(a) 1

(a) 1.0

is given by

(a) both diamagnetic

1.

2.

3.

4.

On the basis o LCAO-MO theory, the magnetic characteristics of  $\mathbf{N}_2$  and  $\mathbf{N}_2^+$  are

The  $v_{ms}$  of a gas at 300 K is 30 R  $\frac{1}{2}$ . The molar mass of the gas, in kg mol<sup>-1</sup>, is

## **CHEMISTRY-CY**

In units of  $\frac{h^2}{8mt^2}$ , the energy difference between levels corresponding to 3 and 2 node eigenfunctions for a

(c)  $1.0 \times 10^{-2}$ 

The coefficient of performance of a perfect refrigerator working reversibly between the temperature  $T_{\rm c}$  and  $T_{\rm h}$ 

(b) both paramagnetic

(d)7

(d)  $1.0 \times 10^{-3}$ 

(d)  $N_2$  paramagnetic and  $N_2^+$  diamagnetic

Q.1 - Q.30: Carry ONE mark each.

(c)  $N_2$  dimagnetic and  $N_2^+$  paramagnetic

particle of mass m in a one dimensional box of length  $\ell$  is

(b)  $1.0 \times 10^{-1}$ 

(b) 3

	$(a) \frac{T_{c} - T_{h}}{T_{c}}$	(b) $\frac{T_h - T_c}{T_c}$	$(c) \frac{T_c}{T_h - T_c}$	(d) $\frac{T_h}{T_h - T_c}$			
5.	_		_	omponent system shows a binodal curve. ent, among the choices given below, is (d) carbon tetrachloride			
6.	A certain reaction proceeds in a sequence of three elementary steps with the rate constants $k_1, k_2$ and $k_3$ . In						
	the observed rate constant $(k_{obs})$ of the reaction is expressed as $k_{obs} = k_3 (k_1/k_2)^{1/2}$ , the observed activation						
	energy $(E_{obs})$ of the	e reaction is					
	(a) $\frac{1}{2} \left[ \frac{E_1}{E_2} \right] + E_3$	(b) $\frac{E_3 + E_1}{E_2}$	(c) $E_3 \left[ \frac{E_1}{E_2} \right]^{\frac{1}{2}}$	(d) $E_3 + \frac{1}{2}(E_1 - E_2)$			
7.	Which one of the following is an example of a maximum boiling azeotrope?						
	(a) H <sub>2</sub> O—HCl	(b) $H_2O - C_2H_6O$	H (c) CHCl <sub>3</sub> —CH <sub>3</sub> C	OH (d) CCl <sub>4</sub> —CH <sub>3</sub> OH			
8.	For the reaction, $A + B \rightleftharpoons X^{+} \rightarrow P$ , $Ea = 20.0 \text{ kJ mol}^{-1}$ at 300 K. The enthalpy change for the formation of the activated complex from the reactants in kJ mol $^{-1}$ is						
	(a) 12	(b) 15	(c) 23	(d) 25			
9.	` '		<b>\</b>	of density ( $\rho$ ) versus concentration ( $gL^{-1}$ )			
	was made at a temperature T. The slope of the plot will be equal to (where g, given in the choices below, is the acceleration of free fall)						
	(a) $\frac{\rho RT}{gM}$	(b) $\frac{gRT}{\rho M}$	(c) $\frac{RT}{\rho gM}$	(d) $\frac{gRM}{\rho T}$			
10.	If 0.001 M of a substance quenches the efficiency of fluorescence by 20%, the value of Stem-Volmer constant						
	in M <sup>-1</sup> is (a) 100	(b) 150	(c) 200	(d) 250			
www.thechemistryguru.com							

- 11. Which one of the following is NOT a photodetector?
  - (a) Bolometer

(b) Charge-transfer device

(c) Photomultiplier tube

- (d) Silicon diode
- 12. The nature of excitation signal used for cyclic voltametry is
  - (a) linear scan
- (b) differential pulse
- (c) triangular
- (d) square wave

- 13. The structure of  $SF_4$  is
  - (a) octahedral

(b) tetrahedral

(c) trigonal bipyramidal

- (d) square planar
- 14. The number of metal-metal bonds present in  $Ir_4(CO)_{12}$  are
  - (a) 4
- (b) 5

