

Test Booklet No.

प्रश्नपत्रिका क्र.

M

## Paper-III

### CHEMICAL SCIENCE

Seat No.

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(In figures as in Admit Card)

Seat No. ....

(In words)

OMR Sheet No.

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(To be filled by the Candidate)

**Signature and Name of Invigilator**

1. (Signature) .....

(Name) .....

2. (Signature) .....

(Name) .....

**DEC - 33313****Time Allowed : 2½ Hours]****[Maximum Marks : 150****Number of Pages in this Booklet : 32****Number of Questions in this Booklet : 75****Instructions for the Candidates**

- Write your Seat No. and OMR Sheet No. in the space provided on the top of this page.
- This paper consists of 75 objective type questions. Each question will carry two marks. All questions of Paper-III will be compulsory, covering entire syllabus (including all electives, without options).
- At the commencement of examination, the question booklet will be given to the student. In the first 5 minutes, you are requested to open the booklet and compulsorily examine it as follows :
  - To have access to the Question Booklet, tear off the paper seal on the edge of this cover page. Do not accept a booklet without sticker-seal or open booklet.
  - Tally the number of pages and number of questions in the booklet with the information printed on the cover page. Faulty booklets due to missing pages/questions or questions repeated or not in serial order or any other discrepancy should not be accepted and correct booklet should be obtained from the invigilator within the period of 5 minutes. Afterwards, neither the Question Booklet will be replaced nor any extra time will be given. The same may please be noted.**
  - After this verification is over, the OMR Sheet Number should be entered on this Test Booklet.
- Each question has four alternative responses marked (A), (B), (C) and (D). You have to darken the circle as indicated below on the correct response against each item.  
**Example :** where (C) is the correct response.  

(A)	(B)	(C)	(D)
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- Your responses to the items are to be indicated in the **OMR Sheet given inside the Booklet only**. If you mark at any place other than in the circle in the OMR Sheet, it will not be evaluated.
- Read instructions given inside carefully.
- Rough Work is to be done at the end of this booklet.
- If you write your Name, Seat Number, Phone Number or put any mark on any part of the OMR Sheet, except for the space allotted for the relevant entries, which may disclose your identity, or use abusive language or employ any other unfair means, you will render yourself liable to disqualification.
- You have to return original OMR Sheet to the invigilator at the end of the examination compulsorily and must not carry it with you outside the Examination Hall. You are, however, allowed to carry the Test Booklet and duplicate copy of OMR Sheet on conclusion of examination.
- Use only Blue/Black Ball point pen.**
- Use of any calculator or log table, etc., is prohibited.**
- There is no negative marking for incorrect answers.**

**विद्यार्थ्यांसाठी महत्वाच्या सूचना**

- परिक्षार्थींनी आपला आसन क्रमांक या पृष्ठावरील वरच्या कोपऱ्यात लिहावा. तसेच आपणांस दिलेल्या उत्तरपत्रिकेचा क्रमांक त्याखाली लिहावा.
- सदर प्रश्नपत्रिकेत 75 बहुपर्यायी प्रश्न आहेत. प्रत्येक प्रश्नास दोन गुण आहेत. या प्रश्नपत्रिकेतील सर्व प्रश्न सोडविणे अनिवार्य आहे. सदरचे प्रश्न हे या विषयाच्या संपूर्ण अभ्यासक्रमावर आधारित आहेत.
- परीक्षा सुरु झाल्यावर विद्यार्थ्यांला प्रश्नपत्रिका दिली जाईल. सुरुवातीच्या 5 मिनीटांमध्ये आपण सदर प्रश्नपत्रिका उघडून खालील बाबी अवश्य तपासून घ्याव्यात.
  - प्रश्नपत्रिका उघडण्यासाठी प्रश्नपत्रिकेवर लावलेले सील उघडावे. सील नसलेली किंवा सील उघडलेली प्रश्नपत्रिका स्विकारू नये.
  - पहिल्या पृष्ठावर नमूद केल्याप्रमाणे प्रश्नपत्रिकेची एकूण पृष्ठे तसेच प्रश्नपत्रिकेतील एकूण प्रश्नांची संख्या पडताळून घ्यावी. पृष्ठे कमी असलेली/कमी प्रश्न असलेली/प्रश्नांचा चुकीचा क्रम असलेली किंवा इतर त्रुटी असलेली सदोष प्रश्नपत्रिका सुरुवातीच्या 5 मिनिटातच पर्यवेक्षकाला परत देऊन दुसरी प्रश्नपत्रिका मागवून घ्यावी. त्यानंतर प्रश्नपत्रिका बदलून मिळणार नाही तसेच वेळही वाढवून मिळणार नाही याची कृपया विद्यार्थ्यांनी नोंद घ्यावी.
  - वरीलप्रमाणे सर्व पडताळून पहिल्यानंतरच प्रश्नपत्रिकेवर ओ.एम.आर. उत्तरपत्रिकेचा नंबर लिहावा.
- प्रत्येक प्रश्नासाठी (A), (B), (C) आणि (D) अशी चार विकल्प उत्तरे दिली आहेत. त्यातील योग्य उत्तराचा रकाना खाली दर्शविल्याप्रमाणे ठळकपणे काळा/निळा करावा.  
**उदा. :** जर (C) हे योग्य उत्तर असेल तर.  

