and BH_3 and BF_3 are soft and hard bases respectively

13. Using chlorobenzene as solvent, the reagents needed for an efficient synthesis of borazine are

(a) NH_4Cl and BCl_3 (b) NH_4Cl and BCl_3 and $NaBH_4$

(c) NH_4Cl and $NaBH_3$ (d) NH_3 and BCl_3

▾ *Solution Points*

GATE 2001

▾ *Solution Points*

14. The first ionization potential of Mg, Al, P and S follows the order

(a) Mg < Al < P < S (b) Al < Mg < P < S

(c) Al < Mg < S < P (d) Mg < Al < S < P

GATE 2000

15. The order of acidity in boron trihalides is

(a) $BF_3 > BCl_3 > BBr_3$ (b) $BBr_3 > BCl_3 > BF_3$

(c) $BF_3 > BBr_3 > BCl_3$ (d) $BBr_3 > BF_3 > BCl_3$

16. Among the following diatomic molecules, the one shows EPR signal, is

(a) Li_2 (b) B_2

(c) C_2 (d) N_2

GATE 2011

(2 Marks Questions)

Common Data for Questions 26 and 27

Na_2HPO_4 and NaH_2PO_4 on heating at high temperature produce a chain sodium pentaphosphate quantitatively.

17. The ideal molar ratio of Na_2HPO_4 to NaH_2PO_4 is

(a) 4 : 1 (b) 1 : 4

(c) 3 : 2 (d) 2 : 3

18. The total charge on pentaphosphate anion is

(a) −5 (b) −3

(c) −7 (d) −9

GATE 2010

19. The most populated rotational state for HCl ($B = 8.5\ cm^{-1}$) at 300 K is

(a) 2 (b) 3

(c) 5 (d) 7

GATE 2007

20. The reaction of ammonium chloride with BCl_3 at 140°C followed $NaBH_4$ gives product *X*. The formula of *X* is

(a) $B_3N_3H_3$ (b) $B_3N_3H_6$

(c) $B_3N_3H_{12}$ (d) $[BH\ldots NH]_n$

21. Which of the following statements is/are true for *X*?

(i) *X* is not isoelectronic with benzene.

(ii) *X* undergoes addition reaction with HCl.

(iii) Electrophilic substitution reaction on *X* is much faster than that of benzene.

(iv) *X* undergoes polymerization at 90°C.

(a) (i) and (ii) (b) (ii) only

(c) (ii) and (iii) (d) (i) and (iv)

▾ *Solution Points*

22. The correct classification of $[B_5H_5]^{2-}$, B_5H_9 and B_5H_{11} respectively is

(a) closo, arachno, nido (b) arachno, closo, nido

(b) closo, nido, arachno (d) nido, arachno, closo

Statement for Linked Answer Questions 23 and 24

Triphosphazene is prepared by reacting *X* and *Y* in equimolar ratio at 120-150°C using appropriate solvents.

23. The reactants *X* and *Y* respectively, are

(a) PCl_3; NH_3

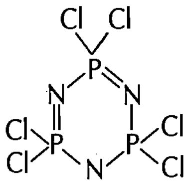
(b) PCl_5; NH_3

(c) PCl_5; NH_4Cl

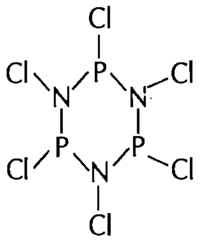
(d) PCl_3; NH_4Cl

24. The structure of triphosphazene is

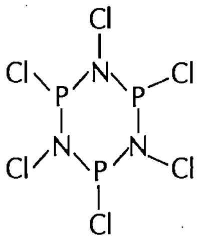
(a)



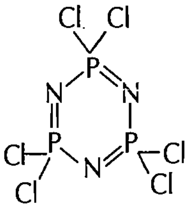
(b)



(c)



(d)



GATE 2004

25. The overall charge present on the cyclic silicate anion $[Si_6O_{18}]^{n-}$ is

(a) 6 (b) 12

(c) 18 (d) 24

26. The reagents required for the synthesis of cyclic phosphazene $N_4P_4Cl_8$ are

(a) PCl_5 and NH_3

(b) $POCl_3$ and NH_4Cl

(c) $POCl_3$ and NH_3

(d) PCl_5 and NH_4Cl

27. According to Wade's rule, the structures of $B_{10}C_2H_{12}$ and $[B_9C_2H_{11}]^{2-}$ respectively are

(a) closo and arachno (b) nido and closo

(c) closo and nido (d) nido and arachno

28. The perxenate ion XeO_4^{4-} can be prepared by

(a) direct reaction of Xe with oxygen

(b) reaction of XeF_6 with oxygen

(c) hydrolysis of XeF_6 in acidic medium

(d) hydrolysis of XeF_6 in basic medium

GATE 2003

29. Match the silicate minerals (Column I) with their compositions (Column II) and order of hardness (Column III).

	Column I		Column II		Column III
P	Talc	U	$KAl_2AlSi_3O_{10}(OH)_2$	X	High
Q	Muscovite	V	$Mg_3Si_4O_{10}(OH)_2$	Y	Low
R	Margarite	W	$CaAl_2\,AlSi_3O_{10}\,(OH)_2$	Z	Intermediate

(a) P, V,Y—Q, U, Z—R, W, X
(b) P, U, X—Q, V, Z—R, W, Y
(c) P, W, X—Q, V, Y—R, U, Z
(d) P, V, Z—Q, U, Y—R, W, X

30. Using the Wade rule, the structure of $B_{10}C_2H_{12}$ can be predicted. The structure and the number of isomers of $B_{10}C_2H_{12}$ respectively, are

(a) nido are two
(b) closo and three
(c) nido and one
(d) closo and two

GATE 2001

31. Which one of the following will show closo structure?

(a) B_5H_9
(b) $B_{12}H_{12}^{2-}$
(c) B_4H_{10}
(d) B_5H_{11}

GATE 2000

32. Which of the following is an arachno borane?

(a) $[B_6H_6]^{2-}$
(b) $[B_5H_9]$
(c) $[B_2H_6]$
(d) $[B_6H_{12}]$

▾ *Solution Points*

Answers with Explanations

1. (c) SF_6 is chemically inert, so it does not undergo rapid hydrolysis.

BCl_3, $SiCl_4$ and PCl_5 get readily hydrolysed to give orthoboric, orthosilicic and phosphoric acid respectively.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$
$$SiCl_4 + 4H_2O \longrightarrow H_4SiO_4 + 4HCl$$
$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$
$$\xrightarrow[\text{(excess)}]{H_2O} H_3PO_4 + HCl$$

[**Note** Al_2Cl_6 is soluble in non-polar solvents.]

2. (c) XeF_2 (Xenon difluoride) acts as a fluoride donor and thus, forms complex when mixed with covalent pentafluorides like AsF_5.

$$\underset{1}{XeF_2} + \underset{1}{AsF_5} \longrightarrow [XeF]^+ [AsF_6]^-$$

3. (b) In BF_3, boron has a vacant $2p$-orbital and each fluorine has completely filled unutilised $2p$-orbital. Fluorine transfers these two $2p$-electrons to vacant $2p$-orbital of boron. This bond reduces electron deficiency of boron and hence, also the Lewis acidity. Tendency of formation of such bond is more in fluorine due its small size.

4. (b) In pyroxenes, there is a total of 3 oxygen atoms per silicon atom, so the simplest repeating unit is $[SiO_3]^{2-}$ or $(SiO_3)^{2n-}$.

5. (d) In $[B_{12}H_{12}]^{2-}$ anion, $m = 12$ (where m = number of BH units).

According to Wades' rules, each BH unit contributes two electrons to the framework bonding in the borane and the negative charge is also assumed to be used up in the framework bonding.

Thus, the total number of electrons in

$$[B_{12}H_{12}]^{2-} = \underbrace{12 \times 2}_{\text{due to BH unit}} + \underbrace{2}_{\text{negative charge}} = 24 + 2 = 26$$

Thus, the number of electron pairs $= \dfrac{26}{2} = 13$

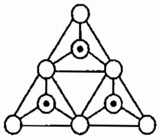
6. (b) P_4 molecule has tetrahedral structure. According to Wade, one P is equivalent to BH_2

So, $P_4 \approx (BH_2)_4 = B_4H_8$ or $B_4H_4^{4-}$

Thus, it should belong to nido system.

7. (c) In boron trihalide, BF_3 is least acidic. Due to its small size, F has a tendency to back donate its lone pair of electrons to B. Due to this electron transfer, the electron deficiency of B is reduced. Such tendency to back donate the electron pair is least in Br. So, the order of acidity is $BBr_3 > BCl_3 > BF_3$.

8. (b) The primary unit of $BaTi(Si_3O_9)$ or $(Si_3O_9^{6-})$ is $(SiO_3)^{2-}$ (as $n = 3$). Thus, it is formed by sharing of two oxygen per Si atom and results in the formation of cyclic silicate.



• = Silicon atom

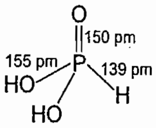
O = Oxygen atom

9. (a) Chrysotile $(Mg_6Si_4O_{10}(OH)_8)$ is commercially known as asbestos.

10. (d) Triple superphosphate is produced by the action of 54% phosphoric acid over phosphate mineral.

$$Ca_3(PO_4)_2 + 4H_3PO_4 \longrightarrow 3Ca(H_2PO_4)_2$$

11. (b) Phosphorus acid (H_3PO_3) has two OH groups.



12. (a) $BH_3 \cdot CO$ is more stable then $BF_3 \cdot CO$ because BH_3 is a soft acid and CO is a soft base and soft acids react faster and form stronger bonds with soft bases.

13. (b) Borazine can be prepared by using NH_4Cl, BCl_3 and $NaBH_4$. It is a two-step process. In the first step, NH_4Cl and boron trichloride react together to give trichloro borazine in chlorobenzene solvent.

$$3BCl_3 + 3NH_4Cl \longrightarrow Cl_3B_3H_3N_3 + 9HCl$$

In second step, B—Cl bonds are subsequently converted to B—H bonds.

$$2Cl_3B_3H_3N_3 + 6NaBH_4 \longrightarrow \underset{\text{borazine}}{2B_3H_6N_3} + 3B_2H_6 + 6NaCl$$

14. (d) Though ionization potential increases on moving across the period as nuclear attraction increases but phosphorus has half-filled $3p$ orbital and Mg completely filled $3s$-orbital which are more stable than incompletely filled orbital. Thus, a large amount of energy is required to remove an electron. Thus, IE of S is less than that of P and IP of Al is less than that of Mg. Order of IE is

$$Al < Mg < S < P$$

15. (b) In boron trihalide BF_3 is least acidic. This is because, due to its small size of F, it has a tendency to back donate its lone pair of electrons to B. Due to this electron transfer the electron deficiency of B is reduced. Such tendency to back donate the electron pair is least in Br. So, the order of acidity is

$$BBr_3 > BCl_3 > BF_3$$

16. (b) EPR signal is given by paramagnetic species. Li_2, C_2 and N_2 have no unpaired electrons and are diamagnetic. B_2 contains unpaired electron and is paramagnetic, so it can give EPR signals.

17. (d) When Na_2HPO_4 and NaH_2PO_4 are heated in the ratio of 2 : 3, a chain sodium pentaphosphate is formed.

$$2Na_2HPO_4 + 3NaH_2PO_4 \longrightarrow \underset{\text{sodium pentaphosphate}}{Na_7P_5O_{16}} + 4H_2O$$

18. (c) Sodium pentaphosphate is $Na_7P_5O_{16}$. Thus, pentaphosphate anion is $P_5O_{16}^{7-}$, *i.e.*, this anion carries −7 charge.

19. (b) Most populated rotational state,

$$j_{\max} = \frac{1}{2}\left[\sqrt{\frac{2kT}{B}} - 1\right]$$

$$B = 8.5\text{cm}^{-1} = 6.6 \times 10^{-34} \times 3 \times 10^8 \times 8.5 \times 100\,\text{J}$$

$$= 1.68 \times 10^{-22}$$

$$\because \quad j_{\max} = \frac{1}{2}\left[\sqrt{\frac{2 \times 1.38 \times 10^{-23} \times 300}{1.68 \times 10^{-22}}} - 1\right]$$

$$= \frac{1}{2}[7 - 1] = \frac{1}{2} \times 6 = 3$$

20. (b) Preparation of borazine is a two-step process. In this process, boron trichloride is first converted to trichloroborazine.

$$3BCl_3 + 3NH_4Cl \longrightarrow Cl_3B_3H_3N_3 + 9HCl$$

The B—Cl bonds are subsequently converted to B—H bonds.

$$2Cl_3B_3H_3N_3 + 6NaBH_4 \longrightarrow 2B_3H_6N_3 + 3\,B_2H_6 + 6NaCl$$

21. (b) X is borazine. It is isoelectronic with benzene. It reacts with hydrogen chloride to give an addition product.

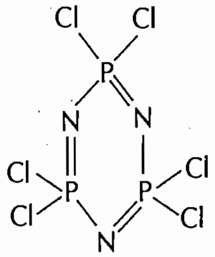
$$B_3N_3H_6 + 3HCl \longrightarrow B_3N_3H_9Cl_3$$

22. (c) The formulae for closo, nido and arachno borane are $[B_nH_n]^{2-}$, B_nH_{n+4} and B_nH_{n+6} respectively. Thus, $[B_5H_5]^{2-}$ is a closo borane. B_5H_9 $[B_5H_{5+4}]$ is a nido borane and B_5H_{11} $[B_5H_{5+6}]$ is a arachno borane.

23. (c) Triphosphazene is prepared by reacting PCl_5; NH_4Cl in equimolar ratio at 120-150°C. A halo hydrocarbon is used as solvent.

$$nPCl_5 + nNH_4Cl \xrightarrow{120-150°C} [NPCl_2]_n + 4n\,HCl$$

24. (d) Structure of triphosphazene is as



25. (b) The overall charge present on Si_6O_{18} is −12 as $x = 6$ in $(SiO_3)_x^{2x-}$.

26. (d) By the reaction of PCl_5 and NH_4Cl, substances with the empirical formula $PNCl_2$ are formed, which on purification by sublimation gives mainly the trimer $(PNCl_2)_3$ and tetramer $(PNCl_2)_4$.

$$nPCl_5 + nNH_4Cl \xrightarrow{130°C} (NPCl_2)_n + 4nHCl$$

27. (c) According to Wade's rule, carboranes are obtained by replacing BH unit by CH^+ unit. So

	Carborane	Borane formula (By replacing CH^+ by BH)	Type
(i)	$B_{10}H_{12}C_2$ or $B_{10}H_{10}C_2H_2$	$B_{10}H_{10} \cdot B_2H_2^{2-}$ or $B_{12}H_{12}^{2-}$	Closo
(ii)	$[B_9C_2H_{11}]^{2-}$ or $[B_9H_9C_2H_2]^{2-}$	$B_9H_9 \cdot B_2H_2^{4-}$ or $B_{11}H_{11}^{4-}$	Nido

28. (d) When XeF_6 is hydrolyzed in a strongly alkaline medium a major portion is precipitated as perxenate salt (XeO_4^{4-}).

29. (a) Talc is $Mg_3Si_4O_{10}(OH)_2$ and its hardness is less. Moscovite is $KAl_2AlSi_3O_{10}(OH)_2$, its hardness is intermediate. Margarite is $CaAl_2AlSi_3O_{10}(OH)_2$, its hardness is high.

30. (b) Structure of $B_{10}C_2H_{12}$ is icosahedral (closo structure). It exists in three isomeric forms. They are orthocarborane (1, 2-$C_2B_{10}H_{12}$), metacarborane (1, 7-$C_2B_{10}H_{12}$), paracarborane (1, 12-$C_2B_{10}H_{12}$).

31. (b) According to Wade's rule, boranes having a formula of $(BH)^{2-}$ show closo structure. So, out of the given compounds, $B_{12}H_{12}^{2-}$ will show closo structure.

32. (d) In archno structure, the formula B_nH_{n+6} is used. Alternative $[B_6H_{12}]$ satisfies this condition.

4

Transition Elements

Syllabus

Transition Elements General characteristics of d and f-block elements ; Coordination chemistry : structure and isomerism, stability, theories of metal-ligand bonding (CFT and LFT), mechanisms of substitution and electron transfer reactions of coordination complexes. Electronic spectra and magnetic properties of transition metal complexes, lanthanides and actinides. Metal carbonyls, metal-metal bonds and metal atom clusters, metallocenes ; Transition metal complexes with bonds to hydrogen, alkyls, alkenes and arenes ; Metal carbenes ; Use of organometallic compounds as catalysts in organic synthesis. Bio-inorganic chemistry of Na, K, Mg, Ca, Fe, Co, Zn, Cu and Mo.

GATE 2011

(1 Mark Questions)

▾ *Solution Points*

1. John-Teller distortion of $CuSO_4 \cdot 5H_2O$ acts to
(a) raise symmetry
(b) remove an electronic degeneracy
(c) cause loss of H_2O ligand
(d) promote a *d*-electron to an antibonding molecular orbital

2. A well known naturally occurring organometallic compound is
(a) vitamin B_{12} coenzyme
(b) chlorophyll
(c) cytochrome P-450
(d) myoglobin

3. The complex that exists as a pair of enantiomers is
(a) *trans*-$[Co(H_2NCH_2CH_2NH_2)_2Cl_2]^+$
(b) *cis*-$[Co(NH_3)_4Cl_2]^+$
(c) $[Pt(PPh_3)(Cl)(Br)(CH_3)]^-$
(d) $[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$

4. The red colour of oxyhaemoglobin is mainly due to the
(a) d-d transition
(b) metal to ligand charge transfer transition
(c) ligand to metal charge transfer transition
(d) intraligand π-$\overset{*}{\pi}$ transition

GATE 2010

▾ *Solution Points*

5. Structurally nickelocene is similar to ferrocene. Nickelocene attains stability due to the formation of
   (a) a mono cation
   (b) a di cation
   (c) a mono anion
   (d) a di anion

6. Among the following pair of metal ions present in nature, the first one functions as an electron transfer agent and the second one catalyzes the hydrolysis reactions. The correct pair is
   (a) Fe and Zn
   (b) Mg and Fe
   (c) Co and Mo
   (d) Ca and Cu

GATE 2009

7. The correct statement about the Cu—N bond distances in $[Cu(NH_3)_6]^{2+}$ is
   (a) all the bond distances are equal
   (b) the axial bonds are longer than the equatorial ones
   (c) the equatorial bonds are longer than the axial ones
   (d) all the bond distances are unequal

8. In the transformation of oxyhaemoglobin to deoxyhaemoglobin
   (a) Fe^{2+} in the low spin state changes to Fe^{2+} in the high spin state
   (b) Fe^{2+} in the low spin state changes to Fe^{2+} in the low spin state
   (c) Fe^{2+} in the high spin state changes to Fe^{2+} in the low spin state
   (d) Fe^{2+} in the high spin state changes to Fe^{2+} in the high spin state

GATE 2008

9. In biological systems, the metal ions involved in electron transport are
   (a) Na^+ and K^+
   (b) Zn^{2+} and Mg^{2+}
   (c) Ca^{2+} and Mg^{2+}
   (d) Cu^{2+} and Fe^{2+}

10. The structures of the complexes $[Cu(NH_3)_4](ClO_4)_2$ and $[Cu(NH_3)_4](ClO_4)$ in the solution respectively are
    (a) square planar and tetrahedral
    (b) octahedral and square pyramidal
    (c) octahedral and trigonal bipyramidal
    (d) tetrahedral and square planar

11. The spectroscopic ground state symbol and the total number of electronic transitions of $[Ti(H_2O)_6]^{2+}$ are
    (a) $^3T_{1g}$ and 2
    (b) $^3A_{2g}$ and 3
    (c) $^3T_{1g}$ and 3
    (d) $^3A_{2g}$ and 2

12. Metal-metal quadruple bonds are well known for the metal
    (a) Ni
    (b) Co
    (c) Fe
    (d) Re

13. The magnetic moment of $[Ru(H_2O)_6]^{2+}$ corresponds to the presence of
    (a) four unpaired electrons
    (b) three unpaired electrons
    (c) two unpaired electrons
    (d) zero unpaired electrons

▾ *Solution Points*

GATE 2007

14. In photosynthesis, the predominant metal present in the reaction centre of photosystem II is

(a) Zn (b) Cu
(c) Mn (d) Fe

15. The octahedral complex/complex ion which shows both facial and meridional isomers is

(a) triglycinato cobalt (III)
(b) tris (ethylene diamine)) cobalt (III)
(c) dichloro diglycinato cobalt (III)
(d) trioxalate cobaltate (III)

16. The difference in the measured and calculated magnetic moment (based on spin-orbit coupling) is observed for

(a) Pm^{3+} (b) Eu^{3+}
(c) Dy^{3+} (d) Lu^{3+}

GATE 2006

17. Iron-sulphur clusters in biological systems are involved in

(a) proton transfer (b) atom transfer
(c) group transfer (d) electron transfer

18. The correct statement regarding the thermodynamic stability and kinetic reactivity of metal ion complexes is that

(a) more stable complexes are less reactive
(b) there exists a dependence on the bulkiness of the ligand
(c) there exists no direct relation between these two phenomenon
(d) there exists a dependence on the size of the metal ion

GATE 2005

19. The complexes $[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Br_2]Cl \cdot H_2O$ are examples of

(a) ionization isomerism (b) linkage isomerism
(c) geometrical isomerism (d) optical isomerism

20. In the trigonal bipyramidal crystal field, the *d* orbital with the highest energy is

(a) d_{xy} (b) $d^2_{x^2-y^2}$
(c) d_{yz} (d) d^2_z

21. The metal present at the active site of the protein carboxypeptidase *A* is

(a) zinc (b) molybdenum
(c) magnesium (d) cobalt

22. The neutral complex which follows the 18-electron rule is

(a) $(\eta^5 - C_5H_5)\,Fe(CO)_2$ (b) $(\eta^5 - C_5H_5)\,Mo(CO)_3$
(c) $(\eta^5 - C_5H_5)_2\,Co$ (d) $\eta^5 - C_5H_5)Re(\eta^6 - C_6H_6)$

GATE 2004

23. The absorption of $[Co(NH_3)_6]^{2+}$ is
(a) stronger than that of $[Co(NH_3)_5Cl]^{2+}$
(b) stronger than that of $[MnCl_4]^{2-}$
(c) weaker than that of $[MnCl_4]^{2-}$ but stronger than that of $[Co(NH_3)_5Cl]^{2+}$
(d) weaker than those of both $[MnCl_4]^{2-}$ and $[Co(NH_3)_5Cl]^{2+}$

24. The number of metal-metal bonds present in $Ir_4(CO)_{12}$ are
(a) 4 (b) 5 (c) 6 (d) 8

GATE 2003

25. The ligand field bands of lanthanide complexes are generally sharper than those of transition metal complexes because
(a) transitions are allowed for lanthanide complexes
(b) intensity of the bands are higher for lanthanide complexes
(c) *f*-orbital have higher energy than *d*-orbital
(d) *f*-orbital, compared to *d*-orbital interact less effectively with ligand

26. Nature has chosen Zn(II) ion at the active site of many hydrolytic enzymes because
(a) Zn(II) is a poor Lewis acid
(b) Zn(II) does not have chemically accessible redox states
(c) Zn(II) forms both four and higher coordination complexes
(d) Zn(II) forms weak complexes with oxygen donor ligands

GATE 2002

27. Electron transfer from $Fe(H_2O)_6^{2+}$ to $Fe(H_2O)_6^{3+}$ is likely to occur *via*
(a) *d-d* transitions (b) inner sphere electron transfer
(c) S_N1 mechanism (d) outer sphere electron transfer

28. The complex formed in the brown ring test for nitrates is
(a) $[Fe(H_2O)_5NO]^{3+}$ (b) $[Fe(H_2O)_5NO]^{2+}$
(c) $[Fe(H_2O)_4(NO)]^{2+}$ (d) $[Fe(H_2O)_4(NO)]^{3+}$

29. The complex which obeys the 18-electron rule is
(a) $Fe(CO)_4$ (b) $Ni(CO)_3(PPh_3)$
(c) $Cr(CO)_5$ (d) $Cr(C_5H_5)_2$

30. The existence of two different coloured complexes of $Co(NH_3)_4Cl_2$ is due to
(a) optical isomerism (b) linkage isomerism
(c) geometrical isomerism (d) coordination isomerism

GATE 2001

31. The chromium (III) species formed soon after electron transfer between $IrCl_6^{2-}$ and $Cr(H_2O)_6^{2+}$ is
(a) $Cr(H_2O)_6^{3+}$ (b) $Cr(H_2O)_5Cl^{2+}$
(c) $CrCl_6^{2-}$ (d) $Cr(H_2O)_3Cl_3$

▾ *Solution Points*

▾ ***Solution Points***

32. The metal ion present in carbonic anhydrase is
(a) Mn (b) Zn (c) Cu (d) Fe

GATE 2000

33. The compound which exhibits John-Teller distortion is
(a) $[Mn(H_2O)_6]^{2+}$ (b) $[Mn(H_2O)_6]^{3+}$
(c) $[Cr(H_2O)_6]^{3+}$ (d) $[Fe(CN)_6]^{4-}$

34. The compound which obeys 18-electron rule is
(a) $Mn(CO)_3$ (b) $Fe(CO)_4$ (c) $V(CO)_6$ (d) $Cr(CO)_6$

GATE 2011

(2 Marks Questions)

35. The crystal field stabilization energy (CFSE) value for $[Ti(H_2O)_6]^{3+}$ that has an absorption maximum at 492 nm is
(a) $20325\ cm^{-1}$ (b) $12195\ cm^{-1}$
(c) $10162\ cm^{-1}$ (d) $8130\ cm^{-1}$

36. In the isoelectronic series, VO_4^{3-}, CrO_4^{2-} and MnO_4^-, all members have intense charge transfer (CT) transitions. The incorrect statement is
(a) CT transitions are attributed to excitations of electrons from ligand (σ) to metal (e)
(b) MnO_4^- exhibits charge transfer at shortest wavelength among the three
(c) The wavelengths of transitions increase in the order $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$
(d) The charge on metal nucleus increases in the order $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$

37. The increasing order of wavelength of absorption for the complex ions
(i) $[Cr(NH_3)_6]^{3+}$ (ii) $[CrCl_6]^{3-}$
(iii) $[Cr(OH_2)_6]^{3+}$ (iv) $[Cr(CN)_6]^{3-}$
is
(a) iv < ii < i < iii (b) iv < iii < ii < i
(c) iv < i < iii < ii (c) ii < iii < i < iv

38. The total number of metal-metal bonds in $Ru_3(CO)_{12}$ and $Co_4(CO)_{12}$ respectively, is
(a) 3 and 6 (b) 4 and 5
(c) zero and 4 (d) 3 and 4

39. The product of the reaction between $CH_3Mn(CO)_5$ and ^{13}CO is
(a) $(CH_3^{13}CO)Mn(CO)^5$ (b) $(CH_3CO)Mn(CO)_4(^{13}CO)$
(c) $(^{13}CH_3CO)Mn(CO)_5$ (d) $CH_3Mn(CO)_4$

GATE 2010

40. The number of unpaired electron (s) present in the species $[Fe(H_2O)_5(NO)]^{2+}$ which is formed during brown ring test is
(a) 2 (b) 3 (c) 4 (d) 5

▾ *Solution Points*

41. The *d-d* absorption band of $[Fe(H_2O)_6]^{2+}$ is split due to

(a) presence of octahedral geometry
(b) static John-Teller distortion
(c) dynamic John-Teller distortion
(d) presence of trigonal bipyramidal geometry

42. The crystal-field symbol for the ground state of $[Mn(CN)_6]^{4-}$ is

(a) $^2T_{2g}$ (b) $^1A_{1g}$ (c) ^5E_g (d) $^6A_{1g}$

43. $[CoCl_4]^{2-}$ is a blue coloured complex. Controlled-treatment of this complex with water generates two isomeric light pink coloured complexes of composition $[Co(H_2O)_4Cl_2]$. Identify the correct point groups for $[CoCl_4]^{2-}$ and two isomeric complexes $[Co(H_2O)_4Cl_2]$.

(a) D_{4h} and (C_{2v} and C_{2h}) (b) T_d and (C_{2v} and D_{4h})
(c) D_{4h} and (C_{2v} and D_{4h}) (d) T_d and (C_{2v} and C_{4v})

Common Data for Questions 44 and 45

A six-coordinate transition metal complex is ESR and Mossbauer active. The effective magnetic moment of this complex is ~ 5.9 B.M.

44. The metal-ion along with its oxidation state and the number of unpaired electrons present are

(a) Fe(II) and 4 (b) Mn(II) and 5
(c) Fe(III) and 1 (d) Fe(III) and 5

45. The complex is

(a) $[Mn(H_2O)_6]^{2+}$ (b) $[Fe(CN)_6]^{3-}$
(c) $[Fe(H_2O)_6]^{2+}$ (d) $[Fe(H_2O)_6]^{3+}$

Gate 2009

Common Data for Questions 46 and 47

Treatment of $W(CO)_6$ with I equivalent of $Na(C_5H_5)$ in THF solution gives the ionic compound *M*. Reaction of *M* with glacial acetic acid results in product *N*. The ^{1}H NMR spectrum of *N* displays two singlets of relative intensity 5 : 1. When *N* is heated, hydrogen gas is evolved and *O* is produced. *O* may also be prepared by refluxing $W(CO)_6$ with cyclopentadiene and H_2 is also produced. Treatment of *O* with an equivalent of Br_2 produces *P*. (Use the 18 electron rule as your guide).

46. The compounds *M* and *N*, respectively are

(a) $[(C_5H_5)W(CO)_3]Na$ and $[(C_5H_5)W(CO)_3H]$
(b) $[(C_5H_5)W(CO)_4]Na$ and $[(C_5H_5)W(CO)_4H]$
(c) $[(C_5H_5)W(CO)_3]Na$ and $[(C_5H_5)W(CO)_4H]$
(d) $[(C_5H_5)W(CO)_4]Na$ and $[(C_5H_5)W(CO)_3H]$

47. The compounds *O* and *P*, respectively are

(a) $[(C_5H_5)W(CO)_3]_2$ and $[(C_5H_5)W(CO)_3Br]$
(b) $[(C_5H_5)W(CO)_4]$ and $[(C_5H_5)W(CO)_2Br(THF)]$
(c) $[(C_5H_5)W(CO)_2(THF)]$ and $[(C_5H_5)W(CO)_3Br]$
(d) $[(C_5H_5)W(CO)_3]_2$ and $[(C_5H_5)W(CO)_2Br(THF)]$

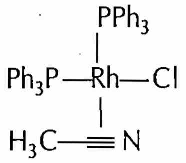
GATE 2008

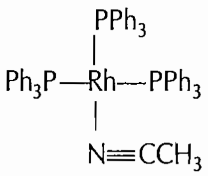
▾ *Solution Points*

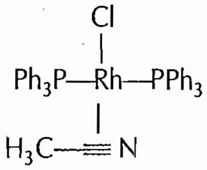
Statement for Linked Answer Questions 48 and 49

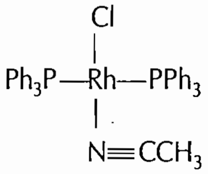
In the reaction, $(PPh_3)_3RhCl \xrightarrow{CH_3CN} X + Y$

48. Compound X is

(a)

$Ph_3P-\underset{\underset{H_3C\equiv N}{|}}{\overset{\overset{PPh_3}{|}}{Rh}}-Cl$

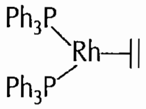
(b)

$Ph_3P-\underset{\underset{N\equiv CCH_3}{|}}{\overset{\overset{PPh_3}{|}}{Rh}}-PPh_3$

(c)

$Ph_3P-\underset{\underset{H_3C\equiv N}{|}}{\overset{\overset{Cl}{|}}{Rh}}-PPh_3$

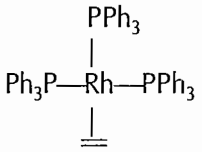
(d)

$Ph_3P-\underset{\underset{N\equiv CCH_3}{|}}{\overset{\overset{Cl}{|}}{Rh}}-PPh_3$

49. $Rh(Ph_3)_3Cl$ reacts very fast with a gaseous mixture of H_2 and C_2H_4 to immediately give Z. The structure of Z is

(a) H_3C-CH_3

(b)


(c) $(PPh_3)_2RhCl\,(\eta^2 - C_2H_4)$

(d)

$Ph_3P-\underset{\underset{=}{|}}{\overset{\overset{PPh_3}{|}}{Rh}}-PPh_3$

GATE 2007

50. The separation of trivalent lanthanide ions, Lu^{3+}, Yb^{3+}, Dy^{3+}, Eu^{3+} can be effectively done by a cation exchange resin using ammonium *o*-hydroxy *iso*-butyrate as the eluent. The order in which the ions will be separated is

(a) $Lu^{3+}, Yb^{3+}, Dy^{3+}, Eu^{3+}$
(b) $Eu^{3+}, Dy^{3+}, Yb^{3+}, Lu^{3+}$
(c) $Dy^{3+}, Yb^{3+}, Eu^{3+}, Lu^{3+}$
(d) $Yb^{3+}, Dy^{3+}, Lu^{3+}, Eu^{3+}$

51. Arrange the following metal complexes in order of their increasing hydration energy

$[Mn(H_2O)_6]^{2+}$	$[V(H_2O)_6]^{2+}$	$[Ni(H_2O)_6]^{2+}$	$[Ti(H_2O)_6]^{2+}$
P	Q	R	S

(a) $P < S < Q < R$
(b) $P < Q < R < S$
(c) $Q < P < R < S$
(d) $S < R < Q < P$

52. Consider the reactions :

1. $[Cr(H_2O)_6]^{2+} + [CoCl(NH_3)_5]^{2+} \longrightarrow [Co(NH_3)_5(H_2O)]^{2+} + [CrCl(H_2O)_5]^{2+}$

2. $[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$

Which one of the following is the correct statement?

(a) Both involve an inner sphere mechanism
(b) Both involve an outer sphere mechanism

(c) Reaction 1 follows inner sphere and reaction 2 follows outer sphere mechanism
(d) Reaction 1 follows outer sphere and reaction 2 follows inner sphere mechanism

53. The compound which shows $L \leftarrow M$ charge transfer is
(a) $Ni(CO)_4$ (b) $K_2Cr_2O_7$
(c) HgO (d) $[Ni(H_2O)_6]^{2+}$

54. The reaction of $[PtCl_4]^{2-}$ with NH_3 gives rise to
(a) $[PtCl_4(NH_3)_2]^{2-}$ (b) *trans*-$[PtCl_4(NH_3)_2]$
(c) $[PtCl_2(NH_3)_4]$ (d) *cis*-$[PtCl_2(NH_3)_2]$

55. Zeise's salt is represented as
(a) H_2PtCl_6 (b) $[PtCl_4]^{2-}$
(c) $[ZnCl_4]^{2-}$ (d) $[PtCl_3(\eta^2{-}C_2H_4]^-$

56. The catalyst used in the conversion of ethylene to acetaldehyde using Wacker process is
(a) $HCo(CO)_4$
(b) $[PdCl_4]^{2-}$
(c) V_2O_5
(d) $TiCl_4$ in the presence of $Al(C_2H_5)_3$

57. In the reaction shown below, *X* and *Y* respectively are
$Mn_2(CO)_{10} \xrightarrow{Na} (X) \xrightarrow{CH_3CoCl} (Y)$
(a) $[Mn(CO)_4]^{2-}$, $[CH_3C(O)Mn(CO)_5]^-$
(b) $[Mn(CO)_5]^-$, $[CH_3C(O)Mn(CO)_5]$
(c) $[Mn(CO)_5]^-$, $[Cl(CO)_5]$
(d) $[Mn(CO)_4]^{2-}$, $[ClMn(CO)_5]^-$

58. $W(CO)_6$ reacts with MeLi to give an intermediate which upon treatment with CH_2N_2 gives a compound *X*, *X* is represented as
(a) WMe_6 (b) $(CO)_5W{-}Me$
(c) $(CO)_5W{=}C(Me)OMe$ (d) $(CO)_5W{\equiv}CMe$

GATE 2006

59. In biological systems, the metal ion involved in the di-oxygen transport besides Fe is
(a) Co (b) Zn
(c) Mg (d) Cu

60. The set of ions expected to show John-Teller distortion in their complexes is
(a) Ti(III), Cu(II), High-spin Fe(III)
(b) Cu(I), Ni(II), High-spin Fe(III)
(c) Cu(II), Low-spin Fe(III), Ti(III)
(d) Low-spin Fe(III), Mn(II), Cu(I)

61. The comlexes $[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)Br_2]\,Cl \cdot H_2O$ are examples of
(a) ionization isomerism (b) linkage isomerism
(c) geometrical isomerism (d) optical isomerism

▼ ***Solution Points***

GATE 2005

▾ ***Solution Points***

62. $[Co(CO)_4]$ is isolobal with
(a) CH_4 (b) CH_3
(c) CH_2 (d) CH

63. Ligand field stabilization energies are smaller for lanthanides compared to transition metals in the same oxidation state because
(a) size of lanthanide ions are larger
(b) *f* orbitals interact less effectively with ligands
(c) size of lanthanide ions are smaller
(d) lanthanides favour oxygen donor ligands

64. The lanthanide complex (where, acac = acetylacetonate; phen 1, 10-phenanthroline) that do not have square antiprismatic structure is
(a) $[Ce(NO_3)_6]^{2-}$ (b) $[La(acac)_3(H_2O)_2]$
(c) $[Ce(acac)_4]$ (d) $[Eu(acac)_3(phen)]$

65. The values of *M*—C stretching frequencies of (i) $[V(CO)_6]^-$; (ii) $[Cr(CO)_6]$ and (iii) $[Mn(CO)_6]^+$ follow the trend
(a) (ii) > (i) > (iii) (b) (ii) > (iii) > (i)
(c) (i) > (ii) > (iii) (d) (iii) > (ii) > (i)

66. For the complex ion $[Cu(NH_3)_6]^{2+}$, the coordination geometry will be
(a) octahedral (b) tetragonally distorted octahedral
(c) trigonal prismatic (d) trigonal antiprismatic

67. In Q 66. the number of possible *d-d* transitions will be
(a) one (b) two
(c) three (d) four

GATE 2004

68. The most suitable route to prepare the *trans* isomer of $[PtCl_2(NH_3)(PPh_3)]$ is
(a) $[PtCl_4]^{2-}$ with PPh_3 followed by the reaction with NH_3
(b) $[PtCl_4]^{2-}$ with NH_3 followed by the reaction with PPh_3
(c) $[Pt(NH_3)_4]^{2+}$ with HCl followed by the reaction with PPh_3
(d) $[Pt(NH_3)_4]^{2+}$ with PPh_3 followed by the reaction with HCl

69. The number of absorption bands observed in $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$, respectively are
(a) 1 and 3 (b) 0 and 1
(c) 0 and 3 (d) 3 and 1

GATE 2003

70. $[CoCl(NH_3)_5]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow [Co(H_2O)(NH_3)_5]^{2+} + [CrCl(H_2O)_5]^{2+}$
The correct statement regarding the above reaction is that
(a) it follows outer sphere mechanism
(b) it follows inner sphere mechanism with NH_3 acting as the bridging ligand
(c) it follows inner sphere mechanism with Cl^- acting as the bridging ligand
(d) it is not an electron transfer reaction

GATE 2002

71. The complexes $V(C_6H_6)_2$ and $Cr(C_6H_6)_2$ are both readily oxidized in air to their respective cations. The number of unpaired electrons, respectively in each are

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

72. The metals involved in nitrogenase are

(a) Fe and Mg
(b) Mo and K
(c) Mo and Fe
(d) Fe and K

GATE 2001

73. Amongst the following, the strongest oxidizing anion is

(a) CrO_4^{2-}
(b) VO_4^{3-}
(c) FeO_4^{2-}
(d) MnO_4^{2-}

74. The compound which has four metal-metal bonds is

(a) $Fe_2(CO)_9$
(b) $Co_2(CO)_8$
(c) $[Re_2Cl_8]^{2-}$
(d) $Ru_3(CO)_{12}$

GATE 2000

75. The complex with spin-only magnetic moment of ~ 4.9 BM is

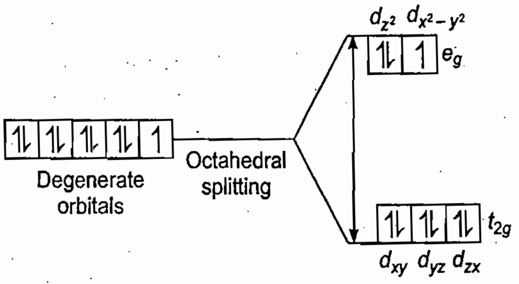
(a) $[Fe(H_2O)_6]^{2+}$
(b) $[Fe(CN)_6]^{3-}$
(c) $[Fe(CN)_6]^{4-}$
(d) $[Fe(H_2O)_6]^{3+}$

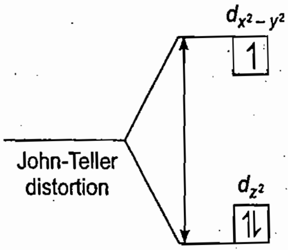
▾ *Solution Points*

Answers with Explanations

1. (b) In $CuSO_4 \cdot 5H_2O$, Cu is present as Cu^{2+}.

$Cu^{2+} = [Ar]\,3d^9$





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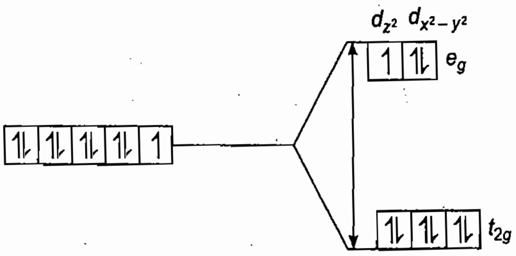
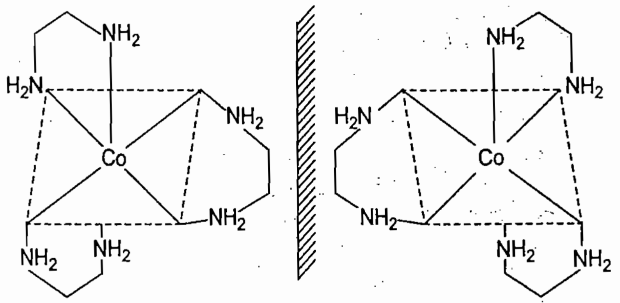


It is clear that the two out of three electrons in e_g orbitals can occupy either d_{z^2} orbital or $d_{x^2-y^2}$ orbital. Since, the e_g level is not symmetrically filled, John-Teller distortion occurs. This removes the degeneracy of the e_g and t_{2g} levels. Thus, the complex is distorted.

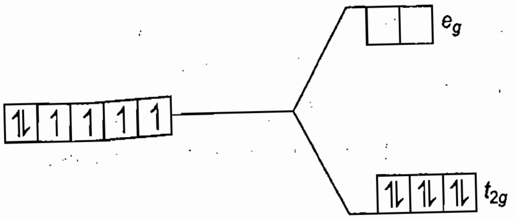
2. (a) Vitamin B_{12} coenzyme is a well known naturally occurring organometallic compound.

3. (d) Complexes of the type $[M(aa)_3]$, $[M(aa)_2b_2]$, $M(aa\,b_2c_2)$ exhibit optical isomerism and exist as a pair of enantiomers.
Thus, $[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$ exists as a pair of enantiomers. The structure of its enantiomers are as



Enantiomers of $[Co(en)_3]^{3+}$

4. (a) When oxygen is bound to Fe^{2+} in heme, all the d-electrons of the Fe atom are forced into the three lower energy t_{2g} orbitals and it produces low spin oxyhaemoglobin.
In oxyhaemoglobin, $Fe^{2+} = [Ar]\,3d^6$



The sharp high energy transition between t_{2g} and e_g levels of the d-electrons is responsible for the bright red colour of oxyhaemoglobin.

5. (b) Nickelocene attains stability due to the formation of a di cation as it contains two electrons in its antibonding molecular orbital, which are easy to remove.

6. (a) Fe act as electron transfer agent in many processes. Zinc (as carboxypeptidase) act as catalyst in hydrolysis reaction specially in enzymatic reactions.

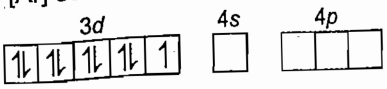
7. (b) In $[Cu(NH_3)_6]^{2+}$, the geometry is distorted octahedral due to John-Teller distortion and axial bonds distances are larger than equatorial bond distances.

8. (a) In deoxyhaemoglobin, the Fe^{2+} is in the high spin state and is paramagnetic. When an oxygen molecule binds to the iron atom of a heme group through its vacant sixth coordination site, the Fe atom becomes low spin. Thus, the transformation of oxyhaemoglobin to deoxyhaelmoglobin involves the change in spin state of Fe^{2+} from low to high.

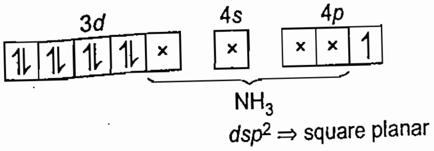
9. (d) Cu^{2+} and Fe^{2+} metal ions are involved in electron transport in biological systems.

10. (a) $[Cu(NH_3)_4](ClO_4)_2$ or $[Cu(NH_3)_4]^{2+}$ contains Cu^{2+} ion.

$Cu^{2+} = [Ar]\,3d^9$



$[Cu(NH_3)_4]^{2+} = [Ar]$



(NH_3 being strong field ligand transfer the upaired electron to $4d$ orbital.)

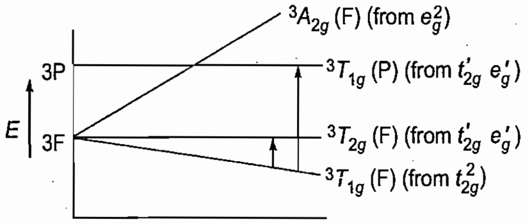
In $[Cu(NH_3)_4]\,ClO_4$ or $[Cu(NH_3)_4]^+$, Cu is present as Cu^+ ion.

$Cu^+ = [Ar]\,3d^{10}\,4s^0\,4p^0$

$$[Cu(NH_3)_4]^+ = [Ar]\,3d^{10}\ \underbrace{\overset{4s}{\boxed{\times}}\ \ \overset{4p}{\boxed{\times|\times|\times}}}_{sp^3 \Rightarrow \text{tetrahedral}}$$

(completely filled orbitals are highly stable, so NH_3 ligand occupy us and up orbitals.)

11. (a) The spectroscopic ground state symbol of $[Ti(H_2O)_6]^{2+}$ is $^3T_{1g}$. In this compound, there will be two electronic transition.



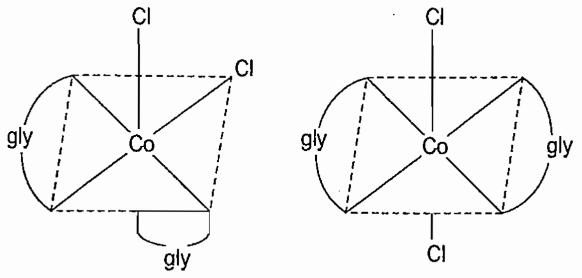
The third electronic transition $^3T_{1g}\,(F) \longrightarrow {}^3A_{2g}$ refers to the simultaneous excitation of both the electrons from t_{2g} to e_g orbitals and is forbidden.

12. (d) Quadruple metal-metal bond is found in Re because it is a member of $5d$ series.

13. (d) $[Ru(H_2O)_6]^{2+}$ is a low spin d^6 compound, it has zero unpaired electrons.

14. (c) The predominant metal present in the reaction centre of photosystem II in photosynthesis is Mn.

15. (c) Complexes of the type $[M(aa)_2xb]$ show geometrical or fac-mer isomerism. (where, aa = bidentate ligand and a and b are monodentate ligands.)
Among the given, dichlorodiglycinato cobalt (III), *i.e.*, $[CoCl_2(gly)_2]$ is such salt, so it will show fac and mer isomerism.



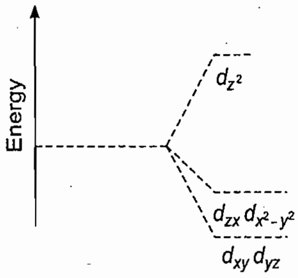
16. (b) For Eu^{3+} the observed value of magnetic moment is 3.4 while calculated value is 3.6.

17. (d) Iron-sulphur cluster is involved in electron transfer.

18. (c) Thermodynamic stability is a measure of the extent to which the complex will form. It depends upon the metal-ligand bond energies, stability constants etc. Kinetic reactivity, on the other hand, refers to the speed with which transformations leading to the attainment of equilibrium will occur. It depends upon the activation energy.
Thus, these two, *i.e.*, thermodynamic stability and kinetic reactivity, have no direct relation. (A stable complex may be inert or labile or an inert complex may be stable or unstable.)

19. (a) The given compounds $[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Br_2]Cl\cdot H_2O$ exhibit ionization isomerism because in ionization isomerism, compounds having same formula differ in their ionic arrangement in solution. The difference occur because of the difference in ions, that are found in the inner and outer coordination sphere of the complex. These complexes also show hydration isomerism.

20. (d) In trigonal bipyramidal crystal field, the d_{z^2} orbital has the highest energy.



Trigonal bipyramidal

21. (a) Zinc metal is present at the active site of enzyme carboxypeptidase A.

22. (d) $(\eta^5-C_5H_5)\,Re(\eta^6-C_6H_6)$ follow 18-electron rule as it contains 18 electrons.
Number of electrons are calculated as

$(\eta^5-C_5H_5)Fe(CO)_2 = 5+8+4=17$

$(\eta^5-C_5H_5)Mo(CO)_3 = 5+6+6=17$

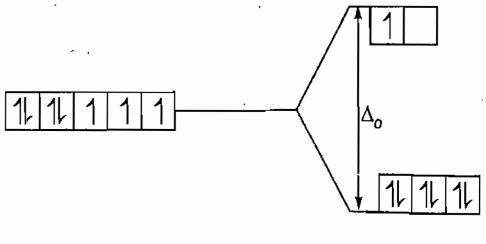
$(\eta^5-C_5H_5)_2\,Co = 10+9=19$

$(\eta^5-C_5H_5)Re(\eta^6-C_6H_6) = 5+7+6=18$

23. (b) $[Co(NH_3)_6]^{2+}$ contains Co^{2+}.

$Co^{2+} = [Ar]\,3d^7$

$$[Co(NH_3)_6]^{2+} = \overset{3d^7}{\boxed{\uparrow\downarrow|\uparrow\downarrow|\uparrow|\uparrow|\uparrow}}$$

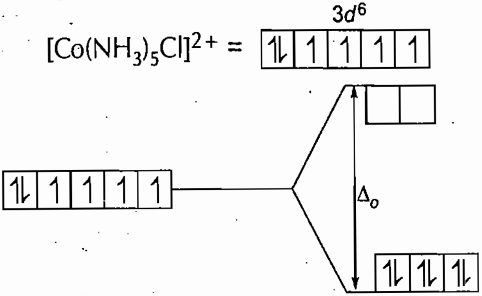


$CFSE = -0.4 \times 6 + 0.6 \times 1 = -2.4 + 0.6 = -1.8$

In $[Co(NH_3)_5Cl]^{2+}$, cobalt is present as Co^{3+}.

$Co^{3+} = [Ar]\ 3d^6$

$[Co(NH_3)_5Cl]^{2+} =$

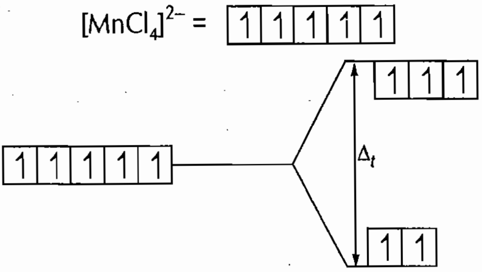


$CFSE = -0.4 \times 6 = -2.4$

In $[MnCl_4]^{2-}$, Mn is present as Mn^{2+}.

$Mn^{2+} = [Ar]\ 3d^5$

$[MnCl_4]^{2-} =$



$CFSE = -0.6 \times 2 + 0.4 \times 3 = 0$

24. (c) Number of *M*—*M* bonds are calculated as

$\Rightarrow 2 \times m + An + 2L = Zn$

where, m = number of *M*—*M* bond

A = atomic number of metal atom

n = number of metals in the formula

L = number of CO ligands

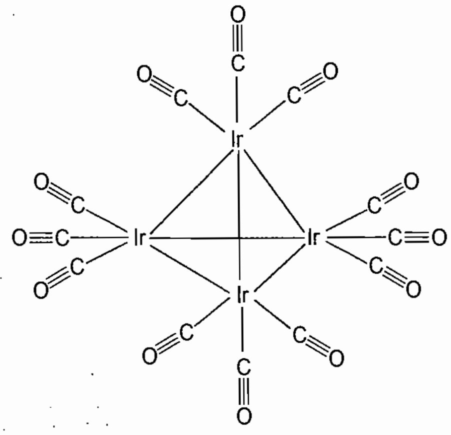
Z = atomic number of nearest inert gas

$$2 \times x + 77 \times 4 + 2 \times 12 = 86 \times 4$$

$$2x + 332 = 344$$

$$x = \frac{12}{2} = 6$$

Thus, it has 6 metal-metal bonds as



25. (d) Electron in *f*-subshell do not screen the nuclear charge effectively so the nuclear charge increases. With this increase, there is a decrease in size and thus, electronic repulsion increases. So, chances of interaction with the ligands become less.

26. (d) Zinc can form complexes with oxygen donor complex, e.g., in carboxypeptidase it forms complex with CO_2.

27. (d) In outer sphere electron transfer no bond making/breaking or ligand exchange takes place.
So, the following self exchange reaction

$$[Fe(H_2O)]_6^{2+} + [Fe(H_2O)_6]^{3+} \rightarrow [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$$

will proceed *via* outer sphere electron transfer.

28. (b) The brown ring test is used to detect the presence of NO_3^- radical. In this test we add freshly prepared ferrous sulphate solution to the salt solution and then conc. H_2SO_4 is added through the walls of the tube. A brown ring is formed at the junction of the two solutions. The reactions, involved in the test are :

$$NO_3^- + H_2SO_4 \longrightarrow HSO_4^- + HNO_3$$

$$6Fe^{2+} + 3H_2SO_4 + 2HNO_3 \longrightarrow 6Fe^{3+} + 4H_2O + 2NO$$

$$Fe^{2+} + NO + 5H_2O \longrightarrow \underset{\text{dark brown ring}}{[Fe(H_2O)_5NO]^{2+}}$$

29. (d) Compounds containing 18 electrons, follow 18-electron rule,
Number of electrons are calculated as

(a) $Fe(CO)_4$ = valance electrons of Fe + 2 × no. of CO ligands

$$= 8 + 2 \times 4 = 16$$

[∵ Fe has $3d^6\,4s^2$ outer configuration]

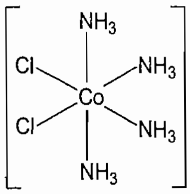
(b) $Ni(CO)_3(PPh_3) = 10 + 2 \times 3 + 2 \times 1 = 18$

(c) $Cr(CO)_5 = 6 + 2 \times 5 = 16$

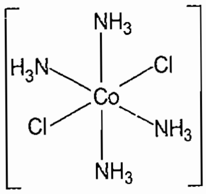
(d) $Cr(C_5H_5)_2 = 6 + 2 \times 5 = 16$

[∵ one C_5H_5 donates 5 electrons]

30. (c) Complex $Co(NH_3)_4Cl_2$ exhibits geometrical isomerism. *Cis* isomer is violet while *trans* isomer is green in colour.



cis $[(Co(NH_3)_4Cl_2)]$
(violet)



trans $[(Co(NH_3)_4Cl_2)]$
(green)

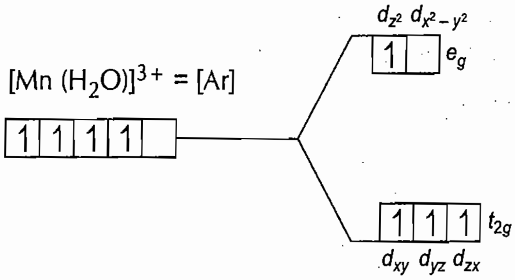
31. (a) The reaction between $IrCl_6^{2-}$ and $Cr(H_2O)_6^{2+}$ takes place *via* inner sphere electron transfer mechanism. The products formed are $[IrCl_6]^{3-}$ and $Cr(H_2O)_6^{3+}$. The reaction is

$$IrCl_6^{2-} + Cr(H_2O)_6^{2+} \longrightarrow [IrCl_6]^{3-} + Cr(H_2O)_6^{3+}$$

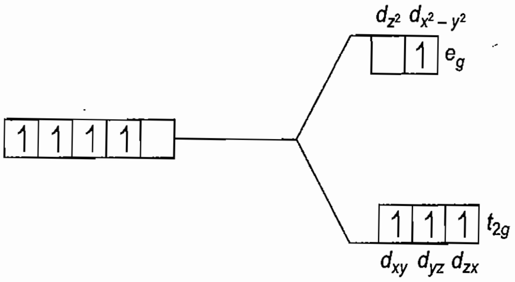
32. (b) The metal ion present in carbonic anhydrase is zinc.

