## GATE-CY 2007

## Section-A

## Q. 1 - Q. 20 : Carry ONE mark each.

1. The rate of sulphonation of benzene can be significantly enhanced by the use of
(a) a mixture of $\mathrm{HNO}_{3}$ and $\mathrm{H}_{2} \mathrm{SO}_{4}$
(b) conc. $\mathrm{H}_{2} \mathrm{SO}_{4}$
(c) a solution of $\mathrm{SO}_{3}$ in $\mathrm{H}_{2} \mathrm{SO}_{4}$
(d) $\mathrm{SO}_{3}$
2. The reaction,

is an example of a
(a) Birch reduction
(b) Clemmenson reduction
(c) Wolff-Kishner reduction
(d) hydride reduction
3. The major product $(\mathrm{X})$ of the monobromination reaction is

(a)

(b)


(d)

4. Benzene can not be iodinated with $\mathrm{I}_{2}$ directly. However, in presence of oxidants such as $\mathrm{HNO}_{3}$, iodination is possible. The electrophile formed in this case is
(a) $\left[\mathrm{I}^{+}\right]$
(b) $I^{*}$
(c) $\left[\begin{array}{ll}{ }^{*} \delta & \stackrel{\delta}{\mathrm{I}} . . . . . \mathrm{O}_{\mathrm{O}} \mathrm{H}_{2}\end{array}\right]^{+}$
(d) $\left[\begin{array}{cc}\left.\begin{array}{c}\delta \\ \mathrm{I} \\ \mathrm{I} \\ \ldots\end{array}\right] . \mathrm{O}_{2} \mathrm{OH}_{2}\end{array}\right]^{+}$
5. Classify the following species as electrophiles $(\mathrm{E})$ and nucleophiles $(\mathrm{N})$ in routine organic synthesis

$$
\begin{array}{lllll}
\mathrm{SO}_{3} & \mathrm{Cl}^{+} \mathrm{CH}_{3} \mathrm{NH}_{2} & \mathrm{H}_{3} \mathrm{O}^{+} & \mathrm{BH}_{3} & \mathrm{CN}^{-}
\end{array}
$$

(a) $\mathrm{E}=\mathrm{SO}_{3}, \mathrm{Cl}^{+}, \mathrm{BH}_{3} \quad ; \mathrm{N}=\mathrm{CH}_{3} \mathrm{NH}_{2}, \mathrm{H}_{3} \mathrm{O}^{+}, \mathrm{CN}^{-}$
(b) $\mathrm{E}=\mathrm{Cl}^{+}, \mathrm{H}_{3} \mathrm{O}^{+} \quad ; \mathrm{N}=\mathrm{SO}_{3}, \mathrm{CH}_{3} \mathrm{NH}_{2}, \mathrm{BH}_{3}, \mathrm{CN}^{-}$
(c) $\mathrm{E}=\mathrm{Cl}^{+}, \mathrm{H}_{3} \mathrm{O}^{+}, \mathrm{BH}_{3} \quad ; \mathrm{N}=\mathrm{SO}_{3}, \mathrm{CH}_{3} \mathrm{NH}_{2}, \mathrm{H}_{3} \mathrm{O}^{+}, \mathrm{CN}^{-}$
(d) $\mathrm{E}=\mathrm{SO}_{3}, \mathrm{Cl}^{+}, \mathrm{H}_{3} \mathrm{O}^{+}, \mathrm{BH}_{3} ; \quad \mathrm{N}=\mathrm{CH}_{3} \mathrm{NH}_{2}, \mathrm{CN}^{-}$
6. The major product obtained upon treatment of compound X with $\mathrm{H}_{2} \mathrm{SO}_{4}$ at $80^{\circ} \mathrm{C}$ is:

(X)
(a)

(b)

(c)

(d)

