## CHEM 102

## General Chemistry II

## CHEM 101 Review

## $>$ Units

Mass, Temperature, Amount, Volume, Dimensional analysis, Density, Uncertainties, and Significant Figures.
$>$ Periodic Table, Atoms, and Ions
$\underset{\text { Atomic Number } \longrightarrow \mathrm{Z}}{\text { Mass Number }} \mathrm{X}^{ \pm \mathrm{c}}$ Element Symbol
$>$ Stiochiometry


## $>$ Concentration units

Mass Percent (\%), Mole Fraction (X), Molarity(M), Molality (m), Normality (N)

## CHEM 101 Review

$>$ Reaction: Balance and Stoichiometry
Types: Precipitation, Acid-base, Redox..

$>$ Thermochemistry
First law of thermodynamics: $\Delta E=q+w$

$$
q=\mathrm{C} \Delta t=m s \Delta t \quad \text { and } \quad w_{\text {exp }}=-P \Delta V
$$

$>$ Gas Laws

$$
P \times V=n R T \quad<\text { Ideal Gas Law }
$$



## CHEM 101 Review

$>$ Molecules and Geometry
Ionic, Covalent, Lewis Structure, VSEPR, Hybridization, Molecular Orbital Model
$>$ Liquid and Solids
IMF (Dipole-dipole, Dispersion, Hydrogen Bonding), Solids (Unit cell-SC, BCC, FCC),..


Octahedral

$>$ Properties of Solutions
Vapor Pressure Lowering, Boiling Point, Elevation
 Freezing Point Depression, Osmotic Pressure..



## Course Outline

Chemical Kinetics (Chap.12)
Chemical Equilibrium (Chap. 13)
Acid-Base and Aqueous Equilibria (chap. 14 \& 15)
Spontaneity, Entropy, and Free Energy (Chap. 16)
Electrochemistry (chap. 17)
The nucleus: A chemist View (Chap. 18)
The Representative Elements: 1A to 8A (Chap. 19 \& 20)
Transition Chemistry: Coordination Chemistry (Chap. 21)
Organic Chemistry: Biological Molecules (Chap. 22)

## Chemical Kinetics

- Reaction Rates

Stoichiometry, Conditions, Concentration

- Rate Laws

Types (Order), Initial Rate, First Order, Second Order and Zero Order Rxns

- Reaction Mechanisms and Model of Chemical Kinetics
- Catalysis

Heterogeneous and Homogeneous

- The main goal of Chemical Kinetics is to understand the steps by which a reaction take place.
- The understanding will allow us to find ways to facilitate or inhibit the reactions,
e.g., Haber process for Ammonia production requires high temperature (more cost for commercially feasibility), while presence of iron oxide speeds up the reaction.

Thermodynamics - does a reaction take place?
Kinetics - how fast does a reaction proceed?


Reaction rate is the change in the concentration of a reactant or a product with time (M/s).

Figure 12.1 Following reaction at $300^{\circ} \mathrm{C}$ and Oxygen are Plotted versus Time
$\mathbf{2 N O} \mathbf{2}(\mathrm{g}) \longrightarrow \mathbf{2 N O}(\mathrm{g})+\mathbf{O}_{\mathbf{2}}(\mathrm{g})$
Average Rate $=\frac{\Delta M}{\Delta t}$
Rate of the disappearance of $\mathbf{N O 2}$ is equal in magnitude but opposite in sign to the rate of the appearance of NO and half of the appearance of $\mathbf{O}_{\mathbf{2}}$


### 12.1 Reaction Rate

- Average Rate-- $\Delta$ mol (or concentration) over a period of time, $\Delta t$
- Instantaneous Rate-- slope of the tangent at a specific time, t
- Initial Rate-- instantaneous rate at $\mathrm{t}=0$


## $[M]$




### 12.1 Reaction Rates Examples

$\mathrm{Br}_{2}(a q)+\mathrm{HCOOH}(a q) \longrightarrow 2 \mathrm{Br}^{-}(a q)+2 \mathrm{H}^{+}(a q)+\mathrm{CO}_{2}(g)$


### 12.1 Reaction Rates Examples

$\mathrm{Br}_{2}(a q)+\mathrm{HCOOH}(a q) \longrightarrow 2 \mathrm{Br}^{-}(a q)+2 \mathrm{H}^{+}(a q)+\mathrm{CO}_{2}(g)$


