

## Lecture Presentation

## Chapter 13

## Chemical Kinetics

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## Reaction Rates

Chemical Kinetics: The area of chemistry concerned with reaction rates and the sequence of steps by which reactions occur

Reaction Rate: Either the increase in the concentration of a product per unit time or the decrease in the concentration of a reactant per unit time

## Reaction Rates

TABLE 13.1 Concentrations as a Function of Time at $55^{\circ} \mathrm{C}$ for the Reaction $2 \mathrm{~N}_{2} \mathrm{O}_{5}(\mathrm{~g}) \longrightarrow 4 \mathrm{NO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$

| Time (s) | $\mathbf{N}_{2} \mathbf{O}_{5}$ | Concentration (M) <br> $\mathbf{N O}_{2}$ | $\mathbf{O}_{2}$ |
| :--- | :--- | :--- | :--- |
| 0 | 0.0200 | 0 | 0 |
| 100 | 0.0169 | 0.0063 | 0.0016 |
| 200 | 0.0142 | 0.0115 | 0.0029 |
| 300 | 0.0120 | 0.0160 | 0.0040 |
| 400 | 0.0101 | 0.0197 | 0.0049 |
| 500 | 0.0086 | 0.0229 | 0.0057 |
| 600 | 0.0072 | 0.0256 | 0.0064 |
| 700 | 0.0061 | 0.0278 | 0.0070 |

Note that the concentrations of $\mathrm{NO}_{2}$ and $\mathrm{O}_{2}$ increase as the concentration of $\mathrm{N}_{2} \mathrm{O}_{5}$ decreases.

## Reaction Rates

## $2 \mathrm{~N}_{2} \mathrm{O}_{5}(g) \longrightarrow 4 \mathrm{NO}_{2}(g)+\mathrm{O}_{2}(g)$

The concentrations of $\mathrm{O}_{2}$ and $\mathrm{NO}_{2}$ increase as the concentration of $\mathrm{N}_{2} \mathrm{O}_{5}$ decreases.


The rate of formation of $\mathrm{O}_{2}$ is one-fourth the rate of formation of $\mathrm{NO}_{2}$ and one-half the rate of decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$.

## Reaction Rates

## $2 \mathrm{~N}_{2} \mathrm{O}_{5}(g) \longrightarrow 4 \mathrm{NO}_{2}(g)+\mathrm{O}_{2}(g)$

Rate of decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$ :

$$
\begin{aligned}
\frac{\Delta\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]}{\Delta t} & =\frac{-(0.0101 \mathrm{M}-0.0120 \mathrm{M})}{(400 \mathrm{~s}-300 \mathrm{~s})} \\
& =1.9 \times 10^{-5} \frac{\mathrm{M}}{\mathrm{~s}}
\end{aligned}
$$

## Reaction Rates

$$
2 \mathrm{~N}_{2} \mathrm{O}_{5}(g) \longrightarrow 4 \mathrm{NO}_{2}(g)+\mathrm{O}_{2}(g)
$$

## General rate of reaction:

$$
\text { rate }=-\frac{1}{2} \frac{\Delta\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]}{\Delta t}=\frac{1}{4} \frac{\Delta\left[\mathrm{NO}_{2}\right]}{\Delta t}=\frac{\Delta\left[\mathrm{O}_{2}\right]}{\Delta t}
$$

$$
a \mathrm{~A}+b \mathrm{~B} \longrightarrow d \mathrm{D}+e \mathrm{E}
$$

$$
\text { rate }=-\frac{1}{a} \frac{\Delta[\mathrm{~A}]}{\Delta t}=-\frac{1}{b} \frac{\Delta[\mathrm{~B}]}{\Delta t}=\frac{1}{d} \frac{\Delta[\mathrm{D}]}{\Delta t}=\frac{1}{e} \frac{\Delta[\mathrm{E}]}{\Delta t}
$$

## Reaction Rates

## $2 \mathrm{~N}_{2} \mathrm{O}_{5}(g) \longrightarrow 4 \mathrm{NO}_{2}(g)+\mathrm{O}_{2}(g)$



The slope of the tangent at time $t$ is defined as the instantaneous rate at that particular time. The initial rate is the slope of the tangent to the curve at $t=0$.

## Rate Laws and Reaction Order

Rate Law: An equation that shows the dependence of the reaction rate on the concentration of each reactant
$a \mathrm{~A}+b \mathrm{~B} \longrightarrow$ products
rate $\alpha[\mathrm{A}]^{m}[\mathrm{~B}]^{n}$
rate $=k[\mathrm{~A}]^{m}[\mathrm{~B}]^{n}$
$k$ is the rate constant.

## Rate Laws and Reaction Order

## The values of the exponents in the rate law must be determined by experiment; they cannot be deduced from the stoichiometry of the reaction.

