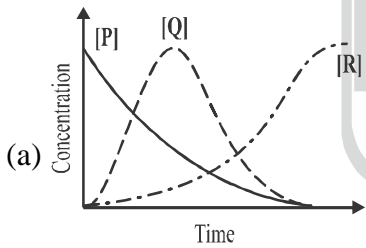
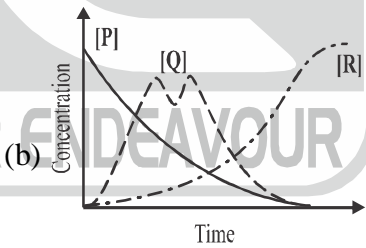
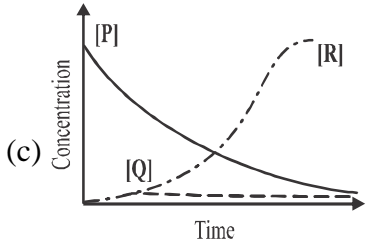
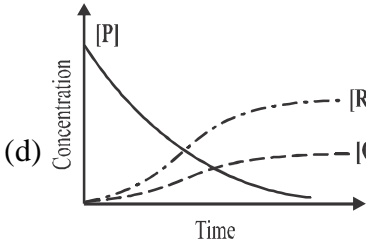
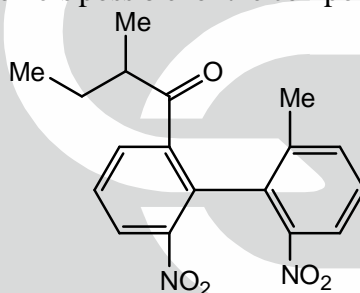


## CHEMISTRY-CY

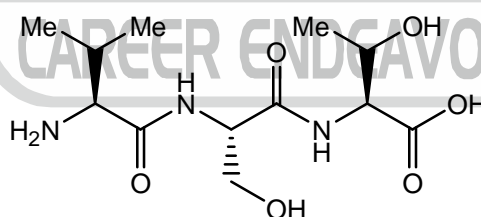
## Q.1 – Q.25 : Carry ONE mark each.

- The point group symmetry of  $\text{CH}_2 = \text{C} = \text{CH}_2$  is:
  - $D_{2h}$
  - $C_{2h}$
  - $C_{2v}$
  - $D_{2d}$
- Two trial wave function  $\phi = c_1x(a-x)$  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:
  - $E_0 = E_1 = E_2$
  - $E_0 < E_1 < E_2$
  - $E_0 < E_2 < E_1$
  - $E_0 > E_2 = E_1$
- The ground state energies of H atom and  $\text{H}_2$  molecule are  $-13.6$  eV and  $-31.7$  eV, respectively. The dissociation energy of  $\text{H}_2$  is \_\_\_\_\_ eV.
- A 2 L vessel containing 2g of  $\text{H}_2$  gas at  $27^\circ\text{C}$  is connected to a 2L vessel containing 176 g of  $\text{CO}_2$  gas at  $27^\circ\text{C}$ . Assuming ideal behaviour of  $\text{H}_2$  and  $\text{CO}_2$ , the partial pressure of  $\text{H}_2$  at equilibrium is \_\_\_\_\_ bar.
- Consider the reaction,  $2\text{C}(s) + \text{O}_2(g) \rightleftharpoons 2\text{CO}(g)$  at equilibrium, The equilibrium can be shifted towards the forward direction by
  - Increasing the amount of carbon in the system
  - Decreasing the volume of the system.
  - Decreasing the pressure of the system.
  - Increasing the temperature of the system
- A sparingly soluble electrolyte  $\text{M}_2\text{X}$  ionizes as  $\text{M}_2\text{X} \rightleftharpoons 2\text{M}^+ + \text{X}^{2-}$ . The solubility product ( $K_{sp}$ ), molal solubility ( $S$ ) and molal activity coefficient ( $\gamma_{\pm}$ ) are related by
  - $K_{SP} = S^2\gamma_{\pm}^2$
  - $K_{SP} = S^3\gamma_{\pm}^3$
  - $K_{SP} = 4S^3\gamma_{\pm}^2$
  - $K_{SP} = 4S^3\gamma_{\pm}^3$
- For the first order consecutive reaction,  $\text{P} \rightarrow \text{Q} \rightarrow \text{R}$ , under steady state approximation to  $[\text{Q}]$ , the variation of  $[\text{P}]$ ,  $[\text{Q}]$  and  $[\text{R}]$  with time are best represented by
  - 
  - 
  - 
  - 
- 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 \_\_\_\_\_  $\text{bar}^{-1}$ .
- Conversion of boron trifluoride to tetrafluoroborate accompanies
  - Increase in symmetry and bond elongation
  - Increase in symmetry and bond contraction
  - Decrease in symmetry and bond contraction
  - Decrease in symmetry and bond elongation.

