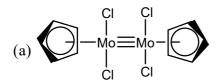
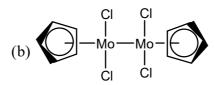
GATE-CY 2016

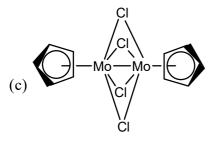
Section-A

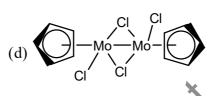
Q.1 – Q.25 : Carry ONE mark each.

[CpMoCl₂]₂ obeys the 18 electron rule. The correct structure of this compound is (atomic number of Mo 1. =42)









- During oxygen transport by hemerythrin, oxygen is bound as 2.
 - (a) O₂ to one Fe(III) only
- (b) HO₂ to one Fe(HI)
- (c) O_2^{2-} to one Fe(III) and one Fe(III)
- (d) O_2^{2-} to two Fe(II)
- Among the following, the most stable isotope to radioactive decay is 3.
 - (a) $_{82}^{206}$ Pb
- (b) $^{210}_{82}$ Pb

- At pH 7.2 and 10 Torr oxygen partial pressure, the extent of O, binding is 4.
 - (a) high for both haemoglobin and myoglobin
 - (b) high for haemoglobin and low for myoglobin
 - (c) high for myoglobin and low for haemoglobin
 - (d) low for both haemoglobin and myoglobin
- In the first row high-spin transition metal complexes [M(H₂O)₆]Cl₂ with d⁵ and d⁷ metal ions, the d-d 5. transitions are
 - (a) spin-forbidden for both
 - (b) spin-allowed for both
 - (c) spin-forbidden for d³ and spin-allowed for d⁷
 - (d) spin-allowed for d and spin-forbidden for d
- Among the given boranes and heteroboranes, the example which belongs to 'closo' type is 6.
 - (a) B_5H_8
- (b) $[C_2B_0H_{11}]^{2-}$
- (c) $GeC_2B_0H_{11}$
- $(d) B_6 H_{10}$

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- The reaction of P₂O₅ with HNO₃ and HClO₄, respectively, gives 7.
 - (a) NO, and ClO,

(b) N₂O₅ and Cl₂O₆ (d) N₂O₅ and Cl₂O₇

(c) N₂O₃ and Cl₂O₇

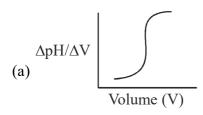
- When crystals of sodium chloride are heated in the presence of sodium vapor, they turn yellow. This is 8. due to the formation of
 - (a) Schottky defects

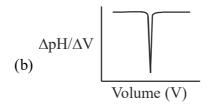
(b) Frenkel defects

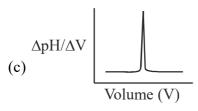
(c) F-centres

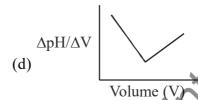
- (d) H-centres
- One mole of an ideal gas is compressed from 5L to 2L at constant temperature. The change in entropy, 9. in J K^{-1} , of the gas is _____ . (R = 8.314 J K^{-1} mol $^{-1}$)

- The linear momentum of a particle described by the wavefunction e^{-ikx} is 10.
 - (a) *kh*
- (b) -kh
- (c) $k\hbar$
- (d) $-k\hbar$
- For an elementary bimolecular gas phase reaction, activation energy is 5.5 kJ mol⁻¹. Enthalpy of activa-11. tion, in kJ mol⁻¹, at 300K is $(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$
- The titration of a strong acid with a strong base is represented by the plot 12.