TABLE 13.2 Balanced Chemical Equations and Experimentally Determined Rate Laws for Some Reactions

| Reaction | Rate Law |
| :--- | :--- |
| $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CBr}($ soln $)+\mathrm{H}_{2} \mathrm{O}($ soln $) \longrightarrow\left(\mathrm{CH}_{3}\right)_{3} \mathrm{COH}($ soln $)+\mathrm{H}^{+}($soln $)+\mathrm{Br}^{-}($soln $)$ | Rate $=k\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CBr}\right]$ |
| $\mathrm{HCO}_{2} \mathrm{H}(a q)+\mathrm{Br}_{2}(a q) \longrightarrow 2 \mathrm{H}^{+}(a q)+2 \mathrm{Br}^{-}(a q)+\mathrm{CO}_{2}(g)$ | Rate $=k\left[\mathrm{Br}_{2}\right]$ |
| $\mathrm{BrO}_{3}^{-}(a q)+5 \mathrm{Br}^{-}(a q)+6 \mathrm{H}^{+}(a q) \longrightarrow 3 \mathrm{Br}_{2}(a q)+3 \mathrm{H}_{2} \mathrm{O}(l)$ | Rate $=k\left[\mathrm{BrO}_{3}^{-}\right]\left[\mathrm{Br}^{-}\right]\left[\mathrm{H}^{+}\right]^{2}$ |
| $\mathrm{H}_{2}(g)+\mathrm{I}_{2}(g) \longrightarrow 2 \mathrm{HI}(g)$ | Rate $=k\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]$ |

In general, the exponents in the rate law are not the same as the stoichiometric coefficients in the balanced chemical equation for the reaction.
*In the first reaction, "(soln)" denotes a nonaqueous solution.

## Experimental Determination of a Rate Law

$$
\begin{gathered}
2 \mathrm{NO}(g)+\mathrm{O}_{2}(g) \longrightarrow 2 \mathrm{NO}_{2}(g) \\
\text { rate }=k[\mathrm{NO}]^{m}\left[\mathrm{O}_{2}\right]^{n}
\end{gathered}
$$

Compare the initial rates to the changes in initial concentrations.
TABLE 13.3 Initial Concentration and Rate Data for the Reaction $2 \mathrm{NO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{NO}_{2}(\mathrm{~g})$

| Experiment | Initial [NO] | Initial $\left[\mathbf{O}_{2}\right]$ | Initial Reaction Rate <br> $(\mathbf{M} / \mathbf{s})$ |
| :--- | :--- | :--- | :--- |
| 1 | 0.015 | 0.015 | 0.024 |
| 2 | 0.030 | 0.015 | 0.096 |
| 3 | 0.015 | 0.030 | 0.048 |
| 4 | 0.030 | 0.030 | 0.192 |

## Experimental Determination of a Rate Law

$$
\begin{gathered}
2 \mathrm{NO}(g)+\mathrm{O}_{2}(g) \longrightarrow 2 \mathrm{NO}_{2}(g) \\
\text { rate }=\mathrm{k}[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]^{n}
\end{gathered}
$$

The concentration of NO doubles, the concentration of $\mathrm{O}_{2}$ remains constant, and the rate quadruples.

$$
2^{m}=4 \quad m=2
$$

TABLE 13.3 Initial Concentration and Rate Data for the Reaction $2 \mathrm{NO}(g)+\mathrm{O}_{2}(g) \longrightarrow 2 \mathrm{NO}_{2}(g)$

| Experiment | Initial $[\mathbf{N O}]$ | Initial $\left[\mathbf{O}_{2}\right]$ | Initial Reaction Rate <br> $(\mathbf{M} / \mathbf{s})$ |
| :--- | :--- | :--- | :--- |
| 1 | 0.015 | 0.015 |  |
| 2 | 0.030 | 0.015 | 0.024 |
| 3 | 0.015 | 0.030 | 0.096 |
| 4 | 0.030 | 0.030 | 0.192 |

## Experimental Determination of a Rate Law

$$
\begin{gathered}
2 \mathrm{NO}(g)+\mathrm{O}_{2}(g) \longrightarrow 2 \mathrm{NO}_{2}(g) \\
\text { rate }=k[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]
\end{gathered}
$$

The concentration of $\mathrm{O}_{2}$ doubles, the concentration of NO remains constant, and the rate doubles.

$$
2^{n}=2 \quad n=1
$$

TABLE 13.3 Initial Concentration and Rate Data for the Reaction $2 \mathrm{NO}(g)+\mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{NO}_{2}(\mathrm{~g})$

| Experiment | Initial [NO] | Initial $\left[\mathbf{O}_{2}\right]$ | Initial Reaction Rate <br> $(\mathbf{M} / \mathbf{s})$ |
| :--- | :--- | :--- | :--- |
| 1 | 0.015 | 0.015 | 0.024 |
| 2 | 0.030 | 0.015 | 0.096 |
| 3 | 0.015 | 0.030 | 0.048 |
| 4 | 0.030 | 0.030 | 0.192 |

## Experimental Determination of a Rate Law

$$
\begin{gathered}
2 \mathrm{NO}(g)+\mathrm{O}_{2}(g) \longrightarrow 2 \mathrm{NO}_{2}(g) \\
\text { rate }=k[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]
\end{gathered}
$$

Reaction Order With Respect to a Reactant

- NO: second-order
- $\mathrm{O}_{2}$ : first-order

Overall Reaction Order

- $2+1=3$ (third-order)


