Kinetics and Rate Law

AP Chemistry – Unit 8

Overview - Kinetics

2 NO + $Cl_2 \rightarrow$ 2NOCl			
Trial	[NO]	[Cl_2]	Rate M/s
1	1.32	.363	1.598
2	2.64	.736	12.784
3	2.64	.363	6.392

- **What we are looking at in Chemical Kinetics:**

1. **Rate** (speed) at which reactants are converted to products during the course of a chemical reaction

2. Factors that affect the rate of the chemical reaction

3. Sequence of steps, or the **Mechanism**, believed to occur when the reactants are converted to products

- This implies that much of kinetics is derived from observation – the math backs up what we see

  - We use what we observe/Experiments to make general statements about our systems
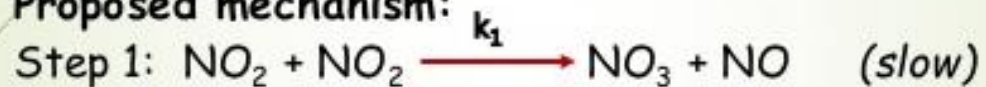
Overview - Terms

Mechanism

- The sequence of steps by which an overall reaction occurs.

  - How many reactions occur in one step (elementary steps) ? (by shoving two things together?)

  - If more than one step is needed for a reaction to happen, how do we figure out the rate?

Overall reaction:
$$NO_2 + CO \longrightarrow NO + CO_2$$

Proposed mechanism:
Step 1: $NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$ (slow)

Step 2: $NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2$

$NO_2 + NO_2 + NO_3 + CO \rightarrow NO_3 + NO + NO_2 + CO_2$

$NO_2 + CO \longrightarrow NO + CO_2$ First hurdle is crossed...

Overview - Terms

Collision Theory
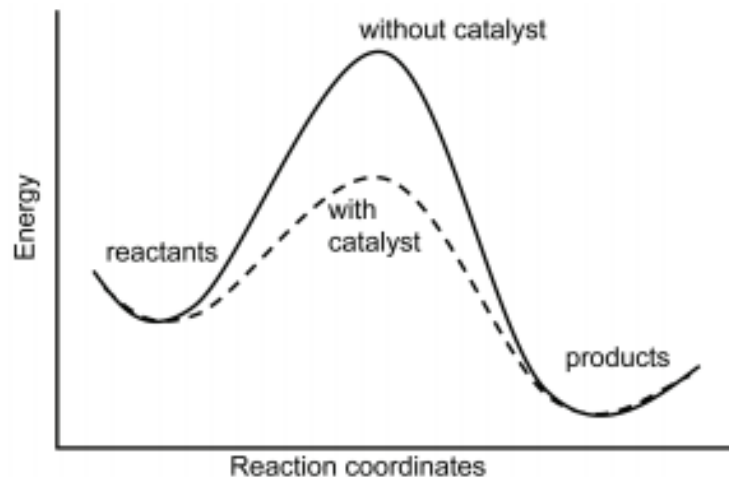
- In order for reactions to occur, we need **EFFECTIVE COLLISIONS**

