### **CHEMISTRY-CY**









- 11. In the carbylamine reaction, R-X is converted to R-Y via the intermediate Z. R-X, R-Y and Z, respectively, are
  - (a)  $R-NH_2$ , R-NC, carbene (b)  $R-NH_2$ , R-NC, nitrene
  - (c) R-NC,  $\text{R-NH}_2$ , carbene (d) R-OH, R-NC, nitrene
- 12. The compound that is NOT oxidized by  $KMnO_4$  is:



- 13. Cyanogen bromide (CNBr) specifically hydrolyses the peptide bond formed by the C-side of (a) methionine (b) glycine (c) proline (d) serine
- 14. The Hammett reaction constant  $\rho$  is based on
  - (a) the rates of alkaline hydrolysis of substituted ethyl benzoates
  - (b) the dissociation constants of substituted acetic acids
  - (c) the dissociation constants of substituted benzoic acids
  - (d) the dissociation constants of substituted phenols
- 15. The lifetime of a molecule in an excited electronic state is  $10^{-10}$  s. The uncertainty in the energy (eV) approximately is

(d) 200

(a) 
$$2 \times 10^{-5}$$
 (b)  $3 \times 10^{-6}$  (c) 0 (d)  $10^{-12}$ 

- 16. For a one component system, the maximum number of phases that can coexist at equilibrium is (a) 3 (b) 2 (c) 1 (d) 4
- 17. At T = 300 K, the thermal energy  $(k_B T)$  in cm<sup>-1</sup> is approximately (a) 20000 (b) 8000 (c) 5000
- 18. For the reaction  $2X_3 = 3X_2$ , the rate of formation of X, is:

(a) 
$$3(-d[X_3]/dt)$$
 (b)  $\frac{1}{2}(-d[X_3]/dt)$  (c)  $\frac{1}{3}(-d[X_3]/dt)$  (d)  $\frac{3}{2}(-d[X_3]/dt)$ 

- 19.The highest occupied molecular orbital of HF is:<br/>(a) bonding(b) antibonding(c) ionic(d) nonbonding.
- 20. The residual entropy of the asymmetric molecule  $N_2O$  in its crystalline state is 5.8 J K<sup>-1</sup> mol<sup>-1</sup> at absolute zero. The number of orientations that can be adopted by  $N_2O$  in its crystalline state is (a) 4 (b) 3 (c) 2 (d) 1