### 12.1 Reaction Rates Examples



$$
2 \mathrm{H}_{2} \mathrm{O}_{2}(a q) \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}(I)+\mathrm{O}_{2}(g)
$$

$$
P V=n R T
$$

$$
P=\frac{n}{V} R T=\left[\mathrm{O}_{2}\right] R T
$$

$$
\left[\mathrm{O}_{2}\right]=\frac{1}{R T} P
$$

rate $=\frac{\Delta\left[\mathrm{O}_{2}\right]}{\Delta t}=\frac{1}{R T} \frac{\Delta \mathrm{P}}{\Delta t}$

measure $\Delta P$ over time

### 12.1 Reaction Rates

## Reaction Rates and Stoichiometry

$$
2 A \longrightarrow B
$$

Two moles of $A$ disappear for each mole of $B$ that is formed.

$$
\text { rate }=-\frac{1}{2} \frac{\Delta[\mathrm{~A}]}{\Delta t} \quad \text { rate }=\frac{\Delta[\mathrm{B}]}{\Delta t}
$$

1
Write the rate expression for the following reaction:
$\mathrm{CH}_{4}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$

$$
\text { rate }=-\frac{\Delta\left[\mathrm{CH}_{4}\right]}{\Delta t}=-\frac{1}{2} \frac{\Delta\left[\mathrm{O}_{2}\right]}{\Delta t}=\frac{\Delta\left[\mathrm{CO}_{2}\right]}{\Delta t}=\frac{1}{2} \frac{\Delta\left[\mathrm{H}_{2} \mathrm{O}\right]}{\Delta t}
$$

### 12.2 Rate Laws:



The rate law expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.

$$
\begin{aligned}
& a \mathrm{~A}+b \mathrm{~B} \longrightarrow c \mathrm{C}+d \mathrm{D} \\
& \text { Rate }=k[A] \frac{1}{2}[B]
\end{aligned}
$$

reaction is $\boldsymbol{x t h}$ order in $A$ reaction is $y$ th order in $B$ reaction is $(x+y)$ th order overall
$\boldsymbol{k}$ is the rate constant for the reaction
Types of Rate Laws
A. Differential rate law: how rate depend on concentration.
B. Integrated rate law: how the concentration depend on time.

## Examples:

- $2 \mathrm{~N}_{2} \mathrm{O}_{5} \quad=>4 \mathrm{NO}_{2}+\mathrm{O}_{2}$ rate $=\mathrm{k}\left[\mathrm{N}_{2} \mathrm{O}_{5}\right] \quad 1^{\text {st }}$ order
- 2NO + $\mathrm{Cl}_{2} \quad=2 \mathrm{NOCl}$ rate $=\mathrm{k}\left[\mathrm{NO}^{2}\left[\mathrm{Cl}_{2}\right] \quad 3^{\text {rd }}\right.$ order
- $2 \mathrm{NH}_{3}=>\mathrm{N}_{2}+3 \mathrm{H}_{2}$

$$
\text { rate }=\mathrm{k}\left[\mathrm{NH}_{3}\right]^{0}=\mathrm{k} \quad 0^{\text {th }} \text { order }
$$

### 12.2 Rate Law Summary

- Rate laws are always determined experimentally.
- Reaction order is always defined in terms of reactant (not product) concentrations.
- The order of a reactant is not related to the stoichiometric coefficient of the reactant in the balanced chemical equation.

$$
\begin{gathered}
\mathrm{F}_{2}(\mathrm{~g})+2 \mathrm{ClO}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{FClO}_{2}(\mathrm{~g}) \\
\text { rate }=k\left[\mathrm{~F}_{2}\right]\left[\mathrm{ClO}_{2} \mathrm{1}\right.
\end{gathered}
$$

12.3 Determination of the Form of Rate Law
Figure 12.3 A Plot of the Concentration of $\mathrm{N}_{2} \mathrm{O}_{5}$ as a Function of Time for the Reaction $\mathbf{2} \mathbf{N}_{2} \mathrm{O}_{\mathbf{5}}($ soln $) \rightarrow \mathbf{4 N O}($ soln $)+\mathbf{O}_{\mathbf{2}}(g)$

$$
\text { rate }=-\frac{\Delta\left[\mathbf{N}_{2} \mathbf{O}_{5}\right]}{\Delta t}=k\left[\mathbf{N}_{2} \mathbf{O}_{5}\right]^{n}
$$

at $M_{1}=0.90 \mathrm{Mol} / \mathrm{L} \ldots r_{1}=5.4 \times 10^{-4} \mathrm{Mol} / \mathrm{L} . \mathrm{s}$
at $M_{2}=0.45 \mathrm{Mol} / \mathrm{L} \ldots r_{2}=2.7 \times 10^{-4} \mathrm{Mol} / \mathrm{L} . \mathrm{s}$

| Exponent Value | [conc] | rate |
| :---: | :---: | :---: |
| 0 | double | same |
| 1 | double | double |
| 2 | double | $\times 4$ |
| 3 | double | $\times 8$ |
| 4 | double | $\times 16$ |