33. (b) John-Teller distortion is exhibited when the *d*-electrons are asymmetrically arranged as they repel some ligands in the complex more than others.

In $[Mn(H_2O)_6]^{3+}$ d = electrons are arranged asymmetrically as



or



Thus, it exhibits John-Teller distortion.

34. (d) Complex compound which contains 18 valence electrons, obeys 18-electron rule.

$Mn(CO)_3 = 7 + 2 \times 3 = 13$

$Fe(CO)_4 = 8 + 2 \times 4 = 16$

$V(CO)_6 = 5 + 2 \times 6 = 17$

$Cr(CO)_6 = 6 + 2 \times 6 = 18$

Thus, $Cr(CO)_6$ obeys 18-electron rule.

35. (a) Absorption maximum, $\lambda = 492$ nm

$$= 492 \times 10^{-7} \text{ cm}$$

$$\text{CFSE (in cm}^{-1}) = \frac{1}{\lambda}$$

$$= \frac{1}{492 \times 10^{-7}}$$

$$= 20325 \text{ cm}^{-1}$$

36. (b) CT (charge transfer) transitions are attributed to excitations of electron from ligand to metal or *vice-versa*.

Higher the oxidizing power of metal, higher is the wavelength of transition.

Order of oxidizing power is

$$V^{5+} < Cr^{6+} < Mn^{7+}$$

∴ The order of wavelength of transition is

$$VO_4^{3-} < CrO_4^{2-} < MnO_4^-$$

The order of charge is

$$V^{5+} < Cr^{6+} < Mn^{7+}$$

37. (c) If metal is same,

CFSE ∝ Field strength of ligand

$$\propto \frac{1}{\lambda}$$

The order of field strength of ligands is

$$Cl < H_2O < NH_3 < en < CN$$

Therefore, the increasing order of wavelength of absorption is

$[Cr(CN)_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(OH_2)_6]^{3+} < [CrCl_6]^{3-}$

38. (a) Number of M—M bonds in metal carbonyls

$\Rightarrow 2 \times M + A \times n + 2 \times L$

= Atomic number of nearest inert gas × n

where, M = number of M—M (metal-metal) bonds

A = atomic number of metals

n = number of metal atoms

L = number of carbonyl (CO) molecules

In $Ru_3(CO)_{12}$,

Number of M—M bonds

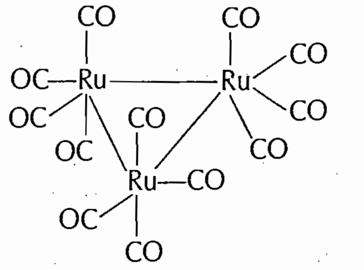
$\Rightarrow 2 \times x + 44 \times 3 + 2 \times 12 = 54 \times 3$

$\Rightarrow \quad 2x + 156 = 54 \times 3$

$$2x = 162 - 156$$

$$x = \frac{6}{2} = 3$$

Thus, $Ru_3(CO)_{12}$ contains 3 M—M bonds as



In $Co_4(CO)_{12}$,

Number of M—M bonds

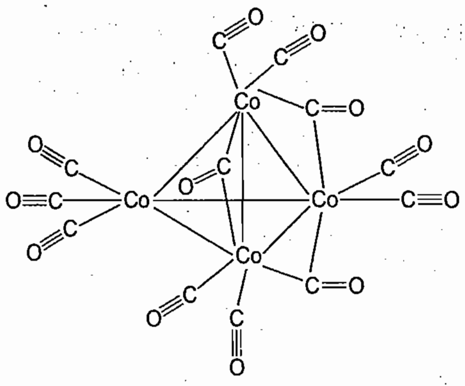
$\Rightarrow 2 \times x + 27 \times 4 + 2 \times 12 = 36 \times 4$

$\Rightarrow \quad 2x + 108 + 24 = 144$

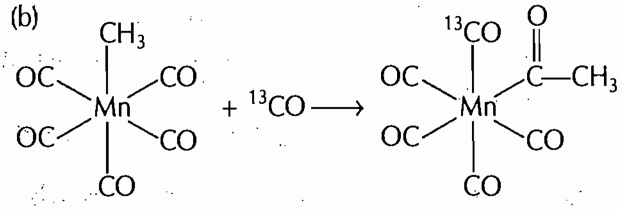
$$2x = 144 - 132$$

$$x = \frac{12}{2} = 6$$

Thus, $Co_4(CO)_{12}$ contains 6 *M—M* bonds as



39. (b)

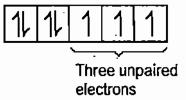


This is an insertion reaction and such reactions actually involve a methyl migration, a concomitant breaking of metal-methyl bond.

40. (b) In $[Fe(H_2O)_5(NO)]^{2+}$, Fe is in +1 oxidation state with five H_2O neutral ligands and one unipositive NO^+ ligand. During the formation of this complex, NO gives its unpaired electron to Fe^{2+} and change it into Fe^+.

$$Fe = [Ar]\, 3d^6\, 4s^2$$

$$Fe = [Ar]\, 3d^7\, 4s^0$$



41. (c) Dynamic John-Teller distortion is exhibited when there is a small distortion.

In $[Fe(H_2O)_6]^{2+}$, distortion is small, since degeneracy occurs in t_{2g} orbitals, so it shows dynamic John-Teller distortion.

42. (a) Crystal field symbol for the ground state of $[Mn(CN)_6]^{4-}$ $^2T_{2g}$ as spin multiplicity $(2s+1)$ is 2 because of the presence of only one unpaired electron.

$$S = \frac{1}{2} \times n = \frac{1}{2} \times 1 = \frac{1}{2}$$

$$2S + 1 = 2 \times \frac{1}{2} + 1 = 2$$

43. (b) The point group for $[CoCl_4]^{2-}$ is T_d as it has tetrahedral geometry. Point groups for two isomers of $[Co(H_2O)_4Cl_2]$, *i.e.*, for *cis* $[Co(H_2O)_4Cl_2]$ and *trans* $[Co(H_2O)_4Cl_2]$ are C_{2v} and D_{4h} respectively.

44. (d) Given, $\mu = 5.9$ BM

$\mu = \sqrt{n(n+2)}$

$(5.9)^2 = n^2 + 2n$

On solving, we get $n = 5$

Mn (II) and Fe (III) both contains five unpaired electrons. Thus, both are ESR active. But Mossbauer active is only Fe (III), not Mn (II).

So, the metal ion must be Fe (III) with 5 unpaired electrons.

Note : In first transition series, only Fe, Ni and Zn are Mossbauer active elements.

45. (d) In $[Fe(H_2O)_6]^{3+}$, Fe is present in (+III) oxidation state and contains 5 unpaired electrons, so the complex is $[Fe(H_2O)_6]^{3+}$.

46. (a) $W(CO)_6 + Na(C_5H_5) \longrightarrow [(C_5H_5)W(CO)_3]\,Na$

$[(C_5H_5)W(CO)_3]\,Na + CH_3COOH \longrightarrow [(C_5H_5)W(CO)_3H]$

In $[(C_5H_5)W(CO)_3]\,Na$, no. of electrons

$$= 5 + 6 + (2 \times 3) + 1 = 18$$

In $[(C_5H_5)W(CO)_3H]$, no. of electrons

$$= [5 + 6 + (2 \times 3) + 1] = 18$$

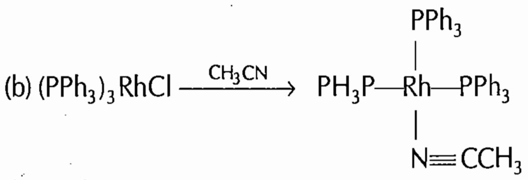
Thus, both obey 18-electron rule.

47. (a) $[(C_5H_5)W(CO)_3H] \xrightarrow{\text{Heat}} [(C_5H_5)W(CO)_3]_2$

$+ W(CO)_6 \rightarrow [(C_5H_5)W(CO)_3]_2$

$[(C_5H_5)W(CO)_3]_2 + Br_2 \rightarrow 2\,[(C_5H_5)W(CO)_3Br]$

48. (b)



$$(PPh_3)_3RhCl \xrightarrow{CH_3CN} PH_3P\text{—}\underset{\underset{N\equiv CCH_3}{|}}{\overset{\overset{PPh_3}{|}}{Rh}}\text{—}PPh_3$$

49. (c) $Rh(Ph_3)_3Cl + C_2H_4 + H_2 \longrightarrow (PPh_3)_2RhCl(\eta^2\text{–}C_2H_4)$

50. (a) In lanthanides, as the atomic number increases, size of lanthanide ion (La^{3+}) decreases. A smaller lanthanide ion forms a stable complex with *o*-hydroxy isobutyrate ion.

Hence, a Lu^{3+}–*o*-hydroxy isobutyrate complex ion comes out first and Eu^{3+} comes out last, *i.e.*, the order is

$$Lu^{3+} > Yb^{3+} > Dy^{3+} > Eu^{3+}$$

51. (a) The hydration energy of transition metals increases with increase in atomic number and decrease in size. But for Mn (d^5) its value is less. So, for the given metals the correct order is

$$Mn < Ti < V < Ni$$

52. (c) Reaction,

$$[Cr(H_2O)_6]^{2+} + [CoCl(NH_3)_5]^{2+} \longrightarrow [Co(NH_3)_5(H_2O)]^{2+} + [CrCl(H_2O)_5]^{2+}$$

follows inner sphere mechanism because it involves exchange of ligand. While reaction ,

$$[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$$

follows outer sphere mechanism because it involves only transfer of charge.

53. (a) $Ni(CO)_4$ show $L \leftarrow M$ transition as in it ligand (CO) is capable to accept *d*-electron of metal.

54. (d) In the reaction between NH_3 and $[PtCl_4]^{2-}$, *cis* $[PtCl_2(NH_3)_2]$ is formed.

$$[PtCl_4]^{2-} + NH_3 \longrightarrow cis\ [PtCl_2(NH_3)_2]$$

(NH_3 ligand mainly gives *cis* product.)

55. (d) Zeise's salt is $[PtCl_3(\eta^2-C_2H_4]^-$.

56. (b) In Wacker process of conversion of acetylene into acetaldehyde palladium(II) chloride $[PdCl_4]^{2-}$ is used as catalyst.

57. (b) Reduction of $Mn_2(CO)_{10}$ gives the manganese pent carbonyl anion

$$Mn_2(CO)_{10} + 2Na \rightarrow 2Na[Mn(CO)_5] \xrightarrow{CH_3COCl} CH_3C(O)Mn(CO)_5$$

58. (c) $W(CO)_6 + MeLi \longrightarrow [W(CO)_5(COCH_3)]\ Li \longrightarrow (CO)_5W{=}C(Me)OMe$

59. (d) Besides Fe, the other metal involved in dioxygen transport is Cu.

60. (c) John-Teller distortion is found in the complexes of Cu(II), Low-spin Fe(III), Ti(III) as these contain asymmetric *d*-electrons.

61. (a) $[Co(NH_3)_4](H_2O)\ Cl]Br_2 \rightleftharpoons [Co(NH_3)_4(H_2O)\ Cl]^{2+} + 2Br^-$

$$[Co(NH_3)_4Br_2]\ Cl \cdot H_2O \rightleftharpoons [Co(NH_3)_4Br_2]^+ + Cl^- + H_2O$$

Since, the above two complexes give different ions on ionization, so they exhibit ionization isomerism.

62. (b) $[Co(CO)_4]$ is compound with 17 electrons. Since, it has one electron less than the 18 electrons so it is isolobal with CH_3 which has one electron less than octet.

63. (b) Electrons in *f*-subshell does not screen the nuclear charge effectively, so the nuclear charge increases. Which results in decreased size and increased electronic repulsion. So, chances of interaction with the ligands becomes less and hence, LFSE are small.

64. (a) $[Ce(NO_3)]^{2-}$ has icosahedral structure. Other given complexes have eight coordination number and thus, have square antiprismatic structure.

65. (d) Any factor which increases the electron charge density in π^* orbital of the ligated CO, would decrease the C—O bond order and also the vibrational frequency of C—O bond. The presence of positive charge on metal carbonyl would resist the flow of the metal electron charge to π^* orbitals of CO. Thus, CO in metal carbonyl cation would absorb at a higher frequency. The value of *M*—C stretching frequency for the given complexes is $[V(CO)_6]^{-1} = 1859\ cm^{-1}$

$$[Cr(CO)_6] = 2000\ cm^{-1}$$

$$[Mn(CO)_6]^+ = 2090\ cm^{-1}$$

66. (a) The complex ion $[Cu(NH_3)_6]^{2+}$ has octahedral geometry.

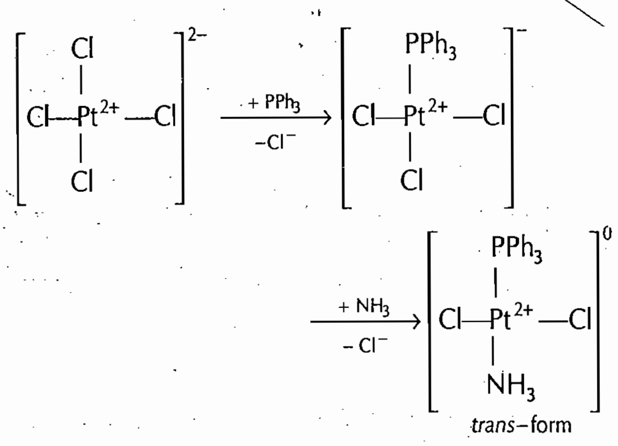
67. (a) Since, the metal in $[Cu(NH_3)_6]^{2+}$ contains only one unpaired electron, spin multiplicity 2-is written above the free ion energy configuration. The ground state energy level $2E_g$ contains two degenerate energy levels corresponding to the orbital arrangements $t_{2g}^6\ d_{z^2}^2\ d_{x^2-y^2}^1$ and $t_{2g}^6\ d_{z^2}^1\ d_{x^2-y^2}^2$. The excited state energy levels contains three degenerate energy levels from three degenerate orbital arrangements $d_{xz}^2\ d_{yz}^1\ d_{xy}^1\ e_g^4$, $d_{xz}^1\ d_{yz}^2\ d_{xy}^1\ e_g^4$ and $d_{xz}^1\ d_{yz}^1\ d_{x^2-y^2}^1\ e_g^4$.

Thus, the absorption band is assigned to only one $2E_g \rightarrow {}^2T_{2g}$ transition.

68. (a) *trans* $[PtCl_2(NH_3)(PPh_3)]$ is prepared by the reaction of $[PtCl_4]^{2-}$ with PPh_3 followed by the reaction with NH_3. This is because both of *trans* effect is

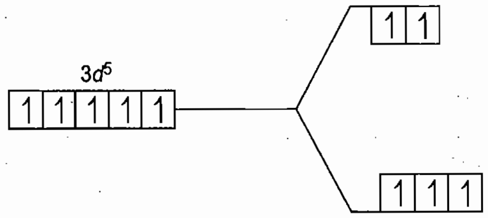
$$PPh_3 > Cl^- > NH_3$$

(*trans*-effect is the ability of a group to direct an incoming group to occupy the position *trans* to that group.)



69. (b) In $[FeF_6]^{3-}$, iron is present as Fe^{3+}

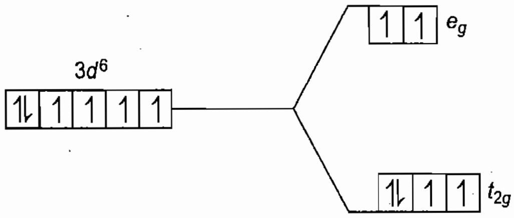
$Fe^{3+} = [Ar]\, 3d^5$



It has symmetrical orbital, so no transition occurs.

In $[CoF_6]^{3-}$, cobalt is present as Co^{3+}.

$Co^{3+} = [Ar]\, 3d^6$



Because of asymmetric geometry one transition $({}^5T_{2g} \rightarrow {}^5E_g)$ occurs. Thus, its electronic spectrum shows one absorption band.

70. (c) The reaction,

$$[CoCl(NH_3)_5]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow [Co(H_2O)(NH_3)_5]^{2+} + [CrCl(H_2O)_5]^{2+}$$

involves the following steps :

$$\text{I. } [Cr(H_2O)_6]^{2+} + [Co(NH_3)_5Cl]^{2+} \xrightarrow{\text{Slow}} [(H_2O)_5Cr{-}Cl{-}Co(NH_3)_5]^{4+} + H_2O$$

$$\text{II. } [(H_2O)_5Cr{-}Cl{-}Co(NH_3)_5]^{4+} \xrightarrow[\text{Fast}]{\text{Hydrolysis}} [Cr(H_2O)_5Cl]^{2+} + [Co(NH_3)_5(H_2O)]^{2+}$$

Transfer of electrons is involved so the reaction will follow inner sphere mechanism.

In this reaction Cl^- is bounded with both the metals in the electron transfer transition state. So, it acts as the bridging ligand.

71. (c) $V(C_6H_6)_2^+$ $(5 + 12 - 1 = 16)$ has zero unpaired electron while $Cr(C_6H_6)_2^+$ $(6 + 12 - 1 = 17)$ has one unpaired electron.

72. (c) Nitrogenase enzyme has Mo and Fe metals.

73. (a) CrO_4^{2-} has a tendency to get reduced (oxidize others). So, it acts as strong oxidizing agent.

74. (c) Number of metal-metal bonds are calculated as

In $Fe(CO)_9$,

$$2 \times m + A \times n + 2 \times L = \text{At no. of nearest inert gas} \times n$$

$$2 \times x + 26 \times z + 2 \times 9 = 36 \times 2$$

$$2x + 52 + 18 = 72$$

$$x = 1$$

In $Co_2(CO)_8$,

$$2 \times x + 27 \times 2 + 2 \times 8 = 36 \times 2$$

$$x = 1$$

In $[Re_2Cl_8]^{2-}$

$$2 \times m + 75 \times 2 + 2 \times 8 - 2 = 86 \times 2$$

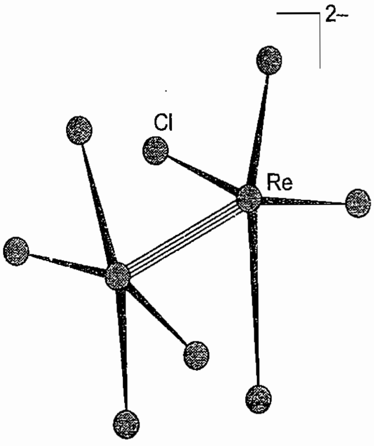
$$m = \frac{8}{2} = 4$$

In $Ru_3(CO)_{12}$,

$$2 \times m + 44 \times 3 + 2 \times 12 = 54 \times 3$$

$$m = \frac{6}{2} = 3$$

Thus, $[Re_2Cl_8]^{2-}$ has four metal-metal bonds as



Structure of $[Re_2Cl_8]^{2-}$

75. (a) $\mu = \sqrt{n(n+2)} = 4.9$

$\therefore \quad n = 4$

Fe^{2+} in $[Fe(H_2O)_6]^{2+}$, has 4 unpaired electrons. Thus, its magnetic moment is 4.9 BM.

5

Chemical and Ionic Equilibrium

Syllabus

Chemical and Ionic Equilibrium Kinetic theory of gases, ideal and non-ideal solutions, phase transformation : phase rule and phase diagram. One, two and three component systems, chemical equilibrium, response of chemical equilibrium to temperature and pressure, colligative properties.

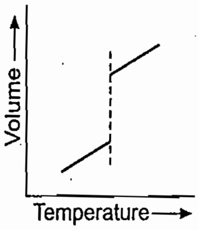
GATE 2011

(1 Mark Questions)

1. The freezing point constant for water is 1.86 K(mol/kg)$^{-1}$. The freezing point when 0.01 mol glucose is added to 1 kg water is
(a) 1.86 K (b) −1.86 K (c) 0.0186 K (d) −0.0186 K

2. On the pressure-temperature diagram for a one-component system, the point where the solid-liquid and the liquid-gas curves intersect is
(a) triple point (b) critical point
(c) melting point (d) boiling point

3.



According to the Ehrenfest classification of phase transition the above diagram refers to
(a) zeroth order phase transition (b) first order phase transition
(c) second order phase transition (d) λ transition

GATE 2010

4. For the pair of reactions given below,

(i) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (ii) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

If at a particular temperature, K_{p1} and K_{p2} are the equilibrium constants for reactions (i) and (ii) respectively then,

▾ *Solution Points*

(a) $K_{p_1} = 2K_{p_2}$ (b) $K_{p_1} = K_{p_2}^2$
(c) $2K_{p_1} = K_{p_2}$ (d) $K_{p_1}^2 = K_{p_2}$

5. For an ideal gas,
(a) $(\partial p/\partial T)_V(\partial T/\partial V)_p(\partial V/\partial p)_T = 0$ (b) $(\partial p/\partial T)_V(\partial T/\partial V)_p(\partial V/\partial p)_T = -1$
(c) $(\partial p/\partial T)_V(\partial T/\partial V)_p(\partial V/\partial p)_T = +1$ (d) $(\partial p/\partial T)_V(\partial T/\partial V)_p(\partial V/\partial p)_T = +2$

GATE 2009

6. The number of degrees of freedom of a system consisting of solid sucrose in equilibrium with an aqueous solution of sucrose is
(a) 0 (b) 1 (c) 2 (d) 3

GATE 2008

7. If a gas obeys equation of state $p(V - nb) = nRT$, the ratio $\dfrac{(C_p - C_V)}{(C_p - C_V)_{\text{ideal}}}$ is
(a) >1 (b) <1 (c) 1 (d) $(1 - b)$

8. The Bronsted acidity of boron hydrides follows the order
(a) $B_2H_6 > B_4H_{10} > B_5H_9 > B_{10}H_{14}$ (b) $B_2H_6 = B_4H_{10} > B_5H_9 = B_{10}H_{14}$
(c) $B_{10}H_{14} > B_5H_9 > B_4H_{10} > B_2H_6$
(d) $B_5H_9 > B_4H_{10} > B_2H_6 > B_{10}H_{14}$

GATE 2006

9. As per the kinetic theory of ideal gases, which of the following statements is not correct?
(a) Gas particles have mass but no volume
(b) Particles are in a Brownian motion between collisions
(c) During the collision, the system does not lose energy
(d) Particles exert same force per unit area on all sides of the container

GATE 2005

10. The triple point for water is
(a) unique
(b) depends on p but is independent of T
(c) depends on T but is independent of p
(d) depends on both p and T

GATE 2003

11. The internal pressure of a van der Waals' gas is
(a) independent of the molar volume
(b) inversely proportional to the molar volume
(c) inversely proportional to square of the molar volume
(d) directly proportional to the molar volume

▾ ***Solution Points***

GATE 2011

(2 Marks Questions)

12. For 1 mol of a monoatomic ideal gas, the relation between pressure (p), volume (V) and average molecular kinetic energy ($\bar{\varepsilon}$) is

(a) $p = \dfrac{N_A \bar{\varepsilon}}{V}$ (b) $p = \dfrac{N_A \bar{\varepsilon}}{3V}$

(c) $p = \dfrac{2N_A \bar{\varepsilon}}{3V}$ (d) $p = \dfrac{2N_A}{2V\bar{\varepsilon}}$

GATE 2009

13. Among the following, the equilibrium which is not affected by an increase in pressure is

(a) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

(b) $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$

(c) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

(d) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

GATE 2007

14. The number of degrees of freedom for a system consisting of NaCl(s), Na^+(aq) and Cl^- (aq) at equilibrium is

(a) 2 (b) 3

(c) 4 (d) 5

15. In the mixture obtained by mixing 25.0 mL $\times 1.2 \times 10^{-3}$ M$MnCl_2$ and 35.0 mL of 6.0×10^{-4} M KCl solution, the concentration (M) of Mn^{2+}, K^+ and Cl^- ions respectively are

(a) $6.0 \times 10^{-4}, 3.0 \times 10^{-4}, 1.5 \times 10^{-3}$

(b) $6.0 \times 10^{-4}, 3.0 \times 10^{-4}, 9 \times 10^{-4}$

(c) $5.0 \times 10^{-4}, 3.5 \times 10^{-4}, 13.5 \times 10^{-3}$

(d) $5.0 \times 10^{-4}, 3.5 \times 10^{-4}, 8.5 \times 10^{-4}$

GATE 2000

16. An aqueous solution containing m moles of non-volatile solute freezes at $-0.186°C$. The elevation in the boiling point of the same aqueous solution ($K_f = 1.86°$, $K_b = 0.512°$) would be

(a) 0.186 (b) 0.512

(c) 0.0512 (d) 0.51/1.86

17. Under the equilibrium conditions for the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the total pressure is 12 atm. The value of K_p is

(a) 16 (b) 0.5 (c) 2 (d) 32

18. The pH of buffer solution containing 4×10^{-3} and 0.4 moles of acetic acid ($pK_a = 4.76$) and sodium acetate respectively will be

(a) 6.76 (b) 4.76 (c) 2.76 (d) 0.76

▾ *Solution Points*

Answers with Explanations

1. (d) We know that depression in freezing point,

$$\Delta T_f = i\, K_f \cdot m$$

Glucose is a non-electrolyte, so $i = 1$

Given, $K_f = 1.86$ K (mol/kg)$^{-1}$

$$\text{Molality } m = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}} = \frac{0.01}{1} = 0.01$$

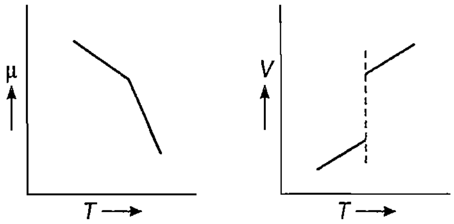
$$\Delta T_f = 1 \times 1.86 \times 0.01 = 0.0186 \text{ K}$$

$$T_f = 0 - 0.0186 = -0.0186 \text{ K}$$

2. (a) Triple point is the point on the p-T diagram for one component system at which the solid-liquid and the liquid-gas curves intersect. In other words, at this point all the three phases (solid, liquid and vapour) can coexist in equilibrium.

3. (b) $\left(\frac{\partial \mu_\beta}{\partial p}\right)_T - \left(\frac{\partial \mu_\alpha}{\partial p}\right)_T = V_{\beta m} - V_{\alpha, n} = \Delta_{trs} V$

According to Ehrenfest classification a transition for which the first derivative of the chemical potential with respect to temperature is discontinuous is classified as first order phase transition.



(μ = chemical potential and V = volume)

4. (b)

$$K_{p_1} = \frac{p^2_{NH_3}}{p_{N_2} \cdot p^3_{H_2}} \quad \text{...(i)}$$

$$K_{p_2} = \frac{p_{NH_3}}{p^{1/2}_{N_2} \cdot p^{3/2}_{H_2}}$$

$$K^2_{p_2} = \frac{p^2_{NH_3}}{p_{N_2} \cdot p^3_{H_2}} \quad \text{...(ii)}$$

Dividing Eq. (ii) by Eq. (i),

$$\frac{Kp_1}{Kp_2^2} = 1 \quad \text{or} \quad Kp_1 = K^2_{p_2}$$

5. (a) For an ideal gas,

At constant volume

$$\frac{p}{T} = \text{constant}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = 0$$

Similarly, $\left(\frac{\partial T}{\partial V}\right)_p = 0$ and $\left(\frac{\partial V}{\partial p}\right)_T = 0$

Thus, $(\partial p/\partial T)_V \, (\partial T/\partial V)_p \, (\partial V/\partial p)_T = 0$

6. (c) Since, solid sucrose is also present in the solution, so there will be two phases ($P = 2$). There will be two components. So, according to phase rule

$$F = C - P + 2$$

$$F = 2 - 2 + 2$$

$$F = 2$$

7. (c) For ideal gas, $pV = RT$

Change in enthalpy (ΔH) can be given by

$$\Delta H = \Delta E + p\Delta V$$

For 1 mol of an ideal gas,

$$pV_1 = RT_1 \quad \text{and} \quad pV_2 = RT_2$$

$$p(V_2 - V_1) = R(T_2 - T_1)$$

or $$p\Delta V = R\Delta T$$

Hence, $$\Delta H = \Delta E + R\Delta T$$

or $$\frac{\Delta H}{\Delta T} = \frac{\Delta E}{\Delta T} + R$$

If ΔH and ΔE are infinitely small, we have

or $$C_p = C_V + R$$

or $$C_p - C_V = R$$

In case of real gas, volume is $V - b$ and thus, the gas equation becomes $p(V - nb) = nRT$

For 1 mol of real gas,

$$p(V_1 - b) = RT_1$$

and $$p(V_2 - b) = RT_2$$

$$p(V_2 - V_1) = R(T_2 - T_1)$$

$$p\Delta V = R\Delta T$$

$$C_p - C_V = R$$

$$\frac{(C_p - C_V)}{(C_p - C_V)_{\text{ideal}}} = 1$$

8. (c) Bronsted acidity of boron hydride follows the order $B_{10}H_{14} > B_5H_9 > B_4H_{10} > B_2H_6$

This is because acidity increases with increase in the size of borane. In larger borane, the charge formed upon deprotonation can be better delocalised over a large anion with many boron atoms than over a small one.

9. (d) According to kinetic theory of gases,

(i) Gases are made up of small units, called atom or molecules. Volume of individual atom or molecule is considered negligible.

(ii) Gas molecules are always in rapid random motion colliding with each other and with the wall of container. So, they do not exert same force per unit area (*i.e.*, pressure) on all sides of the container.

(iii) The collisions among the gas molecules are perfectly elastic *i.e.*, involves no loss of energy.

10. (d) Triple point of water exist at temperature 0.0098° C and 4.58 mm pressure. In case of any change in temperature and pressure, the triple point vanishes.

11. (c) Internal pressure, $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$

$$\because \quad \partial U = \left(\frac{\partial U}{\partial S}\right)_T \cdot dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

On dividing by dV, we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T \cdot \left(\frac{\partial S}{\partial V}\right)_T - p$$

$$\therefore \quad \pi_T = T\left(\frac{\partial p}{\partial T}\right)_T - p$$

$$p = \frac{nRT}{V} \text{ (for ideal gas)}$$

In case of van der Waals' gas,

$$p = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}$$

$$\therefore \quad \pi_T = \frac{an^2}{V^2}$$

Thus, internal pressure varies inversely with the square of molar volume.

12. (c) Kinetic gas equation is

$$pV = \frac{1}{3} mN_A u^2$$

$$\text{KE}(\bar{\varepsilon}) = \frac{1}{2} mv^2$$

$$pV = \frac{1}{3} mN_A u^2 \times \frac{2}{2}$$

$$= \frac{2}{3} \times \frac{1}{2} \mu^2 \cdot N_A$$

$$= \frac{2}{3} \bar{\varepsilon} N_A$$

$$p = \frac{2\bar{\varepsilon} N_A}{3V}$$

13. (d) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

In this equation, the number of moles of gaseous reactants and products are same. So, it will not be affected by change in pressure.

14. (b) The given system has two phases solid NaCl and aqueous solution and three components, *i.e.*, NaCl(*s*), Na^+ (*aq*) Cl^- (*aq*).

$$F = C - P + 2$$

$$F = 3 - 2 + 2 = 3$$

15. (c) For $MnCl_2$ solution, the initial volume was 25 mL. After addition of 35 mL KCl solution the solution is diluted by to 60 mL, so the concentration of Mn^+ ion will become $= 1.2 \times 10^{-3} \times \frac{25}{60} = 5 \times 10^{-4}$.

In case of KCl solution, the concentration of K^+ is

$$= 6 \times 10^{-4} \times \frac{35}{60} = 3.5 \times 10^{-4}$$

$MnCl_2$ on ionization will give $2Cl^-$ ions and KCl will give one Cl^- ion per molecule so the concentration of

$$Cl^- = 2 \times 5 \times 10^{-4} + 3.5 \times 10^{-4}$$

$$= 13.5 \times 10^{-4} \text{ or } 1.35 \times 10^{-3}$$

16. (c) We know that, $m = \frac{\Delta T_f}{K_f} = \frac{0.186}{1.86} = 0.1$

$$\Delta T_b = K_b \times m$$

$$\Delta T_b = 0.512 \times 0.1$$

$$\Delta T_b = 0.0512°C$$

17. (a) At equilibrium, the pressure of CO_2 is p. In the reaction

$$CO_2(g) + C(s) \rightleftharpoons 2CO$$

Pressure at equilibrium $\quad p \quad 0 \quad 2p$

or $\quad p + 2p = 12$

$$p = 4$$

Partial pressure of CO_2 = 4

Partial pressure of CO = 2 × 4 = 8

$$K_p = \frac{(p_{CO})^2}{(p_{CO_2})} = \frac{(8)^2}{4} = 16$$

18. (a) $\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

$$= 4.76 + \log \frac{0.4}{4 \times 10^{-3}}$$

$$= 4.76 + \log 100 = 4.76 + 2$$

$$= 6.76$$

6

Electrochemistry

Syllabus

Electrochemistry Debye-Huckel Theory : Thermodynamics of electrochemical cells; Standard electrode potentials; applications, corrosion and energy conversion. Activity coefficient, fugacity and fugacity coefficient.

GATE 2010

(1 Mark Questions)

▼ *Solution Points*

1. The standard reduction potentials at 298 K for single electrodes are given below.

Electrode	Electrode potential (volt)
Mg^{2+}/Mg	−2.34
Zn^{2+}/Zn	−0.76
Fe^{2+}/Fe	−0.44

From this we can infer that
(a) Zn can reduce both Mg^{2+} and Fe^{2+}
(b) Fe can reduce both Mg^{2+} and Zn^{2+}
(c) Mg can reduce both Zn^{2+} and Fe^{2+}
(d) Mg can reduce Zn^{2+} but not Fe^{2+}

GATE 2009

2. According to the Debye-Huckel limiting law, if the concentration of a dilute aqueous solution of KCl is increased 4-fold, the value of $\ln \gamma_z$ (γ_z is the molar mean ionic activity coefficient) will
(a) decrease by a factor of 2
(b) increase by a factor of 2
(c) decrease by a factor of 4
(d) increase by a factor of 4

GATE 2006

3. Given the standard potential for the following half-cell reaction at 298 K,

$$Cu^{+}(aq) + e^{-} \longrightarrow Cu(s); \qquad E^{\circ} = 0.52\ V$$

$$Cu^{2+}(aq) + e^{-} \longrightarrow Cu^{+}(aq); \quad E^{\circ} = 0.16\ V$$

Calculate the $\Delta G°$ (kJ) for the reaction, [$2Cu^+(aq) \longrightarrow Cu(s) + Cu^{2+}$]

(a) −34.740
(b) −65.720
(c) −69.480
(d) −131.440

GATE 2002

4. The Nernst equation for the reaction, $A^{2+} + 2e^- \to B$, in terms of the free energy change is

(a) $\Delta G = \Delta G° + 2.303RT \log\frac{[B]}{[A]}$

(b) $\Delta G = \Delta G° - 2.303\,RT \log\frac{[B]}{[A]}$

(c) $-\Delta G = -\Delta G° + 2.303RT \log\frac{[B]}{[A]}$

(d) $\Delta G = -\Delta G° + 2.303RT \log\frac{[B]}{[A]}$

GATE 2011

(2 Marks Questions)

5. For the concentration cell,

$$M|M^+\ (aq, 0.01\ \text{mol/dm}^3)\ ||\ M^+\ (aq), 0.1\ \text{mol/dm}^3\,|\,M$$

the EMF (E) of the cell at a temperature (T) equals

(a) $2.303\frac{RT}{F}$
(b) $-2.303\frac{RT}{F}$
(c) $E^{\circ}_{M^+|M} + 2.303\frac{RT}{F}$
(d) $E^{\circ}_{M^+|M} - 2.303\frac{RT}{F}$

6. For a 2 molal aqueous NaCl solution, the mean ionic activity coefficient ($\gamma_\pm$) and the Debye-Huckel Limiting Law constant (A) are related as

(a) $\log\gamma_\pm = \sqrt{2}\,A$
(b) $\log\gamma_\pm = -\sqrt{2}\,A$
(c) $\gamma_\pm = 10^4$
(d) $\gamma_\pm = 10^{-4}$

7. The activity of water at 11 bar and 298 K is

(a) 1.101
(b) 1.007
(c) 0.998
(d) 0.898

GATE 2007

8. Given that $E°(Fe^{3+}, Fe) = -0.4$ V and $E°(Fe^{2+}, Fe) = -0.44$ V, the value of $E°(Fe^{3+}, Fe^{2+})$ is

(a) 0.76 V
(b) −0.40 V
(c) −0.76 V
(d) 0.40 V

9. A student recorded a polarogram of 2.0 mM Cd^{2+} solution and forget to add KCl solution. What type of error do you expect in his results?

(a) Only migration current will be observed
(b) Only diffusion current will be observed
(c) Both migration current as well as diffusion current will be observed
(d) Both catalytic current as well as diffusion current will be observed

▾ ***Solution Points***

GATE 2003

▾ *Solution Points*

10. For the reaction,

$Hg_2Cl_2(s) + H_2(g) \rightarrow 2Hg(liq) + 2HCl(aq)$, the correct representation of the cell and the thermodynamic properties ΔG, ΔH and ΔS at 298 K respectively, are (Given : $E_{298} = 0.2684$ V and temperature coefficient $= 3 \times 10^{-4}$ VK^{-1})

(a) $Pt|H_2(g, 1\ atm)|HCl(aq)|Hg_2Cl_2(g)|Hg(liq)$
$\Delta G = -51.8$ kJ mol^{-1}, $\Delta H = -69$ kJmol^{-1}, $\Delta S = -58$ JK^{-1} mol^{-1}

(b) $Pt|H_2(g, 1\ atm)|HCl(aq)|Hg_2Cl_2(g)|Hg(liq)$
$\Delta G = -25.9$ kJ mol^{-1}, $\Delta H = -34.5$ kJ mol^{-1}, $\Delta S = -29$ JK^{1} mol^{-1}

(c) $Hg(liq)|Hg_2Cl_2(g)|HCl(aq)|H_2(g, 1\ atm)|Pt$
$\Delta G = -51.8$ kJ mol^{-1}, $\Delta H = -69$ kJ mol^{-1}, $\Delta S = -58$ JK^{-1} mol^{-1}

(d) $Hg(liq)|Hg_2Cl_2(g)|HCl(aq)|H_2(g, 1\ atm)|Pt$
$\Delta G = 51.8$ kJmol^{-1}, $\Delta H = 69$ kJmol^{-1}, $\Delta S = 58$ JK^{-1} mol^{-1}

Answers with Explanations

1. (c) Metals with lower SRP can displace the metal with higher SRP from their solutions. Mg with lower SRP (−2.34) can reduce both Zn^{2+} (−0.76) and Fe^{2+} (−0.44).

2. (a) Debye-Huckel equation is

$$\ln(\gamma_z) = -AZ_i^2\sqrt{I}$$

where, A = constant depends upon the solvent

Z_i = charge number of ionic species i

I = ionic strength

Let the concentration of ions is C in dilute solution.

$$\ln\gamma_t = -A\sqrt{C}$$

$$[\because I = \frac{1}{2}[K^+]\times(1)^2 + \frac{1}{2}[Cl^-]\times(1)^2$$

$$= \frac{1}{2}\times C\times 1 + \frac{1}{2}\times C + 1 = C]$$

When concentration is increased four times,

$$C = 4C$$

$$I = \frac{1}{2}(4C)\times(1)^2 + \frac{1}{2}(4C)\times(1)^2 = 4C$$

$$(\ln\gamma_t)_2 = -A\sqrt{4C} = -2\cdot A\sqrt{C} = 2\times\ln\gamma_t$$

Thus, $\ln\gamma_z$ is decreased by a factor of 2.

3. (a) $Cu^+ + e^- \longrightarrow Cu;\ E^\circ = 0.52V$

$$\Delta G_1 = -nFE^\circ = -1\times 96500\times 0.52 \ \ldots(i)$$

$$Cu^{2+} + e^- \longrightarrow Cu^+;\ E^\circ = 0.16\ V$$

or $$Cu^+ \longrightarrow Cu^{2+} + e^-;\ E^\circ = -0.16\ V$$

$$\Delta G_2 = -1\times 96500\times(-0.16) \ldots(ii)$$

On adding Eqs. (i) and (ii), we get

$$2Cu^+ \longrightarrow Cu + Cu^{2+},$$

$$\Delta G = \Delta G_1 + \Delta G_2$$

$$= (-96500\times 0.52) + (96500\times 0.16)$$

$$= 96500(-0.52 + 0.16)$$

$$= -(96500\times 0.36)$$

$$= -34{,}740\ J = -34.740\ kJ$$

4. (a) Nernst equation for the reaction, $A^{2+} + 2e^- \rightarrow B$, in terms of the free energy change is

$$\Delta G = \Delta G^\circ + 2.303RT\log\frac{[B]}{[A]}$$

5. (a) For the cell,

$M|M^+(aq, 0.01\,mol\,dm^{-3})\,||\,M^+(aq, 0.1\,mol/dm^3)|M$

the cell reaction is

$$M + M^+(0.1) \longrightarrow M^+(0.01) + M$$

$$\text{Emf} = E^\circ - \frac{2.303RT}{nF}\log\frac{[M^+]_{(0.01)}}{[M^+]_{0.1}}$$

$$= E^\circ - \frac{2.303RT}{1\times F}\log\frac{(0.01)}{(0.1)}$$

$$[\because E^\circ = E_{M|M^+} + E_{M^+|M}]$$

$$= 0 - \frac{2.303RT}{F}\log(0.1)$$

$$= \frac{-2.303RT}{F}\times(-1)$$

$$= +\frac{2.303RT}{F}$$

6. (b) $\log\gamma_\pm = -Az_\pm^2\sqrt{I}$

$$I = \frac{1}{2}[2\times(1)^2 + 2\times(1)^2] = 2$$

$$\therefore\ \log\gamma_\pm = -A(1)^2\cdot(2)^{1/2} = -A\sqrt{2} = -\sqrt{2}A$$

7. (b) At NTP, concentration of water = 55.5 mol/L

$$\pi = CRT$$

$$\frac{\pi_1}{C_1RT_1} = \frac{\pi_2}{C_2RT_2}$$

(At 11 bar and 298K) (At NTP)

$$\frac{11}{C_1\times 298} = \frac{1}{55.5\times 273}$$

$$C_1 = 559.28$$

$$a_w = \frac{C_1}{C_2} = \frac{559.28}{55.5}$$

$$= 10.07$$

$$= \frac{10.07\times 100}{1000}\ \text{(in percentage)}$$

$$= 1.007$$

8. (a) $Fe^{3+} + 3e^- \longrightarrow Fe;\ E^\circ = -0.4\ V$

$$\Delta G_1^\circ = -3\times F\times(-0.4)$$

$$= +0.12\ F \qquad \ldots(i)$$

$$Fe^{2+} + 2e^- \longrightarrow Fe;\ E^\circ = -0.44\ V$$

On inverting, we get

$$Fe \longrightarrow Fe^{2+} + 2e^-;\ E^\circ = +0.44\ V$$

$$\Delta G_2^\circ = -2\times F\times 0.44$$

$$= -0.88\ F \qquad \ldots(ii)$$

On adding Eqs. (i) and (ii), we get

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}; \Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$
$$= [+0.12\,F + (-0.88F)]$$
$$= -0.76\,F$$
$$\Delta G^\circ = -nFE^\circ_{cell}$$
$$-0.76F = -1 \times F \times E^\circ_{cell}$$
$$E^\circ_{cell} = +0.76\text{ V}$$

9. (d) KCl gives K^+ ion to form a counter ion that shields the negative charge on the drop and prevents metal ion reduction. In the presence of KCl only diffusion current is observed. Otherwise both migration current as well as diffusion current will be observed.

10. (a) $\Delta G = -nFE_{cell}$

$$\Delta G = -2 \times 96500 \times 0.2684$$

(Here, $n = 2$ as two electrons are taking part in the cell reaction.)

$$\Delta G = -51801.2\text{ J mol}^{-1} = -51.8\text{ kJ mol}^{-1}$$

We know that

$$\Delta G = \Delta H - T\Delta S$$
$$\Delta S = -nF\left(\frac{\partial E}{\partial T}\right)_p$$

(where, $\left(\frac{\partial E}{\partial T}\right)_p$ = temperature coefficient)

and $\Delta G = -nFE_{cell}$

$$\Rightarrow \quad -nFE_{cell} = \Delta H - \left[-nF\left(\frac{\partial E}{\partial T}\right)_p\right]T$$
$$\Delta H = -nFE_{cell} - nFT\left(\frac{\partial E}{\partial T}\right)_p$$
$$= -nF\left[E_{cell} + T\left(\frac{\partial E}{\partial T}\right)_p\right]$$
$$= -2 \times 96500\,[0.2684 + (298 \times 3 \times 10^{-4})]$$
$$= -69.055\text{ kJ}$$
$$\Delta S = -nF\left(\frac{\partial E}{\partial T}\right)_p$$
$$= -2 \times 96500 \times 3 \times 10^{-4}$$
$$= -6 \times 9.65$$
$$= -57.9\text{ JK}^{-1}\text{ mol}^{-1}$$

The oxidation and reduction half reactions are as

At cathode $2Hg_2^{2+} + 2e^- \longrightarrow 2Hg$ (Reduction)

At anode $H_2 \longrightarrow 2H^+ + e^-$ (Oxidation)

So, the cell is represented as

$Pt \mid H_2\,(g, 1\text{ atm}) \mid HCl(aq) \parallel Hg_2Cl_2\,(g) \mid Hg(liq)$

7

Chemical Kinetics

Syllabus

Chemical Kinetics Rates of chemical reactions, temperature dependence of chemical reactions; elementary, consecutive and parallel reactions; steady state approximation; theories of reaction rates-collision and transition state theory, relaxation kinetics, kinetics of photochemical reactions and free radical polymerization, homogeneous catalysis, adsorption isotherms and heterogeneous catalysis.

GATE 2011

(1 Mark Questions)

1. For a given first order reaction, the reactant reduces to 1/4th its initial value in 10 min. The rate constant of the reaction is

(a) 0.1386 min^{-1}
(b) 0.0693 min^{-1}
(c) 0.1386 $\text{mol L}^{-1}\text{min}^{-1}$
(d) 0.0693 $\text{mol L}^{-1}\text{min}^{-1}$

Statement for Linked Answer Questions 2 and 3

The decomposition of ozone to oxygen,

$$2O_3(g) \longrightarrow 3O_2(g)$$

occurs by the mechanism

(i) $M(g) + O_3(g) \xrightarrow{k_1} O_2(g) + O(g) + M(g), E_{a_1}$

(ii) $O_2(g) + O(g) + M(g) \xrightarrow{k_2} M(g) + O_3(g), E_{a_2}$

(iii) $O(g) + O_3(g) \xrightarrow{k_3} 2O_2(g), E_{a_3}$

where, M is the catalyst molecule.

k' are rate constants and E_{a_1} is the activation energy for the elementary step.

2. Under the steady state approximation for the intermediates, the rate of decomposition of ozone, $-\dfrac{d[O_3]}{dt}$, is

(a) $\dfrac{2k_1k_3[O_3]^2[M]}{k_2[O_2][M] + k_3[O_3]}$
(b) $\dfrac{2k_1k_3[O_3]^2[M]}{k_2[O_2][M] - k_3[O_3]}$
(c) $\dfrac{2k_2k_3[O_3]\,[M]}{k_2[O_2][M] + k_3[O_3]}$
(d) $\dfrac{2k_1k_2[O_3]^2[M]}{k_2[O_2][M] - k_3[O_3]}$

▾ *Solution Points*

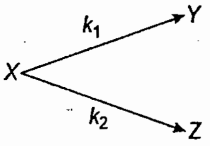
▾ *Solution Points*

3. Assuming $k_3[O_3] >> k_2[O_2][M]$, the activation energy of the overall reaction is

(a) $\frac{E_{a_1} E_{a_3}}{E_{a_2}}$
(b) $E_{a_3} + E_{a_1} - E_{a_2}$
(c) E_{a_2}
(d) E_{a_1}

GATE 2009

4. For the reaction shown below,



the value of k_1 is $1 \times 10^{-4}\,s^{-1}$. If the reaction starts from X, the ratio of the concentrations of Y and Z at any given time during the course of the reaction is found to be $\frac{[Y]}{[Z]} = \frac{1}{4}$. The value of k_2 is

(a) $1 \times 10^{-4}\,s^{-1}$
(b) $2.5 \times 10^{-5}\,s^{-1}$
(c) $4 \times 10^{-4}\,s^{-1}$
(d) $3.5 \times 10^{-4}\,s^{-1}$

GATE 2008

5. At $T = 300\,K$, the thermal energy $[k_B T]$ in cm^{-1} is approximately

(a) 20000
(b) 8000
(c) 5000
(d) 200

6. For the reaction, $2X_3 \rightleftharpoons 3X_2$, the rate of formation of X_2 is

(a) $3(-d[X_3]/dt)$
(b) $\frac{1}{2}(-d[X_3]/dt)$
(c) $\frac{1}{3}(-d[X_3]/dt)$
[✓ (d) $\frac{3}{2}(-d[X_3]/dt)$]

7. In a homogeneous catalytic reaction, 1.0 M of a substrate band 1.0 μM of a catalyst yields 1.0 mM of a product in 10 s. The turnover frequency (TOF) of the reaction (s^{-1}) is

(a) 10^{-2}
(b) 10^{2}
(c) 10^{-3}
(d) 10^{3}

GATE 2007

8. The value of the rate constant for the gas phase reaction, $2NO_2 + F_2 \longrightarrow 2NO_2F$ is 38 $dm^3\,mol^{-1}\,s^{-1}$ at 300K. The order of the reaction is

(a) 0
(b) 1
[✓ (c) 2]
(d) 3

GATE 2005

9. A reaction follows second order rate law, $\frac{-d[A]}{dt} = k[A]^2$, if

(a) a plot of $[A]$ *versus* t is a straight line
[✓ (b) a plot of $1/[A]$ *versus* t is a straight line]

(c) a plot of ln[*A*] *versus* *t* is a straight line
(d) a plot of $e^{[A]}$ *versus* *t* is a straight line

GATE 2003

10. In a consecutive first order reaction,
(where k_1 and k_2 are the respective rate constants) species *B* has transient existence. Therefore,
(a) $k_1 \approx k_2$
(b) $k_1 = 2k_2$
(c) $k_1 >> k_2$
(d) $k_1 << k_2$

GATE 2010

(2 Marks Questions)

11. The specific rate constant of decomposition of a compound is represented by

$$\ln k = 5.0 - \frac{12000}{T}$$

The activation energy of decomposition for this compound at 300 K is
[✓ (a) 24 kcal/mol] (b) 12 kcal/mol
(c) 24 cal/mol (d) 12 cal/mol

GATE 2009

12. The half-life ($t_{1/2}$) for the hydrolysis of an ester varies with the initial concentration of the reactant ($[E]_0$) as follows :

$[E]_0$/10 mol / L	5.0	4.0	3.0
$t_{1/2}$/s	240	300	400

The order of the reaction is
(a) 0 (b) 1 [✓ (c) 2] (d) 3

13. The fluorescence life time of a molecule in solution is 10 ns. If the fluorescence quantum yield is 0.1, the rate constant of fluorescence decay is
(a) $1 \times 10^9\ s^{-1}$ (b) $1 \times 10^8\ s^{-1}$
(c) $1 \times 10^7\ s^{-1}$ (d) $9 \times 10^7\ s^{-1}$

GATE 2007

14. For the reaction, $P + Q + R \rightarrow S$, experimental data for the measured initial rates is given below :

Expt.	Initial conc. *P* (M)	Initial conc. *Q* (M)	Initial conc. *R* (M)	Initial rate (m/s)
1	0.2	0.5	0.4	8.0×10^{-5}
2	0.4	0.5	0.4	3.2×10^{-4}
3	0.4	2.0	0.4	1.28×10^{-3}
4	0.1	0.25	1.6	4.0×10^{-5}

The order of the reaction with respect to *P*, *Q* and *R* respectively, is

▾ *Solution Points*

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

15. Sucrose is converted to a mixture of glucose and fructose in a pseudo first order process under alkaline conditions. The reaction has a half-life of 28.4 min. The time required for the reduction of a 8.0 mM sample of sucrose to 1.0 mM is
(a) 56.8 min (b) 170.4 min (c) 85.2 min (d) 227.2 min

16. The reaction, $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ proceeds *via* the following steps :

$$NO + NO \xrightarrow{K_a} N_2O_2$$

$$N_2O_2 \xrightarrow{K_a'} NO + NO$$

$$N_2O_2 + O_2 \xrightarrow[\text{(slow)}]{k_b} NO_2 + NO_2$$

The rate of this reaction is equal to

(a) $2k_b[NO][O_2]$

(b) $(2K_a k_b[NO]^2[O_2])/(K_a + k_b[O_2])$

(c) $2k_b[NO]^2[O_2]$

(d) $K_a[NO]^2[O_2]$

GATE 2006

17. 1 g of ^{90}Sr gets converted to 0.953 g after 2 yr. The half-life of ^{90}Sr, and the amount of ^{90}Sr remaining after 5 yr are
(a) 1.44 yr and 0.916 g (b) 57.6 yr and 0.75 g
(c) 28.8 yr and 0.887 g (d) 100 yr and 0.982 g

18. Consider an exothermic reaction, $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I$

As the temperature increases

(a) k_1, k_{-1} and k_1/k_{-1} increase

(b) k_1 increases, k_{-1} decreases and k_1/k_{-1} increases

(c) k_1, k_{-1} and k_1/k_{-1} decrease

(d) k_1 and k_{-1} decrease and k_1/k_{-1} increases

19. A reaction proceeds through the formation of an intermediate B in a unimolecular reaction

$$A \xrightarrow{k_a} B \xrightarrow{k_b} C$$

The integrated rate law for this reaction is

(a) $[A] = [A]_0 e^{-k_a t}$

(b) $[A] = [A]_0 (e^{-k_a t} - e^{-k_b t})$

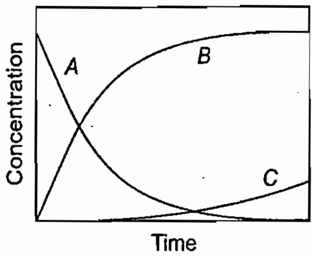
(c) $[A] = \frac{[A]_0}{2}\left(1 + \frac{k_a e^{-k_b t} - k_b e^{-k_a t}}{k_a - k_b}\right)$

(d) $[A] = [A]_0 (1 + e^{-k_a t} - e^{-k_b t})$

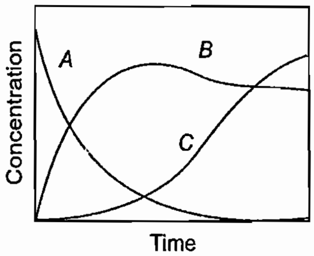
▾ *Solution Points*

20. If $k_a >> k_b$, then concentration *versus* time plot for the reaction is

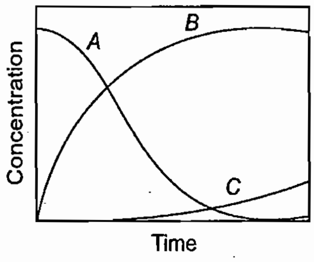
(a)



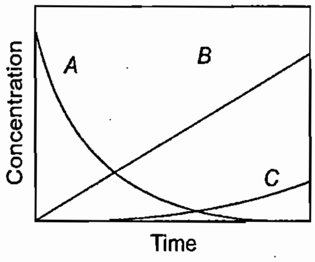
(b)



(c)



(d)



GATE 2003

21. H_2 and Br_2 react to give HBr by the following steps

$$Br_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2Br + M(\text{fast}) \left(\frac{k_1}{k_{-1}} = K\right)$$

$$Br + H_2 \xrightarrow{k_2} HBr + H(\text{slow})$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br\ (\text{fast})$$

The probable rate law for the above sequence is

(a) Rate = $k_2(K)^{1/2}\ [H_2]\ [Br_2]^{1/2}$ (b) Rate = $k_2\ [H_2]\ [Br_2]$

(c) Rate = $k_2\ (k_1)^{1/2}[H_2]\ [Br_2]^{1/2}$ (d) Rate = $k_2\ (K)\ [H_2]^{1/2}[Br_2]^{1/2}$

GATE 2002

22. The half-life of a first order reaction varies with temperature according to

(a) $\ln t_{1/2} \propto 1/T$ (b) $\ln t_{1/2} \propto T$

(c) $t_{1/2} \propto 1/T^2$ (d) $t_{1/2} \propto T^2$

GATE 2000

23. The half-life time for a reaction at initial concentrations of 0.1 and 0.4 mol^{-1} are 200 s and 50 s respectively. The order of the reaction is

(a) 0 (b) 1

(c) 2 (d) 3

▾ *Solution Points*

Answers with Explanations

1. (a) For the first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

Given, $t = 10$ min

$a = a$

$a - x = a/4$

$$k = \frac{2.303}{10} \log \frac{a}{a/4}$$

$$= \frac{2.303 \times 2}{10} \log 2$$

$$= 0.1386 \text{ min}^{-1}$$

2. (a) From the given mechanism,

$$\frac{d[O_3]}{dt} = -k_1[M][O_3] + k_2[O][O_2][M] - k_3[O][O_3] \quad \text{...(i)}$$

$$\frac{d[O]}{dt} = +k_1[M][O_3] - k_2[O_2][O][M] - k_3[O][O_3] \quad \text{...(ii)}$$

On applying steady state approximation for the intermediate,

$$\frac{d[O]}{dt} = 0$$

$$k_1[M][O_3] = k_2[O_2][O][M] + k_3[O][O_3]$$

$$[O] = \frac{k_1[M][O_3]}{k_2[M][O_2] + k_3[O_3]} \quad \text{...(iii)}$$

Putting the value of [O] in equation (i), we get

$$\frac{d[O_3]}{dt} = -k_1[M][O_3] + \frac{k_1k_2[O_2][M]^2[O_3]}{k_2[M][O_2] + k_3[O_3]} - \frac{k_1k_3[M][O_3]^2}{k_2[M][O_2] + k_3[O_3]}$$

$$\frac{d[O_3]}{dt} = \frac{-k_1k_2[M]^2[O_2][O_3] - k_1k_3[O_3]^2[M] + k_1k_2[O_2][M]^2[O_3] - k_1k_3[M][O_3]^2}{k_2[M][O_2] + k_3[O_3]}$$

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_3[M][O_3]^2}{k_2[M][O_2] + k_3[O_3]}$$

3. (d) When $k_3[O_3] >> k_2[O_2][M]$,

$$-\frac{d[O_3]}{dt} \approx \frac{2k_1k_3M[O_3]^2}{k_3[O_3]}$$

$$= 2k_1[M][O_3]$$

Let the overall rate constant, $k = k_1$

$$\frac{d \ln k}{dt} = \frac{d \ln k_1}{dt}$$

i.e., $$\frac{E_a}{RT^2} = \frac{E_{a_1}}{RT^2}$$

$\therefore$ $$E_a = E_{a_1}$$

4. (c) Rate of disappearance of X is

$$dx/dt = k_1(x - a) + k_2(x - a)$$

$$= (k_1 + k_2)(x - a)$$

where x is the initial concentration of x and a is decrease in the concentration at an instant.