7. $\mathrm{BaTi}\left[\mathrm{Si}_{3} \mathrm{O}_{9}\right]$ is a class of
(a) ortho silicate
(b) cyclic silicate
(c) chain silicate
(d) sheet silicate
8. The ground state term fro $\mathrm{V}^{3+}$ ion is
(a) ${ }^{3} \mathrm{~F}$
(b) ${ }^{2} \mathrm{~F}$
(c) ${ }^{3} \mathrm{P}$
(d) ${ }^{2} D$
9. In photosynthesis, the predominant metal present in the reaction centre of photosystem II is
(a) Zn
(b) Cu
(c) Mn
(d) Fe
10. The octahedral complex/complex ion which shows both facial and meridonial isomers is
(a) Triglycinatocobalt (III)
(b) Tris(etihylenediamine) cobalt(III)
(c) Dichlorodiglycinatocobalt(III)
(d) Trioxalactocobaltate (III)
11. Zn in carbonic anhydrase is co-ordinated by three histidine and one water molecule. The reaction of $\mathrm{CO}_{2}$ with this enzyme is an example of
(a) electrophilic addition
(b) electron transfer
(c) nucleophilic addition
(d) electrophilic substitution
12. The difference in the measured and calculated magnetic moment (based on spin-orbit coupling) is observed for
(a) $\mathrm{Pm}^{3+}$
(b) $\mathrm{Eu}^{3+}$
(c) $\mathrm{Dy}^{3+}$
(d) $\mathrm{Lu}^{3+}$
13. For a redox reaction, $\mathrm{Cd}^{2+}+2 \mathrm{e}^{-} \rightleftharpoons \mathrm{Cd}$, the $\left(\mathrm{E}_{\mathrm{p}}\right)_{\text {anodic }}$ observed in cyclic voltametry at hanging mercury drop electrode is -650 mV vs. SCE . The expected valûe for $\left(\mathrm{E}_{\mathrm{p}}\right)_{\text {cathodic }}$ is
(a) -708 mV
(b) -679 mV
(c) 650 mV
(d) -621 mV
14. The dimension of Planck constant is ( $\mathrm{M}, \mathrm{L}$ and $T$ denote mass, length and time respectively)
(a) $M L^{3} T^{-2}$
(b) $M L^{2} T^{-1}$
(c) $M^{2} L^{-1} T^{-1}$
(d) $M^{-1} L^{2} T^{-2}$
15. For a homonuclear diatomic moleculle the bonding molecular orbital is
(a) $\sigma_{u}$ oflowest energy
(b) $\sigma_{u}$ of second lowest energy
(c) $\pi_{\mathrm{g}}$ oflowest energy
(d) $\pi_{u}$ oflowest energy
16. The selection rules for the appearance, of P branch in the rotational-vibrational absorption spectra of a diatomic molecule within rigid rotor-harmonic oscillator model are
(a) $\Delta v= \pm 1$ and $\Delta J= \pm 1$
(b) $\Delta \mathrm{v}=+1$ and $\Delta \mathrm{J}=+1$
(c) $\Delta \mathrm{v}=+1$ and $\Delta \mathrm{J}=-1$
(d) $\Delta \mathrm{v}=-1$ and $\Delta \mathrm{J}=-1$
17. The $S_{2}$ operation on a molecule with the axis of rotation as the z axis, moves a nucleus at $(\mathrm{x}, \mathrm{y}, \mathrm{z})$ to
(a) $(-x,-y, x)$
(b) $(x,-y,-z)$
(c) $(-\mathrm{x}, \mathrm{y},-\mathrm{z})$
(d) $(-x,-y,-z)$
18. The expression which represents the chemical potential of the $i^{\text {th }}$ species $\left(\mu_{\mathrm{i}}\right)$ in a mixture $(\mathrm{i} \neq \mathrm{j})$ is:
(a) $\left(\partial E / \partial n_{i}\right)_{s, v, n j}$
(b) $\left(\partial \mathrm{H} / \partial \mathrm{n}_{\mathrm{i}}\right)_{\mathrm{s}, \mathrm{v}, \mathrm{nj}}$
(c) $\left(\partial \mathrm{A} / \partial \mathrm{n}_{\mathrm{i}}\right)_{\mathrm{s}, \mathrm{v}, \mathrm{nj}}$
(d) $\left(\partial G / \partial \mathrm{n}_{\mathrm{i}}\right)_{\mathrm{s}, \mathrm{v}, \mathrm{nj}}$
19. Which of the following statements is NOT correct for a catalyst?
(a) It increases the rate of a reaction
(b) It is not consumed in the course of a reaction
(c) It provides an alternate pathway for the reaction
(d) It increases the activation energy of the reaction
20. The value of the rate constant for the gas phase reaction $2 \mathrm{NO}_{2}+\mathrm{F}_{2} \rightarrow 2 \mathrm{NO}_{2} \mathrm{~F}$ is $38 \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$ at 300 K . The order of the reaction is
(a) 0
(b) 1
(c) 2
(d) 3

## Q. 21 - Q. 75 : Carry TWO marks each.

21. Boric acid in aqueous solution in presence of glycerol behaves as a strong acid due to the formation of
(a) an anionioc metal-chelate
(b) borate anion
(c) glycerate ion
(d) a charge transfer complex
22. Match the compounds in List I with the corresponding structue / property given in List II

List - I
A. $\left(\mathrm{Ph}_{3} \mathrm{P}\right)_{3} \mathrm{RhCl}$
B. $\mathrm{LiC}_{6}$
C. $\mathrm{PtF}_{6}$
D. $\mathrm{Ni}_{3} \mathrm{~S}_{4}$
(a) A-iii, B-i, C-ii, D-iv
(c) A-iii, B-ii, C-i, D-iv
(i) Spinel