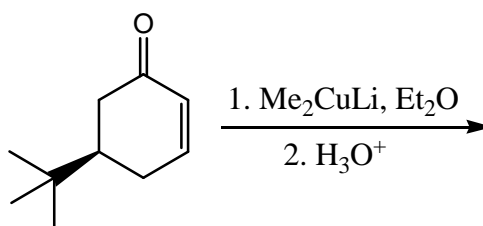
10. The correct statement with respect to the bonding of the ligands,  $\text{Me}_3\text{N}$  and  $\text{Me}_3\text{P}$  with the metal ions  $\text{Be}^{2+}$  and  $\text{Pd}^{2+}$  is,  
 (a) The ligands bind equally strong with both the metal ions as they are dicationic.  
 (b) The ligands bind equally strong with both the metal ions as both the ligands are pyramidal.  
 (c) The binding is stronger for  $\text{Me}_3\text{N}$  with  $\text{Be}^{2+}$  and  $\text{Me}_3\text{P}$  with  $\text{Pd}^{2+}$ .  
 (d) The binding is stronger for  $\text{Me}_3\text{N}$  with  $\text{Pd}^{2+}$  and  $\text{Me}_3\text{P}$  with  $\text{Be}^{2+}$ .
11. A crystal has the lattice parameters  $a \neq b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$ . The crystal system is  
 (a) Tetragonal (b) Monoclinic (c) Cubic (d) Orthorhombic
12. The by-product formed in the characteristic reaction of  $(\text{CO})_5\text{Cr} = \text{C}(\text{OMe})(\text{Me})$  with  $\text{MeNH}_2$  is  
 (a) CO (b) MeOH (c) MeCHO (d)  $\text{MeCONH}_2$ .
13. The catalyst and co-catalyst used in Wacker process, respectively, are  
 (a)  $\text{PdCl}_2$  and Cu (b)  $\text{CuCl}_2$  and  $[\text{PdCl}_4]^{2-}$   
 (c) Pd and CuCl (d)  $[\text{PdCl}_4]^{2-}$  and  $\text{CuCl}_2$ .
14. Oxymyoglobin  $\text{Mb}(\text{O}_2)$  and oxhyhemoglobin  $\text{Hb}(\text{O}_2)_4$ , respectively, are  
 (a) Paramagnetic and paramagnetic (b) Diamagnetic and diamagnetic  
 (c) Paramagnetic and diamagnetic (d) Diamagnetic and paramagnetic.
15. Hapticity of cycloheptatriene in  $\text{Mo}(\text{C}_7\text{H}_8)(\text{CO})_3$  is \_\_\_\_\_
16. The number of oxygen molecule(s) that a molecule of hemerythrin can transport is \_\_\_\_\_
17. The maximum number of stereoisomers possible for the compound given below is \_\_\_\_\_

