GATE – 2003 – Chemistry

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Q.1 – Q.30 Multiple Choice Question (MCQ), carry ONE mark each (for each wrong answer: – 1/3).

1. **Adiabatic reversible expansion of a monoatomic gas (M) and a diatomic gas (D) at an initial temperature T_i , has been carried out independently from initial volume V_1 to final volume V_2. The final temperature attained will be (T_M for monoatomic and T_D for diatomic)**

   (a) $T_M = T_D > T_i$ (b) $T_M < T_D < T_i$
   (c) $T_M > T_D > T_i$ (d) $T_D < T_M < T_i$

2. **The rate of evaporation of a liquid is always faster at a higher temperature because**

   (a) The enthalpy of vaporisation is always endothermic
   (b) The enthalpy of vaporisation is always exothermic
   (c) The enthalpy of vaporisation is zero
   (d) The internal pressure of the liquid is less than that of the gas

3. **The internal pressure of a Vander Waals gas is:**

   (a) Independent of the molar volume
   (b) Inversely proportional to the molar volume
   (c) Inversely proportional to square of the molar volume
   (d) Directly proportional to the molar volume.

4. **In a consecutive first order reaction, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ (where k_1 and k_2 are the respective rate constants) species-B has transient existence. Therefore,**

   (a) $k_1 \approx k_2$ (b) $k_1 = 2k_2$ (c) $k_1 \gg k_2$ (d) $k_1 \ll k_2$

5. **For a free radical polymerisation reaction, the kinetic chain length 'γ', is defined as the ratio**

   (a) $\frac{\text{propagation rate}}{\text{initiation rate}}$ (b) $\frac{\text{initiation rate}}{\text{propagation rate}}$ (c) $\frac{\text{initiation rate}}{\text{termination rate}}$ (d) $\frac{\text{propagation rate}}{\text{termination rate}}$

6. **The reaction that proceeds autocatalytically is**

   (a) an oscillatory reaction (b) hydrolysis of an ester by a mineral acid
   (c) synthesis of ammonia (Haber's process) (d) Ziegler-Natta polymerization

7. **An example for an ion-selective electrode is**

   (a) quinhydrone electrode (b) hydrogen electrode
   (c) glass electrode (d) dropping mercury electrode

8. **The following equilibrium is established for an aqueous acetic acid solution**

$$CH_3COOH \leftrightarrow CH_3COO^- + H^+$$

Upon addition of 1.0 g of solid sodium chloride to 20 ml of 1N solution of acetic acid,

(a) the pH of the solution does not change (b) the pH of the solution decreases

(c) the pH of the solution increases (d) the pH of the solution is 7

9. **According to MO theory, for the species 'C_2'**

(a) bond order is zero and it is paramagnetic (b) bond order is zero and it is diamagnetic

(c) bond order is two and it is paramagnetic (d) bond order is two and it is diamagnetic

10. **The sensitivity of a 600 MHz NMR spectrometer is more than that of a 60 MHz spectrometer because**

(a) Population of spin states is directly proportional to the applied magnetic field

(b) Population of spin states is inversely proportional to the applied magnetic field

(c) According to the Boltzmann distribution law, the excess population in the lower spin state increases with increasing applied magnetic field

(d) The spectral scan width is more for a 600 MHz spectrum compared to a 60 MHz spectrum

11. **The magnetic moment of an octahedral Co (II) complex is 4.0 μ_β. The electronic configuration of the complex is:**

(a) $t_{2g}^5e_g^2$ (b) $t_{2g}^6e_g^1$ (c) $t_{2g}^3e_g^4$ (d) $t_{2g}^4e_g^3$

12. **The square planar complex, $[IrCl(PPh_3)_3]$ undergoes oxidative addition of Cl_2 to give two products, which are**

(a) fac and mer isomers (b) cis and trans isomers

(c) linkage isomers (d) enantiomers

13. **The ligand field bands of lanthanide complexes are generally sharper than those of transition metal complexes because**

(a) transitions are allowed for lanthanide complexes

(b) intensity of the bands are higher for lanthanide complexes

(c) f–orbitals have higher energy than d–orbitals

(d) f–orbitals, compared to d–orbitals, interact less effectively with ligands

14. **Nature has chosen Zn(II) ion at the active site of many hydrolytic enzymes because**

(a) Zn (II) is poor Lewis acid

(b) Zn (II) does not have chemically accessible redox states

(c) Zn (II) forms both four and higher coordination complexes

(d) Zn (II) forms weak complexes with oxygen donor ligands.

15. **$BH_3.CO$ is more stable than $BF_3.CO$ because**

(a) CO is a soft base and BH_3 and BF_3 are soft and hard acids respectively

(b) CO is a hard base and BH_3 and BF_3 are hard and soft acids respectively

(c) CO is a soft base and BH_3 and BF_3 are hard and soft acids respectively

(d) CO is a soft acid and BH_3 and BF_3 are soft and hard bases respectively

16. **Using chlorobenzene as solvent, the reagents needed for an efficient synthesis of borazine are**

(a) NH_4Cl and BCl_3 (b) NH_4Cl, BCl_3 and $NaBH_4$

(c) NH_4Cl and $NaBH_4$ (d) NH_3 and BCl_3

17. **The crystal systems having the highest and the lowest symmetries respectively, are**

(a) cubic and rhombohedral (b) cubic and triclinic

(c) rhombohedral and monoclinic (d) cubic and monoclinic

18. **The dark purple colour of $KMnO_4$ is due to**

(a) d-d transition (b) ligand field transition

(c) charge transfer transition (d) $\sigma \rightarrow \pi^*$ transition

19. **The metallic character of beryllium is due to**

(a) partially filled 2s band (b) completely filled 2s band

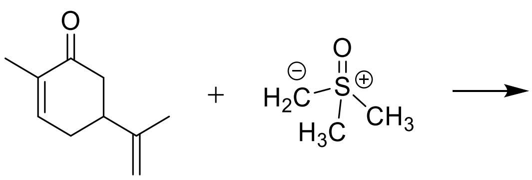
(c) overlap of 2s and 2p bands (d) empty 2p band