List - II
(ii) Intercalation
(iii) Oxidising agent
(iv) Catalyst for alkene hydrogenation
(b) A-iv, B-ii, C-iii, D-i
(d) A-iv, B-iii, C-ii, D-i
23. $\quad \mathrm{W}(\mathrm{CO})_{6}$ reacts with MeLi to give an intermediate which upontreatment with $\mathrm{CH}_{2} \mathrm{~N}_{2}$ gives a compound X . X is represented as
(a) $\mathrm{WMe}_{6}$
(b) $(\mathrm{CQ}), \mathrm{W}-\mathrm{Me}$
(c) $(\mathrm{CO})_{5} \mathrm{~W}=\mathrm{C}(\mathrm{Me}) \mathrm{OMe}$
(d) (CO) ${ }_{5} \mathrm{~W} \equiv \mathrm{CMe}$
24. Considering the quadrupolar nature of $M-M$ bond in $\left[\mathrm{Re}_{2} \mathrm{Cl}_{8}\right]^{2-}$, the $\mathrm{M}-\mathrm{M}$ bond order in $\left[\operatorname{Re}_{2} \mathrm{Cl}_{4}\left(\mathrm{PMe}_{2} \mathrm{Ph}\right)_{4}\right]^{+}$and $\left[\mathrm{Re}_{2} \mathrm{Cl}_{4}\left(\mathrm{PMe}_{2} \mathrm{Ph}\right)_{4}\right]$ respectively are
(a) 3.0 and 3.0
(b) 3.0 and 3.5
(c) 3.5 and 3.5
(d) 3.5 and 3.0
25. A student recorded a polarogram of $2.0 \mathrm{mM} \mathrm{Cd}^{2+}$ solution and forgot to add KCl solution. What type of error do you expect in his results?
(a) Only migration current yill be observed
(b) Only diffusion curcent will be observed
(c) both migration current as well as diffusion current will be observed
(d) Both catalytic current as well as diffusion current will be observed
26. The separation of trivalent lanthanide ions, $\mathrm{Lu}^{3+}, \mathrm{Yb}^{3+}, \mathrm{Dy}^{3+}, \mathrm{Eu}^{3+}$ can be effectively done by a cation exchange resion using ammonia o-hydroxy isobutyrate as the eluent. The order $n$ which the ions will be separated is
(a) $\mathrm{Lu}^{3+}, \mathrm{Yb}^{3+}, \mathrm{Dy}^{3+}, \mathrm{Eu}^{3+}$
(b) $\mathrm{Eu}^{3+}, \mathrm{Dy}^{3+}, \mathrm{Yb}^{3+}, \mathrm{Lu}^{3+}$
(c) $\mathrm{Dy}^{3+}, \mathrm{Yb}^{3+}, \mathrm{Eu}^{3+}, \mathrm{Lu}^{3+}$
(d) $\mathrm{Yb}^{3+}, \mathrm{Dy}^{3+}, \mathrm{Lu}^{3+}, \mathrm{Eu}^{3+}$
27. Arrange the following metal complexes in order of their increasing hydration energy.
$\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
$\left[\mathrm{V}\left(\underset{\mathrm{Q}}{\left.\left.\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}}\right.\right.$
$\left[\underset{R}{\left.\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}}\right.$
$\left[\underset{\mathrm{s}}{\left.\mathrm{Ti}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}}\right.$
(a) P $<$ S $<$ Q $<$ R
(b) P $<$ Q $<$ R $<$ S
(c) Q $<$ P $<$ R $<$ S
(d) S $<$ R $<$ Q $<$ P
28. In the complex, $\left[\mathrm{Ni}_{2}\left(\eta^{5}-\mathrm{Cp}\right)_{2}(\mathrm{CO})_{2}\right]$, the IR stretching frequency appears at $1857 \mathrm{~cm}^{-1}$ (strong) and $1897 \mathrm{~cm}^{-1}$ (weak). The valence electron count and the nature of the M-CO bond respectively are
(a) $16 \mathrm{e}^{-}$, bridging
(b) $17 \mathrm{e}^{-}$, bridging
(c) $18 \mathrm{e}^{-}$, terminal
(d) $18 \mathrm{e}^{-}$, briding.
29. The correct classification of $\left[\mathrm{B}_{5} \mathrm{H}_{5}\right]^{2-}, \mathrm{B}_{5} \mathrm{H}_{9}$ and $\mathrm{B}_{5} \mathrm{H}_{11}$ respectively is
(a) closo, arachno, nido
(b) arachno, closo, nido
(c) closo, nido, arachno
(d) nido, arachno, closo
30. The compounds X and y in the following reaction are

(a) $\mathrm{X}=(\mathrm{Et})_{2} \mathrm{P}(\mathrm{S}) \mathrm{SH} ; \mathrm{Y}=(\mathrm{Et})_{2} \mathrm{P}(\mathrm{S}) \mathrm{Cl}$
(b) $\mathrm{X}=(\mathrm{EtO})_{2} \mathrm{P}(\mathrm{S}) \mathrm{SH} ; \mathrm{Y}=(\mathrm{EtO})_{2} \mathrm{P}(\mathrm{S}) \mathrm{Cl}$
(c) $\mathrm{X}=(\mathrm{EtO})_{2} \mathrm{PSH} \quad ; \mathrm{Y}=(\mathrm{EtO})_{2} \mathrm{PCl}$
(d) $\mathrm{X}=(\mathrm{Et})_{3} \mathrm{PO} \quad ; \mathrm{Y}=(\mathrm{Et})_{3} \mathrm{PCl}$
31. Consider the reactions

1. $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+\left[\mathrm{CoCl}\left(\mathrm{NH}_{3}\right)_{5}\right]^{2+} \rightarrow\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{2+}+\left[\mathrm{CrCl}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}\right]^{2+}$
2. $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}+\left[\mathrm{Mo}(\mathrm{CN})_{8}\right]^{3-} \rightarrow\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-+}+\left[\mathrm{Mo}(\mathrm{CN})_{8}\right]^{4-}$