Rate of formation of $Y = k_1(x - a)$

Rate of formation of $Z = k_2(x - a)$

The ratio of formation of Y and Z is

$$d[Y]/d[Z] = k_1(x - a)/k_2(x - a)$$

$$= k_1/k_2$$

i.e., $$[Y]/[Z] = k_1/k_2$$

$$\frac{1}{4} = \frac{1 \times 10^{-4}}{k_2}$$

$$= 4 \times 10^{-4} \text{ s}^{-1}$$

5. (d) k_B = Boltzmann constant

Value of Boltzmann constant = 0.6950 cm^{-1}/K

Thermal energy = $k_b \times T$

$$= 0.6950 \text{ cm}^{-1}/\text{K} \times 300 \text{ K}$$

$$\simeq 200 \text{ cm}^{-1}$$

6. (d) For the reaction,

$$2X_3 \rightleftharpoons 3X_2$$

Rate of disappearance of $[X_3] = -\frac{d[X_3]}{dt}$

Rate of appearance of $X_2 = +\frac{d[X_2]}{dt}$

Rate of reaction, $-\frac{d[X_3]}{2dt} = \frac{d[X_2]}{3dt}$

$\therefore$ Rate of appearance of $X_2 = \left[\frac{d[X_2]}{dt}\right]$

$$= \frac{3}{2}\left[\frac{-d[X_3]}{dt}\right]$$

7. (b) Rate, $r = \frac{d[\text{product}]}{dt}$

$$= \frac{1 \times 10^{-3}\text{M}}{10}$$

$$= 1 \times 10^{-4} \text{ m/s}$$

Turn over frequency (TOF) $= \frac{r}{Q}$

where, Q = concentration of catalyst

$$= \frac{1 \times 10^{-4} \text{ m/s}}{1 \times 10^{-6} \text{ m/s}}$$

$$= 1 \times 10^{2} \text{ s}^{-1}$$

8. (c) We know that litre = dm^3

So, the unit of rate constant = $\text{Lmol}^{-1}\text{ s}^{-1}$.

Equate it with general expression $(\text{mol/L})^{1-n}\text{s}^{-1}$.

(where, n = order of reaction)

$$\text{Lmol}^{-1}\text{ s}^{-1} = (\text{mol/L})^{1-n}\text{s}^{-1}$$

Therefore, $-1 = 1 - n$

or $n = 2$

9. (b) Rate $= \frac{-d[A]}{dt} = k[A]^2$

or $\frac{-d[A]}{[A]^2} = kdt$ ...(i)

On integrating Eq. (i), we get

$$-\int \frac{d[A]}{[A]^2} = \int k dt$$

$$\frac{1}{A} = kt + C$$

At $t = 0$, $A = [A_0]$ = initial concentration

$$C = \frac{1}{[A_0]}$$

On putting the value of C, we get

$$\frac{1}{A} = kt + \frac{1}{[A_0]}$$

$$kt = \frac{1}{A} - \frac{1}{[A_0]}$$

Thus, a plot of $\frac{1}{A}$ (x) and t (y) is a straight line [from the equation $y = mx + C$ in which graph of y and x is a straight line.]

10. (d) Consecuting reaction is the reaction in which the product formed decays further to form new product. e.g.,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

If k is very low, reactant predominates and if k is high, product dominates.

Since, B has transient existence, thus,

$$k_2 >> k_1$$

11. (a) Given, $\ln k = 5.0 - \frac{12000}{T}$

We know that $\ln k = \ln A - \frac{E_a}{RT}$

Comparing the two, we have

$$E_a/R = 12000$$

$$E_a = 12000 \times 2 = 24.00 \text{ kcal/mol}$$

12. (c) Half-life and initial concentration are related as

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \left[\frac{(E_0)_2}{(E_0)_1}\right]^{1-n}$$

$$\Rightarrow \quad \frac{300}{240} = \left(\frac{4}{5}\right)^{1-n}$$

$$\frac{5}{4} = \left(\frac{4}{5}\right)^{1-n}$$

$$\left(\frac{4}{5}\right)^{-1} = \left(\frac{4}{5}\right)^{1-n}$$

or $-1 = 1 - n$

$$n = 2$$

Further, $\frac{400}{300} = \left(\frac{3}{4}\right)^{1-n}$

$$\frac{4}{3} = \left(\frac{3}{4}\right)^{1-n}$$

$$\left(\frac{3}{4}\right)^{-1} = \left(\frac{3}{4}\right)^{1-n}$$

$$-1 = 1 - n$$

$$n = 2$$

Thus, the reaction is of second order.

13. (c) Rate constant

$$k = \frac{\text{fluorescence quantum yield}}{\text{fluorescence lifetime}}$$

$$= \frac{0.1}{10 \times 10^{-9}} = 1 \times 10^{7} \text{ s}^{-1}$$

14. (c) Let the rate expression be $r = k\,[P]^m[Q]^n[R]^o$

For experiment I,

$$8 \times 10^{-5} = [0.2]^m[0.5]^n[0.4]^o \quad \text{...(i)}$$

Similarly,

$$3.2 \times 10^{-4} = [0.4]^m [0.5]^n [0.4]^o \quad \text{...(ii)}$$

$$1.28 \times 10^{-3} = [0.4]^m [2]^n [0.4]^o \quad \text{...(iii)}$$

$$4 \times 10^{-5} = [0.1]^m [0.25]^n [1.6]^o \quad \text{....(iv)}$$

From Eqs. (i) and (ii),

$$\frac{8 \times 10^{-5}}{3.2 \times 10^{-4}} = \left(\frac{0.2}{0.4}\right)^m$$

$$m = 2$$

From Eqs. (ii) and (iii),

$$\frac{3.2 \times 10^{-4}}{1.28 \times 10^{-3}} = \left(\frac{0.5}{2}\right)^n$$

$$n = 1$$

From Eqs. (i) and (iv)

$$\frac{8 \times 10^{-5}}{4 \times 10^{-5}} = \left(\frac{0.2}{0.1}\right)^m \left(\frac{0.5}{0.25}\right)^n \left(\frac{0.4}{1.6}\right)^o$$

$$o = 1$$

15. (c) For first order reaction,

$$k = \frac{0.693}{t_{1/2}}$$

$$= \frac{0.693}{28.4} = 0.0244$$

$$t = \frac{2.303}{k} \log \frac{a}{(a - x)}$$

$$= \frac{2.303}{0.0244} \log \frac{8}{1}$$

$$= 85.2 \text{ min}$$

16. (c) Reaction, $N_2O_2 + O_2 \xrightarrow{k_b} NO_2 + NO_2$

is the slowest step, so the rate expression is

$$\text{Rate} = k_b [N_2O_2] [O_2] \quad \text{...(i)}$$

Since, N_2O_2 is an intermediate so its concentration should be replaced from Eq. (i). For that purpose consider reaction

$$NO + NO \xrightarrow{K_a} N_2O_2$$

For this reaction equilibrium constant $K_a = \frac{[N_2O_2]}{[NO]^2}$

$$[N_2O_2] = K_a [NO]^2 \quad \text{...(ii)}$$

From Eqs. (i) and (ii)

$$\text{Rate} = k_b \cdot K_a [NO]^2 [O_2]$$

or $$\simeq 2\, k_b [NO]^2 [O_2]$$

17. (c) $k = \frac{2.303}{t} \log \frac{N_0}{N}$

$$k = \frac{2.303}{2} \log \frac{1}{0.953} = 0.0244$$

$$t_{1/2} = 0.693/k = 0.693/0.0244 = 28.79$$

yr

$$\frac{N}{N_0} = \left[\frac{1}{2}\right]^n$$

$$n = \frac{5}{28.8} = 0.1736$$

$$\frac{N}{1} = \left[\frac{1}{2}\right]^{0.1736} = 0.887 \text{ g}$$

18. (a) With increase in temperature, the number of collisions having energy higher than the activation energy increases. Thus, rate and rate constant both increases whether the reaction in exothermic or endothermic.

If k_1 and k_{-1} increases, their ratio also increases.

19. (a) Rate equation for concentration of A is

$$\frac{dA}{dt} = -k_1[A]$$

$$\frac{d[A]}{[A]} = -k_a dt$$

$$\ln[A] = -k_a t + C \quad \text{...(i)}$$

At $t = 0$, $[A] = [A_0]$

On putting these values in Eq. (i), we get

$$\ln[A_0] = -k_a \times 0 + C$$

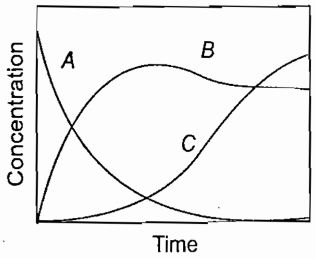
$$C = \ln[A_0]$$

$$\Rightarrow \quad \ln[A] = -k_a t + \ln[A_0]$$

$$\ln[A] - \ln[A_0] = -k_a t$$

$$[A] = [A_0]\, e^{-k_a t}$$

20. (b) If $k_a >> k_b$ all the A present is converted into B, which is slowly used up to form C. So, concentration vs time plot for such reaction is



21. (a) In the given mechanism, step (ii) is the rate of determining step and rate law is

$$\text{Rate} = \frac{d[\text{HBr}]}{dt} = k_2[H_2][\text{Br}] \quad \ldots\text{(i)}$$

Since, Br is one of the reactant, its relationship with other of the reactant must be sought. The rapid reaction in both the directions of step (i) implies the relationship given below.

$$k_1[\text{Br}_2] = k_{-1}[\text{Br}]^2$$

$$[\text{Br}] = ((k_1/k_{-1})[\text{Br}_2])^{1/2}$$

Substituting this value in rate expression (i)

$$\text{Rate} = k_2(k_1/k_{-1})\,[\text{Br}]^{1/2}$$

$$\frac{k_1}{k_{-1}} = k \text{ (new constant)}$$

$$\text{Rate} = k_2(K)^{1/2}[H_2][\text{Br}_2]^{1/2}$$

22. (a) Arrhenius equation is,

$$k = Ae^{-E_a/RT}$$

or $$\ln k = \ln A - \frac{E_a}{RT}$$

For first order reaction,

$$k = \frac{0.693}{t_{1/2}}$$

$$\therefore \quad \ln\left(\frac{0.693}{t_{1/2}}\right) = \ln A - \frac{E_a}{RT}$$

$$\ln 0.693 - \ln t_{1/2} = \ln A - \frac{E_a}{RT}$$

or $$\ln t_{1/2} \propto \frac{1}{T}$$

23. (c) $t_{1/2} \propto \frac{1}{a^{n-1}}$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_1}{a_2}\right)^{1-n}$$

$$\frac{200}{50} = \left(\frac{0.1}{0.4}\right)^{1-n}$$

$$(4) = \left(\frac{1}{4}\right)^{1-n}$$

$$\left(\frac{1}{4}\right)^{-1} = \left(\frac{1}{4}\right)^{1-n}$$

$$-1 = 1 - n$$

$$-1-1 = -n \;\Rightarrow\; n = 2$$

Thus, the order of reaction is 2.

8

Chemical Thermodynamics

Syllabus

Chemical Thermodynamics First law of thermodynamics, heat, energy and work; second law of thermodynamics and entropy; third law and absolute entropy; free energy; partial molar quantities.

GATE 2011

(1 Mark Questions)

▾ *Solution Points*

1. $\left(\frac{\partial G}{\partial p}\right)_T =$

(a) V (b) S (c) $-S$ (d) $-V$

2. According to conventional transition state theory, for elementary bimolecular reactions, the molar entropy of activation $\Delta S^{\pm}$ is

(a) positive
(b) zero
(c) negative
(d) positive for endothermic and negative for exothermic reactions

GATE 2010

3. The molar entropy of crystalline CO at absolute zero is

(a) zero (b) $-R\ln 2$ (c) $R\ln 2$ (d) $2R\ln 2$

4. Among W (work), Q (heat), U (internal energy) and S (entropy)

(a) W and U are path functions but Q and S are state functions
(b) W and S are path functions but Q and U are state functions
(c) S and U are path functions but Q and W are state functions
(d) W and Q are path functions but U and S are state functions

GATE 2009

5. Among the following, the system that would require the least amount of thermal energy to bring its temperature to 80°C is

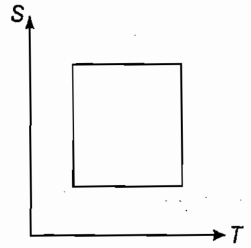
(a) 200 g of water at 40°C (b) 100 g of water at 20°C
(c) 150 g of water at 50°C (d) 300 g of water at 30°C

6. Among the following, the reaction that is accompanied by a decrease in the entropy is
(a) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
(b) $C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$
(c) $PCl_5(s) \longrightarrow PCl_3(l) + Cl_2(g)$
(d) $2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$

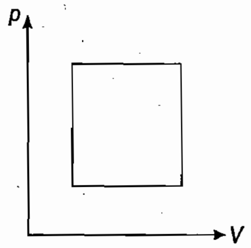
GATE 2006

7. The plot that describes a Carnot cycle is

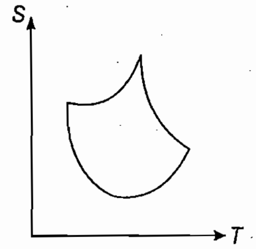
(a)



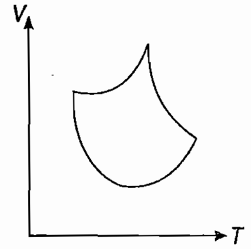
(b)



(c)



(d)



GATE 2003

8. The rate of evaporation of a liquid is always faster at a higher temperature because
(a) the enthalpy of vaporization is always endothermic
(b) the enthalpy of vaporization is always exothermic
(c) the enthalpy of vaporization is zero
(d) the internal pressure of the liquid is less than that of the gas

GATE 2002

9. The enthalpy of formation of AgCl is obtained from the enthalpy change from which one of the following process?
(a) $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
(b) $Ag(s) + 1/2\ Cl_2(g) \longrightarrow AgCl(s)$
(c) $AgCl(s) \longrightarrow Ag(s) + 1/2\ Cl_2(g)$
(d) $Ag(s) + AuCl \longrightarrow Au(s) + AgCl(s)$

GATE 2001

10. For an irreversible adiabatic expansion of a perfect gas from volume V_i to V_f, the change in entropy of the gas is
(a) $nR \ln(V_f/V_i)$
(b) zero
(c) less than zero
(d) greater than zero

▾ *Solution Points*

GATE 2000

▾ *Solution Points*

11. The criterion for the spontaneity of a process is

(a) $\Delta S_{\text{sys}} > 0$ (b) $\Delta S_{\text{surr}} > 0$

(c) $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ (d) $\Delta S_{\text{sys}} - \Delta S_{\text{surr}} > 0$

12. ΔH and ΔE for the reaction,

$Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + H_2O(l)$ at constant temperature are related as

(a) $\Delta H = \Delta E$ (b) $\Delta H = \Delta E + RT$

(c) $\Delta H = \Delta E + 3RT$ (d) $\Delta H = \Delta E - 3RT$

GATE 2011

(2 Marks Questions)

13. For the process,

1 Ar (300 K, 1 bar) → 1Ar (200 K, 10 bar) assuming ideal gas behaviour, the change in molar entropy is

(a) −27.57 J / K / mol (b) +27.57 J / K / mol

(c) −24.20 J / K / mol (d) +24.20 J / K / mol

GATE 2010

14. The change in entropy when two moles of argon gas are heated at constant volume from 300 K to 500 K is

(a) −12.74 J / K / mol (b) −6.37 J / K / mol

(c) 6.37 J / K / mol (d) 12.74 J / K / mol

GATE 2009

15. Given that standard molar enthalpies of formation of NO(g) and $NO_2(g)$ are respectively 90.3 kJ/mol and 33.2 kJ/mol, the enthalpy change for the reaction $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ is

(a) 16.6 kJ (b) −57.1 kJ (c) −114.2 kJ (d) 57.1 kJ

16. The free energy change (ΔG) of 1 mole of an ideal gas that is compressed isothermally from 1 atm to 2 atm is

(a) $RT \ln 2$ (b) $-2RT$

(c) $-RT \ln 2$ (d) $2RT$

GATE 2005

17. Standard entropy of crystalline carbon monoxide (in kJ/mol) at 0 K is around

(a) 0.03 (b) 2.50 (c) zero (d) 5.76

GATE 2004

18. The criterion for spontaneous change in terms of the state functions is

(a) $dU_{S,V} \geq 0$ (b) $dA_{T,V} \geq 0$

(c) $dS_{U,V} \geq 0$ (d) $dG_{p,V} \leq 0$

GATE 2003

19. For the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
compute the entropy change (in J/K/mol) for the process and comment on the sign of the property.

Data	Species	$NH_3(g)$	$N_2(g)$	$H_2(g)$
	$S°$(J/K/mol)	192.3	191.5	130.6

(a) $\Delta S° = -37.65$ J/K/mol; negative sign indicates that there is a decrease in the gaseous species during the reaction.
(b) $\Delta S° = -198.7$ J/K/mol; negative sign indicates that there is a decrease in the gaseous species during the reaction.
(c) $\Delta S° = -31.25$ J/K/mol; negative sign indicates that there is a decrease in the gaseous species during the reaction.
(d) $\Delta S° = +31.25$ J/K/mol; positive sign indicates that the reaction is spontaneous.

20. For the reaction,

$$2Cl(g) \longrightarrow Cl_2(g)$$

the thermodynamic properties
(a) ΔG, ΔH and ΔS are positive
(b) ΔG, ΔH and ΔS are negative
(c) ΔG, ΔH are negative and ΔS is positive
(d) ΔG is negative and ΔH, ΔS are positive

21. The standard free energies of formation of $H_2S(g)$ and CdS(s) at 1000°C are −49.0 kJ/mol and −127.2 kJ/mol respectively. Use these data to predict whether $H_2(g)$ will reduce CdS (s) to metallic Cd at this temperature.
(a) $\Delta G = -78.2$ kJ/mol and H_2 reduces CdS
(b) $\Delta G = -39.1$ kJ/mol and H_2 reduces CdS
(c) $\Delta G = 0$ kJ/mol and the reaction is at equilibrium
(d) $\Delta G = 78.2$ kJ/mol and the reaction is not feasible

GATE 2001

22. Choose the correct criterion of spontaneity in terms of the properties of the system alone.
(a) $(dS)_{U,V} > 0$
(b) $(dS)_{T,p} > 0$
(c) $(dS)_{H,p} < 0$
(d) $(dS)_{T,V} < 0$

▾ *Solution Points*

Answers with Explanations

1. (a) We know that,

Gibbs free energy, $G = H - TS$

and $H = E + pV$

$\therefore \quad G = E + pV - TS$

On differentiating, we get

$$dG = dE + pdV + Vdp - TdS - SdT \qquad \text{...(i)}$$

For an infinitesimal stage of a reversible process,

$$dq = dE + dW \quad \text{and} \quad dS = \frac{dq}{T} \quad [\because W = pdV]$$

$$TdS = dE + pdV \qquad \text{...(ii)}$$

From Eqs. (i) and (ii), we get

$$dG = dE + pdV + Vdp - dE - pdV - SdT$$
$$= Vdp - SdT$$

At constant temperature, $dT = 0$

$$\therefore \quad dG = Vdp$$

$$\left(\frac{dG}{dp}\right)_T = V$$

2. (c) According to conventional transition state theory, for elementary bimolecular reactions, the molar entropy of activation, $\Delta S^{\circ\pm}$ is negative because two reactant species come together to form one species.

3. (c) Although according to the third law of thermodynamics entropy of a perfectly crystalline substance is zero at absolute zero. But CO is not a perfectly crystalline substance and can exist in two ways in crystal lattice.

$$C\equiv O \qquad\qquad O\equiv C$$

Let the amount of two species is equal.

$\therefore$ The entropy of mixing these two species per mole quantity,

$$\Delta S_{\text{mix}} = -n_1 R \ln y_1 - n_2 R \ln y_2$$
$$= -\frac{1}{2} R \ln\left(\frac{1}{2}\right) - \frac{1}{2} R \ln\left(\frac{1}{2}\right)$$
$$= -R \ln \frac{1}{2} = R \ln 2$$

4. (d) Internal energy, U and entropy, S are state functions as they depend only on the initial and final state of the system. Work and heat are path functions as they depend on the path followed.

5. (c) We know that,

$$Q = ms(T_2 - T_1)$$

Now, we will calculate Q in all cases

$$Q = 200 \times 1 \times (80 - 40) = 8000$$
$$Q = 100 \times 1 \times (80 - 20) = 6000$$
$$Q = 150 \times 1 \times (80 - 50) = 4500$$
$$Q = 300 \times 1 \times (80 - 30) = 15000$$

Since, value of Q is least for 150 g water at 50°C. So, it will require least amount of energy.

6. (a) Entropy is the measure of randomness. As the randomness (disorder) increases, entropy increases. The order of entropy is

$$\underset{\substack{\text{(particles}\\ \text{orderly}\\ \text{arranged)}}}{\text{solid}} < \text{liquid} < \underset{\substack{\text{(most}\\ \text{disordered)}}}{\text{gas}}$$

Thus, in reaction,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g),$$

entropy decreases because number of gaseous molecules decreases.

7. (a) In a Carnot cycle there are four processes, two are reversible and two are adiabatic. In the given graphs, graph a satisfies these conditions.

8. (a) At the time of evaporation energy is required to overcome the intermolecular forces between the molecules of liquid. *i.e*, the enthalpy of vaporization is always endothermic. Since, at higher temperature more energy is available, so rate of evaporation is faster at elevated temperature.

9. (b) The enthalpy change accompanying the formation of one mole of a pure substance in its standard state from the constituent elements in their standard state is called enthalpy of formation.

For Ag, standard state is solid and for chlorine, it is gas. Thus, the process that gives the enthalpy of formation of AgCl is

$$Ag(s) + \frac{1}{2}Cl_2(g) \longrightarrow AgCl(s)$$

10. (d), For irreversible adiabatic expansion of a perfect gas,

$$\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$
$$\therefore \quad \Delta S_{\text{surr}} > -\Delta S_{\text{sys}}$$

11. (c) According to second law of thermodynamics the criterion for spontaneity of a process is $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$.

12. (d) For any chemical reaction,

$$\Delta H = \Delta E + \Delta n_g\ RT$$

where, Δn_g = total no. of moles of gaseous product–total no. of moles of gaseous reactants

For the given reaction,

$$\Delta n_g = 0 - 3 = -3$$
$$\Delta H = \Delta E + (-3)RT$$
$$\Delta H = \Delta E - 3\,RT$$

13. (a) $\Delta S = nC_p \ln\frac{T_2}{T_1} - nR\ln\frac{p_2}{p_1}$

$$= 2.303 C_p \log\frac{T_2}{T_1} - 2.303 R \log\frac{p_2}{p_1}$$

For monoatomic gas like Ar, $C_p = \frac{5}{2}R$

$$= \frac{5 \times 8.314}{2} = 20.8$$

$$\Delta S = 2.303 \times 20.8 \log\frac{200}{300} - 2.303 \times 8.314 \log\frac{10}{1}$$
$$= 2.303 \times 20.8 \log\frac{2}{3} - 2.303 \times 8.314$$
$$= 47.9 \times (-0.176) - 19.15$$
$$= -8.43 - 19.15 = -27.58 \text{ J/K/mol}$$

14. (d) $\Delta S = nC_V \ln\frac{T_2}{T_1}$

$$= 2 \times 12.5 \ln\frac{500}{300} \qquad (C_V \text{ for argon} = \frac{3}{2}R = 12.5)$$
$$= 2 \times 12.5(\ln 5 - \ln 3)$$
$$= 25(1.609 - 1.098)$$
$$= 25 \times 0.511\text{d} = 12.74 \text{ J/K/mol}$$

15. (c) $\Delta H = \Sigma\Delta H_{\text{products}} - \Sigma\,\Delta H_{\text{reactants}}$

$$\Delta H = 2(33.2) - [2(90.3) + 0]$$

($\because$ Enthalpy of formation of free element = 0)

$$\Delta H = -114.2 \text{ kJ}$$

16. (a) Work done in isothermal reversible process,

$W_{(\text{rev})} = -nRT\ln\frac{p_1}{p_2}$ [$W_{(\text{rev})}$ is a measure of free energy.]

$$= -1RT\ln\frac{1}{2} = +RT\ln 2 = \Delta G$$

17. (d) Although according to the third law of thermodynamics entropy of a perfectly crystalline substance is zero at absolute zero. But CO is not a perfectly crystalline substance and can exist in two ways in crystal lattice. So, the molar entropy of crystalline CO at absolute zero is $R\ln 2$. (see solution 3)

Standard entropy = $8.314 \times \ln 2$

$$= 8.314 \times 0.693$$
$$= 5.76$$

18. (d) For, spontaneous change, the value of dG should be negative *i.e.*, less than 0 at constant p and V.

or $\qquad dG_{p,V} \leq 0$

19. (b) $\Delta S° = \Sigma S°_{\text{products}} - \Sigma S°_{\text{reactants}}$

$$\Delta S° = 2 \times 192.3 - [191.5 + (3 \times 130.6)]$$
$$= 384.6 - [583.3]$$
$$= -198.7 \text{ J/K/mol}$$

In the reaction two gaseous species are there in the reactant side and number of moles of gaseous species on the product side is 1. So, there is a decrease in number of gaseous species, which is represented by negative sign of entropy.

20. (b) $2\text{Cl(g)} \longrightarrow \text{Cl}_2\text{(g)}$

For this reaction,

$$\Delta H = -\text{ ve}$$

because energy is released during the formation of a bond among isolated gaseous atoms. (or bond formation is an exothermic process.

Number of gaseous particles towards reactant side = 2

Number of gaseous particles towards product side = 1

Thus, entropy decreases due to decrease in number of gaseous particles (*i.e.*, randomness).

The given reaction is spontaneous, so the value of ΔG is also negative.

21. (d) For a reaction to be spontaneous, ΔG should be negative.

The reaction is

$$\text{CdS} + \text{H}_2 \longrightarrow \text{H}_2\text{S}$$
$$\Delta G = \Sigma\Delta G_{\text{products}} - \Sigma\Delta G_{\text{reactants}}$$
$$= -49 - (-127.2) = 78.2 \text{ kJ/mol}$$

Since, the value of ΔG is positive, *i.e.*, 78.2 kJ/mol, the reaction is not feasible.

22. (a) $dS = \frac{dq}{T_{\text{surr}}}$

$$dU = dq + dW$$
$$dU + p_{\text{ext}}dV - T_{\text{surr}}dS < 0$$

For isolated system,

$$q = \omega = 0, \Delta V = 0 \text{ and } dU = 0$$
$$(dS)_{UV} > 0$$

9

Basics of Organic Reaction Mechanism

Syllabus

Organic Chemistry

Stereochemistry Chirality of organic molecules with or without chiral centres. Specification of configuration in compounds having one or more stereogenic centres. Enantiotopic and diastereotopic atoms, groups and faces. Stereoselective and stereospecific synthesis. Conformational analysis of acyclic and cyclic compounds. Geometrical isomerism. Configurational and conformational effects on reactivity and selectivity/specificity.

Reaction mechanism Methods of determining reaction mechanisms. Nucleophilic and electrophilic substitutions and additions to multiple bonds. Elimination reaction. Reactive intermediates : carbocations, carbanions, carbenes, nitrenes, arynes, free radicals. Molecular rearrangements involving electron deficient atoms.

Organic synthesis Synthesis, reactions, mechanisms and selectivity involving the following-alkenes, alkynes, arenes, alcohols, phenols, aldehydes, ketones, carboxylic acids and their derivatives, halides, nitro compounds and amines. Use of compounds of Mg, Li, Cu, B and Si in organic synthesis. Concepts in multistep synthesis-retrosynthetic analysis, disconnections, synthons, synthetic equivalents, reactivity **umpolung**, selectivity, protection and deprotection of functional groups.

Pericyclic reactions Electrocyclic, cycloaddition and sigmatropic reactions. Orbital correlation, FMO and PMO treatments.

Photochemistry Basic principles. Photochemistry of alkenes, carbonyl compounds and arenes. Photooxidation and photoreduction. Di-π-methane rearrangement, Barton reaction.

Heterocyclic compounds Structure, preparation, properties and reactions of furan, pyrrole, thiophene, pyridine, indole and their derivatives.

Biomolecules Structure, properties and reactions of mono and disaccharides, physicochemical properties of amino acids, chemical synthesis of peptides, structural features of proteins, nucleic acids, steroids, terpenoids, carotenoids, and alkaloids.

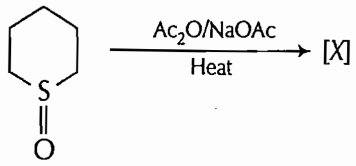
Spectroscopy Principles and applications of UV-visible, IR, NMR and Mass spectrometry in the determination of structures of organic molecules.

GATE 2011

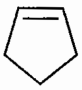
(1 Mark Questions)

▾ *Solution Points*

1. In the following reaction,



the major product [X] is

(a)


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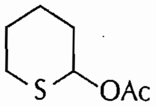

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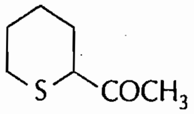

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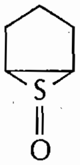
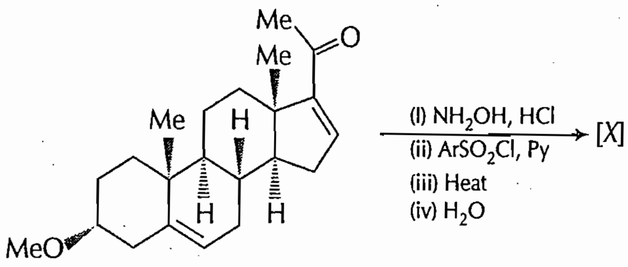
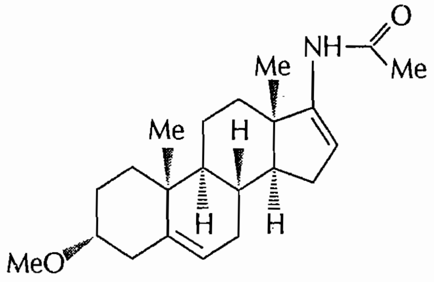


2. In the following reaction sequence,



the major product [X] is

(a)


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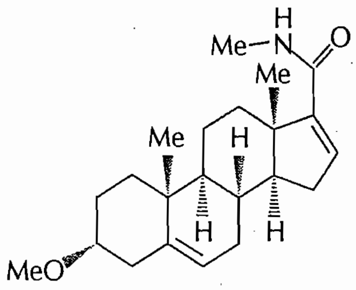

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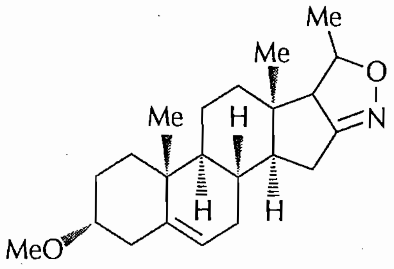
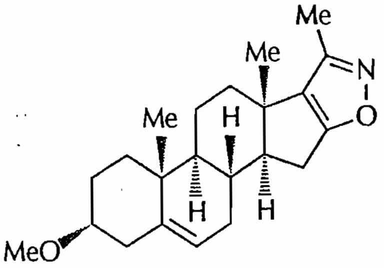
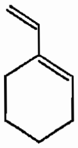


(d)

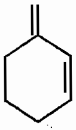


3. The diene which undergoes Diels-Alder reaction with maleic anhydride is

(a)



(b)



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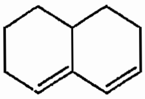
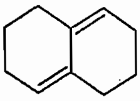


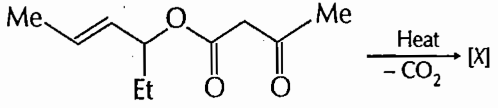
(d)



4. The sequence of an *m*RNA molecule produced from a DNA template strand with the composition 5′-AGCTACACT-3′ is

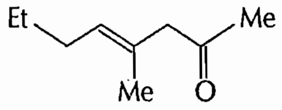
(a) 5′-AGUGUAGCU-3′
(b) 5′-UCGAUGUGA-3′
(c) 5′-AGTGTAGCT-3′
(d) 5′-TCGATGTGA-3′

5. In the following reaction,

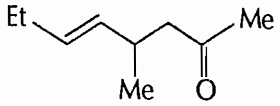


the major product [X] is,

(a)



(b)



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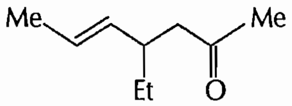
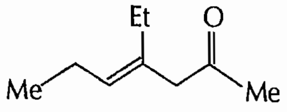
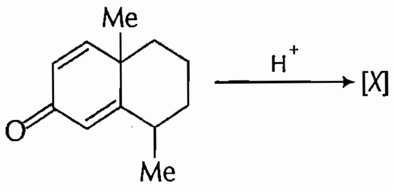


(d)

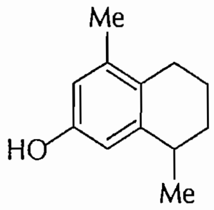


6. In the following reaction,

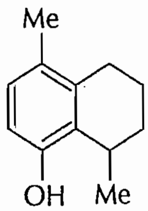


the major product [X] is

(a)



(b)



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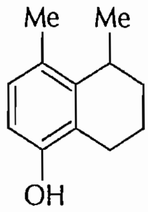
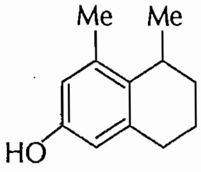


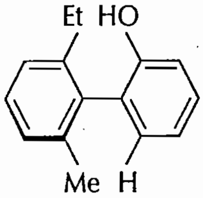
(d)



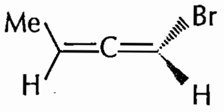
▾ ***Solution Points***

GATE 2010

7. The absolute configuration for compounds *X* and *Y* respectively are



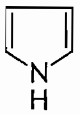
X



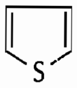
Y

(a) *R*, *S*
(b) *S*, *R*
(c) *R*, *R*
(d) *S*, *S*

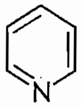
8. The decreasing order of the reactivity of the following compounds towards electrophiles is



I



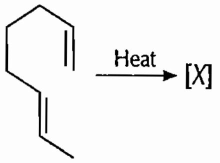
II



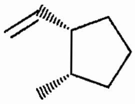
III

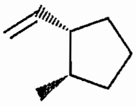
(a) II > I > III
(b) II > III > I
(c) III > I > II
(d) I > II > III

9. In the reaction,



the major product [X] is

(a)


(b)


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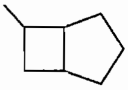
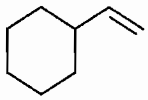
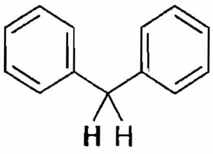
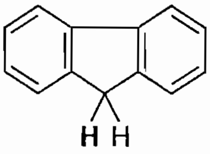


(d)


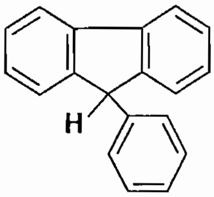
10. The decreasing order of acidity of the marked H of the following molecules is



I



II



III

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

GATE 2009

11. The decreasing order of nucleophilicity for the following anions is

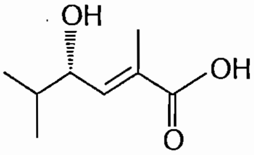
$$CH_3CO_2^-, CH_3O^-, C_6H_5O^-, NO_3^-$$

▾ *Solution Points*

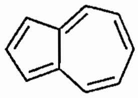
▼ ***Solution Points***

(a) $CH_3CO_2^- > CH_3O^- > C_6H_5O^- > NO_3^-$
(b) $CH_3O^- > NO_3^- > C_6H_5O^- > CH_3CO_2^-$
(c) $CH_3O^- > C_6H_5O^- > CH_3CO_2^- > NO_3^-$
(d) $C_6H_5O^- > CH_3O^- > NO_3^- > CH_3CO_2^-$

12. For the compound,

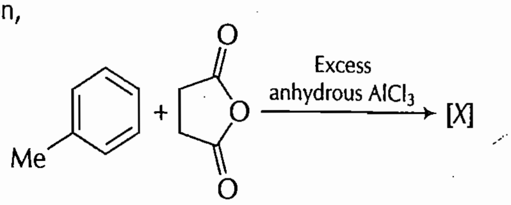


the stereochemical notations are
(a) 2*Z*, 4*R*
(b) 2*Z*, 4*S*
(c) 2*E*, 4*R*
(d) 2*E*, 4*S*

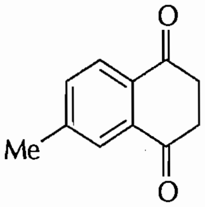
13. The compound  is

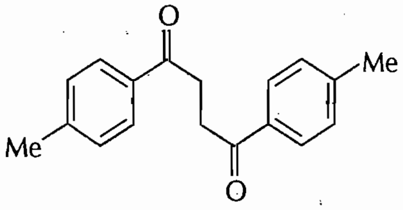
(a) aromatic and high dipole moment
(b) aromatic and has no dipole moment
(c) non-aromatic and has high dipole moment
(d) anti-aromatic and has no dipole moment

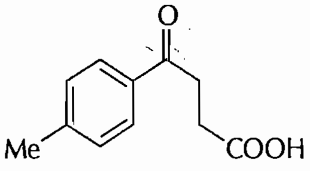
14. In the reaction,

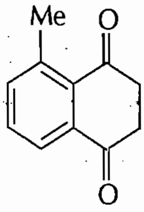


the major product *X* is

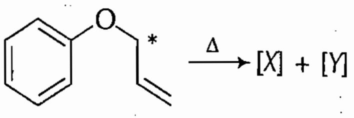
(a) 

(b) 

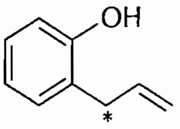
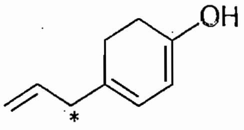
(c) 

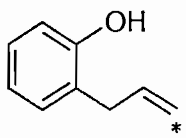
(d) 

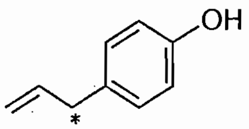
15. In the reaction,

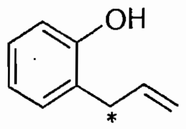


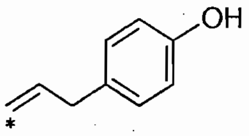
the major product *X* and *Y* are

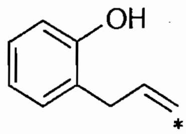
(a)  and 

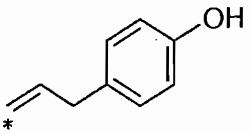
(b) 

and 

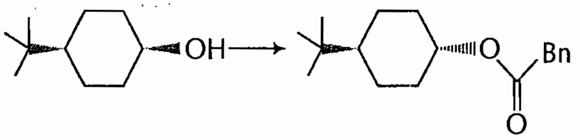
(c) 

and 

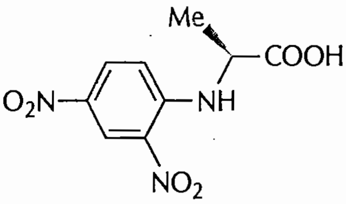
(d) 

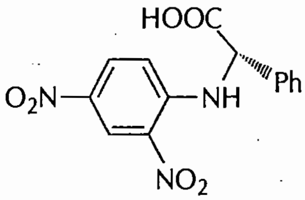
and 

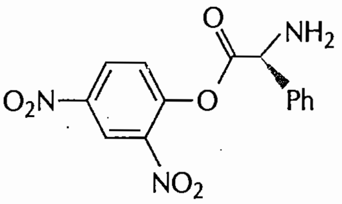
16. The most suitable reagent combination to bring out the following transformation

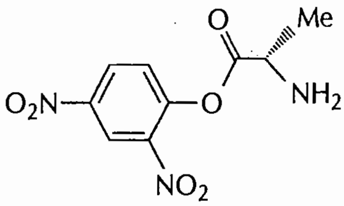


is

(a) 

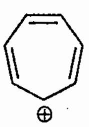
(b) 

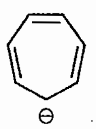
(c) 

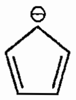
(d) 

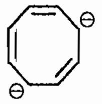
GATE 2008

17. The compound that is not aromatic is

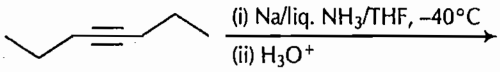
(a) 

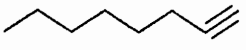
(b) 

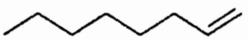
(c) 

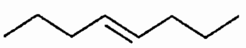
(d) 

18. The major product of the following reaction is



(a) 

(b) 

(c) 

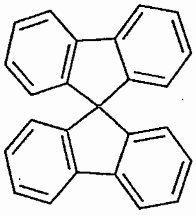
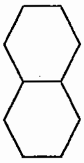
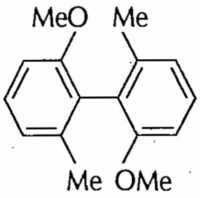
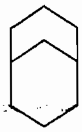
(d) 

19. In the carbylamine reaction, *R–X* is converted to *R–Y* *via* the intermediate *Z*, *R–X*, *R–Y* and *Z*, respectively are

(a) *R*-NH_2, *R*-NC, carbene
(b) *R*-NH_2, *R*-NC, nitrene
(c) *R*-NC, *R*-NH_2, carbene
(d) *R*-OH, *R*-NC, nitrene

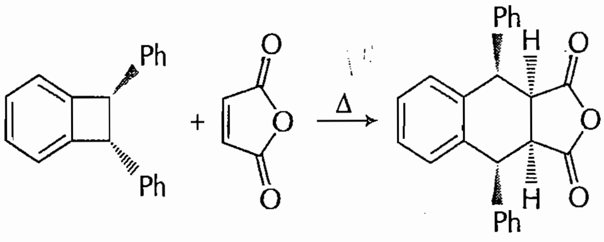
▾ ***Solution Points***

20. Match the entries a-d with their corresponding structures p-s.

a.	Bridged system	p.	
b.	Atropisomeric system	q.	
c.	Spiro system	r.	
d.	Fused system	s.	

(a) a-s; b-r; c-q; d-p (b) a-p; b-s; c-q; d-r
(c) a-q; b-p; c-s; d-r (d) a-s; b-r; c-p; d-q

21. The reaction between *X* and *Y* to give *Z* proceeds *via*



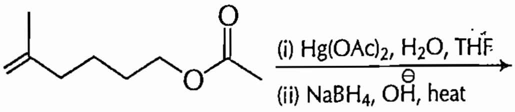
X *Y* *Z*

(a) 4π-conrotatory opening of *X* followed by endo Diels-Alder cycloaddition
(b) 4π-disrotatory opening of *X* followed by endo Diels-Alder cycloaddition
(c) 4π-conrotatory opening of *X* followed by exo Diels-Alder cycloaddition
(d) 4π-disrotatory opening of *X* followed by exo Diels-Alder cycloaddition

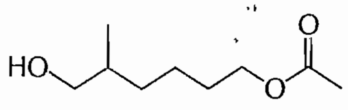
22. *o*-bromophenol is readily prepared from phenol using the following conditions

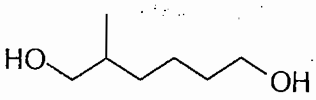
(a) (i) $(CH_3CO)_2O$; (ii) Br_2; (iii) $HCl\text{-}H_2O, \Delta$
(b) (i) H_2SO_4, 100°C (ii) Br_2 (iii) H_3O^+, 100° C
(c) N-bromosuccinimide, dibenzoyl peroxide CCl_4, Δ
(d) $Br_2/FeBr_3$

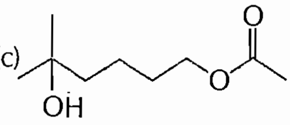
23. The major product of the following reaction is

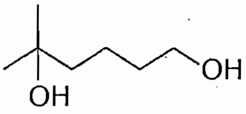


▾ *Solution Points*

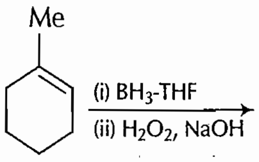
(a) 

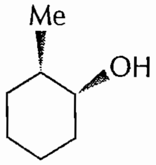
(b) 

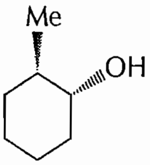
(c) 

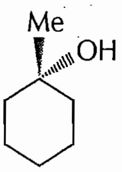
(d) 

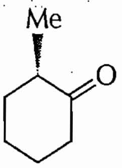
24. The major product of the following reaction is



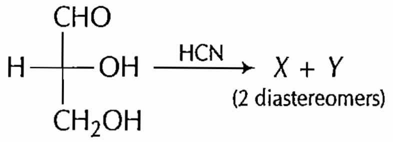
(a) 

(b) 

(c) 

(d) 

25. In the following reaction,



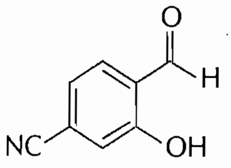
D-glyceraldehyde

the absolute configurations of the chiral centres in *X* and *Y* are

(a) 2*S*, 3*R* and 2*R*, 3*R* (b) 2*R*, 3*R* and 2*R*, 3*S*

(c) 2*S*, 3*S* and 2*R*, 3*R* (d) 2*S*, 3*R* and 2*S*, 3*R*

26. The IR stretching frequencies (cm^{-1}) for the compound *X* are as follows : 3300-3500 (s, br); 3000 (m); 2225 (s); 1680 (s).



X

The correct assignment of the absorption bands is

(a) $\bar{v}_{(OH)} = 3300 - 3500; \bar{v}_{(CH)} = 3000; \bar{v}_{(CN)} = 2225; \bar{v}_{(CO)} = 1680$

(b) $\bar{v}_{(OH)} = 3000; \bar{v}_{(CH)} = 3300 - 3500; \bar{v}_{(CN)} = 2225; \bar{v}_{(CO)} = 1680$

(c) $\bar{v}_{(OH)} = 3300 - 3500; \bar{v}_{(CH)} = 3000; \bar{v}_{(CN)} = 1680; \bar{v}_{(CO)} = 2225$

(d) $\bar{v}_{(OH)} = 3000; \bar{v}_{(CH)} = 3300 - 3500; \bar{v}_{(CN)} = 1680; \bar{v}_{(CO)} = 2225$

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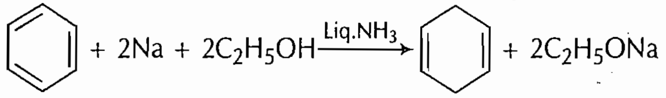
27. The reaction,



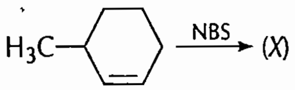
is the example of

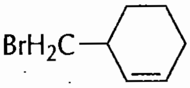
(a) Birch reduction (b) Clemmensen reduction

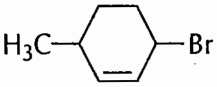
(c) Wolff-Kishner reduction (d) Hydride reduction

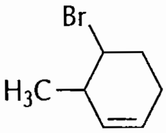
▾ ***Solution Points***

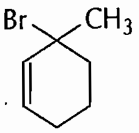
28. The major product (X) of the monobromination reaction is



(a) 

(b) 

(c) 

(d) 

29. Benzene cannot be iodinated with I_2 directly. However, in presence of oxidants such as HNO_3, iodination is possible. The electrophiles formed in the case is

(a) $[I^+]$

(b) $[I^-]$

(c) $\left[\overset{+\delta}{\text{I}}\ldots\overset{+\delta}{\text{OH}_2}\right]^+$

(d) $\left[\overset{+\delta}{\text{I}}\ldots\overset{-\delta}{\text{OH}_2}\right]^+$

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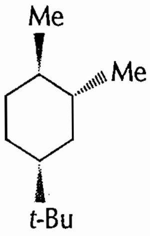
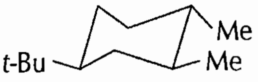
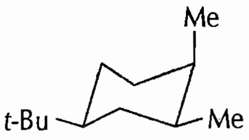
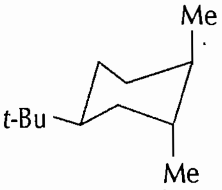
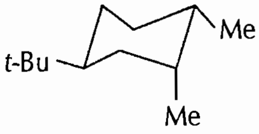
30. The most stable conformation of the following compound is



(a) 

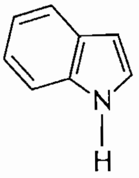
(b) 

(c) 

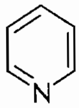
(d) 

31. The correct order of the basicity of the following compounds is

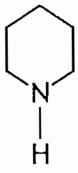
I



II



III

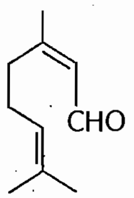


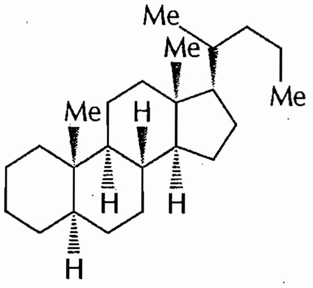
IV

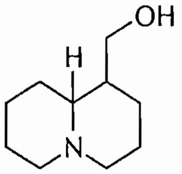
(a) IV > III > II > I
(b) III > IV > I > II
(c) IV > III > I > II
(d) III > IV > II > I

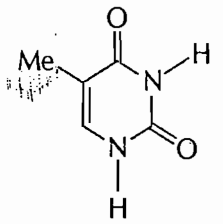
▾ *Solution Points*

32. Match the following compounds with their respective classes


I


II

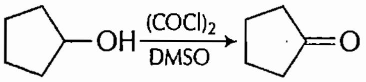

III

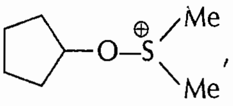

IV

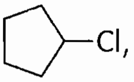
(a) I : steroid; II : terpenoid; III : alkaloid; IV : DNA base
(b) I : terpenoid; II : steroid; III : alkaloid; IV : DNA base
(c) I : terpenoid; II : steroid; III : DNA base; IV : alkaloid
(d) I : steroid; II : terpenoid; III : DNA base; IV : alkaloid

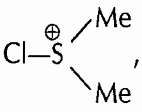
33. Which of the following compounds is expected to show a sharp singlet for one of its protons at $\delta \geq 8$ ppm in ^{1}H NMR spectrum, given that this signal remains unaffected on shaking the solution thoroughly with D_2O?
(a) CH_3CO_2H
(b) $CH_3CONHC_6H_5$
(c) $n\text{-}C_6H_{13}C{\equiv}CH$
(d) $n\text{-}C_6H_{13}CHO$

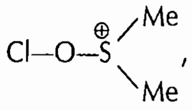
34. Which of the statements is correct about the mechanism of the following reaction?



