CHEMICAL SCIENCES

This Test Booklet will contain 145 (20 Part `A'+50 Part `B+75 Part 'C') Multiple Choice Questions (MCQs). Candidates will be required to answer 15 in part 'A', 35 in Part 'B' and 25 questions in Parts C respectively (No. of question to attempt may vary from exam to exam). In case any candidate answers more than 15, 35 and 25 questions in Parts A, B and C respectively only first 15, 35 and 25 questions in Parts A, B and C respectively will be evaluated. Questions in Parts 'A' and 'B' carry two marks each and Part 'C' questions carry four marks each. There will be negative marking @25% for each wrong answer. Below each question, four alternatives or responses are given. Only one of these alternatives is the 'CORRECT' answer to the question.

MODEL QUESTION PAPER

PART A

May be viewed under heading "General Science"

PART B

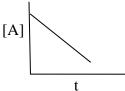
- **21**. [CoCl₄]²- shows a deep blue colour because of
 - 1. metal to ligand charge transfer transition
 - 2. ligand to metal charge transfer transition
 - 3. spin allowed and Laporte forbidden d-d transition
 - 4. spin allowed and Laporte allowed d-d transition
- 22. The violet colour of iodine vapour is due to
 - 1. $n-\pi^*$ transition
 - 2. π - π * transition
 - 3. $n-\sigma^*$ transition
 - 4. $\pi^*-\sigma^*$ transition

20. Choose the correct statement among the rone wing	23.	Choose the correct statement among the following
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- 1. diamond has lower thermal and electrical conductivities compared to graphite
- 2. diamond has similar thermal and electrical conductivities compared to graphite
- 3. diamond has higher thermal conductivity but lower electrical conductivity compared to graphite
- 4. diamond has the same thermal but lower electrical conductivity compared to graphite
- **24.** Which of the following is a nido-borane?
 - 1. B_4H_{10}
 - B_5H_9
 - 3. $[B_6H_6]^{2-}$
 - 4. B_5H_{11}
- **25.** The oxidation number of sulphur in dithionite $[S_2O_4]^{2-}$ and dithionate $[S_2O_6]^{2-}$ are, respectively,
 - 1. +3 and +4
 - 2. +3 and +5
 - 3. +4 and +5
 - 4. +4 and +6
- **26**. Among the three types of orbitals p, d, and f,
 - 1. both p and f orbitals have centre of symmetry
 - 2. both p and d orbitals have centre of symmetry
 - 3. only d orbitals have centre of symmetry
 - 4. f orbitals alone have centre of symmetry
- **27.** The absorbance of solution having 20% transmittance is
 - 1. 0.301
 - 2. 0.699
 - 3. 1.301
 - 4. 1.699
- **28.** The active site of enzyme nitrogenase contains
 - 1. Mo
 - 2. Mn
 - 3. Fe
 - 4. Cu

29.	Which one of the following is a free radical:			
	2.	CO CN ⁻ NO		
		CS		
30.	Choose the 16 e ⁻ complex from the following:			
		$Ni(CO)_4$		
		Rh(PPh ₃) ₃ Cl		
		$Fe(CO)_5$ $(\eta^6-C_6H_6)_2Cr$		
	4.	$(1 - C_6 \Pi_6)_2 C_1$		
31.	The spe	ecies having metal-metal bond is:		
	1.	$Mn_2(CO)_{10}$		
		$Al_2(CH_3)_6$		
		$V_2(O)_{12}$ $Al_2(OPr^i)_{12}$		
	4.	Al ₂ (OFI) ₁₂		
32.	2. Choose the INCORRECT statement from the following			
		Fluorine has higher electronegativity than chlorine Fluorine molecule (F ₂) has lower bond energy than chlorine molecule		
		(Cl_2)		
	3.	Fluorine has higher electron affinity than chlorine		
	4.	Fluorine has a lesser tendency to form cation than chlorine		
33.	The onl	y molecule having bridging oxygen is		
	1.	Phosphorus trioxide		
		Phosphorus pentaoxide		
	3.	Cyclic tetraphosphate		
	4.	Pyrophosphate		
34.	The coo	ordination number of phosphorus in $[PMo_{12}O_{40}]^{3-}$ is		
	1.	2		
	2.	4		
		5		
	4.	6		

- **35.** Using phenolphthalein as the indicator, which of the following titration is possible:
 - 1. acetic acid with pyridine
 - oxalic acid with sodium hydroxide 2.
 - hydrochloric acid with aniline 3.
 - 4. sulphuric acid with aqueous ammonia
- Which of the following species is ESR-active? **36.**
 - 1. $VOSO_4$
 - 2. K₂Cr₂O₇
 - 3. KMnO₄
 - 4. $[Co(NH_3)_6]Cl_3$
- **37.** Ozone (O₃) absorbs UV radiation in the atmosphere and is decomposed mainly into
 - 1.
 - O_2, O O^{2-}, O^{2+} O_2^{2-}, O^+ 2.
 - 3.
 - 4. atomic oxygen
- **38.** Large derivation from Trouton's rule is observed for systems which are
 - having more ordered structure 1.
 - 2. having more disordered structure
 - 3. having low melting points
 - 4. having low boiling points
- **39.** The concentration of a reactant decreases linearly with time. What is the order of the reaction?