Which one of the following is the correct statement?
(i) Both involve an inner sphere mechanism.
(ii) Both involve an outer sphere mechanism
(iii) Reaction 1 follows inner sphere and reaction 2 followsouter sphere mechanism
(iv) Reaction 1 follows outer sphere and reaction 2 follows inner sphere mechanism.
(a) i
(b) ii
(c) iv (d) iii
32. The pair of compounds having the same hybridization for the central atom is
(a) $\mathrm{XeF}_{4}$ and $\left[\mathrm{SiF}_{6}\right]^{2-}$
(b) $\left[\mathrm{NiCl}_{4}\right]^{2-}$ and $\left[\mathrm{PtCl}_{4}\right]^{2-}$
(c) $\mathrm{Ni}(\mathrm{CO})_{4}$ and $\mathrm{XeO}_{2} \mathrm{~F}_{2}$
(d) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ and $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$
33. In the reaction shown below, X and Y respectively are $\mathrm{Mn}_{2}(\mathrm{CO})_{10} \xrightarrow{\mathrm{Na}}(\mathrm{X}) \xrightarrow{\mathrm{CH}_{3} \mathrm{COCl}}(\mathrm{Y})$
(a) $\left[\mathrm{Mn}(\mathrm{CO})_{4}\right]^{2-}\left[\mathrm{CH}_{3} \mathrm{C}(\mathrm{O}) \mathrm{Mn}\left(\mathrm{CO}_{5}\right]^{-}\right.$
(b) $\left[\mathrm{Mn}(\mathrm{CO})_{4}\right]^{2-}, \mathrm{CH}_{3} \mathrm{C}(\mathrm{O}) \mathrm{Mn}(\mathrm{CO})_{5}$
(c) $\left[\mathrm{Mn}(\mathrm{CO})_{5}\right]^{-},\left[\mathrm{ClMn}(\mathrm{CO})_{5}\right]$
(b) $\left[\mathrm{Mn}(\mathrm{CO})_{4}\right]^{2-},\left[\mathrm{ClMn}(\mathrm{CO})_{5}\right]^{-}$
34. The Lewis acid character of $\mathrm{BF}_{3}, \mathrm{BCl}_{3}$ and $\mathrm{BBr}_{3}$ follows the order
(a) $\mathrm{BF}_{3}<\mathrm{BBr}_{3}<\mathrm{BCl}_{3}$
(b) $\mathrm{BCl}_{3}<\mathrm{BBr}_{3}<\mathrm{BF}_{3}$
(c) $\mathrm{BF}_{3}<\mathrm{BCl}_{3}<\mathrm{BBr}_{3}$
(d) $\mathrm{BBr}_{3}<\mathrm{BCl}_{3}<\mathrm{BF}_{3}$
35. The compound which shows $\mathrm{L} \leftarrow \mathrm{M}$ charge transfer is
(a) $\mathrm{Ni}(\mathrm{CO})_{4}$
(b) $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$
(c) HgO
(d) $\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
36. The reaction of $\left[\mathrm{PtCl}_{4}\right]^{2-}$ with $\mathrm{NH}_{3}$ gives rise to
(a) $\left[\mathrm{PtCl}_{4}\left(\mathrm{NH}_{3}\right)_{2}\right]^{2-}$
(b) trans $-\left[\mathrm{PtCl}_{2}\left(\mathrm{NH}_{3}\right)_{2}\right]$
(c) $\left[\mathrm{PtCl}_{2}\left(\mathrm{NH}_{3}\right)_{4}\right]$
(d) cis $-\left[\mathrm{PtCl}_{2}\left(\mathrm{NH}_{3}\right)_{2}\right]$
37. Zeise's salt is represented as
(a) $\mathrm{H}_{2} \mathrm{PtCl}_{6}$
(b) $\left[\mathrm{PtCl}_{4}\right]^{2-}$
(c) $\left[\mathrm{ZnCl}_{4}\right]^{2-}$
(d) $\left[\operatorname{PtCl}_{3}\left(\eta^{2}-\mathrm{C}_{2} \mathrm{H}_{4}\right)\right]^{-}$
38. The catalyst used in the conversion of ethylene to acetaldehyde using Wacker process is
(a) $\mathrm{HCo}(\mathrm{CO})_{4}$
(b) $\left[\mathrm{PdCl}_{4}\right]^{2-}$
(c) $\mathrm{V}_{2} \mathrm{O}_{5}$
(d) $\mathrm{TiCl}_{4}$ in the presence of $\mathrm{Al}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{3}$
39. The temperature of 54 g of water is raised from $15^{\circ} \mathrm{C}$ to $75^{\circ} \mathrm{C}$ at constant pressure. The change in the enthalpy of the system (given that $\mathrm{C}_{\text {p.m }}$ of water $=75 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$ ) is:
(a) 4.5 kJ
(b) 13.5 kJ
(c) 9.0 kJ
(d) 18.0 kJ
40. The specific volume of liquid water is $1.001 \mathrm{~mL} \mathrm{~g}^{-1}$ and that of ice is $1.0907 \mathrm{~mL} \mathrm{~g}^{-1}$ at ${ }^{\circ} \mathrm{C}$. If the heat of fusion of ice at this temperature is $333.88 \mathrm{~J} \mathrm{~g}^{-1}$, the rate of change of melting point of ice with pressure in deg atm ${ }^{-1}$ will be
(a) -0.0075
(b) 0.0075
(c) 0.075
(d) -0.075
41. Given that $\mathrm{E}_{0}\left(\mathrm{Fe}^{3+}, \mathrm{Fe}\right)=-0.04 \mathrm{~V}$ and $\mathrm{E}_{0}\left(\mathrm{Fe}^{2+}, \mathrm{Fe}\right)=-0.44 \mathrm{~V}$, the value of $\mathrm{E}_{0}\left(\mathrm{Fe}^{3+}, \mathrm{Fe}^{2+}\right)$ is:
(a) 0.76 V
(b) -0.40 V
(c) -0.76 V
(d) 0.40 V
42. For the reaction $\mathrm{P}+\mathrm{Q}+\mathrm{R} \longrightarrow \mathrm{S}$, experimental data for the measured intial rates is given below.