(a) DMSO reacts with the alcohol initially to give  which reacts with $(COCl_2)$

(b) $(COCl_2)$ reacts with the alcohol initially to give  which reacts with DMSO

(c) DMSO reacts with $(COCl)_2$ initially to give  $Cl-\overset{\oplus}{S}(Me)_2$, which reacts with the alcohol

(d) $(COCl)_2$ reacts with DMSO initially to give  $Cl-O-\overset{\oplus}{S}(Me)_2$, which reacts with the alcohol

▾ ***Solution Points***

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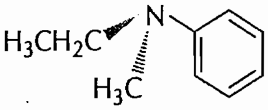
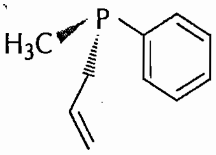
35. Among the following, the optically inactive compound is

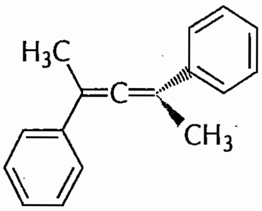
(a)



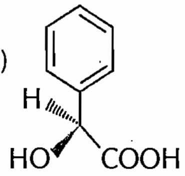
(b)



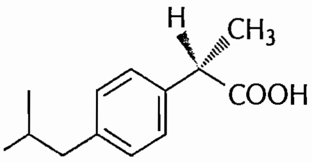
(c)



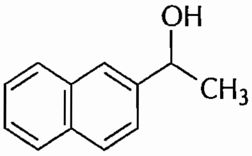
(d)



36. Esterification of the acid *P* with the alcohol *Q* will give



(*S*)-*P*

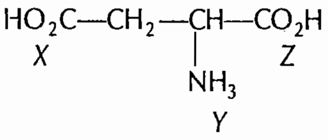


(±)-*Q*

(a) only one enantiomer
(b) a mixture of diastereomers
(c) a mixture of enantiomers
(d) only one diastereomer

37. ^{1}H NMR spectrum of [18]-annulene shows
(a) only one peak at δ 7.2 (18H)
(b) only one peak at δ 5.0 (18H)
(c) two peaks at δ 9.0 (12H) and δ – 3.0 (6H)
(d) two peaks at δ 9.0 (6 H) and δ – 3.0 (12 H)

38. The pK_a values for the three ionisable groups *X*, *Y* and *Z* of glutamic acid are 4.3, 9.7 and 2.2 respectively



$$\underset{X}{HO_2C}—CH_2—\underset{\underset{Y}{NH_3}}{\underset{|}{CH}}—\underset{Z}{CO_2H}$$

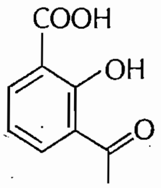
The isoelectric point for the amino acid is

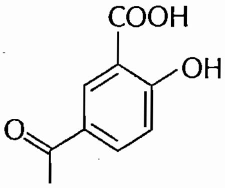
(a) 7.00	(b) 3.25
(c) 4.95	(d) 5.95

39. Bridge-head hydrogen of the conformer of *cis*-decalin is positioned as [a = axial; e = equatorial]
(a) a, a
(b) e, e
(c) a, e
(d) pseudo-a, pseudo-e

▾ ***Solution Points***

40. The major product of the acetylation of salicylic acid with Ac_2O/H^+ followed by heating with anhydrous $AlCl_3$ is

(a)


(b)


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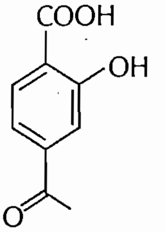

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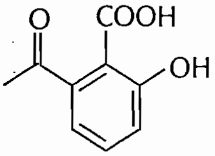
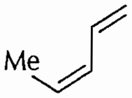
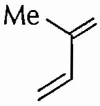


41. Order of reactivity of the following dienes *X*, *Y* and *Z* in Diels-Alder reaction is


X



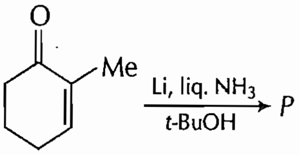
Y

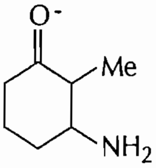


Z

(a) $X > Z > Y$
(b) $Y > X > Z$
(c) $Y > Z > X$
(d) $X > Y > Z$

42. The major product *P* of the following reaction is



(a)


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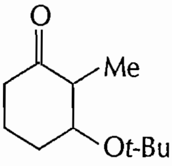
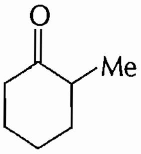
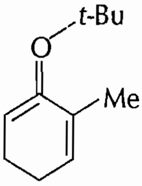
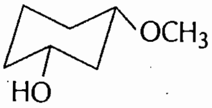


(c)


(d)


43. Among the following, the most stable isomer for 3-methoxycyclohexanol is

(a)


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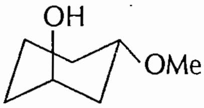
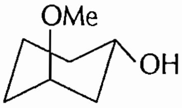


(c)


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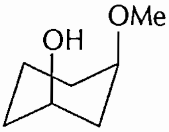
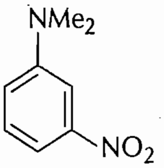


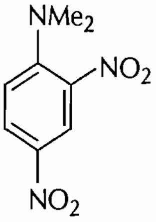
▼ ***Solution Points***

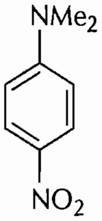
GATE 2004

44. The major product formed on nitration of N, N-dimethylaniline with conc. H_2SO_4, HNO_3 mixture is

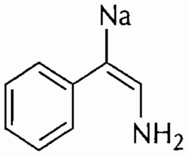
(a)


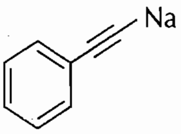
(b)


(c)


(d)


45. Reaction of phenyl acetylene with sodamide in liquid ammonia generates

(a)


(b)


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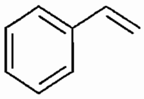
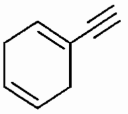
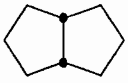
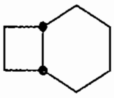
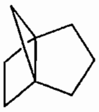


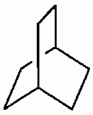
(d)


46. Proton decoupled ^{13}C NMR spectrum of a bicyclooctane (C_8H_{14}), exhibits only two signals. The structure of the compound is

(a)


(b)


(c)


(d)


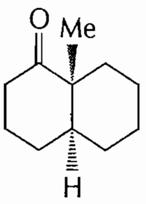
47. Cyclohexyl benzyl ether when reacted with hydrogen in the presence of 10% palladium on charcoal generates a mixture of

(a) cyclohexanol and benzyl alcohol
(b) cyclohexane and benzyl alcohol
(c) cyclohexanol and toluene
(d) cyclohexane and toluene

48. In electrophilic aromatic substitution reactions, nitro group is *meta*-directing because the nitro group

(a) increases electron density at *meta*-position
(b) increases electron density at *ortho* and *para*-positions
(c) decreases electron density at *meta*-position
(d) decreases electron density at *ortho* and *para*-positions

49. The configurations at the two asymmetric centres (C-1 and C-6) in the bicyclo [4.4.0] decane, given below are



(a) 1*R*, 6*R*
(b) 1*R*, 6*S*
(c) 1*S*, 6*S*
(d) 1*S*, 6*R*

▾ ***Solution Points***

▾ ***Solution Points***

50. The reactive intermediate involved in the conversion of phenol to salicylaldehyde using chloroform and sodium hydroxide is

(a) $Cl_2C:$ (b) Cl_2CH^+ (c) Cl_2CH^- (d) Cl_2C^+

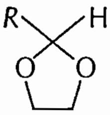
51. Conversion of Ph-NH_2 into Ph-CN can be accomplished by

(a) reaction with sodium cyanide in the presence of nickel catalyst
(b) reaction with chloroform and sodium hydroxide
(c) diazotisation followed by reaction with CuCN
(d) reaction with ethyl formate followed by thermolysis

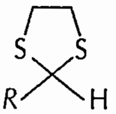
GATE 2003

52. The acylanion equivalents among the following compounds (P-S) are

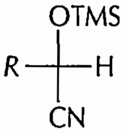
(P)



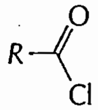
(Q)



(R)



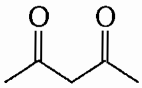
(S)



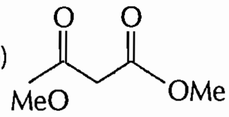
(a) P and Q (b) Q and R
(c) P and S (d) Q and S

53. Among the following compounds, the one that undergoes de-protonation most readily in the presence of base to form a carbanion is

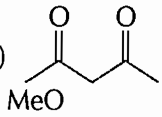
(a)



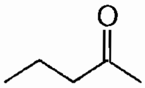
(b)



(c)

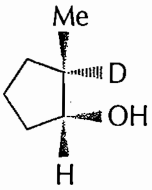


(d)

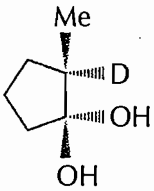


54. Hydroboration of 1-methylcyclopentene using B_2D_6, followed by the treatment with alkaline hydrogen peroxide gives

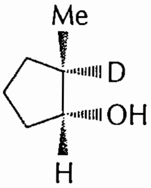
(a)



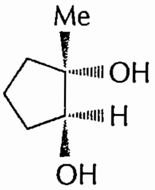
(b)



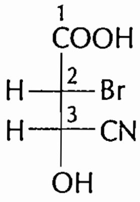
(c)



(d)



55. The absolute configurations of two chiral centres in the following molecule are



(a) 2(*R*), 3(*S*) (b) 2(*R*), 3(*R*) (c) 2(*S*), 3(*S*) (d) 2(*S*), 3(*R*)

GATE 2002

▼ ***Solution Points***

56. In allene, hybridization of the central and terminal carbons respectively, are
(a) sp^2 and sp^2 (b) sp^2 and sp^3
(c) sp and sp^2 (d) sp and sp^3

57. Among the isomers of C_4H_6 given below, the compound which exhibits an absorption band at 3300 cm^{-1} in the IR spectrum, is
(a) 1, 3-butadiene (b) 1- butyne
(c) 2-butyne (d) cyclobutene

58. Among formaldehyde, acetaldehyde and benzaldehyde, the aldehydes which undergo Cannizzaro's reaction are
(a) all the three
(b) formaldehyde and acetaldehyde
(c) acetaldehyde and benzaldehyde
(d) formaldehyde and benzaldehyde

59. Benzaldehyde can be prepared by reacting phenyl magnesium bromide with
(a) N, N-dimethylformamide (b) carbon dioxide
(c) formaldehyde (d) ethyl chloroformate

60. Proteins are biopolymers. The monomer units present in them are
(a) carbohydrates (b) amino acids
(c) fatty acids (d) alkenes

61. Reaction of phenyl acetate with anhydrous aluminium chloride generates a mixture of
(a) *ortho*, *meta* and *para* hydroxyacetophenones
(b) *meta* and *para* hydroxyacetophenones
(c) *ortho* and *meta* hydroxyacetophenones
(d) *ortho* and *para* hydroxyacetophenones

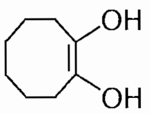
62. The major product formed in the reaction of anisole with lithium, liquid ammonia and *t*-butanol is
(a) 1-methoxycyclohexa-1, 4-diene (b) 2-methoxycyclohexa-1, 3-diene
(c) 1-methoxycyclohexa-1, 3-diene (d) 3-methoxycyclohexa-1, 4-diene

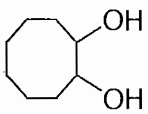
GATE 2001

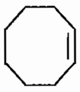
63. 2-phenyl ethanol may be prepared by the reaction of phenyl magnesium bromide with
(a) HCHO (b) CH_3CHO
(c) CH_3COCH_3 (d) 

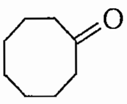
64. Which one of the following molecules will have $n \to \pi^*$ transition at the longest wavelength?
(a) HCHO (b) $CH_3COC_2H_5$
(c) $C_6H_5COC_6H_5$ (d) $CH_3COC_6H_5$

65. The reaction of cyclooctyne with $HgSO_4$ in the presence of aqueous H_2SO_4 gives

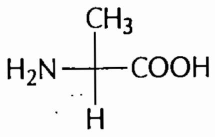
(a) 

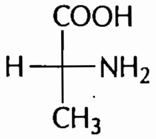
(b) 

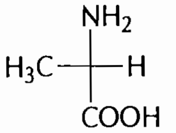
(c) 

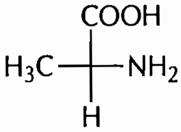
(d) 

66. Among the following amino acids, the (*R*) -enantiomer is represented by

(a) 

(b) 

(c) 

(d) 

GATE 2000

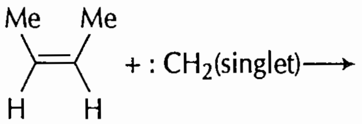
67. Toluene when refluxed with Br_2 in the presence of light mainly gives
(a) *o*-bromotoluene
(b) *p*-bromotoluene
(c) mixture of *o*- and *p*-bromotoluene
(d) benzylbromide

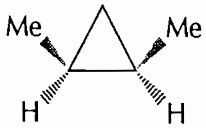
68. Optically active 2-octanol rapidly loses its optical activity when exposed to
(a) dilute acid (b) base
(c) light (d) humidity

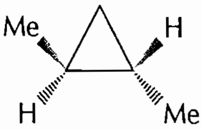
69. 1-hexyne upon treatment with disiamylborane followed by the oxidation with H_2O_2 gives
(a) hexanoic acid
(b) hexenol
(c) hexanal
(d) hexanol

70. (*E*)-3-bromo-3-hexene when treated with CH_3O^- in CH_3OH gives
(a) 3-hexyne
(b) 2-hexyne
(c) 2, 3-hexadiene
(d) 2, 4-hexadiene

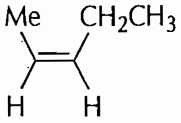
71. The major product formed in the following reaction is



(a) 

(b) 

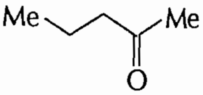
(c) 50 : 50 mixture of above two compounds

(d) 

▾ Solution Points

▼ ***Solution Points***

72. Methyl vinyl ketone upon reaction with $LiCuMe_2$ gives a major product whose structure is

(a)


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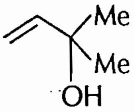
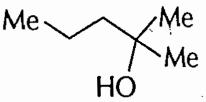
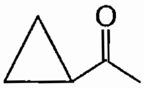
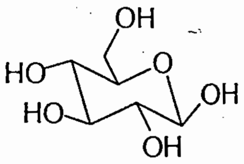


(c)


(d)


73. β-D-glucose is represented as

(a)


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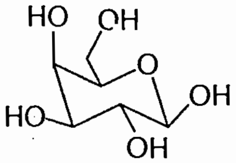
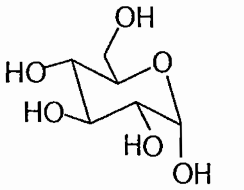
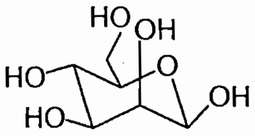


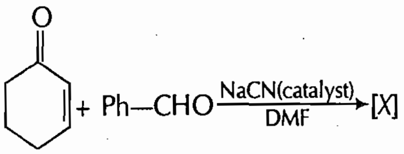
(c)


(d)


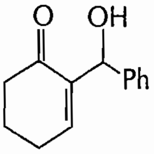
GATE 2011

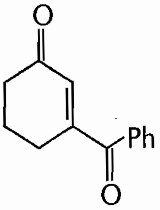
(2 Marks Questions)

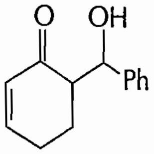
74. In the following reaction,

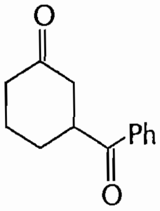


the major product [X] is

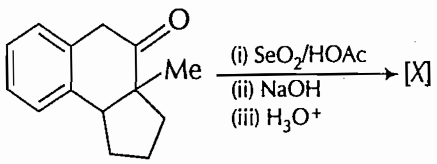
(a)


(b)


(c)


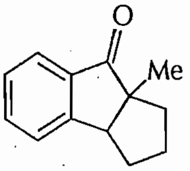
(d)


75. In the following reaction,

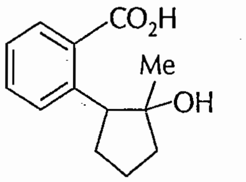


the major product [X] is

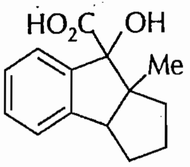
(a)



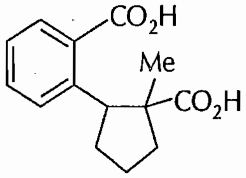
(b)



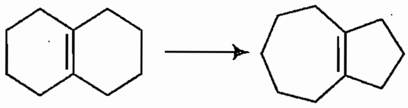
(c)



(d)



76. The most appropriate sequence of the reactions for carrying out the following conversion



is

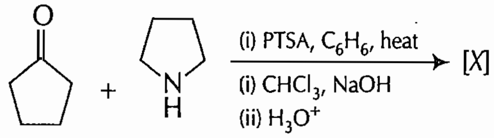
(a) (i) peracid (ii) H^+ (iii) Zn/dil. HCl

(b) (i) Alkaline $KMnO_4$ (ii) $NaIO_4$ (iii) N_2H_4/KOH

(c) (i) Alkaline $KMnO_4$ (ii) H^+ (iii) Zn/dil.HCl

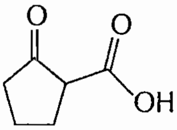
(d) (i) O_3 / Me_2S (ii) NaOEt (iii) N_2H_4/KOH

77. In the following reaction sequence,

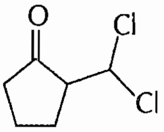


the major product [X] is

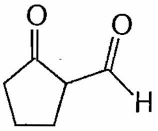
(a)



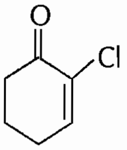
(b)



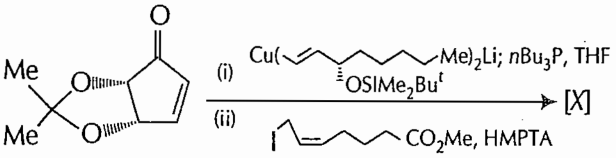
(c)



(d)

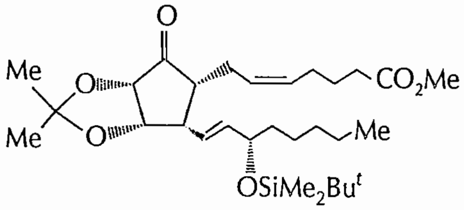


78. In the following conversion,

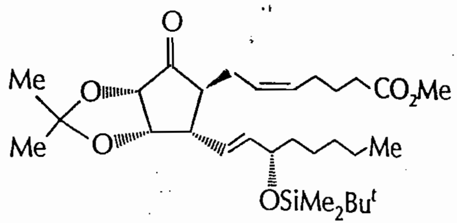


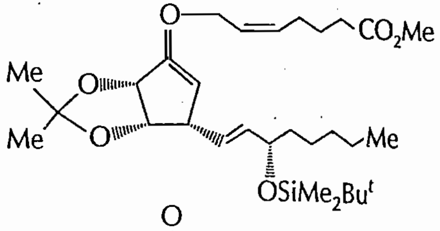
the major product [X] is

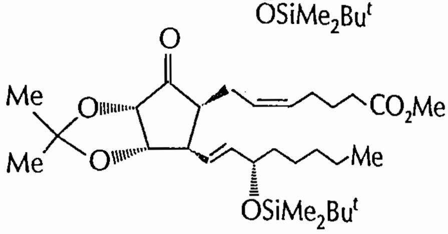
(a)



▾ Solution Points

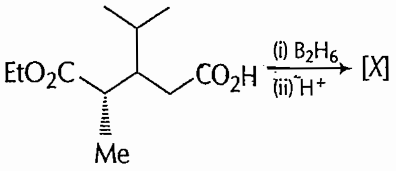
(b)


(c)


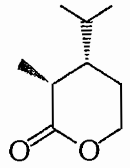
(d)


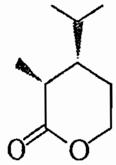
GATE 2010

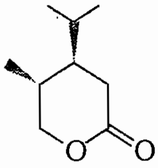
79. In the reaction,

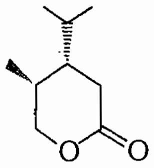


the major product [X] is

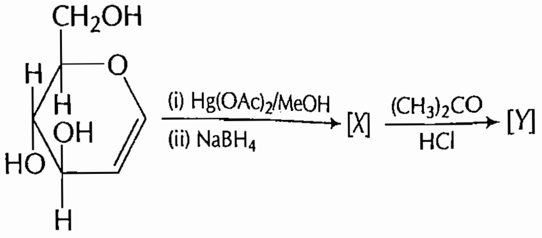
(a)


(b)


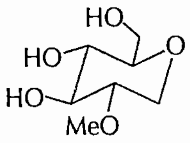
(c)


(d)


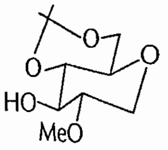
80. In the reaction sequence,



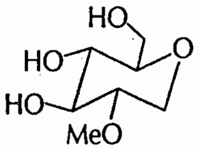
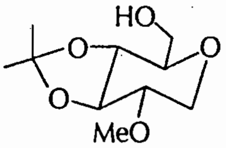
the major products [X] and [Y] respectively are

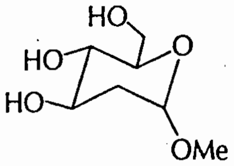
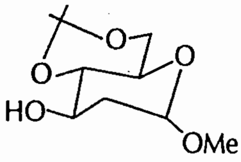
(a)


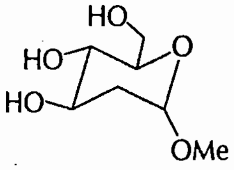
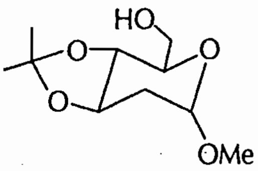
and



▾ ***Solution Points***

(b)  and 

(c)  and 

(d)  and 

GATE 2009

81. In the reaction,

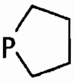
$$Ph_3P \xrightarrow{MeI} [X] \xrightarrow{n\text{-}BuLi} [Y]$$

the compounds *X* and *Y*, respectively, are

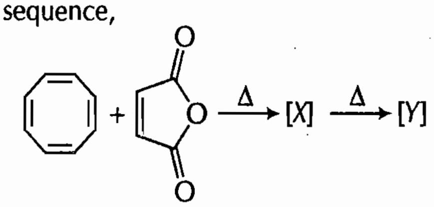
(a) $[Ph_3P(Me)\ I]$; $PH_3P{=}CH{-}CH_2{-}CH_2{-}CH_3$

(b) $[Ph_3P(Me)]\ [I]$; $Ph_3P{=}CH_2$

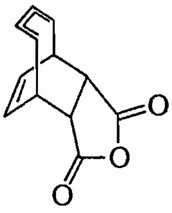
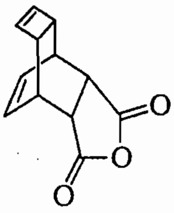
(c) $[Ph_3P(Me)_2]$; $Ph_3P{=}CH_2$

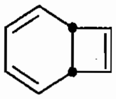
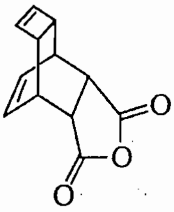
(d) $[Ph_3P(Me)]\ [I]$; Ph_3P 

82. In the reaction sequence,

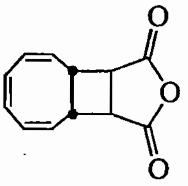


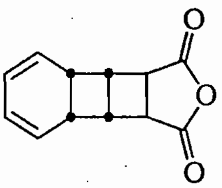
X and *Y* respectively are

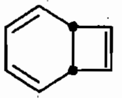
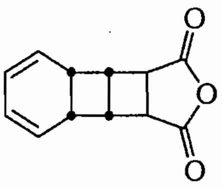
(a)  and 

(b)  and 

▼ ***Solution Points***

(c) 

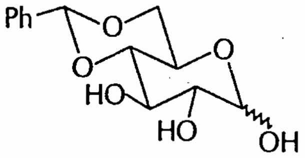
and 

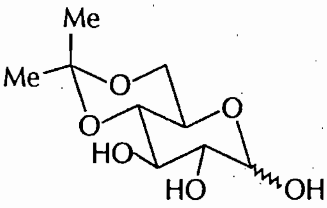
(d) 
and 

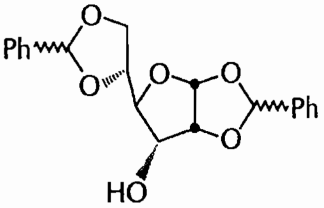
83. In the reactions,

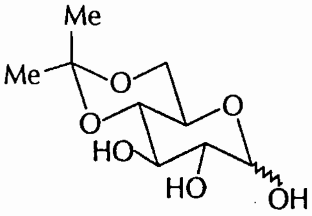
$$[X] \xleftarrow[H^+]{PhCHO} \text{D-glucose} \xrightarrow[H^+]{Acetone} [Y]$$

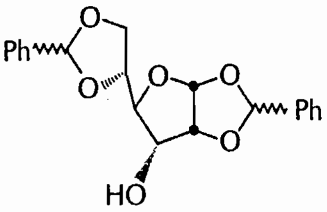
the major product *X* and *Y* respectively, are

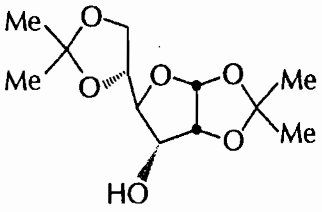
(a) 

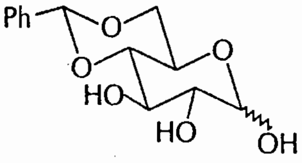
and 

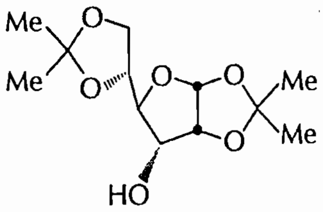
(b) 

and 

(c) 

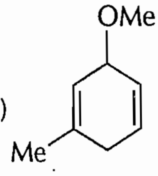
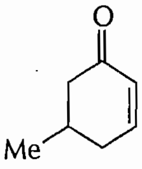
and 

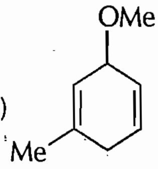
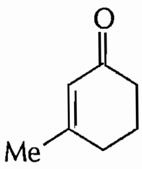
(d) 

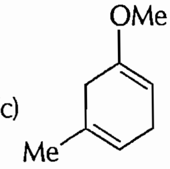
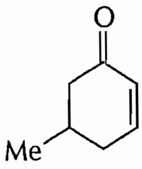
and 

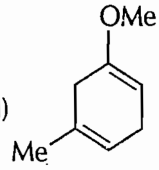
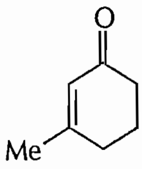
84. Reaction of *m*-methylanisole with lithium in liquid ammonia and *t*-butyl alcohol at 33°C generates compound *X* as the major product. Treatment of the compound *X* with dilute sulphuric acid produces compound *Y* as the major product. The compounds *X* and *Y* respectively are

▾ ***Solution Points***

(a)  and 

(b)  and 

(c)  and 

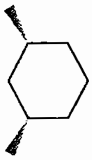
(d)  and 

85. The number of signals that appear in the broad-band decoupled ^{13}C NMR spectrum of *ortho*, *meta* and *para*-dichlorobenzene, respectively are

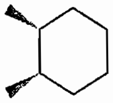
(a) 3, 4 and 2
(b) 3, 3 and 2
(c) 4, 4 and 2
(d) 3, 4 and 4

GATE 2007

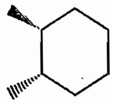
86. The molecules(s) that exist as *meso* structure (s)



(*K*)



(*L*)

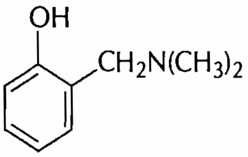


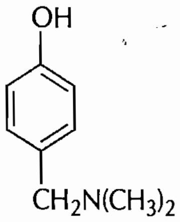
(*M*)

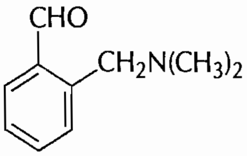
is/are

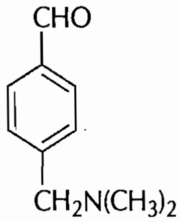
(a) only *M*
(b) both *K* and *L*
(c) only *L*
(d) only *K*

87. Phenol on reaction with formaldehyde and dimethyl amine mainly gives

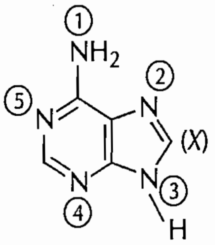
(a) 

(b) 

(c) 

(d) 

88. The mono protonation of adenine (*X*) in acidic solution mainly occurs at

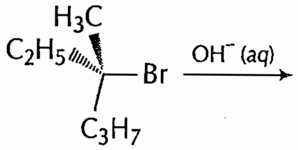


(a) position 1
(b) position 2
(c) position 3
(d) position 4 or 5

▾ *Solution Points*

▾ ***Solution Points***

89. In the reaction,

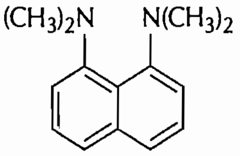


if the concentration of both the reagents is doubled then the rate of the reaction will

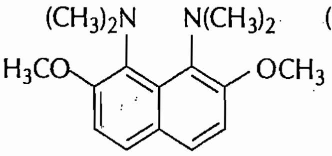
(a) remain unchanged (b) quadruple

(c) reduce to one fourth (d) double

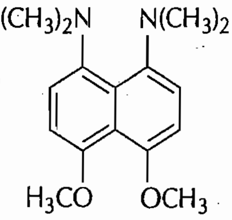
90. The increasing order of basicity among the following is



(X)



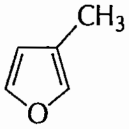
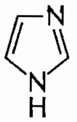
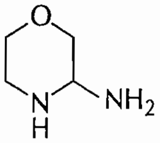
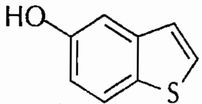
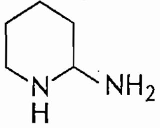
(Y)



(Z)

(a) $Y < X < Z$ (b) $Y < Z < X$ (c) $X < Z < Y$ (d) $X < Y < Z$

91. Match the structures in List I with their correct names in List II.

	List I		List II
(a)		(i)	3-methyl furan
(b)		(ii)	Imidazole
(c)		(iii)	5-hydroxybenzothiazole
(d)		(iv)	2-amino piperidine
(e)		(v)	2-amino morpholine

(a) a-i, b-ii, c-v, d-iii, e-iv (b) a-i, b-iii, c-v, d-ii, e-iv

(c) a-ii, b-i, c-v, d-iii, e-iv (d) a-i, b-ii, c-iv, d-iii, e-v

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92. The amino acid side chain high affinity for Ca^{2+} and Cu^{2+} in metallo-proteins is

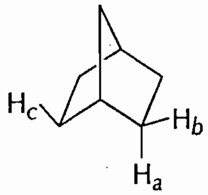
(a) carboxylate in both the cases

(b) imidazole in both the cases

(c) carboxylate for Ca^{2+} and imidazole for Cu^{2+}

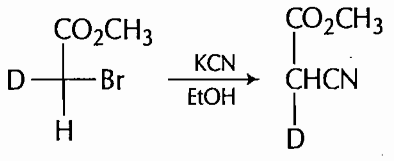
(d) imidazole for Ca^{2+} and carboxylate for Cu^{2+}

93. Identify the correct stereochemical relationship amongst the hydrogen atoms H_a, H_b and H_c in the following molecule



(a) H_a and H_b : enantiotopic
(b) H_a and H_b : diastereotopic
(c) H_a and H_c : enantiotopic
(d) H_a and H_c : diastereotopic

94. The configurations of the reactant and the product in the following reaction, are

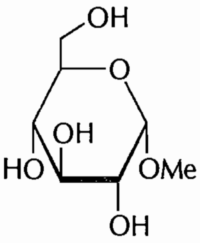


(a) *R*, *R*
(b) *R*, *S*
(c) *S*, *R*
(d) *S*, *S*

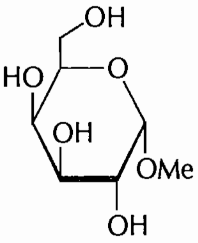
95. On heating with dilute sulphuric acid, naphthalene-1 sulphonic acid gives predominantly

(a) naphthalene
(b) naphthalene-2-sulphonic acid
(c) 1-naphthol
(d) 2-naphthol

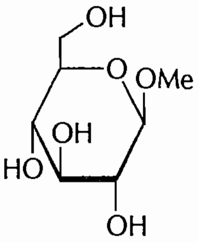
96. Identify the correct set of stereochemical relationships amongst the following monosaccharides I-IV



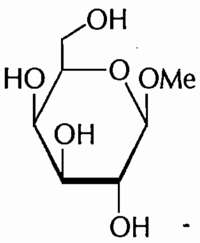
I



II



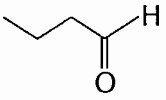
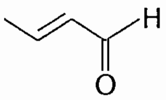
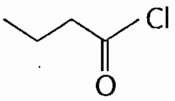
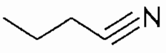
III



IV

(a) I and II are anomers; III and IV are epimers
(b) I and III are epimers; II and IV are anomers
(c) I and II are epimers; III and IV are anomers
(d) I and III are anomers; I and II are epimers

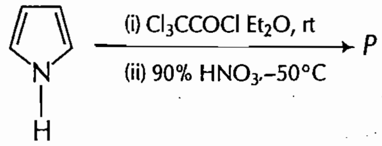
97. Match the compounds in List I with the stretching frequencies (cm^{-1}) of the principal functional groups given in List II.

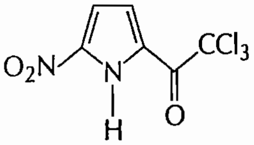
	List I		List II
(a)		(i)	2240
(b)		(ii)	1795
(c)		(iii)	1750
(d)		(iv)	1725
		(v)	1695

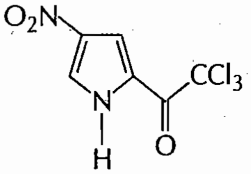
▾ *Solution Points*

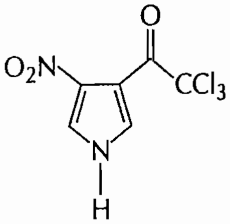
(a) a-iii, b-iv, c-i, d-v
(b) a-iii, b-iv, c-ii, d-v
(c) a-iv, b-v, c-ii, d-i
(d) a-iv, b-iii, c-v, d-i

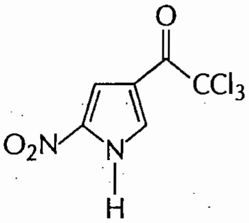
98. Identify the major product *P* in the following two-step reaction :



(a)


(b)


(c)


(d)


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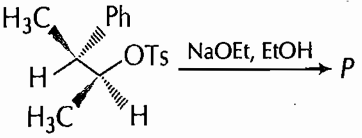
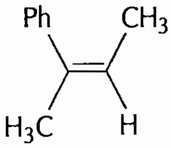
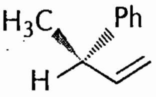
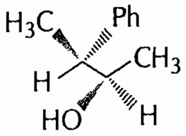
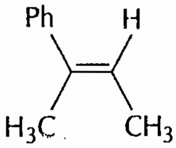
99. The major product *P* formed in the given



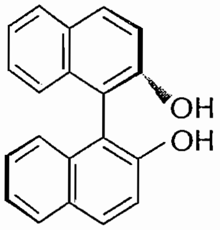
(a)


(b)


(c)


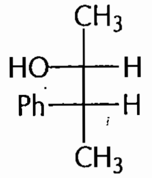
(d)


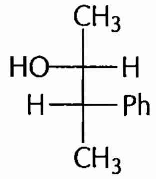
100. The binaphthol (Bnp) is

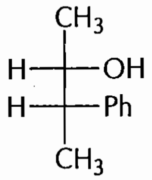


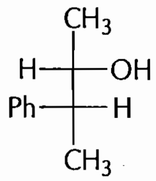
(a) an optically active compound with (*R*)-configuration
(b) an optically inactive compound
(c) a *meso* compound
(d) an optically active compound with (*S*)-configuration

101. The major stereoisomer obtained in the reaction of (S)-2 phenylpropanal with MeMgBr is

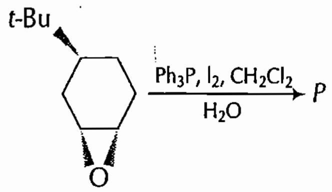
(a) 

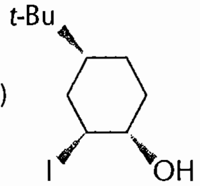
(b) 

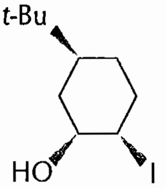
(c) 

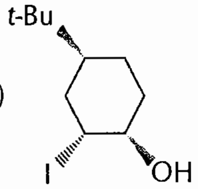
(d) 

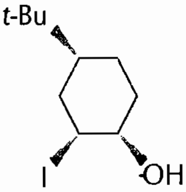
102. The major stereoisomer *P* obtained in the following reaction is



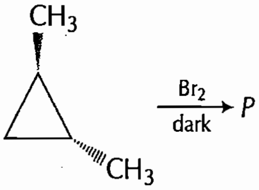
(a) 

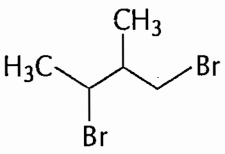
(b) 

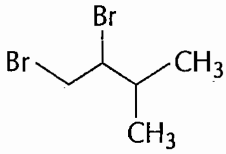
(c) 

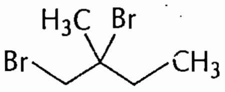
(d) 

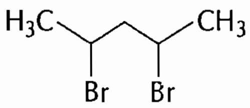
103. The major product *P* of the following reaction is



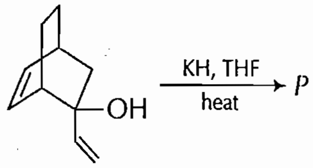
(a) 

(b) 

(c) 

(d) 

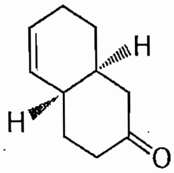
104. The major product *P* of the given reaction is



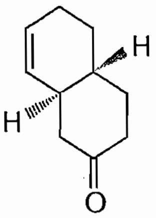
▾ ***Solution Points***

▼ ***Solution Points***

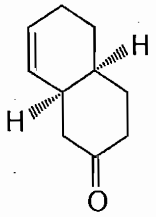
(a)



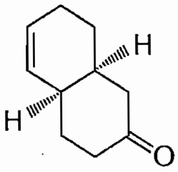
(b)



(c)



(d)



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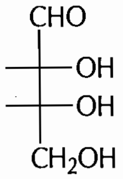
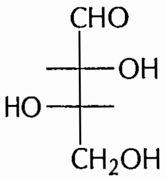
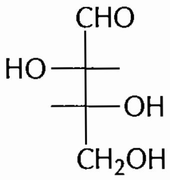
105. For the aldotetroses I-IV, the combination of true statements, among P - T, is



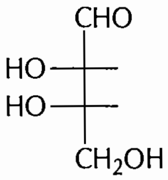
(I)



(II)



(III)



(IV)

P = I and II are diastereomers and II and III are enantiomers

Q = I and IV are mesomers and are optically inactive

R = I and III can be interconverted by a base catalysed isomerisation

S = only I and IV are HIO_4 cleavable

T = I and III are D-sugars and II and IV are L-sugars

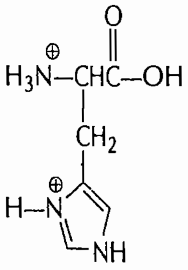
(a) Q, R, T (b) P, R, T (c) Q, R S, T (d) P, Q, S

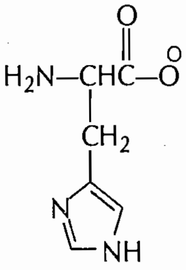
106. Match the compounds P-S with their carbonyl stretching frequencies (cm^{-1}) I-VI in IR spectroscopy.

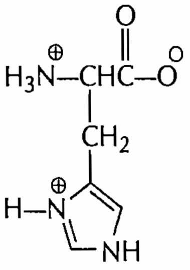
P	Acetone	I	1870
Q	Ethyl acetate	II	1800
R	Acetamide	III	1740
S	Acetyl chloride	IV	1700
		V	1660
		VI	1600

	P	Q	R	S
(a)	IV	III	I	VI
(b)	III	VI	V	II
(c)	IV	III	V	II
(d)	II	V	III	VI

107. Three molecular ionic states, *P-R* are possible for the amino acid histidine. Identify the correct choice of pH values, respectively for the observation of the ionic states *P-R*.

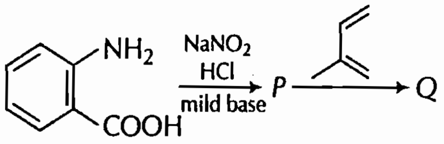


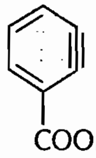


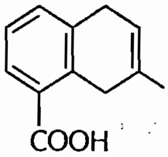


(a) *P* at pH 1; Q at pH 12; *R* at pH 7
(b) *P* at pH 7; Q at pH 1; *R* at pH 12
(c) *P* at pH 12; Q at pH 7; *R* at pH 1
(d) *P* at pH 12; Q at pH 1; *R* at pH 7

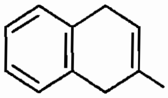
108. In the reaction shown below, identify the correct combination of the intermediate *P* and the product Q.



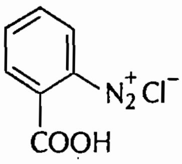
(a) 

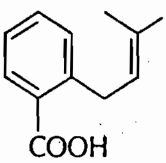
and


P Q

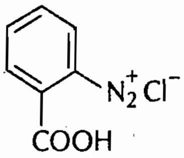
(b) 
and


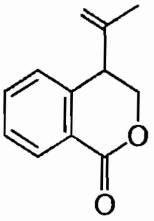
P Q

(c) 

and


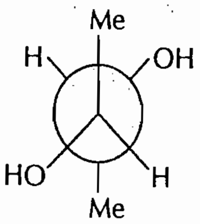
P Q

(d) 

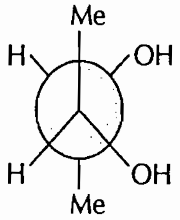
and


GATE 2003

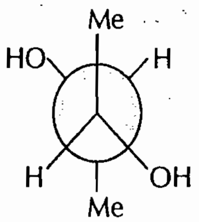
109. Among the following, the Newman projections of *meso*-2, 3-butanediol are



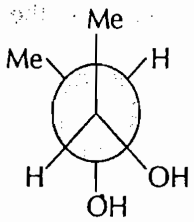
(P)



(Q)



(R)



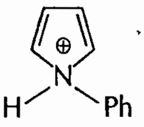
(S)

(a) P, Q (b) P, R (c) R, S (d) Q, S

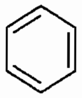
110. Pyrrole + PhMgBr ⟶ *E* + *F*
E + MeCl ⟶ G + *H*
F + MeCl ⟶ no reaction without a catalyst

▾ ***Solution Points***

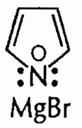
▾ Solution Points



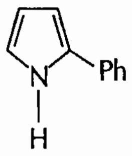
(1)



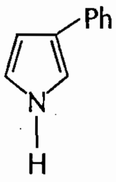
(2)



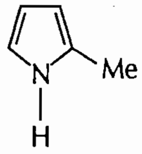
(3)



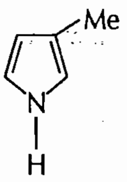
(4)



(5)



(6)



(7)

The structure of products *E* – *H* respectively are

(a) 3, 2, 6, 7 (b) 4, 5, 6, 1

(c) 3, 4, 5, 2 (d) 3, 2, 4, 5

111. Among the carboxylic acid shown below, the ones that exhibit stereoisomerism and also form, cyclic anhydrides on heating are

(I) $HOOCCH(CH_3)CH_2CH_2COOH$
(II) $HOOCCH(C_3H_7)COOH$
(III) $HOOCCH(C_2H_5)CH_2COOH$
(IV) $HOOCC(CH_3)(C_2H_5)COOH$

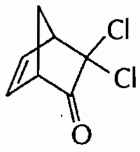
(a) (I) and (II) (b) (I) and (III)

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

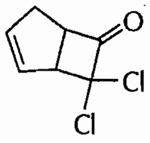
GATE 2002

112. The major product formed in the reaction of cyclo pentadiene with a mixture of dichloro acetyl chloride and triethylamine is

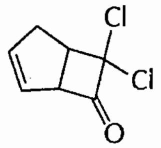
(a)



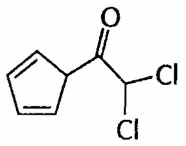
(b)



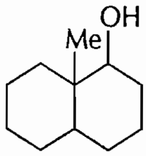
(c)



(d)



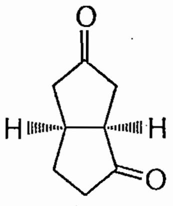
113. The configurations at the three chiral centres in the bicyclodecanol given below, are

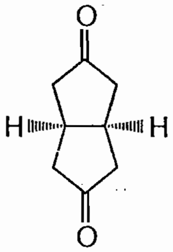


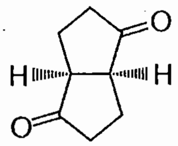
(a) 1*S*, 2*S*, 6*R* (b) 1*S*, 2*S*, 6*S*

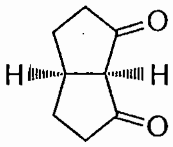
(c) 1*R*, 2*R*, 6*R* (d) 1*R*, 2*S*, 6*R*

114. Among the bicyclo [3.3.0] octane diones given below, which one will exhibit five signals in the broad band decoupled ^{13}C NMR spectrum?

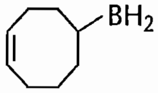
(a) 

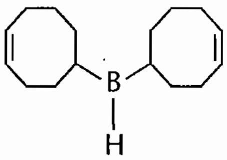
(b) 

(c) 

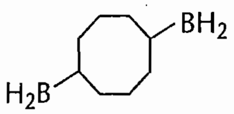
(d) 

115. The major product formed in the reaction of 1, 5-cyclooctadiene with 0.5 equivalent of diborane is

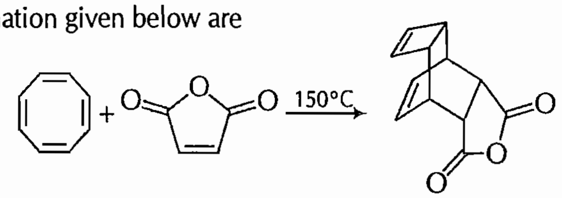
(a) 

(b) 

(c) 

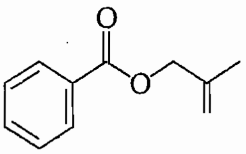
(d) 

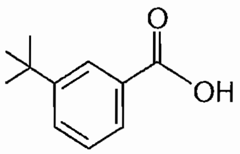
116. The two pericyclic reactions successively involved in the thermal transformation given below are

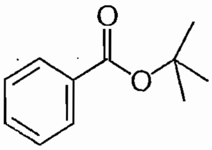


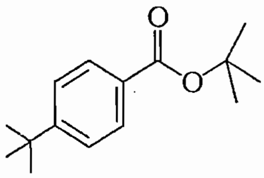
(a) 6π-electrocyclization followed by [4 + 2] π-cycloaddition
(b) 8π-cycloaddition followed by [2 + 2] π-electrocyclization
(c) 6π-cycloaddition followed by [2 + 2] π-electrocyclization
(d) 4π-electrocyclization followed by [4 + 2] π-cycloaddition

117. The major product formed in the reaction of benzoic acid with isobutylene in the presence of catalytic amount of sulphuric acid is

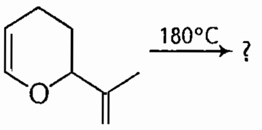
(a) 

(b) 

(c) 

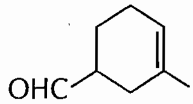
(d) 

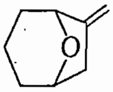
118. The major product formed in the thermal reaction given below, is

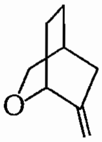


▼ *Solution Points*

(a) 4(H)-pyran

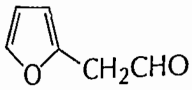
(b)


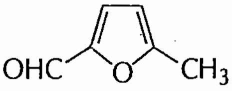
(c)


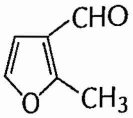
(d)


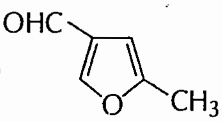
GATE 2001

119. The reaction of 2-methylfuran with DMF-$POCl_3$ would give

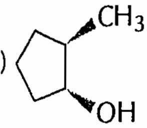
(a)


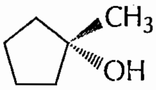
(b)


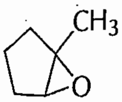
(c)


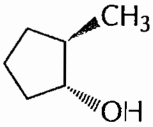
(d)


120. The major product formed during the hydroboration-oxidation of 1-methyl cyclopentene is

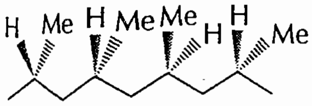
(a)


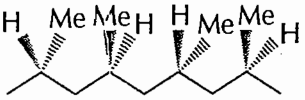
(b)


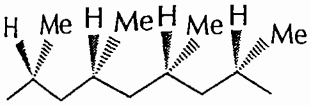
(c)


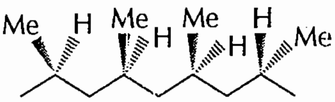
(d)


121. Identify the isotactic polypropylene from the following

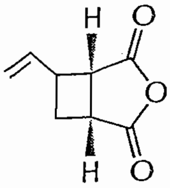
(a)


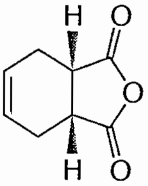
(b)


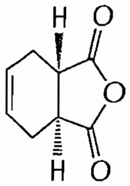
(c)


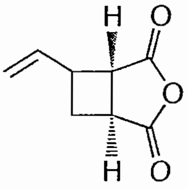
(d)


122. Buta-1, 3-diene on heating with maleic anhydride would give

(a)


(b)


(c)


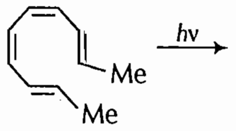
(d)


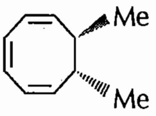
▼ ***Solution Points***

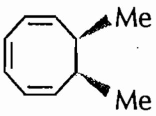
GATE 2000

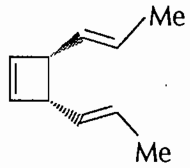
123. Oxymercuration-demercuration reaction of 1-methylcyclohexene gives
- (a) *cis*-2-methylcyclohexanol
- (b) *trans*-2-methylcyclohexanol
- (c) 1-methylcyclohexanol
- (d) mixture of *cis* and *trans*-2-methylcyclohexanol

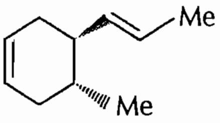
124. The following tetraene upon photolysis gives



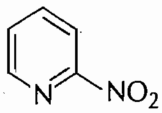
(a)


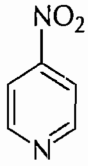
(b)


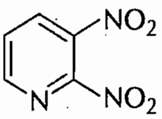
(c)


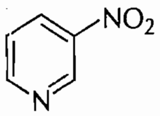
(d)


125. Pyridine undergoes electrophilic nitration at elevated temperatures to give the following as a major product

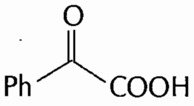
(a)


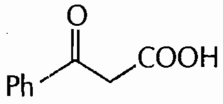
(b)


(c)


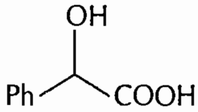
(d)


126. Among the following the acid which undergoes fastest decarboxylation is

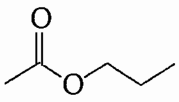
(a)


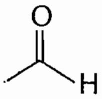
(b)


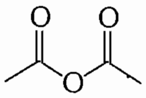
(c) PhCOOH

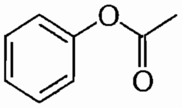
(d)


127. The compound which on reacting with aniline will not form an acetanilide is

(a)


(b)


(c)


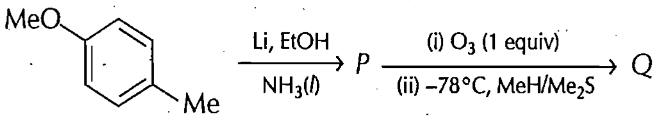
(d)


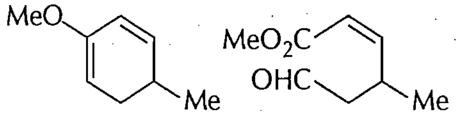
128. Aniline can be distinguished from methyl amine by its reaction with
- (a) p-toluene sulphonyl chloride/KOH
- (b) (i) $NaNO_2/HCl$, 0-5°C (ii) alkaline β naphthol
- (c) Sn/HCl
- (d) Acetyl chloride

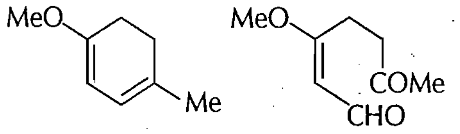
▾ *Solution Points*

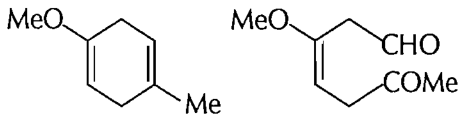
Linked Answer Questions 129 and 130

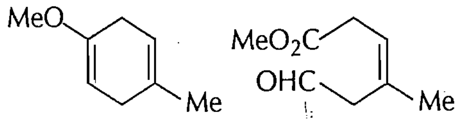
129. The products *P* and *Q* in the following sequence of reactions respectively, are



(a)


(b)


(c)


(d)


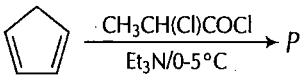
130. The reagent for selective reduction of the aldehyde group in Q obtained in the above reaction is

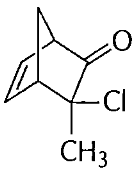
(a) $H_2, (Ph_3P)_3RhCl$ (b) $(H_3C)_2CHCH_2)_2AlH$

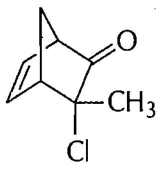
(c) $Na(CH_3COO)_3BH$ (d) $LiAlH_4$

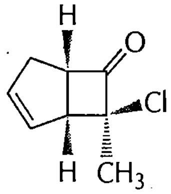
Linked Answer Questions 131 and 132

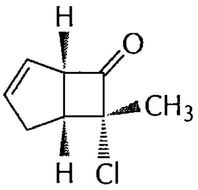
131. Identify the major product *P* in the following reaction



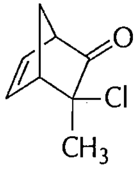
(a)


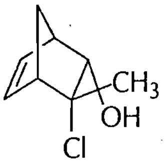
(b)


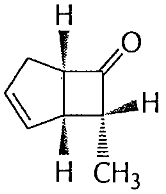
(c)


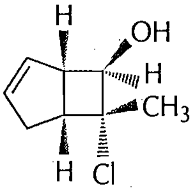
(d)


132. Product P of the above reaction transforms to a product Q on treatment with n-Bu_3SnH in the presence of AlBN in benzene solution. Identify Q.

(a)


(b)


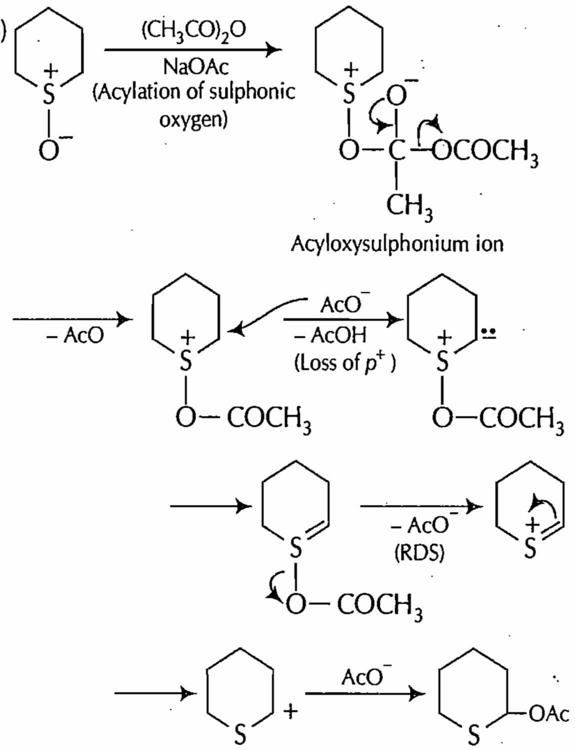
(c)


(d)


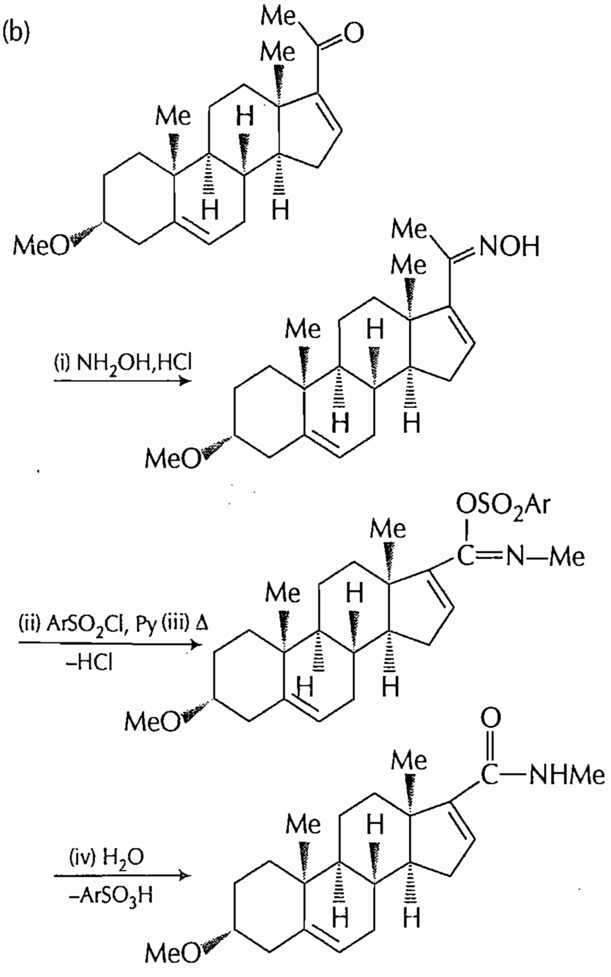
▾ ***Solution Points***

Answers with Explanations

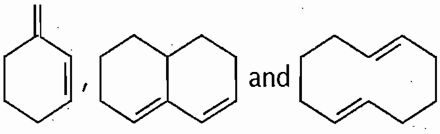
1. (b)



2. (b)



3. (a) Diels-Alder reaction is given by conjugated (s)-*cis* and s-*trans* conformations.