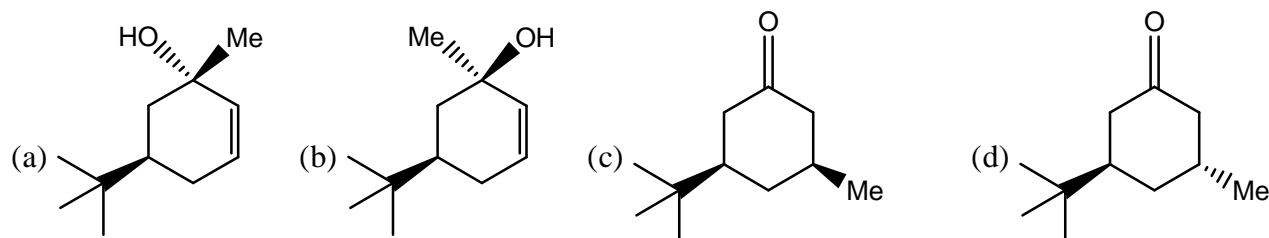


18. The correct sequence of the amino acids present in the tripeptide given below is

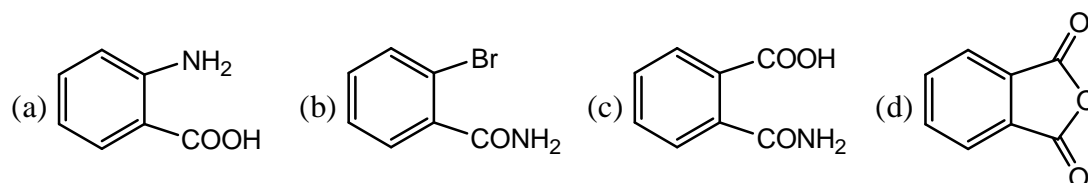
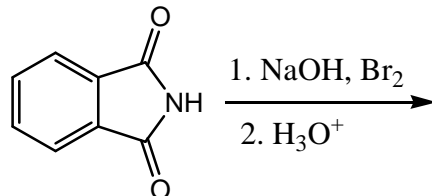


- (a) Val-Ser-Thr (b) Val-Thr-Ser (c) Leu-Ser-Thr (d) Leu-Thr-Ser
19. Among the compounds given in the options (a)–(d), the one that can be used as a formyl anion equivalent (in the presence of a strong base) is:  
 (a) ethylene (b) nitroethane (c) 1, 3-dithiane (d) 1, 4-dithiane
20. The major product formed in the reaction given below is:

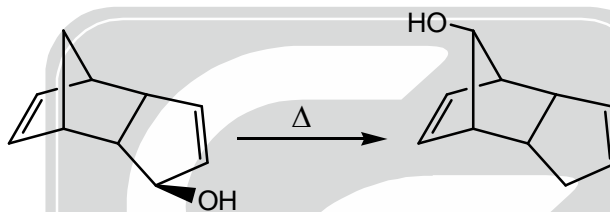




21. The major product formed in the reaction given below is

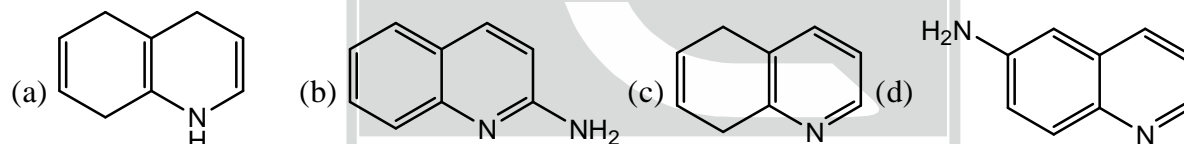


22. The pericyclic reaction given below is an example of



- (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 ( $\text{KNH}_2$ ) in liquid ammonia is:



24. The number of signals that appear in the proton decoupled  $^{13}\text{C}$  NMR spectrum of benzonitrile ( $\text{C}_7\text{H}_5\text{N}$ ) is \_\_\_\_\_

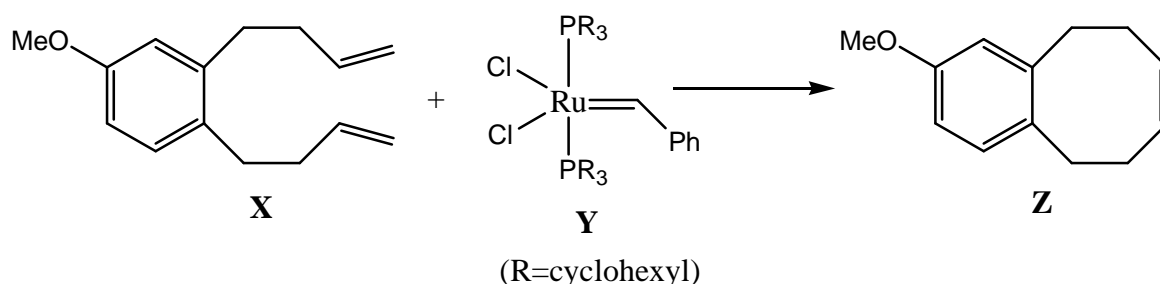
25. Among the compounds given in the option (a) to (d), the one that exhibits a sharp band at around  $3300\text{ cm}^{-1}$  in the IR spectrum is:

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

**Q.26 – Q.55 : Carry TWO marks each.**

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]



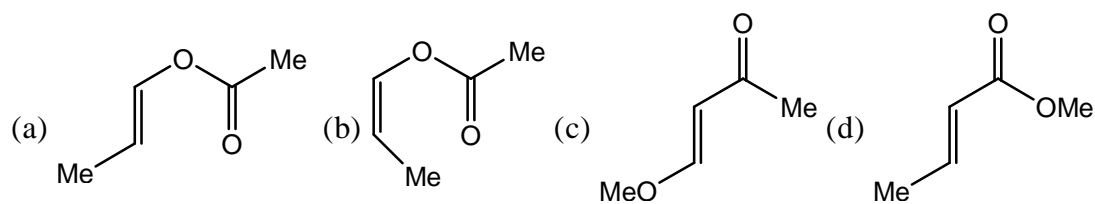
27. An organic compound **Q** exhibited the following spectral data:

IR:  $1760\text{ cm}^{-1}$

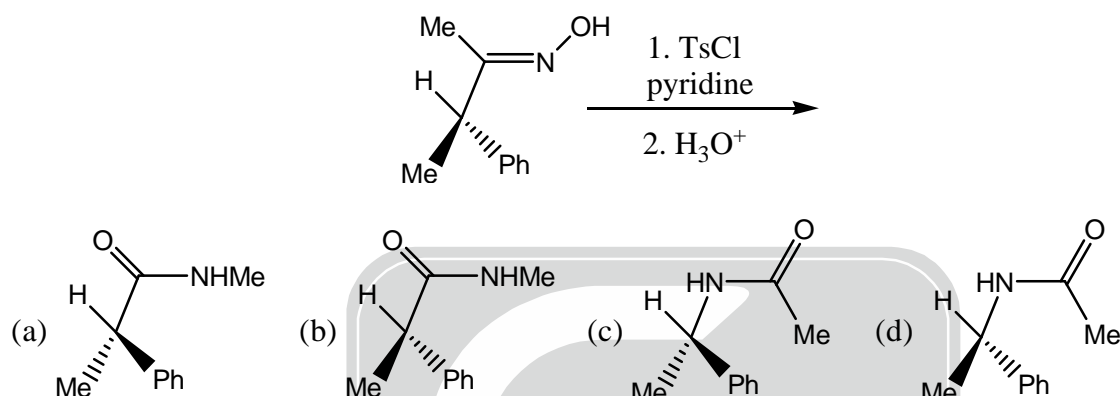
$^1\text{H NMR}$  :  $\delta$  (ppm) : 7.2 (1H, d,  $J = 16.0\text{ Hz}$ ), 5.1 (1H, m), 2.1 (3H, s), 1.8(3H, d,  $J = 7.0\text{ Hz}$ )