### Q.21 – Q.85 : Carry TWO marks each.

The spectroscopic ground state symbol and the total number of electronic transitions of  $\left[ Ti(H_2O)_6 \right]^{2+}$  are 21. (a)  ${}^{3}T_{10}$  and 2 (b)  ${}^{3}A_{2\sigma}$  and 3 (c)  ${}^{3}T_{1\sigma}$  and 3 (d)  ${}^{3}A_{2\sigma}$  and 2 22. The structures of the complexes  $[Cu(NH_3)_4](ClO_4)_2$  and  $[Cu(NH_3)_4](ClO)_4$  in solution respectively (b) octahedral and square pyramidal (a) square planar and tetrahedral (c) octahedral and trigonal bipyramidal (d) tetrahedral and square planar 23. In biological systems, the metal ions involved in electron transport are (b)  $Zn^{2+}$  and  $Mg^{2+}$ (a)  $Na^+$  and  $K^+$ (c)  $Ca^{2+}$  and  $Mg^{2+}$ (d)  $Cu^{2+}$  and  $Fe^{3+}$ In a homogeneous catalytic reaction, 1.0 M of a substrate and 1.0 µM of a catalyst yields 1.0 mM of a 24. product in 10 seconds. The turnover frequency (TOF) of the reaction  $(s^{-1})$  is (a)  $10^{-2}$ (b)  $10^2$ (c)  $10^{-3}$ (d)  $10^3$ The expected magnetic moments of the first-row transition metal complexes and those of the lanthanide metal 25. complexes are usually calculated using (a)  $\mu_{s,0}$  equation (s.o. = spin only) for both lanthanide and transition metal complexes (b)  $\mu_{s,0}$  equation for lanthanide metal complexes and  $\mu_1$  equation for transition metal complexes (c)  $\mu_{s_0}$  equation for transition metal complexes and  $\mu_1$  equation for lanthanide metal complexes (d)  $\mu_{L+S}$  equation for transition metal complexes and  $\mu_{s,o}$  equation for lanthanide metal complexes 26. The Bronsted acidity of boron hydrides follows the order (a)  $B_2H_6 > B_4H_{10} > B_5H_9 > B_{10}H_{14}$ (b)  $B_2H_6 = B_4H_{10} > B_5H_9 = B_{10}H_{14}$ (c)  $B_{10}H_{14} > B_5H_9 > B_4H_{10} > B_2H_6$ (d)  $B_5H_9 > B_4H_{10} > B_2H_6 > B_{10}H_{14}$ NaCl is crystallised by slow evaporation of its aqueous solution at room temperature. The correct statement 27. is (a) The crystals will be non-stoichiometric (b) The crystals should have Frenkel defects (c) The percentage of defects in the crystals will depend on the concentration of the solution and its rate of evaporation (d) The nature of defects will depend upon the concentration of the solution and its rate of evaporation CaTiO<sub>3</sub> has a perovskite crystal structure. The coordination number of titanium in CaTiO<sub>3</sub> is : 28. (a) 9 (b) 6(c) 3(d) 12 If CIF<sub>3</sub> were to be stereochemically rigid, its <sup>19</sup>F NMR spectrum (I for <sup>19</sup>F =  $\frac{1}{2}$ ) would be (assume that Cl is 29. not NMR active) (a) a doublet and a triplet (b) a singlet (c) a doublet and a singlet (d) two singlets. The point group of NSF<sub>3</sub> is: 30. (b)  $C_{3h}$ (a)  $D_{3d}$ (c)  $D_{3h}$ (d)  $C_{3v}$ 



31.	When NiO is heated with a small amount of $Li_2O$ in air at 1200°C, a non-stoichiometric compound						
	$Li_x Ni_{(1-x)}O$ is formed. This compound is						
	(a) an n-type semiconductor containing only $Ni^{1+}$						
	(b) an n-type semiconductor containing $Ni^{1+}$ and $Ni^{2+}$						
	(c) a p-type semiconductor containing $Ni^{2+}$ and $Ni^{3+}$						
	(d) a p-type semiconductor containing only $Ni^{3+}$						
32.	White phosphorus, P <sub>4</sub> , belongs to the (a) closo system (b) nodo system	(c) arachno system (d) hypho system					
33.	Among the compounds $Fe_3O_4$ , $NiFe_2O_4$ and	Mn <sub>3</sub> O <sub>4</sub>					
	(a) NiFe <sub>2</sub> O <sub>4</sub> and Mn <sub>3</sub> O <sub>4</sub> are normal spinels	(b) $\text{Fe}_3\text{O}_4$ and $\text{Mn}_3\text{O}_4$ are normal spinels					
	(c) $\text{Fe}_3\text{O}_4$ and $\text{Mn}_3\text{O}_4$ are inverse spinels	(d) $\text{Fe}_3\text{O}_4$ and $\text{NiFe}_2\text{O}_4$ are inverse spinels					
34.	The number of M-M bonds in Ir $(CO)$ are						
	(a) four (b) six $(a) = \frac{1}{2} (a) + \frac{1}{$	(c) eight (d) zero					
35.	Schrock carbenes are (a) Triplets and nucleophilic (c) Singlets and nucleophilic	<ul><li>(b) Triplets and electrophilic</li><li>(d) Singlets and electrophilic.</li></ul>					
36.	The INCORRECT statement about linear dimethylpolysiloxane, $[(CH_2)_2SiO]_1$ is						
	(a) it is extremely hydrophilic						
	(b) it is prepared by a KOH catalysed ring-opening reaction of $[Me_2SiO]_4$						
	<ul><li>(c) it has a very low glass transition temperature</li><li>(d) it can be reinforced to give silicon elastomers</li></ul>						
37.	Match the entries a-d with their corresponding	structures P-S					
	(A) bridged system						
	(B) atropisometric system	(Q)					
	(C) spiro system	(R) Me Me Me MeO					