(A)	(B)	(C)	(D)
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- या प्रश्नपत्रिकेतील प्रश्नांची उत्तरे ओ.एम.आर. उत्तरपत्रिकेतच दर्शवावीत. इतर ठिकाणी लिहिलेली उत्तरे तपासली जाणार नाहीत.
- आत दिलेल्या सूचना काळजीपूर्वक वाचाव्यात.
- प्रश्नपत्रिकेच्या शेवटी जोडलेल्या कोऱ्या पानावरच कच्चे काम करावे.
- जर आपण ओ.एम.आर. वर नमूद केलेल्या ठिकाणा व्यतिरीक्त इतर कोठेही नाव, आसन क्रमांक, फोन नंबर किंवा ओळख पटेल अशी कोणतीही खूण केलेली आढळून आल्यास अथवा असभ्य भाषेचा वापर किंवा इतर गैरमार्गाचा अवलंब केल्यास विद्यार्थ्यांला परीक्षेस अपात्र ठरविण्यात येईल.
- परीक्षा संपल्यानंतर विद्यार्थ्यांनी मूळ ओ.एम.आर. उत्तरपत्रिका पर्यवेक्षकांकडे परत करणे आवश्यक आहे. तथापी, प्रश्नपत्रिका व ओ.एम.आर. उत्तरपत्रिकेची द्वितीय प्रत आपल्याबरोबर नेण्यास विद्यार्थ्यांना परवानगी आहे.
- फक्त निळा किंवा काळा बॉल पेनचाच वापर करावा.**
- कॅलक्युलेटर किंवा लॉग टेबल वापरण्यास परवानगी नाही.**
- चुकीच्या उत्तरासाठी गुण कपात केली जाणार नाही.**

**DEC - 33313/III**

## Chemical Science

### Paper III

**Time Allowed : 2½ Hours]**

**[Maximum Marks : 150**

**Note :** This Paper contains **Seventy Five (75)** multiple choice questions, each question carrying **Two (2)** marks. Attempt *All* questions.

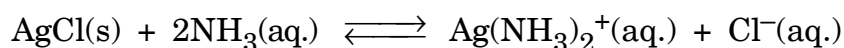
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1. The Bromination of phenol to form tribromophenol :



Change in standard free energy of the system ( $\Delta G^0$ ) is given as :

- (A)  $\Delta G^0 = \frac{1}{3}\mu_{\text{Br}_2}^0 + \mu_{\text{C}_6\text{H}_5\text{OH}}^0 - \frac{1}{3}\mu_{\text{HBr}}^0 - \mu_{\text{TBP}}^0$
- (B)  $\Delta G^0 = \frac{1}{3}\mu_{\text{HBr}}^0 + \mu_{\text{TBP}}^0 - \frac{1}{3}\mu_{\text{Br}_2}^0 - \mu_{\text{C}_6\text{H}_5\text{OH}}^0$
- (C)  $\Delta G^0 = 3\mu_{\text{Br}_2}^0 + \mu_{\text{C}_6\text{H}_5\text{OH}}^0 - 3\mu_{\text{HBr}}^0 - \mu_{\text{TBP}}^0$
- (D)  $\Delta G^0 = 3\mu_{\text{HBr}}^0 + \mu_{\text{TBP}}^0 - 3\mu_{\text{Br}_2}^0 - \mu_{\text{C}_6\text{H}_5\text{OH}}^0$
2. Consider the equation below :



Increase in  $\text{Cl}^-$  concentration causes equilibrium concentration to change favoring :

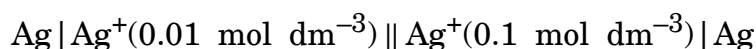
- (A) the formation of  $\text{Ag(NH}_3)_2^+(\text{aq.})$
- (B) a decrease in  $\text{NH}_3(\text{aq.})$  concentration
- (C) the formation of  $\text{AgCl(s)}$
- (D) the decrease in amount of  $\text{AgCl(s)}$
-

3. For 0.01 Molal  $\text{AgNO}_3$  solution, the mean activity coefficient ( $\gamma_{\pm}$ ) is given by expression (assume  $A = \frac{1}{2}$ ) :