$\mathrm{F}_{2}(\mathrm{~g})+2 \mathrm{ClO}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{FClO}_{2}(\mathrm{~g})$
rate $=k\left[\mathrm{~F}_{2}\right]^{x}\left[\mathrm{ClO}_{2}\right]^{y}$


Initial Rates Method

Table 13.2 Rate Data for the Reaction between $\mathrm{F}_{2}$ and $\mathrm{ClO}_{2}$

|  | $\left[\mathrm{F}_{\mathbf{2}}\right](\boldsymbol{M})$ | $\left[\mathrm{ClO}_{\mathbf{2}}\right](\boldsymbol{M})$ |
| :---: | :---: | :---: |
| 1.0 .10 | Initial Rate $(\mathbf{M} / \mathbf{s})$ |  |
| 2.0 .10 | 0.010 | $1.2 \times 10^{-3}$ |
| 3.0 .20 | 0.010 | $4.8 \times 10^{-3}$ |
|  |  | $2.4 \times 10^{-3}$ |

Double $\left[\mathrm{F}_{2}\right]$ with $\left[\mathrm{ClO}_{2}\right]$ constant

Rate doubles
$x=1$

Quadruple $\left[\mathrm{ClO}_{2}\right]$ with $\left[\mathrm{F}_{2}\right]$ constant Rate quadruples

$$
y=1
$$

rate $=k\left[\mathrm{~F}_{2}\right]\left[\mathrm{ClO}_{2}\right]$


Determine the rate law and calculate the rate constant for the following reaction from the following data:

$$
\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}(a q)+3 \mathrm{I}^{-}(a q) \longrightarrow 2 \mathrm{SO}_{4}{ }^{2-}(a q)+\mathrm{I}_{3}^{-}(a q)
$$

| Experiment | $\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2}\right]$ | [ 1 ] | Initial Rate (M/s) | y |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 0.08 | 0.034 | $2.2 \times 10^{-4}$ | $y=1$ |
| 2 | 0.08 | 0.017 | $1.1 \times 10^{-4}$ | $x=1$ |
| 3 | 0.16 | 0.017 | $2.2 \times 10^{-4}$ | rate $=k\left[\mathrm{~S}_{2} \mathrm{O}_{8}{ }^{2-}\right]\left[L^{-}\right]$ |

Double [ $1-$ ], rate doubles (experiment $1 \& 2$ )
Double $\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]$, rate doubles (experiment $2 \& 3$ )

$$
k=\frac{\text { rate }}{\left[\mathrm{S}_{2} \mathrm{O}_{8}^{2}\right]\left[\mathrm{I}^{-}\right]}=\frac{2.2 \times 10^{-4} \mathrm{M} / \mathrm{s}}{(0.08 \mathrm{M})(0.034 \mathrm{M})}=0.08 / \mathrm{M} \cdot \mathrm{~s}
$$

### 12.4 The integrated Rate Law

$\mathrm{A} \longrightarrow$ product rate $=-\frac{\Delta[\mathrm{A}]}{\Delta t} \quad$ rate $=k[\mathrm{~A}]$

## First-Order Reactions

Unit of rate constant:

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

$$
k=\frac{\text { rate }}{[\mathrm{A}]}=\frac{M / s}{M}=1 / \mathrm{s} \mathrm{or} \mathrm{~s}^{-1}
$$

Integrated Form of the first order rate equation:

$$
[\mathrm{A}]=[\mathrm{A}]_{0} \exp (-k t)
$$



$$
-\frac{\Delta[\mathrm{A}]}{\Delta t}=k[\mathrm{~A}]
$$


$[A]$ is the concentration of $A$ at any time $t$
$[A]_{0}$ is the concentration of $A$ at time $t=0$

## First-Order Reactions

Figure 12.4 A Plot of $\ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$ versus Time $\mathbf{2} \mathrm{N}_{2} \mathrm{O}_{5}($ soln $) \rightarrow \mathbf{4 N O} \mathbf{2}($ soln $)+\mathrm{O}_{\mathbf{2}}($ g $)$


## First-Order Reactions

The reaction $2 A \longrightarrow B$ is first order in $A$ with a rate constant of $2.8 \times 10^{-2} \mathrm{~s}^{-1}$ at $8^{\circ} \mathrm{C}$. How long will it take for A to decrease from 0.88 M to 0.14 M ?