- 1st order 1.
- Fractional order 2.
- 2nd order 3.
- 4. Zero order

40.	0. The point group symmetry of the molecule cis -ML ₄ X ₂ is				
	1. $C_{4\nu}$				
	2. D_{4h}				
	C_{2h}				
	$4. \qquad C_{2\nu}$				
41.	The point group symmetries of a square and a rectangle respectively, are				
	1. D_{4h} and D_{2h}				
	2. C_{4h} and C_{2h}				
	3. D_{4h} and C_{2h}				
	4. C_{4h} and D_{2h}				
42 .	The number of rotational degrees of freedom of CO ₂ is				
	1. one				
	2. two				
	3. three				
	4. four				
43.	The magnitude of the nuclear spin angular momentum of a nuclei is $\sqrt{15}/2$ \hbar units. The value of I is				
	1. 5/2				
	2. 1/2				
	3. 1				
	4. 3/2				
	T. 3/2				
44.	Identify the molecule whose rotational constant can not be determined by spectroscopic methods.				
	1. CH ₄				
	2. H ₂				
	CO_2				
	4. HCl				
	4. IICI				
45.	Which of the following transitions in the electronic spectrum of a homonuclear				
	diatomic molecule is forbidden				
	$1. \qquad \sum_{u}^{+} \rightarrow \sum_{g}^{+}$				
	$2. \qquad \sum_{g}^{+} \rightarrow \prod_{u}$				
	·				
	$\sum_{u}^{+} \rightarrow \prod_{g}$				
	$4 \qquad \sum^{+} \rightarrow \Lambda$				

- **46.** The diffraction pattern of a cubic solid has an intense 110 Bragg reflection, but the 100 and 111 Bragg reflections are absent. The structure of the solid is
 - 1. Body-centered cubic
 - 2. Primitive cubic
 - 3. Face-centered cubic
 - 4. Edge-centered cubic
- 47. The logarithmic conductivity of a crystalline solid shows a linear variation with inverse temperature (1/T). The band gap may be obtained from
 - 1. slope of the plot.
 - 2. intercept on the conductivity axis.
 - 3. intercept on the temperature axis.
 - 4. inverse slope
- 48. The molar masses of monodisperse and polydisperse polymers obey respectively the conditions: $(\overline{M}_n = \text{Number average molecular weight and } \overline{M}_w = \text{Weight average molecular weight)}.$
 - 1. $\overline{M}_n > \overline{M}_w$ and $\overline{M}_n < \overline{M}_w$
 - 2. $\overline{M}_n = \overline{M}_w$ and $\overline{M}_n < \overline{M}_w$
 - 3. $\overline{M}_n < \overline{M}_w$ and $\overline{M}_n < \overline{M}_w$
 - 4. $\overline{M}_n = \overline{M}_w \text{ and } \overline{M}_n = \overline{M}_w$
- 49. Curding from milk, an enzyme-catalysed reaction, is most efficient around
 - 1. $0 \, ^{\circ}\text{C} \text{ and pH} \ge 10$
 - 2. $0 \, ^{\circ}\text{C} \text{ and pH} \leq 4$
 - 3. $0 \,^{\circ}\text{C} \text{ and } 4 \leq \text{pH} \leq 10$
 - 4. $25 \, ^{\circ}\text{C} \text{ and } 4 \leq \text{pH} \leq 10$
- 50. The spatial part of hydrogen molecular wavefunction in the simplest molecular orbital theory is given by σ_g^2 where σ_g is normalized linear combination of two hydrogen 1s orbitals. Which of the following is true about the above wavefunction?
 - 1. It contains only covalent terms.
 - 2. It includes only a small amount of ionic terms.
 - 3. It contains only ionic terms.
 - 4. It overestimates the ionic terms.

51. A 2p_z orbital of hydrogen atom is an eigenfunction of

- 1.
- H only. H and L^2 only 2.
- H, L^2 and L_z only H, L^2 , L_z and L_x 3.