$^{13}\text{C NMR}$  :  $\delta$  (ppm); 170 (carbonyl carbon),

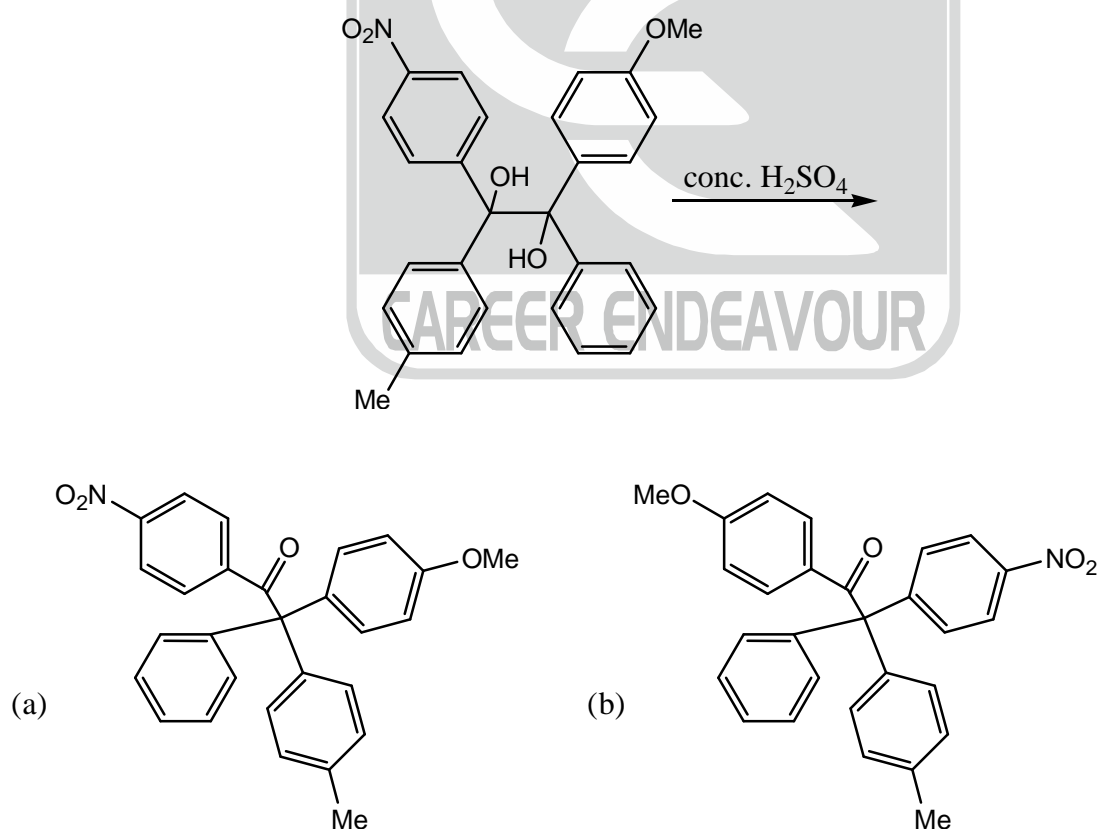
Compound **Q** is

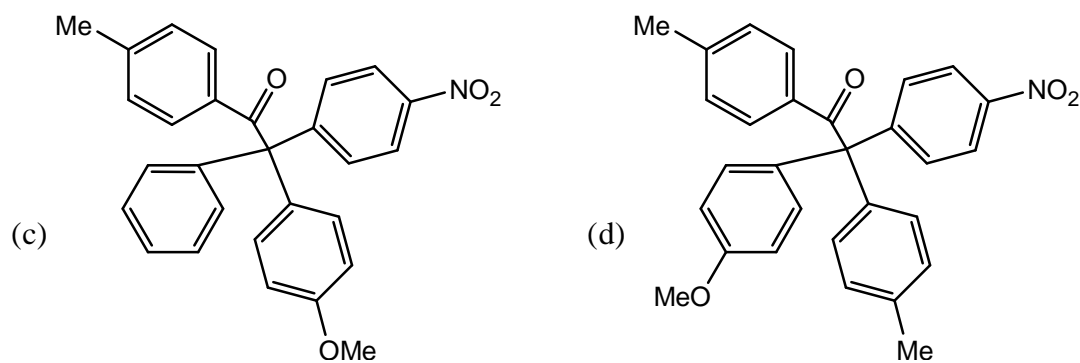


28. The major product formed in the Beckmann rearrangement of the compound given below is:

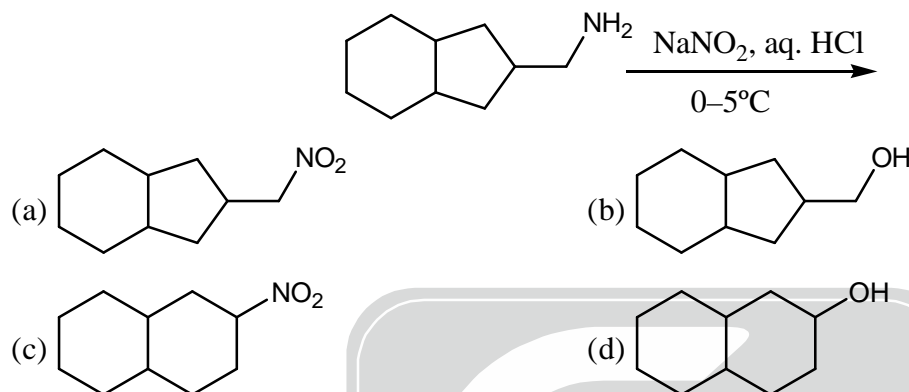


29. The major product formed in the reaction given below is

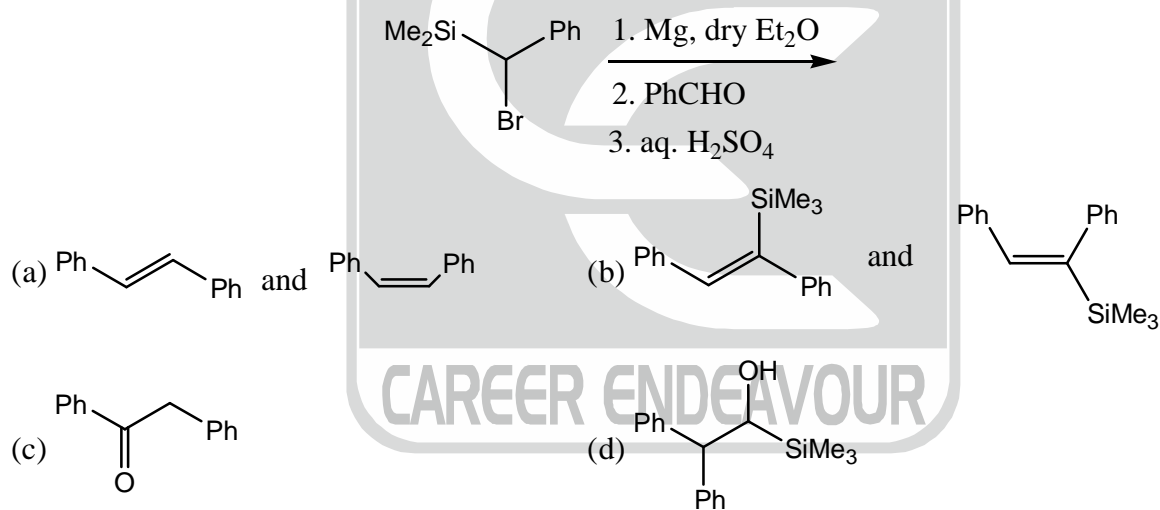




30. The major product formed in the reaction given below is



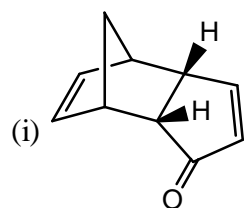
31. The major product(s) formed in the reaction sequence given below is/are



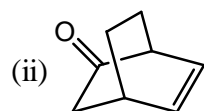
32. Match the compounds in the **Column-I** with photochemical reactions that they can undergo given in the **Column-II**:

Column-I

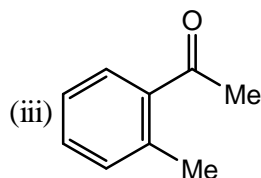
Column-II



(p) oxa-di- $\pi$ -methane rearrangement



(q) Paterno-Buchi reaction



(r) intramolecular [2+2]-cycloaddition.