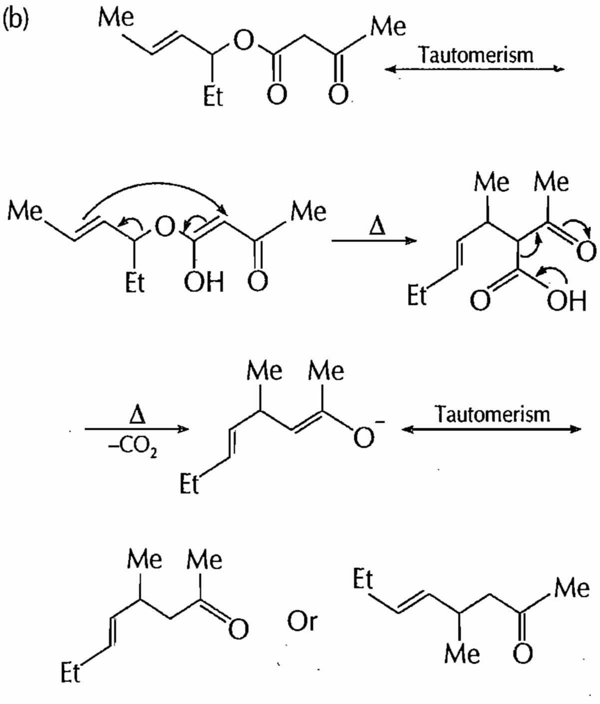
Thus,  do not participate as diene in Diels-Alder reaction.

4. (b) The two strands of DNA are complementary to each other and the bases of one strand are paired with the bases of other strand by means of hydrogen bonding, *i.e.*, A = T and G≡C. But uracil (U) instead of thymine (T) is present in case of RNA. Thus, the sequence of bases on *m*-RNA molecule is

DNA strand 5′-AGCTACACT-3′

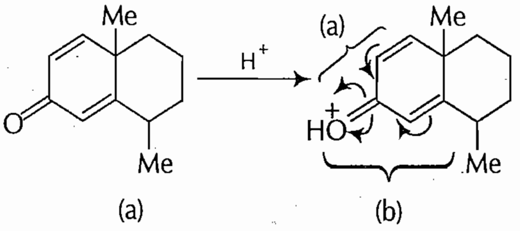
m-RNA 5′-UCG AUG UGA-3′

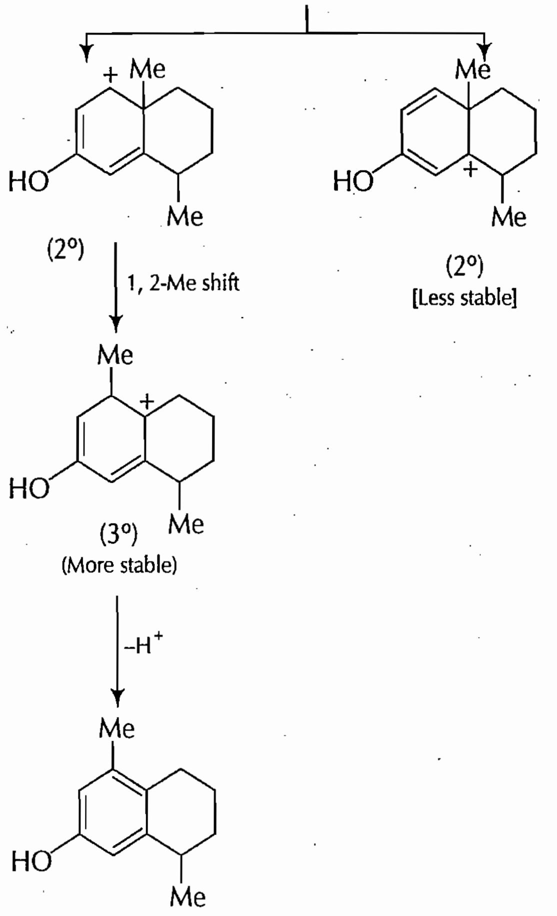
5. (b)



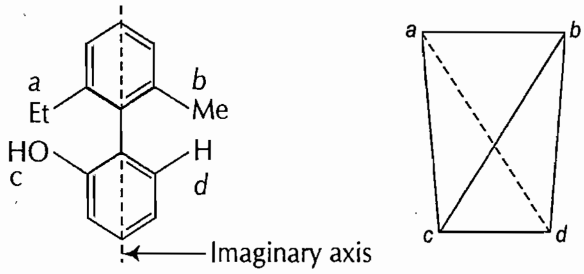
It is an example of carroll rearrangement. It involves the transformation of β-keto allyl ester into α-allyl-β-keto carboxylic acid followed by decarboxylation. Thus, the final product is *s*-allyl ketone.

6. (a)



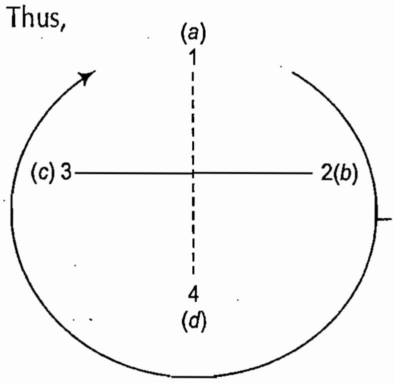


7. (a) In the compound *X* a virtual axis is drawn and arrangement of groups is observed, now the group having more atomic number is given priority. Since, priority groups are arranged in clockwise direction, so the conformation is *R*.



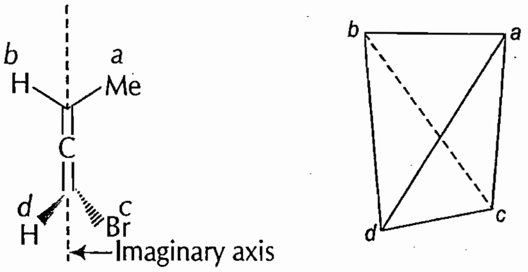
Priority order : a > *b* and c > *d*

Thus,



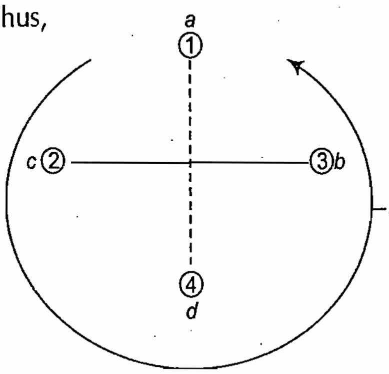
Clockwise so *R* configuration rotation.

In compound *Y* the priority groups are arranged in anti-clockwise direction so the configuration is *S*.



Priority order : *a* > *b* and c > *d*

Thus,

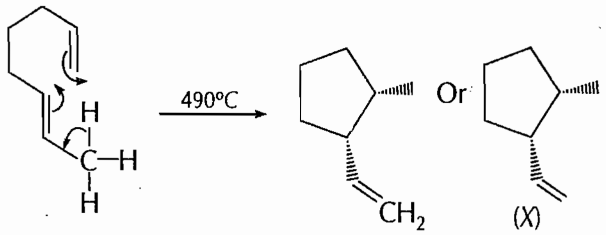


Anti-clockwise so *S* configuration rotation.

8. (d) In pyridine because of the withdrawal of electrons from ring carbon atom by nitrogen, the ring is deactivated towards electrophilic attack. Although both pyrrole and thiophene show reactivity towards electrophiles but pyrrole is more reactive in comparison to thiophene. Thus, correct order is

I > II > III

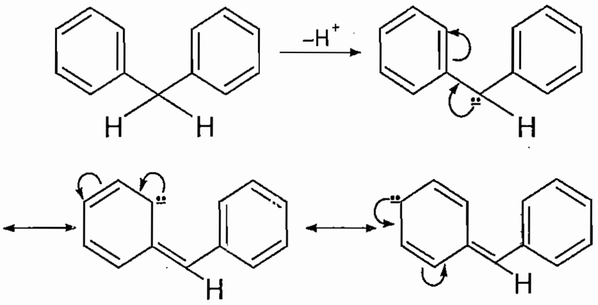
9. (a)

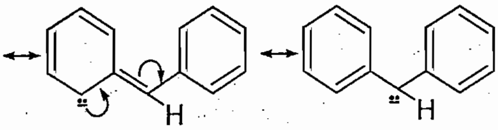


Octa-1,6-diene　　*Cis*-methyl-2-vinyl cyclopentane

It is an example of intramolecular ene reaction.

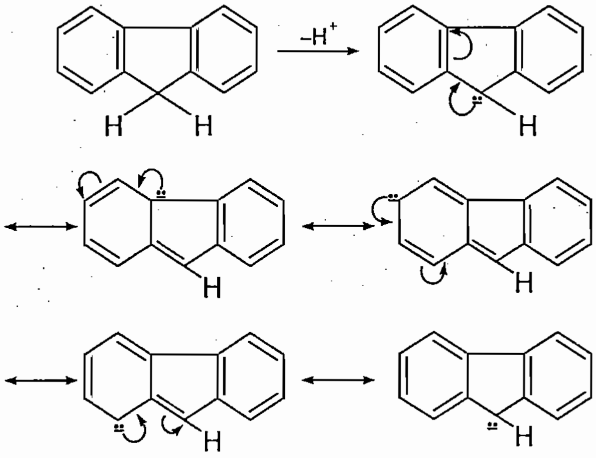
10. (c) Acidity is the measure of proton donating tendency and depends upon the stability of carbanion formed after the removal of a proton.



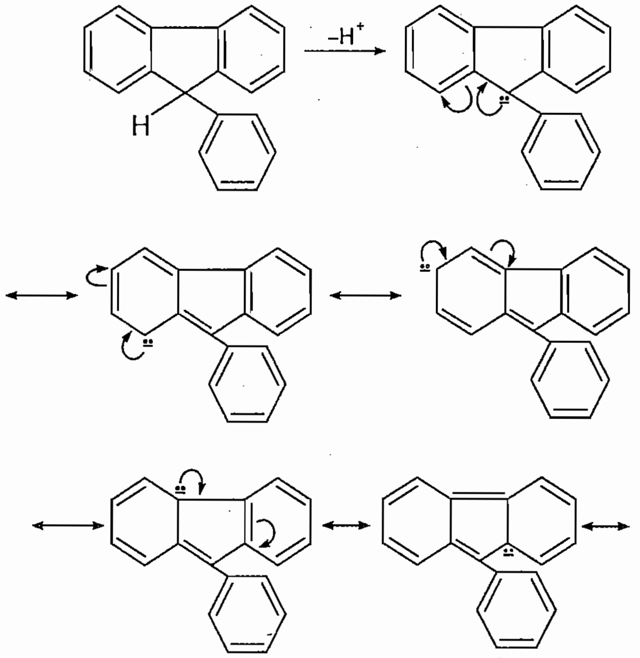


and so on

Similarly,



and so on



so on.

More the number of resonating structures, higher is the stability of carbanion and thus, higher is the acidity of compound.

Thus, the order of acidity is

$$III > II > I$$

11. (c) Since the electron donating atom is same, the nucleophilicity parallels basicity.

A conjugate base of a strong acid is weak and *vice-versa*.

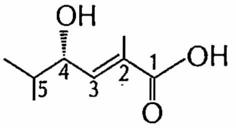
The order of acidity is

$CH_3OH < C_6H_5OH < CH_3COOH < HNO_3$

Thus, the order of basicity and thus, the nucleophilicity is

$CH_3O^- > C_6H_5O^- > CH_3CO_2^- > NO_3^-$

12. (d)

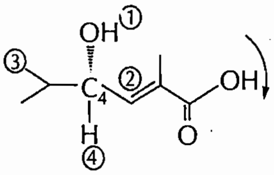


$—COOH > —CH_3$

$—C(OH)CH(CH_3)_2 > —H$

In this compound, the heavier groups attached to the double bonded carbon atoms are at the opposite side, so the configuration of second carbon is *E*.

The fourth carbon can be represented as



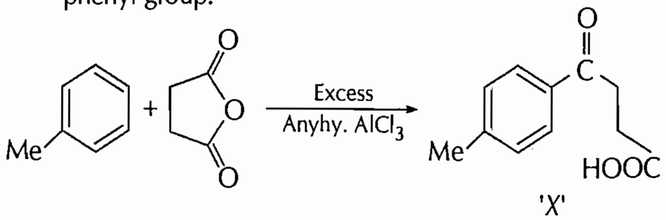
Priority for *R* – *S* configuration,

$$OH > = \text{bond} > R \text{ group} > H$$

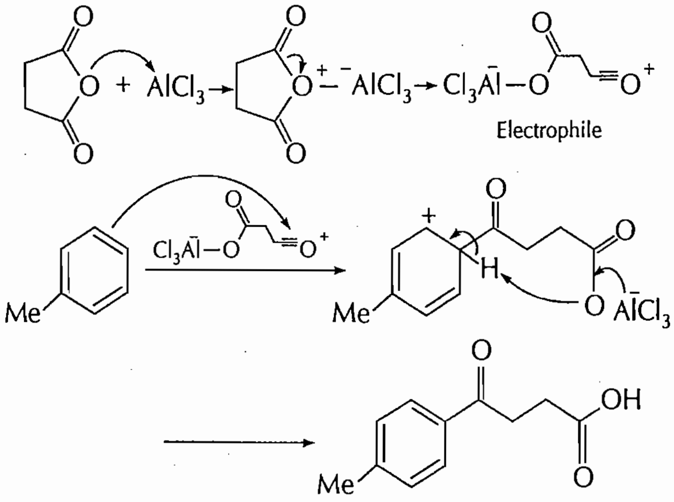
Since, the least prior group is attached to solid line, the clockwise 1 → 2 → 3 rotation gives *S*-configuration.

13. (a) The given compound has 10π electrons, which is in accordance to Huckel's (4*n* + 2)π electrons. So, it is an aromatic compound. This molecule being unsymmetrical possesses a dipole moment of 0.8 Debye.

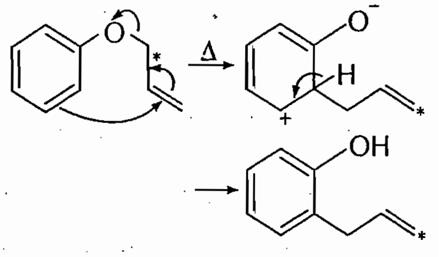
14. (c) It is an example of typical Friedel-Crafts reaction in which anhydride reacts with benzene derivative to give a semicarbazone with a carbonyl, carboxylic and phenyl group.



This reaction involves the following mechanism.

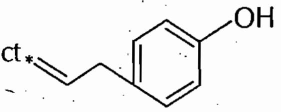


15. (d)

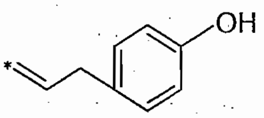


ortho-allylphenol
'X' (85%)

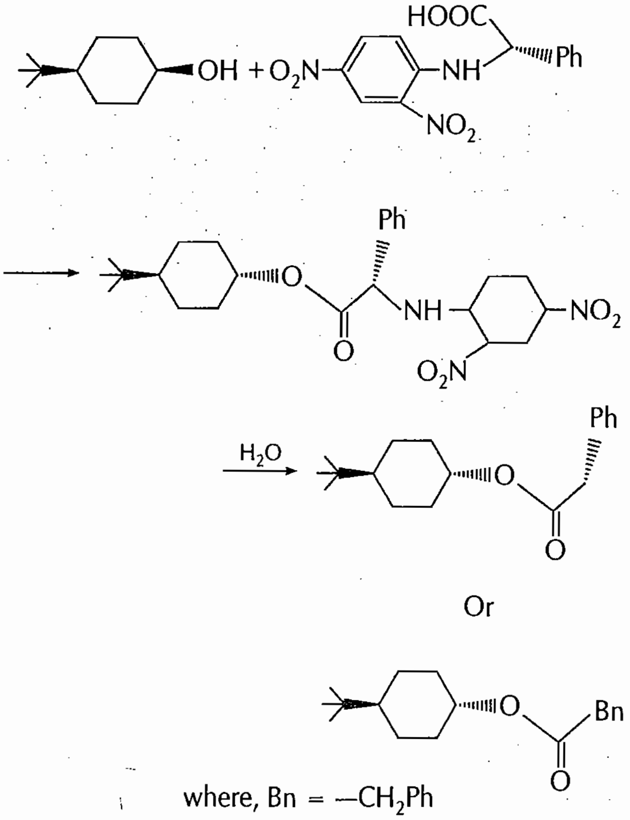
Along with *ortho, para* product



is also formed but as minor product. So Y is

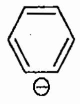


16. (b) Reagent given in option (b) is more suitable to bring out the following transformation.



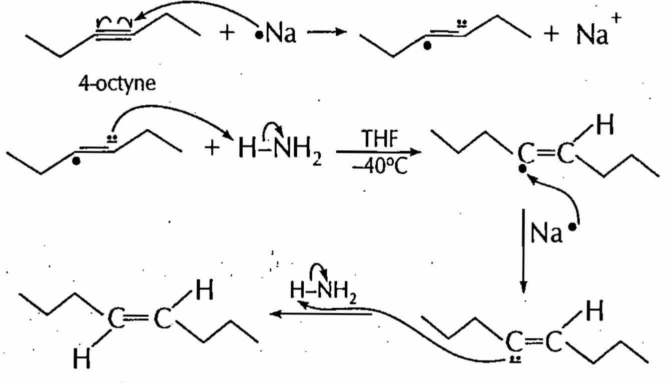
where, Bn = $—CH_2Ph$

17. (b) An aromatic compound must follow Huckel's rule of $(4n + 2)\pi$ electrons. Where $n = 0, 1, 2, 3, \ldots$ etc. that means aromatic compounds should have 2, 6, 10, 14, ... etc electrons. Among the given,



contains $8\pi\ e^-$ that's way it is non-aromatic.

18. (c)



19. (a) In carbylamine reaction, isocyanide (bad smelling compound) is obtained when primary amine (aliphatic as well as aromatic) reacts with chloroform in the presence of alkali. This reaction proceeds through dichlorocarbene intermediate which is obtained by the reaction of chloroform with alkene.

$CHCl_3 + KOH \longrightarrow KCl + H_2O \quad :CCl_2$

Dichlorocarbene
'Z'

$$R\ddot{N}H_2 + :CCl_2 \longrightarrow R\overset{+}{N}H_2\bar{C}Cl_2$$

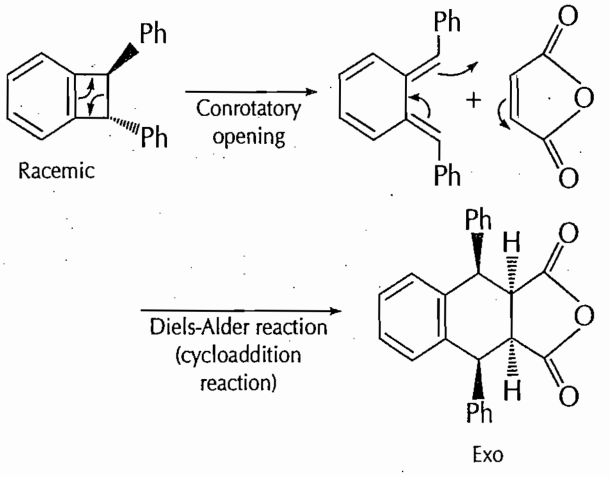
$$\xrightarrow{-H^+} R—\ddot{N}H\ddot{C}Cl_2$$

$$\xrightarrow[-HCl]{} R—N{=}\bar{C}Cl \xrightarrow[-Cl^-]{} R\overset{+}{N}{\equiv}C^-$$

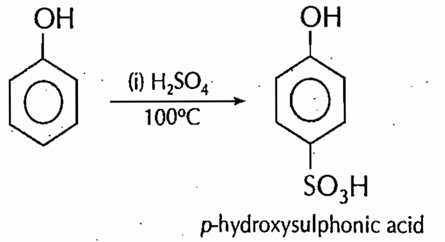
The $X = RNH_2$ and $Y = RNC$.

20. (d) In spiro system, rings are shared by single carbon atom. In fused system, two atoms are shared. Atropisomers are those stereoisomers resulting from hindered rotation about single bond. The hindrance is high enough to allow the isolation of conformers. In bridge system, a bridge joining two carbon atoms is present.
So, the correct match is a – s; b – r; c – p; d – q

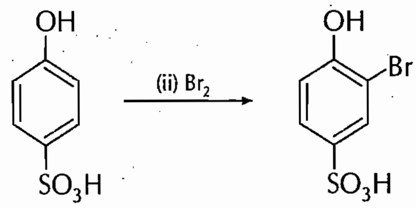
21. (c) Because of the presence of even number of electron pairs, 4π-conrotatory opening occurs.



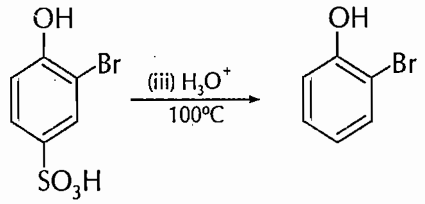
22. (b) At 100°C, phenol mainly gives *p*-hydroxy sulphonic acid with concentrated sulphuric acid.



Since, *p*-position is not free, Br^+ mainly attacks at *ortho* position.

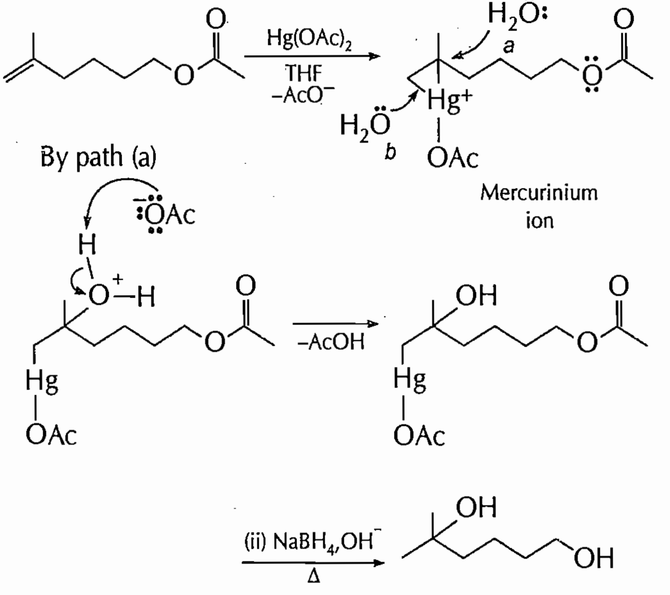


(This is because phenol is less reactive than phenoxide ion.)

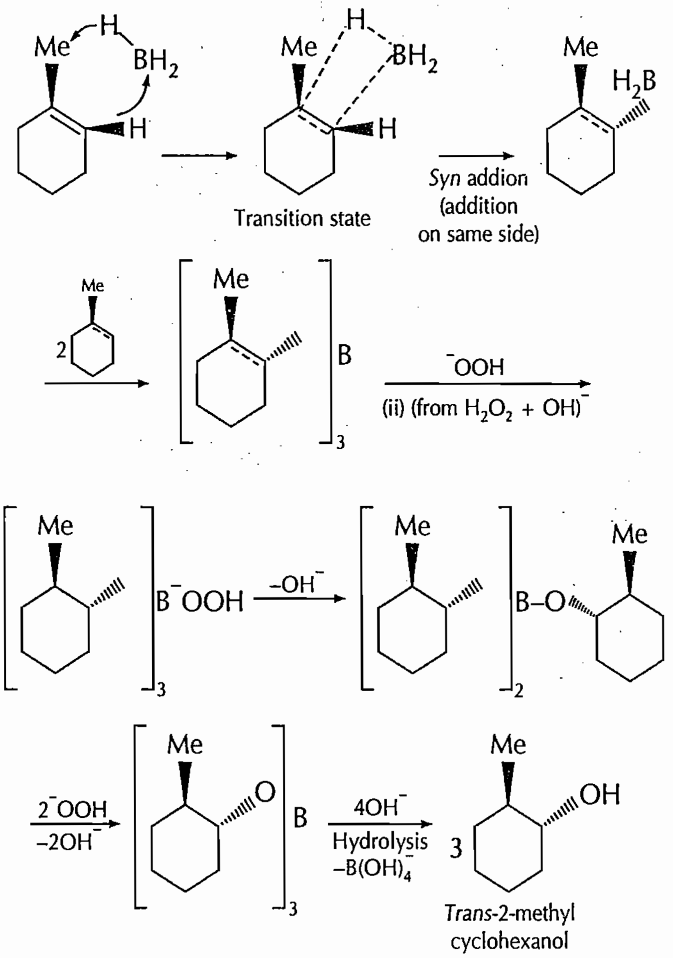


(—SO_3H group is removed by boiling in acid medium.)

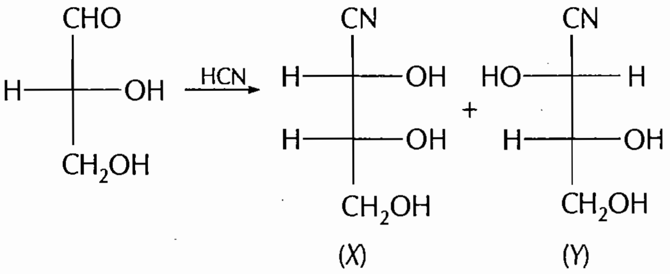
23. (d)

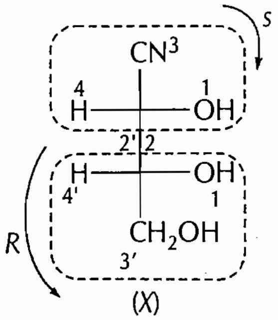


24. (b) BH_3 react rapidly with alkane in THF to give tetra alkyl boranes, which on oxidation with H_2O_2 in NaOH produce primary alcohols.



25. (a) When an aldotriose reacts with HCN, two cyanohydrins are obtained which are non-superimposable and not related to each other as mirror images (*i.e.*, these are diastereomers).

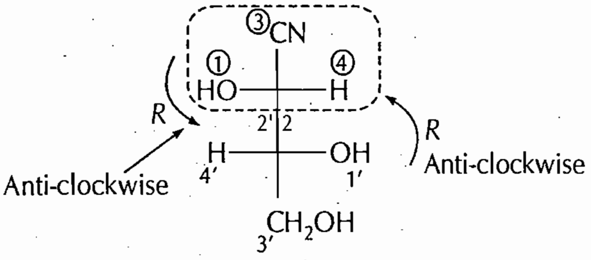




2*s* and 3*R*

Since, H (least priority group is at horizontal position), clockwise rotation gives *S* and anti-clockwise rotation gives *R* configuration.

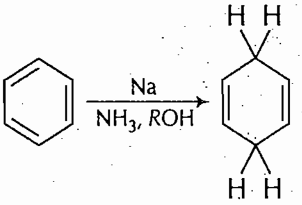
Similarly,



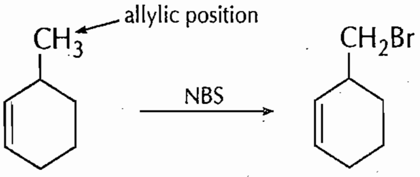
(Y)

26. (a) The IR stretching frequency of —OH group is 3200-3500, —CN group is 2200-2300, —C=O group is 1600-1700 and of —CH group is 3000.

27. (a) Birch reduction is the reduction of aromatic rings in liquid ammonia with sodium, lithium or potassium and an alcohol, such as ethanol.



28. (a) In the mono bromination of cycloalkene with NBS the bromination takes place at the allylic position.



29. (a) In the presence of oxidants such as HNO_3 direct, iodination of benzene is possible. The electrophiles formed in this case is $[I^+]$.

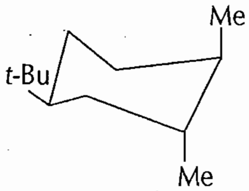
$$H^+ + HNO_3 + \frac{1}{2} I_2 \longrightarrow \underset{\text{Iodine cation}}{I^+} + NO_2 + H_2O$$

30. (c) In the most stable conformation, the bulkiest group occupies the equatorial position. Thus, *t*-Bu occupies equatorial position.

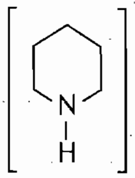
C-1 Me is *cis* to *t*-Bu, thus it should occupy axial position (∵ for *cis* configuration, ae or ea positions are occupied).

C-2 Me being *trans* to C-1 Me, occupy axial position.

Thus, the most stable conformation is

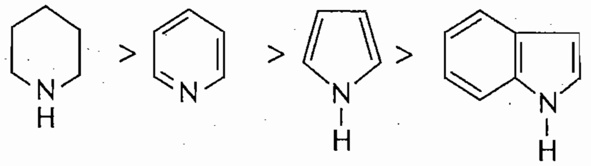


31. (c) Basicity depends upon the availability of lone pair of nitrogen for donation. More the availability of lone pair of nitrogen for donation, more will be the basicity. In piperidine lone pair of nitrogen are easily available for donation, so it is more basic.



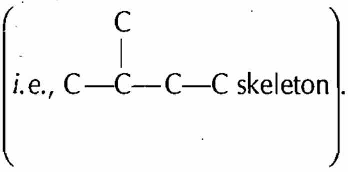
In pyrrole and indole, lone pair of nitrogen takes part in resonance, thus, less available for donation. The lone pair of indole are loss available as compared to pyrrole, so pyrrole is more basic than indole but less basic than pyridine (in which lone pair are not utilised in resonance but less available as present on double bonded *N*) and piperidine.

Thus, the order of basicity is



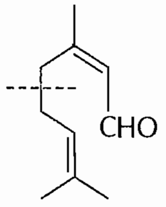
Piperidine (IV) > Pyridine (III) > Pyrrole (I) > Indole (more resonating structures) (II)

32. (b) All naturally occurring terpenoids contain isoperene units



$$\left(i.e., C—\overset{\overset{\Large C}{|}}{C}—C—C \text{ skeleton}\right)$$

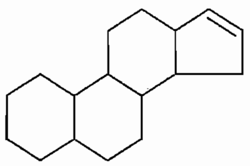
. So,



2-isoprene units

is a terpenoid.

The structure of steroids is based on 1, 2-cyclo pentenophenanthrene skeleton.



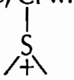
1, 2-cyclopentenophenanthrene

So compound II is a steroid.

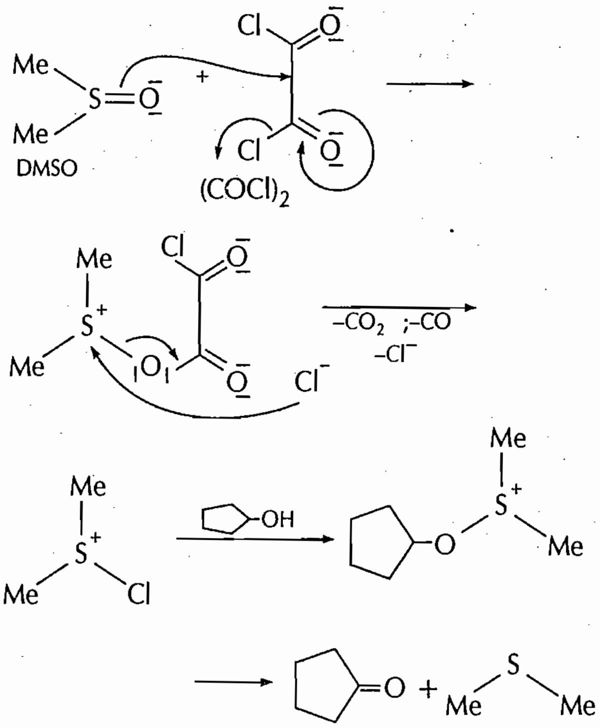
Alkaloids contain at least one N atom in the heterocyclic ring. Thus, III is an alkaloid. IV is thymine, a pyrimidine base present in DNA.

33. (b) At $\delta \geq 8$ ppm in ^1H NMR spectrum, arene proton and N-can give signals. Signals of arene proton are unaffected by D_2O.

34. (c) The given reaction is Swern oxidation. In this reaction, DMSO reacts with $(COCl)_2$ to give,



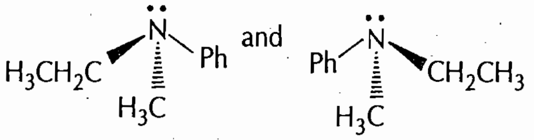
which reacts with alcohol to give carbonyl compound.



35. (a) Phosphorus is attached with bulky groups, so the oscillation becomes zero and it can show optical activity.

Compound (c) is an allene system and is optically active due to molecular symmetry.

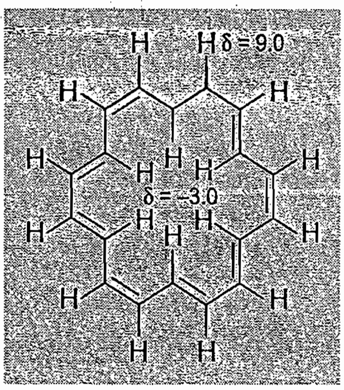
Compound (d) has one chiral carbon atom and thus, is optically active.



are non-separable mirror images, that's why this compound is optically active.

36. (a) Due to steric hindrance only one enantiomer is formed in the given reaction.

37. (c) [18] Annulene has the following structure :



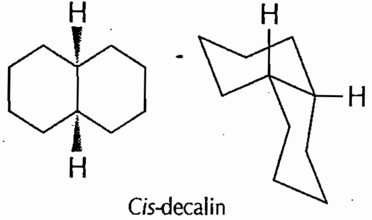
As shown in the figure, 12 protons are outside the ring and are strongly deshielded at $\delta = 9$. Six protons are inside the ring and absorb at $\delta = -3$, the negative value is because of strong shielding.

38. (b) If an amino acid has an ionisable side chain, its pI is the average of the pK_a values of the similarly ionising groups.

In glutamic acid, ionisable side chain is —COOH, hence isoelectric point is the average of pK_a of —COOH group (that remains neutral) and pK_a of other —COOH group that changes to $—COO^-$.

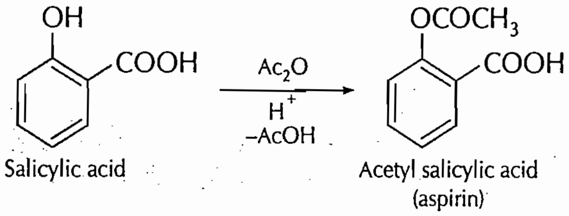
$$\text{Isoelectric point (pI)} = \frac{4.3 + 2.2}{2} = \frac{6.5}{2} = 3.25$$

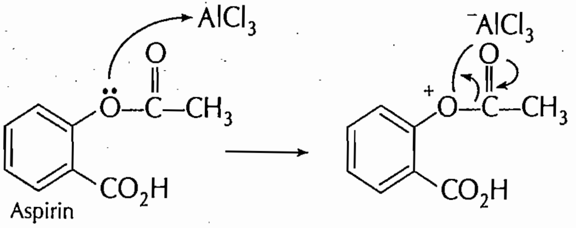
39. (c) In *cis*-decalin two rings of *cis*-conformer undergo ring flip so the position of bridge head hydrogen changes. However, if one bridged H is axial than other occupy equatorial position or *vice-versa*.

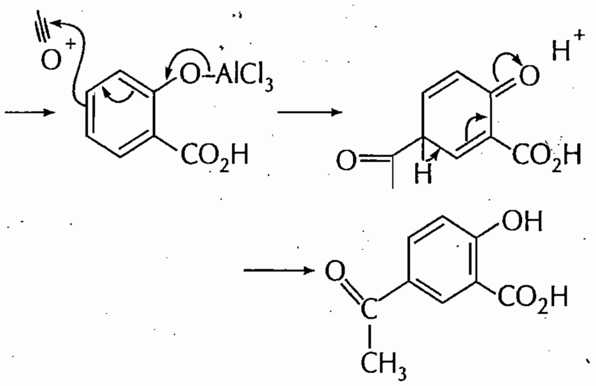


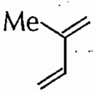
Cis-decalin

40. (b)







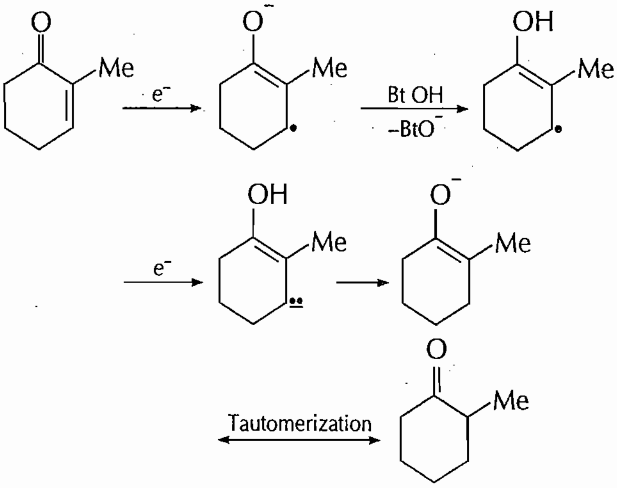
41. (d) *Cis* diene are more reactive than *trans* diene in Diels-Alder reaction. Cyclopentadiene is most reactive while Me is least reactive among the given.

Thus, the order of reactivity is

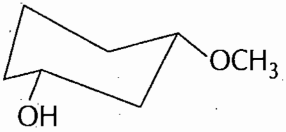
$$X > Y > Z$$

42. (c) By Li, Liq NH_3, α, β-unsaturated carbonyl compounds are reduced in a 1, 4 fashion to give an enolate which can subsequently trap the electrophile.

$$\underset{}{Li + NH_3} \rightleftharpoons \underset{\text{Solvated electron}}{NH_3e^-} + Li^+$$



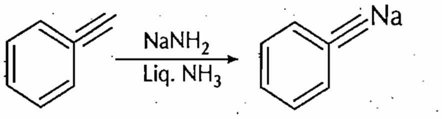
43. (a) In stable conformation, the bulkier groups occupy equatorial position. Since both the groups are present at equatorial position in *cis*-conformation of 3-methoxy cyclohexanol, the *cis*-conformation, *i.e.*,



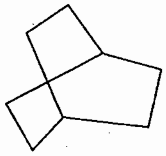
is most stable.

44. (a) Nitration of N,N-dimethyl aniline with conc. H_2SO_4, HNO_3 mixture give a mixture of *meta* and *para* nitro isomers. In which *meta* isomer is the major product.

45. (b) In this reaction, sodium alkylide is formed.



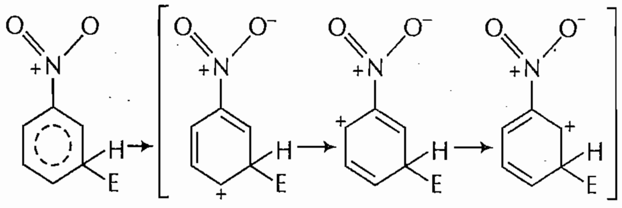
46. (d) Number of signals in ^{13}CNMR spectrum depends upon the types of carbon atoms present in the compound.



contains only two types of carbon atoms, so it exhibits only two signals in proton decoupled ^{13}C NMR spectrum.

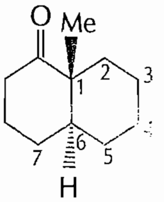
47. (d) Cyclohexyl benzyl ether when reacted with hydrogen in the presence of 10% palladium on charcoal generates a mixture of cyclo hexane and toluene as during the reaction dehydration takes place.

48. (d) In electrophilic aromatic substitution reactions, nitro group is an electron withdrawing group so, it decreases electron density at *ortho* and *para* positions but at *meta* position electron density remains the same. So, substitution takes place at *meta* position, which has more electron density as compared to *o*/*p*-positions.



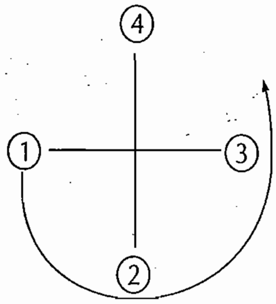
Meta substitution on nitrobenzene.

49. (c) According to sequence rule both the asymmetric centres (C_1 and C_6) has *S* configuration.



Priority order for C_1;

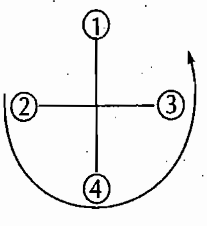
—CO.....> C_6 carbon > C_2 carbon > Me



Anti-clockwise,
so *S* configuration.

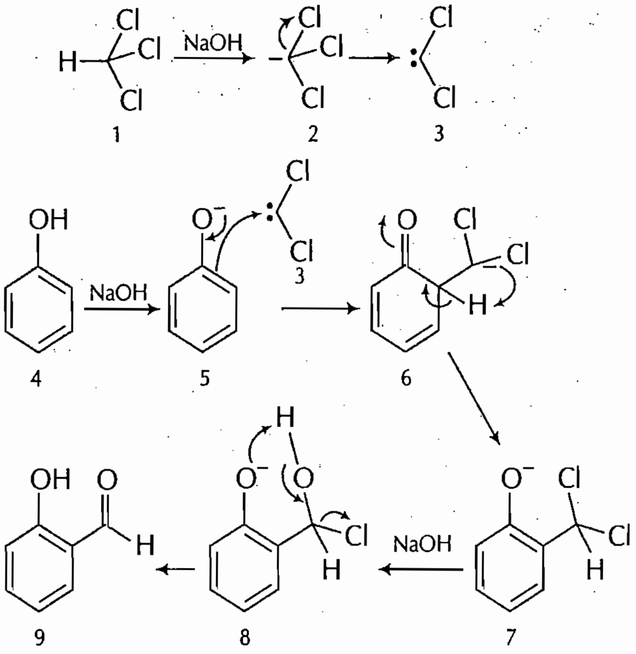
Priority order for C_6 :

$$C_1 > C_7 > C_5 > H$$

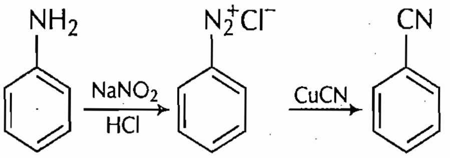


Anti-clockwise, so *S* configuration.

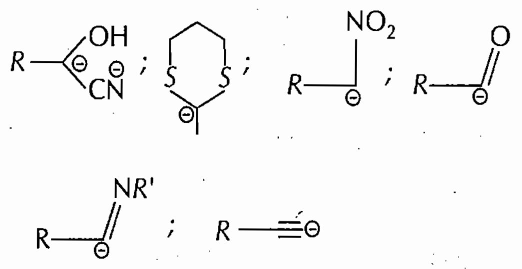
50. (a) The reaction of conversion of phenol to salicylaldehyde using chloroform and sodium hydroxide involves dichloro carbene intermediate.



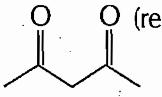
51. (c) Aniline reacts with $NaNO_2 + HCl$ to give benzene diazonium chloride. Which reacts with CuCN to give phenyl cyanide.

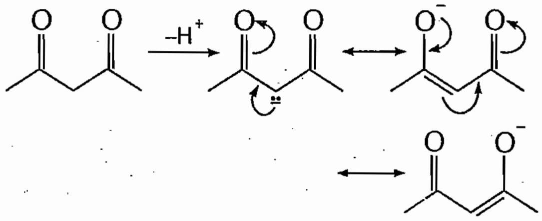


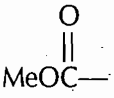
52. (d) The following anions are equivalent to acyl anion.



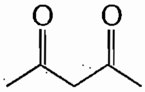
53. (a) The compound which give a stable carbanion, readily undergoes de-protonation.

Since, the negative charge of carbanion is stabilized by neighbouring electron withdrawing group. (like $>C{=}O$), so  (resonance stabilized) is most reactive towards deprotonation.





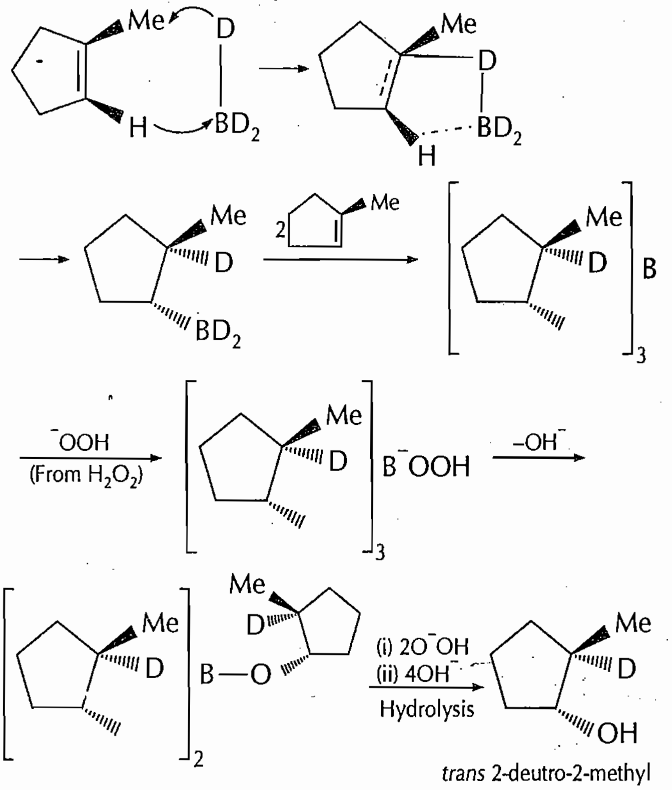
$\mathrm{MeO\overset{\overset{O}{\|}}{C}}$— group (ester group) also stabilizes carbanion but less in comparison to carbonyl group. This is because —OMe group decreases the electron deficiency of carbonyl carbon. That's why



gets readily deprotonated among the given.

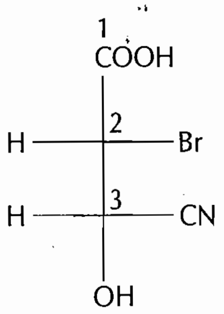
54. (c) Hydroboration of 1-methylcyclopentene using B_2D_6, followed by the treatment with alkaline hydrogen peroxide gives deutrated alcohol with D—OH adding across the C=C.

This reaction involves *syn* addition.



trans 2-deutro-2-methyl cyclopentan-1-ol

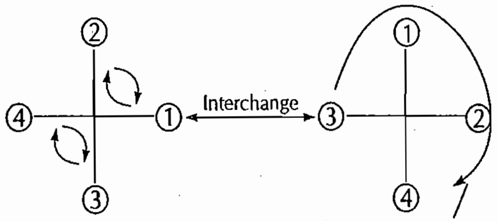
55. (b)



According to sequence rule, for C-2, priority order is

—Br > —COOH > —CH(OH)(CN) > —H

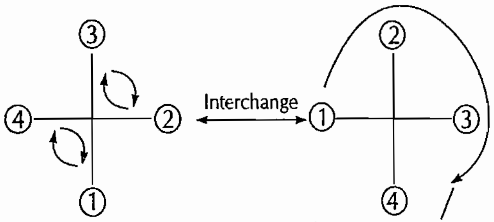
i.e.,



Clockwise rotation, *R*-configuration.

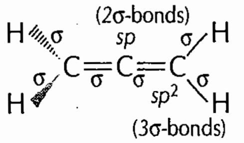
For C-3, priority order is

—OH > —CN > —CH(Br) (COOH) > —H



Clockwise rotation, *R*-configuration.

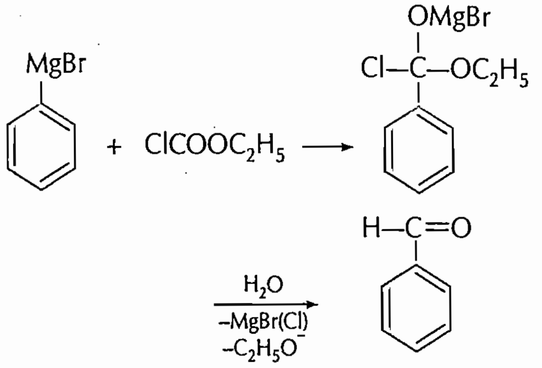
56. (c) In allene, central carbon has *sp* and terminal carbon has sp^2 hybridization.



57. (b) Compounds containning (C≡C—H) group exhibit an absorption band at 3300 cm^{-1} in the IR spectrum. Among the given isomers, only 1-butyne ($CH_3CH_2C{\equiv}CH$) contains (C≡C—H) group. That's why it exhibits an absorption band at 3300 cm^{-1}.

58. (d) Cannizzaro reaction is given by those aldehydes which have no α hydrogen. So, this reaction is given by formaldehyde (HCHO) and benzaldehyde (C_6H_5CHO).

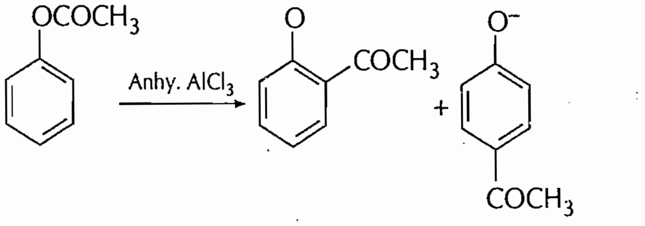
59. (d) Benzaldehyde is prepared by the reaction of phenyl magnesium bromide with ethyl chloroformate.



Benzaldehyde

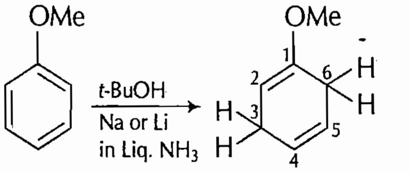
60. (b) Proteins are the biopolymers of amino acids.

61. (a) When phenyl acetate is heated with anhydrous $AlCl_3$, it undergoes Fries rearrangement to give *ortho* and *para* hydroxyacetophenones as OH group is *o*/*p* directing.



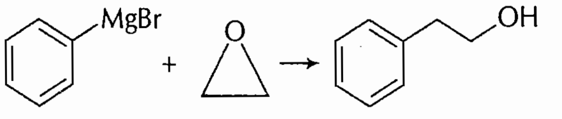
o and *p*-hydroxyacetophenone

62. (a) A carbon bearing electron releasing group is not reduced in Birch reduction.

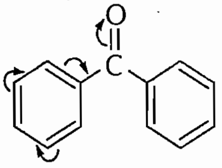


1-methoxy cyc ilohexa-1, 4-diene

63. (d)

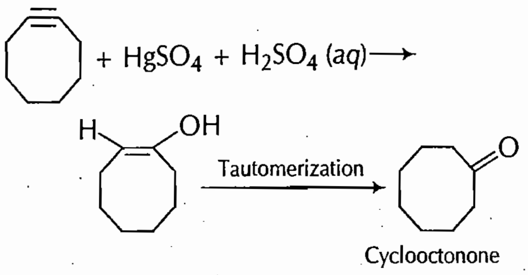


64. (c) Wavelength of transition depends upon the extent of conjugation. More the conjugation, longer is the wavelength. Phyenyl group is some what electron withdrawing in nature and has alternate = bond. Thus, $C_6H_5COC_6H_5$ because of the presence of two electron withdrawing Ph groups has the longest wavelength.

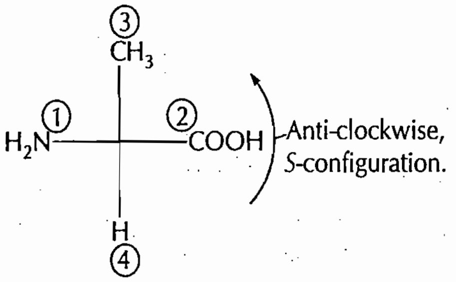


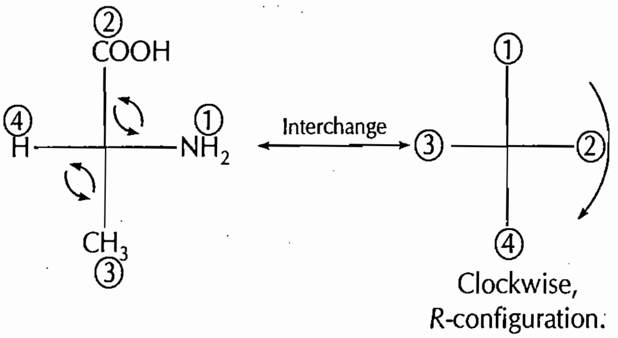
($C_6H_5COC_6H_5$)

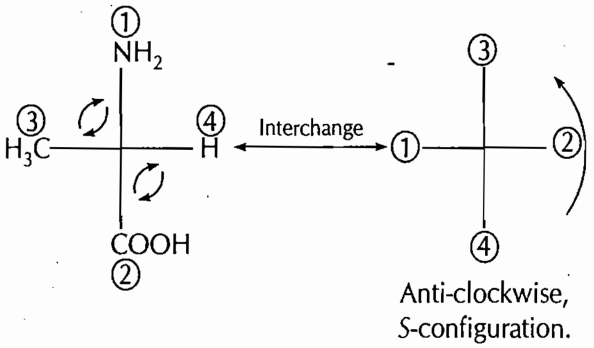
65. (d)

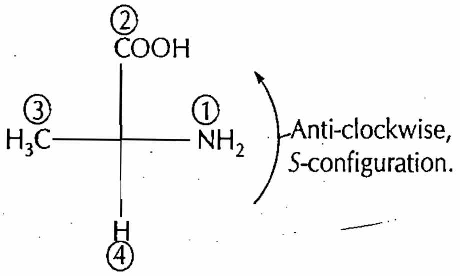


66. (b)

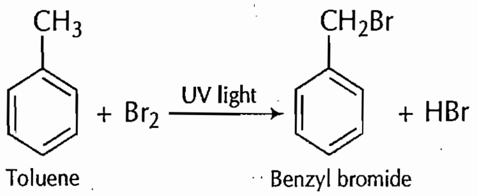






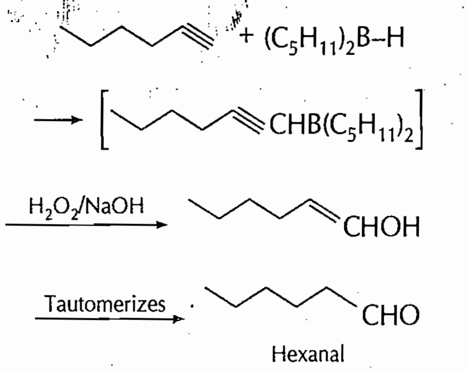


67. (d) In the presence of light, Br• (bromine free radicals are generated and substitution occurs in the side chain. Thus, the major product is benzyl bromide.

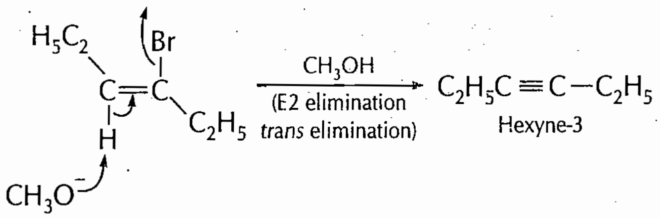


68. (b) Base reacts with optically active 2-octanol and gives a racemic mixture.