52. By a reversible process, we mean one that always

- takes infinite time for completion 1.
- 2. satisfies ΔS (universe) = 0
- 3. satisfies $\Delta G = 0$.
- 4. gives maximum work

53. A hydrogenic 3p orbital has the following form of the radial wavefunction (α_i = constant):

- 1.
- $r(\alpha_1 r)e^{-\alpha_2 r}$ $r^2 e^{-\alpha_3 r}$ $r(\alpha_4 r)(\alpha_5 r)e^{-\alpha_6 r}$
- 4.

The wavefunction $\sin^{-1} x$ is not acceptable because it is **54**.

- 1. not continuous
- 2. not differentiable
- 3. not an eigenfunction of kinetic energy operator
- 4. not a single-valued function

55. IUPAC name for the compound given below is

- 1. *E*-5-ethylhept-5-en-2-one
- 2. Z-5-ethylhept-5-en-2-one
- 3. E-3-ethylhept-2-en-6-one
- Z-3-ethylhept-2-en-6-one

56. The most suitable reagent for the following transformation is

- 1. NaBH₄
- B_2H_6
- 3. Zn-Hg / HCl
- 4. NH_2NH_2/HCl

57. Acetophenone can be converted to phenol by reaction with

- 1. *m*-CPBA followed by base catalysed hydrolysis
- 2. conc. HNO₃
- 3. iodine and NaOH
- 4. singlet oxygen followed by base catalysed hydrolysis

58. Reaction of phenyl benzoate with an excess of methylmagnesium bromide gives a mixture of

- 1. triphenylmethanol and phenol
- 2. 2-phenylpropan-2-ol and phenol
- 3. acetophenone and toluene
- 4. 2-phenylbenzoic acid and toluene

59. The major product formed in the reaction of 2-methylbut-3-en-2-ol with HBr is

60. Among dimethylcyclobutanes, which one can exhibit optical activity?

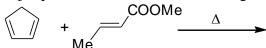
- 1. *cis*-1,2-dimethylcyclobutane
- 2. *trans*-1,2-dimethylcyclobutane
- 3. *cis*-1,3-dimethylcyclobutane
- 4. *trans*-1,3-dimethylcyclobutane

61. The monomer of biopolymer DNA is a

- 1. nucleotide
- 2. amino acid
- 3. disaccharide
- 4. fatty acid

- 62. The order of chemical shifts (δ value) in the 1H NMR spectrum of crotonaldehyde is
 - 1. olefinic > CHO > Me
 - 2. CHO > Me > olefinic
 - 3. CHO > olefinic > Me
 - 4. olefinic > Me > CHO
- **63.** Natural sugars and aminoacids are predominantly
 - 1. D-sugars and L-amino acids
 - 2. D-sugars and D-amino acids
 - 3. L-sugars and D-amino acids
 - 4. L-sugars and L-amino acids
- **64.** The product formed in the reaction given below is

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



1. Me

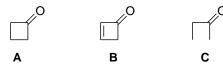


- 2. COOMe
- 3. MeOOC
- 4. Me COOMe
- **66.** The conversion of excited singlet state (S_1) of a molecule to triplet state (T_1) is known as
 - 1. fluorescence
 - 2. phosphorescence
 - 3. intersystem crossing
 - 4. internal conversion
- 67. The decreasing order of stability of the free radicals A, B and C is

- 1. A > B > C
- $2. \qquad C > A > B$
- $3. \qquad B > A > C$
- 4. A > C > B

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

- 1. OH
- 2. OH
- 3. N₃
- 4. "N₃
- **69.** The rates of keto-enol tautomerism in the ketones **A-C**, given below, are in the order

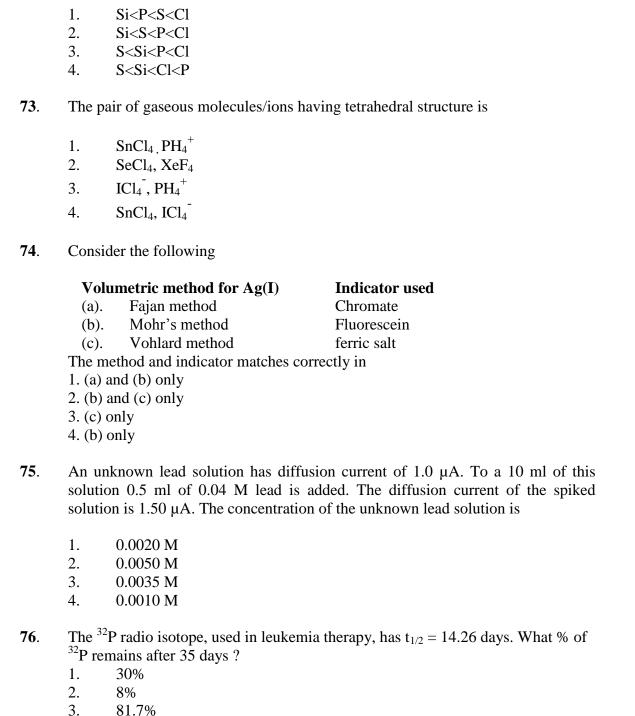


- $1. \qquad A > B > C$
- $2. \qquad A > C > B$
- $3. \qquad C > A > B$
- 4. C > B > A
- **70.** The reaction given below is an example of