(D) Fused system



(a) A-S, B-R, C-Q, D-P (c) A-Q B-P, C-S, D-R (b) A-P, B-S, C-Q, D-R (d) A-S, B-R, C-P, D-Q

38. The reaction between X and Y to give Z proceeds via



- (a)  $4\pi-$  conrotatory opening of X followed by endo Diels-Alder cycloaddition.
- (b)  $4\pi$  distortary opening of X followed by endo Diels-Alder cycloaddition.
- (c)  $4\pi$  conrotatory opening of X followed by exo Diels-Alder cycloaddition
- (d)  $4\pi$ -disrotatory opening of X followed by exo Diels -Alder cycloaddition.
- 39. The Major products  $P_1$  and  $P_2$ , respectively, in the following reaction sequenc are





40. The products Y and Z are formed, respectively, from X via



- (a) hu. conrotatory opening and  $\Delta$ , disrotatory opening.
- (b) hu, disrotatory opening and  $\Delta$ , controtatory opening.
- (c)  $\Delta$ , conrotatory opening and hu, disrotatory opening.
- (d)  $\Delta$ , disrotatory opening and hu, conrotatory opening.
- 41. o-Bromophenol is readily prepared from phenol using the following conditions
  - (a) (i)  $(CH_3CO)_2O$ ; (ii)  $Br_2$ ; (iii)  $HCl-H_2O$ ,  $\Delta$ (b) (i)  $H_2SO_4$ , 100°C (ii)  $Br_2$  (iii)  $H_2O^+$ , 100°C
  - (c) N-Bromosuccinimide, dibenzoyl peroxide,  $CCl_4$ ,  $\Delta$

(d) 
$$\operatorname{Br}_2 / \operatorname{FeBr}_3$$

42. The major product of the following reaction is



- 43. The photochemical reaction of 2-methylpropane with  $F_2$  gives 2-fluoro-2-methylpropane and 1-fluoro-2methylpropane in 14:86 ratio. The corresponding ratio of the bromo products in the above reaction using  $Br_2$  is most likely to be (a) 14:86 (b) 50:50 (c) 1:9 (d) 99:1
- 44. The major product P of the following reactions is











45. The reagent X in the following reaction is



46. The major product of the following reactions is



48. In the following compound, the hydroxy group that is most readily methylated with CH<sub>2</sub>N<sub>2</sub> is:





49. The most appropriate sequence of reactions for carrying out the following transformations.



- (a) (i)  $O_3/H_2O_2$ ; (ii) excess SOCl<sub>2</sub>/pyridine; (iii) excess NH<sub>3</sub>; (iv) LiAlH<sub>4</sub> (b) (i)  $O_3/Me_2S$ ; (ii) excess SOCl<sub>2</sub>/pyridine; (iii) LiAlH<sub>4</sub>; (iv) excess NH<sub>3</sub> (c) (i)  $O_3/H_2O_2$ ; (ii) excess SOCl<sub>2</sub>/pyridine; (iii) LiAlH<sub>4</sub>; (iv) excess NH<sub>3</sub>
- (d) (i)  $O_3^{\prime}/Me_2S$ ; (ii) excess SOCl<sub>2</sub>/pyridine; (iii) excess NH<sub>3</sub>; (iv) LiAlH<sub>4</sub>
- 50. The number of optically active stereoisomers possible for 1,3-cyclohexanediol in its chair conformation is (a) 4 (b) 3 (c) 2 (d) 1
- 51. The major product of the following reactions is



2225 (s); 1680(s).