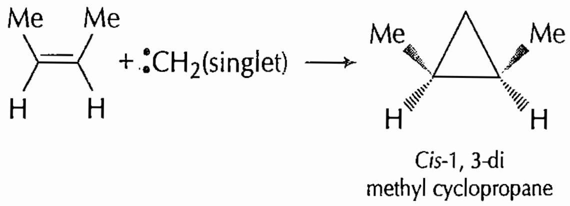
69. (c) Disiamyl borane/H_2O_2 reacts with terminal alkynes and converts them into less substituted α, β-unsaturated alcohol which readily tautomerises into aldehyde. 1-hexyne being a terminal alkyne, gives the similar reaction.



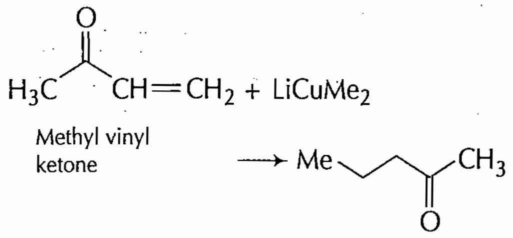
70. (a)



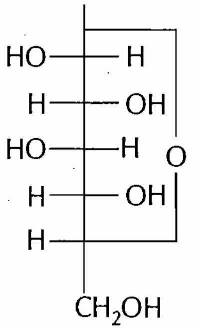
71. (a) Singlet carbene generally undergoes cheletropic reaction. It is an stereospecific reaction and gives only one enantiomer.



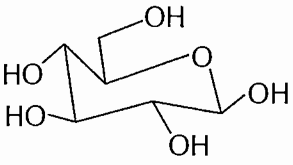
72. (a)



73. (a) Fischer formula of β-D-glucose is

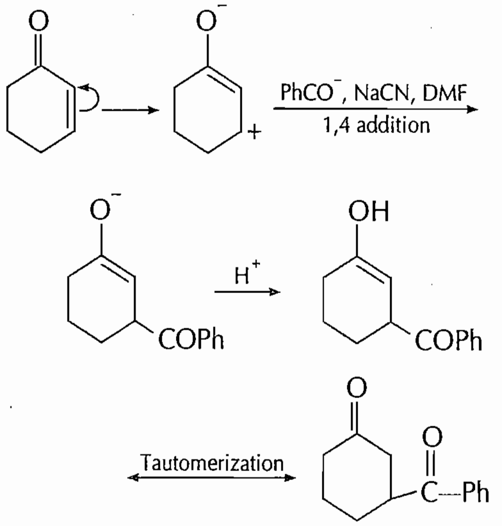


In Haworth formula, all the —OH groups on the right in the Fischer's formula are directed below the plane of the ring while those on the left go above the plane. Thus, the Haworth formula of β-D-glucose is

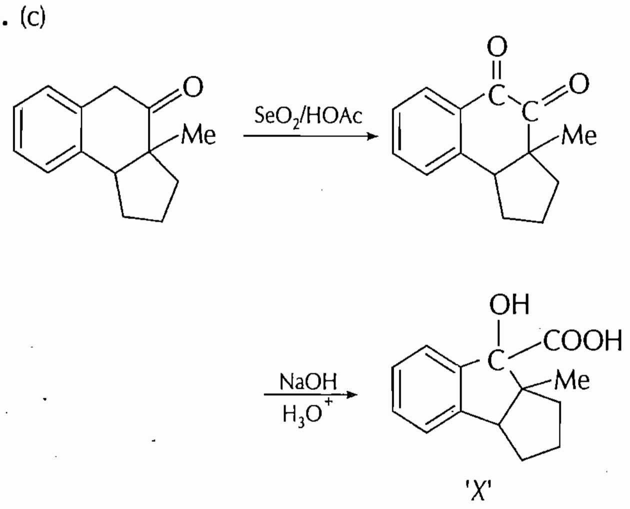


β-D-glucose

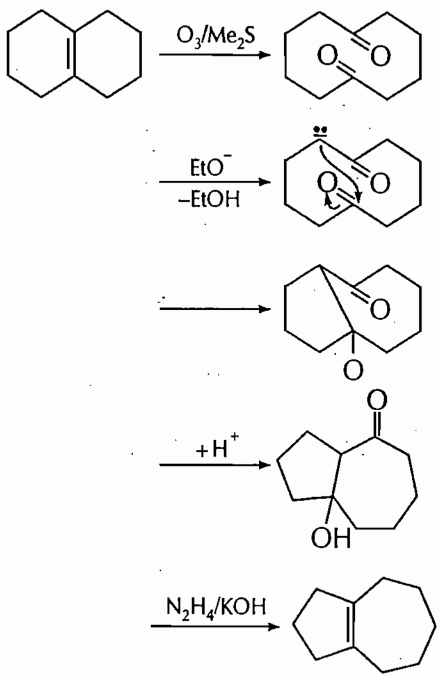
74. (d)



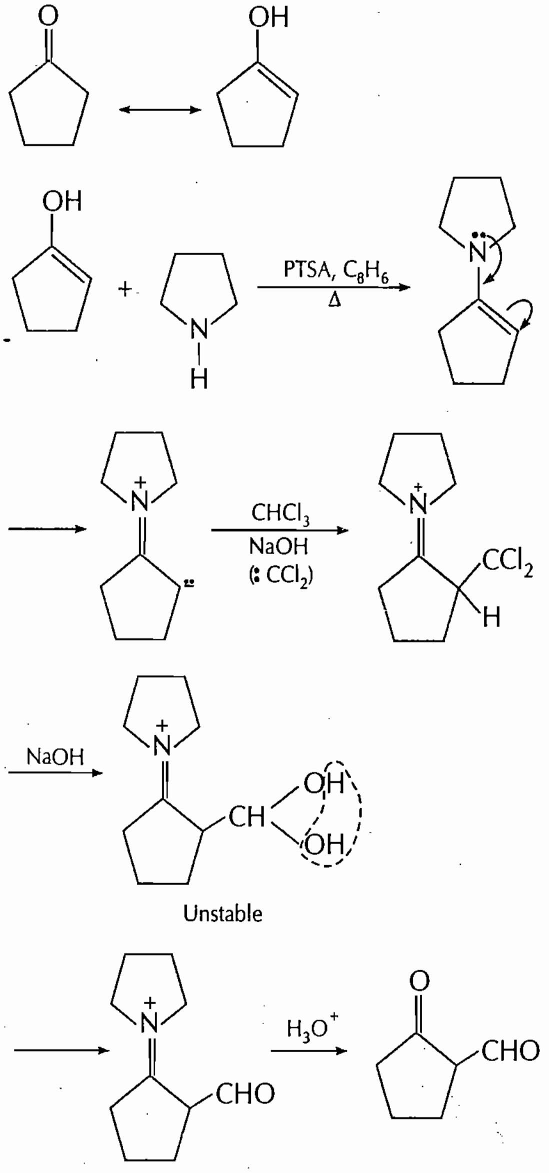
75. (c)



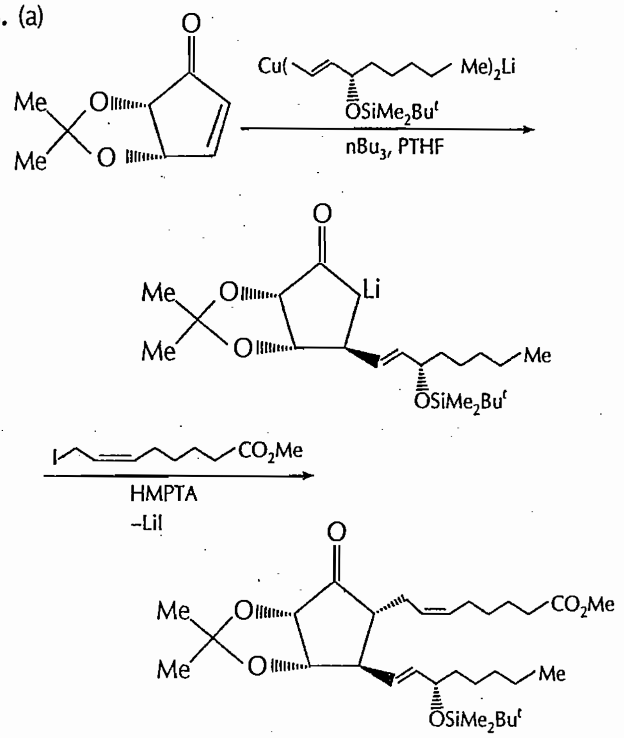
76. (d)



77. (c)

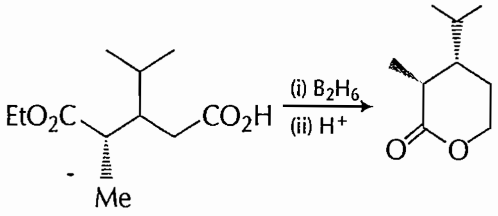


78. (a)

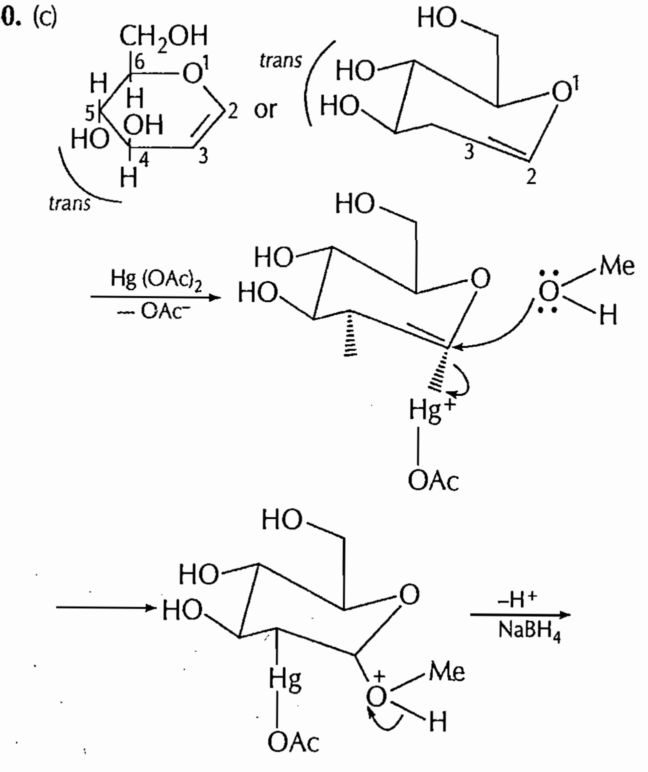


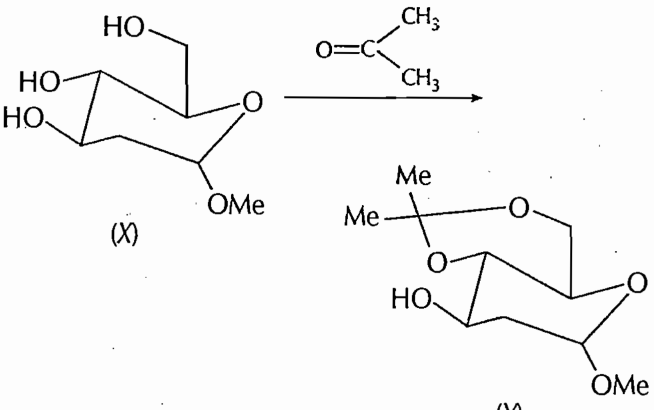
'X'

79. (a) B_2H_6 first reduced —COOH group to —CH_2OH.



80. (c)

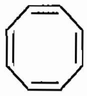


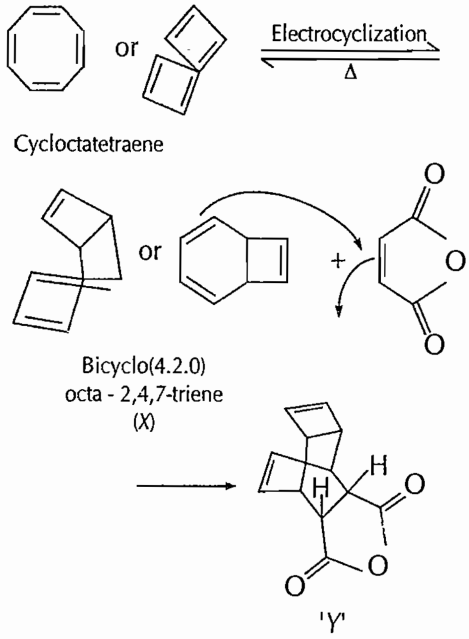


(X)

(Y)

81. (b) $Ph_3P + MeI \longrightarrow \underset{(X)}{(Ph_3\overset{+}{P}\cdot CH_3)I^-} \xrightarrow[-LiI\ -nC_4H_{10}]{n\,BuLi(base)} \underset{(Y)}{Ph_3P{=}CH_2}$

82. (b)  does not contain any coplanar double bond, so it is unreactive towards nucleophile but it changes to its isomer bicyclo (4.2.0) octa-2, 4, 7-triene by electrocyclic isomerization, which because of the presence of coplanar double bonds reacts with succinic anhydride to give diels alder product.

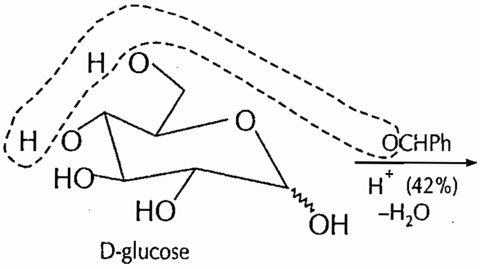


Cyclooctatetraene

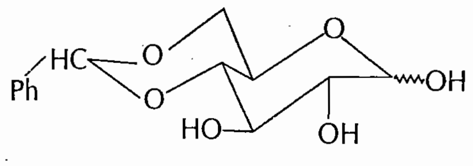
Bicyclo(4.2.0)
octa - 2,4,7-triene
(X)

'Y'

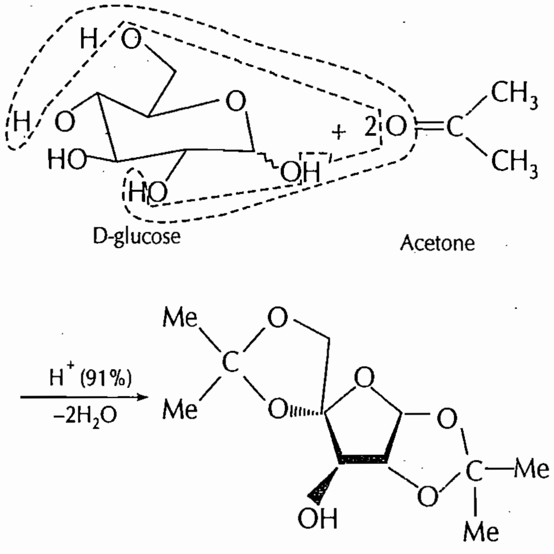
83. (d)



D-glucose

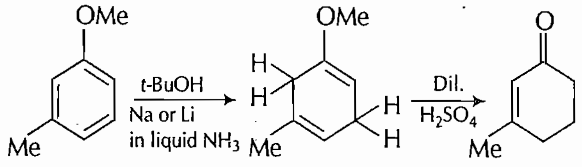


'X'

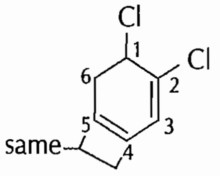


'Y'

84. (d)



85. (a) In ^{13}C NMR spectrum, the number of signals depends upon the types of carbon atoms present in the compound.

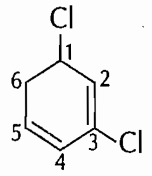


o-dichlorobenzene

$$\left.\begin{array}{l} C_1 = C_2 \\ C_3 = C_6 \\ C_4 = C_5 \end{array}\right] \text{Three types of carbon}$$

Thus, three signals are appeared in the ^{13}C NMR spectrum of o-dichlorobenzene.

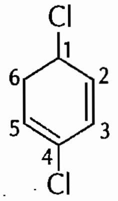
Similarly,



m-dichlorobenzene

Carbon present = C_2, $C_1 = C_3$, $C_4 = C_6$; C_5

Thus, four signals are appeared in the ^{13}C NMR spectrum of *m*-dichlorobenzene.



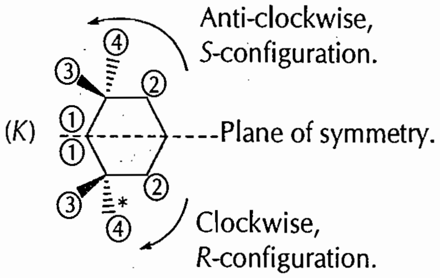
p-dichlorobenzene

$C_1 = C_4$

$C_2 = C_3 = C_5 = C_6$

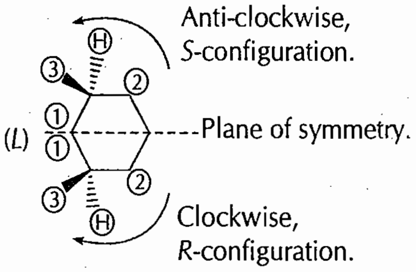
Thus, two signals are present in the ^{13}C NMR spectrum of *p*-dichlorobenzene.

86. (b)

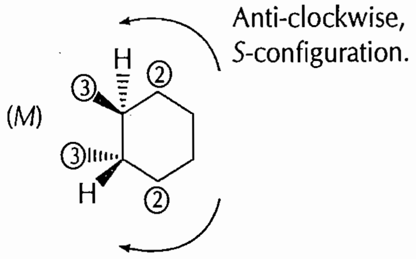


(C* = chiral centre)

This molecule contains plane of symmetry and rotation of upper half part is cancelled by rotation of lower half part as these are in opposite direction. In other words, this molecule is optically inactive due to internal compensation, so it is a *meso*-compound.



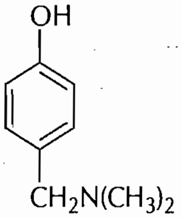
Thus, it is also a *meso* compound.



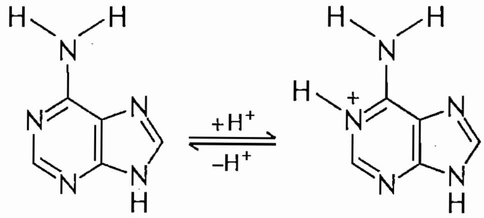
clockwise but configuration is *S* as H is attached with solid line.

Thus, there is no internal compensation in this molecule, so it is not a *meso*-compound.

87. (b) Phenol reacts with formaldehyde and dimethyl amine to give *p*-product.



88. (d) For monoprotonation position 4 and 5 are more reactive.



Adenine

89. (d) 3° alkyl halides undergo nucleophilic substitution by S_N1 mechanism, *i.e.*, the rate depends only on the concentration of alkyl halide but not on the concentration of OH^- ion. In other words,

$$\text{Rate, } r_1 = k\,[C\,(CH_3)\,(C_2H_5)\,(C_3H_7)\,Br]$$

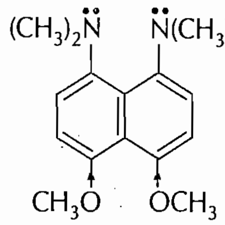
If concentration of halide is doubled,

$$\text{Rate} = k_1\; 2\,[C(CH_3)\,(C_2H_5)\,(C_3H_7)Br]$$
$$= 2r_1$$

i.e., the rate of the reaction will double.

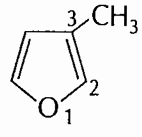
90. (a) Electron releasing substituent like —CH_3—OCH_3 increase the basicity of amines by dispersing positive charge of the anilium ion. However, their presence at *ortho* position decreases the basicity due to *ortho* effect.

Thus, Z

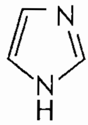


is most basic and compound Y is least basic.

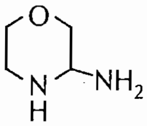
91. (d)



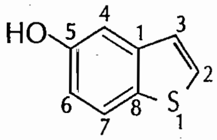
is 3-methyl furan;



is imidazole;

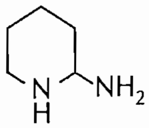


is 2-amino morpholine;



is 5-hydroxybenzothiazole

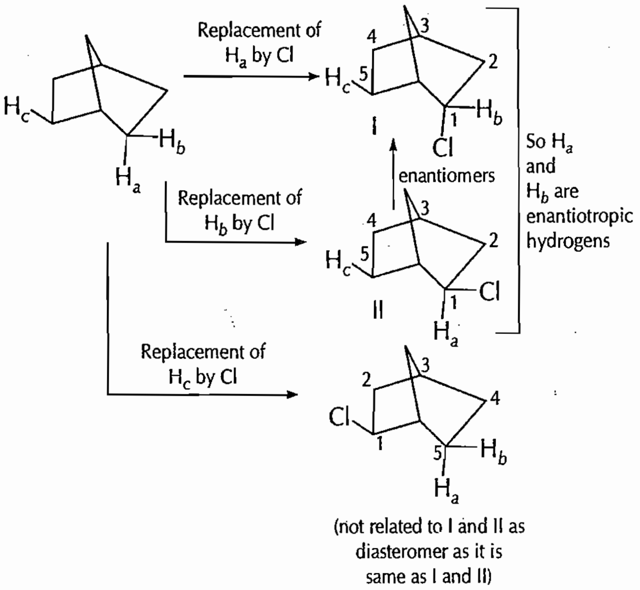
and



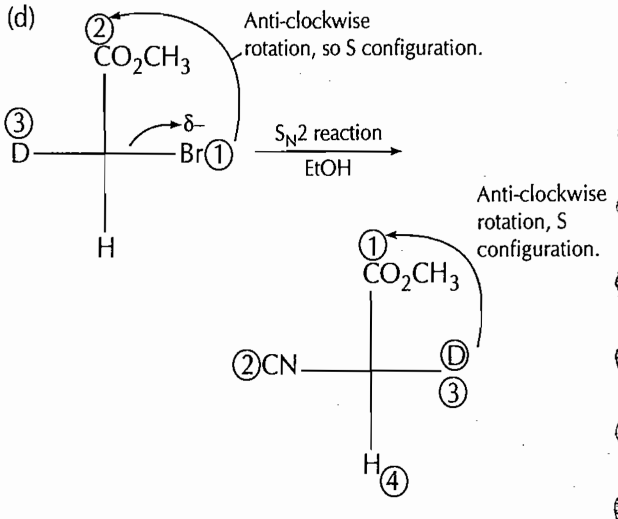
is 2-amino piperidine.

92. (c) In amino acid side chain Ca^{2+} and Cu^{2+} are bounded with carboxylate unit and imidazole rings.

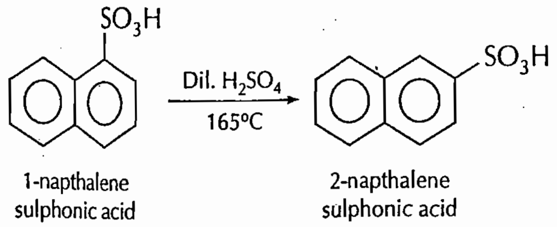
93. (a) H_a and H_b are enantiotropic because if one of the two hydrogen atoms (either H_a or H_b) is replaced, it would generate a chiral compound.



94. (d)

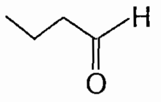
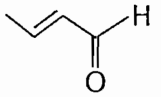
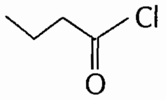
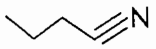


95. (b) Naphthalene-1 sulphonic acid when treated with dilute sulphuric acid at high temperature, gives its isomer naphthalene-2-sulphonic acid.

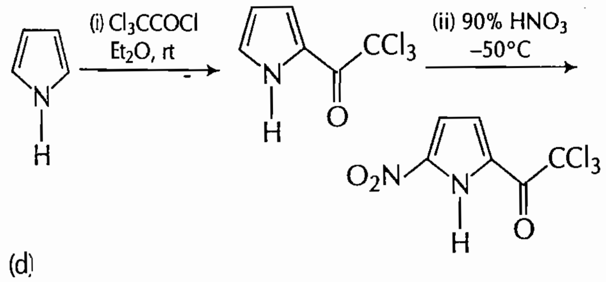


96. (d) I and III are anomers because they have different configuration at C-1 position. I and II are epimers because they have change in configuration at the carbon other than C-1.

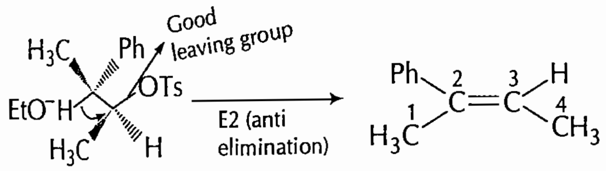
97. (c)

Functional group	Stretching frequency (in cm^{-1})
	1725
	1695
	1795
	2240

98. (a)

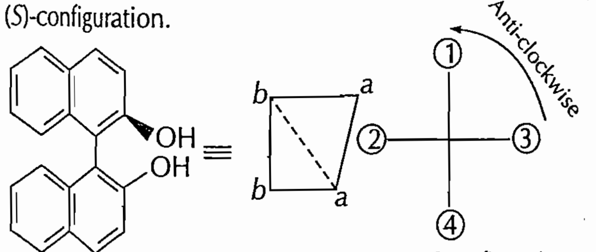


99. (d)



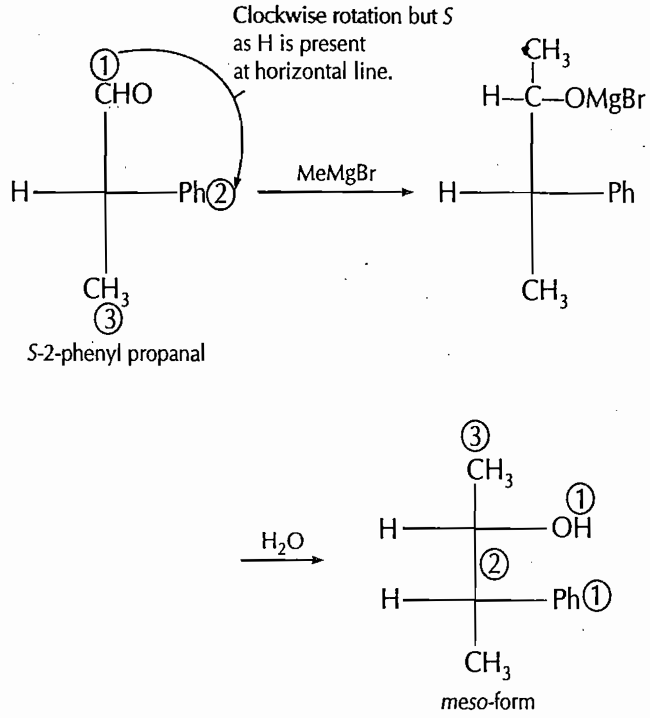
cis-2-phenyl-but-2-ene (P)

100. (d) Bnp is an optically active compound with (*S*)-configuration.

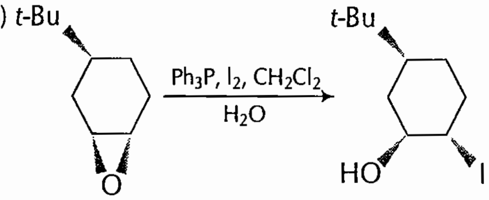


So, *S* configuration.

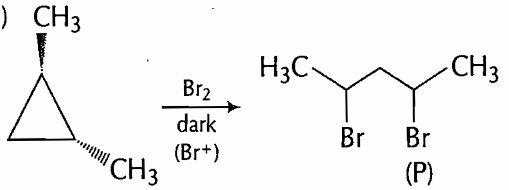
101. (c)



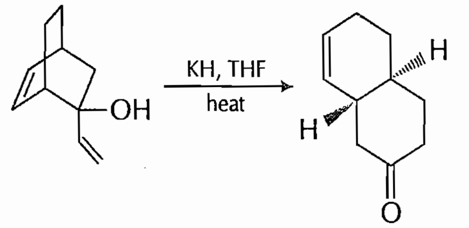
102. (b)



103. (d)



104. (b)



105. (d) Diastereomers are not mirror image and they differ in arrangement of group at one carbon atom. So, (I) and (II) or (I) and (III) are diastereomers. Enantiomers are optically active compound and are mirror image of each other. II and III are enantiomers. (I) and (IV) are optically inactive due to plane of symmetry.

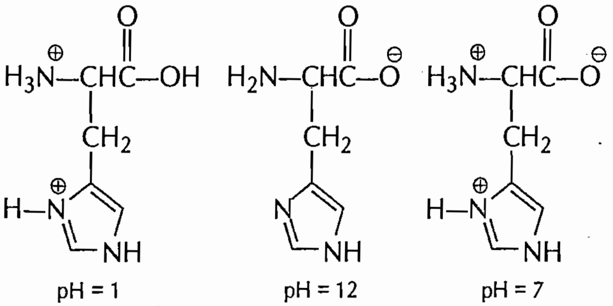
(I) and (IV) are *cis*-diol so, are HIO_4 cleavable.

I and III are D-sugar and II and IV are L-sugars.

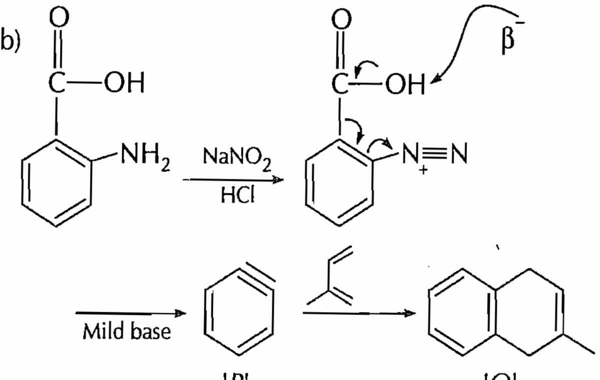
106. (c) Carbonyl stretching frequencies (cm^{-1}) in IR spectroscopy for the given compounds are :

Compound	Carbonyl stretching frequencies (cm^{-1})
Acetone	1700
Ethyl acetate	1740-1760
Acetamide	1660
Acetyl chloride	1803

107. (a) At low pH value, cationic species (species containing only $\overset{+}{N}H_3$) is found. At high pH, anionic species is found and at moderate pH neutral (Zwitter ion) is found.

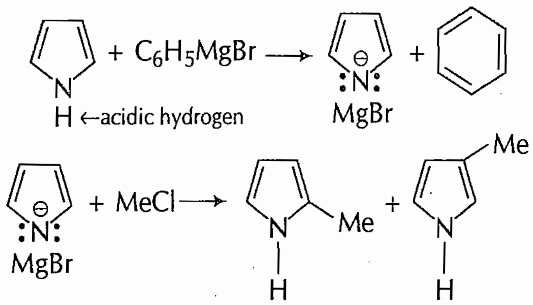


108. (b)



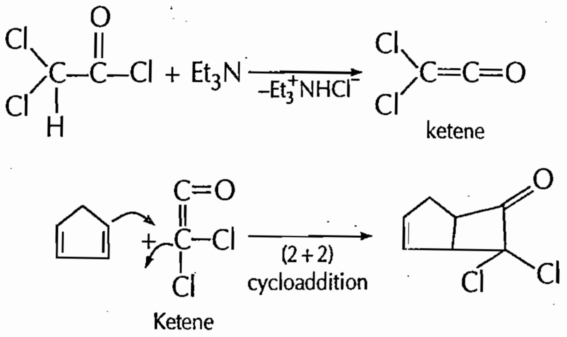
109. (b) Compound *P*, *R* has plane of symmetry so they are *meso* forms.

110. (a)

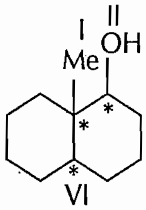


111. (b) $HOOC\overset{*}{C}H(CH_3)CH_2CH_2COOH$ and $HOOC\overset{*}{C}H(C_2H_5)CH_2COOH$ both have asymmetric carbon atom ($\overset{*}{C}$ = asymmetric or chiral carbon atom) so they will show optical isomerism. They will also form cyclic anhydride on heating.

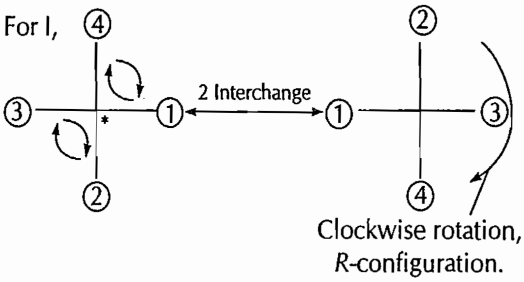
112. (b)



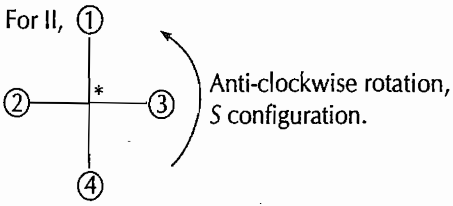
113. (d)



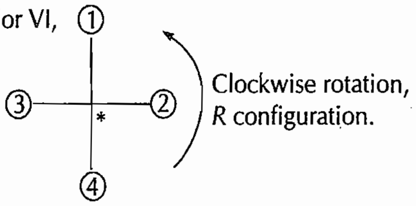
For I,



For II,

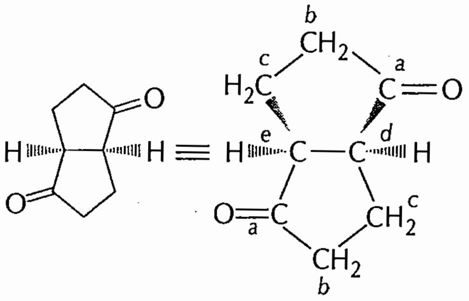


For VI,

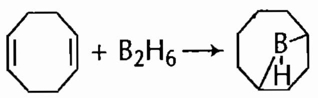


Thus, the configuration of the chiral carbons is 1*R*, 2*S*, 6*R*.

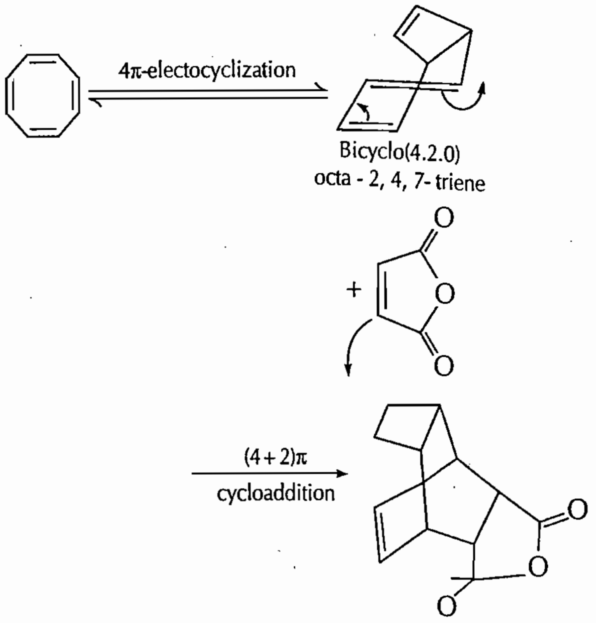
114. (c) Compound shown below will exhibit five signals in the broad band decoupled ^{13}C NMR spectrum as it contains five such C atoms which are in different environment.



115. (c)



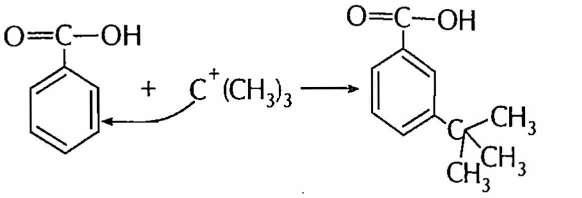
116. (d) 1, 3, 5, 7-octa-tetraene, because of the absence of coplanar double bond, first isomerises into bicyclo [4. 2. 0] octa-2, 4, 7-triene, which reacts with succinic anhydride to give the given diels-Alder adduct.



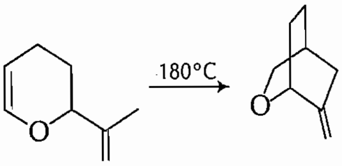
117. (b) $(CH_3)_2C{=}CH_2 \xrightarrow[\text{from } H_2SO_4]{H^+} (CH_3)_3C^+$

3° carbocation
(Highly stable)

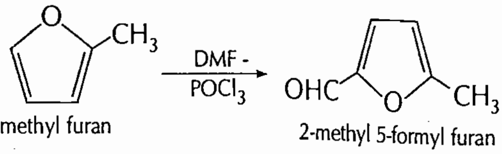
—COOH group is *m*-directing and deactivating group.



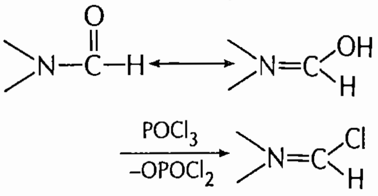
118. (d)

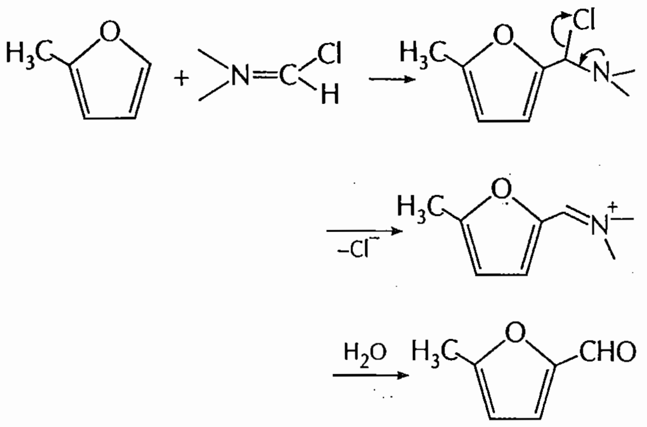


119. (b)

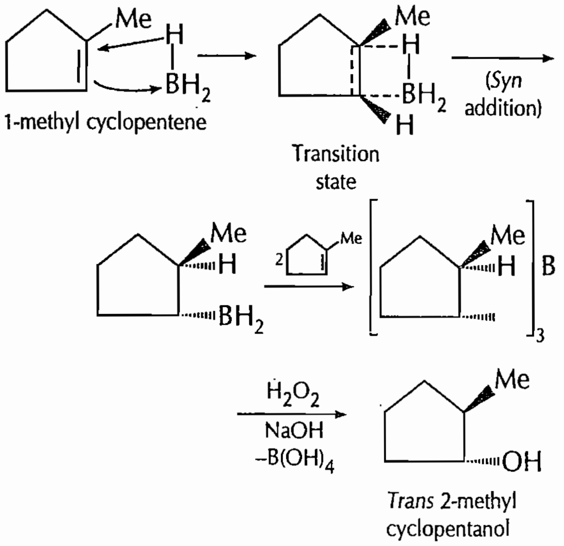


It involves the following steps :



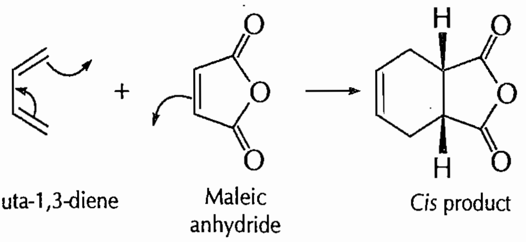


120. (d)

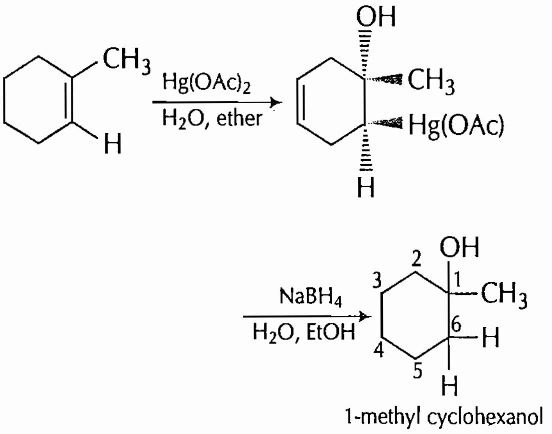


121. (c) In isotactic arrangement, same groups are present on the same side of carbon backbone.

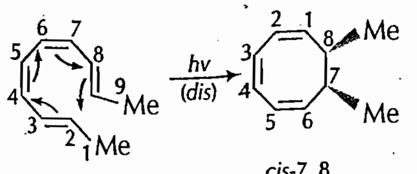
122. (b)



123. (c)



124. (b)

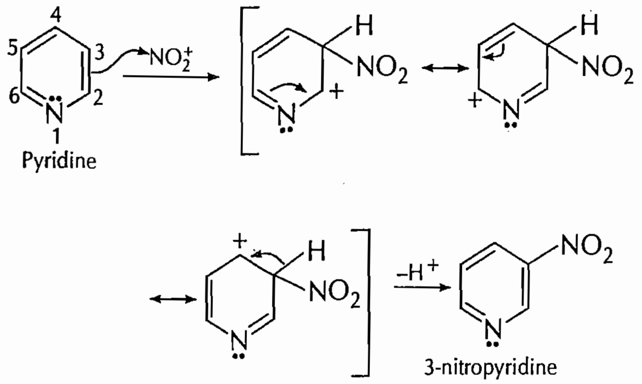


trans, *cis*, *cis*, *trans*-2, 4, 6, 8-nonatetraene

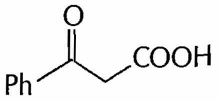
cis-7, 8 dimethyl-1, 3, 5-cycloocta triene

125. (d) Pyridine undergoes electrophilic substitution at C-3 position under vigorous conditions. This is because electron density is more at C-3 position.

$$NO_3^- + H_2SO_4 \longrightarrow \underset{\text{Electrophile}}{NO_2^+} + H_2O + HSO_4^-$$

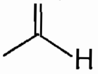


126. (b)

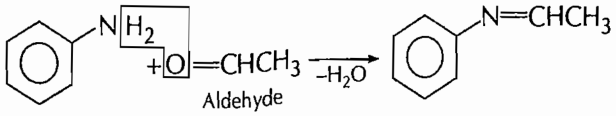


is a β keto acid and β keto acids decarboxylate at a faster rate.

127. (b) Acetanilide is obtained by the reaction of aniline with derivatives of carboxylic acids. Thus, O(CH$_3$CHO) does not give acetanilide with aniline



but it gives

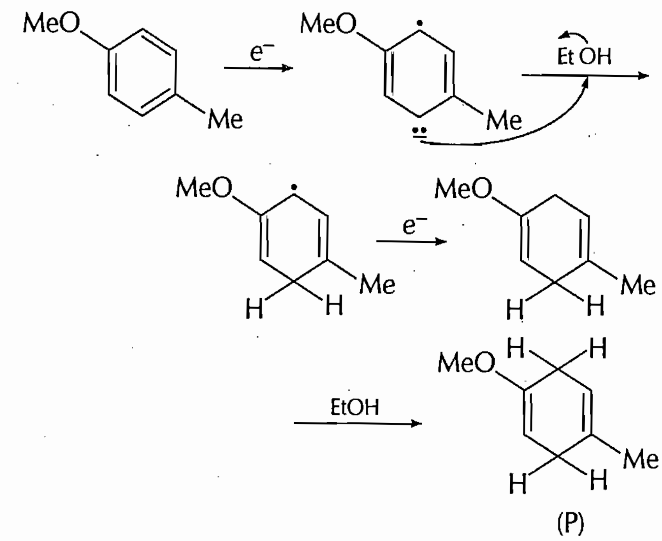


Ethyledeneaniline (Schiff's base)

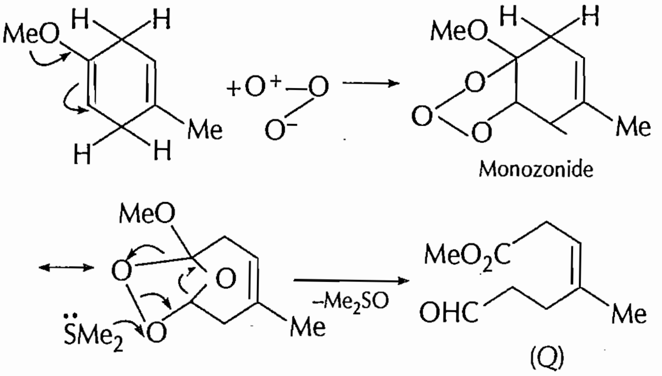
Other given reagents give acetanilide with aniline.

128. (b) Methyl amino when reacts with NaNO$_2$ and HCl gives N$_2$, while aniline gives diazonium salt. Diazonium salt so formed give red colour dye with alkaline β-naphthol. Methyl amine however does not produce dye. So these two can be distinguished by using these reagents.

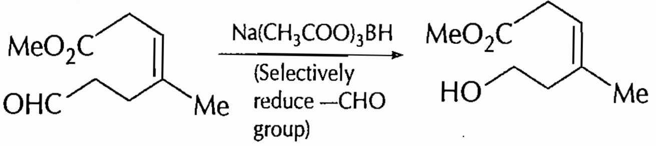
129. (d) $Li + NH_3 \longrightarrow \underset{\text{Solvated electron}}{(NH_3)x^{e^-}} + Li^+$



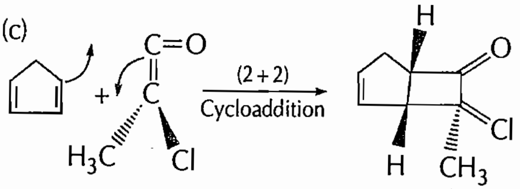
(Presence of the methoxy group activates the double bond towards electrophilic reagents like O$_3$).



130. (c)

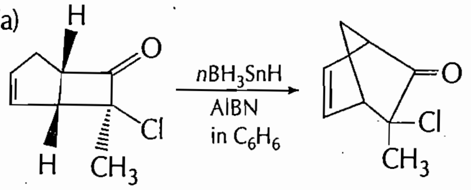


131. (c)



Ketene (P)

132. (a)



10

General Aptitude

Syllabus

Verbal Ability *English grammar, sentence completion, verbal analogies, word groups, instructions, critical reasoning and verbal deduction.*

Numerical Ability *Numerical computation, numerical estimation, numerical reasoning and data interpretation.*

GATE 2011 *(1 Mark Questions)*

1. Choose the word from the options given below that is most nearly opposite in meaning to the given word.

Amalgamate

(a) Merge

(b) Split

(c) Collect

(d) Separate

2. Which of the following options is the closest in the meaning to the word below?

Inexplicable

(a) Incomprehensible

(b) Indelible

(c) Inextricable

(d) Infallible

3. If $\log P = \left(\frac{1}{2}\right)\log Q = \left(\frac{1}{3}\right)\log R$, then which of the following options is true?

(a) $P^2 = Q^3R^2$ (b) $Q^2 = PR$

(c) $Q^2 = R^3P$ (d) $R = P^2Q^2$

4. Choose the most appropriate word(s) from the options given below to complete the following sentence.

I contemplated .... Singapore for my vacation but decided against it.

(a) to visit (b) having to visit

(c) visiting (d) for a visit

5. Choose the most appropriate word from the options given below to complete the following sentence.

If you are trying to make a strong impression on your audience, you cannot do so by being understated, tentative or ....

(a) hyperbolic

(b) restrained

(c) argumentative

(d) indifferent

6. Choose the most appropriate word from the options given below to complete the following sentence.

It was her view that the country's problems had been .... by foreign technocrats, so that to invite them to come back would be counter-productive.

(a) identified (b) ascertained

(c) exacerbated (d) analysed

7. Choose the word from the options given below that is most nearly opposite in meaning to the given word.

Frequency

(a) Periodicity

(b) Rarity

(c) Gradualness

(d) Persistency

8. Choose the most appropriate word from the options given below to complete the following sentence.

Under ethical guidelines recently adopted by the Indian Medical Association, human genes are to be manipulated only to correct diseases for which .... treatments are unsatisfactory.

(a) similar (b) most

(c) uncommon (d) available

9. The question below consists of a pair of related words followed by four pairs of words. Select the pair that best expresses the relation in the original pair.
Gladiator : Arena
(a) Cancer : Stage
(b) Commuter : Train
(c) Teacher : Classroom
(d) Lawyer : Courtroom

10. There are two candidates P and Q in an election. During the campaign, 40% of the voters promised to vote for P, and rest for Q. However, on the day of election 15% of the voters went back on their promise to vote for P and instead voted for Q. 25% of the voters went back on their promise to vote for Q and instead voted for P. Suppose P lost by 2 votes, then what was the total number of voters?
(a) 100 (b) 110 (c) 90 (d) 95

GATE 2010

11. Which of the following options is the closest in meaning to the word given below?
Circuitous
(a) Cyclic (b) Indirect
(c) Confusing (d) Crooked

12. The question below consists of a pair of related words followed by four pairs of words. Select the pair that best expresses the relation in the original pair.
Unemployed : Worker
(a) Fallow : Land (b) Unaware : Sleeper
(c) Wit : Jester (d) Renovated : House

13. Choose the most appropriate word from the options given below to complete the following sentence.
If we manage to .... our natural resources, we would leave a better planet for our children.
(a) uphold (b) restrain
(c) cherish (d) conserve

14. Choose the most appropriate word from the options given below to complete the following sentence.
His rather casual remarks on politics .... his lack of seriousness about the subject.
(a) masked (b) belied
(c) betrayed (d) conserve

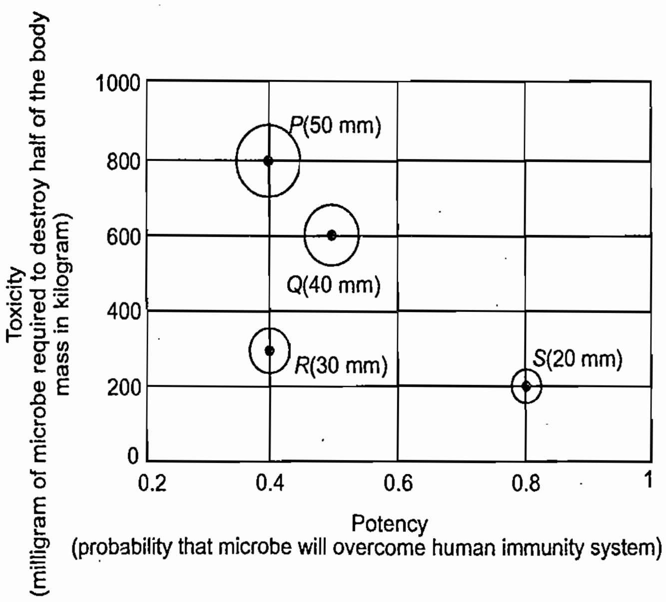
15. 25 persons are in a room, 15 of them play hockey, 17 of them play football and 10 of them play both hockey and football. Then, the number of persons playing neither hockey nor football is
(a) 2 (b) 17
(c) 13 (d) 3

GATE 2011 *(2 Marks Questions)*

16. A container originally contains 10 L of pure spirit. From this container 1 L of spirit is replaced with 1 L of water. Subsequently, 1 L of the mixture is again replaced with 1 L of water and this process is repeated one more time. How much spirit is now left in the container?
(a) 7.58 L (b) 7.84 L
(c) 7 L (d) 7.29 L

17. Few school curriculum include a unit on how to deal with bereavement and grief, and yet all students at some point in their lives suffer from losses through death and parting.
Based on the above passage which topic would not be included in a unit on bereavement?
(a) How to write a letter of condolence
(b) What emotional stages are passed through in the healing process
(c) What the leading causes of death are
(d) How to give support to a grieving friend

18. P, Q, R and S are four types of dangerous microbes recently found in a human habitat. The area of each circle with its diameter printed in brackets represents the growth of a single microbe surviving human immunity system within 24 h of entering the body. The danger to human beings varies proportionately with the toxicity, potency and growth attributed to a microbe shown in the figure ahead.



A pharmaceutical company is contemplating the development of a vaccine against the most dangerous microbe. Which microbe should the company target in its first attempt?

(a) *P* (b) *Q*
(c) *R* (d) *S*

19. The variable cost (*V*) of manufacturing a product varies according to the equation $V = 4q$, where q is the quantity produced. The fixed cost (*F*) of production of same product reduces with q according to the equation $F = 100/q$. How many units should be produced to minimize the total cost $(V + F)$?
(a) 5 (b) 4
(c) 7 (d) 6

20. A transporter receives the same number of orders each day. Currently, he has some pending orders (backlog) to be shipped. If he uses 7 trucks, then at the end of the 4th day he can clear all the orders. Alternatively, if he uses only 3 trucks, then all the orders are cleared at the end of the 10th day. What is the minimum number of trucks so that there will be no pending order at the end of the 5th day?
(a) 4 (b) 5
(c) 6 (d) 7

21. Three friends *R*, *S* and *T* shared toffees from a bowl. *R* took 1/3rd of the toffees, but returned four to the bowl. *S* took 1/4th of what was left but returned three toffees to the bowl. *T* took half of the remainder but returned two back into the bowl. If the bowl had 17 toffees left, how many toffees were originally there in the bowl?
(a) 38 (b) 31
(c) 48 (d) 41

22. Given that $f(y) = |y|/y$ and q is any non-zero real number, the value of $|f(q) - f(-q)|$ is
(a) 0 (b) −1
(c) 1 (d) 2

23. The sum of n terms of the series 4 + 44 + 444 + ... is

(a) $\left(\frac{4}{81}\right)(10^{n+1} - 9n - 1)$

(b) $\left(\frac{4}{81}\right)(10^{n-1} - 9n - 1)$

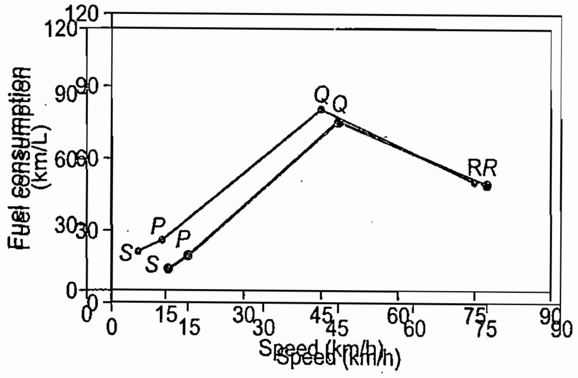
(c) $\left(\frac{4}{81}\right)(10^{n+1} - 9n - 10)$

(d) $\left(\frac{4}{81}\right)(10^{n} - 9n - 10)$

24. The horse has played a little known but very important role in the field of medicine. Horses were injected with toxins of diseases until their blood built up immunities. Then a serum was made from their blood. Serums to fight with diphtheria and tetanus were developed this way.

It can be inferred from the passage, that horses were
(a) given immunity to diseases
(b) generally quite immune to diseases
(c) given medicines to fight toxins
(d) given diphtheria and tetanus serums

25. The fuel consumed by a motorcycle during a journey while travelling at various speeds is indicated in the graph below.



The distances covered during four laps of the journey are listed in the table below.

Lap	Distance (km)	Average speed (km/h)
P	15	15
Q	75	45
R	40	75
S	10	10

From the given data, we can conclude that the fuel consumed per kilometre was least during the lap
(a) *P* (b) *Q*
(c) *R* (d) *S*

GATE 2010

26. Modern warfare has changed from larger scale clashes of armies to suppression, of civilian populations. Chemical agents that do their work silently appear to be suited to such warfare; and regretfully, there exist people in military establishment who think that chemical agents are useful tools for their cause.
Which of the following statements best sums up the meaning of the above passage?
(a) Modern warfare has resulted in civil strife
(b) Chemical agents are useful in modern warfare
(c) Use of chemical agents in warfare would be undesirable
(d) People in military establishments like to use chemical agents in war

27. If 137 + 276 = 435, how much is 731 + 672?
(a) 534 (b) 1403 (c) 1623 (d) 1513

28. 5 skilled workers can build a wall in 20 days; 8 semi-skilled workers can build a wall in 25 days; 10 unskilled workers can build a wall in 30 days. If a team has 2 skilled, 6 semi-skilled and 5 unskilled workers, how long will it take to build the wall?
(a) 20 days (b) 18 days
(c) 16 days (d) 15 days

29. Given digits 2, 2, 3, 3, 3, 4, 4, 4, 4, how many distinct 4 digit numbers greater than 3000 can be formed?
(a) 50 (b) 51
(c) 52 (d) 54

30. Hari (H), Gita (G), Irfan (I) and Saira (S) are siblings (*ie*, brothers and sisters). All were born on 1st January. The age difference between any two successive siblings (that is born one after another) is less than 3 yr. Given the following facts :

i. Hari's age + Gita's age > Irfan's age + Saira's age.
ii. The age difference between Gita and Saira is 1 yr. However, Gita is not the oldest and Saira is not the youngest.
iii. There are not twins.