- (c)6
- (d) 8
- 15. The zero magnetic moment of octahedral K<sub>2</sub>NiF<sub>6</sub> is due to
  - (a) low spin d<sup>6</sup>Ni(IV) complex
- (b) low spin d<sup>8</sup>Ni(II) complex.
- (c) high spin d<sup>8</sup>Ni(II) complex
- (d) high spin d<sup>6</sup>Ni(IV) complex.
- 16. The number of hyperfine split lines observed in ESR spectrum of methyl radical is
  - (a) 1

- (b) 4
- (c) 6
- (d) 8

- 17. The absorption of  $Co(NH_3)_6^{2+}$  is:
  - (a) stronger than that of  $\left[ \text{Co} \left( \text{NH}_3 \right)_5 \text{Cl} \right]^{2+}$
  - (b) stronger than that of  $[MnCl_4]^{2-}$
  - (c) weaker than that of  $[MnCl_4]^2$  but stronger than that of  $[CO(NH_3)_5 Cl]^2$
  - (d) weaker than those of both  $[MnCl_4]^{2-}$  and  $[Co(NH_3)_5 Cl]^{2+}$
- 18. Which one of the following statements about ferrocene is FALSE?
  - (a) It obeys the 18-electron rule
- (b) It is diamagnetic

(c) It is an orange solid

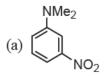
(d) It resists electrophilic substitution

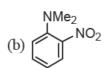
- 19. The bond angle of Cl<sub>2</sub>O is
  - (a) smaller than that of  $F_3O$

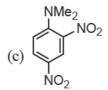
(b) greater than that of H<sub>2</sub>O

(c) smaller than that of H<sub>2</sub>O

- (d) same as that of F<sub>2</sub>O
- 20. The half-wave potential for a reversible reduction of a metal ion in polarography is independent of
  - (a) Concentration of the supporting electrolyte
  - (b) Concentration of the electroactive species.
  - (c) Concentration of the complexing agent.
  - (d) Temperature of the solution.
- 21. The major product formed on nitration of N, N-dimethylaniline with conc. H<sub>2</sub>SO<sub>4</sub>HNO<sub>3</sub> mixture is

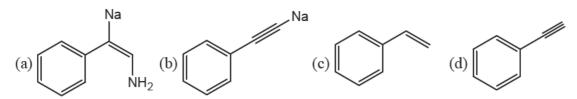




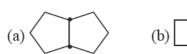




22. Reaction of phenylacetylene with sodamide in liquid ammonia generates



23. Proton decoupled <sup>13</sup>C NMR spectrum of a bicyclooctane (C<sub>8</sub>H<sub>14</sub>) exhibits only two signals. The Structure of the compound is:









24. Cyclohexyl benzyl ether when reacted with hydrogen in the presence of 10% palladium on charcoal generates a mixture of

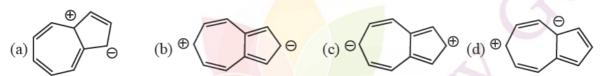
- (a) cyclohexanol and benzyl alcohol
- (b) cyclohexane and benzyl alcohol
- (c) cyclohexanol and toluene

(d) cyclohexane and toluene

25. In electrophilic aromatic substitution reactions, nitro group is meta-directing, because the nitro group

- (a) increase electron density at meta-position (b) increase electron density at ortho-and para-positions
- (c) decreases electron density at meta-position (d) decreases electron density at ortho-and para-positions

26. Among the resonance forms given below, the one which contributes most to the stability of azulene is



27. The configurations at the two asymmetric centres (C-1 and C-6) in the bicyclo [4.4.0] decane, given below are



- (a) 1R, 6R
- (b) 1R, 6S
- (c) 1S, 6S
- (d) 1S, 6R

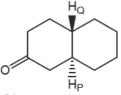
28. The reactive intermediate involved in the conversion of phenol to salicylaldehyde using chloroform and sodium hydroxide is

- (a) Cl<sub>2</sub>C:
- (b) Cl<sub>2</sub>CH<sup>+</sup>
- (c) Cl<sub>2</sub>CH<sup>-</sup>
- (d) Cl<sub>2</sub>CH<sup>+</sup>