| Expt. | Initial conc. P <br> $(\mathrm{M})$ | Initial conc. Q <br> $(\mathrm{M})$ | Initial conc. R <br> $(\mathrm{M})$ | Initial rate <br> $\left(\mathrm{Ms}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 0.2 | 0.5 | 0.4 | $8.0 \times 10^{-5}$ |
| 2 | 0.4 | 0.5 | 0.4 | $3.2 \times 10^{-4}$ |
| 3 | 0.4 | 2.0 | 0.4 | $1.28 \times 10^{-3}$ |
| 4 | 0.1 | 0.25 | 1.6 | $4.0 \times 10^{-5}$ |

The order of the reaction with respect to $P, Q$ and $R$ respectively is:
(a) 22,1
(b) $2,1,2$
(c) $2,1,1$
(d) $1,1,2$
43. Sucrose is converted to a mixt $\begin{gathered}\text { re } \\ \text { of glucose and fructose in a pseudo first order process under alkaline }\end{gathered}$ conditions. The reaction has a half life of 28.4 min . The time required for the reduction of a 8.0 mM sample of sucrose to 1.0 mM is
(a) 56.8 min
(b) 170.4 min
(c) 85.2 min
(d) 227.2 min
44. The reaction, $2 \mathrm{NO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g})$ proceeds via the following steps

$$
\begin{aligned}
\mathrm{NO}+\mathrm{NO} & \xrightarrow{\mathrm{k}_{\mathrm{a}}} \mathrm{~N}_{2} \mathrm{O}_{2} \\
\mathrm{~N}_{2} \mathrm{O}_{2} & \xrightarrow[\mathrm{k}_{\mathrm{a}^{\prime}}]{ } \mathrm{NO}+\mathrm{NO} \\
\mathrm{~N}_{2} \mathrm{O}_{2}+\mathrm{O}_{2} & \xrightarrow{\mathrm{k}_{\mathrm{b}}} \mathrm{NO}_{2}+\mathrm{NO}_{2}
\end{aligned}
$$

The rate of this reaction is equal to
(a) $2 \mathrm{k}_{\mathrm{b}}[\mathrm{NO}]\left[\mathrm{O}_{2}\right]$
(b) $\left(2 \mathrm{k}_{\mathrm{a}} \mathrm{k}_{\mathrm{b}}[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]\right) /\left(\mathrm{k}_{\mathrm{a}}+\mathrm{k}_{\mathrm{b}}\left[\mathrm{O}_{2}\right]\right)$
(c) $2 \mathrm{k}_{\mathrm{b}}[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]$
(d) $\mathrm{k}_{\mathrm{a}}[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]$
45. 40 millimoles of NaOH are added to 100 mL of a 1.2 MHA and Y M NaAbuffer resulting in a solution of pH 5.30. Assuming that the volume of the buffer remains unchanged, the pH of the buffer $\left(\mathrm{K}_{\mathrm{HA}}=1.00 \times 10^{-5}\right)$ is
(a) 5.30
(b) 5.00
(c) 0.30
(d) 10.30
46. The entropy of mixing of 10 moles of helium and 10 moles of oxygen at constant temperature and pressure, assuming both to be ideal gas, is:
(a) $115.3 \mathrm{JK}^{-1}$
(b) $5.8 \mathrm{JK}^{-1}$
(c) $382.9 \mathrm{JK}^{-1}$
(d) $230.6 \mathrm{JK}^{-1}$
47. The ionisation potential of hydrogen atom is 13.6 eV . The first ionistaion potential of a sodium atom, assuming that the energy of its outer electron can be represented by a H -atom like model with an effective nuclear charge of 1.84 , is
(a) 46.0 eV
(b) 11.5 eV
(c) 5.1 eV
(d) 2.9 eV
48. The quantum state of a particle moving in a circular path in a plane is given by

$$
\psi_{\mathrm{m}}(\phi)=(1 / \sqrt{2 \pi}) \mathrm{e}^{\mathrm{i} m \phi}, \mathrm{~m}=0, \pm 1, \pm 2, \ldots \ldots
$$