In what order were they born (oldest first)?
(a) HSIG (b) SGHI
(c) IGSH (d) IHSG

Some More Questions for Practice

(1 Mark Questions)

1. Which of the following options is the closest in meaning to the word given below?
Mirth
(a) Anger
(b) Merriment
(c) Audacity
(d) Blunder

2. Which of the following options is the closest in meaning to the word given below?
Ruminate
(a) Run fast
(b) Reprimand
(c) Think deeply
(d) Spend lavishly

3. Which of the following options is the farthest in meaning to the word given below?
Confidant
(a) Turncoat (b) Arrogant
(c) Confederate (d) Firm

4. Which of the following options is the farthest in meaning to the word given below?
Perfunctory
(a) Quick (b) Slow
(c) Careful (d) Loud

5. Which of the following options is the closest in meaning to the word given below?
Prepossessing
(a) Economical (b) Pleasing
(c) Selfish (d) Wise

Directions (Q. Nos. 6 to 10)
Each of these questions consists of a pair of related words followed by four pairs of words. Select the pair which best expresses the relation in the original pair.

6. Day : Week
(a) Week : Year (b) Second : Time
(c) Time : Duration (d) Week : Month

7. Arc : Curve
(a) Triangle : Base
(b) Rectangle : Square
(c) Revolution : Distance
(d) Square : Polygon

8. Jackal : Dog
(a) Crow : Bat
(b) Orange : Lemon
(c) Tiger : Wolf
(d) Ant : Antepol

9. Error : Mistake
(a) Connection : Retaliation
(b) Literature : Poetry
(c) Music : Art
(d) Doubt : Suspicion

10. Hockey : Game
(a) King : Rule
(b) Constitution : Assembly
(c) Book : Read
(d) Latin : Language

Directions (Q. Nos. 11 to 15)
Choose the most appropriate word from the options given below to complete each sentence.

11. No man had a more .... love for literature or a higher respect for it than Dr. Samuel Johnson.
(a) animated (b) adroit
(c) ardent (d) arduous

12. My father was too .... to open the heavy door.
(a) faint (b) feeble
(c) timid (d) faltering

13. The government should provide attractive tax .... to create the market for quality goods.
(a) revenues (b) structuret
(c) incentives (d) controls

14. The Hubble space telescope will search for planets around other stars, a key to the .... for extraterrestrial life, and examine interstellar dust and gases out of which stars are born.
(a) perception (b) discovery
(c) enquiry (d) quest

15. He knew everything better than anybody else, and it was an effront to his .... vanity that you should disagree with him.
(a) overstrung (b) overweening
(c) overwhelming (d) overwrought

16. A train travels from A to B at the rate of 60 km/h and from B to A at the rate of 40 km/h, then the average rate for the whole journey is
(a) 46 km/h (b) 48 km/h
(c) 50 km/h (d) 52 km/h

17. A watch is offered for sale at ₹ 115 and if that price is reduced by 5%, the dealer who is selling it will still make $9\frac{1}{4}$% profit. How much did the watch cost him?
(a) ₹ 129.25 (b) ₹ 109
(c) ₹ 105 (d) ₹ 100

18. A company buys equal number of red pencils and green pencils. It uses $\frac{7}{8}$ of the red pencils and $\frac{5}{6}$ of the green pencils. Find what fraction of pencils bought remain unused?
(a) $\frac{7}{24}$ (b) $\frac{17}{24}$
(c) $\frac{13}{48}$ (d) $\frac{7}{48}$

19. If a man takes 2 h to row 7 km upstream or 15 km downstream, what is the speed of the current (in km/h)?
(a) 2 (b) 10.5
(c) 3.5 (d) 7.5

20. A reduction of 30% in the price of sugar enables a housewife to buy 6 kg more sugar for ₹ 20. What was the price per kg of sugar before the price reduction?
(a) ₹ $2\frac{1}{3}$ (b) ₹ $3\frac{1}{3}$
(c) ₹ $3\frac{1}{7}$ (d) ₹ $1\frac{3}{4}$

21. Printer A can complete 50 pages in 12 min. Printer B can print the same manuscript in 30 min. In how many minutes will it take for both printers to print a 100 page manuscript?
(a) $17\frac{1}{7}$ (b) $20\frac{1}{7}$
(c) 24 (d) 42

22. The areas of two squares are in the ratio 3 : 1, what is the ratio for their perimeters?
(a) 3 : 1 (b) $1 : \sqrt{3}$ (c) $\sqrt{3} : 1$ (d) 1 : 3

23. The average weight of 24 students in a class is 40 kg. If the weight of the teacher is included, the weight is increased by 500 g. The weight of the teacher is
(a) 52 kg (b) 52.5 kg
(c) 69 kg (d) 53.3 kg

24. A man wishes to divide his monthly savings of ₹ 846 between his two sons and one daughter in the ratio $\frac{1}{4} : \frac{1}{5} : \frac{1}{3}$ respectively. How much did his daughter get?
(a) 270 (b) 216 (c) 360 (d) 300

25. In a fraction, the numerator 8 is less than the denominator. If 3 is added to the numerator, the fraction becomes $\frac{2}{3}$. Then, the fraction is
(a) $\frac{7}{15}$ (b) $\frac{2}{5}$ (c) $\frac{3}{11}$ (d) $\frac{7}{16}$

(2 Marks Questions)

26. Instead of walking along the adjacent sides of a rectangular field, a boy takes a short cut along the diagonal of the field and saves a distance equal to half the longer side. The ratio of the shorter side to that of the longer side is
(a) 1 : 2 (b) 2 : 3
(c) 1 : 4 (d) 3 : 4

27. The proportion of milk and water in two samples is 5 : 2 and 7 : 5. If a mixture comprising of equal quantities of the two samples is made, the proportion of milk and water in the mixture is
(a) 12 : 7
(b) 7 : 12
(c) 109 : 59
(d) 59 : 109

28. An express train moving at a speed of 80 km/h, overtakes a goods train twice as long as the express train and moving in the same direction at a speed of 40 km/h, in 54 s. The time taken by express train to go through a station 400 m long is
(a) 27 s (b) 54 s
(c) 18 s (d) None of these

29. A child was asked to add first few natural numbers (that is, 1 + 2 + 3 + ...) so long his patience permitted. As he stopped, he gave the sum as 575. When the teacher declared the result wrong the child discovered he had missed one number in the sequence during addition. The number he missed was
(a) less than 10 (b) 10
(c) 15 (d) more than 15

30. A colony of bacteria in a container grows by each bacterium splitting into eight next generation bacteria. However, because of environmental conditions only 50% of the bacteria in a generation can split as above. A colony of first generation was put in container and it was found that the number of seventh generation bacteria was 4096 million. What was the size of the first generation population initially put in the container?
(a) 2 million (b) 8 million
(c) 1 million (d) 4 million

31. *N* persons stand on the circumference of a circle at distinct points. Each possible pair of persons, not standing next to each other, sings a two-minute song one pair after the other. If the total time taken for singing is 28 min, what is *N*?
(a) 5 (b) 7
(c) 9 (d) None of these

32. Ram has to travel from Hyderabad to Chennai which is a certain distance apart. 23% of the distance was travelled by bus, 50% of the remaining by train and rest of the distance 231 km by taxi. Find the distance between Hyderabad and Chennai in km.
(a) 600 (b) 462
(c) 231 (d) 856

33. A and *B* can do a piece of work in 45 days and 40 days respectively. They began to do the work together but *A* leaves after some days and then *B* completed the remaining work in 23 days. The number of days after which *A* left the work was how many days?
(a) 6 days (b) 9 days
(c) 12 days (d) 15 days

34. A dishonest businessman professes to sell his articles at cost price but he uses false weight with which he cheats by 10% while buying and by 10% while selling. Find his profit percentage.
(a) 20% (b) 21%
(c) 22.22% (d) 25%

35. In nuts and bolts factory, one machine produces only nuts at the rate of 100 nuts per minute and needs to be cleaned for 5 min after production of every 1000 nuts. Another machine produces only bolts at the rate of 75 bolts per minute and needs to be cleaned for 10 min after production of every 1500 bolts. If both the machines start production at the same time, what is the minimum duration required for producing 9000 pairs of nuts and bolts?
(a) 130 min (b) 135 min
(c) 170 min (d) 180 min

36. Consider a 99 digit number created by writing side by side the first fifty four natural numbers as follows

1 2 3 4 5 6 7 8 9 10 11 12 13............53 54

The above number when divided by 8 will leave a remainder of
(a) 6 (b) 4
(c) 2 (d) 0

37. The distance between two stations *A* and *B* is 600 km. One train leaves station *A* towards station *B* at the average speed of 54 km/h. After an hour another train left station *B* towards station *A* at the average speed of 66 km/h. The distance from station *A* where the two trains meet is?
(a) 272.7 km
(b) 299.7 km
(c) 333.3 km
(d) 387.3 km

38. Amol was asked to calculate the arithmetic mean of ten positive integers each of which had two digits. By mistake, he interchanged the two digits say a and *b*, in one of these ten integers. As a result, his answer for the arithmetic mean was 1.8 more than what it should have been. Then (*b* – *a*) equals.
(a) 1 (b) 2
(c) 3 (d) None of these

39. In a number system, the product of 44 and 11 is 1034. The number 3111 of this system, when converted to the decimal number system, becomes

(a) 406 (b) 1086

(c) 213 (d) 691

40. Three consecutive positive integers are raised to the first, second and third powers respectively and then added. The sum so obtained is a perfect square whose square root equals the total of the three original integers. Which of the following best describes the minimum, say *m*, of these three integers?

(a) $1 \le m \le 3$ (b) $4 \le m \le 6$

(c) $7 \le m \le 9$ (d) $10 \le m \le 12$

41. Speed of a railway engine is 42 km/h when no compartment is attached and the reduction in speed is directly proportional to the square root of the number of compartments attached. If speed of the train carried by this engine is 24 km/h when 9 compartments are attached, then maximum number of compartments that can be carried by the engine is

(a) 49 (b) 48

(c) 46 (d) 47

42. There is a leak in the bottom of a cistern. When the cistern had no leak, it was filled in 2.5 h. It now takes half an hour longer. If the cistern is full of water, how long will it take in leaking itself empty, in case the water leaks out at double the rate after half the cistern becomes empty?

(a) 15 h (b) 11 h 15 min

(c) 11 h 25 min (d) 7.5 h

43. A certain basketball team that has played 2/3 of its games has a record of 17 wins and 3 losses. What is the greatest number of the remaining games that the team can lose and still win at least 3/4 of the total games played?

(a) 4 (b) 7

(c) 5 (d) 6

44. Two typists undertake to do a job. The second typist begins working one hour after the first. Three hours after the first typist has begun working there is still 9/20th of the work to be done. When the assignment is completed, it turns out that each typist has done half the work. How many hours would it take each one to do the whole job individually?

(a) 12, 8 h (b) 8, 5.6 h

(c) 10, 8 h (d) 5, 4 h

45. A student took five papers in an examinations, where the full marks were the same for each paper. His marks in these papers were in the proportion of 6 : 7 : 8 : 9 : 10. In all papers together, the candidate obtained 60% of the total marks. Then, the number of papers in which he got more than 50% marks is

(a) 2 (b) 3

(c) 4 (d) 5

46. Company Alpha buys free-travel coupons from people who are awarded the coupons by Bravo Airlines for flying frequently on Bravo Airplanes. The coupons are sold to people who pay less for the coupons than they would pay by purchasing tickets from Bravo. This marketing of coupons results in lost revenue for Bravo.

To discourage the buying and selling of free-travel coupons, it would be best for Bravo Airlines to restrict the

(a) number of coupons that a person can be awarded in a particular year

(b) limiting the use of the coupons to those who were awarded the coupons and members of the immediate families

(c) days that the coupons can be used from Monday through Friday

(d) amount of time that the coupons can be used after they are issued

47. Opponents of laws that require automobile drivers and passengers to wear seat belts argue that in a free society people have the right to take risks as long as the people do not harm others as a result of taking the risks. As a result, they conclude that it should be each person's decision whether or not to wear a seat belt.

Which of the following, if true, most seriously weaken the conclusion drawn above?

(a) Many new cars are built with seat belts that automatically fasten when someone sits in the front seat

(b) Automobile insurance rates for all automobile owners are higher because of the need to pay for the increased injuries or deaths of people not wearing seat belts

(c) Passengers in airplanes are required to wear seat belts during take-offs and landings

(d) The rate of automobile fatalities in states that do not have mandatory seat belt laws is greater than the rate of fatalities in states that do have such laws

Common Data for Questions 48 and 49

The average life expectancy for the United States population as a whole is 73.9 yr, but children born in Hawaii will live an average of 77 yr, and those born in Louisiana, 71.7 yr. If a newly wed couple from Louisiana were to begin their family in Hawaii, their children would live longer than if the couple began their family in Louisiana.

48. Which of the following, if true, would most significantly strengthen the conclusion drawn in the passage?

(a) 25% of all Louisianians who move to Hawaii live longer than 22 yr

(b) Over the last decade, average life expectancy has risen at a higher rate for Louisianians than for Hawaiians

(c) Environmental factors tending to favour longevity are abundant in Hawaii and less numerous in Louisiana

(d) As population density increases in Hawaii, life expectancy figures for the state are likely to be revised downward

49. Which of the following, if true, would most seriously weaken the conclusion drawn in the passage?

(a) Insurance company statisticians do not believe that moving to Hawaii will significantly lengthen the average Louisiana life

(b) The governor of Louisiana has falsely alleged that statistics of his state are inaccurate

(c) The longevity attributed to Hawaii's current population is attributed mostly to genetically determined factors

(d) 30% of all Louisianians can expect to live longer than 77 yr

50. Blood banks will shortly start to screen all donors for NANB hepatitis. Although the new screening tests are estimated to disqualify upto 5% of all prospective blood donors, they will still miss two-thirds of donors carrying NANB hepatitis. Therefore, about 10% of actual donors will still supply NANB contaminated blood.

The argument above depends on which of the following assumptions?

(a) Donors carrying NANB hepatitis do not, in a large percentage of cases, carry other infections for which reliable screening tests are routinely performed

(b) Donors carrying NANB hepatitis do not, in a large percentage of cases, develop the disease themselves at any point

(c) The number of donors who would be disqualified by tests for NANB hepatitis has been underestimated

(d) The incidence of NANB hepatitis is lower among the potential blood donors then it is in the population at large

Answers with Explanations

1. (b) Amalgamate means combine or unite to form an organization or structure when two companies or organizations merge and become finally one organization, process to becoming a one is amalgamation. So, the best option here is split. Separate on the other hand, although a close synonym, it is too general to be the best antonym in the given question while merge is the synonym, collect is not related.

2. (a) Inexplicable means not explicable, that cannot be explained, understood, or accounted for. So, the best synonym here is incomprehensible.

3. (b) $\log P = \frac{1}{2}\log Q = \frac{1}{3}\log R = k$

∴ $P = b^k, Q = b^{2k}, R = b^{3k}$

Now, $Q^2 = b^{4k} = b^{3k}\, b^k = PR$

4. (c) Contemplate is a transitive verb and hence is followed by a gerund. Hence, the correct usage of contemplate is verb + ing form.

5. (b) The tone of the sentence clearly indicates a word that is similar to understated is needed for the blank. Alternatively, the word should be antonym of strong (fail to make strong impression). Therefore, the best choice is restrained which means controlled/reserved/timid.

6. (c) **7.** (a) **8.** (b) **9.** (b)

10. (a) $P = 40$ votes

$Q = 60$ votes

P loses 15% of 40 votes, *ie*, 6 votes

And Q loses 25% of 60 votes, *ie*, 15 votes

So, finally P got $= 40 - 6 + 15 = 49$ votes

Q got $= 60 - 15 + 6 = 51$ votes

Difference $= 51 - 49 = 2$ votes

So, the total votes is 100.

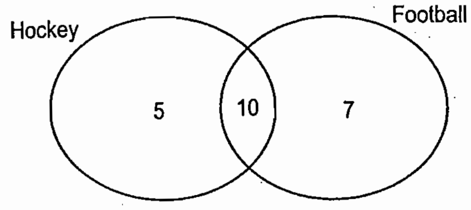
11. (b) Circuitous means round about or indirect.

12. (a) Relationship between the given word is that first word tells the negative quality of record.
So, option (a) is correct because fallow means uncultivated land which is a negative quality.

13. (d) Conserve is the most appropriate word because it means protect or safe.

14. (c) Betrayed is the most appropriate word because it means to tell identity unintentionally.

15. (d)



From the Venn-diagram, it is clear that 5 persons play only hockey.
7 persons play only football.
Total number of persons playing either game

$= 5 + 10 + 7 = 22.$

So, number of persons playing neither hockey nor football $= 25 - 22 = 3$

16. (d) $10\left(\frac{10-1}{10}\right)^3 = 10\left(\frac{9}{10}\right)^3 = 10 \times \frac{729}{1000} = \frac{729}{100}$

∴ $\frac{729}{100} \times 1 = 7.29$ L

17. (c) The given passage clearly deals with how to deal with bereavement and grief. So, after the tragedy occurs and not about precautions. Therefore, irrespective of the causes of death, a school student rarely gets into details of causes which is beyond the scope of the context. Rest all are important in dealing with grief.

18. (d) By observation of the table, we can say S.

	P	Q	R	S
Requirement	800	600	300	200
Potency	0.4	0.5	0.4	0.8

19. (a) Checking with all options in formula

$(4q + 100/q)$ *ie*, $(V + F)$.

Option (a) gives the minimum cost.

20. (c) Let each truck carries 100 units.

$2800 = 4n + e$ (n = normal)

$3000 = 10n + e$ (e = excess/pending)

∴ $n = \frac{100}{3}, \quad e = \frac{8000}{3}$

5 days ⇒ $500x = \frac{5.100}{3} + \frac{8000}{3}$

$$x = \frac{8500}{3 \times 500} = 5.6 \text{ days}$$

So, $x > 5$ days

So, minimum possible days = 6

Hint 7 trucks × 4 days × 100 units = 2800

21. (c) Let the total toffee is x.

R took 1/3, *ie*, $\frac{x}{3}$ but returned 4.

Finally R taken $= \left(\frac{x}{3} - 4\right)$

Remaining toffee $= x - \left(\frac{x}{3} - 4\right)$

$$= x - \frac{x}{3} + 4 = \frac{2x}{3} + 4$$

S took $\frac{1}{4}$, *ie*, $\left(\frac{2x}{3} + 4\right)\frac{1}{4}$ but returned 3.

So, finally S taken $= \left(\frac{2x}{3} + 4\right)\frac{1}{4} - 3 = \frac{x}{6} - 2$

Remainder $= \left(\frac{2x}{3} + 4\right) - \left(\frac{x}{6} - 2\right)$

$$= \frac{2x}{3} + 4 - \frac{x}{6} + 2 = \frac{3x}{6} + 6 = \frac{x}{2} + 6$$

T took half of the remainder, *ie*, $\left(\frac{x}{2} + 6\right)\frac{1}{2}$ but return 2 toffees.

So, T finally taken $= \left(\frac{x}{2} + 6\right)\frac{1}{2} - 2 = \frac{x}{4} + 1$

Remaining $= \left(\frac{x}{2} + 6\right) - \left(\frac{x}{4} + 1\right)$

$$= \frac{x}{2} + 6 - \frac{x}{4} - 1 = \frac{x}{4} + 5$$

and $\frac{x}{4} + 5 = 17$

$$x = (17 - 5) \times 4 = 48$$

22. (d) **23.** (c) **24.** (a) **25.** (b)

26. (d) From the statement of the passage, it is clear that people in military establishments think that chemical agents are useful tool for their cause.
It is not given in the passage that chemical agents are useful or undesirable in modern warfare.

27. (a) 137 + 276 = 435

If 137 and 276 are written in reverse order, then 731 and 672 are obtained.

So, 731 + 672 = reverse order of 435 = 534.

28. (d) 5 skilled workers can build a wall in 20 days.

∴ 2 skilled workers can build the wall in

$$\frac{20 \times 5}{2} \text{ days} = 50 \text{ days}$$

8 semi-skilled workers can build a wall in 25 days.

∴ 6 semi-skilled workers can build the wall in

$$\frac{25 \times 8}{6} \text{ days} = \frac{100}{3} \text{ days}$$

10 unskilled workers can build a wall in 30 days.

∴ 5 unskilled workers can build the wall in 60 days.

One day work of a team of 2 skilled, 6 semi-skilled and 5 unskilled workers

$$= \frac{1}{50} + \frac{3}{100} + \frac{1}{60}$$

$$= \frac{6 + 9 + 5}{300} = \frac{20}{300} = \frac{1}{15}$$

So, this team can complete the work in 15 days.

29. (b) As the number should be greater than 3000.

So, thousand's place can be filled by 3 or 4, *ie*, 2 ways.

Hundred's place can be filled by 2, 3 or 4, *ie*, 3 ways.

Tenth place can be filled by 2, 3 or 4, *ie*, 3 ways.

First place can be filled by 2, 3 or 4, *ie*, 3 ways.

But when all 2's and 3's are used, *ie*, 333, 322, and 422 then there is a limitation for first place.

So, total three such types of numbers have limitation.

Total number of numbers greater than 3000

$$= 2 \times 3 \times 3 \times 3 - 3$$

$$= 54 - 3 = 51$$

30. (b) The age difference between any two successive siblings should be at least 1 yr and at most 2 yr.

So, Gita and Saira are successive siblings.

If Gita is older than Saira,

Then, Hari's age + Gita's age

> Irfan's age + (Gita's age − 1)

⇒ Hari's age > Irfan's age − 1

As there is at least 1 yr age difference.

So, Hari is older than Irfan.

If Gita is younger than Saira,

Then, Hari's age + Gita's age > Irfan's age + (Gita's age + 1)

⇒ Hari's age > Irfan's age + 1

So, Hari is older than Irfan in this case also.

As Gita is not the oldest.

So, correct order is SGHI.

Some More Questions for Practices

1. (b) Mirth means laughter or merriment.

2. (c) Ruminate means musing on a subject or think deeply.

3. (a) Confidant means a person trusted with knowledge on one's private affairs while turncoat means a person who changes sides in a conflict.

4. (c) Perfunctory means something done in a careless manner.

5. (b) Prepossessing means attractive or appealing or pleasing.

6. (d) Immediate upper unit of time after day is week. Similarly, immediate upper unit of time after week is month.

7. (d) An arc is a curve, similarly a square is a polygon.

8. (b) As jackal and dog belong to same class, similarly orange and lemon belong to same class.

9. (d) As error and mistake are synonyms to each other, similarly doubt and suspicion are synonyms to each other.

10. (d) Hockey is a game, similarly Latin is a language.

11. (c) Ardent means intense and it is used for love.

12. (b) The sense in this sentence is that due to physical weakness my father was unable to open the heavy door. So, feeble is the best word to complete the sentence.

13. (c) Incentives means rewads or concession. So, it is the best word to complete the sentence.

14. (d) For can be used only with quest which means search.

15. (b) Overweening means too much pride. So, it is the best word to complete the sentence.

16. (b) As the train travels equal distance on both sides.

So, $\quad \text{average speed} = \dfrac{2 \times 60 \times 40}{60 + 40}$

$$= \frac{4800}{100} = 48 \text{ km/h}$$

17. (d) Marked price of watch = ₹ 115

SP of watch $= 115 \times 0.95 =$ ₹ 109.25

$\therefore \quad \text{CP of watch} = \dfrac{109.25}{109.25} \times 100 =$ ₹ 100

18. (a) Let company buys x number of each type of pencil.

$\therefore \quad \text{Used pencils} = \dfrac{7}{8}x + \dfrac{5}{6}x$

$$= \frac{21x + 20x}{24} = \frac{41x}{24}$$

$\therefore$ Unused pencils $= 2x - \dfrac{41x}{24} = \dfrac{7}{24}x$

So, fraction of pencils remains unused $= \dfrac{7}{24}$

19. (a) Let the speed of man in still water be x and speed of current be y.

$\therefore$ Upstream speed $= x - y$

$\Rightarrow \quad x - y = \dfrac{7}{2} \quad$ ...(i)

$\therefore$ Downstream speed $= x + y$

$\Rightarrow \quad x + y = \dfrac{15}{2} \quad$ ...(ii)

On solving Eqs. (i) and (ii), we get

$x = 5.5$ km/h and $y = 2$ km/h

20. (d) Let the initial price be ₹ x per kg.

$\therefore$ Initial quantity of sugar for ₹ 20 $= \dfrac{20}{x}$ kg

Now, the price of sugar $= 0.7x$ per kg

$\therefore$ New quantity of sugar for ₹ 20

$$\frac{20}{0.7x} - \frac{20}{x} = 6$$

$\Rightarrow \quad \dfrac{20 - 14}{0.7\,x} = 6$

$\Rightarrow \quad 6 = 4.2\,x$

$\Rightarrow \quad x = \dfrac{6}{4.2} = \dfrac{60}{42}$

$$= 1\frac{3}{7} \text{ per kg}$$

21. (a) Printer A can print 50 pages in 12 min.
So, printer A can print 100 pages in 24 min.
Printer B can print 50 pages in 30 min.
So, printer B can print 100 pages in 60 min.

So, both printers can print 100 pages in $\dfrac{24 \times 60}{24 + 60}$ min

$$= \frac{1440}{84} \text{ min} = 17\frac{1}{7} \text{ min}$$

22. (c) Ratio of areas of two squares $= 3:1$

∴ Ratio of sides of two squares $= \sqrt{3}:1$

∴ Ratio of perimeters of two squares $= \sqrt{3}:1$

23. (b) Average weight of 24 students = 40 kg

Total weight of 24 students = 960 kg

Average weight of 24 students and the teacher

= 40.5 kg

Total weight of 24 students and the teacher

= 1012.5 kg

∴ Weigth of teacher = 1012.5 − 960 = 52.5 kg

24. (c) Ratio of amount $= \frac{1}{4}:\frac{1}{5}:\frac{1}{3}$

$= 15:12:20$

So, amount of daughter $= \frac{20}{15+12+20} \times 846$

$= \frac{20}{47} \times 846 =$ ₹ 360

25. (a) Let the denominator be x.

So, the numerator $= x - 8$

Now, $\frac{x-8+3}{x} = \frac{2}{3}$

$\Rightarrow \quad 3x - 15 = 2x$

$\Rightarrow \quad x = 15$

∴ Fraction $= \frac{15-8}{15} = \frac{7}{15}$

26. (d) Let shorter side be x and longer side be y.

∴ Length of diagonal $= \sqrt{x^2+y^2}$

$$(x+y) - \sqrt{x^2+y^2} = \frac{1}{2}y$$

$$\Rightarrow \quad x + \frac{1}{2}y = \sqrt{x^2+y^2}$$

$$\Rightarrow x^2 + \frac{1}{4}y^2 + 2 \times \frac{1}{2}xy = x^2 + y^2$$

$$\Rightarrow \quad xy = \frac{3}{4}y^2$$

$$\Rightarrow \quad x = \frac{3}{4}y$$

$$\Rightarrow \quad \frac{x}{y} = \frac{3}{4}$$

27. (c) LCM of (5 + 2) and (7 + 5) = 84

Let 84 L of each sample is mixed.

Quantity of milk in this mixture $= \frac{5}{7} \times 84 + \frac{7}{12} \times 84$

$= 109$ L

Quantity of water in this mixture $= \frac{2}{7} \times 84 + \frac{5}{12} \times 84$

$= 59$ L

∴ Required ratio $= 109:59$

28. (a) Let the length of express train be x metre.

As both trains are running in opposite directions.

So, relative speed = 80 − 40

= 40 km/h

$= 40 \times \frac{5}{18}$ m/s

Distance = Speed × Time

$$x + 2x = 40 \times \frac{5}{18} \times 54$$

$$\Rightarrow \quad 3x = 40 \times 5 \times 3$$

$$\Rightarrow \quad x = 200 \text{ m}$$

∴ Required time $= \frac{200+400}{80 \times \frac{5}{18}}$

$= \frac{600 \times 18}{80 \times 5} = 27$ s

29. (d) Let the child was asked to add first n natural numbers and the number missed was x.

$$\therefore \quad (1+2+3+\ldots n) - x = 575$$

$$\Rightarrow \quad \frac{n(n+1)}{2} - x = 575$$

For $n = 33$,

$$\frac{n(n+1)}{2} = 561$$

For $n = 34$,

$$\frac{n(n+1)}{2} = 595$$

So, $x = 595 - 575 = 20$

So, x is more than 15.

30. (c) Bacteria are increasing by four times in next generation.

So, they are forming a GP with common ratio 4.

Let the size of first generation be a million.

$$\therefore \quad a(r)^{7-1} = 4096$$

$$\Rightarrow \quad a \times 4^6 = 4096$$

$$\Rightarrow \quad a = \frac{4096}{4096} = 1$$

31. (b) Each person can be paired with $(N-3)$ persons. (*ie*, excluding himself and the adjacent two persons)

So, total number of pairs $= \dfrac{N(N-3)}{2}$

Total time taken for ringing $= \dfrac{N(N-3)}{2} \times 2$

$$\Rightarrow \quad N(N-3) = 28$$
$$\Rightarrow \quad N^2 - 3N - 28 = 0$$
$$\Rightarrow \quad (N-7)(N+4) = 0$$
$$\Rightarrow \quad N = 7 \text{ as } N \neq -4$$

32. (a) Let the distance between Hyderabad and Chennai be x km.

$\therefore$ Distance travelled by bus $= 0.23x$

Distance travelled by train $= \dfrac{1}{2} \times 0.77x$

$$= 0.385\,x$$

$\therefore$ Remaining distance $= x - (0.23x + 0.385x)$

$$= 0.385\,x$$
$$0.385\,x = 231$$
$$\therefore \quad x = \frac{231}{0.385} = 600 \text{ km}$$

33. (b) 1 day work of A and $B = \dfrac{1}{45} + \dfrac{1}{40} = \dfrac{17}{360}$

So, A and B together can complete the work in $\dfrac{360}{17}$ days.

23 days work of $B = \dfrac{23}{40}$

$\therefore$ Work done by A and $B = 1 - \dfrac{23}{40} = \dfrac{17}{40}$

So, A and B can do $\dfrac{17}{40}$ part of work in $\dfrac{17}{40} \times \dfrac{360}{17}$ days

$= 9$ days

So, A left the work after 9 days.

34. (c) In place of 100 g weight, he uses 110 g weight while buying and 90 g weight while selling.

So, he gained 20 g after selling 90 g.

$\therefore$ Profit percentage $= \dfrac{20}{90} \times 100 = 22.22\%$

35. (c) Time required to produce 1000 nuts = 10 min

Now, machine needs to be cleaned for 5 min.

So, time required to produce 8000 nuts

$$= 8 \times 15 = 120 \text{ min}$$

Time required to produce 900 nuts = 130 min

Time required to produce 1500 bolts = 20 min

Now, machine needs to be cleaned for 10 min.

So, time required to prodcue 7500 bolts = 150 min

Time required to produce 900 bolts = 170 min

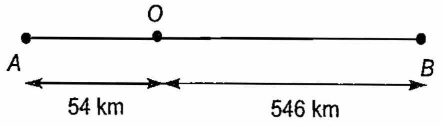
So, time required to produce 9000 pairs of nuts and bolts = 170 min

36. (c) We know that, if a number formed from the last 3 digits of a number is divisible by 8, then the whole number is also divisible by 8.

So, required remainder

= Remainder when 354 is divided by 8 = 2

37. (b)



In 1h, first train covers 54 km.

As trains are running in opposite directions.

So, relative speed = 54 + 66 = 120 km/h

$\therefore$ Required time $= \dfrac{546}{120} = 4.55$ h

Distance travelled by first train before the meeting of trains = 54 + 4.55 × 54 = 299.7 km

38. (b) Arithmetic mean of 10 integers is increased by 1.8.

So, sum of these 10 integers in increased by 18.

$$(10b + a) - (10a + b) = 18$$
$$\Rightarrow \quad 9b - 9a = 18$$
$$\Rightarrow \quad b - a = 2$$

39. (a)

$$\begin{array}{r} 4\;4 \\ \times\;1\;1 \\ \hline 4\;4 \\ 4\;4 \\ \hline 1\;0\;3\;4 \end{array}$$

From the above calculation it is clear that the base of given number system is 5.

$$(3111)_5 = 3 \times 5^3 + 1 \times 5^2 + 1 \times 5^1 + 1 \times 5^0$$
$$= 375 + 25 + 5 + 1$$
$$= 406$$

40. (a) Three positive integers are m, $(m+1)$ and $(m+2)$.

$$m + (m+1)^2 + (m+2)^3 = (m + m + 1 + m + 2)^2$$
$$\Rightarrow \quad m + m^2 + 1 + 2m + m^3 + 8 + 6m(m+2) = (3m+3)^2$$
$$\Rightarrow \quad m^3 - 2m^2 - 3m = 0$$
$$\Rightarrow \quad m^2 - 2m - 3 = 0$$

$$\Rightarrow \quad (m-3)(m+1)=0$$

So, $\quad m = 3 \quad \text{as} \quad m \neq -1$

41. (b) $S = 42 - k\sqrt{n}$

where, S is the speed of the engine.
k is the constant.
n is the number of compartments.

$$24 = 42 - k\sqrt{9}$$

$$\Rightarrow \quad 3k = 18$$

$$\Rightarrow \quad k = 6$$

$$S = 42 - 6\sqrt{n}$$

For $n = 49$, $S = 0$

So, maximum number of compartments that can be carried by the engine is 48.

42. (c) Let leak can empty the cistern in x hour at normal rate.

$$\frac{1}{2.5} - \frac{1}{x} = \frac{1}{3}$$

$$\Rightarrow \quad \frac{1}{x} = \frac{1}{2.5} - \frac{1}{3}$$

$$\Rightarrow \quad x = 15 \text{ h}$$

Now, half the cistern becomes empty in 7.5 h after this rate of emptying doubles.

So, remaining half part of cistern empty in $\frac{7.5}{2}$ h.

$$\therefore \quad \text{Total time} = \left(7.5 + \frac{7.5}{2}\right) \text{h}$$

$$= 11.25 \text{ h} = 11 \text{ h } 25 \text{ min}$$

43. (a) $\frac{2}{3}$ of total games $= 17 + 3$

$\therefore$ Total number of games $= 20 \times \frac{3}{2} = 30$

$\frac{3}{4}$ of total games $= \frac{3}{4} \times 30 = 22.5$

So, team has to win at least 23 games.
So, team can lose at most 4 more games.

44. (c) Let first typist takes x hour to complete the job while second typist takes y hour to complete the job.
When first typist typed for 3 h, second typist typed for 2 h.

Total work was completed $= \frac{11}{20}$

$$\therefore \quad \frac{3}{x} + \frac{2}{y} = \frac{11}{20} \qquad \text{...(i)}$$

Since, both typists had done half the work.

So, first typist typed for $\frac{x}{2}$ h while second typist typed for $\frac{y}{2}$ h.

$$\text{But} \quad \frac{x}{2} - \frac{y}{2} = 1 \qquad \text{...(ii)}$$

On solving Eqs. (i) and (ii), we get

$$x = 10 \text{ h} \quad \text{and} \quad y = 8 \text{ h}$$

45. (c) Let the marks obtained in five papers be $6x$, $7x$, $8x$, $9x$ and $10x$.

$$\frac{6x + 7x + 8x + 9x + 10x}{5} = 60\% \text{ of total marks}$$

$$\Rightarrow \quad \frac{40x}{5} = 60\% \text{ of total marks}$$

$$\Rightarrow \quad 8x = 60\% \text{ of total marks}$$

$$\Rightarrow \quad x = 7.5\% \text{ of total marks}$$

So, except the subject in which he got $6x$ marks, in other 4 subjects he got more than 50% of marks.

46. (b) The loss for Bravo is due to the marketing of the coupons. These coupons are used by other persons in place of those who were awarded the coupons. So, the use of coupons should be limited to those who were awarded the coupons and their immediate family members.

47. (b) The conclusion of the paragraph is that, automobile drivers and passengers not wearing seat belts should be allowed to do it as we are living in a free society where people can take risks on themselves. But option (b) goes against it.

48. (c) It is given in the paragraph that life expectancy in Hawaii is more than that of in Louisiana. This may be due to some environmental factors tending to favour longevity are more in Hawaii and less in Louisiana.

49. (c) From the paragraph it can be concluded that if couples from other places began their family in Hawaii then their children will live longer. This is because in Hawaii geography and living conditions are much better than other places. But this is not because genetically determined factros as given in option (c). If it is true then only those person have higher life expectancy who have their roots in Hawaii.

50. (a) From the paragraph it can be concluded that about 10% of actual donors will supply NANB contaminated blood even after the screening of all donors. It should be confirmed that these donors do not have any other infections for which reliable screening tests are routinely performed.

GATE

Practice Sets (1-3)

Practice Set 1

GATE Chemistry

Duration : 3 Hours **Maximum Marks : 100**

1. All questions in this paper are of objective type.
2. There are total of 65 questions carrying 100 marks.
3. Questions 1-25 will carry 1 mark each and questions 26-55 will carry 2 marks each.
4. Questions 48-51 (2 pairs) are common data questions and question pairs 52-55 are linked answer questions. The answer to the second question of the linked answer questions depends on the answer to the first question of the pair. If the first question in the linked pair is wrongly answered or is unattempted, then the answer to the second question in the pair will not be evaluated.
5. Questions 56 to 65 belong to General Aptitude (GA). Questions 56-60 will carry 1 mark each and questions (61-65) will carry 2 marks each.
6. Unattempted questions will carry zero marks.
7. Wrong answers will carry **negative** marks. For 1-25 and 56-60, $\frac{1}{3}$ marks will be deducted for each wrong answer. For 26 to 51 and 61 to 65, $\frac{2}{3}$ mark will be deducted for each wrong answer. The question pairs 52-53 and 54-55 are questions with linked answers. There will be negative marks only for wrong answer to the first question of the linked answer question pair *i.e.*, for Q. 52 and Q. 54, $\frac{2}{3}$ mark will be deducted for each wrong answer. There is no negative marking for Q. 53 and Q. 55.

(1 Mark Questions)

1. For which one of the following ions, the colour is not due to *d*-*d* transition ?

(a) CrO_4^{2-} (b) $Cu(NH_3)_4^{2+}$

(c) $Ti(H_2O)_6^{3+}$ (d) CoF_6^{3-}

2. Suppose an electron moves with one half of the velocity of light. To which part of the electromagnetic spectrum would its de-Broglie wavelength correspond?

(a) γ-rays

(b) X-rays

(c) Ultraviolet radiation

(d) Visible radiation

3. A particle of mass *m* is confined to a cubical box of side length, a. Its zero point energy is

(a) zero (b) $h^2/8ma^2$

(c) $3h^2/8ma^2$ (d) $6h^2/8ma^2$

4. A particle of mass *m* is confined to a square of side length, a. Its first excited state is

(a) non degenerate with energy $= h^2/4ma^2$

(b) two fold degenerate with energy $= 5h^2/8ma^2$

(c) two fold degenerate with energy $= 3h^2/8ma^2$

(d) non degenerate with energy $= 5h^2/8ma^2$

5. The benzene molecule has

(a) non degenerate MO_s

(b) three degenerate bonding MO_s

(c) one pair of degenerate MO_s

(d) two pairs of degenerate MO_s

6. In CH_4, the contribution α of the 2*s* orbital of carbon to each of the hybrid orbitals (of the form $\alpha\psi_{2s} + \beta_1\psi_{2px} + \beta_2\psi_{2py} + \beta_3\psi_{2px}$) is

(a) 1/3 (b) $1/\sqrt{2}$

(c) $1/\sqrt{3}$ (d) 1/2

7. The number of nodes in a 4*p* orbital is

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

8. A positron and an electron by mutual annihilation produce

(a) either one photon or two photons

(b) only one photon

(c) either two photons or three photons

(d) one, two or three photons depending on the conditions

9. Which one of the following is most easily reduced?
(a) $H_4P_2O_7$ (b) $Cr(CO)_6$
(c) $Fe(CO)_5$ (d) $Ni(CO)_4$

10. Which one of the following molecules exists as a monomer under ambient conditions?
(a) Trimethyl aluminium
(b) Triethyl aluminium
(c) Triphenyl aluminium
(d) Trimesityl aluminium

11. Which one of the following complex ions shows the minimum intensity of adsorption in the UV-visible region?
(a) $[Cr(H_2O)_6]^{2+}$ (b) $[V(H_2O)_6]^{2+}$
(c) $[Mn(H_2O)_6]^{2+}$ (d) $[Co(H_2O)_6]^{2+}$

12. Diels-Alder reaction normally yields endo-adducts as a major product. This is due to
(a) higher stability of the product
(b) faster rate of formation of the endo-adduct
(c) steric hindrance
(d) secondary orbital interaction between a diene and a dienophile

13. The perhydroxylation of maleic and fumaric acids using $KMnO_4$ leads respectively to the following tartaric acids
(a) meso and meso
(b) *d*, *l* racemate and meso
(c) meso and *d*, *l* racemate
(d) *d*, *l* racemate and *d*, *l* racemate

14. Lithium dialkyl amide base on reaction with cyclohexanone, abstracts
(a) axial hydrogen preferentially
(b) equatorial hydrogen preferentially
(c) axial and equatorial hydrogen in non-preferentially manner
(d) neither axial nor equatorial hydrogen

15. How many states (distinguished by the quantum number m_l) being to the ground state of the chlorine (atomic number : 17) atom?
(a) 4 (b) 1 (c) 3 (d) 2

16. Which one of the following statements for haemoglobin is not true?
(a) The binding with O_2 is weaker in comparison with myoglobin
(b) Iron is 5-coordinated
(c) Iron is coplanar with prorphyrin ring in the absence of oxygen
(d) The oxidation state of iron is +2

17. For $H_3(PMo_{12}O_{40})$ which one of the following statements is not true?
(a) The nearest neighbours of P are 4 oxygen atoms
(b) The nearest neighbours of Mo are 6 oxygen atoms
(c) It is called a 12-heteropoly acid
(d) It is synthesized by heating phosphate solution with ammonium molybdate and NaOH

18. Which one of the following statements for borazine is not correct?
(a) It has six B—H bonds
(b) It has three B═N bonds
(c) It has three N—H bonds
(d) It has a cyclic structure

19. One mole of an ideal gas ($C_p = 29.234\ JK^{-1}mol^{-1}$) is expanded reversibly and adiabatically from 1 dm^3 to 10 dm^3. If the initial temperature is 750 K, the final temperature will be
(a) 1000 K (b) 750 K (c) 300 K (d) 100 K

20. The dissociation constant of a weak acid *HA* is 2.5×10^{-5} at 25°C. The degree of hydrolysis of 0.01 M of its sodium salt Na*A* will be approximately
(a) 2×10^{-10} (b) 2×10^{-14}
(c) 0.02 (d) 2×10^{-4}

21. The overall rate $d[P]/dt$ for the reaction $2A \overset{K}{\rightleftharpoons} B;\ B + C \xrightarrow{k_t} P$ is given by
(a) $Kk_t[A]^2[C]$ (b) $K[A][B]$
(c) $k_t[B][C]$ (d) $Kk_t[A]^2[B][C]$

22. The wavelength of light emitted when electron falls from the $n = 50$ orbit to the $n = 49$ orbit of the H-atom, is
(a) 55 nm (b) 0.55 cm (c) 0.55 Å (d) 55 m

23. Energy of activation of an exothermic reaction is
(a) negative (b) positive
(c) zero (d) can't be predicted

24. The strongest acid (in the gas phase) is
(a) H_2O (b) HCl (c) HI (d) CH_4

25. NO_2^+ is
(a) oxidizing agent (b) Lewis base
(c) non-linear (d) nitrating agent

(2 Marks Questions)

26. The reaction of potassium phthalimide with ethyl chloroacetate followed by hydrolysis results in
(a) glycine (b) alanine
(c) leucine (d) valine

27. The compressibility factor for an ideal gas is
(a) 1 (b) 1.5
(c) 2 (d) ∞

28. The point group symmetry of *p*-dichlorobenzene is
(a) C_{2v} (b) D_{2h}
(c) D_3 (d) C_{2h}

29. A certain buffer solution contains equal concentrations of A^- and HA. The K_b for A^- is 10^{-10}. The pH of the buffer is
(a) 7 (b) 10
(c) 4 (d) 14

30. Nitrous acid can behave
(a) only as an oxidant
(b) only as a reductant
(c) both as oxidant and reductant
(d) as a drying agent

31. The structure of XeF_4 is
(a) tetrahedral (b) square pyramid
(c) square planar (d) octahedral

32. XeF_2 on hydrolysis yields
(a) $XeOF_4$ (b) XeO_3
(c) XeO_2F_2 (d) Xe

33. Which of the following compounds is optically active ?
(a) $Pt(NH_3)_2Cl_2$ (b) $Ni(CO)_2(PPh_3)_2$
(c) *Trans*-Co $(en)_2Cl_2$ (d) *Cis*-Co $(en)_2Cl_2$

34. The complexes $[Co(1, 2\text{-diaminopropane})_2\ Cl_2]^+$ and $[Co(1, 3\text{-diaminopropane})_2Cl_2]^+$ represent an example of
(a) ligand isomerism
(b) linkage isomerism
(c) ionization isomerism
(d) coordination isomerism

35. Aqueous titanium (IV) solution develops intense orange colour on addition of H_2O_2. The colour is due to
(a) *d-d* transition
(b) IV → II transition of the peroxo group
(c) reduction of the Ti(IV) to Ti(III)
(d) charge transfer transition

36. The enthalpy of vaporization of water is zero
(a) at 0°C
(b) at the critical temperature
(c) at the boiling point
(d) under no conditions

37. Which one of the following metals could not be obtained on electrolysis of aqueous solution of its salts?
(a) Mg (b) Ag
(c) Cu (d) Cr

38. On passing 0.1 Faraday of electricity through aluminium, metal deposited on cathode is (Al = 27)
(a) 0.3 g (b) 0.6 g
(c) 0.9 g (d) 1.2 g

39. For the reaction, $2A + B \rightarrow$ products, rate law, $r = k[A][B]$ the active mass of *B* is kept constant and of *A* is doubled. The rate of reaction will be then
(a) decrease 4 times (b) decrease 2 times
(c) increase 4 times (d) increase 2 times

40. The minimum energy required for a molecule to take part in a reaction is called
(a) threshold energy
(b) nuclear energy
(c) potential energy
(d) kinetic energy

41. In an isochoric process, the increase in internal energy is
(a) equal to the heat absorbed
(b) equal to the heat evolved
(c) equal to the work done
(d) equal to the sum of the heat adsorbed and work done

42. For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter, ΔU and W correspond to
(a) $\Delta U < 0, W = 0$ (b) $\Delta U = 0, W < 0$
(c) $\Delta U > 0, W = 0$ (d) $\Delta U = 0, W > 0$

43. A container has hydrogen and oxygen mixture in ratio of 1:1 by weight, then
(a) internal energy of the mixture decreases
(b) internal energy of the mixture increases
(c) entropy of the mixture increases
(d) entropy of the mixture decreases

44. Which of the following can act both as Bronsted acid and Bronsted base?
(a) Cl^- (b) HCO_3^-
(c) H_3O^+ (d) OH^-

45. K_{sp} of an electrolyte *AB* is 1×10^{-10}, $[A^+] = 10^{-5}$M. Which concentration of B^- will not give precipitate of *AB*?
(a) 5×10^{-6} (b) 1×10^{-5}
(c) 2×10^{-5} (d) 5×10^{-5}

46. Chemical equations convey quantitative information on the
(a) type of atom/molecules taking part in the reaction
(b) relative number of moles of reactants and products involved in the reaction
(c) number of atom/molecules of the reactants and products involved in the reaction
(d) quantity of reactant consumed and quantity of product formed

47. The effect of increasing the pressure on the equilibrium, $2A + 3B \rightleftharpoons 3A + 2B$, is
(a) forward reaction is favoured
(b) backward reaction is favoured
(c) no effect
(d) None of the above

Common Data for Questions 48 to 51

Elements of boron family have two electrons in the *s*-orbital and one electron in the *p*-orbital of the valence shell. These elements are expected to exhibit a oxidation state of +3 uniformly. Actually boron and aluminium exhibit a oxidation state of +3 only but other elements *i.e.*, gallium, indium and thallium besides group oxidation states, exhibit a lower oxidation state.

48. Elements of group 13
(a) exhibit a oxidation state of +1 only
(b) form M^{2+} and M^{3+} ions
(c) exhibit oxidation state of +1 and +3
(d) form M^- and M^{3-} ions

49. Ga^+ and In^+ undergo disproportionation reaction in aqueous reaction because
(a) in Ga and In +3 oxidation state is less stable than +1 oxidation state
(b) in Ga and In +1 oxidation state is less stable than +3 oxidation state
(c) in aqueous solution, Ge^+ has a tendency to convert into Ge^{3+} only
(d) None of the above

50. Which of the following is correct?
(a) Tl^{3+} salts are strong reducing agent
(b) Ge^+ undergoes self oxidation in aqueous solution
(c) In boron +1 oxidation state is more stable
(d) In^+ undergoes self oxidation and reduction in aqueous solution

51. Which of the following is the strongest oxidizing agent?
(a) Tl^{3+} (b) In^{3+}
(c) Ga^{3+} (d) Al^{3+}

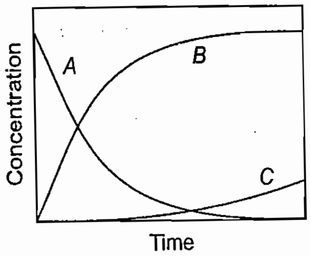
Statement for Linked Answer Questions 52 and 53

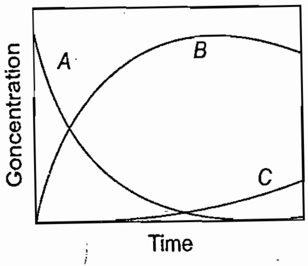
A reaction proceeds through the formation of an intermediate *B* in a unimolecular reaction

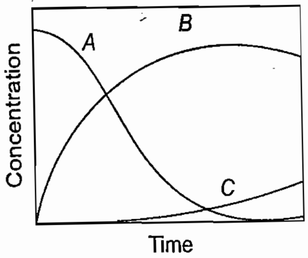
$$A \xrightarrow{k_a} B \xrightarrow{k_b} C$$

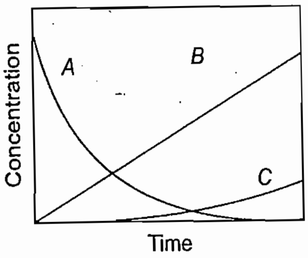
52. The integrated rate law for this reaction is
(a) $[A] = [A]_0 e^{-k_a t}$
(b) $[A] = [A]_0 (e^{-k_a t} - e^{-k_b t})$
(c) $[A] = \dfrac{[A]_0}{2}\left(1 + \dfrac{k_a e^{-k_b t} - k_b e^{-k_a t}}{k_a - k_b}\right)$
(d) $[A] = [A]_0(1 + e^{-k_a t} - e^{-k_b t})$

53. If $k_a >> k_b$, then concentration *vs* time plot for the above reaction is

(a)


(b)


(c)


(d)


Linked Answer Questions 54 and 55

54. For the complex ion $[Cu(NH_3)_6]^{2+}$, the coordination geometry will be
(a) octahedral
(b) tetragonally distorted octahedral

(c) trigonal prismatic
(d) trigonal and prismatic

55. The number of possible *d-d* transitions will be
(a) one (b) two (c) three (d) four

General Aptitude

56. Which of the following options is closest in meaning to the word given below?
Pinnacle
(a) Foothills (b) Pass
(c) Peak (d) Excess

57. The question below consists of a pair of related words followed by four pairs of words. Select the pair which best expresses the relation in the original pair.
Water : Oxygen
(a) Helium : Nitrogen (b) Salt : Sodium
(c) Tree : Plant (d) Food : Hunger

58. Choose the most appropriate word from the options given below to complete the following sentence Comparatively few rock musicians are willing to laugh at themselves, although a hint of ...... can boost sales of video clips very nicely.
(a) self deprecation (b) congeniality
(c) cynicism (d) embarrassment

59. In a direct election between two contestants, 4% of the votes cast are declared to be illegal. One contestant secures 55% of the valid votes and wins with a majority of 240 votes. What is the total number of votes cast?
(a) 2455 (b) 2400
(c) 2500 (d) None of these

60. There are two groups *A* and *B* consisting of 30 and 70 students respectively. If the average weight of group *A* is 30 kg and that of group *B* is 70 kg. Find the average weight of all the students of group *A* and group *B*.
(a) 58 kg (b) 50 kg
(c) 40 kg (d) 42 kg

61. A program instituted in a particular state allows parents to prepay their children's future college tuition fee at current rates. The program then pays the tuition annually for the child at any of the state's public colleges in which the child enrolls. Parents should participate in the program as a means of decreasing the cost of their children's college education.

Which of the following, if true is the most appropriate reason for parents not to participate in the program?
(a) The parents are unsure about which public college in the state the child will attend
(b) The amount of money accumulated by putting the prepayment funds in an interest bearing account today will be greater than the total cost of tuition for any of the public colleges when the child enrolls
(c) The annual cost of tuition at the state's public colleges is expected to increase at a faster rate than the annual increase in the cost of living
(d) Some of the state's public colleges are contemplating large increases in tuition next year

62. The value of a silver coin is directly proportional to the $(\text{diameter})^2$ when the thickness is same and is directly proportional to thickness when the diameter is same. If two silver coins have their diameters in the ratio of 4 : 3, then what is the ratio of thicknesses of the two silver coins, if value of 1st coin is 4 times that of the 2nd coin?
(a) 4 : 9 (b) 9 : 4
(c) 9 : 16 (d) 16 : 9

63. A man can row 15 km upstream and 22 km downstream in 5 h. Also he can row 20 km upstream and 27.5 km downstream in $6\frac{1}{2}$ h. Find the rate of current and the speed of the man in still water respectively.
(a) 8 km/h, 3 km/h (b) 3 km/h, 8 km/h
(c) 5 km/h, 11 km/h (d) 11 km/h, 5 km/h

64. *A* supplies 20 men who work for 8 h a day for 6 days. *B* supplies 15 men working at 9 h day for 7 days and C supplies 10 men working 6 h a day for 8 days to do a certain job. If ₹ 636 is paid for all the labour, what is C's share ?
(a) ₹ 102 (b) ₹ 128 (c) ₹ 136 (d) ₹ 144

65. In a certain township 1/5 of the housing units are equipped with cable television 1/10 of the housing units are equipped with videocassette recorders and 1/3 of those having cable television have videocassette recorders. What fraction of the housing units have neither cable television nor videocassette recorder?
(a) 7/10 (b) 23/30
(c) 11/15 (d) 1.6

Answers with Explanations

1. (a) In CrO_4^{2-}, Cr (VI) has d^0 configuration. So, there is no *d-d* transition. The colour is due to charge transfer.

2. (a) $\lambda = h/m_0v$, Given, $v = 0.5\ c$

We have
$$\lambda = \frac{h}{(0.5 \times m_0c)}$$
$$= 2 \times \frac{h}{m_0c} = 2 \times 2.425\ \text{pm}$$
$$= 4.850 \times 10^{-12}\ \text{m}$$
$$= 0.0485\ \text{Å}$$

So, the wavelength corresponds to gamma rays.

3. (c) $\frac{h^2}{8ma^2}(n_1^2 + n_2^2 + n_3^2)$, where, $n_1 = n_2 = n_3 = 1$ for zero point energy.

So, we have $\frac{3h^2}{8ma^2}$ = zero point energy

4. (b) $E = \frac{h^2}{8ma^2}(n_1^2 + n_2^2)$

First excited state corresponds to $(n_1 = 1, n_2 = 2)$ and $(n_1 = 2, n_2 = 1)$

So, two-fold degeneracy.

$$\therefore \qquad \text{Energy} = \frac{5h^2}{8ma^2}$$

5. (d) It has two pairs of degenerate orbitals (e_{1g}) giving the ground state configuration $a_{2u}^2 e_{1g}^4$.

6. (d) Since, the orbitals are equally divided among the four hybrids, $\alpha^2 = \frac{1}{4}$

So, $\qquad \alpha = \frac{1}{2}$

7. (b) Number of nodes $= n - 1 = 4 - 1 = 3$. (One nodal plane and two nodal spheres).