- 1. aldol condensation
- 2. Knoevenagel condensation
- 3. Dieckmann condensation
- 4. acyloin condensation

PART C

- 71. The covalent radii vary gradually in the Periodic Table. From the orders given below for such radii, the correct ones are
 - (a) Ce > Lu, (b) Co > Ti, (c) Sr > Ca, (d) I > Se



The first ionization energy for the elements Si, P, S and Cl, follows the order

1.

2.

3.

4.

72.

(a) and (b) only

(a) and (c) only

(a), (c) and (d) only

(b), (c) and (d) only

- 4. 18.3%
- 77. On a 30 cm column, the t_R of **A** and **B** respectively are 16.40 and 17.63 minutes. The t_0 of the column is 1.30 minutes. The peak width at base lines for **A** and **B** are 1.11 and 1.21 minutes respectively. The column resolution R_S is
 - 1. 1.06
 - 2. 1.23
 - 3. 2.12
 - 4. 2.23
- **78**. Which one of the following pairs of electronic configurations of high-spin transition metal ions (3d) in an octahedral field undergoes a substantial Jahn-Teller distortion:
 - d^3 . d^9 1.
 - d^{4}, d^{9} d^{5}, d^{9} 2.
 - 3.
 - d^6, d^9 4.
- **79**. Which one of the following pairs consists of a good oxidizing and a good reducing agent respectively:
 - 1. Ce(IV), Ln(III)
 - 2. Ln(III), Eu(II)
 - 3. Ce(IV), Eu(II)
 - 4. Ln(III), Ce(III)
- Which one of the pairs of following statements about reduction of [CoCl(NH₃)₅]²⁺ **80**. by Cr(II) is correct:
 - (A). Reactant $\left[CoCl(NH_3)_5 \right]^{2+}$ has non-labile coordination sphere
 - (B). Reaction proceeds by outer-sphere mechanism
 - (C). Reactant $[CoCl(NH_3)_5]^{2+}$ has labile coordination sphere
 - (D). Reaction proceeds by inner-sphere mechanism
 - 1. (A) and (B)
 - 2. (A) and (D)
 - 3. (C) and (B)
 - (C) and (D) 4.
- **81**. Hemocyanin contains
 - a dinuclear copper core and binds dioxygen in the cuprous state. 1.
 - 2. a dinuclear copper core and binds dioxygen in the cupric state.
 - 3. a mononuclear copper core and binds dioxygen in the cuprous state
 - 4. a mononuclear copper core and binds dioxygen in the cupric state.

82.	The ^{31}P NMR spectrum of $PF_4N(CH_3)_2$ at room temperature and low temperature (173 K) respectively shows (assume that N and H do not couple):		
	1. 2. 3. 4.	triplet and quintet quintet and triplet quintet and triplet of triplets triplet and triplet of triplets	
83.	The number of hyperfine lines in the EPR spectrum of a one electron reduce product of $[Co_3(CO)_9Se]$ (I = 7/2 for Co nucleus) is:		
	1. 2. 3. 4.	8 15 22 1	
84.	The highest oxidation state of a metal in the following compounds is : $(\eta^6-C_6H_6)_2Cr$, $Mn(CO)_5Cl$, $Na_2[Fe(CO)_4]$, $K[Mn(CO)_5]$ and $K[Mo(CO)_5Br]$		
	1. 2. 3. 4.	1 2 -1 -2	
85.	The maximum number of valence electrons of a metal in these complexes are: $Mn_2(CO)_{10}$, $(\eta^5-C_5H_5)Mo(CO)_3Cl$, $(\eta^5-C_5H_5)_2Ni$, and $(\eta^5-C_5H_5)_2TiCl_2$		
	1. 2. 3. 4.	16 18 20 22	
86 . The number of bridging and terminatemperature are respectively:		number of bridging and terminal carbonyls present in $Co_4(CO)_{12}$ at low trature are respectively:	
	1. 2. 3. 4.	3 and 9 4 and 8 6 and 6 0 and 12	
87 .	Olefin	hydrogenation using Wilkinson's catalyst initiates with:	

olefin addition to $Rh(PPh_3)_2Cl$ olefin addition to $Rh(PPh_3)_3Cl$

a phosphine dissociation from Rh(PPh₃)₃Cl

1.