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

- (b) (i)-(r); (ii)-(p); (iii)-(s)  
(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  $2885 \text{ cm}^{-1}$ . The zero point energy of HCl molecule under hamonic oscillator approximation is:

- (a)  $2.8665 \times 10^{-22} \text{ J}$  (b)  $2.8665 \times 10^{-20} \text{ J}$   
(c)  $5.7330 \times 10^{-22} \text{ J}$  (d)  $5.7330 \times 10^{-20} \text{ J}$

35. For the reaction  $X_2O_4(\ell) \rightarrow 2XO_2(g)$  at 298K, given the values,

given the values,  $\Delta U = 9 \text{ kJ}$  and  $\Delta S = 84 \text{ J K}^{-1}$ ,  $\Delta G$  is

- (a) -11.08 kJ (b) +11.08 kJ (c) -13.55 kJ (d) +13.55 kJ

36. The change in enthalpy when 3 mol of liquid benzene transforms to the vapour state at its boiling temperature ( $80^\circ\text{C}$ ) and at 1 bar pressure is \_\_\_\_\_ kJ.

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

38. For a reaction of the type  $X \xrightleftharpoons[k_2]{k_1} Y$ , the correct rate expression is ( $[X]_0$  and  $[X]$  corresponds to the concentration 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 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-exponential factor for a reaction of the type given below is

linear molecule + linear molecule  $\rightleftharpoons$  non-linear linear transition state  $\longrightarrow$  products.

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

40. Decarbonylation reaction of  $[\text{cis}-(\text{CH}_3\text{CO})\text{Mn}(\text{CO})_4]$  yields X, Y and Z, where  $X = [(\text{CH}_3)\text{Mn}(\text{CO})_5]$ ;  $Y = [\text{cis}-(\text{CH}_3)\text{Mn}(\text{CO})_4]$ ;  $Z = \text{trans}-(\text{CH}_3)\text{Mn}(\text{CO})_4]$ . 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

41. According to polyhedral electron count rule, the structure of  $\text{Rh}_6(\text{CO})_{16}$  is:  
 (a) closo (b) nido (c) arachno (d) hypho
42. The increasing order of melting points of the halides NaCl, CuCl and NaF is:  
 (a)  $\text{CuCl} < \text{NaCl} < \text{NaF}$  (b)  $\text{NaF} < \text{NaCl} < \text{CuCl}$   
 (c)  $\text{NaF} < \text{CuCl} < \text{NaCl}$  (d)  $\text{CuCl} < \text{NaF} < \text{NaCl}$
43. The correct electronic configuration and spin only magnetic moment of  $\text{Gd}^{3+}$  (atomic number 64) are  
 (a)  $[\text{Xe}]4f^7$  and 7.9 BM (b)  $[\text{Xe}]4f^7$  and 8.9 BM  
 (c)  $[\text{Xe}]4f^65d^1$  and 7.9 BM (d)  $[\text{Rn}]5f^7$  and 7.9 BM
44. Among the following octahedral complexes, the one that has the highest enthalpy of hydration is  
 (a)  $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$  (b)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  (c)  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$  (d)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
45. A metal crystallizes in the face-centered cubic lattice parameter of  $4.20\text{\AA}$ . The shortest atom to atom contact distance in the lattice is  
 (a)  $4.20\text{\AA}$  (b)  $2.97\text{\AA}$  (c)  $2.42\text{\AA}$  (d)  $2.10\text{\AA}$
46. Polarographic method of analysis to obtain individual amounts of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  in a given mixture of the two ions ( $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ) is achieved by measuring their  
 (a) half-wave potentials (b) migration currents  
 (c) decomposition potentials (d) diffusion currents
47. The ground state term  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is:  
 (a)  ${}^3T_{1g}$  (b)  ${}^3T_{2g}$  (c)  ${}^3A_{2g}$  (d)  ${}^4T_{1g}$

**Common Data Questions:****Common data for Q.48 and Q.49:**

N, N-Dimethylformamide (DMF) gives different patterns of signals for the methyl protons when its  ${}^1\text{H}$  NMR spectrum is recorded at different temperatures.

48. Match the patterns of the NMR signals given in the **Column-I** with temperatures given in the **Column-II**.
- | <b>Column-I</b>   | <b>Column-II</b>                 |
|---|----------------------------------|
| (i) Two singlets, for three protons each, at $\delta$ 2.87 and 2.97 ppm | (x) $25^\circ\text{C}$           |
| (ii) One sharp singlet for six protons at $\delta$ 2.92 ppm             | (y) $120^\circ\text{C}$          |
| (iii) One broad signal for six protons                                  | (z) $150^\circ\text{C}$          |
| (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.

