## REVIEW QUESTIONS

## Chapter 14

1. Consider the reaction shown below:

$$
\mathrm{A}+3 \mathrm{~B} \rightarrow 2 \mathrm{C}+2 \mathrm{D}
$$

a) Express the rate of this reaction in terms of concentrations of A, B, C and D.
b) At some point in the reaction $[\mathrm{B}]=0.9986 \mathrm{M}$ and 13.20 minutes later $[B]=0.9746$. Based on this data, what is the average rate of the reaction during this time in $\mathrm{Ms}^{-1}$ ?
2. The following data was collected for the reaction shown below:

$$
2 \mathrm{HgCl}_{2}+\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-} \rightarrow 2 \mathrm{Cl}^{-}+2 \mathrm{CO}_{2}+\mathrm{Hg}_{2} \mathrm{Cl}_{2}
$$

| Expt. | $\left[\mathrm{HgCl}_{2}\right]$ <br> M | $\left[\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}\right]$ <br> M | Initial Rate <br> M min |
| :---: | :---: | :---: | :---: |
| 1 | 0.105 | 0.15 | $1.8 \times 10^{-5}$ |
| 2 | 0.105 | 0.30 | $7.1 \times 10^{-5}$ |
| 3 | 0.052 | 0.30 | $3.5 \times 10^{-5}$ |

Determine the rate law for this reaction.
3. The following data was collected for the reaction shown below:

$$
\mathrm{A}+\mathrm{B} \rightarrow \mathrm{C}+\mathrm{D}
$$

| Expt. | $[\mathrm{A}]$ <br> M | $[\mathrm{B}]$ <br> M | Initial Rate <br> $\mathrm{M} \mathrm{s}^{-1}$ |
| :---: | :---: | :---: | :---: |
| 1 | 0.185 | 0.133 | $3.35 \times 10^{-4}$ |
| 2 | 0.185 | 0.266 | $1.35 \times 10^{-3}$ |
| 3 | 0.370 | 0.133 | $6.75 \times 10^{-4}$ |
| 4 | 0.370 | 0.266 | $? ? ? ?$ |

a) Determine the rate law for this reaction.
b) Calculate the value of k for this reaction.
c) Calculate the rate of experiment 4 .
4. The thermal decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$ to form $\mathrm{NO}_{2}$ and $\mathrm{O}_{2}$ is a first order reaction. The rate constant for the reaction is $5.1 \times 10^{-4} \mathrm{~s}^{-1}$ at 318 K . Calculate the half-life of this reaction.
5. The thermal decomposition of phosphine $\left(\mathrm{PH}_{3}\right)$ to phosphorus and hydrogen gas is a first order reaction, with a half-life of 35 s at $680^{\circ} \mathrm{C}$.
a) Calculate the rate constant for this reaction.
b) Calculate the time required for $95 \%$ of phosphine to decompose.
6. The rate constant for the $2^{\text {nd }}$ order reaction shown below is $0.54 \mathrm{M}^{-1}$ at $300^{\circ} \mathrm{C}$. How many seconds would it take for the concentration of $\mathrm{NO}_{2}$ to decrease from 0.62 M to 0.28 M ?
7. The gas phase decomposition of $\mathrm{NO}_{2}$ to form NO and $\mathrm{O}_{2}$ was studied at $383^{\circ} \mathrm{C}$ and the following data was collected:

| Time $(\mathrm{s})$ | $\left[\mathrm{NO}_{2}\right], \mathrm{M}$ |
| :---: | :---: |
| 0.0 | 0.100 |
| 5.0 | 0.017 |
| 10.0 | 0.0090 |
| 15.0 | 0.0062 |
| 20.0 | 0.0047 |

Determine the order of this reaction with respect to $\left[\mathrm{NO}_{2}\right]$ and calculate the rate constant.
8. The reaction $2 \mathrm{~N}_{2} \mathrm{O}_{5} \rightarrow 4 \mathrm{NO}_{2}+\mathrm{O}_{2}$ has an activation energy of $100 \mathrm{~kJ} / \mathrm{mol}$ and an enthalpy of $-23 \mathrm{kj} / \mathrm{mol}$. Sketch a potential energy diagram for this reaction and determine the activation energy for the reverse reaction?
9. Shown below is an Arrhenius plot for the reaction:

$$
\mathrm{CO}(\mathrm{~g})+\mathrm{NO}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{NO}(\mathrm{~g})
$$

Based on this information, determine the activation energy $\left(\mathrm{E}_{\mathrm{a}}\right)$ and the frequency factor (A) for this reaction. (Estimate your calculations to 3 sig figs.)