29. Conversion of Ph-NH, into Ph-CN can be accomplished by

- (a) reaction with sodium cyanide in the presence of nickel catalyst
- (b) reaction with chloroform and sodium hydroxide
- (c) diazotisation followed by reaction with CuCN
- (d) reaction with ethyl formate followed by thermolysis

30. The vicinal coupling constant J expected for the protons H<sub>p</sub> and H<sub>Q</sub> in the compound given below will be in the range



- (a) 0-2 Hz
- (b)  $4-6 \, \text{Hz}$
- (c)  $8-10 \,\mathrm{Hz}$
- (d)  $12-15 \,\mathrm{Hz}$

## Q.31 - Q.90: Carry TWO marks each.

For one mole of an ideal gas  $\left(\frac{\partial P}{\partial T}\right)_{v} \left(\frac{\partial V}{\partial T}\right)_{r} \left(\frac{\partial V}{\partial P}\right)_{r} =$ 31.

(a) - 1

(b)  $-\frac{R^2}{\mathbf{p}^2}$ 

(d)  $\frac{R^2}{P^2}$ 

32. Neglecting the mass of hydrogen (1.0 amu) and deuterium (2.0 amu) with respect to that of iodine (127 amu), the ratio between fundamental vibrational frequencies of HI and DI is:

(a)  $\frac{1}{2}$ 

(b) 2

(c)  $\frac{1}{\sqrt{2}}$ 

(d)  $\sqrt{2}$ 

The population of  $J^{th}$  rotational level  $N_i$  is given by  $N_i = N_0 (2J+1) e^{\left[j(j+1)B\right]/kT}$ . The J value of rotational 33. level with maximum population  $(J_{max})$  is given by

(a)  $\frac{(2k \text{ T/B})-1}{\sqrt{2}}$  (b)  $\frac{\sqrt{2k \text{ T/B}}-1}{2}$  (c)  $\frac{k\text{T}}{\text{B}}$ 

(d)  $\frac{B}{1-T}$ 

The fugacity coefficient  $\phi$  is given by  $\ln \phi = \int_{1}^{p} \left(\frac{z-1}{p}\right) dp$  where z is the compressibility factor, and p the 34.

pressure. The fugacity of a gas governed by the gas law  $p(V_m - b) = RT$  is

(a)  $p \ln (V_m / RT)$  (b)  $pe^{b/RT}$ 

(c)  $ne^{-bp/RT}$ 

(d)  $pe^{bp/RT}$ 

The number and symmetry type of normal modes of vibration of H<sub>2</sub>O are 35.

(a) 3 and  $2A_1 + B_2$ 

(c) 3 and  $2A_1 + B_1$ 

(b) 3 and  $2A_1 + A_2$ (d) 4 and  $3A_1 + B_2$ 

The gaseous reaction  $2A + B \rightarrow C$ , with partial pressures of  $p_A = 0.1$  atm;  $p_B = 0.001$  atm and  $p_C = 1.0$ 36. atm, proceeds to the left at 298 K. The equilibrium constant,  $K_p$  for the above reaction is

(a)  $1.0 \times 10^4$ 

(b)  $1.0 \times 10^5$ 

(c)  $1.0 \times 10^6$ 

The change in entropy when one mole of an ideal gas is compressed to one-fourth of its initial volume and 37. simultaneously heated to twice its initial temperature is

(a)  $(C_{-}-R)\ln 4$ 

(b)  $(C_v - 2R) \ln 2$  (c)  $(C_v - 2R) \ln 4$  (d)  $(C_v + 2R) \ln 2$ 

For the reaction,  $A(s) \rightleftharpoons B(l) + 2C(g)$ ,  $\Delta G^{\circ}$  (in Joules) = 90800 - 100T. The partial pressure of C(g)38. at 600 K in Torr is

(a) 15

(c)35

(d) 46

39. Match the following:

 $P \cdot \left( \frac{\partial U}{\partial S} \right)$ 

I.A

 $Q \cdot \left( \frac{\partial U}{\partial V} \right)_{c}$ 

II. -S

 $R.\left(\frac{\partial G}{\partial P}\right)$ 

III. T

48.