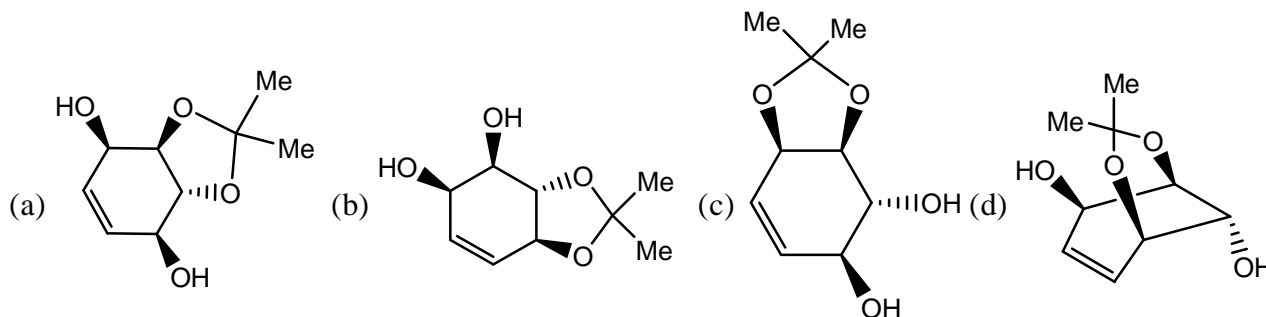
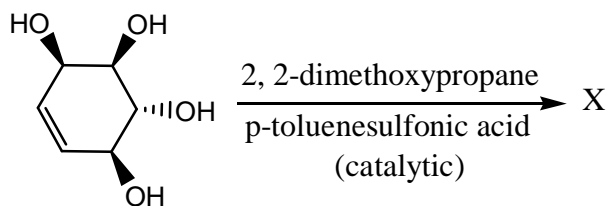
**Common data for Q.50 and Q.51:**

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

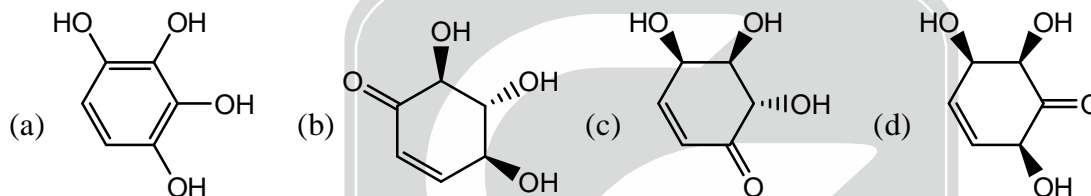
50. Compound X is:  
 (a)  $\text{NH}_4[\text{BH}_4]$  (b)  $[(\text{NH}_3)_2\text{BH}_2][\text{BH}_4]$   
 (c)  $\text{N}_3\text{B}_3\text{H}_6$  (d)  $\text{N}_3\text{B}_3\text{H}_{12}$
51. Compound X is an example of  
 (a) Ionic liquid (b) saturated heterocycle  
 (c) molecular cage (d) unsaturated heterocycle.

**Linked Answer Q.52 and Q.53:**

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

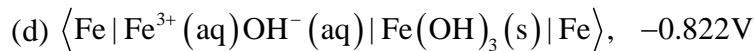
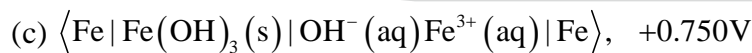
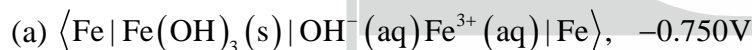


53. Oxidation of the product X, obtained in the above reaction, with active manganese dioxide, followed by acidic hydrolysis gives

**Statement for Linked Answer Q.54 and Q.55:**

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

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



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

- (a)  $-38.2$       (b)  $+87.6$       (c)  $-96.0$       (d)  $-87.6$

\*\*\*\*\* END OF THE QUESTION PAPER \*\*\*\*\*