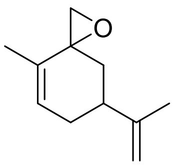
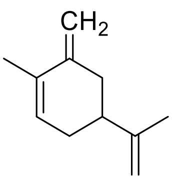
20. **The values of CO stretching frequencies of I - III follow the trend,**

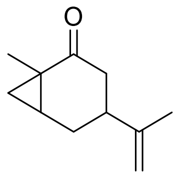
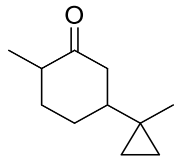
I	II	III
$[Ni(CO)_4]$	$[Ni(CO)_3(PMe_3)]$	$[Ni(CO)_2(PMe_3)_2]$

(a) I > II > III (b) III > II > I (c) I > III > II (d) II > III > I

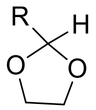
21. **The products formed in the following reaction are**

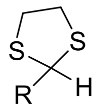


(a)  + DMSO (b)  + $CH_3SO_2CH_3$

(c)  + DMSO (d)  + DMSO

22. **The acyl anion equivalents, among the following compounds (P–S), are**


P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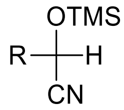
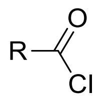

R


S

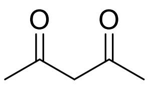
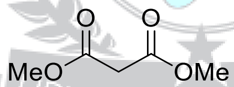
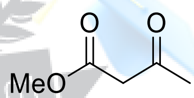
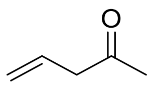
(a) P and Q (b) Q and R (c) P and S (d) Q and S

23. **^{1}H–NMR spectrum of a compound with molecular formula $C_4H_9NO_2$ shows δ 5.30 (broad, 1H), 4.10 (q, 2H), 2.80 (d, 3H), 1.20 (t, 3H) ppm. The structures of the compound that is consistent with the above data is:**

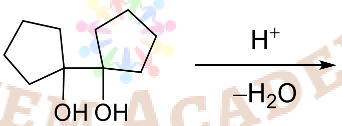
(a) $CH_3NHCOOCH_2CH_3$ (b) $CH_3CH_2NHCOOCH_3$

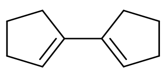
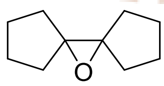
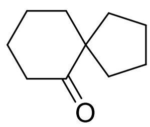
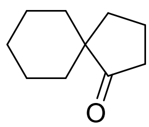
(c) $CH_3OCH_2CONHCH_3$ (d) $CH_3CH_2OCH_2CONH_2$

24. **Among the following compounds, the one that undergoes deprotonation most readily in the presence of a base, to form a carbanion is:**

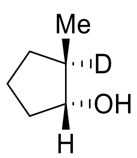
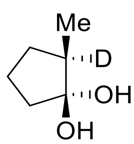
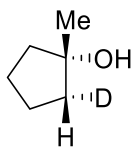
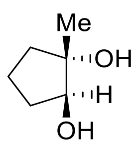
(a)  (b)  (c)  (d) 

25. **The structure of the product formed in the reaction given below is**

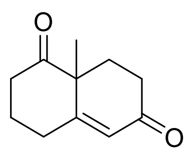


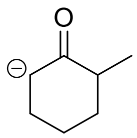
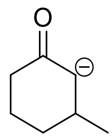
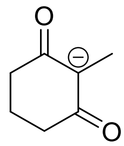
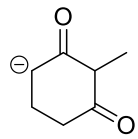
(a)  (b)  (c)  (d) 

26. **Hydroboration of 1-methylcyclopentene using B_2D_6, followed by treatment will alkaline hydrogen peroxide, gives**

(a)  (b)  (c)  (d) 

27. **The enolate ion that reacts with 3-buten-2-one to form (Y) is**

Y = 

(a)  (b)  (c)  (d) 

28. **Electrocyclization of E,Z,E-octa-2,4,6-triene under photochemical condition,**

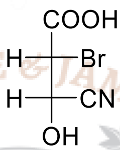
(a) trans-5,6-dimethylcyclohexa-1,3-diene

(b) cis-5,6-dimethylcyclohexa-1,3-diene

(c) a mixture of trans and cis-5,6-dimethylcyclohexa-1,3-diene

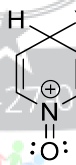
(d) 1,2-dimethylcyclohexa-1,3-diene

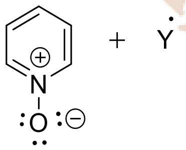
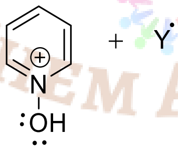
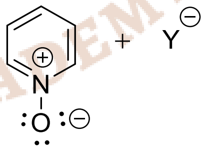
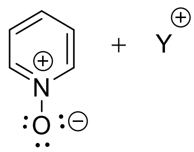
29. **The absolute configurations of the two chiral centers in the following molecule are**



(a) 2R, 3S (b) 2R, 3R (c) 2S, 3S (d) 2S, 3R

30. **A pyridine derivative-P reacts with (Y). (Y) can be a free radical, cation or anion. The structure of intermediate-Q formed in the reaction is given below. (P) and (Y) respectively, are**



(a)  (b)  (c)  (d) 

Q.31 – Q.90 Multiple Choice Question (MCQ), carry TWO mark each (for each wrong answer: – 2/3).

31.

	Column-I		Column-II
P.	$ZnSO_{4(aq)} + K_4[Fe(CN)_6]_{(aq)} \longrightarrow$ **Products**	**(i)**	**Enzymatic reaction**
Q.	$Zn_{(s)} + CuSO_{4(aq)} \longrightarrow$ **Products**	**(ii)**	**Chain reaction**
R.	$H_2 + Cl_2 \xrightarrow{\Delta}$ **Products**	**(iii)**	**Redox reaction**
S.	**Fischer-Tropsch synthesis of hydrocarbons**	**(iv)**	**Precipitation reaction**
		(v)	**Surface reaction**
		(vi)	**Hydrolysis reaction**

	(P)	(Q)	(R)	(S)		(P)	(Q)	(R)	(S)
(a)	(ii)	(iv)	(v)	(vi)	(b)	(i)	(iii)	(ii)	(iv)
(c)	(iv)	(iii)	(ii)	(v)	(d)	(i)	(vi)	(ii)	(v)

32.