    - This means just bumping two molecules together doesn't mean they will react

    1. The particles must collide with enough KE to overcome the activation energy requirements

    2. The molecules must collide with the proper orientation (facing the right direction)

NO O_3 Ineffective collision   NO O_3

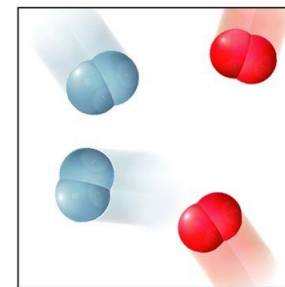NO O_3 Effective collision NO_2 O_2
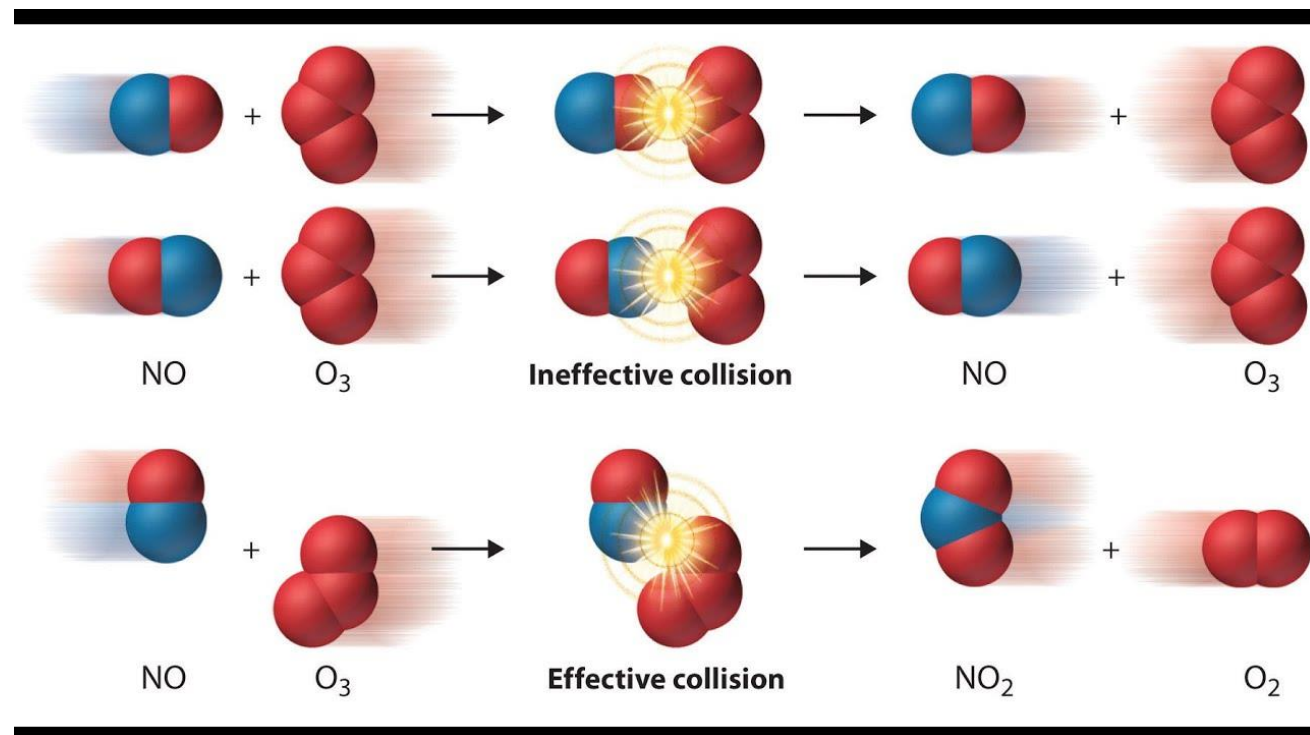
Overview – Reaction Rates
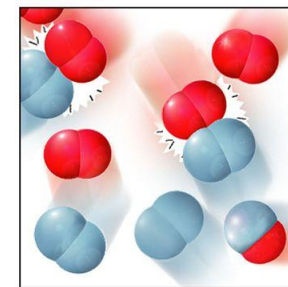
Factors that influence **Reaction Rates:**

- **Nature of Reactants**

- **Concentration of reactants**

- **Temperature**

- **Surface area of reactants**
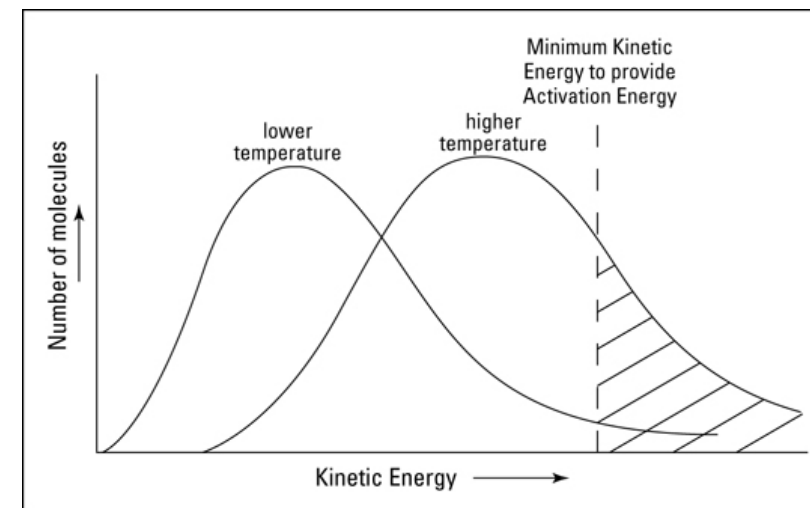
- **Catalysts**