## Experimental Determination of a Rate Law

$$
\begin{gathered}
2 \mathrm{NO}(g)+\mathrm{O}_{2}(g) \longrightarrow 2 \mathrm{NO}_{2}(g) \\
\text { rate }=k[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]
\end{gathered}
$$

Units of $k$ for this third-order reaction:

$$
k=\frac{\text { rate }}{\left[\mathrm{NO}^{2}\left[\mathrm{O}_{2}\right]\right.}=\frac{\frac{\mathrm{M}}{\mathrm{~s}}}{\left(\mathrm{M}^{2}\right)(\mathrm{M})}=\frac{1}{\mathrm{M}^{2} \mathrm{~s}}
$$

## Experimental Determination of a Rate Law

## $2 \mathrm{NO}(g)+\mathrm{O}_{2}(g) \longrightarrow 2 \mathrm{NO}_{2}(g)$ <br> rate $=k[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]$

| Rate Law | Overall Reaction Order | Units for $\boldsymbol{k}$ |
| :--- | :--- | :--- |
| Rate $=k$ | Zeroth order | $\mathrm{M} / \mathrm{s} \mathrm{or} \mathrm{M} \mathrm{s}^{-1}$ |
| Rate $=k[\mathrm{~A}]$ | First order | $1 / \mathrm{sor} \mathrm{s}^{-1}$ |
| Rate $=k[\mathrm{~A}][\mathrm{B}]$ | Second order | $1 /(\mathrm{M} \cdot \mathrm{s})$ or $\mathrm{M}^{-1} \mathrm{~s}^{-1}$ |
| Rate $=k[\mathrm{~A}][\mathrm{B}]^{2}$ | Third order | $1 /\left(\mathrm{M}^{2} \cdot \mathrm{~s}\right){\text { or } \mathrm{M}^{-2} \mathrm{~s}^{-1}}^{\text {R }}$ |

## Zeroth-Order Reactions

A plot of [A] versus time gives a straight-line fit and the slope will be $-\boldsymbol{k}$.


Time

## Zeroth-Order Reactions

For a zeroth-order reaction, the rate is independent of the concentration of the reactant.

$$
\begin{gathered}
\mathrm{A} \longrightarrow \text { product(s) } \\
\text { rate }=k[\mathrm{~A}]^{0}=\mathrm{k} \quad-\frac{\Delta[\mathrm{A}]}{\Delta t}=k
\end{gathered}
$$

Calculus can be used to derive an integrated rate law.


## Zeroth-Order Reactions

## $2 \mathrm{NH}_{3}(g) \longrightarrow \mathrm{N}_{2}(g)+3 \mathrm{H}_{2}(g)$

## rate $=k\left[\mathrm{NH}_{3}\right]^{0}=k$

Most of the $\mathrm{NH}_{3}$ molecules are in the gas phase above the surface and are unable to react.


Because only the $\mathrm{NH}_{3}$ molecules on the surface react under these conditions, the reaction rate is independent of the total concentration of $\mathrm{NH}_{3}$.

## Integrated Rate Law for a First-Order Reaction

$$
\begin{gathered}
\mathrm{A} \longrightarrow \text { product(s) } \\
\text { rate }=k[\mathrm{~A}] \quad-\frac{\Delta[\mathrm{A}]}{\Delta t}=k[\mathrm{~A}]
\end{gathered}
$$

Calculus can be used to derive an integrated rate law.

$$
\begin{aligned}
& \qquad \ln \left(\frac{[\mathrm{A}]_{t}}{[\mathrm{~A}]_{0}}\right)=-k t\left\{\begin{array}{cc}
{[\mathrm{A}]_{t}} & \text { concentration of } \mathrm{A} \text { at time } t \\
{[\mathrm{~A}]_{0}} & \text { initial concentration of } \mathrm{A}
\end{array}\right. \\
& \text { Using: } \ln \left(\frac{\mathrm{x}}{\mathrm{y}}\right)=\ln (x)-\ln (y) \quad \begin{array}{c}
\ln [\mathrm{A}]_{t}=-\mathrm{k} t+\ln [\mathrm{A}]_{0} \\
\mathrm{y}=\mathrm{mx}+\mathrm{b}
\end{array}
\end{aligned}
$$

## Integrated Rate Law for a First-Order Reaction

$$
\begin{aligned}
\ln [\mathrm{A}]_{t} & =-k \boldsymbol{t}+\ln [\mathrm{A}]_{0} \\
y & =m x+b
\end{aligned}
$$

A plot of $\operatorname{In}[A]$ versus time gives a straight-line fit and the slope will be $-k$.