	Column-I		Column-II
P.	Supporting electrolyte	(i)	Overpotential
Q.	$Zn(Hg)_{Q=1} \mid ZnCl_{2(aq)} \mid Zn(Hg)_{Q=2}$	(ii)	Residual current
R.	Inversion temperature	(iii)	Electrolyte concentration cell
S.	Entropy of vapourisation	(iv)	Electrode concentration cell
		(v)	Trouton's rule
		(vi)	Joule-Thomson expansion

	(P)	(Q)	(R)	(S)		(P)	(Q)	(R)	(S)
(a)	(ii)	(iv)	(vi)	(v)	(b)	(ii)	(iv)	(iii)	(vi)
(c)	(i)	(iv)	(vi)	(iii)	(d)	(i)	(iii)	(vi)	(vi)

33.

	Column-I		Column-II
P.	Kroenecker delta	(i)	Electronic transition
Q.	Franck-Condon principle	(ii)	Isothermal process
R.	Kirchoff's equation	(iii)	Orthonormal set
S.	Glass transition temperature	(iv)	Reaction enthalpy
		(v)	Turnover number
		(vi)	Polymer

	(P)	(Q)	(R)	(S)		(P)	(Q)	(R)	(S)
(a)	(i)	(iii)	(v)	(vi)	(b)	(iii)	(i)	(iv)	(vi)
(c)	(i)	(iii)	(v)	(ii)	(d)	(iii)	(i)	(vi)	(ii)

34.

	Enzyme		Metal at the Active site
P.	Liver alcohol dehydrogenase	(i)	Cu
Q.	Cytochrome C oxidase	(ii)	Fe and Cu
R.	Hemocyanin	(iii)	Zn

S.	**Myoglobin**	**(iv)**	**Fe**
		(v)	**Mo**
		(vi)	**Cu and Zn**

	(P)		(Q)		(R)		(S)
(a)	(vi)	;	(ii)	;	(i)	;	(iv)
(b)	(iii)	;	(ii)	;	(i)	;	(vi)
(c)	(iii)	;	(ii)	;	(iv)	;	(v)
(d)	(v)	;	(vi)	;	(i)	;	(ii)

35.

	Column-I		**Column-II**
P.	$[(PPh_3)_3RhCl]$	**(i)**	**Friedel-Crafts catalyst**
Q.	$[Rh(CO)_2I_2]$	**(ii)**	**Hydroformylation of alkenes**
R.	$[PdCl_4]^{2-}$	**(iii)**	**Hydrogenation process**
S.	$[HCo(CO)_4]$	**(iv)**	**The Wacker process**
		(v)	**Monsanto acetic acid synthesis**
		(vi)	**Reppe catalyst**

	(P)		(Q)		(R)		(S)
(a)	(iii)	;	(v)	;	(iv)	;	(ii)
(b)	(iv)	;	(i)	;	(vi)	;	(ii)
(c)	(v)	;	(iv)	;	(ii)	;	(i)
(d)	(iii)	;	(ii)	;	(i)	;	(v)

36.

	List-I		**List-II**
P.	$[Cr(H_2O)_6]^{3+}$	**(i)**	C_{3V}
Q.	$Fe_2(CO)_9$	**(ii)**	D_{3h}
R.	**Eclipsed ferrocene**	**(iii)**	O_h
S.	**Staggered ferrocene**	**(iv)**	D_5
T.	**Skew ferrocene**	**(v)**	D_{5h}
		(vi)	D_{5d}

	(P)		(Q)		(R)		(S)		(T)
(a)	(iii)	;	(ii)	;	(v)	;	(vi)	;	(iv)
(b)	(ii)	;	(iv)	;	(i)	;	(iii)	;	(v)
(c)	(vi)	;	(ii)	;	(v)	;	(i)	;	(iv)
(d)	(iii)	;	(vi)	;	(iv)	;	(v)	;	(i)

37. **For the reaction, $Hg_2Cl_{2(s)} + H_{2(g)} \longrightarrow 2Hg_{(l)} + 2HCl_{(aq)}$, the correct representation of the cell and the thermodynamic properties ΔG, ΔH and ΔS at 298 K respectively, are (given : $E_{298} = 0.2684$ V and temperature coefficient $= -3 \times 10^{-4}$ V K^{-1})**

(a) $Pt|H_2(g, 1atm)|HCl(aq)|Hg_2Cl_2(s)|Hg(\ell)$

$\Delta G = -51.8$ kJ mol^{-1}, $\Delta H = -69$ kJ mol^{-1}, $\Delta S = -58$ J K^{-1} mol^{-1}

(b) $Pt|H_2(g, 1atm)|HCl(aq)|Hg_2Cl_2(s)|Hg(\ell)$

$\Delta G = -25.9$ kJ mol^{-1}, $\Delta H = -34.5$ kJ mol^{-1}, $\Delta S = -29$ J K^{-1} mol^{-1}

(c) $Hg(\ell)\,|\,Hg_2Cl_2(s)|HCl(aq)|H_2(g, 1atm)|Pt$

$\Delta G = -51.8$ kJ mol^{-1}, $\Delta H = -69$ kJ mol^{-1}, $\Delta S = 58$ JK^{-1} mol^{-1}

(d) $Hg(\ell)\,|\,Hg_2Cl_2(s)|HCl(aq)|H_2(g, 1atm)|Pt$

$\Delta G = 51.8$ kJ mol^{-1}, $\Delta H = 69$ kJ mol^{-1}, $\Delta S = 58$ JK^{-1} mol^{-1}

38. **Among CH_3Cl, CH_2Cl_2, $CHCl_3$, CH_3Br and CH_3I in the gaseous state, the one having highest molar entropy value at room temperature is**