$$
\begin{array}{lc}
\ln [\mathrm{A}]=\ln [\mathrm{A}]_{0}-k t & {[\mathrm{~A}]_{0}=0.88 \mathrm{M}} \\
k t=\ln [\mathrm{A}]_{0}-\ln [\mathrm{A}] & {[\mathrm{A}]=0.14 \mathrm{M}} \\
t=\frac{\ln [\mathrm{A}]_{0}-\ln [\mathrm{A}]}{k}=\frac{\ln \frac{[\mathrm{A}]_{0}}{[\mathrm{~A}]}}{k}=\frac{\ln \frac{0.88 \mathrm{AM}}{0.14 \mathrm{M}}}{2.8 \times 10^{-2} \mathrm{~s}^{-1}}=66 \mathrm{~s}
\end{array}
$$

## Half-life time of the First-Order Reactions

The half-life, $\boldsymbol{t}_{1 / 2}$, is the time required for the concentration of a reactant to decrease to half of its initial concentration.

$$
t_{1 / 2}=t \text { when }[\mathrm{A}]=[\mathrm{A}]_{0} / 2
$$

$$
t=\frac{\ln [\mathrm{A}]_{0}-\ln [\mathrm{A}]}{k}=\frac{\ln \frac{[\mathrm{A}]_{0}}{[\mathrm{~A}]}}{k}
$$

$$
t_{1 / 2}=\frac{\ln \frac{[A]_{0}}{[A]_{0} / 2}}{k}=\frac{\ln 2}{k}=\frac{0.693}{k}
$$



What is the half-life of $\mathrm{N}_{2} \mathrm{O}_{5}$ if it decomposes with a rate constant of 5.7 $\times 10^{-4} \mathrm{~s}^{-1}$ ?

$$
t_{1 / 2}=\frac{\ln 2}{k}=\frac{0.693}{5.7 \times 10^{-4} \mathrm{~s}^{-1}}=1200 \mathrm{~s}=20 \text { minutes }
$$

$\mathrm{A} \longrightarrow$ product rate $=-\frac{\Delta[\mathrm{A}]}{\Delta t} \quad$ rate $=k[\mathrm{~A}]^{2}$
$\mathrm{A} \longrightarrow$ product $\quad$ rate $=-\frac{\Delta[\mathrm{A}]}{\Delta t} \quad$ rate $=k[\mathrm{~A}]^{0}$

## Second-Order Reactions Zero-Order Reactions

Unit of rate constant

$$
k=\frac{\text { rate }}{[\mathrm{A}]^{2}}=\frac{M / s}{M^{2}}=1 / M \cdot s \quad k=\frac{\text { rate }}{[\mathrm{A}]^{0}}=M / \mathrm{s}
$$

Integrated Form of the first order rate equation

$$
\begin{aligned}
& -\frac{\Delta[\mathrm{A}]}{\Delta t}=k[\mathrm{~A}]^{2} \\
& \frac{1}{[\mathrm{~A}]}=\frac{1}{[\mathrm{~A}]_{0}}+k t
\end{aligned}
$$

$$
-\frac{\Delta[\mathrm{A}]}{\Delta t}=k
$$

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

$$
t_{1 / 2}=t \quad \text { when } \quad[\mathrm{A}]=[\mathrm{A}]_{0} / 2
$$

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

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

## Equation for a Straight Line

$$
\begin{aligned}
& y=b x+a \quad\left\{\begin{array}{l}
b=\text { slope } \\
a=y \text { intercept } \\
x=\text { time }
\end{array}\right. \\
& \ln [\mathrm{A}]_{t}=-k t \quad+\ln [\mathrm{A}]_{0} \quad \text { 1st order } \\
& \frac{1}{[\mathrm{~A}]_{t}}=\mathrm{kt}+\frac{1}{[\mathrm{~A}]_{0}} \quad \text { 2nd order } \\
& {[\mathrm{A}]_{t}=k t+[\mathrm{A}]_{0} \quad \text { Zero order }}
\end{aligned}
$$

### 12.5 Rate Laws: A Summary

- The used laws contain reactant concentration only
- Rate types: Differential or Integral rate laws
- The common experimental methods:
- For differential rate law is the initial concentration method
- For integral rate law graphical method
- For reactions with several reactants the integral method can be applied only if the concentration of one reactant only can be treated (Pseudo rate law), i.e.