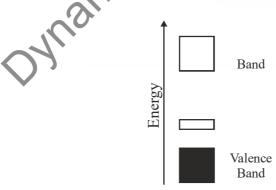




- Of the following inequalities, the criteria for spontaneity of a chemical reaction is/are 13.
- (i) $(\Delta G)_{T,P} < 0$ (ii) $(\Delta U)_{S,V} > 0$ (iii) $(\Delta S)_{U,V} > 0$ (a) (i) only (b) (ii) only (c) (i) and (ii)

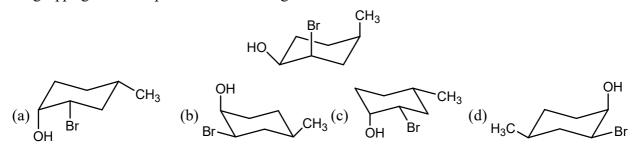
- (d) (i) and (iii)
- 14. A protein sample consists of an equimolar mixture of ribonuclease (molar mass = 13.7 kg mol⁻¹), hemoglobin (molar mass = 15.5 kg mol⁻¹), and myoglobin (molar mass = 17.2 kg mol⁻¹). The statement that is true about the weight-average molar mass $(\overline{M}_{\scriptscriptstyle W})$, the number-average molar mass $(\overline{M}_{\scriptscriptstyle n})$, and the polydispersity index (PDI) for this sample is
 - dispersity index (PDI) for this sample is

 (a) $\bar{M}_w > \bar{M}_n = 15.5 \ kg \ mol^{-1}$ and PDI > 1 (b) $\bar{M}_w > \bar{M}_n = 15.5 \ kg \ mol^{-1}$ and PDI < 1 (c) $\bar{M}_w = 15.5 \ kg \ mol^{-1} > \bar{M}_n$ and PDI < 1 (d) $\bar{M}_w = 15.5 \ kg \ mol^{-1} < \bar{M}_n$ and PDI < 1
- The band structure given below represent a 15.



- (a) *n*-type semiconductor formed by doping Si with B
- (b) *n*-type semiconductor formed by doping Si with P
- (c) p-type semiconductor formed by doping Si with P
- (d) p-type semiconductor formed by doping Si with B
- 16. The experimental ionization energies of hydrogen and helium atoms in their ground states are, respectively, 13.6 eV and 24.6 eV. The ground state energy of helium atom, in eV, is
 - (a) $-\frac{1}{2}(13.6) 24.6$ (b) -4(13.6) 24.6 (c) $-\frac{1}{4}(13.6) 24.6$ (d) -2(13.6) 24.6

17. Ring flipping of the compound in the following conformation leads to



18. The total number of lines expected (due to spin-spin coupling of proton with fluorine and deuterium nuclei) in the ¹H NMR spectrum of the following compound is

19. The compound in 'R' configuration is

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(a)
$$H_3$$
 (b) H_3 (c) H_3 (d) H_3 (d) H_4 (d) H_5 (e) H_5 (d) H_5 (d) H_5 (e) H_5 (e) H_5 (f) H_5 (f)

20. The most suitable reagent for performing the following transformation, is

O
$$CH_3$$
 O CH_3 O CH_3 O CH_3 NH₂
(a) LiAlH₄ (b) H₂, Pd/C (c) PPh₃, H₂O (d) Li, Liq. NH₃

21. The major product obtained in the following reaction, is

22. The Favourable transition state leading to the formation of the product in the following reaction, is

$$\begin{array}{c} \text{B(Chx)}_2\\ \\ \text{Ph} \\ \\ \text{CH}_3 \end{array} \xrightarrow{\text{(i) PhCHO, } -78^{\circ}\text{C}} \begin{array}{c} \text{O} \\ \\ \\ \text{E} \\ \\ \text{CH}_3 \end{array} \begin{array}{c} \text{O} \\ \\ \text{CH}_3 \end{array} \begin{array}{c} \text{O} \\ \\ \text{CH}_3 \end{array}$$