When a perturbation $\mathrm{H}_{1}=\mathrm{P} \cos \phi$ is applied ( P is a constant), what will be the first order correction to the energy of the $\mathrm{m}^{\text {th }}$ state
(a) 0
(b) $\mathrm{P} /(2 \pi)$
(c) $\mathrm{P} /(4 \pi)$
(d) $\cdot \mathrm{Pm}^{2}+\left(4 \pi^{2}\right)$
49. The correct statement(s) among the following is/are
(i) The vibrational energy levels of a real diatomic molecule are equally spaced.
(ii) At 500 K , the reaction $\mathrm{A} \rightarrow \mathrm{B}$ is spontaneous when $\Delta \mathrm{H}=18.83 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and $\Delta \mathrm{S}=41.84 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$.
(iii) The process of fluorescence involves transition from a singlet electronc state to another singlet electronic state by absorption of light.
(iv) When a constant P is added to each of the possibteenergies of a system, its entropy remains unchanged.
(a) Only i
(b) Only ii
(c) Both i and iii
(d) Both ii and iv
50. Assuming $\mathrm{H}_{2}$ and HD molecules having equal lengths, the ratio of the rotational partition functions of these molecules, at temperature above 100 K is
(a) $3 / 8$
(b) $3 / 4$
(c) $1 / 2$
(d) $2 / 3$
51. N non-interacting molecules are distributed among three non-degenerate energy levels $\varepsilon_{0}=0, \varepsilon_{1}=1.38 \times 10^{-21} \mathrm{~J}$ and $\varepsilon_{2}=2.76 \times 10^{-21} \mathrm{~J}$, at 100 K . If the average total energy of the system at this temperature is $1.38 \times 10^{-118} \mathrm{~J}$, the number of molecules in the system is:
(a) 1000
(b) 1503
(c) 2354
(d) 2987
53. The rate constants of two reactions at temperature $T$ are $k_{1}(T)$ and $k_{2}(T)$ and the corresponding activation energies are $E_{1}$ and $E_{2}$ with $E_{2}>E_{1}$. When temperature is raised from $T_{1}$ and $T_{2}$, which one of the following relations is correct?
(a) $\frac{\mathrm{k}_{1}\left(\mathrm{~T}_{2}\right)}{\mathrm{k}_{1}\left(\mathrm{~T}_{1}\right)}=\frac{\mathrm{k}_{2}\left(\mathrm{~T}_{2}\right)}{\mathrm{k}_{2}\left(\mathrm{~T}_{1}\right)}$
(b) $\frac{\mathrm{k}_{1}\left(\mathrm{~T}_{2}\right)}{\mathrm{k}_{1}\left(\mathrm{~T}_{1}\right)}>\frac{\mathrm{k}_{2}\left(\mathrm{~T}_{2}\right)}{\mathrm{k}_{2}\left(\mathrm{~T}_{1}\right)}$
(c) $\frac{\mathrm{k}_{1}\left(\mathrm{~T}_{2}\right)}{\mathrm{k}_{1}\left(\mathrm{~T}_{1}\right)} \geq \frac{\mathrm{k}_{2}\left(\mathrm{~T}_{2}\right)}{\mathrm{k}_{2}\left(\mathrm{~T}_{1}\right)}$
(d) $\frac{k_{1}\left(T_{2}\right)}{k_{1}\left(T_{1}\right)}<\frac{k_{2}\left(T_{2}\right)}{k_{2}\left(T_{1}\right)}$
54. The number of degrees of freedom for a system consisting of $\mathrm{NaCl}(\mathrm{s}), \mathrm{Na}^{+}(\mathrm{aq})$ and $\mathrm{Cl}^{-}(\mathrm{aq})$ at equilibrium is
(a) 2
(b) 3
(c) 4
(d) 5
55. Match the structures in List - I with their correct names in List - II.
List - I
List - II
(P)

(i) 3-methyl furan
(Q)

(ii) Imidazole
(R)

(iii) 5-hydroxybenzothiazole
(S)

(iv) 2-amino piperidine.
(T)

(v) 2-aminomorpholine
(a) P-i, Q-ii, R-v, S-iii, T-iv
(b) P-ii, Q-iii, R-iv, S-v, T-i
(c) P-iii, Q-iv, R-v, S-i, T-ii
(d) P-iv, Q-v, R-i, S-ii, T-iii
56. The result of the reduction of either (R) or (S) 2-methylcyclohexanone, in separate reactions, using $\mathrm{LiAlH}_{4}$ is that the reduction of
(a) The R enantiomer is stereoselective
(b) The R enantiomer is stereospecific.
(c) The S enantiomer is stereospecific
(d) Both the R and S enantiomers is stereoselective.
57. The increasing order of basicity among the following is

(X)

(Y)

(Z)
(a) Y $<$ X $<$ Z
(b) Y $<$ Z $<$ X
(c) $\mathrm{X}<\mathrm{Z}<$ Y
(d) X $<$ Y $<$ Z
58. In the reaction,

if the concentration of both the reactants is doubled, then the rate of the reaction will
(a) remain unchanged
(b) quadruple
(c) reduce to one fourth
(d) double
59. Match the structures in List - I with the coupling constant $\left[{ }^{1} \mathrm{H} \mathrm{J}(\mathrm{Hz})\right]$ given in List - II

## List - I

(1)
(2)

(3)