Rate $=k[A]^{n}[B]^{m}[C]^{p}$
To be reduced to
Rate $=k^{\prime}[A]^{n}$
Concentration-Time
Equation

| Order | Rate Law | Equation | Half-Life |
| :---: | :--- | :---: | :---: |
| 0 | rate $=k$ | $[\mathrm{~A}]=[\mathrm{A}]_{0}-k t$ | $t_{1 / 2}=\frac{[\mathrm{A}]_{0}}{2 k}$ |
| 1 | rate $=k[\mathrm{~A}]$ | $\ln [\mathrm{A}]=\ln [\mathrm{A}]_{0}-k t$ | $t_{1 / 2}=\frac{\ln 2}{k}$ |
| 2 | rate $=k[\mathrm{~A}]^{2}$ | $\frac{1}{[\mathrm{~A}]}=\frac{1}{[\mathrm{~A}]_{0}}+k t$ | $t_{1 / 2}=\frac{1}{k[\mathrm{~A}]_{0}}$ |

### 12.6 Reaction Mechanisms



Many Chemical reactions occur by a series of steps called the Reaction Mechanism.

$$
\begin{array}{cc}
2 \mathrm{O}_{3} \rightarrow & 3 \mathrm{O}_{2} \\
\mathrm{O}_{3} \rightarrow \mathrm{O}_{2}+\mathrm{O} & \text { rate }=\mathrm{k}\left[\mathrm{O}_{3}\right] \\
\mathrm{O}_{3}+\mathrm{O} \rightarrow 2 \mathrm{O}_{2} & \text { rate }=\mathrm{k}^{\prime}\left[\mathrm{O}_{3}\right][\mathrm{O}]
\end{array}
$$

Intermediates are species that appear in a reaction mechanism but not in the overall balanced equation.

## Reaction Mechanisms

The overall progress of a chemical reaction can be represented at the molecular level by a series of simple elementary steps or elementary reactions.

The sequence of elementary steps that leads to product formation is the reaction mechanism.

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

$\mathrm{N}_{2} \mathrm{O}_{2}$ is detected during the reaction!
Elementary step: $\quad \mathrm{NO}+\mathrm{NO} \longrightarrow \mathrm{N}_{2} \boldsymbol{\sigma}_{2}$

$+$| Elementary step: |
| :---: |
| Overall reaction: |
| $\mathrm{N}_{2} \mathrm{O}_{2}+\mathrm{O}_{2} \longrightarrow 2 \mathrm{NO}_{2}$ |
| $2 \mathrm{O} \longrightarrow 2 \mathrm{NO}_{2}$ |

### 12.6 Reaction Mechanisms

- Elementary Step equation describing a single molecular event
- Molecularity

■ Unimolecular rate $=\mathrm{k}[\mathrm{A}]$
■ Bimolecular
rate $=k[A][B]$ or rate $=k[A]^{2}$

- Termolecular rate $=\mathrm{k}[\mathrm{A}]^{2}[\mathrm{~B}]$

$$
2 \mathrm{O}_{3} \quad \rightarrow \quad 3 \mathrm{O}_{2}
$$



### 12.6 Reaction Mechanisms

The proposed Reaction Mechanism will be coorected if it satisfy the following two requirements:

- The sum of the elementary steps give the overall balanced equation.
- The rate of the mechanism agrees the experimental rate law.

For example: Given the following reaction and rate law:

$$
\mathrm{NO}_{2(\mathrm{~g})}+\mathrm{CO}_{(\mathrm{g})} \Rightarrow \mathrm{CO}_{2(\mathrm{~g})}+\mathrm{NO}_{(\mathrm{g})} \quad \text { rate }=\mathrm{k}\left[\mathrm{NO}_{2}\right]^{2}
$$

- Does the reaction occur in a single step?
- Which of the following two mechanisms is most likely:

Mechanism A:
$\mathrm{NO}_{2}+\mathrm{NO}_{2} \rightarrow \mathrm{NO}_{3}+\mathrm{NO}$
$\mathrm{NO}_{3}+\mathrm{CO} \rightarrow \mathrm{NO}_{2}+\mathrm{CO}_{2}$
VI. IVIUISy

Mechanism B:
$\mathrm{NO}_{2} \rightarrow \mathrm{NO}+\mathrm{O}$
$\mathrm{CO}+\mathrm{O} \rightarrow \mathrm{CO}_{2}$

The experimental rate law for the reaction between $\mathrm{NO}_{2}$ and CO to produce NO and $\mathrm{CO}_{2}$ is rate $=k\left[\mathrm{NO}_{2}\right]^{2}$. The reaction is believed to occur via two steps:


What is the equation for the overall reaction?

$$
\mathrm{NO}_{2}+\mathrm{CO} \longrightarrow \mathrm{NO}+\mathrm{CO}_{2}
$$

What is the intermediate?

$$
\mathrm{NO}_{3}
$$

What can you say about the relative rates of steps 1 and 2?

$$
\begin{aligned}
& \text { rate }=k\left[\mathrm{NO}_{2}\right]^{2} \text { is the rate law for step } 1 \text { so } \\
& \text { step } 1 \text { must be slower than step } 2
\end{aligned}
$$