(A)  $\log \gamma_{\pm} = \frac{\sqrt{2}}{2}$  (B)  $\log \gamma_{\pm} = -\frac{\sqrt{2}}{2}$

(C)  $\gamma_{\pm} = 10^{0.05}$  (D)  $\gamma_{\pm} = 10^{-0.05}$

4. For the concentration cell,

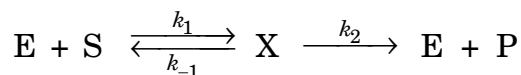


EMF of the cell reaction at temperature (T) is equal to :

(A)  $2.303 \frac{RT}{F}$  (B)  $-2.303 \frac{RT}{F}$

(C)  $E_{\text{Ag}^+/\text{Ag}}^0 + 2.303 \frac{RT}{F}$  (D)  $E_{\text{Ag}^+/\text{Ag}}^0 - 2.303 \frac{RT}{F}$

5. For the enzymolysis with the following mechanism :



Applying steady state approximation on the rate law, the concentration of an intermediate will become :

$$[x] = \frac{k_1 E_0 S_0}{k_1 S_0 + k_{-1} + k_2}$$

Based on this, the initial rate of a reaction is worked out to be :

(A)  $v_0 = \frac{k_1 k_2 E_0}{k_1 + \frac{k_{-1} + k_2}{S_0}}$  (B)  $v_0 = \frac{k_1 k_2 E_0}{k_2 + \frac{k_{-1} + k_1}{S_0}}$

(C)  $v_0 = \frac{k_1 k_2 E_0}{k_{-1} + \frac{k_1 + k_2}{S_0}}$  (D)  $v_0 = \frac{k_1 k_2 E_0}{k_1 + \frac{k_{-1} + k_2}{S_0}}$

6. For the reaction given below, the relaxation time ( $\tau$ ) is found to be  $10^{-9}$  s. If 10% of cis-dichloroethene remains at equilibrium, then the value of  $k_1(\text{s}^{-1})$  is :



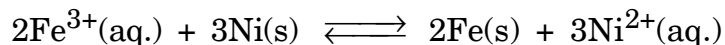
- (A)  $-9 \times 10^{-8}$  (B)  $10^{-8}$   
 (C)  $10^8$  (D)  $9 \times 10^{-8}$
7. The following are the comparison between bimolecular rate constants predicated from Collision Theory (CT) and the corresponding experimental values, for the various gaseous phase reactions :

$\xrightleftharpoons[k_{-1}]{k_1}$	<b>k(Expt.),</b> <b>L mol<sup>-1</sup> s<sup>-1</sup></b>	<b>k(Collision Theory),</b> <b>L mol<sup>-1</sup> s<sup>-1</sup></b>
$2\text{NaCl} \rightarrow 2\text{Na} + 2\text{Cl}$	$9.4 \times 10^9$	$5.9 \times 10^{10}$
$2\text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	$6.3 \times 10^7$	$2.5 \times 10^{10}$
$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	$1.24 \times 10^6$	$7.3 \times 10^{11}$

These results suggest that CT over-estimates the rate constants. This limitation of CT is due to :

- (A) favorable orientation is needed to be considered for the successful reaction  
 (B) experimental errors in the measurements  
 (C) activation energy is involved in the reaction  
 (D) molecules are assumed as hard sphere

8. Which of the answers below is the correct short hand representation for the galvanic cell having the following over all reaction ?



- (A)  $\text{Fe}^{3+}(\text{aq.}) | \text{Fe}(\text{s}) || \text{Ni}(\text{s}) | \text{Ni}^{2+}(\text{aq.})$   
(B)  $\text{Fe}^{3+}(\text{aq.}) | \text{Ni}(\text{s}) || \text{Fe}(\text{s}) | \text{Ni}^{2+}(\text{aq.})$   
(C)  $\text{Ni}(\text{s}) | \text{Ni}^{2+}(\text{aq.}) || \text{Fe}(\text{s}) | \text{Fe}^{3+}(\text{aq.})$   
(D)  $\text{Ni}(\text{s}) | \text{Ni}^{2+}(\text{aq.}) || \text{Fe}^{3+}(\text{aq.}) | \text{Fe}(\text{s})$
9. What would happen to the state of a substance represented by this phase diagram, if the pressure changed from Point 'A' to Point 'B' (holding temperature constant) ?

