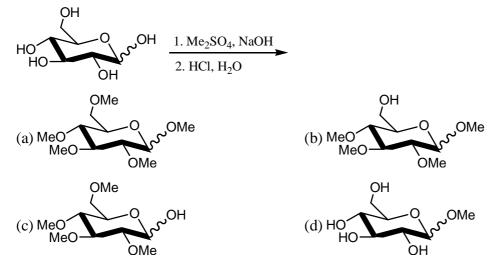
## GATE-CY 2014

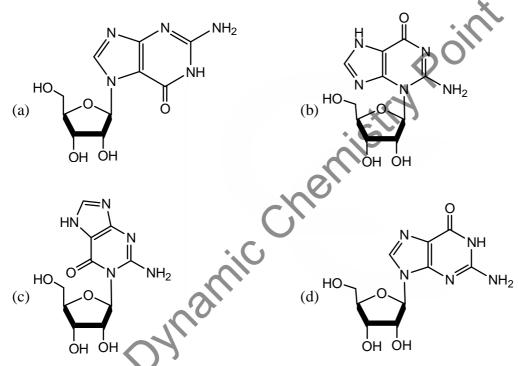
## Section-A

	Q.1 – Q.25 : Carry ONE mark each.
1.	The maximum non-PV work that a system can perform at constant P is
	(a) $\Delta H$ (b) $\Delta G$ (c) $\Delta S$ (d) $\Delta A$
2.	Consider the reaction :
	A + B  C
	The unit of the thermodynamic equilibrium constant for the reaction is (a) mol $L^{-1}$ (b) $L$ mol <sup>-1</sup> (c) mol <sup>2</sup> $L^{-2}$ (d) dimensionless
3.	The number of IR active vibrational normal modes of CO <sub>2</sub> is
4.	The number of $C_2$ axes in $CCl_4$ is
5.	The value of the magnetic quantum number of a $p_x$ orbital is (a) $-1$ (b) 0 (c) $+1$ (d) undefined.
6.	The molecular partition function for a system in which the energy levels are equispaced by $\epsilon$ , is
	(a) $\frac{1}{1+e^{\beta\epsilon}}$ (b) $\frac{1}{1-e^{\beta\epsilon}}$ (c) $\frac{1}{1+e^{-\beta\epsilon}}$ (d) $\frac{1}{1-e^{-\beta\epsilon}}$
7.	A monoatomic gas, X, adsobred on a surface, Langmuir adsorption isotherm. A plot of the fraction of surface coverage, $\theta$ against the concentration of the gas [X], for very low concentration of the gas, is described by the equation
	equation (a) $\theta = K[X]$ (b) $1 - \theta = \frac{1}{K[X]}$ (c) $\theta = K^{1/2}[X]^{1/2}$ (d) $\theta = \frac{K[X]}{1 - K[X]}$
8.	At a given temperature and pressure, the ratio of the average speed of hydrogen gas to that of helium gas is approximately
9.	An example of nido-borane from the following is (a) $B_4H_{10}$ (b) $B_6H_{40}$ (c) $B_6H_{12}$ (d) $B_8H_{14}$
10.	The geometries of Ni(CO), and [NiCl,] <sup>2-</sup> , respectively, are(a) tetrahedral and square planar(b) square planar and tetrahedral(c) tetrahedral and tetrahedral(d) square planar and square planar
11.	The number of S–S bonds in $H_2S_5O_6$ is
12.	In atomic absorption spectroscopy, the atomization process utilizes (a) flame (b) electric field (c) magnetic field (d) electron beam
13.	At room temperature, the number of singlet resonances observed in the <sup>1</sup> H NMR spectrum of $Me_3CC(O)NMe_2$ (N N-dimethyl pivalamide) is
14.	Amongst the following, the metal that does NOT form homoleptic polynuclear carbonyl is (a) Mn (b) Fe (c) Cr (d) Co
15.	The reaction of $[Cp_2TaMe_2]I(Cp = C_5H_5^-)$ with NaOMe yields. (a) $[Cp_2Ta(OMe)_2]I$ (b) $[Cp_2Ta(Me)OMe]I$ (c) $Cp_2Ta(Me) = CH_2$ (d) $Cp_2Ta(OMe) = CH_2$
16.	The complexes $[Co(H_2O)_4Cl_2]NO_2$ and $[Co(H_2O)_4Cl(NO_2)]Cl$ are (a) linkage isomers (b) positional isomers (c) ionization isomers (d) optical isomers