### 12.7 A Model for Chemical Kinetics

## Temperature Effects

- Rates typically increase with T increase
- Collisions between molecules increase
- Energy of collisions increase
- Even though only a small fraction of collisions lead to reaction
- Minimum Energy necessary for reaction is the Activation Energy


## Molecular Theory (Collision Theory)

- Activation Energy varies greatly

Activation Energy, Ea

- almost zero to hundreds of kJ
- size of $E_{a}$ affects reaction rates
- Concentration
- more molecules, more collisions
- Molecular Orientation
- collisions must occur "sterically"


Reaction Progress

$$
\Delta H_{r x t n}=E a_{\text {forward }}-E a_{\text {reverse }}
$$

## The Arrhenius Equation



- increase temperature, increase reaction rates
- reaction rates are $\alpha$ to energy, collisions, temperature \& orient

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

$\mathrm{k}=$ rate constant
A = frequency of collisions
$-E_{a} / R T=$ fraction of molecules with energy necessary for reaction



$$
\ln \frac{k_{2}}{k_{1}}=-\frac{E_{a}}{R}\left(\frac{1}{T_{2}}-\frac{1}{T_{1}}\right)
$$

## Problem:

Data for the following reaction are listed in the table. Calculate $\mathrm{E}_{\mathrm{a}}$ graphically, calculate A and find k at 311 K .

| In k | $\mathrm{k}, \mathrm{min}^{-1}$ | $\mathrm{~T}(\mathrm{~K})$ | $1 / \mathrm{T} \times 10^{-3}$ |
| :---: | :---: | :---: | :---: |
| -3.20 | 0.0409 | 298 | 3.35 |
| -2.50 | 0.0818 | 308 | 3.25 |
| -1.85 | 0.157 | 318 | 3.14 |

$$
\mathrm{Mn}(\mathrm{CO})_{5}\left(\mathrm{CH}_{3} \mathrm{CN}\right)^{+}+\mathrm{NC}_{5} \mathrm{H}_{5}=>\mathrm{Mn}(\mathrm{CO})_{5}\left(\mathrm{NC}_{5} \mathrm{H}_{5}\right)^{+}+\mathrm{CH}_{3} \mathrm{CN}
$$

$$
\begin{aligned}
& \text { slope }=-6419.9=-E a / R \\
& E a=(-6419.9)\left(-8.31 \times 10^{-3} \mathrm{~kJ} / \mathrm{K} \mathrm{~mol}\right) \\
& =53.3 \mathrm{~kJ} \\
& y \text { intercept }=18.327=\ln \mathrm{A} \\
& \qquad \mathrm{~A}=8.0 \times 10^{7}
\end{aligned}
$$



## Problem:

The energy of activation for

$$
\mathrm{C}_{4} \mathrm{H}_{8(\mathrm{~g})}=>2 \mathrm{C}_{2} \mathrm{H}_{4(\mathrm{~g})}
$$

is $260 \mathrm{~kJ} / \mathrm{mol}$ at 800 K and $\mathrm{k}=0.0315 \mathrm{sec}$
Find k at 850 K .

$$
\begin{gathered}
\ln \frac{k_{2}}{k_{1}}=-\frac{E_{a}}{R}\left(\frac{1}{T_{2}}-\frac{1}{T_{1}}\right) \\
\mathrm{k} \text { at } 850 \mathrm{~K}=0.314 \mathrm{sec}^{-1}
\end{gathered}
$$

A catalyst is a substance that increases the rate of a chemical reaction without itself being consumed.
-homogeneous
-Heterogeneous
Facilitates the progress of a reaction by lowering the

$k=A \cdot \exp \left(-E_{a} / R T\right) \quad E_{a} \downarrow \quad k \uparrow$ rate $_{\text {catalyzed }}>$ rate $_{\text {uncatalyzed }}$


## Uncatalyzed Reaction:

$\mathrm{O}_{3(\mathrm{~g})}<=>\quad \mathrm{O}_{2(\mathrm{~g})}+\mathrm{O}_{(\mathrm{g})}$
$\mathrm{O}_{(\mathrm{g})}+\mathrm{O}_{3(\mathrm{~g})}=>2 \mathrm{O}_{2(\mathrm{~g})}$ Catalyzed Reaction:

Step 1: $\quad \mathrm{Cl}_{(\mathrm{g})}+\mathrm{O}_{3(\mathrm{~g})}+\mathrm{O}_{(\mathrm{g})} \Rightarrow \quad \mathrm{ClO}_{(\mathrm{g})}+\mathrm{O}_{2(\mathrm{~g})}+\mathrm{O}_{(\mathrm{g})}$
Step 2: $\quad \mathrm{ClO}_{(\mathrm{g})}+\mathrm{O}_{2(\mathrm{~g})}+\mathrm{O}_{(\mathrm{g})}=>\mathrm{Cl}_{(\mathrm{g})}+2 \mathrm{O}_{2(\mathrm{~g})}$
Overall rxn: $\quad \mathrm{O}_{3(\mathrm{~g})}+\mathrm{O}_{(\mathrm{g})} \quad=>\mathbf{2 O}_{2(\mathrm{~g})}$

### 12.8 Catalysis

$\mathrm{E}_{\mathrm{a}}$ uncatalyzed rxn


### 12.8 Examples

In heterogeneous catalysis, the reactants and the catalysts are in different phases.

- Haber synthesis of ammonia
- Ostwald process for the production of nitric acid
- Catalytic converters

In homogeneous catalysis, the reactants and the catalysts are dispersed in a single phase, usually liquid.

- Acid catalysis
- Base catalysis


## Haber Process



$$
\mathrm{N}_{2}(g)+3 \mathrm{H}_{2}(g) \frac{\mathrm{Fe} / \mathrm{Al}_{2} \mathrm{O}_{3} / \mathrm{K}_{2} \mathrm{O}}{\text { catalyst }} 2 \mathrm{NH}_{3}(g)
$$

Heterogeneous Catalysis involves:
$\checkmark$ Adsorption and activation of reactants
$\checkmark$ Migration of the adsorbed reactants on the surface
$\checkmark$ Reaction of the adsorbed substances
$\checkmark$ Escape, or desorption, of the product

## Ostwald Process

$$
\begin{gathered}
4 \mathrm{NH}_{3}(g)+5 \mathrm{O}_{2}(\mathrm{~g}) \xrightarrow{\text { Pt catalyst }} 4 \mathrm{NO}(\mathrm{~g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \\
2 \mathrm{NO}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{NO}_{2}(\mathrm{~g}) \\
2 \mathrm{NO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longrightarrow \mathrm{HNO}_{2}(\mathrm{aq})+\mathrm{HNO}_{3}(\mathrm{aq})
\end{gathered}
$$



Pt-Rh catalysts used in Ostwald process


Hot Pt wire over $\mathrm{NH}_{3}$ solution

$\mathrm{CO}+$ Unburned Hydrocarbons $+\mathrm{O}_{2} \xrightarrow[\text { converter }]{\text { catalytic }} \mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$

$2 \mathrm{NO}+2 \mathrm{NO}_{2} \xrightarrow[\text { converter }]{\text { catalytic }} 2 \mathrm{~N}_{2}+3 \mathrm{O}_{2}$


## Review Problems:

- Consider the reaction $X \rightarrow Y+Z$

Which of the following is a possible rate law?
a) Rate $=k[X]$
b) Rate $=k[\mathrm{Y}]$
c) Rate $=k[Y][Z]$
d) Rate $=k[\mathrm{X}][\mathrm{Y}]$
e) Rate $=k[Z]$

ANS: a) SECTION: 12.2 LEVEL: easy

## Review Problems:

- For a reaction in which $A$ and $B$ react to form $C$, the following initial rate data were obtained:

| $[\mathrm{A}]$ | $[\mathrm{B}]$ | Initial Rate of Formation of C <br> $(\mathrm{mol} / \mathrm{L})$ |
| :--- | :--- | :--- |
| $(\mathrm{mol} / \mathrm{L})$ | $(\mathrm{mol} / \mathrm{L} \times \mathrm{s})$ |  |
| 0.10 | 0.10 | 1.00 |
| 0.10 | 0.20 | 4.00 |
| 0.20 | 0.20 | 8.00 |

What is the rate law for the reaction?
a) Rate $=k[\mathrm{~A}][\mathrm{B}]$
b) $\quad$ Rate $=k[\mathrm{~A}]^{2}[\mathrm{~B}]$
c) $\quad$ Rate $=k[\mathrm{~A}][\mathrm{B}]^{2}$
d) Rate $=k[\mathrm{~A}]^{2}[\mathrm{~B}]^{2}$
e) $\quad$ Rate $=k[\mathrm{~A}]^{3}$

ANS:c) SECTION: 12.3 LEVEL: medium

- A first-order reaction is 45\% complete at the end of 35 minutes. What is the length of the half-life of this reaction?
a) 41 min
b) 39 min
c) $30 . \mathrm{min}$
d) 27 min
e) none of these