- |                 |                |
|-----------------|----------------|
| (A) Melting     | (B) Deposition |
| (C) Sublimation | (D) Freezing   |

10. What will be the number of possible arrangements for a hypothetical system consisting of 5 molecules and 2 quanta ?
- (A) 21 (B) 3  
(C) 15 (D) 2
11. Nylon is *not* a :
- (A) Co-polymer (B) Condensation polymer  
(C) Polyamine (D) Homopolymer
12. A liquid *does not* wet the surface of a solid if the angle of contact is :
- (A) Zero (B) 90°  
(C) 30° (D) 120°
13. Radioactive disintegration differs from a chemical change in being :
- (A) A unimolecular first order reaction  
(B) A spontaneous process  
(C) A bimolecular process  
(D) A nuclear process
14. Predict the value for the standard constant volume heat capacity ( $C_v^\circ$ ) of a closed shell heteronuclear diatomic molecule at high temperature :
- (A)  $\frac{5}{2}R$  (B)  $\frac{7}{2}R$   
(C)  $\frac{3}{2}R$  (D)  $\frac{9}{2}R$
15. The radio carbon dating method was developed by :
- (A) A. Yukawa (B) J.J. Thomson  
(C) Willard Libby (D) Enrico Fermi

16. The commutator of  $[x^2, p_x]$  is equal to :

- (A)  $\frac{hx}{\pi i}$  (B)  $\frac{2hx}{\pi i}$   
 (C)  $\frac{hx^2}{2\pi i}$  (D)  $-\frac{hx}{\pi i}$

17. The life time of a state that gives rise to a spectral line of width  $0.1 \text{ cm}^{-1}$  is :

- (A) 53 nm (B) 53 pm  
 (C) 33 nm (D) 33 pm

18. The wave function for a particle in a 1-D box of length 'L' is given as  $\psi = A \sin \frac{\pi x}{L}$ . The value of 'A' for a box of length 50 nm is :

- (A)  $5\sqrt{2} \text{ (nm)}^{1/2}$  (B)  $0.2 \text{ (nm)}^{-1/2}$   
 (C)  $0.2 \text{ (nm)}^{1/2}$  (D)  $\sqrt{5}/10 \text{ (nm)}^{-1/2}$

19. The quantum state of a particle in a circular path in a plane is given by :

$$\psi_m(\phi) = \left( \frac{1}{\sqrt{2\pi}} \right) e^{-im\phi}, m = 0, \pm 1, \pm 2, \dots$$

When a perturbation  $H' = P \cos \theta$  is applied (P is a constant), what will be the first order correction to the energy of the  $m$ th state ?

- (A) 0 (B)  $P/(2\pi)$   
 (C)  $P/(4\pi)$  (D)  $Pm^2/(4\pi^2)$



20. The molecular orbitals of 1, 3-butadiene (not in proper order) are given below :

( $f_1, f_2, f_3, f_4$  are the  $2p_z$  orbitals on carbon atoms.)

$$\psi_1 = 0.372f_1 - 0.602f_2 + 0.602f_3 - 0.372f_4$$

$$\psi_2 = 0.602f_1 + 0.372f_2 - 0.372f_3 - 0.602f_4$$

$$\psi_3 = 0.372f_1 + 0.602f_2 + 0.602f_3 + 0.372f_4$$

$$\psi_4 = 0.602f_1 - 0.372f_2 - 0.372f_3 + 0.602f_4$$





The *correct* order of the orbitals with increasing energy is :

- (A)  $\psi_1 < \psi_2 < \psi_3 < \psi_4$                       (B)  $\psi_3 < \psi_2 < \psi_4 < \psi_1$   
 (C)  $\psi_3 < \psi_4 < \psi_1 < \psi_2$                       (D)  $\psi_4 < \psi_3 < \psi_2 < \psi_1$
21. The infrared spectrum of a diatomic molecule exhibits transitions at  $2143.0 \text{ cm}^{-1}$  and  $4260.0 \text{ cm}^{-1}$  corresponding to excitations from the ground state to first and second vibrational states respectively. The value of the fundamental frequency,  $\bar{\omega}_e$  ( $\text{cm}^{-1}$ ) for the molecule is :
- (A) 2156    (B) 2169  
 (C) 2182    (D) 2195
22. The ratio of the translational partition functions of  $\text{D}_2$  and  $\text{H}_2$  at the same temperature and pressure is :
- (A) 1.59    (B) 2.83  
 (C) 2.00    (D) 0.35
23. The  $T_d$  point group has 24 elements and 5 classes. Given that it has two three-dimensional irreducible representations, the number of one-dimensional irreducible representations is :
- (A) 1    (B) 6  
 (C) 2    (D) 3

24. In which of the following will the energy level separation be maximum ?
- (A) A  $^{13}\text{C}$  nucleus in a 400 MHz NMR instrument
- (B) A  $^{95}\text{Mo}$  nucleus in a 600 MHz NMR instrument
- (C) A  $^{31}\text{P}$  nucleus in a 600 MHz NMR instrument
- (D) An unpaired electron in a magnetic field of 0.33 T
25. The  $^{129}\text{I}$  Mössbauer spectral data for the compounds  $\text{I}_2\text{Cl}_6$  and  $\text{I}_2\text{Br}_2\text{Cl}_4$  are given below :