IV.-P V. H VI. V (a) P-III Q-IV R-VI S-II (b) P-III Q-I R-II S-V (c) P-I Q-III R-V S-II P-IV Q-III R-VI S-V (d) 40. Match the following: P. 4n+2 rule Woodward-Hoffmann rule Q. single valued II. Bound system R.  $< p_{v} > = 0$ III. Hurtree-Fock Theory S. photochemically allowed IV. Huckel theory V. Wave function VI. unbound system Codes: (b) P-IV, O-V, R-II, S-VI (a) P-I, Q-III, R-IV, S-VI (c) P-II, Q-VI, R-III, S-I (d) P-IV, O-V, R-II, S-I The solubility product of silver sulphate at 298 K is  $1.0 \times 10^{-5}$ . If the standard reduction potential of the half-41.  $cell~Ag^{+} + e \rightarrow Ag~is~0.80~V, the~standard~reduction~potential~of~the~half-cell~Ag_{2}SO_{4} + 2e \rightarrow 2Ag + SO_{4}^{2-}~is:$ (b) 0.22 V (a) 0.15 V (c) 0.65 V 42. The criterion for spontaneous change in terms of the state functions is: (d)  $dG_{TV} \leq 0$ (b)  $dA_{TV} \ge 0$ (c)  $dS_{uv} \ge 0$ (a)  $dU_{sv} \ge 0$ One mole of an ideal gas  $(C_v = 1.5 \, \text{R})$  at a temperature 500 K is compressed from 1.0 atm to 2.0 atm by a 43. reversible isothermal path. Subsequently, it is expanded back to 1.0 atm by a reversible adiabatic path. The volume of the final state in litre is: (c) 31.1 (d) 41.0 (a) 15.6 (b) 20.5The vapour pressures of the pure components P and Q are 700 Torr and 500 Torr, respectively. When the 44. two phases are in equilibrium at 1.0 atm, the mole fraction of P in the liquid phase is 0.6 and in the vapour phase 0.4. The activity co-efficient of component P in the solution on the basis of Raoult's law is (a) 0.60(b) 0.72The concentration of oxygen in water in mg L<sup>-1</sup>. If the Henry's law constant for oxygen at 298 K is 45.  $2.80 \times 10^7$  Torr, the partial pressure of oxygen in the atmosphere in Torr is, (a) 28 (b) 32(c) 50 (d) 15.68 Decomposition of ammonia on tungsten at 850°C has a rate constant value of 0.10 Torr s<sup>-1</sup>. If the initial 46. pressure of ammonia is 100 Torr, the pressure of ammonia (in Torr) at t = 200 s is (a) 10 (b) 20 For the reaction of the type  $P \xrightarrow{k_1} Q \xrightarrow{k_2} R$ , given that  $\left[P\right]_0 = 1.0M; k_1 = 1 \times 10^{-3} \text{ s}^{-1}$  and 47.  $k_2=1\times 10^{-4}\,\mathrm{s^{-1}}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ respectively, is } 10^{-4}\,\mathrm{s^{-1}}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ respectively, is } 10^{-4}\,\mathrm{s^{-1}}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ respectively, is } 10^{-4}\,\mathrm{s^{-1}}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ respectively, is } 10^{-4}\,\mathrm{s^{-1}}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ respectively, is } 10^{-4}\,\mathrm{s^{-1}}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ respectively, is } 10^{-4}\,\mathrm{s^{-1}}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ respectively, is } 10^{-4}\,\mathrm{s^{-1}}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ respectively, } 10^{-4}\,\mathrm{s^{-1}}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.5966\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ the time at which the concentrations of } Q \text{ and } R \text{ are } 0.59660\,\mathrm{M} \text{ and } 0.0355\mathrm{M}, \text{ the time at which the concentrations of } Q \text{ and } Q \text{$ (b) 750 s (a) 500s (c) 1000 s (d) 1500 s

(a) inverse and inverse (b) inverse and normal (c) normal and normal (d) normal and inverse

The spinels CoFe<sub>2</sub>O<sub>4</sub> and FeFe<sub>2</sub>O<sub>4</sub>, respectively, are