2.3.

- 4. a phosphine addition to Rh(PPh₃)₂Cl
- **88**. Although Fe(III) is a better Lewis acid compared to Zn(II), most hydrolytic enzymes contain Zn(II) at the active site because
 - 1. Fe(III) is a redox active ion.
 - 2. Fe(III) has less abundance compared to Zn(II).
 - 3. Fe(III) generally makes octahedral complexes while Zn(II) makes tetrahedral complexes
 - 4. Zn(II) makes kinetically labile complexes.
- **89**. Considering the two complexes (A) $[Ni(H_2O)_6]^{2+}$ and (B) $[Ni(NH_3)_6]^{2+}$, the right statement is
 - 1. Complex (A) is diamagnetic and complex (B) is paramagnetic
 - 2. Complex (A) is paramagnetic and complex (B) is diamagnetic
 - 3. Both are paramagnetic
 - 4. Both are diamagnetic
- **90**. Unlike d-d transitions, the f-f transitions
 - 1. do not change much with change in ligand
 - 2. change significantly with change in ligand
 - 3. appear at low energies i.e., at the near-IR region
 - 4. appear as broad bands
- 91. The solvent that will enhance electrical conductivity of N_2O_4 considerably is
 - 1. hexane
 - 2. benzene
 - 3. nitromethane
 - 4. carbon tetrachloride
- 92. The major product obtained by the reaction of PCl₅ with NH₃, NH₄Cl and $(NH_4)_2SO_4$ respectively are
 - 1. $(PNCl_2)_n$, $P(NH_2)_4Cl$ and $Cl_3P=NPOCl_2$
 - 2. $P(NH_2)_4Cl$, $(PNCl_2)_n$ and $Cl_3P=NPOCl_2$
 - 3. $Cl_3P=NPOCl_2$, $(PNCl_2)_n$ and $P(NH_2)_4Cl$
 - 4. $(PNCl_2)_n$ only
- **93**. Strongest superacid among the following is a
 - 1. solution of HNO₃ in H₂SO₄
 - 2. solution of HClO₄ in H₂SO₄
 - 3. solution of SbF₅ in HF
 - 4. solution of SbCl₅ in HCl

- **94**. Consider the following statements regarding borazine,
 - A. It is isoelectronic with benzene
 - B. Each nitrogen receives more σ -electron density from neighbouring boron than it gives away as a π -donor
 - C. It does not undergo addition reactions
 - D. Nitrogen retains its basicity and boron its acidity.

The true statements among the above are

- 1. A, C and D
- 2. A, B and D
- 3. A and C only
- 4. B, C, and D
- **95**. Which of the following has linear shape
 - 1. $H_3C-N=C=S$
 - 2. $H_3Si-N=C=S$
 - 3. H₃C-N=C=O
 - 4. H₃C-O-CH₃
- **96**. For a diffusion-controlled bimolecular reaction, the rate constant (k_D) is proportional to $(T = temperature; \eta = coefficient of viscosity of medium).$
 - 1. ηT
 - 2. $\frac{1}{\eta T}$
 - 3. $\frac{T}{\sqrt{\eta}}$
 - 4. $\frac{T}{n}$
- **97**. Consider the unimolecular reaction

$$A(g) \rightarrow products$$

for which the following remarks were made.

- A. The reaction is second order at low pressure and becomes first order at high pressure.
- B. The reaction is first order at low pressure and becomes second order at high pressure.
- C. The reaction is zero order

Which of these is correct?

1. A and B

- 2. B and C
- 3. Only C
- 4. only A
- 98. A random distribution of errors obeys the Gaussian form $\sqrt{A/\pi} \exp[-Ax^2]$. The mean and standard deviation of this distribution obeys
 - 1. $< x > = 0 \text{ and } \sigma_x = 1/\sqrt{A}$
 - 2. $\langle x \rangle \neq 0$ and $\sigma_x = 1/\sqrt{A}$
 - 3. $\langle x \rangle = 0$ and $\sigma_x = \sqrt{A}$
 - 4. $\langle x \rangle = 0$ and $\sigma_x = A$
- **99**. The function $\sin^{-1} x$ is not an acceptable wave function because
 - 1. it is not differentiable
 - 2. its first derivative is not continuous
 - 3. it does not cover the entire space
 - 4. it is not a single-valued function
- **100**. The following is true of $2p_x$, $2p_y$ and $2p_z$ orbitals of a H atom.
 - 1. All are eigen functions of L_z
 - 2. Only $2p_x$ and $2p_z$ orbitals are eigen functions of L_z
 - 3. Only $2p_y$ orbital is an eigen function of L_z .
 - 4. Only $2p_z$ orbital is an eigen function of L_z .
- **101**. Given two Hermitian operators A and B, we construct the following four additional operators

AB, ABA,
$$i[A,B]$$
, A^2B .