Higher concentration = more collisions

Less concentrated

More concentrated

without catalyst

with catalyst

reactants

products

Energy

Reaction coordinates

Minimum Kinetic Energy to provide Activation Energy

lower temperature

higher temperature

Number of molecules

Kinetic Energy

Factors that influence Reaction Rates:

Nature of Reactant

- From slowest to fastest, how does phase (liquid, gas, solid) influence how fast a reaction occurs? Think of why when justifying your answer

  - What is the energy associated with each state? What is the motion? What is the average kinetic energy of the sample?

  - Solid, liquid, gas

- **Charge** (if applicable)

  - Ions of opposite charge react quickly

  - Like charges repel and do not have productive interactions which are unlikely to further the reaction

Factors that influence Reaction Rates

Nature of Reactant

- How do the number of bond between reaction molecules influence the rate of the reaction? Think of large vs. small covalent compounds

- **Answer**: the more bonds that have to be broken and rearranged, the slower the reaction is likely to occur.

  - If more bonds have to be accounted for, the more steps for the reaction are likely needed.

Factors that influence Reaction Rates
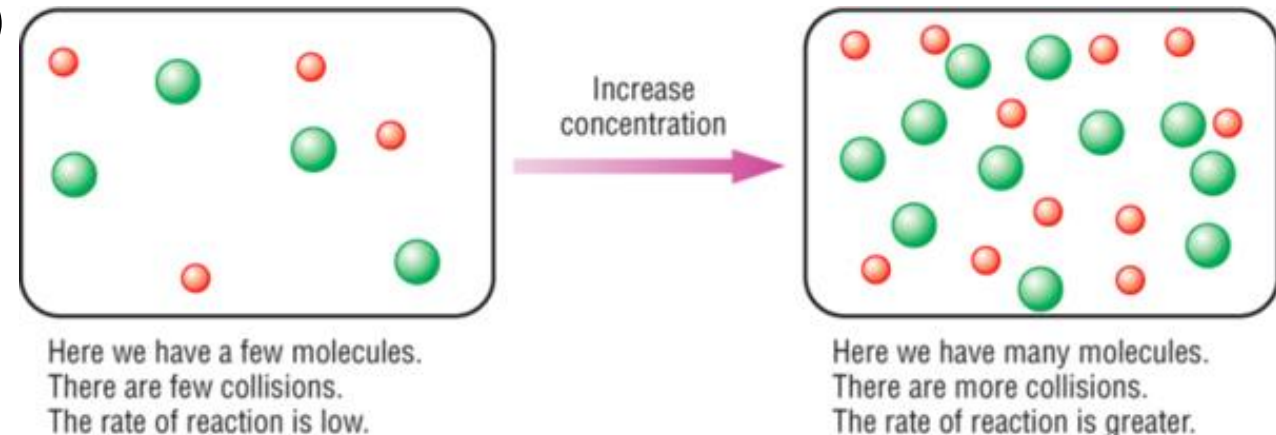
Temperature

- What is the effect of raising the temperature on the rate of a reaction?

- **Answer**: Increase temp → increase reaction rate

  - rule of thumb is if you increase temp by 10 degrees Kelvin, the reaction rate doubles