Compound	Isomer Shift (mm/s)	Quadrupole Splitting (MHz)
$\text{I}_2\text{Cl}_6$	3.50	3060
$\text{I}_2\text{Br}_2\text{Cl}_4$	2.82	2920
	3.49	3055

The structure of  $\text{I}_2\text{Br}_2\text{Cl}_4$  can be represented as :

- (A)  (B) 
- (C)  (D) 
26. When a KCl crystal is strongly heated, it loses some chlorine. The resulting structure then has :
- (A) F centers (B) Schottky defects
- (C) Frenkel defects (D) Metal deficiency defects

27.  $\text{PbTiO}_3$  and  $\text{YBa}_2\text{Cu}_3\text{O}_7$  both are having :
- (A) Semiconducting property
  - (B) Superconducting property
  - (C) Piezoelectric property
  - (D) Common structural features
28. Magnetic measurements indicate that  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  has 3 unpaired electrons. Therefore, the hybridization of the metal orbitals in  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is :
- (A)  $d^2sp^3$
  - (B)  $sp^3d^2$
  - (C)  $dsp^2$
  - (D)  $sp^2d$
29. Which of the statements is *false* ?
- (A) In an octahedral crystal field, the electrons fill the  $e_g$  level first, followed by  $t_{2g}$  level.
  - (B) Diamagnetic metal ions cannot have an odd number of electrons.
  - (C) Low-spin complexes can be paramagnetic.
  - (D) In high-spin octahedral complexes  $\Delta_{\text{oct}}$  is less than the electron pairing energy, and is relatively every small.
30. The complex  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  shows an absorption band at  $20,000 \text{ cm}^{-1}$ . Therefore, the CFSE of this complex is :
- (A)  $8,000 \text{ cm}^{-1}$
  - (B)  $12,000 \text{ cm}^{-1}$
  - (C)  $-8,000 \text{ cm}^{-1}$
  - (D)  $-12,000 \text{ cm}^{-1}$

31. The first excited state configuration of low-spin octahedral  $d^4$  system is :  
 (A)  ${}^2E_g$  (B)  ${}^5T_{2g}$   
 (C)  ${}^5E_g$  (D)  ${}^3T_{2g}$
32. Coordinated water molecules of Cd(II) complex can be successively replaced by  $\text{Br}^-$  finally to result in  $[\text{CdBr}_4]^{2-}$ . In this process, the fourth equilibrium constant ( $K_4$ ) is observed to be higher than the third one, because :  
 (A) Equilibrium constant for the last step is always the highest  
 (B) Three molecules of  $\text{H}_2\text{O}$  are released during the fourth step  
 (C) The aqua  $\text{Cd}^{2+}$  complex is octahedral  
 (D) A  $\text{Br}^-$  anion replaces a neutral ( $\text{H}_2\text{O}$ ) molecule from the coordination sphere
33. The reaction :  

$$[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]^{2+} + [\text{Cr}(\text{H}_2\text{O})_6]^{2+} \rightarrow [\text{Co}(\text{H}_2\text{O})_6]^{2+} + [\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$$
 is an example of :  
 (A) isomerization  
 (B) nucleophilic substitution  
 (C) inner-sphere electron transfer  
 (D) outer-sphere electron transfer
34. Reducing ability of the oxyanions of sulphur change as :  
 (A)  $\text{S}_2\text{O}_3^{2-} > \text{SO}_3^{2-} > \text{S}_2\text{O}_8^{2-}$  (B)  $\text{SO}_3^{2-} > \text{S}_2\text{O}_8^{2-} > \text{S}_2\text{O}_3^{2-}$   
 (C)  $\text{SO}_3^{2-} > \text{S}_2\text{O}_3^{2-} > \text{S}_2\text{O}_8^{2-}$  (D)  $\text{S}_2\text{O}_8^{2-} > \text{S}_2\text{O}_3^{2-} > \text{SO}_3^{2-}$
35. Match the following class of boranes with their examples :  
 (a) closo (i)  $\text{B}_8\text{H}_{14}$   
 (b) nido (ii)  $(\text{B}_{10}\text{H}_{10})^{2-}$   
 (c) arachno (iii)  $\text{B}_9\text{H}_{13}$   
 (A) (a)—(iii), (b)—(i), (c)—(ii)  
 (B) (a)—(i), (b)—(iii), (c)—(ii)  
 (C) (a)—(ii), (b)—(i), (c)—(iii)  
 (D) (a)—(ii), (b)—(iii), (c)—(i)