Choose the correct option from below.

- 1. All these 4 operators are Hermitian
- 2. Only 3 of these operators are Hermitian
- 3. Only 2 of these operators are Hermitian
- 4. Only 1 of these operators is Hermitian
- 102. The first-order correction to energy for the ground state of a particle-in-a-box due to a perturbation λx would be
 - 1. $\lambda L/2$
 - 2. λL
 - 3. 2λL
 - 4. 2

Characters of a few symmetry operations are given below. Identify the character **103**. of the irreducible representation $A_{2g}^{'}$

	E	C_n	C_2	i	$\sigma_{\rm h}$
1	1	1	1	-1	-1
2	1	1	-1	1	1
3	1	-1	-1	1	1
4	1	1	-1	-1	1

The character of the irreducible representation A_1 in $C_{3\nu}$ point group is given **104**. below

Identify one irreducible representation orthogonal to A₁among the following.

	Е	$2C_3$	$3\sigma_{\rm v}$
Γ_1	1	-1	1
Γ_2	2	-1	0
Γ_3	2	0	-1
Γ_4	1	-1	-1

- 1.
- 2.
- 3.
- 4.
- The energy levels of cyclopropene are $\alpha + 2\beta$, $\alpha \beta$, and $\alpha \beta$. The **105**. delocalization energy in C₃H₃ is
 - 2β 1.
 - 2. 0
 - 3. β
 - 3β
- The rotational constant (B) of H³⁵Cl, H³⁷Cl and D³⁵Cl follow the order **106**.
 - 1.

 - $\begin{array}{l} H^{35}Cl \ > \ D^{35}Cl \ > H^{37}Cl \\ H^{35}Cl \ > \ H^{37}Cl \ > D^{35}Cl \\ D^{35}Cl \ > \ H^{35}Cl \ > H^{37}Cl \\ H^{37}Cl \ > \ H^{35}Cl \ > D^{35}Cl \end{array}$
- **107**. Observe the following statements

- I. Atomic mass of isotopes can be obtained from rotational spectra
- **II.** The separation between two successive rotational spectral lines of gaseons NO is 2B cm⁻¹
- III. The nmr spectrum of a compound gave a singlet at 300 H_z away from TMS using a nmr spectrometer operating at 60 MH_z . Its chemical shif is 3 ppm.

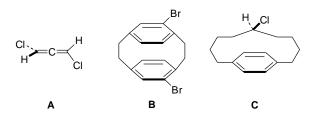
Which of the following is correct?

- 1. I, II and III are correct.
- 2. Only III is correct.
- 3. I and II are correct.
- 4. Only I is correct.
- 108. In a crystal, atom A is at the corners of the unit cell, B is at the centre of the cell and the oxygen atoms are at the face-centred positions. What is the formula per unit cell?
 - 1. A_8BO_6
 - ABO_6
 - A_8BO_3
 - 4. ABO_3
- **109**. On mixing 100 mL of 0.1 M CH₃COOH and 50 mL of 0.1 M NaOH, the pH of the solution will be
 - 1. $pk_a + 0.301$
 - pk_a
 - 3. $pk_a 0.301$
 - 4. $pk_a + 0.477$
- 110. Using the fundamental equation dA = -SdT P dV, the Maxwell relation is
 - 1. $\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial S}\right)_V$
 - 2. $\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial P}{\partial T}\right)_V$
 - 3. $\left(\frac{\partial T}{\partial V}\right)_{S} = \left(\frac{\partial P}{\partial S}\right)_{T}$
 - 4. $\left(\frac{\partial S}{\partial V}\right)_{T} = \left(\frac{\partial P}{\partial T}\right)_{V}$