(a) $CHCl_3$ (b) CH_3Cl (c) CH_3Br (d) CH_3I

39. **Two solid components form a congruent melting solid in situ. The phase diagram of the system has**

(a) five invariant points, two equilibria involving three phases and two equilibria involving two phases

(b) three invariant points, two equilibria involving three phases and three equilibria involving two phases

(c) five invariant points, two equilibria involving three phases and three equilibria involving two phases

(d) three invariant points, three equilibria involving three phases and two equilibria involving two phases

40. **H_2 and Br_2 react to give HBr by the following steps**

$$Br_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br + M \quad \text{(fast)} \quad (K = k_1/k_{-1})$$

$$Br + H_2 \xrightarrow{k_2} HBr + H \text{ (slow)}$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br \text{ (fast)}$$

The probable rate law for the above sequence is:

(a) rate $= k_2[H_2][Br_2]^{1/2}$ (b) rate $= k_2[H_2][Br_2]$

(c) rate $= k_2(k)^{1/2}[H_2][Br_2]^{1/2}$ (d) rate $= k_2(k)^{1/2}[H_2][Br_2]^{1/2}$

Common data for Q. 41 and Q. 42.

For the opposing reaction, $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$

The forward reaction has values $E_a = 100\ kJ\ mol^{-1}$ and $A = 1.0 \times 10^{10}\ M^{-1}s^{-1}$. The equilibrium concentration of A, B, C and D are 1.0 M, 2.0 M, 5.0 M and 4.0 M respectively, at 700 K.

41. **The values of k_1 and k_{-1}, respectively, at this temperature are**

(a) $20\ M^{-1}s^{-1}$ and $2.0\ M^{-1}s^{-1}$ (b) $345\ M^{-1}s^{-1}$ and $34.5\ M^{-1}s^{-1}$

(c) $34.5\ M^{-1}s^{-1}$ and $3.45\ M^{-1}s^{-1}$ (d) $200\ M^{-1}s^{-1}$ and $20\ M^{-1}s^{-1}$

42. **The rate constant (k_1) for the forward reaction at 1000 K is:**

(a) $5.98 \times 10^4\ M^{-1}min^{-1}$ (b) $5.98 \times 10^2\ M^{-1}s^{-1}$

(c) $1.00 \times 10^3\ M^{-1}s^{-1}$ (d) $5.98 \times 10^4\ M^{-1}s^{-1}$

43. **For the reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, Compute the entropy change (in J/K/mol) for the process and comment on the sign of the property**

Species	$NH_{3(g)}$	$N_{2(g)}$	$H_{2(g)}$
S^0 (J/K/mol)	192.3	191.5	130.6

(a) $\Delta S^0 = -37.65$ J/K/mol; negative sign indicates that there is a decrease in the gaseous species during the reaction

(b) $\Delta S^0 = -198.7$ J/K/mol; negative sign indicates that there is a decrease in the gaseous species during the reaction.

(c) $\Delta S^0 = -31.25$ J/K/mol; negative sign indicates that there is a decrease in the gaseous species during the reaction.

(d) $\Delta S^0 = +31.25$ J/K/mol; the positive sign indicates that the reaction is spontaneous.

44. **The translational partition function of a hydrogen molecule confined in a 100 mL flask at 298 K (Mol. wt. of hydrogen = 2.016) is:**

(a) 2.8×10^{20} (b) 2.8×10^{25} (c) 2.8×10^{26} (d) 2.8×10^{27}

45. **ΔH^0_{298} for the reaction, $C_2H_4O_{(g)} \longrightarrow CH_{4(g)} + CO_{(g)}$, is –16.0 kJ. From the given data, evaluate the temperature at which ΔH will be zero.**

Substance:	$C_2H_4O_{(g)}$	$CH_{4(g)}$	$CO_{(g)}$
C_P (J/K/mol)	50	36	30

(a) 1298 K (b) 1000 K (c) 1298 °C (d) 1100 °C

46. **At 273 K, N_2 is adsorbed on a mica surface. A plot of $1/V$ vs $1/P$ (V in m^3 and P in torr) gives a straight line with a slope equal to 2.0×10^{-5} torr m^{-3} and an intercept equivalent V_m equal to 4.0×10^{-8} m^3. The adsorption coefficient and the number of molecules of N_2 forming the mono layer, respectively, are**

(a) 1.25×10^{12} torr^{-1} and 1.075×10^{18} (b) 2.5×10^{12} torr^{-1} and 1.075×10^{18}

(c) 2.5×10^{12} torr^{-1} and 1.75×10^{18} (d) 1.25×10^{10} torr^{-1} and 1.075×10^{18}

47. **For the reaction, $2Cl_{(g)} \longrightarrow Cl_{2(g)}$; the thermodynamics properties:**

(a) ΔG, ΔH and ΔS are positive

(b) ΔG, ΔH and ΔS are negative

(c) ΔG and ΔH are negative and ΔS is positive

(d) ΔG is negative and ΔH and ΔS are positive

48. **The standard free energies of formation of $H_2S_{(g)}$ and $CdS_{(s)}$ at 100 ℃ are -49.0 kJ/mol and -127.2 kJ/mol, respectively. Use these data to predict whether $H_{2(g)}$ will reduce $CdS_{(s)}$ to metallic Cd at this temperature**

(a) $\Delta G = -78.2$ kJ/mol and H_2 reduces CdS

(b) $\Delta G = -39.1$ kJ/mol and H_2 reduces CdS

(c) $\Delta G = 0$ kJ/mol and the reaction is at equilibrium

(d) $\Delta G = +78.2$ kJ/mol and the reaction is not feasible

49. **From the data of two half-cell reactions:**

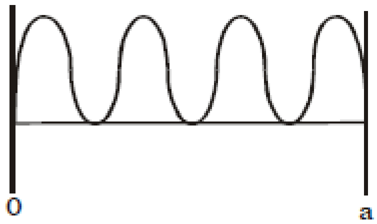
$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq) \qquad E^0 = +0.22\ V$$