36. The molecule  $\text{BrF}_5$ , interconverts between :
- (A) trigonal-bipyramidal and tetrahedral structure
  - (B) square pyramidal and pentagonal structure
  - (C) trigonal-bipyramidal and square planar structure
  - (D) square pyramidal and trigonal-bipyramidal structure
37. Among the following statements :
- (a) Sheet silicates have general formula  $[\text{Si}_2\text{O}_5]_n^{2n-}$
  - (b)  $\text{ZrSiO}_4$  is an example for orthosilicate
  - (c)  $\text{Si}_2\text{O}_7^{6-}$  is a cyclosilicate
  - (d)  $\text{BaTiSi}_3\text{O}_9$  is a pyrosilicate
- (A) Only (a) is correct                      (B) (a), (c) are correct  
(C) (a), (b) are correct                      (D) (b), (c) are correct
38. The type of hybridisation of carbon atoms in graphene sheets is :
- (A) only  $sp^2$                                       (B)  $sp^2$  and  $sp^3$
  - (C) only  $sp^3$                                       (D)  $sp$  and  $sp^2$
39. Which of the following ligands will form a stable complex with  $\text{Ln}^{3+}$  ions ?
- (A)  $\text{H}_2\text{O}$     (B) CO
  - (C)  $\text{C}_2\text{H}_4$     (D)  $\text{PPh}_3$

40. The ligand field bands of lanthanide complexes are generally sharper than those of transition metal complexes because :
- (A) The corresponding transitions are allowed  
 (B) The bands are more intense  
 (C) *f*-orbitals have higher energy than *d*-orbitals  
 (D) The interaction of ligands with *f*-orbitals is less effective than with *d*-orbitals
41. The reaction of an alkylbromide with  $[\text{IrCl}(\text{CO})(\text{PMe}_3)_2]$  is :
- (A) oxidative addition (B) substitution  
 (C) alkylation (D) halogenation
42.  $\text{M}_4$  carbonyl clusters A and B have CVE count of 60 and 62, respectively. Therefore the cluster geometries should be, respectively :
- (A) square planar and tetrahedral  
 (B) tetrahedral and butterfly  
 (C) square planar and butterfly  
 (D) tetrahedral and square planar
43. The *correct* order  $\nu_{\text{CO}}$  in the given compounds is :
- (A)  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2] < [\text{Rh}(\eta^5\text{-C}_5\text{F}_5)](\text{CO})_2 < [\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$   
 (B)  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2] < [\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2] < [\text{Rh}(\eta^5\text{-C}_5\text{F}_5)(\text{CO})_2]$   
 (C)  $[\text{Rh}(\eta^5\text{-C}_5\text{F}_5)(\text{CO})_2] < [\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2] < [\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$   
 (D)  $[\text{Rh}(\eta^5\text{-C}_5\text{F}_5)(\text{CO})_2] < [\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})] < [\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$

44. In oxyhaemoglobin, the iron centre is best described as :
- (A) high-spin Fe(III)                      (B) high-spin Fe(II)  
 (C) low-spin Fe(III)                      (D) low-spin Fe(II)
45. Iron is stored in the body as :
- (A) transferrin                              (B) haemoglobin  
 (C) ferritin                                  (D) siderophore
46. In zinc enzymes binding of water to zinc ion induces :
- (A) formation of hydronium ion  
 (B) conformational change in the binding site  
 (C) ionization of a histidine residue  
 (D) formation of a zinc bound hydroxide ion
47. Identify the *correct* response given in column 2 to analyte concentration measured in the following electroanalytical techniques given in column 1 :

<b>Column 1</b>	<b>Column 2</b>
(a) Coulometry	(i) Cathodic current
(b) Polarography	(ii) Coulombs
(c) Voltammetry	(iii) Conductivity
(d) Conductometry	(iv) Cathodic or anodic current
(A) (a)—(i), (b)—(ii), (c)—(iii), (d)—(iv)	
(B) (a)—(ii), (b)—(i), (c)—(iv), (d)—(iii)	
(C) (a)—(iv), (b)—(i), (c)—(ii), (d)—(iii)	
(D) (a)—(ii), (b)—(iv), (c)—(ii), (d)—(iii)	

48. The amount of  $[\text{Al}_2(\text{SO}_4)_3] \cdot 18\text{H}_2\text{O}$  (MW = 662.42) required to prepare a litre of 1 M Al solution is :
- (A) 331.21 g (B) 662.42 g  
(C) 33.121 g (D) 66.42 g
49. Which of the following molecules contains the highest % of sulphur by mass ?
- (A)  $\text{Na}_2\text{SO}_4$  (B)  $\text{Li}_2\text{SO}_4$   
(C)  $\text{H}_2\text{SO}_4$  (D)  $\text{PbSO}_4$
50. On a 20 cm column, the retention times  $t_R$  of A and B are 16.40 and 17.63 minutes, respectively. The peak width at base lines for A and B are 1.15 and 1.31 minutes, respectively. The column resolution  $R_S$  is :
- (A) 0.10 (B) 0.50  
(C) 1.00 (D) 1.50
51. A 10 mg sample containing  $\text{CaCO}_3$  and  $\alpha\text{-Al}_2\text{O}_3$  was analysed by thermogravimetry between 30—800°C. A weight loss of 2.2 mg was observed. The %  $\text{CaCO}_3$  in the mixture is .....
- (Given : M.W.  $\text{CaCO}_3$  = 100.0)
- (A) 50% (B) 45%  
(C) 55% (D) 75%