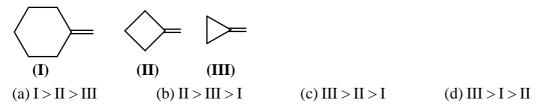
17. The major product of the following reaction is



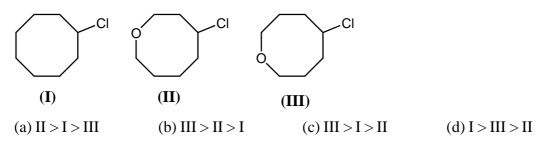
18. Amongst the following, the structure of guanosine is



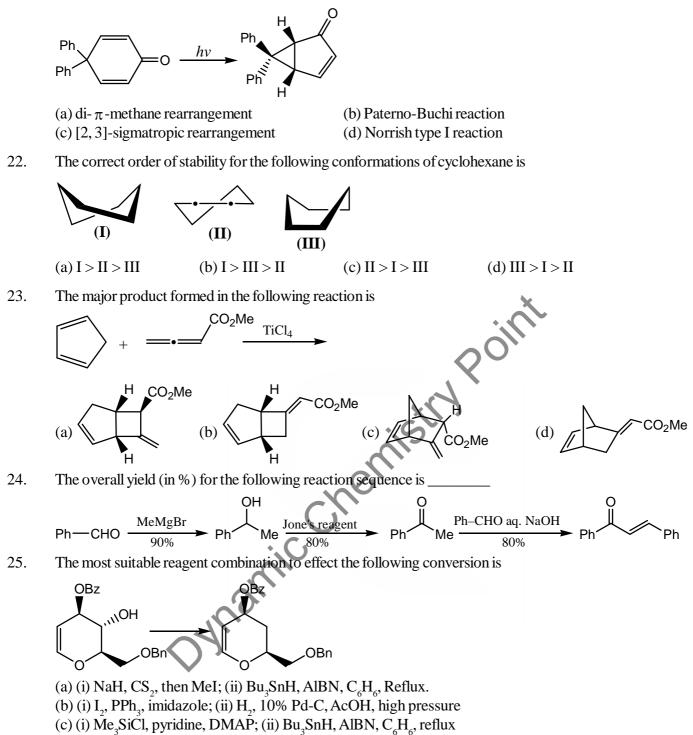
19. The correct order of IR stretching frequency of the C = C in the following olefins is



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



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



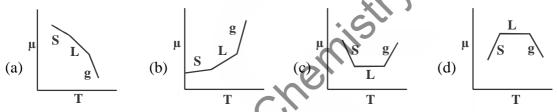
(d) (i) MsCl, pyridine, DMAP; (ii) LiAlH<sub>4</sub>, THF, reflux,