The correct assignment of the absorption bands is:

- (a)  $\overline{v}_{(OH)} = 3300 3500; \overline{v}_{(CH)} = 3000; \overline{v}_{(CN)} = 2225; \overline{v}_{(CO)} = 1680$
- (b)  $\overline{v}_{(OH)} = 3000; \overline{v}_{(CH)} = 3300 3500; \overline{v}_{(CN)} = 2225; \overline{v}_{(CO)} = 1680$
- (c)  $\overline{v}_{(OH)} = 3300 3500; \overline{v}_{(CH)} = 3000; \overline{v}_{(CN)} = 1680; \overline{v}_{(CO)} = 2225$
- (d)  $\overline{v}_{(OH)} = 3000; \overline{v}_{(CH)} = 3300 3500; \overline{v}_{(CN)} = 1680; \overline{v}_{(CO)} = 2225$



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54.	The Td point group has 24 elements and 5 classes. Given that it has two 3-dimensional irreducible represen- tation, the number of one dimensional irreducible representation is: (a) 1 (b) 2 (c) 0 (d) 3								
55.	The total number of w magnetic field is; (a) 1	ays in which two nonid	entical spin- <sup>1</sup> / <sub>2</sub> particles	can be oriented relative to a constant					
56.	Approximately one hydroximately one hydroximate	drogen atom per cubic n $(10^{-10})$ the mean free p (b) $10^{19}$	meter is present in interst bath (m) approximately i (c) 10 <sup>24</sup>	ellar space. Assuming that the H- s (d) 10 <sup>14</sup> .					
57.	The wavefunction of a electrons of the bond v	diatomic molecule has t vill be found on the same	the form $\psi = 0.89 \varphi_{conva}$ e atom in 100 inspection	$h_{lent} + 0.45 \phi_{ionic}$ . The chance that both s of the molecule approximately is					
	(a) 79	(b) 20	(c) 45	(d) 60					
58.	For the reaction given value of $k_1(s^{-1})$ is	below, the relaxation tin	ne is 10 <sup>-6</sup> s. Givem that 1	0% of A remains at equilibrium, the					
$A \xrightarrow{k_1} B$									
	(a) $9 \times 10^5$	(b) 10 <sup>-5</sup>	(c) $10^5$	(d) $9 \times 10^{-5}$					
59.	The minimum number (a) 1	of electrons needed to fo (b) 2	orm a chemical bond bet (c) 3	ween two atoms is (d) 4					
60.	The ground state electrical $(a) - 1.0$	ronic energy (Hartree) of (b) –0.5	f a helium atom, neglecti (c) -2.0	ng the inter-electron repulsion, is (d) –4.0					
61.	A particle is confined to a one-dimensional box of length 1 mm. If the length is changed by $10^9$ m, the % change in the ground state energy is								
	(a) $2 \times 10^{-4}$	(b) $2 \times 10^{-7}$	(c) $2 \times 10^{-2}$	(d) 0					
62.	A certain molecule can be treated as having only a doubly degenerate state lying at $360 \text{ cm}^{-1}$ above the non- degenerate ground state. The approximate temperature (K) at which 15% of the molecules will be in the upper state is (a) $500$ (b) $150$ (c) $200$ (d) $300$								
63.	A box of volume V co occupying one half of t	A box of volume V contains one mole of an ideal gas. The probability that all N particles will be four occupying one half of the volume leaving the other half empty is							
	(a) 1/2	(b) 2/N	(c) $(1/2)^{N}$	(d) $(1/2)^{6N}$					
64.	According to the Debye-Huckel limiting law, the mean activity coefficient of $5 \times 10^{-4}$ mol kg <sup>-1</sup> aqueous solution of CaCl <sub>2</sub> at 25°C is (the Debye-Huckel constant 'A' can be taken to be 0.509) (a) 0.63 (b) 0.72 (c) 0.80 (d) 0.91								
65.	The operation of the co	ommutator $[x, d/dx]$ on	a function $f(x)$ is equal to	0					
	(a) 0	(b) f(x)	(c)-f(x)	(d) $x df/dx$					
66.	If a gas obeys the equa	tion of state $P(V-nb)$	$=$ nRT, the ratio $\frac{(C_{I})}{(C_{P})}$	$\frac{(-C_v)}{(-C_v)_{ideal}}$ is:					
	(a) >1	(b) <1	(c) 1	(d) (1–b)					