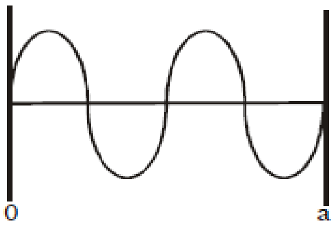
$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad E^0 = +0.80\ V$$

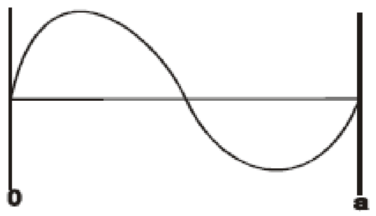
the solubility product of AgCl at 298 K, is calculated to be

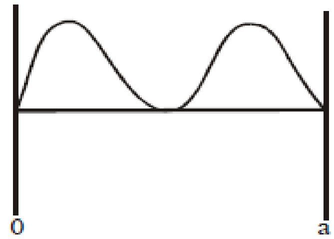
(a) 1.5×10^{-10} (b) 2.1×10^{-7} (c) 3.0×10^{-3} (d) 1.2×10^{-5}

50. **For the energy level $(2h^2/ma^2)$ the probability for a particle of mass 'm' over the length 'a' of a one-dimensional box is depicted by**

(a) 

(b) 

(c) 

(d) 

51. **Among the following complexes the 18-electron rule is not followed in**

I	II	III	IV
$[(C_6H_6)_2Cr]$	$[HMn(CO)_5]$	$[(CH_3CO)Rh(CO)I_3]^-$	$[CpFe(CO)_2(CH_3)]$

(a) III only (b) II and III (c) I and IV (d) II only

52. **The incorrect statement regarding the Fischer-type metal carbene complexes is that**

(a) carbene acts as a σ donor and π acceptor

(b) all atoms directly connected to carbene C atom are coplanar

(c) the bond between the metal and the carbene C atom has partial double bond character

(d) the carbene C atom is nucleophilic

53. **The xenon compounds that are iso-structural with IBr_2^- and BrO_3^- respectively are**

(a) linear XeF_2 and pyramidal XeO_3 (b) bent XeF_2 and pyramidal XeO_3

(c) bent XeF_2 and planar XeO_3 (d) linear XeF_2 and tetrahedral XeO_3

54. **The reagents needed for an efficient synthesis of borazine are**

(a) NH_4Cl and BCl_3 (b) NH_4Cl with $NaBH_4$ on Δ

(c) NH_3 and $NaBH_4$ (d) NH_3 and BCl_3

55. **The number of manganese ions in tetrahedral and octahedral sites, respectively in Mn_3O_4 are**

(a) one Mn^{2+} and two Mn^{3+} (b) one Mn^{3+} and two Mn^{2+}

(c) two Mn^{3+} and one Mn^{2+} (d) two Mn^{2+} and one Mn^{3+}

56. **Gold crystallizes in face-centered-cubic lattice. The atomic weight and density of gold are 196.97 and 19.4 g/cm^3 respectively. The length of the unit cell is**

(a) 2.563 Å (b) 3.230 Å (c) 4.070 Å (d) 8.140 Å

57. **Solid $Co_2(CO)_8$ shows infrared CO stretching bands at 1857, 1886, 2001, 2031, 2044, 2059, 2071 and 2112 cm^{-1}. When $Co_2(CO)_8$ is dissolved in hexane, the carbonyl bands at 1857 and 1886 cm^{-1} disappear. These changes in the infrared spectrum in hexane are due to.**

(a) Loss of terminal CO

(b) Structural change of $Co_2(CO)_8$ involving conversion of terminal CO to bridging CO

(c) Dissociation of $Co_2(CO)_8$ to $Co(CO)_4$

(d) Structural changes of $Co_2(CO)_8$, involving conversion of bridging CO to terminal CO

58. **Match the silicate minerals (column I) with their compositions (column II) and order of hardness (column III)**

	I		II		III
P	**talc**	**U**	**$KAl_3Si_3O_{10}(OH)_2$**	**X**	**high**
Q	**muscovite**	**V**	**$Mg_3Si_4O_{10}(OH)_2$**	**Y**	**low**
R	**margarite**	**W**	**$CaAl_4Si_2O_{10}(OH)_2$**	**Z**	**intermediate**

(a) P-V-Y ; Q-U-Z ; R-W-X
(b) P-U-X ; Q-V-Z ; R-W-Y
(c) P-W-X ; Q-V-Y ; R-U-Z
(d) P-V-Z ; Q-U-Y ; R-W-X

59. **The structure of $P_4N_4Cl_8$ is puckered whereas that of $P_4N_4F_8$ is planar because**

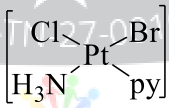
(a) F is more electronegative than Cl

(b) F is smaller in size than that of Cl

(c) F is more polarizable than Cl

(d) Extent of π –electron delocalization is more in $P_4N_4Cl_6$ than in $P_4N_4F_6$.

60. **The correct order of addition of NH_3, pyridine (py) and Br^- to $[PtCl_4]^{2-}$ to obtain**



is

(a) py, Br^- and NH_3
(b) Br^-, py and NH_3
(c) NH_3, py and Br^-
(d) NH_3, Br^- and py

61. **$[Ru(C_2H_5)Cl(PPh_3)_3]$ is stable only under a pressure of ethene because**

(a) it is a 16-electron complex

(b) it forms an 18-electron adduct with ethene

(c) one of the decomposition products is ethene

(d) it prevents α–elimination of ethene

62. **The ground state term symbols for p^3 and d^3 electronic configuration respectively, are**

(a) ^4S and ^4F
(b) ^4D and ^4F
(c) ^1D and ^4F
(d) ^4S and ^2G

63. **The "styx" code for diborane is**

(a) 2020
(b) 2200
(c) 2002
(d) 0220

64. $[CoCl(NH_3)_5]^{3+} + [Cr(H_2O)_6]^{2+} \longrightarrow [Co(H_2O)(NH_3)_5]^{2-} + [CrCl(H_2O)_5]^{3+}$