49.	According to Wade's i	rule, the structures of 1	$\mathrm{B}_{10}\mathrm{C}_2\mathrm{H}_{12}$ and $\mathrm{B}_9\mathrm{C}_2\mathrm{H}_{11}$	] <sup>2-</sup> , respectively, are		
	(a) closo and arachno	(b) nido and closo	(c) closo and nido	(d) nido and arachno		
50.	The overall charge present on the cyclic silicate anion $\left[Si_6O_{18}\right]^{n-}$ is					
	(a) 6	(b) 12	(c) 18	(d) 24		
51.	The ground state term (a) ${}^3S$ and ${}^6S$	symbols for high spin of (b) <sup>6</sup> P and <sup>3</sup> S	1 <sup>5</sup> s <sup>1</sup> and d <sup>5</sup> configuratio (c) <sup>7</sup> S and <sup>6</sup> S	ns, respectively, are (d) <sup>7</sup> P and <sup>6</sup> S		
52.	The reagents required for the synthesis of cyclic phosphazene N <sub>4</sub> P <sub>4</sub> Cl <sub>8</sub> are					
	(a) PCl <sub>5</sub> and NH <sub>3</sub> (c) POCl <sub>3</sub> and NH <sub>3</sub>		(b) POCl <sub>3</sub> and NH <sub>4</sub> Cl (d) PCl <sub>5</sub> and NH <sub>4</sub> Cl	Cl		
53.	The isomerisms that are possible in the Co(III) complexes $\left(\text{Co}\left(\text{NH}_{3}\right)_{3}\left(\text{NO}_{2}\right)_{3}\right)$ and $\left[\text{Co}\left(\text{NH}_{3}\right)_{5}\text{NO}_{2}\right]\text{Cl}_{2}$					
	respectively, are (a) co-ordination and p (c) geometrical and link		(b) optical and linkag (d) optical and optica			
54.	The perxenate ion XeO <sub>4</sub> <sup>4-</sup> can be prepared by					
	<ul><li>(a) direct reaction of XeF</li><li>(c) hydrolysis of XeF</li></ul>		(b) reaction of XeF <sub>6</sub> (d) hydrolysis of Xe			
55.	In tetrahedral geometry tion to the magnetic mo		wing sets of electronic c	onfigurations will have orbital contribu		
	(a) d <sup>3</sup> , d <sup>4</sup> , d <sup>8</sup> and d <sup>9</sup> (c) d <sup>3</sup> , d <sup>4</sup> , d <sup>7</sup> and d <sup>9</sup>		(b) d <sup>1</sup> , d <sup>6</sup> , d <sup>7</sup> and d <sup>9</sup> (d) d <sup>1</sup> , d <sup>3</sup> , d <sup>4</sup> and d <sup>9</sup> .			
56.	The most suitable route to prepare the trans isomer of $[PtCl_2(NH_3)(PPh_3)]$ is:					
	(a) [PtCl <sub>4</sub> ] <sup>2-</sup> with PPh <sub>3</sub> followed by reaction with NH <sub>3</sub> .					
	(b) $[PtCl_4]^{2-}$ with NH <sub>3</sub> followed by reaction with PPh <sub>3</sub> .					
	(c) $\left[ Pt(NH_3)_4 \right]^{2+}$ with HCl followed by reaction with PPh <sub>3</sub> .					
	(d) $\left[ \text{Pt} \left( \text{NH}_3 \right)_4 \right]^{2+}$ with PPh <sub>3</sub> followed by reaction with HCl.					
57.	A solution containing 5 ppm of KMnO <sub>4</sub> (F.W. = 159) has a transmittance of 0.360 measured in a 1 cm cell a 500 nm. The molar absorptivity of KMnO <sub>4</sub> in L mol <sup>-1</sup> cm <sup>-1</sup> is					
	(a) $1.1 \times 10^4$	(b) $1.4 \times 10^4$	(c) $1.9 \times 10^4$	(d) $2.7 \times 10^4$		
58.	Match the following: P. Coulometry Q. Ion selective electrode R. Polarography S. Amperometry		I. Dropping mercury of II. Current efficiency III. Dead stop end po IV. Membrane potent V. Conductometer VI. Actinometer.	pint		
	(a) P-II, Q-IV, R-I, S- (c) P-VI, Q-V, R-III,		(b) P-I, Q-II, R-III, S (d) P-III, Q-IV, R-I,			

59. Match the following:

> P: Ferritin I. electron transport

Q: Vitamin B<sub>12</sub> II. Ionophore

R: Cytochromes III. Oxygen transport S: Valinomycin IV. Nitrogen fixation

V. Organometallic enzyme

VI. Iron storage.

S-I (a) P-VI Q-IV R-II (b) P-I Q-III S-IV R-VI

(c) P-III R-IV S-VI (d) P-VI R-I S-II

The number of absorption bands observed  $[FeF_6]^{3-}$  and  $[CoF_6]^{3-}$ , respectively, are 60.