ANS: a) SECTION: 12.4 LEVEL: medium

## $H$ Y <br> Review Problems:

- The reaction $2 \mathrm{NO} \rightarrow \mathrm{N}_{2}+\mathrm{O}_{2}$ has the following rate law:

$$
-\Delta[\mathrm{NO}] / \Delta \mathrm{t}=2 k[\mathrm{NO}]^{2} .
$$

After a period of $2.0 \times 10^{3} \mathrm{~s}$, the concentration of NO falls from an initial value of $2.8 \times 10^{-3} \mathrm{~mol} / \mathrm{L}$ to $2.0 \times 10^{-3} \mathrm{~mol} / \mathrm{L}$. What is the rate constant, $k$ ?
a) $7.2 \times 10^{-2} \mathrm{M}^{-1} / \mathrm{s}$
b) $1.7 \times 10^{-4} \mathrm{M}^{-1} / \mathrm{s}$
c) $4.0 \times 10^{-4} \mathrm{M}^{-1} / \mathrm{s}$
d) $4.0 \times 10^{-7} \mathrm{M}^{-1} / \mathrm{s}$
e) $3.6 \times 10^{-2} \mathrm{M}^{-1} / \mathrm{s}$

ANS:e) SECTION: 12.4 LEVEL: medium

## Review Problems:

- The reaction $2 \mathrm{NO}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2}$ obeys the rate law

$$
-\Delta[\mathrm{NO}] / \Delta \mathrm{t}=k_{\mathrm{obsd}}[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right] .
$$

Which of the following mechanisms is consistent with the experimental rate law?
a) $\mathrm{NO}+\mathrm{NO} \rightarrow \mathrm{N}_{2} \mathrm{O}_{2}$ (slow)

$$
\mathrm{N}_{2} \mathrm{O}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2} \quad \text { (fast) }
$$

b) $\mathrm{NO}+\mathrm{O}_{2} \rightleftharpoons \mathrm{NO}_{3}$
(fast equilibrium)
$\mathrm{NO}_{3}+\mathrm{NO} \rightarrow 2 \mathrm{NO}_{2}$
(slow)
c) $2 \mathrm{NO} \rightleftharpoons \mathrm{N}_{2} \mathrm{O}_{2}$
$\mathrm{N}_{2} \mathrm{O}_{2} \rightarrow \mathrm{NO}_{2}+\mathrm{O}$
$\mathrm{NO}+\mathrm{O} \rightarrow \mathrm{NO} 2$
(fast equilibrium)
$\mathrm{O}_{2}+\mathrm{O}_{2} \rightarrow \mathrm{O}_{2}+\mathrm{O}_{2}$
(slow)
d) $\mathrm{O}_{2}+\mathrm{O}_{2} \rightarrow \mathrm{O}_{2}+\mathrm{O}_{2}$
(fast)
$\mathrm{O}_{2}+\mathrm{NO} \rightarrow \mathrm{NO}_{2}+\mathrm{O}$
$\mathrm{O}+\mathrm{NO} \rightarrow \mathrm{NO}_{2}$
(slow)
(fast)
(fast)
e) none of these

ANS:b)
SECTION: 12.6
LEVEL: medium

## Review Problems:

- Use the following information to determine the activation energy for the reaction shown here:

$$
2 \mathrm{NO} \rightarrow \mathrm{~N}_{2}+\mathrm{O}_{2}
$$

Temperature (K) Rate Constant (L/mol $\times \mathrm{s}$ ) ..... 1400 ..... 0.143

$1500 \quad 0.659$
a) $3.2 \times 10^{4} \mathrm{~J} / \mathrm{mol}$
b) $9.5 \times 10^{6} \mathrm{~J} / \mathrm{mol}$
c) $2.8 \times 10^{4} \mathrm{~J} / \mathrm{mol}$
d) $6.8 \times 10^{5} \mathrm{~J} / \mathrm{mol}$
e) $2.7 \times 10^{5} \mathrm{~J} / \mathrm{mol}$ ANS: $)^{\text {) }}$

SECTION: 12.7
LEVEL: easy

## Review Problems:

- The reaction $2 \mathrm{H}_{2} \mathrm{O}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2}$ has the following mechanism:

$$
\begin{aligned}
& \mathrm{H}_{2} \mathrm{O}_{2}+\mathrm{I}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{IO}^{-} \\
& \mathrm{H}_{2} \mathrm{O}_{2}+\mathrm{IO}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2}+\mathrm{I}^{-}
\end{aligned}
$$

The catalyst in the reaction is:
a) $\mathrm{H}_{2} \mathrm{O}$
b) $\mathrm{I}^{-}$
c) $\mathrm{H}_{2} \mathrm{O}_{2}$
d) $\mathrm{IO}^{-}$

ANS:b)
SECTION: 12.6,8
LEVEL: easy