The correct statement regarding the above reaction is that

(a) it follows outer-sphere mechanism

(b) it follows inner-sphere mechanism with NH_3 acting as the bridging ligand

(c) it follows inner-sphere mechanism with Cl^- acting as the bridging ligand

(d) it is not an electron-transfer reaction

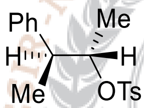
65. **The percentage transmittance of a transition metal complex at 360 nm and at 25 ℃ is 25 % for a 6×10^{-4} molL^{-1} solution in a 1 cm cell. The molar adsorption coefficient in the unit of L mol^{-1} cm^{-1} is:**

(a) $\sim 1.0 \times 10^{-3}$ (b) $\sim 1.0 \times 10^{3}$ (c) $\sim 2.0 \times 10^{3}$ (d) $\sim 1.0 \times 10^{4}$

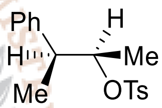
66. **The bond order of the metal-metal bonds in $[Re_2Cl_8]^{2-}$, $[Re_2Cl_6(P(C_2H_5)_3)_2]$ and $[Re_2Cl_4P(C_2H_5Ph_2)_4]$ respectively are**

(a) 4, 4 and 3 (b) 3, 4 and 4 (c) 4, 2 and 3 (d) 2, 3 and 4

67.



(I)



(II)

Statement : **solvolysis of tosylates (I) and (II) shown above, in acetic acid yield the corresponding acetates.**

Reason : **Due to neighbouring group participation(NGP) of the bridge phenonium ion, achiral intermediates are formed in both cases of (I) and (II).**

Assertion : **Tosylate (I) gives an acetate with retention of configuration and tosylate (II) gives a racemic mixture of acetates.**

(a) both R and A are correct (b) both R and A are wrong

(c) R is correct but A is wrong (d) R is wrong but A is correct

68. **Statement** : **Cyclopentadiene can potentially undergo Diels-Alder reaction $(4\pi + 2\pi)$ and $2\pi + 2\pi$ cycloaddition reactions with ketenes. However, it reacts to give stereospecifically only one product.**

Reason : **Due to sp hybridisation of the ketene carbon $2\pi_s + 2\pi_a$ cycloaddition is feasible and thermally this reaction is symmetry allowed.**

Assertion : **Ketenes undergo only $2\pi + 2\pi$ cycloaddition reaction with 1, 3-dienes.**

(a) both R and A are correct (b) both R and A are wrong

(c) R is correct but A is wrong (d) R is wrong but A is correct

69. **Statement** : **1,3-Dichloroallene is optically active and the enantiomers are resolvable.**

Reason : **Optical activity is due to the presence of a chiral center in the molecule.**

Assertion : **The enantiomers are resolvable because interconversion of enantiomers is possible only if there is a free rotation about C=C bonds, which is absent.**

(a) both R and A are correct (b) both R and A are wrong

(c) R is correct but A is wrong (d) R is wrong but A is correct

70. **Statement** : **At 273 K, the fugacities (in atm) of N_2 are 97.03 and 1839 at the experimental pressures (atm) of 100 and 1000, respectively.**

Reason : **At 1000 atm, the system is above the critical temperature and pressure.**

Assertion : **The contribution of the repulsive forces is more dominant at 1000 atm.**

(a) both R and A are correct (b) both R and A are wrong

(c) R is correct but A is wrong (d) R is wrong but A is correct

71. **Statement** : **for the equilibrium, $Ag_2CO_3(s) \leftrightarrow Ag_2O(s) + CO_2(g)$. A plot of ln K_p vs 1/T gives a linear relationship with a positive slope.**

Reason : **The reaction is exothermic.**

Assertion : **The free energy change for the reaction is more negative at higher temperatures.**

(a) both R and A are correct (b) both R and A are wrong

(c) R is correct but A is wrong (d) R is wrong but A is correct

72. **Statement** : **The potential for the cell, $Pt|H_2(1\ atm)|HCl(m)|AgCl(s)|Ag(s)$ decreases as the concentration of HCl is increased.**

Reason : **The mean ionic activity coefficient decreases with increase in HCl concentration.**

Assertion : **In a plot of E vs [HCl], the intercept at the potential axis is equal to the standard reduction potential of the hydrogen electrode.**

(a) both R and A are correct (b) both R and A are wrong

(c) R is correct but A is wrong (d) R is wrong but A is correct

73. **Statement : Oxygen is preferred to air for welding metals using acetylene gas.**

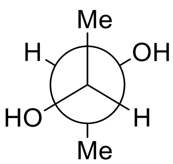
Reason : With air, metal nitrides are formed resulting in poor welding.

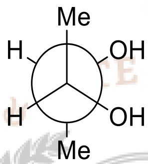
Assertion : With air, inert nitrogen dissipates the heat of combustion and hence, the maximum temperature attained is less than that with oxygen.

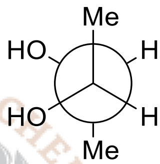
(a) both R and A are correct (b) both R and A are wrong

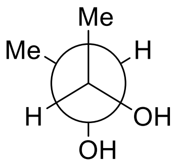
(c) R is correct but A is wrong (d) R is wrong but A is correct

74. **Among the following, the Newmann projections of meso-2, 3-butanediol are**

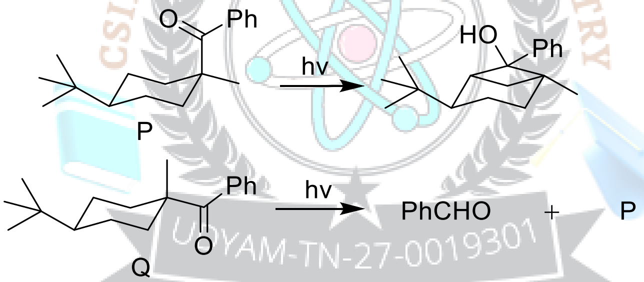
(a) 

(b) 

(c) 

(d) 

75. **The correct description of the following two reactions is that**



(a) Both P and Q undergo α −cleavage reaction

(b) P undergoes only Norrish type II reaction whereas Q undergoes only Norrish type I reaction.

