## Assignment for B.Sc. Part I (Chem (H)

1. F or the radioactive isotope ${ }^{131} \mathrm{I}$, the time required for $50 \%$ disintegration is 8 days. The time required for the $99.9 \%$ disintegration of 5.5 g of ${ }^{131} \mathrm{I}$ is (Up to one decimal place)
a) 70 days
b) 16 days
c) 32 days
d) 80 days
2. The rate constant of a first order reaction, $1.6 \times 10^{-3} \mathrm{is} \mathrm{s}^{-1}$ at 300 K . Given that the activation energy of the reaction is $28 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and assuming Arrhenius behavior for the temperature dependence, the total time required to obtain $90 \%$ of Y at 350 K is (in seconds) - (Up to one decimal place. Use $\mathrm{R}=8.31 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ )
a) 350
b) 250
c) 280
d) 310
3. The rate constant of a reaction is $1.25 \times 10^{-4} \mathrm{molL}^{-1} \mathrm{~s}^{-1}$. If the initial concentration of reactant is $0.250 \mathrm{MolL}^{-1}$, the total time (in second) required for complete conversion is-
a) 2000
b) 1500
c) 200
d) 150
4. For the following consecutive first order reactions

$$
\mathrm{X} \xrightarrow{\mathrm{k}_{1}=2.0 \mathrm{~s}^{-1}} \mathrm{Y} \xrightarrow{\mathrm{k}_{2}=0.1 \mathrm{~s}^{-1}} \mathrm{Z}
$$

the time (in seconds) required for Y to reach its maximum concentration (assuming only X is present at time $=0$ ) is
a) 1.50
b) 1.60
c) 1.70
d) 1.65
5. The concentration of a reactant R varies with time for two different reactions as shown in the following plots



The orders of these two reactions I and II, respectively, are
a) zero and one
b) one and zero
c) zero and two
d) two and zero
6. For the following reactions
 $\frac{d[B]}{d t}$ is given by
a) $k_{1}[A]-k_{-1}[B]^{2}-2 k_{2}[B]$
b) $2 k_{1}[A]-2 k_{-1}[B]^{2}-k_{2}[B]$
c) $\frac{1}{2} k_{1}[A]-\frac{1}{2} k_{-1}[B]^{2}-k_{2}[B]$
d) $2 k_{1}[A]-2 k_{-1}[B]^{1 / 2}-k_{2}[B]$
7. The expression for the equilibrium constant $\left(\mathrm{K}_{\mathrm{eq}}\right)$ for the enzyme catalyzed reaction given below, is

$$
\mathrm{E}+\mathrm{S} \underset{k_{2}}{\stackrel{k_{1}}{\rightleftarrows}} \mathrm{ES} \underset{k_{4}}{\stackrel{k_{3}}{\rightleftarrows}} \mathrm{P}+\mathrm{E}
$$

(a) $\frac{k_{1} k_{3}}{k_{2} k_{4}}$
(b) $\frac{k_{1} k_{2}}{k_{3} k_{4}}$
(c) $\frac{k_{2} k_{3}}{k_{1} k_{4}}$
(d) $\frac{k_{1} k_{4}}{k_{2} k_{3}}$
8. For a reaction type

$$
\mathrm{X} \xlongequal[\mathrm{k}_{2}]{\stackrel{\mathrm{k}_{1}}{\rightleftharpoons} \mathrm{Y}}
$$

The correct rate expression is $\left([\mathrm{X}]_{0}\right.$ and $[\mathrm{X}]$ correspond to the concentrations of X at time $\mathrm{t}=0$ and $t=t$, respectively)
a) $-\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{dt}}=\mathrm{k}_{1}[\mathrm{X}]_{0}-\left(\mathrm{k}_{1}+\mathrm{k}_{2}\right)[\mathrm{X}]$
b) $-\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{dt}}=\left(\mathrm{k}_{1}+\mathrm{k}_{2}\right)[\mathrm{X}]-\mathrm{k}_{2}[\mathrm{X}]_{0}$
c) $-\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{dt}}=\left(\mathrm{k}_{1}+\mathrm{k}_{2}\right)[\mathrm{X}]_{0}-\mathrm{k}_{1}[\mathrm{X}]$
d) $-\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{dt}}=\left(\mathrm{k}_{1}-\mathrm{k}_{2}\right)[\mathrm{X}]-\mathrm{k}_{1}[\mathrm{X}]_{0}$
9. For a reaction involving two steps given below