Chx = cyclohexyl

23. The major product of the following reaction is,

$$(CH_3CO)_2O$$

$$BF_3Et_2O, 0^{\circ}C$$

$$CH_3$$

$$(b)$$

$$CH_3$$

$$(c)$$

$$CH_3$$

$$(d)$$

$$CH_3$$

$$(d)$$

$$H_3C$$

$$CH_3$$

24. The major product obtained in the following reaction, is

$$H-C \equiv C-CH_2OH \xrightarrow{(i) \text{ LiNH}_2 \text{ (2equiv.)/liq. NH}_3}$$

$$(ii) C_2H_5Br(1 \text{ equiv.)}$$

$$(ii) H_3O^+$$

$$CH_2OH \qquad \qquad (b) H-C \equiv C-CH_2OCH_2CH_3$$

$$CH_2NH_2 \qquad \qquad (d) H-C \equiv C-CH_2NH-CH_2CH_3$$

25. The major product formed in the following reaction, is

$$(a) \begin{array}{c} (i) CH_3I \\ (ii) NaHCO_3/MeOH, warm \\ (b) \\ (c) \\ (d) \\$$

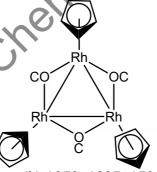
Q.26 - Q.55: Carry TWO marks each.

- 26. The Larmor frequency of 1 H at 1 Tesla (T) is 42.57 MHz. If the magnetogyric ratios for 1 H and 13 C are 26.75 \times 10 7 rad T $^{-1}$ s $^{-1}$ and 6.72 \times 10 7 rad T $^{-1}$ s $^{-1}$, respectively, the Larmor frequency of 13 C, in MHz, at 1 Tesla will be
- 27. At 1 bar and 298K, for the process $A(s) \rightarrow A(\ell)$, the ΔG is 200 J mol⁻¹ and ΔV_m is -2×10^{-6} m³ mol⁻¹. The minimum pressure, in bar, at which the process becomes spontaneous at 298K is ______. (1 bar = 10^5 Pa).
- 28. The reaction, $A \rightleftharpoons B$, is first order in both the directions. The forward and reverse rate constants are $4.2 \times 10^{-4} \, \text{s}^{-1}$ and $1.04 \times 10^{-3} \, \text{s}^{-1}$, respectively. The relaxation time for this reaction, in seconds, in a temperature jump experiment is ______
- 29. Adsorption of CO on charcoal at 273K follows Langmuir isotherm. A plot of P(kPa)/V(cm³) versus P (kPa) is linear with a slope of 0.01 y-intercept of 0.5. The equilibrium constant, K (kPa⁻¹), for the adsorption is
- 30. For the following reaction,

$$A + B \xrightarrow{\frac{k_1 = 10^5 L \text{ mol}^{-1} s^{-1}}{k_{-1} = 10^4 s^{-1}}} I \xrightarrow{k_2 = 10 s^{-1}} P$$

if steady state approximation can be applied on [I], the observed rate constant of product formation, in L mol⁻¹ s⁻¹, will be

31. The correct set of infra-red spectral bands (in cm⁻¹) for the v_{CO} stretching mode of the given carbonyl complex is



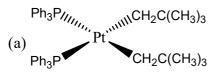
- (a) 1827, 1783, 1766
- (c) 1833, 1775, 1650

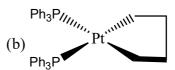
- (b) 1973, 1827, 1794
- (d) 1960, 1918
- 32. The ¹⁹F NMR spectrum of ClF₃ when measured at -60°C will be observed as a
 - (a) singlet

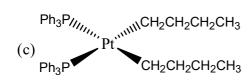
(b) doublet

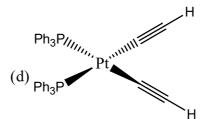
(c) doublet and triplet

- (d) doublet of doublet and a doublet of triplet
- 33. Among the given platinum(II) complexes, the one that is thermally the most unstable is