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67.	Physisorbed particles undergo desorption at 27 °C with an activation energy of 16.628 kJ mol <sup>-1</sup> . Assuming first-order process and a frequency factor of 10 <sup>12</sup> Hz, the average residence time (in seconds) of the particles on the surface is								
	(a) $8 \times 10^{-10}$	) (1	b) $8 \times 10^{-11}$		(c) $2 \times 10^{-9}$		(d) $1 \times 10^{-12}$		
68.	The rotational constants for CO in the ground and the first excited vibrational states are 1.9 and 1.6 cm respectively. The % change in the internuclear distance due to vibrational excitation is								
	(a) 9	(	b) 30		(c) 16		(d) 0		
69.	The mechanism of enzyme (E) catalysed reaction of a substrate (S) to yield product (P) is:								
	If a small am	$E + S \xrightarrow{k_1}_{k_{-1}}$	$ \geq [ES] \frac{k_2}{k_{-2}} $	E + P;	$\frac{-d[S]}{dt} =$	$= \frac{k_1 k_2}{k_1 [S]_0}$ the react	$\frac{[S]_{0}+k_{2}k_{-2}[P]}{k_{-2}[P]+k_{-1}+k_{2}}[E]$ ion will be observed to	[] <sub>0</sub>	
	(a) $(k_1 + k_2)$	$) >> k_1[S]$		, ,	(b) $(k_1 + k_2)$	<< k.[S]			
	(c) $(k_1 + k_2)$	$(k_{1}) >> k_{1}(s)$			(d) $k < k$	1 L <sup></sup> J(	)		
	$(\mathbf{c})$ $(\mathbf{k}_1 + \mathbf{k}_2)$	2) > × • • • • • • • • • •			$(\mathbf{u}) \mathbf{k}_2 < < \mathbf{k}_1$				
70.	The lowest energy state of the $(1s)^2 (2s)^1 (3s)^1$ configuration of Be is:								
	(a) ${}^{1}S_{0}$	(	b) ${}^{1}D_{2}$		(c) ${}^{3}S_{1}$		(d) ${}^{3}P_{1}$		
	Common D	Data for Q. 7	1 , Q.72 and	Q.73					
	An electron planes have	An electron accelerated through a potential difference of $\varphi$ volts impinges on a nickel surface, whose (100) planes have a spacing d = 351.5×10 <sup>-12</sup> m (351.5 pm)							
71.	The de-Brog	glie waveleng	gth of the elect	ron is – F	$\frac{\lambda}{m} = \left(\frac{a}{\varphi}\right)^{1/2}$ . The second s	he value o	of 'a' in volts is		
	(a) 1.5×10 <sup>-</sup>	-18 (1	b) 1.5×10 <sup>6</sup>		(c) $6.63 \times 10^{-5}$	5	(d) $2.5 \times 10^{18}$		
72.	The condition	on for observi	ng diffraction	from th	e nickel surface	is			
	(a) $\lambda >> 2d$	(	b) $\lambda \leq 2d$		(c) $\lambda \leq ad$		(d) $\lambda \ge ad$		
73.	The minimu (a) 3000	m value of φ	(V) for the el b) 300	ectron t	o diffract from ( (c) 30	the (100)	planes is (d) 3		

## Common Data for Q. 74 and Q.75

An iron complex  $[FeL_6]^{2+}$  (L = neutral monodentate ligand) catalyses the oxidation of  $(CH_3)_2 S$  by perbenzoic acid.