Assume that the first step attains equilibrium rapidly. The rate of formation of P is proportional to
a) $[G]^{1 / 2}$
b) $[\mathrm{G}]$
c) $[G]^{2}$
d) $[\mathrm{G}]^{3 / 2}$
10. The specific rate constant of decomposition of a compound is represented by

$$
\ln K=5.0-\frac{12000}{\mathrm{~T}}
$$

The activation energy of decomposition for this compound at 300 K is:
(a) $\mathrm{kcal} / \mathrm{mole}$
b) $12 \mathrm{kcal} / \mathrm{mole}$
c) $24 \mathrm{cal} / \mathrm{mole}$
d) $12 \mathrm{cal} / \mathrm{mole}$
11. The half-life for the hydrolysis of an ester varies with the initial concentration of the reactant $\left[\mathrm{E}_{0}\right]$ as follows:

| $\left[\mathrm{E}_{0}\right] / 10^{-2}$ <br> $\mathrm{molL}^{-1}$ | 5.0 | 4.0 | 3.0 |
| :--- | :---: | :---: | :---: |
| Half-life | 240 | 300 | 400 |

The order of the reaction is
a) 0
b) 1
c) 2
d) 3
12. For the first order consecutive $\mathrm{P} \rightarrow \mathrm{Q} \rightarrow \mathrm{R}$, under steady state approximation to [Q], the variation of $[P],[Q]$ and $[R]$ with time are best represented by
(a)

(b)

(c)

(d)

13. In the reaction mechanism given

$$
\mathrm{X}+\mathrm{Y} \underset{\mathrm{k}_{2}, \mathrm{E}_{\mathrm{A}, 2}}{\stackrel{\mathrm{k}_{1} \cdot \mathrm{E}_{\mathrm{A}, 1}}{\rightleftharpoons}} \mathrm{Z} \xrightarrow{\mathrm{k}_{3}, \mathrm{E}_{\mathrm{A}, 3}} \mathrm{P}
$$

where, k 's represent rate constants, $\mathrm{E}_{\mathrm{A}}$ 's represent activation energies and $\mathrm{k}_{2} \gg \mathrm{k}_{3}$
The overall rate constant for the formation of P can be expressed as
a) $\mathrm{k}_{1} \mathrm{k}_{3} / \mathrm{k}_{2}$
b) $\mathrm{k}_{1}$
c) $\mathrm{k}_{1} /\left(\mathrm{k}_{2}+\mathrm{k}_{3}\right)$
d) $k_{1} /\left(k_{2}-k_{3}\right)$
14. The overall activation energy for the formation of $P$ can be expressed as
(a) $\frac{E_{A, 1} \cdot E_{A, 3}}{E_{A, 2}}$
(b) $\mathrm{E}_{\mathrm{A}, 1}$
(c) $\mathrm{E}_{\mathrm{A}, 1}+\mathrm{E}_{\mathrm{A}, 3}-\mathrm{E}_{\mathrm{A}, 2}$
(d) $\frac{E_{A, 1}}{E_{A, 2}+E_{A, 3}}$
15. For the reaction given below, the relaxation time is $10^{-6} \mathrm{~s}$. Given that $10 \%$ of A remains at equilibrium, the value of $\mathrm{k}_{1}\left(\mathrm{~s}^{-1}\right)$ is-

$$
\mathrm{A} \stackrel{\mathrm{k}_{1}}{\underset{\mathrm{k}_{-1}}{\rightleftharpoons}} \mathrm{~B}
$$