- 111. The relationship between mean ionic activity coefficient for Ca₃(PO₄)₂ and its ions is given by
 - $$\begin{split} \gamma_{\pm} &= \gamma_{+}^{\ 3} \ \gamma_{-}^{\ 2} \\ \gamma_{\pm} &= \gamma_{+}^{\ 2} \ \gamma_{-}^{\ 3} \\ \gamma_{\pm}^{\ 5} &= \gamma_{+}^{\ 3} \ \gamma_{-}^{\ 2} \\ \gamma_{\pm}^{\ 5} &= \gamma_{+}^{\ 2} \ \gamma_{-}^{\ 3} \end{split}$$
- Assuming that C-H and C-X bond lengths in X-112. the molar residual entropy at 0 K is
 - 0 1.
 - 2. Rln2
 - 3. Rln3
 - 4. Rln6
- 113. The contributions to the molar entropy by translational (tr), rotational (rot), vibrational (vib) and electronic (ele) degrees of freedom is in order
 - 1. tr > rot > vib > ele
 - 2. rot > vib > tr > ele
 - 3. ele > vib > rot > tr
 - 4. vib > rot > tr > ele
- 114. A binary mixture of A₂ and B₂ will show negative deviation from Raoult's law when
 - A-A and B-B interactions are stronger than A-B 1.
 - 2. A-A and B-B interactions are weaker than A-B
 - 3. Both A-A and B-B interactions are equal to A-B
 - 4. Either A–A or B–B interactions is equal to A–B
- In the presence of external magnetic field the transition ${}^3D_1 \rightarrow {}^3P_1$ splits into 115.
 - 3 1.
 - 2. 5
 - 3. 7
 - 4. 9
- The term symbol for the ground state of rhodium (Rh, atomic number 45) is ⁴F. **116**. The electronic configuration for this term symbol is
 - [Kr] $4d^7 5s^2$ 1.
 - $[Kr] 4d^8 5s^1$ 2.
 - 3.
 - [Kr] $4d^9 5s^0$ [Kr] $4d^7 5s^1 5p^1$ 4.

- Ionic equivalent conductance value for Ca²⁺ is 0.0119 (S m² mol⁻¹) and for Cl⁻ is 117. 0.0076 (S m² mol⁻¹). The correct expected molar conductivity at infinite dilution for CaCl2 is
 - $\begin{array}{c} 0.0195 \; S \; m^2 \; mol^{\text{-}1} \\ 0.0271 \; S \; m^2 \; mol^{\text{-}1} \\ 0.0542 \; S \; m^2 \; mol^{\text{-}1} \end{array}$ 1.
 - 2.
 - 3.
 - 0.01355 S m² mol⁻¹
- Find correct pair for ionic strengths of (a) a 0.02 molal solution of KCl and 118. a 0.02 molal solution of K₂SO₄.

 - 2.
 - 3.
 - $\begin{array}{l} \text{(a) } 0.020 \text{ mol } \text{Kg}^{\text{-1}} \text{ (b) } 0.020 \text{ mol } \text{Kg}^{\text{-1}} \\ \text{(a) } 0.020 \text{ mol } \text{Kg}^{\text{-1}} \text{ (b) } 0.060 \text{ mol } \text{Kg}^{\text{-1}} \\ \text{(a) } 0.020 \text{ mol } \text{Kg}^{\text{-1}} \text{ (b) } 0.050 \text{ mol } \text{Kg}^{\text{-1}} \\ \text{(a) } 0.020 \text{ mol } \text{Kg}^{\text{-1}} \text{ (b) } 0.030 \text{ mol } \text{Kg}^{\text{-1}} \end{array}$ 4.
- 119. The term symbol for the ground state configuration of NO is
 - 1. $^{2}\Pi_{u}$
 - $^{2}\Pi_{\alpha}$ 2.
 - $^{1}\Pi_{\mu}$ 3.
- **120**. The kinetic chain length (v) is a measure of chain propagation. If the rates of consumption are denoted by R_c and rates of production by R_p; M and M[•] denote the monomer and the active center, respectively. The correct definition of v is
 - 1. $R_{c}(M)/R_{p}(M^{\bullet})$
 - $R_{p}\left(M^{\bullet}\right)/R_{c}\left(M\right)$
 - $R_c(M^{\bullet})/R_p(M)$ 3.
 - $R_c(M)/R_c(M^{\bullet})$
- 121. Amongst the following the correct statement for the compounds A, B, and C, is



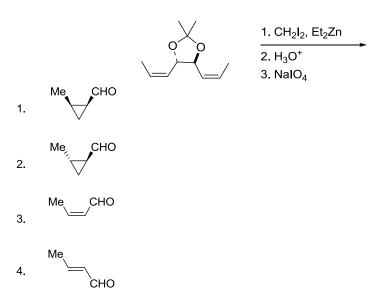
- A and B are achiral and C is chiral 1.
- 2. A is chiral and B and C are achiral
- A and B are chiral and C is achiral 3.