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

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

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

- 27. The van der waals constant a and b of CO<sub>2</sub> are  $3.64 L^2$  bar mol<sup>-2</sup> and  $0.04 L \text{ mol}^{-1}$ , respectively. The value of R is 0.083 bar dm<sup>3</sup> mol<sup>-1</sup>K<sup>-1</sup>. If one mole of CO<sub>2</sub> is confined to a volume of 0.15L at 300K, then the pressure (in bar) exerted by the gas, is \_\_\_\_\_
- 28. A plot of osmotic pressure against concentration  $(gL^{-1})$  of a polymer is constructed. The slope of the plot (a) increases with increase in temperature
  - (b) increases with increase in molar mass of the polymer
  - (c) decreases with decrease in concentration of the polymer
  - (d) decreases with increase in temperature.
- 29. A platinum electrode is immersed in a solution containing  $0.1 \text{ M Fe}^{2+}$  and  $0.1 \text{ M Fe}^{3+}$ . Its potential is found to be 0.77V against SHE. Under standard conditions and considering activity coefficients to be equal to unity, the potential of the electrode, when the concentration of Fe<sup>3+</sup> is increased to 1 M, is \_\_\_\_\_
- 30. Molybdenum crystallizes in a bcc structure with unit cell dimensions of 0.314 nm. Considering the atomic mass of molybdenum to be 96, its density (in kg  $m^{-3}$ ) is \_\_\_\_\_
- 31. The ratio of molecules distributed between two states is  $9.22 \times 10^6$  at 300K. The difference in energy (in kJ mol<sup>-1</sup>) of the two states is \_\_\_\_\_
- 32. A Carnot engine operates at 55% efficiency. If the temperature of reject steam is 105°C, then the absolute temperature of input steam is \_\_\_\_\_
- 33. Of the following plots, the correct representation of chemical potential (µ) against absolute temperature (T) for a pure substance is (S, L and g denote solid, liquid and gas phases, respectively)



- 34. The enthalpy of fusion of ice at 273K is 6.01 kJ mol<sup>-1</sup> and the enthalpy of vaporization of water at 273K is  $44.83 \text{ kJ mol}^{-1}$ . The enthalpy of sublimation (in kJ mol<sup>-1</sup>) of ice at 273K, is \_\_\_\_\_\_
- 35. Suppose  $\psi_1$  and  $\psi_2$ , are two hybrid orbitals:  $\psi_1 = 0.12 \psi_{3s} + 0.63 \psi_{3p_x} + 0.77 \psi_{3p_y}$  and  $\psi_2 = 0.12 \psi_{3s} - 0.63 \psi_{3p_x} - 0.77 \psi_{3p_y}$ The angle (in degrees) between them is \_\_\_\_\_

36. BCl<sub>3</sub> and NH<sub>4</sub>Cl were heated at 140°C to give compound X, which when treated with NaBH<sub>4</sub> gave another compound Y. Compounds X and Y are (a)  $X = B_3N_3H_3Cl_3$  and  $Y = B_3N_3H_6$  (b)  $X = B_3N_3H_9Cl_3$  and  $Y = B_3N_3H_6$ (c)  $X = B_3N_3H_3Cl_3$  and  $Y = B_3N_3H_{12}$  (d)  $X = B_3N_3Cl_6$  and  $Y = B_3N_3H_6$ 

37. The number of microstates in term  ${}^{1}G$  is \_

38. The set of protons (underlined) in CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> that would exhibit different splitting patterns in high (500 MHz) and low (60 MHz) field <sup>1</sup>H NMR, is
(a) CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>
(b) CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>

- (a)  $\underline{CH}_{3}\underline{CH}_{2}\underline{CH}_{2}\underline{OCH}_{3}$ (b)  $\underline{CH}_{3}\underline{CH}_{2}\underline{CH}_{2}\underline{OCH}_{3}$ (c)  $\underline{CH}_{3}\underline{CH}_{2}\underline{CH}_{2}\underline{OCH}_{3}$ (d)  $\underline{CH}_{3}\underline{CH}_{2}\underline{CH}_{2}\underline{OCH}_{3}$
- 40. Amonst the following, the metal carbonyl species having the highest  $v_{CO}$  stretching frequency is (a)  $[Mn(CO)_6]^+$  (b)  $Cr(CO)_6$  (c)  $[V(CO)_6]^-$  (d)  $[Fe(CO)_4]^{2-}$

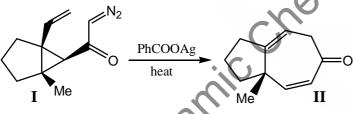
- 41. The correct order of thermal stability for the given compounds is (a)  $TiMe_4 > Ti(CH_2CMe_3)_4 > TiEt_4$  (b)  $TiEt_4 > Ti(CH_2CMe_3)_4 > TiMe_4$ (c)  $TiMe_4 > TiEt_4 > Ti(CH_2CMe_3)_4$  (d)  $Ti(CH_2CMe_3)_4 > TiMe_4 > TiEt_4$
- 42. Amongst the following, the complex ion that is expected to the highest magnetic moment at room temperature is