## Integrated Rate Law for a First-Order Reaction

$$
\ln [\mathrm{A}]_{t}=-k \boldsymbol{t}+\ln [\mathrm{A}]_{0}
$$

(a) Reactant concentration versus time


# This is a plot of [A] versus time. 

## The best-fit is a curve and not a line.

## Integrated Rate Law for a First-Order Reaction

## $\ln [\mathrm{A}]_{t}=-k t+\ln [\mathrm{A}]_{0}$

(a) Reactant concentration versus time


Time $\longrightarrow$
(b) Natural logarithm of reactant concentration versus time


Time $\longrightarrow$

## Integrated Rate Law for a First-Order Reaction

$$
\begin{gathered}
2 \mathrm{~N}_{2} \mathrm{O}_{5}(g) \longrightarrow 4 \mathrm{NO}_{2}(g)+\mathrm{O}_{2}(g) \\
\text { rate }=k\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]
\end{gathered}
$$

| Time (s) | $\left[\mathbf{N}_{\mathbf{2}} \mathrm{O}_{5}\right]$ | $\ln \left[\mathrm{N}_{\mathbf{2}} \mathrm{O}_{5}\right]$ |
| :---: | :---: | :---: |
| 0 | 0.0200 | -3.912 |
| 100 | 0.0169 | -4.080 |
| 200 | 0.0142 | -4.255 |
| 300 | 0.0120 | -4.423 |
| 400 | 0.0101 | -4.595 |
| 500 | 0.0086 | -4.756 |
| 600 | 0.0072 | -4.934 |
| 700 | 0.0061 | -5.099 |



Slope $=-k$

## Integrated Rate Law for a First-Order Reaction

$$
\begin{gathered}
2 \mathrm{~N}_{2} \mathrm{O}_{5}(g) \longrightarrow 4 \mathrm{NO}_{2}(g)+\mathrm{O}_{2}(g) \\
\text { rate }=k\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]
\end{gathered}
$$

Calculate the slope:
$\frac{-5.02-(-4.17)}{650 s-150 s}=-0.0017 \frac{1}{s}$

$$
k=0.0017 \frac{1}{\mathrm{~s}}
$$

Slope $=-k$


## Half-Life of a First-Order Reaction

Half-Life: The time required for the reactant concentration to drop to one-half of its initial value

$$
\begin{gathered}
\mathrm{A} \longrightarrow \operatorname{product}(\mathrm{~s}) \\
\operatorname{rate}=k[\mathrm{~A}] \\
\ln \left(\frac{[\mathrm{A}]_{t}}{[\mathrm{~A}]_{0}}\right)=-k t\left\{\begin{array}{l}
t=t_{1 / 2} \\
{[\mathrm{~A}]_{t_{1 / 2}}=\frac{[\mathrm{A}]_{0}}{2}}
\end{array}\right. \\
\ln \left(\frac{1}{2}\right)=-k t_{1 / 2} \text { or } t_{1 / 2}=\frac{0.693}{k}
\end{gathered}
$$

## Half-Life of a First-Order Reaction

$$
t_{1 / 2}=\frac{0.693}{k}
$$

For a first-order reaction, the half-life is independent of the initial concentration.

## Each successive half-life is an equal period of time.



## Radioactive Decay Rates

$$
\begin{gathered}
{ }_{6}^{14} \mathrm{C} \longrightarrow{ }_{7}^{14} \mathrm{~N}+{ }_{-1}^{0} \mathrm{e} \\
t_{1 / 2}=5715 \mathrm{y} \\
\text { Decay rate }=-\frac{\Delta \mathrm{N}}{\Delta t}=k \mathrm{~N}
\end{gathered}
$$

## Second-Order Reactions

$$
\begin{gathered}
\mathrm{A} \longrightarrow \text { product(s) } \\
\text { rate }=k[\mathrm{~A}]^{2} \quad-\frac{\Delta[\mathrm{A}]}{\Delta \mathrm{D} t}=k[\mathrm{~A}]^{2}
\end{gathered}
$$

Calculus can be used to derive an integrated rate law.


## Second-Order Reactions

## $2 \mathrm{NO}_{2}(g) \longrightarrow 2 \mathrm{NO}(g)+\mathrm{O}_{2}(g)$

| Time (s) | $\left[\mathrm{NO}_{2}\right]$ | $\ln \left[\mathrm{NO}_{2}\right]$ | $\mathbf{1} /\left[\mathrm{NO}_{2}\right]$ |
| :---: | :---: | :---: | :---: |
| 0 | $8.00 \times 10^{-3}$ | -4.828 | 125 |
| 50 | $6.58 \times 10^{-3}$ | -5.024 | 152 |
| 100 | $5.59 \times 10^{-3}$ | -5.187 | 179 |
| 150 | $4.85 \times 10^{-3}$ | -5.329 | 206 |
| 200 | $4.29 \times 10^{-3}$ | -5.451 | 233 |
| 300 | $3.48 \times 10^{-3}$ | -5.661 | 287 |
| 400 | $2.93 \times 10^{-3}$ | -5.833 | 341 |
| 500 | $2.53 \times 10^{-3}$ | -5.980 | 395 |

## Second-Order Reactions

$$
2 \mathrm{NO}_{2}(g) \longrightarrow 2 \mathrm{NO}(g)+\mathrm{O}_{2}(g)
$$



# Plotting $\operatorname{In}\left[\mathrm{NO}_{2}\right]$ versus time gives a curve and not a straight-line fit. 

Therefore, this is not a firstorder reaction.

## Second-Order Reactions

$$
2 \mathrm{NO}_{2}(g) \longrightarrow 2 \mathrm{NO}(g)+\mathrm{O}_{2}(g)
$$

## Plotting $\frac{1}{\left[\mathrm{NO}_{2}\right]}$ versus <br> $\left[\mathrm{NO}_{2}\right]$

time gives a straight-line fit.
Therefore, this is a secondorder reaction.