(ii) $\sim 10 \mathrm{~Hz}$
(iii) $\sim 15 \mathrm{~Hz}$
(a) 1-(i), 2- (ii), 3-(iii)
(b) 1-(ii), 2-(iii), 3-(i)
(c) 1-(iii), 2-(ii), 3-(i)
(d) 1-(iii), 2-(i), 3-(ii)
60. Phenol on reaction with formaldehyde and dimethyl amine mainly gives
(a)

(b)

(c)

(d)

61. The mono protonation of adenine $(\mathrm{X})$ in acidic solution

(X)
mainly occurs at
(a) position 1
(b) position 2
(c) position 3
(d) either position 4 or 5 .
62. In the following reaction,

$(\mathrm{X})$ and $(\mathrm{Y})$ respectively are
(a) ${ }^{1}: \mathrm{CH}_{2}$ and cis 1, 2-dimethylcyclopropane
(b) ${ }^{3}: \mathrm{CH}_{2}$ and cis 1, 2-dimethylcyclopropane
(c) ${ }^{1}: \mathrm{CH}_{2}$ and a mixture of cis/trans 1, 2-dimethylcyclopropane
(d) ${ }^{3}: \mathrm{CH}_{2}$ and a mixture of cis/trans 1, 2-dimethylcyclopropane
63. The major products obtained upon treating a mixture of

with a strongly acidic solution of $\mathrm{H}_{2} \mathrm{SO}_{4}$ is
(a)
 and

(b)
 and

(c)
 and

(d)
 and

64. Match the observed pricipal absorptions in the visible spectrum shown in List - I with the bond shows this absorption in List - II.

## List - I

(1) $\sigma \rightarrow \sigma^{*}$
(2) $n \rightarrow \sigma^{*}$
(3) $n, \pi^{*}$
(3) $\pi, \pi^{*}$
(a) 1-(i), 2-(ii), 3-(iii), 4-(iv)
(c) 1-(ii), 2-(i), 3-(iv), 4-(iii)
-(i), 2-(iii), 3-(ii), 4-(iv)
(d) 1-(iv), 2-(ii), 3-(iii), 4-(i)

## List - II

(i) $\mathrm{C}-\mathrm{C}$
(ii) $\mathrm{C}-\mathrm{O}$
(iii) $\mathrm{C}=\mathrm{O}$
(iv) $\mathrm{C}=\mathrm{C}$
65. Among the isomers $\mathrm{C}_{10} \mathrm{H}_{14}$ shown,


P


Q


R


S
the isomer that can be identified uniquely by mass spectrometry alone is:
(a)P
(b) Q
(c) R
(d) S
66. The direction of rotation of the following thermal electrocyclic ring closures.

respectively is:
(a) Disrotory, disrotatory, disrotatory
(b) Conrotatory, conrotatory, conrotatory
(c) Disrotatory, disrotatory, conrotatory
(d) Disrotatory, conrotatory, disrotatory.
67. The molecules (s) that exist as meso structure (s).

(K)

(L)

(M)
is/are:
(a) Only M
(b) Both K and L
(c) Only L
(d) Only K
68. Stereochemical descriptors for the atoms labeled $\mathrm{H}_{a}$ and $\mathrm{H}_{\mathrm{b}}$ in the structures.


(Y)

(Z)
respectively are:
(a) X-homotopic, Y-enantiotopic and Z-diastereotopic
(b) X-enantiotopic, Y-homotopic and Z-diastereotopic
(c) X-diastereotopic, Y-homotopic and Z-enantiotopic
(d) X-homotopic, Y-diastereotopic and Z-enantiotopic.
69. Treatment of the pentapeptide Gly-Arg-Phe-Ala-Ala, in separate experiments, with the enzymes Trypsin, Chyemotrypsin and Carboxypeptidase A respectively, gives :
(a) Gly-Arg + Phe-Ala-Ala; Gly-Arg-Phe + Ala-Ala; Gly-Arg-Phe-Ala+Ala
(b) Gly-Arg-Phe+Ala-Ala; Gly-Arg-Phe+Ala-Ala; Gly-Arg-Phe-Ala+Ala
(c) Gly-Arg+Phe-Ala-Ala; Gly-Arg-Phe-Ala+Ala; Gly-Arg-Phe+Ala-Ala
(d) Gly-Arg + Phe-Ala-Ala; Gly-Arg-Phe+Ala-Ala; Gly+Arg-Phe-Ala + Ala
70. Hordenine (x), an alkaloid, undergoes Hoffmann degradation to give compound (Y).