(c) 0 and 3 (a) 1 and 3 (b) 0 and 1

Regarding the catalytic cycle of hydrogenation of alkenes involving RhCl(PPh<sub>2</sub>)<sub>3</sub> as the catalyst, the correct 61. statements is:

- (a) Only 18-electron Rh complex is involved.
- (b) 14-, 16- and 18-electron Rh complexes are involved.
- (c) 14- and 16-electron Rh complexes are involved.
- (d) 16- and 18-electron Rh complexes are involved.

The infra-red stretching frequency  $V_{CO}$  of P-S follows the order 62.

(R)  $H_3B \leftarrow CO$ (b) S > P > R > Q(d) R > Q > P > S(P)  $\operatorname{Mn}(\operatorname{CO})_{6}^{+}$ (a) P > R > S > Q

(c) Q > S > P > R

63. The structures of  $N(CH_3)_3$  and  $N(SiH_3)_3$ , respectively, are

(a) trigonal planar and pyramidal (b) pyramidal and trigonal planar

(c) pyramidal and pyramidal (d) trigonal planar and trigonal planar

Which one of the following is NOT correct in chromatography? 64.

 $t_{\rm M} = {
m Retention}$  time for a species that is not retained by the stationery phase.

 $T_R$  = Retention time for the analyte

 $(t_R)_n$  = Retention time for the component n

 $W_n$  = Width of the peak at its base for the component n

(a) Resolution =  $\frac{\left(t_{R}\right)_{2} - \left(t_{R}\right)_{1}}{2\left(W_{1} + W_{2}\right)}$ (b) Capacity factor =  $\frac{t_R - t_M}{t_M}$ 

(d) No. of theoretical plates =  $16 \left( \frac{t_R}{W} \right)^2$ (c) Separation factor =  $\frac{(t_R)_2 - t_M}{(t_R)_2 - t_M}$ 

65. Thermal reaction of allyl phenyl ether generates a mixture of ortho-and para-allyl phenols. The para-allyl phenol is formed via

(a) a[3, 5]-sigmatropic shift

(b) first ortho-allyl phenol is formed, which then undergoes a [3, 3]-sigmatropic shift

(c) two consecutive [3, 3]-sigmatropic shifts

(d) dissociation to generate allyl cation, which then adds at para-position

Of the favour vicinal diols shown below, only three are cleaved by  $\mathrm{HIO_4}$ , the diol which is NOT cleaved  $\mathrm{HIO_4}$  is

67. With respect to the two reactions shown below, the correct statements about their stereochemical nature is [LDA=LiN(iPr<sub>2</sub>)]

- (a) The reactions are stereoselective, because P and Q are the same.
- (b) The reactions are non-stereoselective, because P and Q are the same.
- (c) The reactions are stereoselective, because P and Q are diastereomers.
- (d) The reactions are enantioselective, because P and Q are enantiomers.
- 68. For the reactions shown below, identify the correct statement with regard to the products formed.

(S)-styreneoxide

- (S)-styreneoxide
- (a) P and Q are identical, both are optically active.
- (b) P and Q are positional isomers, P is racemic and Q is optically active.
- (c) P and Q are positional isomers, P is optically active and Q is racemic.
- (d) P and Q are positional isomers, both are optically active.
- 69. In the reaction shown below, identify the correct combination of the intermediate P and the product Q.