## Slope $=k$



## Second-Order Reactions

$$
2 \mathrm{NO}_{2}(g) \longrightarrow 2 \mathrm{NO}(g)+\mathrm{O}_{2}(g)
$$

Calculate the slope:
Slope $=k$
$\frac{(340-150) \frac{1}{M}}{400 \mathrm{~s}-50 \mathrm{~s}}=0.54 \frac{1}{\mathrm{Ms}}$

$$
k=0.54 \frac{1}{\mathrm{M} \mathrm{~s}}
$$



## Second-Order Reactions

Half-life for a second-order reaction
$\mathrm{A} \longrightarrow$ product(s)
rate $=k[\mathrm{~A}]^{2}$

$$
\begin{aligned}
& \frac{1}{[\mathrm{~A}]_{t}}=k t+\frac{1}{[\mathrm{~A}]_{0}} \quad\left\{\begin{array}{l}
t=\boldsymbol{t}_{1 / 2} \\
{[\mathrm{~A}]_{t_{1 / 2}}=\frac{[\mathrm{A}]_{0}}{2}}
\end{array}\right. \\
& \frac{2}{[\mathrm{~A}]_{0}}=k t_{1 / 2}+\frac{1}{[\mathrm{~A}]_{0}} \quad t_{1 / 2}=\frac{1}{k[\mathrm{~A}]_{0}}
\end{aligned}
$$

## Second-Order Reactions

$$
t_{1 / 2}=\frac{1}{k[\mathrm{~A}]_{0}}
$$

## For a second-order reaction, the half-life is dependent on the initial concentration.

## Each successive half-life is twice as long as the preceding one.

## TABLE 13.4 Characteristics of Zeroth-, First-, and Second-Order Reactions of the

 Type A $\rightarrow$ Products|  | Zeroth-Order | First-Order | Second-Order |
| :---: | :---: | :---: | :---: |
| Rate law | $-\frac{\Delta[\mathrm{A}]}{\Delta t}=k$ | $-\frac{\Delta[\mathrm{A}]}{\Delta t}=k[\mathrm{~A}]$ | $-\frac{\Delta[\mathrm{A}]}{\Delta t}=k[\mathrm{~A}]^{2}$ |
| Integrated Rate Law | $[\mathrm{A}]_{t}=-k t+[\mathrm{A}]_{0}$ | $\ln [\mathrm{A}]_{t}=-k t+\ln [\mathrm{A}]_{0}$ | $\frac{1}{[\mathrm{~A}]_{t}}=k t+\frac{1}{[\mathrm{~A}]_{0}}$ |
| Linear graph | [A] versus $t$ | $\ln [\mathrm{A}]$ versus $t$ | $\frac{1}{[\mathrm{~A}]} \text { versus } t$ |
|  | [A] |  |  |
| Graphical determination of $k$ | $k=-($ Slope $)$ | $k=-($ Slope $)$ | $k=$ Slope |
| Half-life | $t_{1 / 2}=\frac{[\mathrm{A}]_{0}}{2 k}$ <br> (not constant) | $\begin{aligned} & t_{1 / 2}=\frac{0.693}{k} \\ & \text { (constant) } \end{aligned}$ | $t_{1 / 2}=\frac{1}{k[\mathrm{~A}]_{0}}$ <br> (not constant) |

## Reaction Rates and Temperature: The Arrhenius Equation

Typically, as the temperature increases, the rate of reaction increases.

$$
\begin{gathered}
2 \mathrm{~N}_{2} \mathrm{O}_{5}(g) \longrightarrow 4 \mathrm{NO}_{2}(g)+\mathrm{O}_{2}(g) \\
\text { rate }=k\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]
\end{gathered}
$$

The rate constant is dependent on temperature.

## Reaction Rates and Temperature: The Arrhenius Equation

Magnesium is inert<br>in cold water.

Magnesium reacts
in hot water.


$$
\mathrm{Mg}(s)+2 \mathrm{H}_{2} \mathrm{O}(l) \longrightarrow \mathrm{Mg}^{2+}(a q)+2 \mathrm{OH}^{-}(a q)+\mathrm{H}_{2}(g)
$$

The formation of bubbles of gas and the pink color of phenolphthalein, which indicates an alkaline solution, provide evidence of the reaction.

## Reaction Rates and Temperature: The Arrhenius Equation

Transition State: The configuration of atoms at the maximum in the potential energy profile. This is also called the activated complex.


Reaction progress $\longrightarrow$

## Reaction Rates and Temperature: The Arrhenius Equation

Collision Theory: As the average kinetic energy increases, the average molecular speed increases, and thus the collision rate increases.