10. The reaction $2 \mathrm{NO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g})$ was studied and the following mechanism was proposed:
(1) $\quad \mathrm{NO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \leftrightarrow \mathrm{NO}_{3}(\mathrm{~g}) \quad$ (fast)
(2) $\quad \mathrm{NO}_{3}(\mathrm{~g})+\mathrm{NO}(\mathrm{g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g}) \quad$ (slow)

Determine the rate law based on this mechanism.
11. Assuming the activation energies are equal, which of the following reactions will occur at a higher rate at $50^{\circ} \mathrm{C}$ ? (Hint: What factors affect the rate of a reaction)

$$
\begin{gathered}
\mathrm{NH}_{3}(\mathrm{~g})+\mathrm{HCl}(\mathrm{~g}) \rightarrow \mathrm{NH}_{4} \mathrm{Cl}(\mathrm{~s}) \\
\mathrm{N}\left(\mathrm{CH}_{3}\right)_{3}(\mathrm{~g})+\mathrm{HCl}(\mathrm{~g}) \rightarrow\left(\mathrm{CH}_{3}\right)_{3} \mathrm{NHCl}(\mathrm{~s})
\end{gathered}
$$

12. The following rate data was collected for the reaction shown below:

| $\mathrm{A}+\mathrm{B} \rightarrow \mathrm{C}+\mathrm{D}$ |  |  |  |
| :---: | :---: | :---: | :---: |
| Exp. \# | $[\mathrm{A}]$ <br> $(\mathrm{M})$ | $[\mathrm{B}]$ <br> $(\mathrm{M})$ | Initial Rate <br> $(\mathrm{M} / \mathrm{min})$ |
|  | 0.50 | 1.50 | $4.2 \times 10^{-3}$ |
| 2 | 1.50 | 1.50 | $1.3 \times 10^{-2}$ |
| 3 | 3.00 | 3.00 | $5.2 \times 10^{-2}$ |

Determine the Rate Law and calculate the rate constant (k) for this reaction.
13. The following mechanism has been proposed for reaction of HBr with $\mathrm{O}_{2}$ to form $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{Br}_{2}$

$$
\begin{gathered}
\mathrm{HBr}+\mathrm{O}_{2} \rightarrow \mathrm{HOOBr} \\
\mathrm{HOOBr}+\mathrm{HBr} \rightarrow 2 \mathrm{HOBr} \\
\mathrm{HOBr}+\mathrm{HBr} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{Br}_{2}
\end{gathered}
$$

a) Identify all reaction intermediates in this reaction.
b) Write a balanced overall equation for this reaction. (Hint: you may have to multiply all the coefficients of an elementary reaction before adding)
14. The following mechanism has been proposed for the reaction of NO with $\mathrm{H}_{2}$ to form $\mathrm{N}_{2} \mathrm{O}$ and $\mathrm{H}_{2} \mathrm{O}$.

$$
\begin{aligned}
2 \mathrm{NO}(\mathrm{~g}) & \rightarrow \mathrm{N}_{2} \mathrm{O}_{2}(\mathrm{~g}) \\
\mathrm{N}_{2} \mathrm{O}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g}) & \rightarrow \mathrm{N}_{2} \mathrm{O}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
\end{aligned}
$$

The observed rate law for this reaction is: Rate $=\mathrm{k}[\mathrm{NO}]^{2}\left[\mathrm{H}_{2}\right]$. If the proposed mechanism is correct, what can we conclude about the relative speeds of the first and the second steps?
15. The reaction below has been studied and the following experimental rate law determined:

$$
\mathrm{H}_{2}+2 \mathrm{ICl} \rightarrow 2 \mathrm{HCl}+\mathrm{I}_{2} \quad \text { Rate }=\mathrm{k}\left[\mathrm{H}_{2}\right][\mathrm{ICl}]
$$

Three mechanisms have been proposed for this reaction. Predict the rate law based on each mechanism and determine which is consistent with the experimental rate law?
a) $\quad 2 \mathrm{ICl}+\mathrm{H}_{2} \rightarrow 2 \mathrm{HCl}+\mathrm{I}_{2}$
b)

$$
\begin{align*}
& \mathrm{H}_{2}+\mathrm{ICl} \rightarrow \mathrm{HI}+\mathrm{HCl} \\
& \mathrm{HI}+\mathrm{ICl} \rightarrow \mathrm{HCl}+\mathrm{I}_{2}
\end{align*} \quad \text { (slow) }
$$

c)

$$
\begin{aligned}
& \mathrm{H}_{2}+\mathrm{ICl} \rightarrow \mathrm{HI}+\mathrm{HCl} \\
& \mathrm{HI}+\mathrm{ICl} \rightarrow \mathrm{HCl}+\mathrm{I}_{2}
\end{aligned}
$$

16. The following mechanism has been proposed for the catalyzed oxidation of thallium (I) by cerium (IV):

$$
\begin{aligned}
\mathrm{Ce}^{4+}+\mathrm{Mn}^{2+} & \rightarrow \mathrm{Ce}^{3+}+\mathrm{Mn}^{3+} \\
\mathrm{Ce}^{4+}+\mathrm{Mn}^{3+} & \rightarrow \mathrm{Ce}^{3+}+\mathrm{Mn}^{4+} \\
\mathrm{Tl}^{+}+\mathrm{Mn}^{4+} & \rightarrow \mathrm{Tl}^{3+}+\mathrm{Mn}^{2+}
\end{aligned}
$$

a) Identify the catalyst and the intermediates in this mechanism.
b) Determine the overall equation for this reaction.
c) Explain why the reaction would be slow without the catalyst.