52. The extraction of uranyl (VI) ion  $(\text{UO}_2)^{2+}$  from an aqueous solution in concentrated HCl using ether as solvent is an example of :
- (A) neutral metal-chelate extraction
  - (B) ion-pair association
  - (C) supercritical fluid extraction
  - (D) fractional extraction
53. Which of the following is *not* a criteria for aromaticity ?
- (A) Presence of  $(4n + 2)$  delocalizable electrons
  - (B) Diamagnetic character
  - (C) Strong shielding-de-shielding pattern as a result of induced ring current
  - (D) Paramagnetic character
54. Which of the following statements is *correct* regarding fullerene  $\text{C}_{60}$  ?
- (A) 12,500 Resonating structures are possible for  $\text{C}_{60}$
  - (B) Fullerene  $\text{C}_{60}$  is a super aromatic compound
  - (C) Unsubstituted fullerene  $\text{C}_{60}$  can be acylated using Friedel-Crafts acylation
  - (D) Fullerene  $\text{C}_{60}$  is susceptible to attack by nucleophilic reagents

55. Predict the stereochemical outcome of the following reaction :

(A)

(B)

(C)

(D)

56. Study the following reaction sequence, predict the structure of X and choose the *correct* description for the same :

- (A) Both the steps are non-stereoselective and X is
  
  
  
  
  
  
  
  
  
  
- (B) Both the steps are enantioselective and X is
  
  
  
  
  
  
  
  
  
  
- (C) The first step is diastereoselective as well as enantioselective and X is
  
  
  
  
  
  
  
  
  
  
- (D) Both the steps are diastereoselective as well as enantioselective and X is

57. 2-Bromocyclohexanone on reaction with methoxide gives methyl ester of cyclopentane carboxylic acid. Give the name of the reaction and the key intermediate involved in this reaction :
- (A) Favorskii rearrangement with a derivative of cyclopropanone intermediate.
- (B) Favorskii rearrangement with a carbocation as an intermediate.
- (C) Benzylic acid rearrangement with carbocation as an intermediate.
- (D) Baeyer-Villiger reaction with carbocation as an intermediate.
58. Study the following chemical transformation :

The *correct* reagents for the above reaction are :

- (A) *t*-BuOOH, Ti(O-*i*-Pr)<sub>4</sub>, (-)-DET
- (B) *t*-BuOOH, Ti(O-*i*-Pr)<sub>4</sub>, (+)-DET
- (C) H<sub>2</sub>O<sub>2</sub>
- (D) MCPBA

59. Hammett plot for hydrolysis of ethyl benzoates in 99.9%  $\text{H}_2\text{SO}_4$ , has two separate reaction constants,  $\rho = -3.25$  and  $\rho = 2.0$ , for electron donating groups (EDG) and electron withdrawing groups (EWG) respectively.

Which of the following statements *correctly* summarizes the above observation ?

- (A) For EDG, reaction proceeds by  $A_{AC}1$  and for EWG, reaction proceeds by  $A_{AC}2$  mechanism
- (B) For EDG, reaction proceeds by  $A_{AC}1$  and for EWG, reaction proceeds by  $A_{AL}1$  mechanism
- (C) For EDG, reaction proceeds by  $A_{AC}1$  and for EWG, reaction proceeds by  $A_{AC}1$  mechanism
- (D) For EDG, reaction proceeds by  $A_{AL}1$  and for EWG, reaction proceeds by  $A_{AC}1$  mechanism

60. The following are some of the processes used for studying reaction mechanism.

Match them with their specific applications :

- |     |                                |     |  |
|-----|--------------------------------|-----|--|
| (M) | Primary Kinetic isotope effect | (1) | Largely gives information about RDS  |
| (N) | Cross-over experiments         | (2) | Detection of non-isolable suspected intermediate                             |
| (O) | Trapping of intermediates      | (3) | Helps in distinguishing between intramolecular and intermolecular mechanisms |
| (P) | Kinetic studies                | (4) | Helps to find out whether a particular bond is cleaved in the RDS            |

(A) (M)—(1), (N)—(2), (O)—(3), (P)—(4)