# Reaction Rates and Temperature: The Arrhenius Equation 

$$
k=A e^{-E_{\mathrm{a}} / R T}
$$

k Rate constant

A Collision frequency factor
$E_{\mathrm{a}} \quad$ Activation energy
$\boldsymbol{R}$ Gas constant
$\boldsymbol{T} \quad$ Temperature (K)

## Using the Arrhenius Equation

$$
\begin{gathered}
\ln (k)=\ln (A)+\ln \left(\mathrm{e}^{-E_{a} / R T}\right) \\
\ln (k)=\ln (A)-\frac{E_{\mathrm{a}}}{R T} \xrightarrow[\begin{array}{c}
\text { rearrange } \\
\text { the equation }
\end{array}]{\ln (k)=\left(\frac{-E_{\mathrm{a}}}{R}\right)\left(\frac{1}{T}\right)+\ln (A)} \\
y=m x+b
\end{gathered}
$$

## Reaction Mechanisms

Reaction Mechanism: A sequence of reaction steps that describes the pathway from reactants to products

Elementary Reaction (step): A single step in a reaction mechanism

## Reaction Mechanisms

An elementary reaction describes an individual molecular event.

The overall reaction describes the reaction stoichiometry and is a summation of elementary reactions.

## Reaction Mechanisms

Experimental evidence suggests that the reaction between $\mathrm{NO}_{2}$ and CO takes place by a two-step mechanism:
$\mathrm{NO}_{2}(g)+\mathrm{NO}_{2}(g) \longrightarrow \mathrm{NO}(g)+\mathrm{NO}_{3}(g)$ elementary reaction
$\mathrm{NO}_{3}(g)+\mathrm{CO}(g) \longrightarrow \mathrm{NO}_{2}(g)+\mathrm{CO}_{2}(g)$ elementary reaction
$\mathrm{NO}_{2}(g)+\mathrm{CO}(g) \longrightarrow \mathrm{NO}(g)+\mathrm{CO}_{2}(g)$ overall reaction

## Reaction Mechanisms

$\mathrm{NO}_{2}(g)+\mathrm{NO}_{2}(g) \longrightarrow \mathrm{NO}(g)+\mathrm{NO}_{3}(g)$

$\mathrm{NO}_{3}(g)+\mathrm{CO}(g) \longrightarrow \mathrm{NO}_{2}(g)+\mathrm{CO}_{2}(g)$

## Reaction Mechanisms

Experimental evidence suggests that the reaction between $\mathrm{NO}_{2}$ and CO takes place by a two-step mechanism:
$\mathrm{NO}_{2}(g)+\mathrm{NO}_{2}(g) \longrightarrow \mathrm{NO}(g)+\mathrm{NO}_{3}(g)$ elementary reaction
$\mathrm{NO}_{3}(g)+\mathrm{CO}(g) \longrightarrow \mathrm{NO}_{2}(g)+\mathrm{CO}_{2}(g)$ elementary reaction
$\mathrm{NO}_{2}(g)+\mathrm{CO}(g) \longrightarrow \mathrm{NO}(g)+\mathrm{CO}_{2}(g)$ overall reaction

A reactive intermediate is formed in one step and consumed in a subsequent step.

## Reaction Mechanisms-Molecularity

Molecularity: A classification of an elementary reaction based on the number of molecules (or atoms) on the reactant side of the chemical equation

# Reaction Mechanisms-Molecularity 

## Unimolecular Reaction

$$
\mathrm{O}_{3}{ }^{*}(g) \longrightarrow \mathrm{O}_{2}(g)+\mathrm{O}(g)
$$



# Reaction Mechanisms-Molecularity 

## Bimolecular Reaction

$$
\mathrm{O}_{3}(g)+\mathrm{O}(g) \longrightarrow 2 \mathrm{O}_{2}(g)
$$



# Reaction Mechanisms-Molecularity 

Termolecular Reaction
$\mathrm{O}(g)+\mathrm{O}(g)+\mathrm{M}(g) \longrightarrow \mathrm{O}_{2}(g)+\mathrm{M}(g)$


## Rate Laws for Elementary Reactions

The rate law for an elementary reaction follows directly from its molecularity because an elementary reaction is an individual molecular event.

## Rate Laws for Elementary Reactions

## Unimolecular Reaction

$$
\mathrm{O}_{3}{ }^{*}(g) \longrightarrow \mathrm{O}_{2}(g)+\mathrm{O}(g) \quad \text { rate }=k\left[\mathrm{O}_{3}\right]
$$

Bimolecular Reaction

$$
\mathrm{O}_{3}(g)+\mathrm{O}(g) \longrightarrow 2 \mathrm{O}_{2}(g) \quad \text { rate }=k\left[\mathrm{O}_{3}\right][\mathrm{O}]
$$

## Termolecular Reaction

$$
\mathrm{O}(g)+\mathrm{O}(g)+\mathrm{M}(g) \longrightarrow \mathrm{O}_{2}(g)+\mathrm{M}(g) \quad \text { rate }=k[\mathrm{O}]^{2}[\mathrm{M}]
$$