(c) Q gives P by photochemical chair to chair interconversion of the cyclohexane Ring

(d) Both P and Q undergo Norrish type I reaction, but only Q gives S through this mechanism.

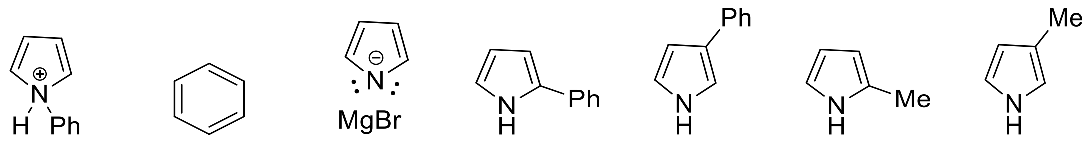
76. **A 10.0 g mixture of n-butane and 2-butene was treated with bromine in CCl_4 and it consumed 8.0 g of bromine (Atomic wt = 80). Another 10.0 g of the same mixture was hydrogenated to get n-butane only. The weight of 2-butene in the original mixture and the gain in the weight of the mixture after hydrogenation, respectively are**

(a) 2.8 g and 0.1 g (b) 5.6 g and 0.4 g (c) 7.2 g and 0.8 g (d) 8.0 g and 1.0 g

77. **Pyrrole + PhMgBr ⟶ E + F**

E + MeCl ⟶ G + H

F + MeCl ⟶ no reaction without catalyst



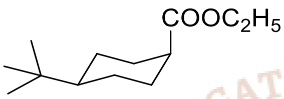
1 2 3 4 5 6 7

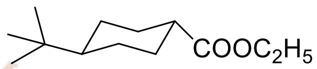
The structure of products E–H, respectively are

	(E)	(F)	(G)	(H)
(a)	(3) ;	(2) ;	(6) ;	(7)
(c)	(3) ;	(4) ;	(5) ;	(2)

	(E)	(F)	(G)	(H)
(b)	(4) ;	(5) ;	(6) ;	(1)
(d)	(3) ;	(2) ;	(4) ;	(5)

78. **Regarding the saponification of M and N shown below, the correct statement is that**





M **N**

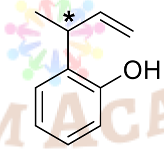
(a) M reacts faster than N because the transition state is less crowded for M than for N

(b) M reacts slower than N because the transition state is more crowded for M than for N

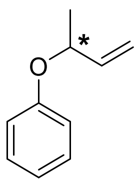
(c) N and M react at the same rate because of formation of tetrahedral intermediate in both cases

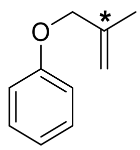
(d) N reacts slower than M because of its greater thermodynamic stability

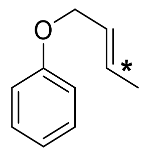
79. **Reactant P labelled with *C (labelled carbon marked with a star) rearranged to product Q on heating. The structure of reactant P is**

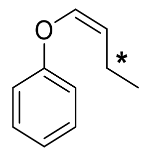


Q

(a) 

(b) 

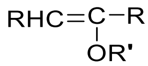
(c) 

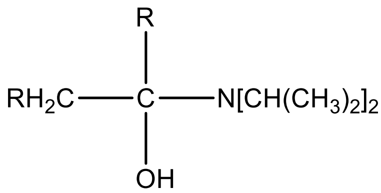
(d) 

80. $$\mathbf{RCH_2COR + R'X \xrightarrow{[(CH_3)_2CH]_2NLi} P + Q}$$

In the above reaction, X is a halogen and the products P and Q are

(I) $R'N[CH(CH_3)_2]_2$ **(II)** $RCH(R')COR$

(III) 

(IV) 

(a) I and II (b) II and III (c) III and IV (d) I and IV

81. **Among the halobenzenes, the one that undergoes electrophilic aromatic substitution most readily and the reason for its higher reactivity are**

(a) fluorobenzene; the benzenonium ion intermediate is stablished by 2p (F), 2p (C) overlap which is most efficient

(b) chlorobenzene; very high electron affinity of chlorine considerably lowers the energy of activation of the reaction

(c) bromobenzene; high polarising power of the halogen atom helps in effective stabilisation of the benzenonium ion intermediate

(d) iodobenzene; iodine atom has the lowest electronegativity and hence electron density of the phenyl ring is least disturbed

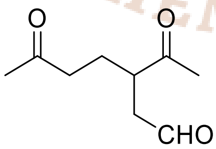
82. **Among the carboxylic acids shown below, the ones that exhibit stereoisomerism an also form cyclic anhydrides on heating are**

(I) $HOOCCH(CH_3)CH_2CH_2COOH$ **(II)** $HOOCCH({}^{i}C_3H_7)COOH$

(III) $HOOCCH(C_2H_5)CH_2COOH$ **(IV)** $HOOCC(CH_3)(C_2H_3)COOH$

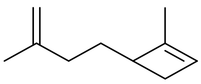
(a) (I) and (II) (b) (I) and (III) (c) (II) and (III) (d) (II) and (IV)