8. (a) A position may be annihilated with a electron by two distinct process. (I) If it is annihilated by a free electron, the energy must reappear in the form of atleast two quanta to satisfy the conservation laws (II) and if it is annihilated by a bound electron, energy may appear in the form of a single quantum since the nucleus of the atom in which the electron is bound, is available to take up excess momentum.

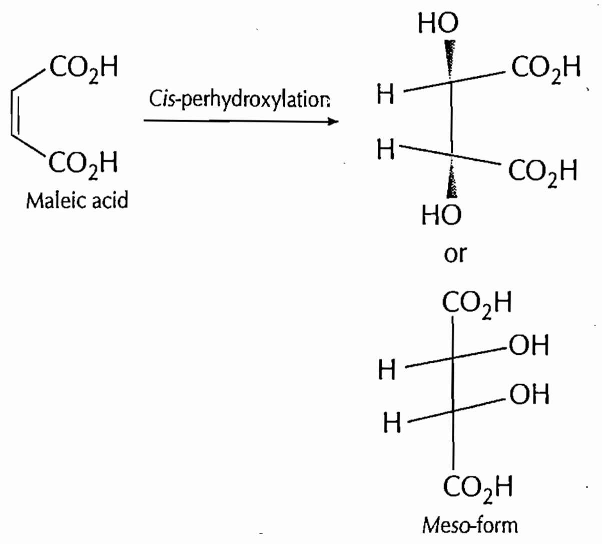
9. (a) $H_4P_2O_7$ as in it P is present in its highest oxidation state, *i.e.*, +5. All other follow 18-electron rule.

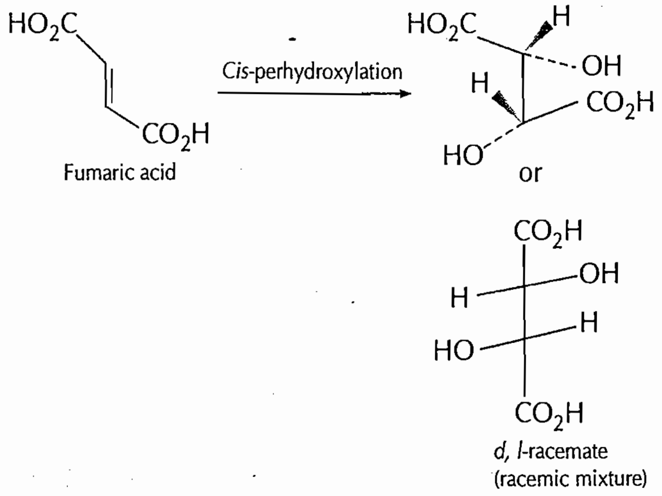
10. (d) Due to steric hindrance, trimesityl aluminium does not dimerize.

11. (c) $[Mn(H_2O)_6]^{2+}$ shows the minimum intensity of adsorption in the UV-visible region, since spin selection rule ($\Delta S = 0$) is not obeyed.

12. (d) The secondary interaction of orbitals in the transition state is not sterically possible for the exo-product.

13. (c)





14. (a) The hydrogen is abstracted from the axial position due to stereo electronic factors.

15. (d) Ground state of Cl atom : $1s^2, 2s^2, 2p^6, 3s^2 3p^5$

$$S = n \times \frac{1}{2} = 1 \times \frac{1}{2} = +1/2$$

∴ Number of possible values of

$$J = 2S + 1 = 2$$

16. (c) In the absence of oxygen, Fe^{2+} is not coplanar with the porphyrin ring.

17. (d) Conc. HNO_3 should be used in the place of NaOH.

18. (a) Borazine has three B—H bonds and not six.

19. (c) $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$ $\frac{T_2}{T_1} = \left(\frac{1}{10}\right)^{0.397}$

$$\left(\frac{C_p}{C_V} = \frac{29.234}{29.234 - 8.314} = 1.397\right)$$

$$\frac{T_2}{T_1} = 0.4009\ ;\ T_2 = 750 \times 0.4009 = 300.7\ \text{K}$$

20. (d)
$$K_h = \frac{10^{-14}}{2.5 \times 10^{-5}}$$

$$0.4 \times 10^{-9} = 4 \times 10^{-10}$$

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$h = \sqrt{\frac{k_b}{c}} = \sqrt{\frac{4 \times 10^{-10}}{0.01}}$$

$$\alpha = 2 \times 10^{-4}$$

21. (a) $\frac{d[P]}{dt} = k_t[B][C]$ ...(i)

Equilibrium constant,

$$K = \frac{[B]}{[A]^2} \quad \text{or} \quad [B] = K[A]^2 \qquad \text{(ii)}$$

From Eqs. (i) and (ii),

$$\frac{d[P]}{dt} = k_t K[A]^2[C]$$

22. (b) $\bar{v} = 1.097 \times 10^5\ \text{cm}^{-1}\left(\frac{1}{(49)^2} - \frac{1}{(50)^2}\right)$

$$= 1.097 \times 10^5\ (4.165 \times 10^{-4} - 4.0 \times 10^{-4})\ \text{cm}^{-1}$$

$$= 1.097 \times 10^5 \times 1.65 \times 10^{-5}\ \text{cm}^{-1} = 1.81\ \text{cm}^{-1}$$

The corresponding wavelength $= \frac{1}{1.81}$ cm = 0.55 cm

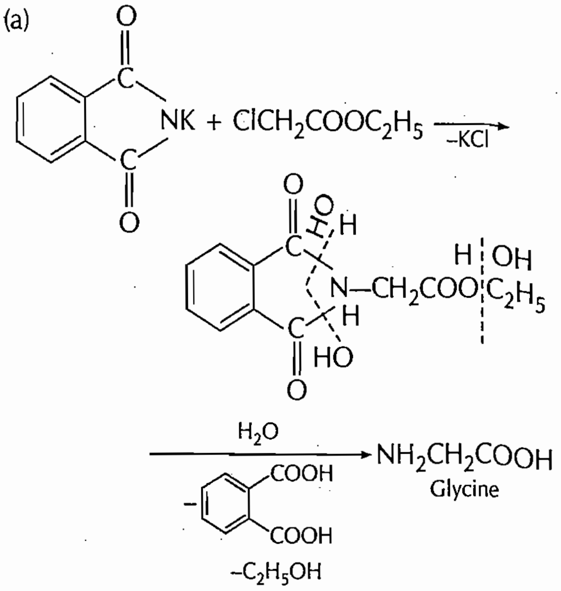
23. (b) Activation energy of a reaction is always positive.

24. (c) The acidity of hydrides increases in a period. Thus, HCl and HI are more acidic than the H_2O and CH_4. Between HCl and HI, HI is the stronger acid because of weaker H—I bond.

25. (d) $NO_2^+ \Rightarrow \underset{\text{linear}}{O{=}\overset{+}{N}{=}O}$

NO_2^+ (nitronium ion) is a nitrating agent.

26. (a)



27. (a) Compressibility factor, $Z = \frac{pV}{RT} = 1$ for ideal gas.

28. (b) *Para* position of halogen atom make it D_{2h}.

29. (c) For acidic buffer,

$$\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$K_a \cdot K_b = K_\omega$$

$$K_a = \frac{K_\omega}{K_b} = \frac{10^{-14}}{10^{-10}} = 10^{-4}$$

$$\text{pH} = -\log 10^{-4} + \log\frac{[A]}{[HA]}$$

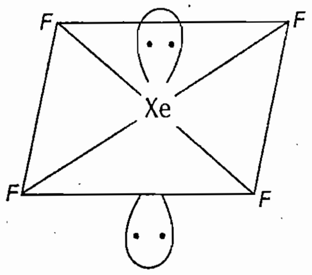
$\because$ $[A^-] = [HA]$

$\therefore$ pH = 4

30. (c) In nitrous acid, HNO_2, oxidation state of N is +3, an intermediate oxidation state (as oxidation state of N varies from –3 to +5). Thus, it can be oxidized to +5 state or can be reduced to lower oxidation state. Hence, it can behave like reductant as well as oxidant.

31. (d) $XeF_4 = 4bp + 2lp \Rightarrow 6$ hybrid orbitals

Thus, hybridization is sp^3d^2 and structure should be octahedral. However, its actual geometry is square planar because of the presence of two lone pairs of electrons.

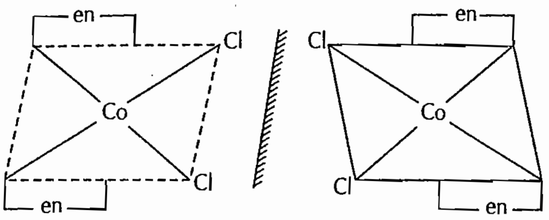


Square planar

32. (d) XeF_2 on hydrolysis gives Xe, HF and O_2.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

33. (d) *Cis* form of the compound containing bidentate ligand is usually optically active, so *cis*-$Co(en)_2Cl_2$ is optically active.



34. (a) 1, 2-diaminopropane and 1, 3-diaminopropane are the isomers so the given complexes exhibit ligand isomerism.

35. (b) Ti(IV) solutions give yellow-orange colour on addition of H_2O_2 due to the formation of peroxo complex.

$$TiO(SO_4) + H_2O_2 \longrightarrow \underset{\text{Yellow orange colour}}{TiO_2(SO_4)} + H_2O$$

36. (d) Vaporization of water always needs certain amount of energy.

37. (a) The reduction potential of Mg is less than that of water ($E° = -0.83$V). Hence, its ions in the aqueous solution cannot be reduced, instead water will be reduced.

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

38. (c) At cathode

$$Al^{3+} + 3e^- \longrightarrow Al$$

$$E_{Al} = \frac{27}{3} = 9$$

$$W_{Al} = E_{Al} \times \text{no. of Faradays}$$
$$= 9 \times 0.1 = 0.9 \text{ g}$$

39. (d) $2A + B \longrightarrow$ products

It is a second order reaction. Rate of reaction

$$r_1 = k[A][B]$$

If the concentration of A becomes double then the rate will be

$$r_2 = k[2A][B]$$
$$r_2 = 2k[A][B]$$
$$r_2 = 2r_1$$

40. (a) The minimum energy required for a molecule to take part in a reaction is called threshold energy.

41. (a) For isochoric process $\Delta V = 0$, so $q_V = \Delta E$ *i.e.*, heat given to a system under constant volume is used up in increasing ΔE.

42. (a) Bomb calorimeter is commonly used to find the heat of combustion of organic substances which consists of a sealed combustion chamber, called a bomb. If a process is run in a sealed container then no expansion or compression is allowed, so, $W = 0$ and $\Delta U = q$. $\Delta U < 0, W = 0$.

43. (c) Entropy of the mixture increases due to increase in impurity.

44. (b) Those substances that accept the proton are called Bronsted base and which have a tendency to donate a proton are called Bronsted acid. e.g., HCO_3^-

45. (a) For precipitation,

$$K_{sp} < \text{ionic product}$$
$$1 \times 10^{-10} < [A^+][B^-] < (10^{-5})[B^-]$$
$$[B^-] > \frac{1 \times 10^{-10}}{10^{-5}}$$
$$[B^-] \geq 1 \times 10^{-5}$$

Thus, 5×10^{-6} concentration of B^- will not give the precipitate of AB.

46. (b) Chemical reactions quantitatively depend on the moles of reactant and product involved in the reaction.

47. (c) Here, $\Delta n_g = 0$. Thus, no effect of pressure.

48. (c) Group 13 elements possess 2*s* and 1*p* electrons in the valence shell. So, they exhibit a oxidation state of +3 but due to inert pair effect they also exhibit a oxidation state of +1.

49. (b) Ga^+ and In^+ undergo disproportionation because in Ga^+ and In^+, +3 oxidation state is more stable than +1 oxidation state.

50. (d) In^+ undergoes self oxidation and reduction in aqueous solution. For example

$$3\overset{+1}{In}X(s) \longrightarrow 2\overset{0}{In}(s) + \overset{3+}{In}(aq) + 3X^-(aq)$$

51. (a) In Tl, +1oxidation state is more stable. So, Tl^{3+} acts as a strong oxidizing agent.

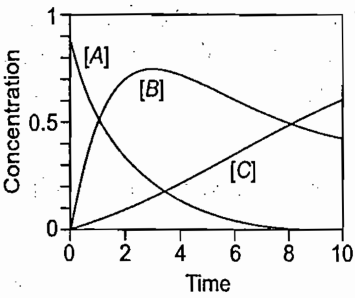
52. (a) Rate equation for concentration of A.

$$\frac{dA}{dt} = -k_1[A]$$

Integrated rate law for A

$$d[A] = [A]_0^{e^{-k_a t}}$$

53. (b) If $K_a >> K_b$, all the *A* present is converted into *B*, which is slowly used up to form *C*. So, concentration *vs* time plot for the given reaction is



54. (a) The complex ion $[Cu(NH_3)_6]^{2+}$ has octahedral geometry.

55. (a) Complex ion $[Cu(NH_3)_6]^{2+}$ has one *d-d* transition.

56. (c) Pinnacle means climax on endeavour or success. So, peak is most closet to pinnacle.

57. (b) As water contains oxygen, similarly salt contains sodium.

58. (a) According to the sentence, very few musicians want to laugh at themselves but this can boost the sale of video clips.

59. (c) Let total number of votes cast be *x*.

∴ Total number of valid votes = 0.96 *x*

Winner contestant secures 55% of valid votes.

So, looser contestant secures 45% of valid votes.

∴ Majority = (55 − 45)% of valid votes

$\Rightarrow$ 240 = 10% of 0.96*x*

$$\Rightarrow \quad x = \frac{240}{0.96} \times \frac{100}{1} = 2500$$

60. (a) Average weight of group *A* = 30 kg

Total weight of group *B* = 30 × 30 = 900 kg

Average weight of group *B* = 70 kg

Total weight of group *B* = 70 × 70 = 4900 kg

$$\text{Average weight of groups } A \text{ and } B = \frac{900 + 4900}{30 + 70}$$

$$= \frac{5800}{100} = 58 \text{ kg}$$

61. (b) The conclusion from the paragraph is that parents can prepay their children's future college tuition fee at current rates as it is expected that in future college tuition fee may increase. However, one drawback of this program is that, if interest on principal amount is more than the increase in fee then parents will not participate in this program.

62. (b) Value of a silver coin ∝ (Diameter)^2

Value of a silver coin ∝ Thickness

$$\therefore \quad \frac{v_1}{v_2} = \left(\frac{d_1}{d_2}\right)^2 \cdot \left(\frac{t_1}{t_2}\right)$$

$$\Rightarrow \quad \frac{4}{1} = \left(\frac{4}{3}\right)^2 \cdot \left(\frac{t_1}{t_2}\right)$$

$$\Rightarrow \quad \frac{t_1}{t_2} = \frac{9}{4}$$

63. (b) Let rate of current be *x* and the speed of man in still water be *y*.

∴ Upstream speed = $y - x$

Downstream speed = $y + x$

$$5 = \frac{15}{y - x} + \frac{22}{y + x} \quad \text{...(i)}$$

$$6\frac{1}{2} = \frac{20}{y - x} + \frac{27}{y + x} \quad \text{...(ii)}$$

On solving Eqs. (i) and (ii),

$$y - x = 5 \quad \text{...(iii)}$$

$$y + x = 11 \quad \text{...(iv)}$$

On solving Eqs. (iii) and (iv), we get

$y = 8$ km/h

$x = 3$ km/h

64. (b) Ratio of total man hours supplied by *A*, *B* and *C*

$= (20 \times 8 \times 6) : (15 \times 9 \times 7) : (10 \times 6 \times 8)$

$= (4 \times 8 \times 2) : (3 \times 3 \times 7) : (2 \times 2 \times 8)$

$= 64 : 63 : 32$

$$\therefore \quad C\text{'s share} = \frac{32}{64 + 63 + 32} \times 636 = ₹\,128$$

65. (b) Cable television = $\frac{1}{5}$

Videocassette recorder = $\frac{1}{10}$

Having both = $\frac{1}{3} \times \frac{1}{5} \times \frac{1}{15}$

Housing units having either television or videocassette recorder

$$= \frac{1}{5} + \frac{1}{10} - \frac{1}{5}$$

$$= \frac{6 + 3 - 2}{30} = \frac{7}{30}$$

Housing units having neither television nor videocassette recorder = $1 - \frac{7}{30} = \frac{23}{30}$

Practice Set 2

GATE Chemistry

Duration : 3 Hours **Maximum Marks : 100**

1. All questions in this paper are of objective type.
2. There are total of 65 questions carrying 100 marks.
3. Questions 1-25 will carry 1 mark each and questions 26-55 will carry 2 marks each.
4. Questions 48-51 (2 pairs) are common data questions and question pairs 52-55 are linked answer questions. The answer to the second question of the linked answer questions depends on the answer to the first question of the pair. If the first question in the linked pair is wrongly answered or is unattempted, then the answer to the second question in the pair will not be evaluated.
5. Questions 56 to 65 belong to General Aptitude (GA). Questions 56-60 will carry 1 mark each and questions (61-65) will carry 2 marks each.
6. Unattempted questions will carry zero marks.
7. Wrong answers will carry **negative** marks. For 1-25 and 56-60, $\frac{1}{3}$ marks will be deducted for each wrong answer. For 26 to 51 and 61 to 65, $\frac{2}{3}$ mark will be deducted for each wrong answer. The question pairs 52-53 and 54-55 are questions with linked answers. There will be negative marks only for wrong answer to the first question of the linked answer question pair *i.e.*, for Q. 52 and Q. 54, $\frac{2}{3}$ mark will be deducted for each wrong answer. There is no negative marking for Q. 53 and Q. 55.

(1 Mark Questions)

1. For a second order reaction, $2B \rightarrow$ products, if the initial concentration of the species B is $[B]_0$ and the rate constant is k, then $t_{1/2}$ can be expressed as

(a) $1/[B]_0k$ (b) $1/k$

(c) $[B]_0k$ (d) $\frac{1}{2}[B]_0k$

2. If the heats of reaction of the following transformations $C + O_2(g) \rightarrow CO_2(g)$, $C + \frac{1}{2}O_2(g) \rightarrow CO(g)$ and $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ are Q, 11.5 J and 10.5 J respectively then Q in joules is equal to

(a) 120.75 (b) 1

(c) −1 (d) 22

3. The spontaneity of a reaction can be judged from the sign of the emf (E) and the free energy (G) of the cell. The criteria are

(a) $\Delta G \approx +$ve, $E \approx -$ ve

(b) $\Delta G \approx 0, E \approx -0$

(c) $\Delta G \approx -$ve, $E \approx +$ve

(d) $\Delta G \approx -$ ve, $E \approx -$ ve

4. Two moles of a gas expand at 25°C against a constant pressure of 1 atm, the change in the volume being 82.1 mL. The work done by the gas is

(a) 2 cal

(b) 4 cal

(c) 821 L atm

(d) 2 × 298 cal

5. The heteronuclear diatomic molecule that is isoelectronic to HCN is

(a) NO (b) CO

(c) BO (d) SO

6. The bond order in Be_2, molecule can be expected to be

(a) 0 (b) 1

(c) 2 (d) 3

7. The intense colour of $KMnO_4$ is due to

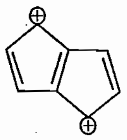
(a) electronic transition from one energy level to another in Mn

(b) electronic transition from one energy level to another in O

(c) charge transfer from Mn to O

(d) charge transfer from O to Mn

8. Of the following, the compounds that are aromatic are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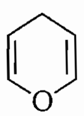
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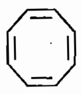
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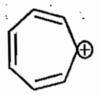
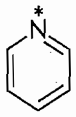
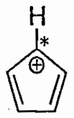
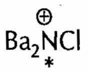

(4)

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

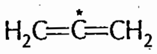
9. The hybridization of the atoms indicated by asterisk in the following compounds in a sequence (from 1 to 4) is given by


(1)


(2)


$Ba_2\underset{*}{\overset{\oplus}{N}}Cl$

(3)

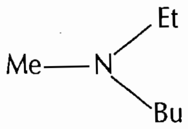

$H_2C{=}\overset{*}{C}{=}CH_2$

(4)

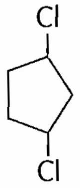
(a) sp^4, sp^2, sp^3, sp (b) sp^2, sp^2, sp^3, sp^2

(c) sp^2, sp^2, sp^3, sp (d) sp^4, sp^3, sp^3, sp

10. Which of the following compounds can have enantiomers?



(1)



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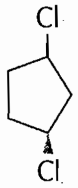

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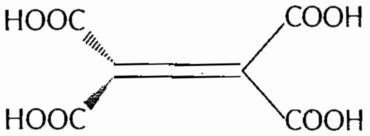


(4)

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

11. The rate constant for a certain reaction is found to be doubled when the temperature is raised from 27°C to 37°C. The activation energy for this reaction in kJ is

(a) 26.8 (b) 107.2 (c) 53.6 (d) 50.0

12. The standard potential for the electrodes $Hg|Hg_2^{2+}$ and Hg/Hg^{2+} are –0.799 V and –0.855 V at 25°C, respectively. The equilibrium constant for the reaction $Hg + Hg^{2+} \rightleftharpoons Hg_2^{2+}$ is

(a) 85.12 (b) 79.12 (c) 70 (d) 90.20

13. The ion conductance of the alkali metal cation at a given concentration follow the following order

(a) $Li^+ > Na^+ > K^+ > Rb^+$

(b) $Li^+ < Na^+ < K^+ > Rb^+$

(c) $Li^+ < Na^+ < K^+ < Rb^+$

(d) $Li^+ = N^+ > K^+ > Rb^+$

14. The total pressure for the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ under the equilibrium condition is 15 atm. The value of K_p is

(a) 16 (b) 2 (c) 20 (d) 25

15. The bond angle in CO_2 is

(a) 90° (b) 104° (c) 120° (d) 180°

16. Reverse osmosis is an example of

(a) reversible process
(b) irreversible process
(c) equilibrium process
(d) non-spontaneous process

17. The crystal field stabilization energy and the spin only magnetic moment of $[CoF_6]^{4-}$ are respectively

(a) $0.4\Delta_n$ and 4.9 BM (b) $0.8\ \Delta_n$ and 3.8 BM

(c) $1.8\ \Delta_n$ and 1.7 BM (d) $2.4\ \Delta_n$ and 0 BM

18. Which one of the following free ions has the lowest magnetic moment?

(a) Ce^{3+} (b) Nd^{3+} (c) Sm^{3+} (d) Gd^{3+}

19. Which one of the following has the largest energy band gap?

(a) Germanium (b) Silicon
(c) Telliurium (d) Diamond

20. The number of possible isomers for the octahedral complex ion $[Co(en)Cl_2Br_2]^-$ is

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

21. How many stereoisomers are there for tartaric acid?

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

22. When methyl group is in the axial position in methyl cyclohexane, the molecule has

(a) one *n*-butane gauche interaction
(b) two *n*-butane gauche interaction
(c) no *n*-butane gauche interaction
(d) three *n*-butane gauche interaction

23. $S_N1$reaction on optically active substrates mainly gives

(a) retention in configuration
(b) inversion in configuration
(c) racemic product
(d) No product

24. The absorption isotherm is defined as the dependence of

(a) surface coverage on the temperature at a fixed pressure
(b) surface coverage on the pressure at a fixed temperature
(c) surface coverage on the oxidation state of the surface material
(d) rate of a surface reaction on the pressure at a fixed temperature

25. The minimum energy for an endothermic reaction will be
(a) not less than ΔH for the reaction
(b) less than ΔH for the reaction
(c) zero
(d) equal to the solvation energy

(2 Marks Questions)

26. The triple point of water is at
(a) 273.16 K
(b) 273.16 K and 760 Torr
(c) 273.16 K and 4.58 Torr
(d) 760 Torr

27. The diffusion current in polarogram is proportional to
(a) the residual current
(b) the migration current
(c) the wave height
(d) the concentration of the supporting electrolyte

28. The net work turned out by a Carnot's engine operating between 27°C and 127°C is......kcal, if it absorbs 400 kcal from the hot reservoir.
(a) 50 (b) 100 (c) 4 (d) 300

29. A refrigerator absorbs 100 cal of heat from the cold reservoir and the mechanical work done to reject heat into the hot reservoir is 200 cal. The coefficient of performance of the refrigerator is
(a) 1/2 (b) 2 (c) 3 (d) 3/2

30. The reversible and irreversible entropy changes of a system on going from state 1 to state 2 are $\Delta S_{12}^{\text{rev}}$ and $\Delta S_{12}^{\text{irrev}}$ respectively. The correct relationship between the two entropy changes is
(a) $\Delta S_{12}^{\text{irrev}} > \Delta S_{12}^{\text{rev}}$ (b) $\Delta S_{12}^{\text{irrev}} < \Delta S_{12}^{\text{rev}}$
(c) $\Delta S_{12}^{\text{irrev}} = \Delta S_{12}^{\text{rev}}$ (d) $\Delta S_{12}^{\text{irrev}} = -\Delta S_{12}^{\text{rev}}$

31. The boiling point of a normal liquid is 27°C. Its molar enthalpy of vaporization is likely
(a) 567 cal mol^{-1} (b) 6300 cal mol^{-1}
(c) 3150 cal mol^{-1} (d) 1575 cal mol^{-1}

32. $\frac{1}{2}$ mole of gas *A* and $\frac{1}{2}$ mole of gas *B* (both ideal gases) are allowed to mix freely at a constant pressure of 1 atm and a constant temperature of 300 K. The entropy change during mixing is
(a) 300 cal K^{-1}
(b) 300×1.987 cal K^{-1}
(c) $2.303 \times 1.987 \log \frac{1}{2}$ cal K^{-1}
(d) $2.303 \times 1.987 \log 2$ cal K^{-1}

33. The thermodynamic property that may be utilized from specifying the direction of time is
(a) *E* (b) *H* (c) *S* (d) *G*

34. System *A* is 1 mole of ice at −10° C and system *B* is 1 mole of super-cooled water at −10°C. Choose the correct statement.
(a) *A* has greater vapour pressure than *B*
(b) *A* has greater free energy than *B*
(c) *A* has lower free energy than *B*
(d) Both *A* and *B* have the same free energy

35. The specific rate constants for a given reaction are $3.76 \times 10^3\ h^{-1}$ and $1.16 \times 10^4\ h^{-1}$ at 812°C and 852.3°C respectively. Calculate energy of activation.
(a) 68.28 kcal mol^{-1} (b) 34.14 kcal mol^{-1}
(c) 136.56 kcal mol^{-1} (d) 17.7 kcal mol^{-1}

36. The rate of decomposition of a substance increases by a factor 2.25 for 1.5 times increase in concentration of substance at same temperature. Find out order of reaction.
(a) 1 (b) 4
(c) 2 (d) 8

37. In a reaction, $H_2 + I_2 \rightarrow 2HI$, the rate of disappearance of I_2 is found to be 10^{-6} mol L^{-1} s^{-1}. What would be the corresponding rate of appearance of HI?
(a) 2×10^{-5} mol L^{-1} s^{-1}
(b) 1×10^{-6} mol L^{-1} s^{-1}
(c) 4×10^{-6} mol L^{-1} s^{-1}
(d) 2×10^{-6} mol L^{-1} s^{-1}

38. Calculate the frequency (in H_2) of an X-ray having a wavelength of 1.5×10^{-10}m.
(a) 1×10^{10} (b) 2×10^{19}
(c) 2×10^{-10} (d) 2×10^{18}

39. Compare the energies of two radiations, one with $\lambda = 10000$ Å and other with $\lambda = 5000$ Å.
(a) 2 : 1 (b) 1 : 2
(c) 2 : 5 (d) 4 : 2

40. The radius of the fourth orbit in H atom is 0.85 nm. Calculate the velocity of electron in this orbit. ($m_e = 9.1 \times 10^{-31}$ kg)
(a) 5.44×10^5 ms (b) 5.44×10^5 cms^{-1}
(c) 2.77×10^5 ms^{-1} (d) 2.77×10^5 cms^{-1}

41. Calculate the Bohr's radius for first orbit of H atom.
(a) 0.529 Å (b) 0.529 cm
(c) 0.529 nm (d) 0.529 mm

42. Calculate the work of expansion when 2 moles of an ideal gas expands isothermally and reversibly from 10 L to 20 L at 300 K.

(a) 826.5 cal (b) 413.25 cal
(c) – 826.5 cal (d) – 413.25 cal

43. Predict whether at 27°C, the following change is spontaneous or not?

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6\ H_2O(l).$$

Given, $\Delta H = +9080\ \text{J mol}^{-1}$

and $\Delta S = +35.7\ \text{JK}^{-1}\ \text{mol}^{-1}$.

(a) $\Delta G = 1630$ J, so spontaneous
(b) $\Delta G = -1630$ J, so non-spontaneous
(c) $\Delta G = 1630$ J, so non-spontaneous
(d) $\Delta G = -1630$ J, so spontaneous

44. Calculate the change in entropy when 1 mole of N_2 gas expands isothermally and reversibly from an initial volume of 1 L to a final volume of 10 L at 27°C.

(a) 19.15 $\text{kJ}^{-1}\ \text{mol}^{-1}$ (b) 19.15 $\text{JK}^{-1}\text{mol}^{-1}$
(c) 9.57 $\text{JK}^{-1}\text{mol}^{-1}$ (d) 9.57 $\text{kJ}^{-1}\text{mol}^{-1}$

45. Calculate the enthalpy of vaporization for ethanol, Given, $\Delta S = 109.8\ \text{JK}^{-1}\text{mol}^{-1}$ and boiling point of ethanol is 78.5° C.

(a) 38.595 kJ mol^{-1} (b) 38.595 JK mol^{-1}
(c) 19.25 kJ mol^{-1} (d) 19.25 JK mol^{-1}

46. How much quantity of electricity is required to liberate 112 mL of H_2 at 27°C and 760 mm?

(a) 877.6 C (b) 877.6 A
(c) 438.8 C (d) 438.8 A

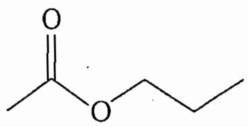
47. A reaction proceeds in 3 steps. The first stage is a fast second order reaction. The second stage is slow and of first order. The third stage is fast again and is a third order reaction. The overall order of the reaction is

(a) zero order (b) first order
(c) second order (d) third order

Common Data for Questions 48 and 49

Reactivity of aryl amines towards electrophilic aromatic substitution is much higher than that of aliphatic amines. Hence, differential reactivity of the amino group is desirable in many reactions.

48. The compound which on reacting with aniline will not form an acetanilide is

(a)


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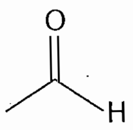
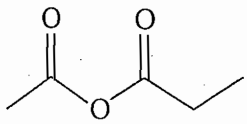


(c)


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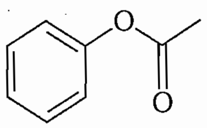


49. Aniline can be distinguished from methyl amine by its reaction with

(a) *p*-toluene sulphonyl chloride/KOH
(b) (i) $NaNO_2$/HCl, 0-5°C (ii) alkaline β naphthol
(c) Sn/HCl
(d) Acetyl chloride

Common Data for Questions 50 and 51

General electronic configuration of group 14 elements is ns^2np^2. So, they should show an oxidation state of +4. First two member *i.e.*, carbon and silicon show a oxidation state of +4. But other elements of this group show a oxidation state of +2 with + 4, due to inert pair effect.

50. Which of the following is the strongest reducing agent?

(a) $GeCl_2$ (b) $SnCl_2$ (c) $SnCl_4$ (d) $PbCl_2$

51. Which of the following is a electron precise molecule?

(a) $SnCl_2$ (b) $GeCl_2$
(c) CCl_4 (d) All of these

Statement for Linked Answer Questions 52 and 53

The reaction of ammonium chloride with BCl_3 at 140°C followed by reduction with $NaBH_4$ gives product *X*.

52. The formula of *X* is

(a) $B_3N_3H_3$ (b) $B_3N_3H_6$
(c) $B_3N_3H_{12}$ (d) $[BH \ldots NH]_n$

53. Which of the following statements is/are true for *X*?

(i) *X* is not isoelectronic with benzene.
(ii) *X* undergoes addition reaction with HCl.
(iii) Electrophilic substitution reaction on *X* is much faster than that of benzene.
(iv) *X* undergoes polymerization at 90°C.

(a) i and ii (b) only ii (c) ii and iii (d) i and iv

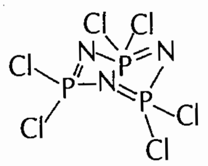
Statement for Linked Answer Questions 54 and 55

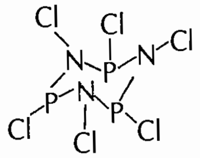
Triphosphazene is prepared by reacting *X* and *Y* in equimolar ratio at 120-150°C using appropriate solvents.

54. The reactants *X* and *Y* respectively are

(a) PCl_3; NH_3 (b) PCl_5; NH_3
(c) PCl_5; NH_4Cl (d) PCl_3; NH_4Cl

55. The structure of triphosphazene is

(a)


(b)


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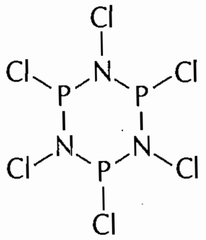

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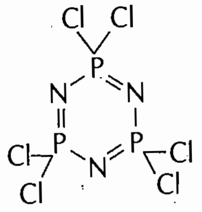


General Aptitude

56. Which of the following options is farthes in meaning to the word given below?

Gloomy

(a) Discouraging (b) Disguising

(c) Bright (d) Tragic

57. The question below consists of a pair of related words followed by four pairs of words. Select the pair which best expresses the relation in the original pair.

Paper : Blackboard

(a) Filter : Air (b) Pencil : Pen

(c) Eraser : Chalk (d) Polish : Shoe

58. Choose the most appropriate word from the options given below to complete the following sentence. It has been argued that politics as ...... whatever its transcendental claims, has always been the systematic organization of common hatreds.

(a) a theory (b) an ideal

(c) a practice (d) a contest

59. Choose the most appropriate word from the options given below to complete the following sentence. Although adolescent maturational and developmental states occur in an orderly sequence, their timing ...... with regard to onset and duration.

(a) lasts (b) varies

(c) falters (d) accelerates

60. The annual salaries of Mr. John, Mr. Adam and Mr. Joe are in the ratio 2 : 3 : 5. If the salary of Mr. Joe is ₹ 90000 more than that of Mr. John, then the monthly slalary of Mr. Adam is

(a) ₹ 7500 (b) ₹ 75000

(c) ₹ 90000 (d) None of these

61. The ice on the front windshield of the car had formed when moisture condensed during the night. The ice melted quickly after the car was warmed up the next morning because the defrosting vent, which blows only on the front windshield was turned on full force.

Which of the following, if true, most seriously jeopardizes the validity of the explanation for the speed with which the ice melted?

(a) The side windows have no ice condensation on them

(b) Even though no attempt was made to defrost the back window, the ice there melted at the same rate as did the ice on the front windshield

(c) The speed at which ice on a window melts increases as the temperature of the air blown on the window increases

(d) The warm air from the defrosting vent for the front windshield cools rapidly as it dissipates throughout the rest of the car

62. The cost of turfing a uniform circular road round a circular garden at ₹ 20 per m^2 is ₹ 21560 and the area of the garden is 1386 m^2. Find the breadth of the circular road.

(a) 7 m (b) 14 m

(c) 10 m (d) None of these

63. $\left[1-\frac{1}{3}\right]\left[1-\frac{1}{4}\right]\left[1-\frac{1}{5}\right]\dots\left[1-\frac{1}{n}\right]=?$

(a) $\frac{2}{n}$ (b) $\frac{1}{n}$

(c) $\frac{3}{n}$ (d) $n-\frac{1}{n}$

64. Two flask of liquid contain liquid of mixture of liquids A and B. In the first flask $A : B :: 7 : 3$ and in the second flask $A : B :: 3 : 1$. In what ratio must the mixtures from the two flask be taken to give a mixture in which $A : B :: 11 : 4$?

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

65. A and B can complete a piece of work in 80 and 120 days respectively. They together start the work but A left after 20 days. After another 12 days C joined B and now they complete the work in 28 more days. In how many days C can complete the work, working alone?

(a) 92 days (b) 102 days

(c) 112 days (d) 124 days

Answers

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

Practice Set 3

GATE Chemistry

Duration : 3 Hours **Maximum Marks : 100**

1. All questions in this paper are of objective type.
2. There are total of 65 questions carrying 100 marks.
3. Questions 1-25 will carry 1 mark each and questions 26-55 will carry 2 marks each.
4. Questions 48-51 (2 pairs) are common data questions and question pairs 52-55 are linked answer questions. The answer to the second question of the linked answer questions depends on the answer to the first question of the pair. If the first question in the linked pair is wrongly answered or is unattempted, then the answer to the second question in the pair will not be evaluated.
5. Questions 56 to 65 belong to General Aptitude (GA). Questions 56-60 will carry 1 mark each and questions (61-65) will carry 2 marks each.
6. Unattempted questions will carry zero marks.
7. Wrong answers will carry **negative** marks. For 1-25 and 56-60, $\frac{1}{3}$ marks will be deducted for each wrong answer. For 26 to 51 and 61 to 65, $\frac{2}{3}$ mark will be deducted for each wrong answer. The question pairs 52-53 and 54-55 are questions with linked answers. There will be negative marks only for wrong answer to the first question of the linked answer question pair *i.e.*, for Q. 52 and Q. 54, $\frac{2}{3}$ mark will be deducted for each wrong answer. There is no negative marking for Q. 53 and Q. 55.

(1 Mark Questions)

1. Choose the correct statement.
- (a) For a real gas, C_p changes with temperature but does not change with pressure.
- (b) For an ideal gas, C_p changes neither with temperature nor with pressure.
- (c) For a ideal gas, C_p changes with temperature, but not with pressure.
- (d) For an ideal gas, C_p changes with both temperature and pressure.

2. van der Waals' equation for n moles of a gas is
- (a) $\left[p + \frac{a}{V^2}\right](V - b) = RT$
- (b) $\left[p + \frac{n^2a^2}{V^2}\right](V - nb) = nRT$
- (c) $\left[p + \frac{na^2}{V^2}\right](V - nb) = nRT$
- (d) $\left[p + \frac{n^2a}{V^2}\right](V - nb) = nRT$

3. The correct decreasing rate of hydrogenation of the olefins

I. $Me_2C{=}CMe_2$ II. $Me_2C{=}CH_2$
III. $CH_3CH{=}CHCH_3$ IV. $CH_2{=}CH_2$
is
- (a) I > II > III > IV (b) IV > II > III > I
- (c) IV > III > I > II (d) I > III > II > IV

4. The compressibility factor of a van der Waals' gas at the critical state is
- (a) 1/3 (b) 3/8
- (c) 8/27 (d) 3

5. Camphor is often used in molecular weight determinations because
- (a) it has high cryoscopic constant
- (b) it is readily available
- (c) it is volatile
- (d) it is a solvent for organic substances

6. An example of a colligative property is
- (a) boiling point (b) freezing point
- (c) osmotic pressure (d) vapour pressure

7. One of the following is not perfect differential
- (a) dQ (b) dH
- (c) dT (d) dG

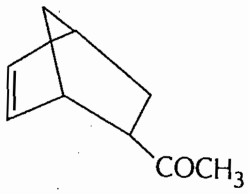
8. Kelvin's thermodynamic scale of temperature is based on
(a) Charles' law (b) Joule's law
(c) Amagat's law (d) Carnot's principle

9. A condition for equilibrium is
(a) $dG = 0$ (b) $\partial G_{T,V} = 0$
(c) $\partial G_{p,V} = 0$ (d) $\partial G_{T,p} = 0$

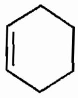
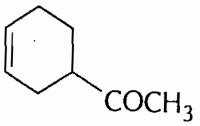
10. $\left[\dfrac{\partial E}{\partial V}\right]_T$ for a van der Waals' gas is
(a) a/V^2 (b) a
(c) b (d) b/V^2

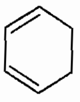
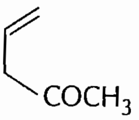
11. The reversible work done by one mole of an ideal gas when it is compressed isothermally at 27°C from 1 atm pressure to 10 atm is
(a) 1381 cal (b) −1381 cal
(c) 270 cal (d) 243 cal

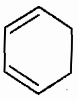
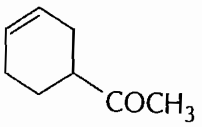
12. For the synthesis of

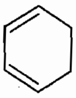
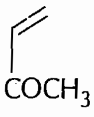


using Diel's Alder reaction, the reactants required are

(a)  and 

(b)  and 

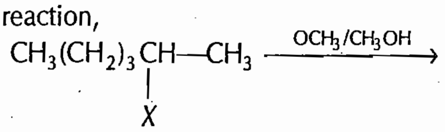
(c)  and 

(d)  and 

13. Which one of the following statements is correct for XeO_2F_2?
(a) It has a square planar structure
(b) It has a trigonal bipyramid based structure
(c) It is isostructural with XeF_4
(d) It has tetrahedral structure

14. $B_{10}C_2H_{12}$ is isoelectronic with
(a) $B_{12}H_{12}^{2-}$ (b) $B_{12}H_{12}$
(c) $B_{12}H_{12}^{+}$ (d) $B_{12}H_{12}^{2+}$

15. In the reaction,



$$CH_3(CH_2)_3\underset{\displaystyle X}{\underset{|}{CH}}{-}CH_3 \xrightarrow{OCH_3/CH_3OH}$$

if $X = F$ in the first case and $X = Br$ in the second case, the major products formed will be respectively.
(a) 1-hexene and 1-hexene
(b) 1-hexene and 2-hexene
(c) 2-hexene and 2-hexene
(d) 2-hexene and 1-hexene

16. Which one of the following IR frequency is closest to that of a triply bridged CO group?
(a) 1700 cm^{-1} (b) 1810 cm^{-1}
(c) 1920 cm^{-1} (d) 2140 cm^{-1}

17. Which one of the following is a monobasic acid?
(a) $H_4P_2O_7$ (b) H_3PO_4 (c) H_3PO_3 (d) H_3PO_2

18. The ionic compounds MgO and CaO have the same crystal structure except that the interionic distances are 2.10 Å and 2.40 Å respectively. The ratio of the lattice energies U(MgO) / U(CaO) is
(a) 0.766 (b) 0.875 (c) 1.143 (d) 1.306

19. Fisher projection indicates
(a) horizontal substituents above the plane
(b) vertical substituents above the plane
(c) both horizontal and vertical substituents below the plane
(d) both horizontal and vertical substituents above the plane

20. Bromination of toluene gives
(a) only *meta*-substituted product
(b) only *para*-substituted product
(c) mixture of *ortho* and *para*-substituted products
(d) mixture of *ortho* and *meta*-substituted products

21. Table sugar is
(a) a disaccharide consisting of D-glucose and D-fructose
(b) a monosaccharide
(c) a disaccharide consisting of two D-glucose units
(d) D-glucose

22. In the reaction of cyclopentadiene with acrylate ester giving Diels–Alder reaction products the interacting frontier orbitals are
(a) HOMO of a diene and LUMO of a dienophile
(b) HOMO of a dienophile and LUMO of a diene
(c) HOMO of a diene and HOMO of a dienophile
(d) LUMO of a diene and LUMO of a dienophile

23. One of the species given below is a Lewis acid. Which one is it?
(a) I (b) I^- (c) I_3^- (d) I_2

24. In E2 elimination, some compounds follow Hofmann rule which means
(a) the double bond goes to the most substituted position
(b) the compound is resistant to elimination
(c) no double bond is formed
(d) the double bond goes mainly towards the least substituted carbon

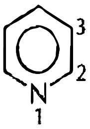
25. The internal pressure of one mole of a van der Waals' gas is equal to
(a) zero (b) b^2 (c) $\frac{a}{V^2}$ (d) $b - \frac{a}{RT}$

(2 Marks Questions)

26. Solid CO_2 is called dry ice because
(a) at 25°C and 1 atm only solid and vapour phases of CO_2 are in equilibrium
(b) the critical temperature of CO_2 is above 25°C
(c) the boiling point of liquid CO_2 is above 100°C
(d) the melting point of solid CO_2 is 0°C

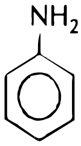
27. An aqueous mixture solution is prepared which contains 0.1 M of KCl and 0.1 MKI. To this solution, a drop of 0.01 M aquaeous solution of $AgNO_3$ is added. Which of the following statements is correct?
(a) A precipitate forms which is primarily AgI
(b) A precipitate forms which is primarily AgCl.
(c) A precipitate forms which has equimolar amounts of AgCl and AgI
(d) There will be no precipitation as there is no common ion between potassium and silver salts.

28.

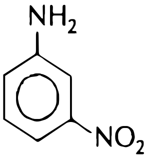


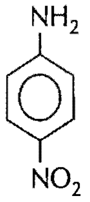
undergoes electrophilic substitution reaction preferentially
(a) position 2 (b) position 3
(c) position 4 (d) positions 2 and 4

29. Among the compounds the order of basicity is

(a)


(b) Et_3N

(c)


(d)


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

30. Which among the following is solvolysed at the faster rate?
(a) $C_6H_5CH_2Cl$ (b) $Me_3C—Cl$
(c) $CH_2=CH—CH_2Cl$ (d) $(C_6H_5)_3C—Cl$

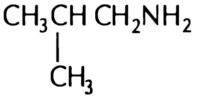
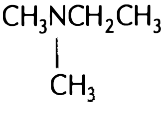
31. What happens when (S) $CH_3CH_2CH_2CHD(I)$ is heated with NaI in acetone?
(a) (*R*) isomer is exclusively formed
(b) Racemisation occurs
(c) 1-butene is formed
(d) No reaction occurs

32. Which among the following has the maximum base character?
(a) $CH_3\overset{\ominus}{N}HNa^+$ (b) CH_3CONH_2
(c) $(CH_3)_3N$ (d) $C_2H_5NH_2$

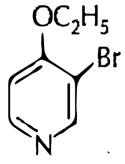
33. Which among the following forms the strongest conjugate acid?
(a) $C_6H_5NH_2$
(b) p-$O_2N\,C_6H_4NH_2$
(c) m-$NO_2C_6H_4NH_2$
(d) p-$H_3C\,COC_6H_4NH_2$

34. Dipole moment of *p*-nitroaniline when compared to $C_6H_5NO_2$(*X*) and aniline (*Y*) will be
(a) greater than *X* and *Y*
(b) smaller than *X* and *Y*
(c) greater than *X* but less than *Y*
(d) equal to zero

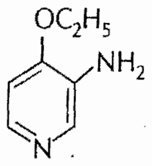
35. Among the following anions (a) CH_3^- (b) NH_2^- (c) OH^- (d) F^-, the correct order of nucleophilicity is
(a) a > b > c > d (b) b > a > c > d
(c) c > b > a > d (d) c > a> b > d

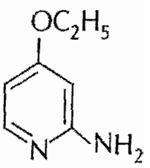
36. An organic compound *X*, $C_4H_{11}N$ reacts with only one mole of CH_3I and the product reacts with Ag_2O and H_2O to give an olefin. The compound *X* is
(a) $CH_3CH_2CH_2CH_2NH_2$
(b)

$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_2NH_2$
(c)

$CH_3\underset{\displaystyle CH_3}{\underset{|}{N}}CH_2CH_3$
(d) $CH_3NH\,CH_2CH_2CH_3$

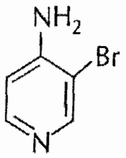
37. The product of reaction between



and $NaNH_2$ in liquid ammonia solvent is

(a)


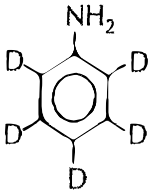
(b)


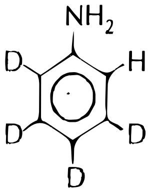
(c)


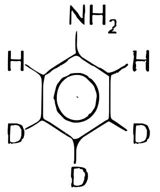
(d) None of these

38. The product of reaction between C_6D_5Br and $NaNH_2$ and NH_3 is

(a) $C_6H_5NH_2$

(b)


(c)


(d)


39. Which among the following has *sp*, *sp*^{2} and *sp*^{3} hybridization for C in it?
(a) $H_2C{=}CH{-}CH{=}CH_2$
(b) $H_2C{=}C{=}CH_2$
(c) $CH_3{-}CH{=}CH{-}CH_3$
(d) $H_2C{=}C{=}CH{-}CH_3$

40. Which among the following has a single absorption in proton nuclear magnetic resonance spectrum?
(a) *n*-pentane
(b) 2-methyl butane
(c) 2, 2-dimethyl propane
(d) 2, 3-dimethyl butane

41. Which among the following has the smallest heat of hydrogenation?
(a) 1-butene (b) 1,3-butadiene
(c) *Cis*-2-butene (d) *Trans*-2-butene

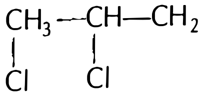
42. The C—H bond distance is the longest in
(a) C_2H_2 (b) C_2H_4
(c) C_2H_6 (d) C_6H_6

43. HBr reacts fastest with
(a) 1-butene (b) 1-pentane
(c) 2-pentane (d) 2-methyl propene

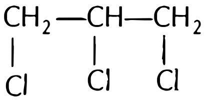
44. Electrophilic substitution on trifluoromethyl benzene gives
(a) *ortho* product (b) *para* product
(c) *meta* product (d) None of these

45. The most stable conformation of ethylene glycol is
(a) anti (b) gauche
(c) partially eclipsed (d) fully eclipsed

46. Propene when heated with chlorine at 500°C gives
(a) $CH_2{=}CHCH_2Cl$

(b)


$CH_3{-}\underset{Cl}{CH}{-}\underset{Cl}{CH_2}$

(c)


$\underset{Cl}{CH_2}{-}\underset{Cl}{CH}{-}\underset{Cl}{CH_2}$

(d) All of these

47. Which xylene is most easily sulphonated?
(a) *Ortho* xylene
(b) *Meta* xylene
(c) *Para* xylene
(d) None of the above

Common Data for Questions 48 and 49

A six-coordinate transition-metal complex is ESR and Mossbauer active. The effective magnetic moment of this complex is ~ 5.9 BM.

48. The metal-ion along with its oxidation state and the number of unpaired electrons present are
(a) Fe(II) and 4
(b) Mn(II) and 5
(c) Fe(III) and 1
(d) Fe(III) and 5

49. The complex is
(a) $[Mn(H_2O)_6]^{2+}$ (b) $[Fe(CN)_6]^{3-}$
(c) $[Fe(H_2O)_6]^{2+}$ (d) $[Fe(H_2O)_6]^{3+}$

Common Data for Questions 50 and 51

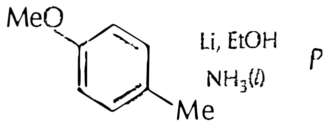
Trans-1,2 difluoro ethylene molecule has a 2-fold rotational axis and an inversion centre.

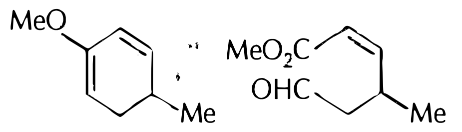
50. The number of distinct symmetry operations that can be performed on the molecule is
(a) 2 (b) 4
(c) 6 (d) 8

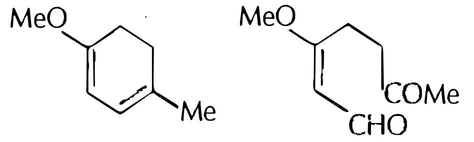
51. The number of irreducible representations of the point group of the molecule is
(a) 1 (b) 2
(c) 3 (d) 4

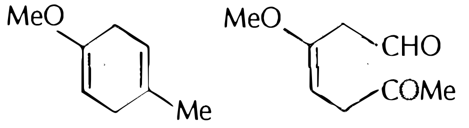
Linked Answer Questions 52 and 53

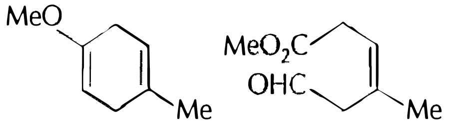
52. The products *P* and *Q* in the following sequence of reactions, respectively are



(a) 

(b) 

(c) 

(d) 

53. The reagent for selective reduction of the aldehyde group in Q obtained in the above reaction is

(a) H_2, $(Ph_3P)_3RhCl$ (b) $((H_3C)_2CHCH_2)_2AlH$

(c) $Na(CH_3COO)_3BH$ (d) $LiAlH_4$

Statement for Linked Answer Questions 54 and 55

Consider a particle of mass m moving in a one-dimensional box under the potential $V = 0$ for $0 \leq x \leq a$ and $V = \infty$ outside the box.

54. When the particle is in its lowest energy state, the average momentum ($< p_x >$) of the particle is

(a) $< p_x > = 0$ (b) $< p_x > = \frac{h}{a}$

(c) $< p_x > = \frac{h}{2a}$ (d) $< p_x > = \frac{h}{2\pi a}$

55. The uncertainty in the momentum (Δp_s) of the particle in its lowest energy state is

(a) $\Delta p_s = 0$ (b) $\Delta p_s = \frac{h}{a}$

(c) $\Delta p_s = \frac{h}{2a}$ (d) $\Delta p_s = \frac{h}{2\pi a}$

General Aptitude

56. Which of the following options is closest in meaning to the word given below?

Elegant

(a) Unrefined (b) Tasteless

(c) Inelegant (d) Graceful

57. The question below consists of a pair of related words followed by four pairs of words. Select the pair which best expresses the relation in the original pair.

Die : Dice

(a) Data : Datas (b) Mouse : Mice

(c) Monkey : Monkies (d) Dates : Datum

58. Choose the most appropriate words from the options given below to complete the following sentence. Congress is having great difficulty in developing a consensus on energy policy primarily because the policy objectives of various members of Congress rest on such...... assumptions.

(a) common place (b) trivial

(c) explicit (d) divergent

59. Choose the most appropriate word from the options given below to complete the following sentence. Because folk art is neither completely rejected nor accepted as an art form by art historians, their final evaluations of it necessarily remain......... .

(a) arbitrary (b) equivocal

(c) orthodox (d) unspoken

60. The price per kg of rice increases by 20%. By what percentage should the consumption be decreased such that expenditure remains the same?

(a) 20% (b) 16.67%

(c) 25% (d) 16.33%

61. One state adds a 7% sales tax to the price of most products purchases within its jurisdiction. This tax, therefore, if viewed as tax on income has the reverse effect of the federal income tax, the lower the income, the higher the annual percentage rate at which the income is taxed.

The conclusion above would be properly drawn, if which of the following were assumed as a premise?

(a) The amount of money citizens spend on products subject to the state sales tax tends to be equal across income levels

(b) The federal income tax favours citizens with high incomes, whereas the state sales tax favours citizens with low incomes

(c) Citizens with low annual incomes can afford to pay a relatively high percentage of their incomes in state sales tax, since their federal income tax is relatively low

(d) The lower a state's sales tax, the more it will tend to redistribute income from the more effluent citizens to the rest of the society

62. A man invests a certain sum of money at 6% per annum simple interest and another sum at 7% per annum simple interest. His income from interest after 2 yr was ₹354. One-fourth of the first sum is equal to one-fifth of the second sum. The total sum invested

(a) ₹ 2600 (b) ₹ 2700

(c) ₹ 2880 (d) ₹ 2900

63. Mr. Tamatar buys some apples at 5 per rupee from one trader and a similar quantity at 7 per rupee from a different trader. He mixes both the varieties and sells the entire lot at 6 per rupee. What is the profit or loss percentage that he makes?

(a) $2\frac{7}{9}\%$ (b) $3\frac{7}{9}\%$

(c) $3\frac{2}{9}\%$ (d) $2\frac{6}{9}\%$

64. A man starts from *B* to *K*, another from *K* to *B* at the same time. After passing each either they complete their journey in $3\frac{1}{3}$ and $4\frac{4}{5}$ h respectively. Find the speed of the second man, if the speed of the first man is 12 km/h.

(a) 8 km/h (b) 10 km/h

(c) 15 km/h (d) 24 km/h

65. *A* and *B* working separately can do a piece of work in 9 and 12 days respectively. If they work for a day alternatively, *A* beginning in how many days the work will be completed?

(a) $7\frac{1}{2}$ days

(b) $9\frac{1}{4}$ days

(c) $10\frac{1}{4}$ days

(d) $12\frac{1}{4}$ days

Answers

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