## Rate Laws for Elementary Reactions

## TABLE 13.5 Rate Laws for Elementary Reactions

| Elementary Reaction | Molecularity | Rate Law |
| :--- | :--- | :--- |
| $\mathrm{A} \rightarrow$ Products | Unimolecular | Rate $=k[\mathrm{~A}]$ |
| $\mathrm{A}+\mathrm{A} \rightarrow$ Products | Bimolecular | Rate $=k[\mathrm{~A}]^{2}$ |
| $\mathrm{~A}+\mathrm{B} \rightarrow$ Products | Bimolecular | Rate $=k[\mathrm{~A}][\mathrm{B}]$ |
| $\mathrm{A}+\mathrm{A}+\mathrm{B} \rightarrow$ Products | Termolecular | Rate $=k[\mathrm{~A}]^{2}[\mathrm{~B}]$ |
| $\mathrm{A}+\mathrm{B}+\mathrm{C} \rightarrow$ Products | Termolecular | Rate $=k[\mathrm{~A}][\mathrm{B}][\mathrm{C}]$ |

## Rate Laws for Overall Reactions

Rate-Determining Step: The slow step in a reaction mechanism since it acts as a bottleneck and limits the rate at which reactants can be converted to products

## Rate Laws for Overall Reactions

## Multistep Reactions with an Initial Slow Step

$\mathrm{NO}_{2}(g)+\mathrm{NO}_{2}(g) \xrightarrow{k_{1}} \mathrm{NO}(g)+\mathrm{NO}_{3}(g)$ slow step
$\mathrm{NO}_{3}(g)+\mathrm{CO}(g) \xrightarrow{k_{2}} \mathrm{NO}_{2}(g)+\mathrm{CO}_{2}(g)$ fast step
$\mathrm{NO}_{2}(g)+\mathrm{CO}(g) \longrightarrow \mathrm{NO}(g)+\mathrm{CO}_{2}(g)$ overall reaction

Based on the slow step: rate $=\boldsymbol{k}_{\mathbf{1}}\left[\mathrm{NO}_{\mathbf{2}}\right]^{\mathbf{2}}$

Rate Laws for Overall Reactions

## Multistep Reactions with an Initial Fast Step

$$
2 \mathrm{NO}(g) \stackrel{k_{1}}{\underset{K_{-1}}{ }} \mathrm{~N}_{2} \mathrm{O}_{2}(g)
$$

$\mathrm{N}_{2} \mathrm{O}_{2}(g)+\mathrm{H}_{2}(g) \xrightarrow{k_{2}} \mathrm{~N}_{2} \mathrm{O}(g)+\mathrm{H}_{2} \mathrm{O}(g)$ slow step
$\mathrm{N}_{2} \mathrm{O}(g)+\mathrm{H}_{2}(g) \xrightarrow{k_{3}} \mathrm{~N}_{2}(g)+\mathrm{H}_{2} \mathrm{O}(g)$ fast step
$2 \mathrm{NO}(g)+2 \mathrm{H}_{2}(g) \longrightarrow \mathrm{N}_{2}(g)+2 \mathrm{H}_{2} \mathrm{O}(g)$ overall reaction Based on the slow step: rate $=\boldsymbol{k}_{\mathbf{2}}\left[\mathbf{N}_{\mathbf{2}} \mathrm{O}_{2}\right]\left[\mathrm{H}_{\mathbf{2}}\right]$

## Rate Laws for Overall Reactions

$$
\text { rate }=k_{2}\left[\mathrm{~N}_{2} \mathrm{O}_{2}\right]\left[\mathrm{H}_{2}\right]
$$

intermediate
First step: $\quad$ Rate $_{\text {forward }}=k_{1}[\mathrm{NO}]^{2} \quad$ Rate reverse $=k_{-1}\left[\mathrm{~N}_{2} \mathrm{O}_{2}\right]$

$$
k_{1}[\mathrm{NO}]^{2}=k_{-1}\left[\mathrm{~N}_{2} \mathrm{O}_{2}\right]
$$



## Rate Laws for Overall Reactions

## Procedure for Studying Reaction Mechanisms



## Using the Arrhenius Equation

$\ln (k)=\left(\frac{-E_{\mathrm{a}}}{R}\right)\left(\frac{1}{T}\right)+\ln (A)$


Plot $\ln (\boldsymbol{k})$ versus $\frac{\mathbf{1}}{\boldsymbol{T}}$

## Catalysis

Catalyst: A substance that increases the rate of a reaction without itself being consumed in the reaction. A catalyst is used in one step and regenerated in a later step.

$$
\mathrm{H}_{2} \mathrm{O}_{2}(\mathrm{aq})+\mathrm{I}^{1-(a q)} \longrightarrow \mathrm{H}_{2} \mathrm{O}(\Lambda)+\mathrm{IO}^{1-}(\mathrm{aq})
$$

rate-determining step

$$
\mathrm{H}_{2} \mathrm{O}_{2}(a q)+10^{1-}(a q) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\lambda)+\mathrm{O}_{2}(g)+\mathrm{I}^{1-}(a q) \text { fast step }
$$

$$
2 \mathrm{H}_{2} \mathrm{O}_{2}(\mathrm{aq}) \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}(\Lambda)+\mathrm{O}_{2}(g) \quad \text { overall reaction }
$$

## Catalysis

Since the catalyst is involved in the rate determining step, it often appears in the rate law.

$$
\text { rate }=k\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]\left[\mathrm{I}^{1-}\right]
$$

$$
\mathrm{H}_{2} \mathrm{O}_{2}(\mathrm{aq})+\mathrm{I}^{1-(a q)} \longrightarrow \mathrm{H}_{2} \mathrm{O}(\Lambda)+\mathrm{IO}^{1-}(a q) \begin{gathered}
\text { rate-determining } \\
\text { step }
\end{gathered}
$$

$$
\mathrm{H}_{2} \mathrm{O}_{2}(a q)+\mathrm{IO}^{1-}(a q) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\Lambda)+\mathrm{O}_{2}(g)+\mathrm{I}^{1-}(a q) \text { fast step }
$$

$$
2 \mathrm{H}_{2} \mathrm{O}_{2}(a q) \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}(\Lambda)+\mathrm{O}_{2}(g) \quad \text { overall reaction }
$$

## Catalysis

The rate of decomposition of aqueous hydrogen peroxide can be monitored qualitatively by collecting the evolved oxygen gas in a balloon.