(a) $9 \times 10^{5}$
(b) $10^{-5}$
(c) $10^{5}$
(d) $9 \times 10^{-5}$
16. The mechanism of enzyme (E) catalyzed reaction of substrate ( S ) to yield product P is:

$$
\mathrm{E}+\mathrm{S} \underset{\mathrm{k}_{-1}}{\stackrel{\mathrm{k}_{1}}{\rightleftharpoons}}[\mathrm{ES}] \underset{\mathrm{k}_{-2}}{\stackrel{\mathrm{k}_{2}}{\rightleftharpoons}} \mathrm{E}+\mathrm{P} ; \quad \frac{-\mathrm{d}[\mathrm{~S}]}{\mathrm{dt}}=\frac{\mathrm{k}_{1} \mathrm{k}_{2}[\mathrm{~S}]_{0}+\mathrm{k}_{2} \mathrm{k}_{-2}[\mathrm{P}]}{\mathrm{k}_{1}[\mathrm{~S}]_{0}+\mathrm{k}_{-2}[\mathrm{P}]+\mathrm{k}_{-1}+\mathrm{k}_{2}}[\mathrm{E}]_{0}
$$

If a small amount of $S$ is converted to $P$, the maximum rate for the reaction will be observed for
(a) $\left(\mathrm{k}_{1}+\mathrm{k}_{2}\right) \gg \mathrm{k}_{1}[\mathrm{~S}]_{0}$
(b) $\left(\mathrm{k}_{-1}+\mathrm{k}_{2}\right) \ll \mathrm{k}_{1}[\mathrm{~S}]_{0}$
(c) $\left(\mathrm{k}_{1}+\mathrm{k}_{2}\right) \gg \mathrm{k}_{1}(\mathrm{~s})_{1}$
(d) $\mathrm{k}_{2} \ll \mathrm{k}_{1}$
17. The reaction $2 \mathrm{NO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g})$, Proceed via the followng mechanism

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

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) $\mathrm{k}_{\mathrm{a}}[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]$
18. The rate constants of two reactions at temperature $T$ are $k_{1}(T)$ and $k_{2}(T)$ and the corresponding activationenergies are $\mathrm{E}_{1}$ and $\mathrm{E}_{2}$ with $\mathrm{E} 2>\mathrm{E}_{1}$. When temperature is raised from $T_{1}$ and $T_{2}$, which one of the followingrelations 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) $\frac{\mathrm{k}_{1}\left(\mathrm{~T}_{2}\right)}{\mathrm{k}_{1}\left(\mathrm{~T}_{1}\right)}<\frac{\mathrm{k}_{2}\left(\mathrm{~T}_{2}\right)}{\mathrm{k}_{2}\left(\mathrm{~T}_{1}\right)}$
19. Consider an exothermic reaction

$$
A \xlongequal[\mathrm{k}_{-1}]{\stackrel{\mathrm{k}_{1}}{\rightleftharpoons}} \mathrm{I}
$$