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

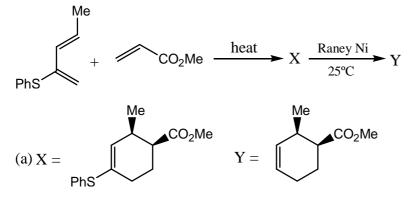
- 43.  $MnCr_2O_4$  is
  - (a) normal spinel with total CFSE of -15.5 Dq
  - (b) inverse spinel with total CFSE of -15.5 Dq
  - (c) normal spinel with total CFSE of -24 Dq
  - (d) inverse spinel with total CFSE of -24 Dq
- 44. Mg<sup>2+</sup> is preferred in photosynthesis by chlorphyll because
  (a) it has strong spin-orbit coupling
  (b) it has weak spin-orbit coupling
  (c) it is a heavy metal
  (d) it binds strongly with chlorophyll
- 45. In Monsanto acetic acid process shown below, the role of HI is

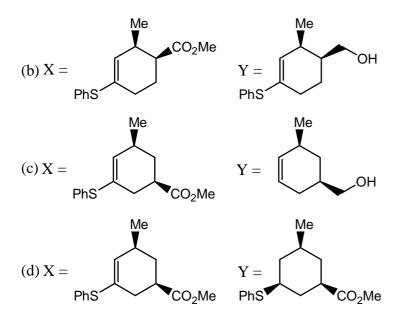
$$CH_3OH + CO \xrightarrow{Rh(\ell) \text{ catalyst/HI}} CH_3CO_2H$$

- (a) to convert  $CH_3OH$  to a stronger nucleophile ( $CH_3O^-$ )
- (b) to reduce the Rh(I) catalyst to a Rh(0) species
- (c) to reduce a Rh(III) active species to a Rh(I) species in the catalytic cycle
- (d) to convert  $CH_3OH$  to  $CH_3I$
- 46. Formation of the ketone H from the diazoketone I involved

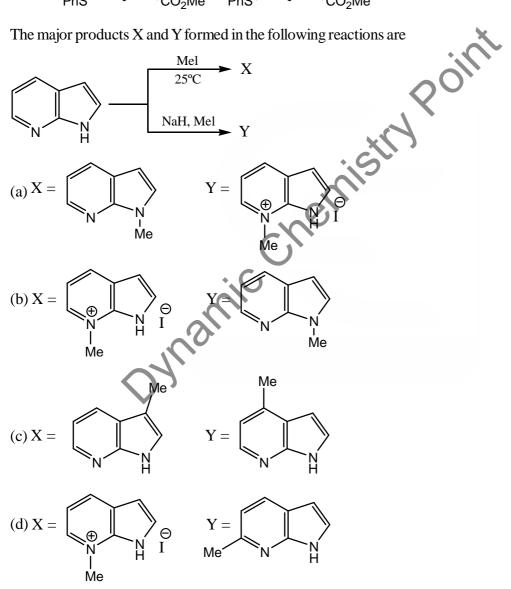


- (a) generation of carbene and a[2, 3]-sigmatropic rearrangement
- (b) generation of carbene and an electrocyclic ring closing reaction
- (c) generation of ketene and a [2+2] cycloaddition
- (d) generation of ketene and a [3, 3] sigmatropic rearrangement
- 47. The major products X and Y formed in the following reaction sequence are