- 74. The formation of the organic product in the above reaction can be monitored by
   (a) gas chromatography
   (b) cyclic voltammetry
   (c) electron spin resonance
   (d) fluorescence spectroscopy
- 75. The oxidation state of the metal ion in the catalyst can be deducted by
  (a) Atomic absorption spectroscopy
  (b) Mossbauer spectroscopy
  (c) HPLC
  (d) Gas Chromatography



# Linked Answer type Q. 76 and Q. 77:

In the reaction,  $(PPh_3)_3$  RhCl $\longrightarrow$ X + Y

76. Compound X is

- $Rh(PPh_3)_3$  Cl reacts very fast with a gaseous mixture of  $H_2$  and  $C_2H_4$  to immediately give Z. The struc-77. ture of Z is

(a) 
$$H_3C - CH_3$$
 (b)  $\begin{array}{c} Ph_3P \\ Rh \end{array}$  (c)  $\left(PPh_3\right)_2 RhCl\left(\eta^2 - C_2H_4\right)$  (d)  $\begin{array}{c} Ph_3P \\ Ph_3P \\ H \end{array}$ 

# Linked Answer Type for Q. 78 and Q. 79:

The reaction of PCl, with methanol in the presence of triethylamine affords compound X. EI mass spectrum of X shows a parent ion peak at m/z = 124. Microanalysis of X shows that it contains C, H, O and P. The <sup>1</sup>H NMR spectrum of X shows a doublet at 4.0 ppm The separation between the two lines of the doublet is

approximately 15 Hz (I for <sup>1</sup>H and <sup>31</sup>P= $\frac{1}{2}$ ).

- 78. Compound X is:

  - (a)  $(CH_{3}O)_{3}P$ (b)  $(CH_{3}O)_{2}P(O)$ (c)  $(CH_{3}O)_{2}P(O)(OH)$ (d)  $(CH_{3}O)_{2}P(O)$
- 79. Upon heating, compound X is converted to Y, which has the same molecular formula as that of X. The <sup>1</sup>H NMR spectrum of Y shows two doublets centered at 3.0 ppm (separation of two lines ~ 20 Hz) and 4.0 ppm (separation of two lines ~ 15 Hz) respectively.

Compound Y is:

(a) 
$$(CH_3O)_2 P(O)(OH)$$
  
(b)  $(CH_3O)_3 P(O)$   
(c)  $(CH_3O)_2 (CH_3)P(O)$   
(d)  $(CH_3O)_2 (CH_3)P(OH)$ 

## Linked Answer Type Q.80 and Q. 81.

For butyrophenone ( $PhCOCH_2CH_2CH_3$ ),

The most probable fragmentation observed in the electron impact ionization (EI) mass spectrometry is: 80.





81. Photoirradiation leads to the following set of products:



#### Linked Answer Q. 82 and Q. 83

In the following reaction,



82. The reactive intermediate I and the product P are



83. The product P shows 'm' and 'n' number of signals in <sup>1</sup>H and <sup>13</sup>C NMR spectra, respectively. The values of 'm' and 'n' are

(a) m = 3 and n = 2 (b) m = 2 and n = 3 (c) m = 2 and n = 2 (d) m = 4 and n = 3

#### Linked Answer Type Q.84 and Q. 85:

The infrared spectrum of a diatomic molecule exhibits transitions at 2144, 4262 and 6354  $\text{cm}^{-1}$  corresponding to excitations from the ground state to the first, second and, third vibration states respectively.

- 84. The fundamental transition  $(cm^{-1})$  of the diatomic molecule is at: (a) 2157 (b) 2170 (c) 2183 (d) 2196
- 85. The anharmonicity constant  $(cm^{-1})$  of the diatomic molecule is: (a) 0.018 (b) 0.012 (c) 0.006 (d) 0.003

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