- 34. The shapes of XeF_5^+ and XeF_5^- , respectively, are
 - (a) pentagonal planar and square pyramidal
 - (b) pentagonal planar and trigonal bipyramidal
 - (c) square pyramidal and pentagonal bipyramidal
 - (d) square pyramidal and pentagonal planar
- 35. Sodium salt of pseudohalogens, X, Y and Z form colorless solutions in water. Solution of X decolorizes I_3^- solution with brisk effervescence. Solution of Y gives an intense red colour on reaction with Fe³⁺ solution. Solution of Z gives an intese blue color on reaction with a solution containing Fe³⁺ and Fe²⁺ ions. The pseudohalogens X, Y and Z respectivley are
 - (a) CN^- , N_3^- and CNS^-

(b) N_3^- , CNS⁻ and CN⁻

(c) N_3^- , CN^- , and CNS^-

- (d) N₃, CNS⁻, and CNO⁻
- 36. On reacting 1.55g of a diol with an excess of methylmagnesium iodide, 1.12L (corrected to STP) of methane gas is liberated. The molecular mass (g mol⁻) of the diol is ______
- 37. The structure of the compound having the following characteristics spectral data, is IR: 1690 cm^{-1} . $^{1}\text{H-NMR}: 1.30 \text{ (3H, t, J} = 7.2 \text{ Hz)}; 2.41 \text{ (2H, q, J} = 7.2 \text{ Hz)}; 2.32 \text{ (3H, s)}; 7.44 \text{ (1H, t, J} = 7.0 \text{ Hz)}; 7.57 \text{ (1H, dt, J} = 7.0, 3.0 \text{ Hz)}; 7.77 \text{ (1H, t, J} = 3.0 \text{ Hz)}; 7.90 \text{ (1H, dt, J} = 7.0, 3.0 \text{ Hz)}; EI mass: m/z 119 (100%); 57 (80%)$

$$(a) \begin{picture}(20,0) \put(0,0){\line(1,0){100}} \put(0,0){\line(1,0)$$

38. The major products X and Y formed in the following formed in the following synthetic scheme, are

$$(ii) \xrightarrow{N}, \text{ cat. } H^{+}$$
benzene (solvent)
$$(iii) \xrightarrow{H^{+}, H_{2}O} (X) \xrightarrow{(H_{3}C)_{2}S \xrightarrow{C} H_{2}} (Y)$$

(iv) aq. NaOH, heat

(a)
$$X = \begin{pmatrix} 0 & 0 & 0 & 0 \\ Y = & \begin{pmatrix} 0 & 0 & 0 \\ Y = & & & \end{pmatrix} \end{pmatrix} \end{pmatrix} \end{pmatrix} \end{pmatrix}$$

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39. The major product S and T formed in the following synthetic schemem, are

$$(a) S = (b) S = (c) S = (c)$$

40. Among the following, the transformation(s) that can be accomplished using umpolung concept is(are)

41. A disaccharide does NOT give a positive test for Tollen's reagent. Upon acidic hydrolysis, it gives an equimolar mixture of two different monosaccharides, both of which can be oxidized by bromine water. This disaccharide is

42. The major products M and N in the following reaction sequence are

43. The major products P and Q in the following reaction sequence, are

$$(a) P = Q = (b) Ph$$

$$(b) P = Q = (c) Ph$$

$$(c) P = Q = (d) Ph$$

$$(d) P = Q = (d) Ph$$

$$(d) P = Q = (d) Ph$$

$$(e) Ph$$

$$(e) P = Q = (d) Ph$$

$$(f) Ph Mg Br (1 equiv.) (Q)$$

44. The major product formed in the following reaction, is

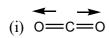
(a)
$$CH_3$$
 (b) C

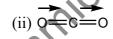
$$(d) \begin{picture}(d){\cite{1.5ex}} \begin{picture}(d){\cite{1.$$

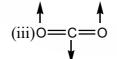
45. The following synthetic transformation can be achieved using

Reagents:

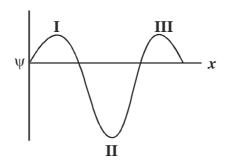
- (p) (i) NH₂OH/H⁺, (ii) H₂SO₄
- $(q) NH_2/H^+$
- (r) (i) NH₂OH/H⁺, (ii) NaOH
- (a) p only
- (b) p and q
- (c) q and r
- (d) r only
- 46. Consider a two-state system at thermal equilibrium with equal degeneracy where the excited state is higher in energy than the ground state by 0.1 eV. The ratio of the population of the excited state to that of the ground state, at a temperature for which $k_B T = 0.05$ eV, is ______
- 47. Of the vibrational modes given below, the IR active mode(s) is(are)







- (a) (ii) only
- (b) (iii) only
- (c) (i) and (ii)
- (d) (ii) and (iii)
- 48. A system is described by the following real wavefunction.



The probability (P) of finding the particle in a region dx around points I, II and III in the figure obeys the trend

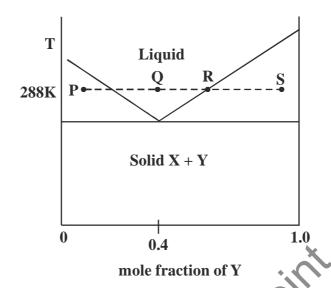
(a) P(I) > P(II) > P(III)

(b) P(II) > P(III) > P(I)

(c) P(II) > P(I) > P(III)

(d) P(III) > P(I) > P(II)

49. The temperature-composition (*T-x*) phase diagram of the two-component system made of X and Y is given below. At a temperature of 288K and starting at the point P, Y is added until the composition reaches S. Which of the following statements is NOTR TRUE?



- (a) At P, the solid and liquid are present in almost equal proportions
- (b) At Q, the system is all liquid
- (c) At S, the system has more solid than liquid
- (d) At R, the liquid is pure X
- 50. For a system subjected to only P-V work, entropy is given by
 - (I) $-\left(\frac{\partial G}{\partial T}\right)_P$
- (II) $\left(\frac{\partial G}{\partial P}\right)_T$
- $(III) \left(\frac{\partial A}{\partial V}\right)_T$
- (IV) $-\left(\frac{\partial A}{\partial T}\right)_{V}$

- (a) I and II
- (b) I and IV
- (c) Lonk
- (d) II only
- 51. According to Irving-Williams series, the number of d electrons for the first row transition metal (M) ion having the highest overall stability cosntant $(\log \beta)$ for $[M(EDTA)]^{2-}$ is
- 52. The magnitude of the difference in the crystal field stabilization energies, in Δ_0 (irnoring pairing energy), of $[\text{Fe}(H_2O)_6]^{2+}$ and $[\text{Fe}(CN)_3]^{4-}$ is
- 53. The calculated and observed magnetic moments differ considerably for an aqua complex of a Lanthanide (III) ion as a result of low lying states of high J. The ion, among the follwing, is

 (a) Ce^{3+} (b) Pr^{3+} (c) Eu^{3+} (d) Yb^{3+}
- 54. In the electronic spectra of $\left[\text{CrF}_6 \right]^{3-}$, absorption bands observed at 670, 440 and 290 nm are, respectively, due to the transitions.
 - (a) ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(P)$, ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(F)$ and ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$
 - (b) ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$, ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$
 - (c) $^4A_{2g} \rightarrow ^4T_{1g}(F)$, $^4A_{2g} \rightarrow ^4T_{1g}(P)$ and $^4A_{2g} \rightarrow ^4T_{2g}$
 - (d) $^4A_{2g} \rightarrow {}^4T_{2g},\, ^4A_{2g} \rightarrow {}^4T_{lg} (F)$ and $^4A_{2g} \rightarrow {}^4T_{lg} (P)$
- 55. Amongst the following, the group that is bound to the metal ion in coenzyme B_{12} is
 - (a) methyl
- (b) cyanide
- (c) adenosyl
- (d) hydroxyl