(B) (M)—(2), (N)—(4), (O)—(1), (P)—(3)

(C) (M)—(4), (N)—(3), (O)—(2), (P)—(1)

(D) (M)—(3), (N)—(2), (O)—(1), (P)—(4)

61. Study the following reaction and identify the process involved :

- (A) Thermal 6 pi electron electrocyclic reaction
- (B) Photochemical 6 pi electron electrocyclic reaction
- (C) (4 pi + 2 pi) electron photochemical cycloaddition reaction
- (D) (4 pi + 2 pi) electron thermal cycloaddition reaction

62. Study the following reaction and identify the processes involved :

- (A) Claisen rearrangement followed by keto-enol tautomerism
- (B) [3, 3] Sigmatropic rearrangement followed by [1, 5]-H-shift
- (C) [3, 3] Sigmatropic rearrangement followed by keto-enol tautomerism
- (D) [1, 3] Sigmatropic rearrangement followed by keto-enol tautomerism

63. In Fischer-indole synthesis of 2-phenylindole, starting materials used are :

- (A) Phenyl hydrazine and acetophenone
- (B) Phenyl hydrazine and benzaldehyde
- (C) Phenyl hydrazine and acetone
- (D) Phenyl hydrazine and acetaldehyde

64. Match the structures in List I with their *correct* names in List II :

**List I****List II**

(L) (1) 5-hydroxybenzothiazole

(M) (2) 2-amino pyridine

(N) (3) 2-methyl furan

(O) (4) 2-amino piperidine

(A) (L)—(1), (M)—(2), (N)—(3), (O)—(4)

(B) (L)—(3), (M)—(2), (N)—(4), (O)—(1)

(C) (L)—(3), (M)—(2), (N)—(1), (O)—(4)

(D) (L)—(2), (M)—(3), (N)—(4), (O)—(1)



65. Lithium isopropylamide (LDA) is a :
- (A) Conjugate base of diisopropylamine which is strongly basic and bulky.
  - (B) Conjugate base of diisopropylamine which is weakly basic and bulky.
  - (C) Conjugate acid of diisopropylamine which is strongly basic and bulky.
  - (D) Conjugate base of diisopropylamine which is strongly basic and small in size.
66. The products formed as **X** and **Y** respectively in the following reactions are :

(A)

(B)

(C)

(D)

67. Dehydrocholesterol is present in the tissues of the skin, where it is transformed to vitamin D<sub>3</sub> by a sun-light induced photochemical reaction :

Choose the *correct* structure of vit. D<sub>3</sub> :

(A)

(B)

(C)

(D)

68. Which of the following structures is the *correct* representation of  $\beta$ -D-glucopyranose ?

(A)

(B)

(C)

(D)

69. The *correct* stereochemical structure of the tetrapeptide, Try-Gly-Gly-Phe, derived from the natural amino acids is :

(A)

(B)

(C)

(D)

70. The following rearrangement occurs when 2, 5-cyclohexadienone [X] is irradiated. The name of the rearrangement is :



- (A) Barton rearrangement
  - (B) Photo Fries rearrangement
  - (C) Dienone-phenol rearrangement
  - (D) Di-pi-methane rearrangement
71. The following photochemical reaction is :



- (A) Norrish type I reaction
- (B) Photochemical reduction
- (C) Paterno-Buchi reaction
- (D) Norrish type II reaction

72. Chymotrypsin preferentially cleaves the carbon side of the peptide bond of :

- (A) Methionine (B) Proline  
(C) Phenyl alanine (D) Alanine

**Linked Problem Q. No. 73 and Q. No. 74 :**

A ketone on treatment with bromine in methanol gives the corresponding monobromo compound **X** having molecular formula  $C_5H_9BrO$ . The compound **X** when treated with NaOMe in MeOH produces **Y** as the major product. The spectral data for the compound **X** are  $^1H$  NMR  $\delta$  1.17(*d*, 6H), 3.02(*m*, 1H), 4.10(*s*, 2H);  $^{13}C$  NMR  $\delta$  17, 37, 39, 210.

73. The compound [**X**] is :

- (A) (B)  
(C) (D)

74. The major product **Y** is :

(A) (B)

(C) (D)

75. Compound **X** and **Y** exhibit two singlets each in  $^1\text{H}$  NMR. The expected chemical shifts are at  $\delta$  :

(A) 6.9 and 2.1 for **X**, 7.7 and 3.9 for **Y**

(B) 6.9 and 3.9 for **X**, 7.7 and 2.1 for **Y**

(C) 7.7 and 3.9 for **X**, 6.9 and 2.1 for **Y**

(D) 7.7 and 2.1 for **X**, 6.9 and 3.9 for **Y**

**DEC - 33313/III**

**ROUGH WORK**