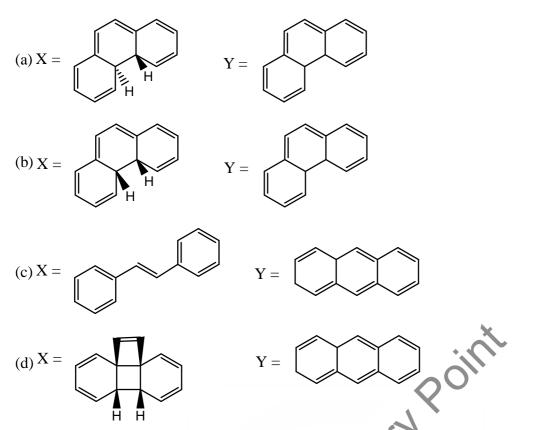




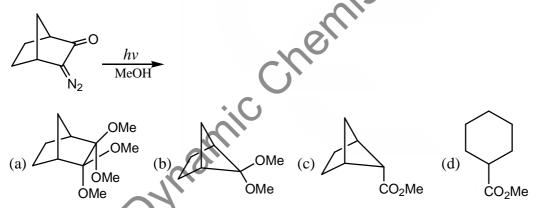
The major products X and Y formed in the following reactions are 48.



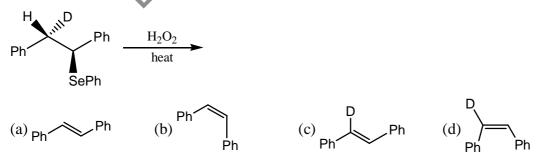
The major product X and Y formed in the following reaction sequence are 49. cis-stilbene  $\xrightarrow{hv} X \xrightarrow{I_2} Y$ 



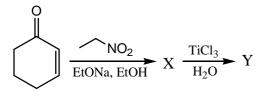
50. The product of the following reaction gave 6 line <sup>13</sup>C NMR spectrum with peaks at  $\delta$  175, 52, 50, 46, 37, 33 ppm. The structure of the product is

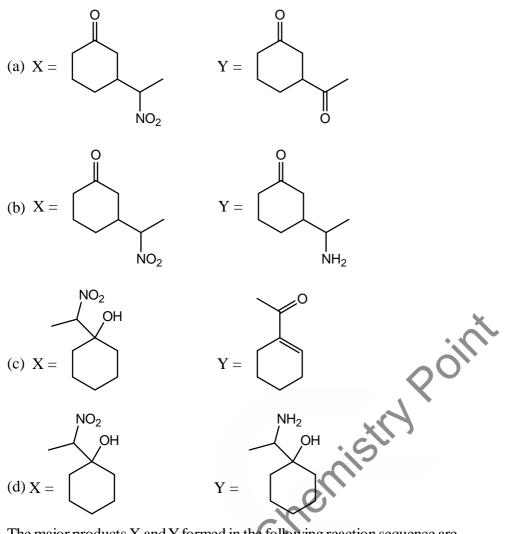


51. The major product formed in the following reaction is

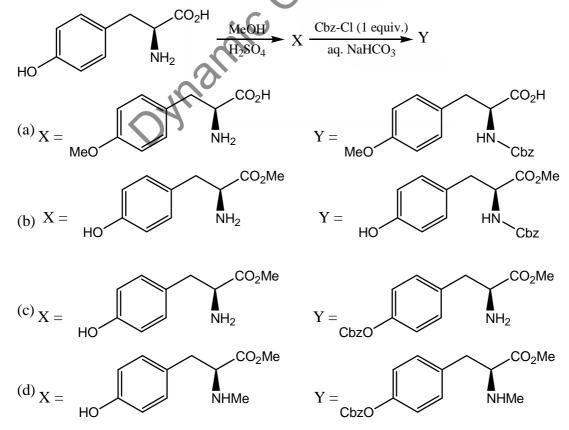


52. The major products X and Y formed in the following reaction sequence are

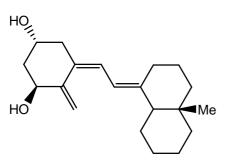




53. The major products X and Y formed in the following reaction sequence are



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



(Use these absorption values for auxochromic groups: alkyl: +5; exo-cyclic double bond: +5; every additional conjugated C = C: +30)

The m/z value of the detectable fragment formed by McLafferty like rearrangement of the following compound 55. in mass spectrometer is \_\_\_\_\_