83. **The reactants that lead to products (X) and (Y) on ozonolysis are**

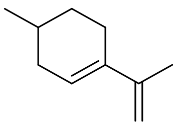


HCHO

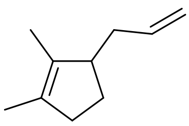
X **Y**



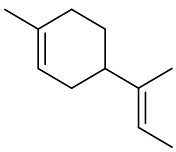
I



II

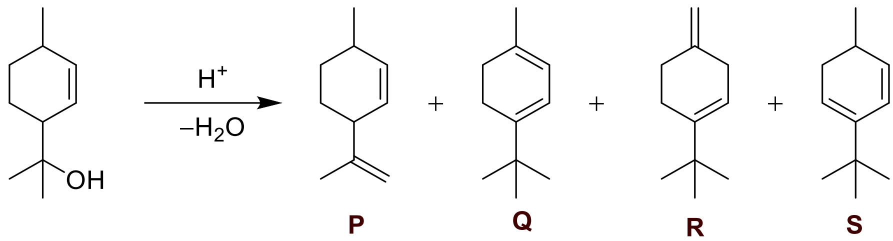


III



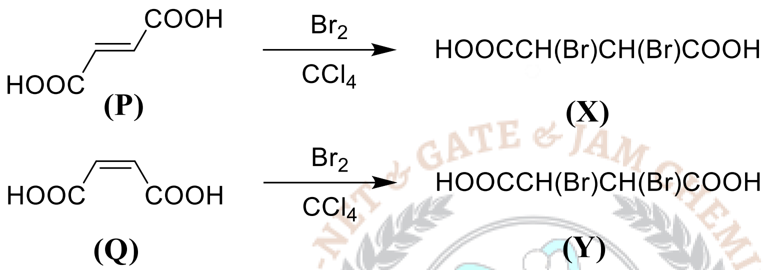
IV

(a) (I) and (IV) (b) (I) and (III) (c) (II) and (III) (d) (II) and (IV)

84. 

On the basis of Woodward-Fieser rules, the dienes that have λ_{max} values in the range 268-273 nm are

(a) P and Q (b) P and R (c) Q and R (d) Q and S

85. 

The correct statements with respect to the above pair of reactions are that

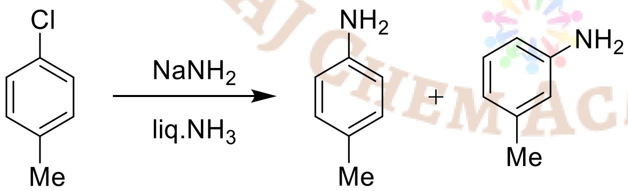
I. The reactions are stereospecific

II. (X) is erythro and (Y) is threo isomer

III. (X) is threo and (Y) is erythro isomer

IV. Each of (P) and (Q) gives a mixture of (X) and (Y)

(a) (I) and (II) (b) (I) and (III) (c) (I) and (IV) (d) (II) and (IV)

86. 

The above reaction is an example of

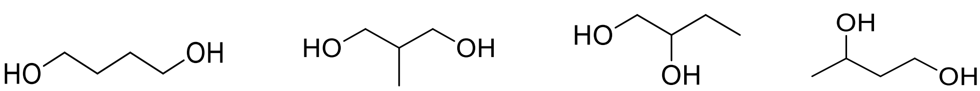
(a) nucleophilic substitution of addition-elimination mechanism

(b) electrophilic substitution by addition-elimination mechanism

(c) radical substitution reaction

(d) nucleophilic substitution involving benzyne intermediate

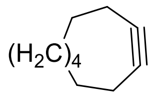
87. **Diols (I-IV) which react with CrO_3 in aqueous H_2SO_4 and yield products that readii undergo decarboxylation on heating, are**



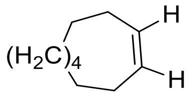
I **II** **III** **IV**

(a) (I) and (II) (b) (II) and (III) (c) (II) and (IV) (d) (I) and (IV)

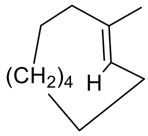
88. **Reactant P gives products Q and/or R.**



(P)



(Q)



(R)

The possible reagents are:

Na/liq.NH_3	**H_2/Pd-$CaCO_3$**	**H_2/Pd/C**
I	**II**	**III**

The correct statement with respect to the conversion is:

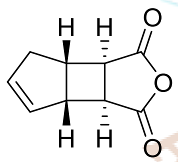
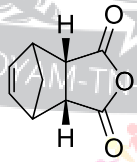
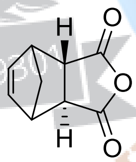
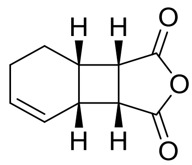
(a) Q is obtained on treatment with reagent (I)

(b) R and Q are obtained on treatment with reagent (III)

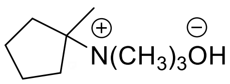
(c) R is obtained on treatment with reagent (I)

(d) R is obtained on treatment with reagent (II)

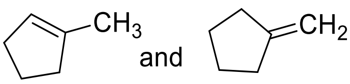
89. **The product obtained in the thermal reaction of cyclopentadiene with maleic anhydride is**

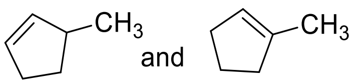
(a) 
(b) 
(c) 
(d) 

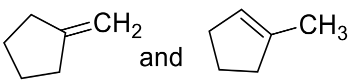
90. **Two alkenes, X (91% yield) and Y (9% yield) are formed when the following is heated.**

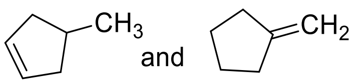


The structures of X and Y, respectively are

(a) 

(b) 

(c) 

(d) 

Answer Key

Q.No	Ans		Q.No	Ans		Q.No	Ans		Q.No	Ans
1.	b		26.	a		51.	a		76.	**
2.	a		27.	c		52.	d		77.	a

3.	c		28.	a		53.	a		78.	b
4.	d		29.	a		54.	b		79.	c
5.	a		30.	d		55.	a		80.	b
6.	a		31.	c		56.	c		81.	a
7.	c		32.	a		57.	d		82.	b
8.	a		33.	b		58.	a		83.	b
9.	d		34.	b		59.	b		84.	d
10.	c		35.	a		60.	a		85.	a
11.	a		36.	a		61.	a		86.	d
12.	a		37.	b		62.	a		87.	c
13.	d		38.	a		63.	c		88.	c
14.	d		39.	c		64.	c		89.	b
15.	a		40.	c		65.	b		90.	c
16.	b		41.	b		66.	a			
17.	b		42.	d		67.	d			
18.	c		43.	b		68.	a			
19.	c		44.	c		69.	d			
20.	a		45.	a		70.	a			
21.	c		46.	a		71.	c			
22.	b		47.	b		72.	a			
23.	a		48.	d		73.	**			
24.	a		49.	a		74.	a			
25.	c		50.	a		75.	b			