4. **A** is achiral and **B** and **C** are chiral

- 122. 4-tert-Butylcyclohexanone on reduction gives two isomeric alcohols which are
 - 1. Enantiomers
 - 2. Diasteromers
 - 3. Rotamers
 - 4. Homomers
- **123**. For the following compounds **A** and **B** the correct statement is



- 1. **A** is aromatic and **B** is antiaromatic
- 2. A is antiaromatic and B is non-aromatic
- 3. **A** and **B** are both aromatic
- 4. **A** and **B** are both non-aromatic
- **124.** Identify the product formed in the following transformations



125. Identify the product formed in the following sequence of reactions

126. Identify the products **A** and **B** in the following reaction sequence

127. Match the following:

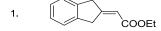
- A. Conversion of 1,7-octadiene to cyclohexene
- B. Conversion of bromobenzene to ethyl cinnamate
- C. Conversion of 1-hexene to 2-hexanone

- i) Wacker Oxidation
- ii) McMurry Coupling
- iii) Heck reaction
- iv) Olefin Metathesis

- 1, A: iv; B: ii; C: iii
- 2. A: ii; B: iv; C: i
- 3. A: iv; B: iii; C: i
- 4. A: i; B: iii; C: iv
- **128.** Reagents that can be used in the following conversion are

- 1. i) Ph₃P=CH₂, ii) HCN, iii) H₃O⁺
- 2. i) HS(CH₂)₂SH, ii) n-BuLi, iii) BrCH₂COOH
- 3. i) EtMgI, ii) KMnO₄
- 4. i) Ph₃P, CBr₄, ii) n-BuLi, iii) CO₂
- **129.** The major product formed in the following reaction is

- 1.
- 2. OH
- 3. OH
- 4.
- **130.** In the following reaction, the structure of the major product is



131. For the following reaction, the structure of the major product is

132. Identify the products **A** and **B** in the following reaction sequence.

- 1. **A** is **Q B** is **Q O**
- 2. **A** is **Q B** is
- 3. **A** is **B** is
- 4. A is 0 B is 0
- **133.** Major product formed in the following reaction is

- MeO CONH
- TMSO COMe 2.
- TMSO NH₂
- 4. TMSO OF
- 134. In the following reaction sequence the structure of the major products \mathbf{X} and \mathbf{Y} are

$$\begin{array}{c} S \\ \\ S \\ \end{array} \begin{array}{c} O \\ \\ \end{array} \begin{array}{c} \text{i. n-BuLi} \\ \text{ii. CH}_3\text{CH}_2\text{CH}_2\text{Br} \end{array} \begin{array}{c} X \\ \end{array} \begin{array}{c} \text{HgSO}_4, \text{ H}_2\text{O} \\ \end{array} \begin{array}{c} Y \\ \end{array}$$

135. Product of Sharpless kinetic resolution of the following alcohol with (-)-diethyl tartrate is

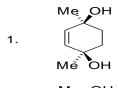
136. Select the product of the reaction of (Z)-(2-methoxyvinyl)benzene with dichloroacetyl chloride in presence of triethyl amine.

137. Identify the product formed in the following reaction

138. The compound formed in the following reaction sequence is

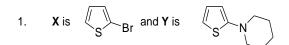
139. Cholestanol on oxidation with chromium trioxide in acetic acid/pyridine gives a dicarboxylic acid, which on pyrolysis in the presence of a catalytic amount of barium hydroxide gives compound **A** as the major product. The structure of **A** is

140. Photolysis of 1,4-dimethyl-1,3-cyclohexadiene in presence of excess oxygen and catalytic amount of Rose Bengal followed by reduction with H₂/Pt provides



141. In the following reaction sequence, the correct structures of the major products ${\bf X}$ and ${\bf Y}$ are

142. Structure of the X and Y in the reaction sequence of thiophene given below are



143. Identify the product of hydrogenation (H₂, Pd/C) of the protected amino acid given below

$$_{2}$$
 $H_{2}N$ COOCH $_{2}$ Ph

144. In the broad band decoupled ¹³C NMR spectrum, the number of signals appear for (a) catechol, (b) resorcinol and (c) hydroquinone, respectively, are

- 1. six, four and two
- 2. six, six and four
- 3. three, four and four
- 4. three, four and two

145. In the proton NMR spectrum, an organic compound exhibited the following spectral data

 δ 7.2 (1H, dd, J = 8 and 1.5 Hz), 6.8 (1H, d, J = 1.5 Hz), 6.7 (1H, d, J = 8 Hz), 4.9 (2H, s), 3.9 (3H, s), 3.85 (3H, s), 3.5 (1H, br s, exchangeable with D₂O)

The compound among the choices given below is