In the absence of a catalyst, little $\mathrm{O}_{2}$ is produced.


After addition of aqueous sodium iodide, by opening the stopcock to add Nal, the balloon rapidly inflates with $\mathrm{O}_{2}$.

## Catalysis

(a) Catalyzed pathway


Reaction progress $\longrightarrow$
(b) Uncatalyzed pathway


The activation energy $E_{\mathrm{a}}$ is lower for the catalyzed pathway. The shape of the barrier for the catalyzed pathway applies to the decomposition of $\mathrm{H}_{2} \mathrm{O}_{2}$.

## Homogeneous and Heterogeneous Catalysts

Homogeneous Catalyst: A catalyst that exists in the same phase as the reactants

Heterogeneous Catalyst: A catalyst that exists in a different phase from that of the reactants

## Homogeneous and Heterogeneous Catalysts


(a) $\mathrm{H}_{2}$ and $\mathrm{C}_{2} \mathrm{H}_{4}$ are adsorbed on the metal surface.

(c) One H atom forms a bond to a C atom of the adsorbed $\mathrm{C}_{2} \mathrm{H}_{4}$ to give a metal-bonded $\mathrm{C}_{2} \mathrm{H}_{5}$ group. A second H atom bonds to the $\mathrm{C}_{2} \mathrm{H}_{5}$ group.

(b) The $\mathrm{H}-\mathrm{H}$ bond breaks as H -metal bonds form, and the H atoms move about on the surface.

(d) The resulting $\mathrm{C}_{2} \mathrm{H}_{6}$ molecule is desorbed from the surface.

## Homogeneous and Heterogeneous Catalysts

## TABLE 13.6 Some Heterogeneous Catalysts Used in Commercially Important Reactions

| Reaction | Catalyst | Commercial Process | Product: Commercial Uses |
| :---: | :---: | :---: | :---: |
| $2 \mathrm{SO}_{2}+\mathrm{O}_{2} \longrightarrow 2 \mathrm{SO}_{3}$ | Pt or $\mathrm{V}_{2} \mathrm{O}_{5}$ | Intermediate step in the contact process for synthesis of sulfuric acid | $\mathrm{H}_{2} \mathrm{SO}_{4}$ : Manufacture of fertilizers, chemicals; oil refining |
| $4 \mathrm{NH}_{3}+5 \mathrm{O}_{2} \longrightarrow 4 \mathrm{NO}+6 \mathrm{H}_{2} \mathrm{O}$ | Pt and Rh | First step in the Ostwald process for synthesis of nitric acid | $\mathrm{HNO}_{3}$ : Manufacture of explosives, fertilizers, plastics, dyes, lacquers |
| $\mathrm{N}_{2}+3 \mathrm{H}_{2} \longrightarrow 2 \mathrm{NH}_{3}$ | $\mathrm{Fe}, \mathrm{K}_{2} \mathrm{O}$, and $\mathrm{Al}_{2} \mathrm{O}_{3}$ | Haber process for synthesis of ammonia | $\mathrm{NH}_{3}$ : Manufacture of fertilizers, nitric acid |
| $\mathrm{H}_{2} \mathrm{O}+\mathrm{CH}_{4} \longrightarrow \mathrm{CO}+3 \mathrm{H}_{2}$ | Ni | Steam-hydrocarbon re-forming process for synthesis of hydrogen | $\mathrm{H}_{2}$ : Manufacture of ammonia, methanol |
| $\mathrm{CO}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{CO}_{2}+\mathrm{H}_{2}$ | ZnO and CuO | Water-gas shift reaction to improve yield in the synthesis of $\mathrm{H}_{2}$ | $\mathrm{H}_{2}$ : Manufacture of ammonia, methanol |
| $\mathrm{CO}+2 \mathrm{H}_{2} \longrightarrow \mathrm{CH}_{3} \mathrm{OH}$ | $\mathrm{Cu}, \mathrm{ZnO}$, and $\mathrm{Al}_{2} \mathrm{O}_{3}$ | Industrial synthesis of methanol | $\mathrm{CH}_{3} \mathrm{OH}$ : Manufacture of plastics, adhesives, gasoline additives; industrial solvent |
|  | $\mathrm{Ni}, \mathrm{Pd}$, or Pt | Catalytic hydrogenation of compounds with $\mathrm{C}=\mathrm{C}$ bonds as in conversion of unsaturated vegetable oils to solid fats | Food products: margarine, shortening |