$$(Ts = 4-methylphenylsulfonyl)$$

$$(A) \qquad (A) \qquad (A$$

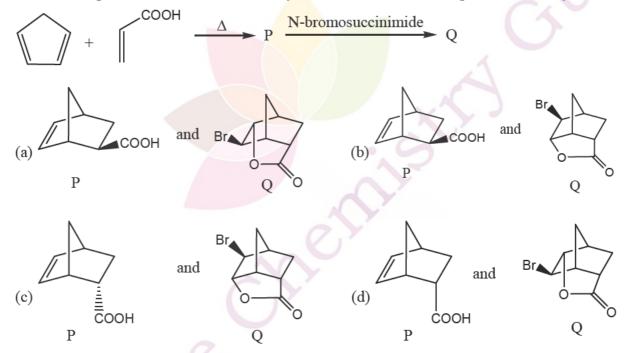
OH

$$(b) \qquad (P) \qquad (Q) \qquad Ph$$

$$(c) \qquad (P) \qquad (Q) \qquad OH$$

$$(d) \qquad (P) \qquad (Q) \qquad OH$$

70. In the two step reaction shown below, identify the correct combination of products P and Q.



71. On the basis of Favorskii rearrangement mechanism, the ratio of the products P, Q and R given below, will be, respectively.

72. An organic compound having molecular formula  $C_6H_{11}BrO_2$  exhibits the following peaks in <sup>1</sup>H NMR spectrum.  $\delta$  4.1 (2H, q, J = 7.5 Hz), 4.0 (2H, t, J = 7.5 Hz), 1.5 – 2.2 (4H, m), 1.25 (3H, t, J = 7.5 Hz)

The structure of the compound is:

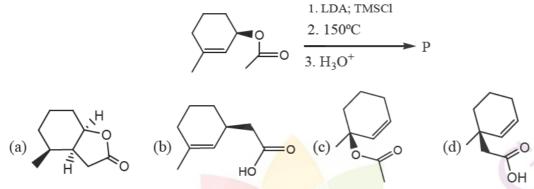
$$(a) \xrightarrow{Br} 0$$

$$(b) \xrightarrow{Br} 0$$

$$(c) \xrightarrow{Br} 0$$

$$(d) \xrightarrow{O} B$$

73. The product P formed in the following three steps reaction is:



74. Identify the correct choice of reagents, among P, Q and R, for the transformation of norbornene into the epoxides I and II

P=H<sub>2</sub>O<sub>2</sub>-AcOH

 $Q = H_2O_2$ -NaOH

R=HOBr followed by aq. NaOH.



- (a) P gives I and Q gives II
- (c) Q gives I and R gives II

- (b) R gives I and P gives II
- (d) P gives I and R gives II

MgBr

75. Reaction of ethyl acetoacetate with one equivalent of methylmagnesium bromide gives

76. For the aldotetroses I-IV, the combination of TRUE statements, among P-T, is:

P=I and II are diastereomers and II and III are enantiomers.

Q=I and IV are mesomers and are optically inactive.

R=I and III can be interconverted by a base catalysed isomerisation.

S=only I and IV are HIO<sub>4</sub> cleavable.

T=I and III are D-sugars and II and IV are L-sugars.

- (a) Q, R, T
- (b) P, R, T
- (c) Q, S, T
- (d) P, Q, S

77. Match the compounds P-S with their carbonyl stretching frequencies (cm<sup>-1</sup>) I–VI in IR spectroscopy.

P. acetone I. 1870
Q. ethyl acetate II. 1800
R. acetamide III. 1740
S. acetyl chloride IV. 1700
V. 1660
VI. 1600

- (a) P-IV, Q-III, R-I, S-VI
- (b) P-III, Q-VI, R-V, S-II
- (c) P-IV, Q-III, R-V, S-II
- (d) P-II, Q-V, R-III, S-VI

78. In the following three step transformation, identify the correct combination of product P, Q and R. [LDA=LiN(iPr)<sub>2</sub>].

$$(a) \longrightarrow_{P} G$$

$$(b) \longrightarrow_{P} G$$

$$(c) \longrightarrow_{P} G$$

$$(d) \longrightarrow_{P} G$$

79. The major product P formed in the following photochemical reaction is:

80. Three molecular ionic states, P-R, are possible for the amino acid histidine. Identify the correct choice of pH values, respectively, for the observation of the ionic states P-R.

$$H_3$$
N-CHC-OH

 $H_2$ N-CHC-O

 $H_3$ N-CHC-O

 $H_3$ N-CHC-O

 $H_4$ N-CHC-O

 $H_4$ N-CHC-O

 $H_5$ N-CHC-O

 $H_5$ N-CHC-O

- (a) P at pH 1; Q at pH 12; R at pH 7
- (b) P at pH 7; Q at pH 1; R at pH 12
- (c) P at pH 12; Q at pH 7; R at pH 1
- (d) P at pH 12; Q at pH 1; R at pH 7