As the temperature increases
(a) $\mathrm{k}_{1}, \mathrm{k}_{-1}$, and $\mathrm{k}_{1} / \mathrm{k}_{-1}$ increases
(b) $\mathrm{k}_{1}$ increases, $\mathrm{k}_{-1}$ decreases, and $\mathrm{k}_{1} / \mathrm{k}_{-1}$ increases.
(c) $\mathrm{k}_{1}, \mathrm{k}_{-1}$ increases and $\mathrm{k}_{1} / \mathrm{k}_{-1}$ decreases
(d) $\mathrm{k}_{1}$ and $\mathrm{k}_{-1}$ decrease, and $\mathrm{k}_{1} / \mathrm{k}_{-1}$ increases.
20. The rate constant for a unimolecular reaction was $2.66 \times 10^{-3} \mathrm{~s}^{-1}$ and $2.2 \times 10^{-1} \mathrm{~s}^{-1}$ at $\mathrm{T}=120 \mathrm{~K}$ and at $\mathrm{T}=360 \mathrm{~K}$ respectively. The rate constant (in s${ }^{-1}$ ) at 240 K would be
a) $2.4 \times 10^{-2} \mathrm{~s}^{-1}$
b) $2.4 \times 10^{-1} \mathrm{~s}^{-1}$
c) $4.8 \times 10^{-2} \mathrm{~s}^{-1}$
d) $1.8 \times 10^{-3} \mathrm{~s}^{-1}$
21. The decomposition of gaseous acetaldehyde at $T(K)$ follow the second order kinetics. The half-life of this reaction is 400 s when the initial pressure is 250 Torr. What will be the rate constant (in Torr ${ }^{-1} \mathrm{~s}^{-1}$ ) and half-life (in s) respectively, if the pressure of the acetaldehyde is 200 Torr at the same temperature?
a) $10^{5}$ and 500
b) $10^{-5}$ and 400
c) $10^{-4}$ and 400
d) $10^{-5}$ and 500
22. For a reaction, the rate constant k at $27^{0} \mathrm{C}$ was found to be $\mathrm{k}=5.4 \times 10^{-11} \mathrm{e}^{-50}$. The activation energy of the reaction is
a) $50 \mathrm{Jmol}^{-1}$
b) $415 \mathrm{Jmol}^{-1}$
c) $15000 \mathrm{Jmol}^{-1}$
d) $125,000 \mathrm{Jmol}^{-1}$
23. The concentrations of a species A undergoing the reaction $\mathrm{A} \rightarrow \mathrm{P}$ is $1.0,0.5,0.33,0.25$ moldm $^{-3}$ at $\mathrm{t}=0,1,2,3$ seconds respectively. The order of the reaction is:
a. a) two
b) one
c) zero
d) three
24. The rate equation for the reaction $2 \mathrm{AB}+\mathrm{B}_{2} \rightarrow 2 \mathrm{AB}_{2}$ is given by rate $=\mathrm{k}[\mathrm{AB}]\left[\mathrm{B}_{2}\right]$, a possible mechanism consistent with this rate law is
(a) $2 \mathrm{AB}+\mathrm{B}_{2} \xrightarrow{\text { slow }} 2 \mathrm{AB}_{2}$
$\mathrm{AB}+\mathrm{AB} \rightleftharpoons \mathrm{A}_{2} \mathrm{~B}_{2}$ (fast)
(b) $\mathrm{A}_{2} \mathrm{~B}_{2}+\mathrm{B}_{2} \xrightarrow{\text { slow }} 2 \mathrm{AB}_{2}$
$\mathrm{AB}+\mathrm{B}_{2} \xrightarrow{\text { slow }} \mathrm{AB}_{3}$
(c) $\mathrm{AB}_{3}+\mathrm{AB} \xrightarrow{\text { fast }} 2 \mathrm{AB}_{2}$

$$
\mathrm{AB}+\mathrm{B}_{2} \rightleftharpoons \mathrm{AB}_{3}(\text { fast })
$$

(d) $\mathrm{AB}_{3}+\mathrm{AB} \xrightarrow{\text { slow }} 2 \mathrm{AB}_{2}$
25. According to Arrhenius equation ( $k=$ rate constant and $T=$ temperature)
a) lnk decreases linearly with $1 / \mathrm{T}$
b) lnk decreases linearly with T
c) lnk increases linearly with $1 / \mathrm{T}$
d) $\ln k$ increases linearly with T
26. In the mechanism of the reaction, $\mathrm{H}_{2}+\mathrm{Br}_{2} \rightarrow 2 \mathrm{HBr}$, the first step is
a) dissociation of $\mathrm{H}_{2}$ into $\mathrm{H}^{\bullet}$ radicals
b) dissociation of $\mathrm{Br}_{2}$ into $\mathrm{Br}^{\bullet}$ radicals
c) reaction of $\mathrm{H}^{\bullet}$ radical with $\mathrm{Br}_{2}$
d) reaction of $\mathrm{Br}^{\bullet}$ radical with $\mathrm{H}_{2}$
27. In the reaction between NO and $\mathrm{H}_{2}$ the following data are obtained

Experiment I: $\mathrm{P}_{\mathrm{H}_{2}}=$ constant

| $\mathrm{P}_{\mathrm{NO}}(\mathrm{mm}$ of Hg$)$ | 359 | 300 | 152 |
| :--- | :--- | :--- | :--- |
| $\frac{-\mathrm{dP}_{\mathrm{NO}}}{\mathrm{dt}}$ | 1.50 | 1.03 | 0.25 |

Experiment II : $\mathrm{P}_{\mathrm{NO}}=$ constant

| $\mathrm{P}_{\mathrm{H}_{2}}(\mathrm{~mm}$ of Hg$)$ | 289 | 205 | 147 |
| :--- | :--- | :--- | :--- |
| $\frac{-\mathrm{dP}_{\mathrm{H}_{2}}}{\mathrm{dt}}$ | 1.60 | 1.10 | 0.79 |