$(\mathrm{Y})$ on treatment with alkaline permanganate $(\mathrm{Z})$. Y and Z respectively are
(a)
 and

(b)
 and

(c)
 and

(d)
 and


## Common data for Q.71, Q.72, Q.73:

Trans 1, 2-difluoroethylene molecule has a 2-fold rotational axis, a symmetry plane perpendicular to the rotatinal axis and an inversion centre.
71. The number of distinct symmetry operations that can be performed on the molecule is:
(a) 2
(b) 4
(c) 6
(d) 8
72. The number of irreducible representations of the point group of the molecule is:
(a) 1
(b) 2
(c) 3
(d) 4
73. If two H atoms of the above molecule are also replaced by F atoms, the point group of the resultant molecule will be
(a) $\mathrm{C}_{\mathrm{i}}$
(b) $\mathrm{C}_{2 \mathrm{~h}}$
(c) $\mathrm{C}_{2 \mathrm{v}}$
(d) $\mathrm{D}_{2 \mathrm{~h}}$

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

Reactivity of aryl amines towards electrophilic aromatic substitution is much higher than that of aliphatic amines.
Hence differential reactivity of the amino group is desirable in many reactions.
74. The compound which on reacting with aniline will NOT form an acetanilide is
(a)

(b)

(c)

(d)

75. Aniline can be distinguished from methylamine by its reaction with
(a) p-toluene sulphonyl chloride $/ \mathrm{KOH}$
(b) (i) $\mathrm{NaNO}_{2} / \mathrm{HCl}, 0-5^{\circ} \mathrm{C}$ (ii) alkaline $\beta$-napthol
(c) $\mathrm{Sn} / \mathrm{HCl}$
(d) acetyl chloride

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

76. In the reaction,


Compound X is
(a)

(b)

(c)

(d)

77. Oxidation of X with chromic acid chiefly gives
(a)

(b)

(c)

(d)


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

78. In the reaction, $\mathrm{AMP} \xrightarrow[175^{\circ} \mathrm{C}]{\text { aq. } \mathrm{NH}_{3}}(\mathrm{X})+\mathrm{H}_{3} \mathrm{PO}_{4}$

Compound X is
(a) Adenine
(b) Xanthine
(c) 2,6-diaminopurine
(d) Adenosine
79. Compound X on treatment with conc. HCl gives
(a) Uric acid
(b) Adenine
(c)Hypoxanthine
(d) Guanine

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

80. The reaction of ammonium chloride with $\mathrm{BCl}_{3}$ at $140^{\circ} \mathrm{C}$ at followed by treatment with $\mathrm{NaBH}_{4}$ gives the product X . The formula of X is
(a) $\mathrm{B}_{3} \mathrm{~N}_{3} \mathrm{H}_{3}$
(b) $\mathrm{B}_{3} \mathrm{~N}_{3} \mathrm{H}_{6}$
(c) $\mathrm{B}_{3} \mathrm{~N}_{3} \mathrm{H}_{12}$
(d) $[\mathrm{BH}-\mathrm{NH}]_{\mathrm{n}}$
81. Which of the following statement(s) is/are true for X ?
(I) X is not isoelectronic with benzene
(II) X undergoes addition reaction with HCl .
(III) Electrophilic substitution reaction on X is much faster than that of benzene
(IV) X undergoes polymerization at $90^{\circ} \mathrm{C}$
(a) I and II
(b) Only II
(c) II and III
(d) I and IV

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

82. Consider a particle of mass moving tinane-dimensional box under the potential $V=0$ for $0 \leq x \leq a$ and $V=\infty$ outside the box. When the particle is in its lowest energy state the average momentum ( $<\mathrm{p}_{\mathrm{x}}>$ of the particle is
(a) $<$ p $\left._{x}\right\rangle=0$
(b) $\left\langle\mathrm{p}_{\mathrm{x}}>=\frac{\mathrm{h}}{\mathrm{a}}\right.$
(c) $\left\langle\right.$ p $\left._{x}\right\rangle=\frac{h}{2 \mathrm{a}}$
(d) $\left.<\mathrm{p}_{\mathrm{x}}\right\rangle=\frac{\mathrm{h}}{2 \pi \mathrm{a}}$
83. The uncertainty in the momentum $\left(\Delta \mathrm{p}_{\mathrm{s}}\right)$ of the particle in its lowest energy state is:
(a) $\Delta p_{x}=0$
(b) $\Delta p_{x}=\frac{h}{a}$
(c) $\Delta \mathrm{p}_{\mathrm{x}}=\frac{\mathrm{h}}{2 \mathrm{a}}$
(d) $\Delta p_{x}=\frac{h}{2 \pi a}$

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

84. In the mixture obtained by mixing $25.0 \mathrm{~mL} 1.2 \times 10^{-3} \mathrm{M} \mathrm{MnCl}_{2}$ and 35.0 mL of $6.0 \times 10^{-4} \mathrm{M} \mathrm{KCl}$ solution, the concentrations $(\mathrm{M})$ of $\mathrm{Mn}^{2+}, \mathrm{K}^{+}$and $\mathrm{Cl}^{-}$ions respectively are
(a) $6.0 \times 10^{-4}, 3.0 \times 10^{-4}, 1.5 \times 10^{-3}$
(b) $6.0 \times 10^{-4}, 3.0 \times 10^{-4}, 9.0 \times 10^{-4}$
(c) $5.0 \times 10^{-4}, 3.5 \times 10^{-4}, 1.35 \times 10^{-3}$
(d) $5.0 \times 10^{-4}, 3.5 \times 10^{-4}, 8.5 \times 10^{-4}$
85. The activity (M) of $\mathrm{Mn}^{2+}$ ions in the above solution is
(a) $1.0 \times 10^{-4}$
(b) $2.0 \times 10^{-4}$
(c) $3.0 \times 10^{-4}$
(d) $4.0 \times 10^{-4}$