81. In the reaction shown below, identify the correct combination of the intermediate P and the product Q.

$$(a) \qquad \text{and} \qquad (b) \qquad \text{and} \qquad (c) \qquad P \qquad Q$$

$$(c) \qquad \text{and} \qquad (d) \qquad (d) \qquad \text{and} \qquad$$

- 82. 90. contain a Statement with a Reason and an Assertion. for each question, choose the correct answer from the following four choices.
- (a) Both Reason and Assertion are correct
- (b) Both reason and Assertion are wrong
- (c) Reason is correct and Assertion is wrong
- (d) Reason is wrong but Assertion is correct
- 82. **Statement:** solid carbon dioxide is called as dry ice.

**Reason**: CO<sub>2</sub> sublimes when kept in open atmosphere.

**Assertion**: Triple point of CO<sub>2</sub> lies above one atmosphere.

83. Statement: Entropy of pure, perfectly crystalline substance is zero at absolute zero of temperature.

**Reason**: At absolute zero, molecules can have only one orientation.

**Assertion:** Statistical definition of entropy is given by the equation, S = k ln W, where W is the probability of orientation

84. **Statement**: Catalytic decomposition of ammonia on platinum takes place at 1000°C.

**Reason**: Ammonia is more strongly adsorbed than hydrogen on platinum.

**Assertion :** The rate law for the decomposition of ammonia on platinum is given as, Rate =  $k \frac{p_{NH_3}}{p_{H_3}}$ 

85. **Statement**:  $CoCl_4^{2-}$  is a regular tetrahedron but  $CuCl_4^{2-}$  is a distorted tetrahedron.

**Reason:** Unsymmetrical distribution of electrons in  $e_g$  orbital leads to distortion in  $CuCl_4^{2-}$ .

**Assertion:** CI<sup>-</sup> ligands interact differently with orbitals of unequal electron population. This leads to distortion in tetrahedral geometry.

86. **Statement:** Schottky and Frenkel defects are stoichiometric defect occurring in crystal lattices.

**Reason**: Schottky defects are due to the absence of one positive and one negative ion and Frenkel defects are due to the presence of one hole and one ion in an interstitial position.

**Assertion:** The ratio of number of atoms of one kind to the number of atoms of the other kind does not correspond exactly to the ideal whole number ratio implied by the formula which leads to stoichiometric defects.

87. **Statement**: Ga is below Al in Group IIIA, yet the atomic size of Ga is almost the same as that of Al.

Reason: Lanthanide contraction

**Assertion:** Poor shielding of nuclear charge results in outer electrons being more firmly held by the nucleus.

88. **Statement:** 5-Bromopyrimidine (C<sub>4</sub>H<sub>3</sub>BrN<sub>2</sub>) exhibits two prominent peaks in the mass spectrum at m/z 158 and 160 in the ratio of 1:1.

**Reason:** There are two basic centres in the molecule, which are protonated.

Assertion: There are two isotopes of bromine, <sup>79</sup>Br and <sup>81</sup>Br, that occur in the ratio of 1:1.

Choose the correct answer from the following four choices.

- (a) Both Reason and Assertion are correct.
- (b) Both Reason and Assertion are wrong
- (c) Reason is correct and Assertion is wrong. (d
  - (d) Reason is wrong but Assertion is correct.
- 89. **Statement**: Pyridine is more basic than pyrrole.

**Reason:** The nitrogen in pyrrole carries a proton while the nitrogen in pyridine does not.

**Assertion:** Nitrogens in trigonal geometry are generally more basic than the nitrogens in tetrahedral geometry.

90. **Statement**: Replacement of CH<sub>3</sub> with CF<sub>3</sub> decreases the rate decreases the rate of reaction I, but increases the rate of reaction II

OMs  $H_2O$ -acetone  $H_2O$ -acetone  $H_3O$ -acetone

**Reason :** Reaction I proceeds through  $SN_1$  mechanism and reaction II proceeds through  $SN_2$  mechanism. **Assertion :** Being an electron withdrawing group,  $CF_3$  destabilizes the transition state in  $SN_1$  reaction, but stabilizes the transition state in  $SN_2$  reaction.

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