28. The order with respect to $\mathrm{H}_{2}$ and NO , respectively are
2 and 1
b) 1 and 2
c) 3 and 1
d) 2 and 2
29. For the following sequence of reactions

$$
2 A \underset{k_{2}}{\stackrel{k_{1}}{\rightleftarrows}} 4 B+3 C ; 2 B \xrightarrow{k_{3}} P
$$

The $\frac{d[B]}{d t}$ is given by
(a) $\frac{1}{4} k_{1}[A]^{2}-\frac{1}{4} k_{2}[B]^{4}[C]^{3}-\frac{1}{2} k_{3}[B]^{2}$
(b) $\frac{1}{2} k_{1}[A]^{2}-\frac{1}{2} k_{2}[B]^{4}[C]^{3}-k_{3}[B]^{2}$
(c) $2 k_{1}[A]^{2}-2 k_{2}[B]^{4}[C]^{3}-k_{3}[B]^{2}$
(d) $4 k_{1}[A]^{2}-4 k_{2}[B]^{4}[C]^{3}-2 k_{3}[B]^{2}$
30. Consider the reactions,
a. $\mathrm{A}+\mathrm{B} \rightarrow$ product
b. $\mathrm{C}+\mathrm{D} \rightarrow$ product.

| Species | $\mathrm{M}(\mathrm{g} / \mathrm{mole})$ | Diameter <br> $(\mathrm{nm})$ |
| :---: | :--- | :--- |
| A | 2 | 1 |
| B | 4 | 2 |
| C | 6 | 3 |
| D | 4 | 4 |

The ratio of squares of pre-exponential factor of reaction (1) and reaction (2) is-
a) $1 / 2$
b) $3 / 4$
c) $1 / 4$
d) $2 / 3$
31. A second order reaction is $50 \%$ completed in 5 mins , the time required for $75 \%$ completion of the reaction is
a) 20 min
b) 25 min
c) 15 min
d) 18 min
32. For a given first order reaction, the reactant reduces to $1 / 4^{\text {th }}$ its initial value in 10 minutes. The rate constant of the reaction is:
a) $0.1386 \mathrm{~min}^{-1}$
b) $0.0693 \mathrm{~min}^{-1}$
c) $0.1386 \mathrm{molL}^{-1} \mathrm{~min}^{-1}$
d) $0.0693 \mathrm{molL}^{-1} \mathrm{~min}^{-1}$
33. The temperature dependence of a reaction is given by $\mathrm{k}=\mathrm{AT}^{5 / 2} \exp \left(-\mathrm{E}_{0} / \mathrm{RT}\right)$, the activation energy of the reaction given by
a) $\mathrm{E}_{0}+5 \mathrm{RT} / 2$
b) $\mathrm{E}_{0}+2 \mathrm{RT} / 5$
c) $\mathrm{E}_{0}+2 \mathrm{RT}$
d) $\mathrm{E}_{0}+5 \mathrm{RT}$
34. For a complex reaction $\mathrm{A} \rightarrow \mathrm{P}, \mathrm{Ea}_{1}=180 \mathrm{~kJ} / \mathrm{mol} ; \mathrm{Ea}_{2}=0 \mathrm{~kJ} / \mathrm{mol} ; \mathrm{Ea}_{3}=50 \mathrm{~kJ} / \mathrm{mol}$; overall constant k is related to individual rate constant by the equation

$$
k=\left(\frac{k_{1} \cdot k_{2}}{k_{3}}\right)^{2 / 3}
$$

Activation energy ( $\mathrm{kJ} / \mathrm{mol}$ ) for the overall reaction is:
a) 100
b) 43.44
c) 150
d) 140
35. A first order reaction is $50 \%$ completed in 20 minutes at $27^{\circ} \mathrm{C}$ and in 5 minutes at $47^{\circ} \mathrm{C}$. The energy of activation of the reaction is:
a) $43.85 \mathrm{~kJ} / \mathrm{mol}$
b) $55.14 \mathrm{~kJ} / \mathrm{mol}$
c) $11.97 \mathrm{~kJ} / \mathrm{mol}$
d) $6.65 \mathrm{~kJ} / \mathrm{mol}$