  - **Why**? Energy. Increase in temp reflects the average kinetic energy of a sample. If the average KE goes up, each particle is more likely to have more energy. This means when the particles collide, they are more likely to have enough energy to overcome the activation energy.
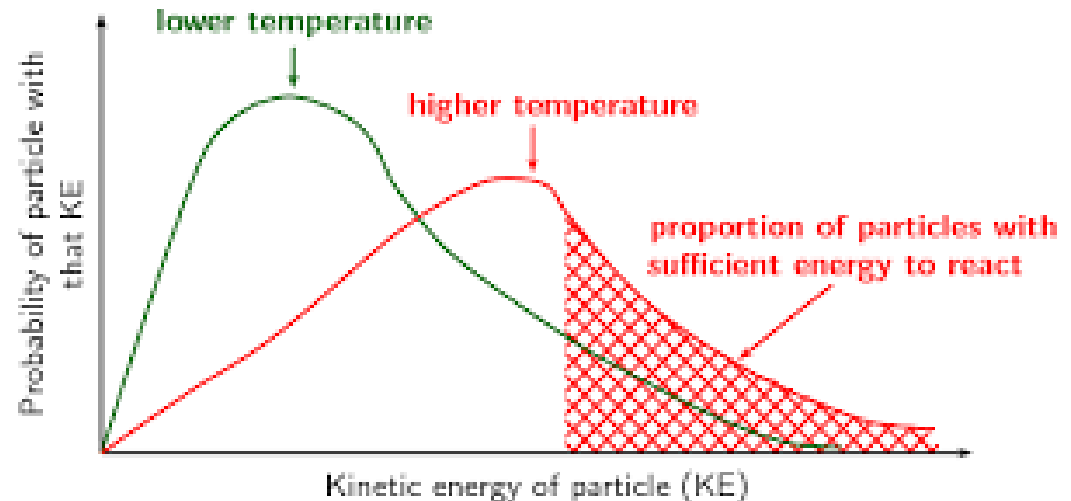
Factors that influence Reaction Rates
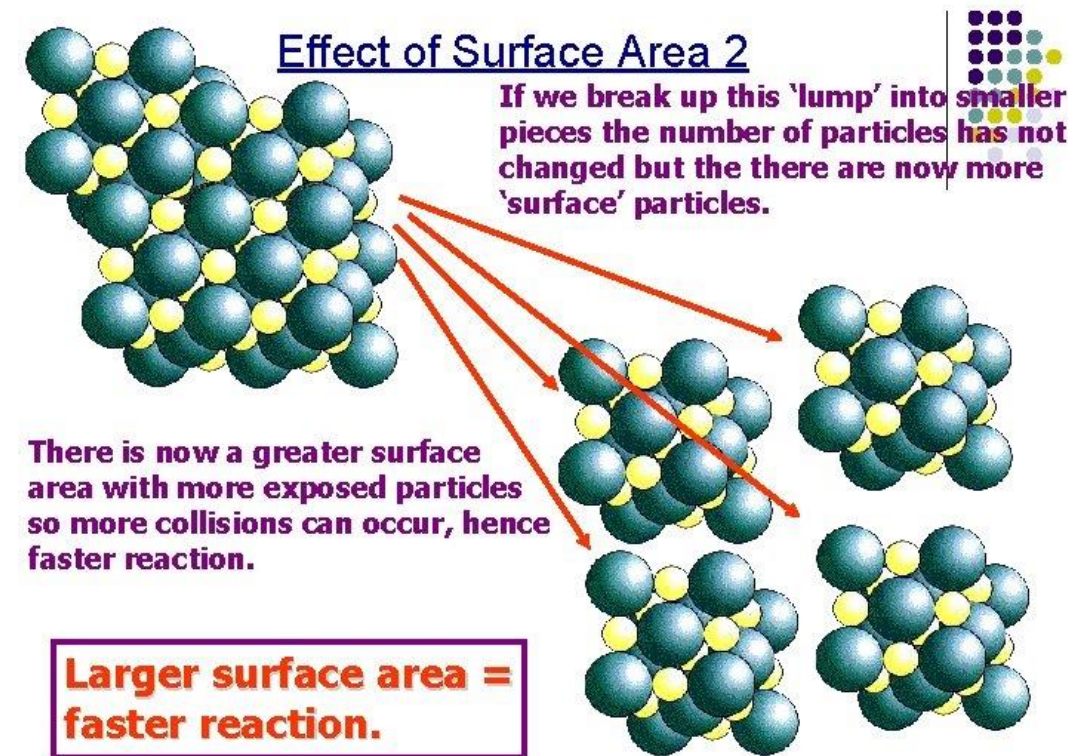
Concentration [ ]

- What does changing the concentration of the reactants do to the rate of the reaction?

- **Answer:** Increasing the concentration of a reaction USUALLY speeds up the reaction (unless it is a Zero order)

- **Why?**

  - Higher concentration of reactants = more likely a collision will occur. If you get more collisions, the chances are greater the that one of them will be productive and result in a reaction (its just a game of numbers!)

Increase concentration

Here we have a few molecules.
There are few collisions.
The rate of reaction is low.

Here we have many molecules.
There are more collisions.
The rate of reaction is greater.

Factors that influence Reaction Rates
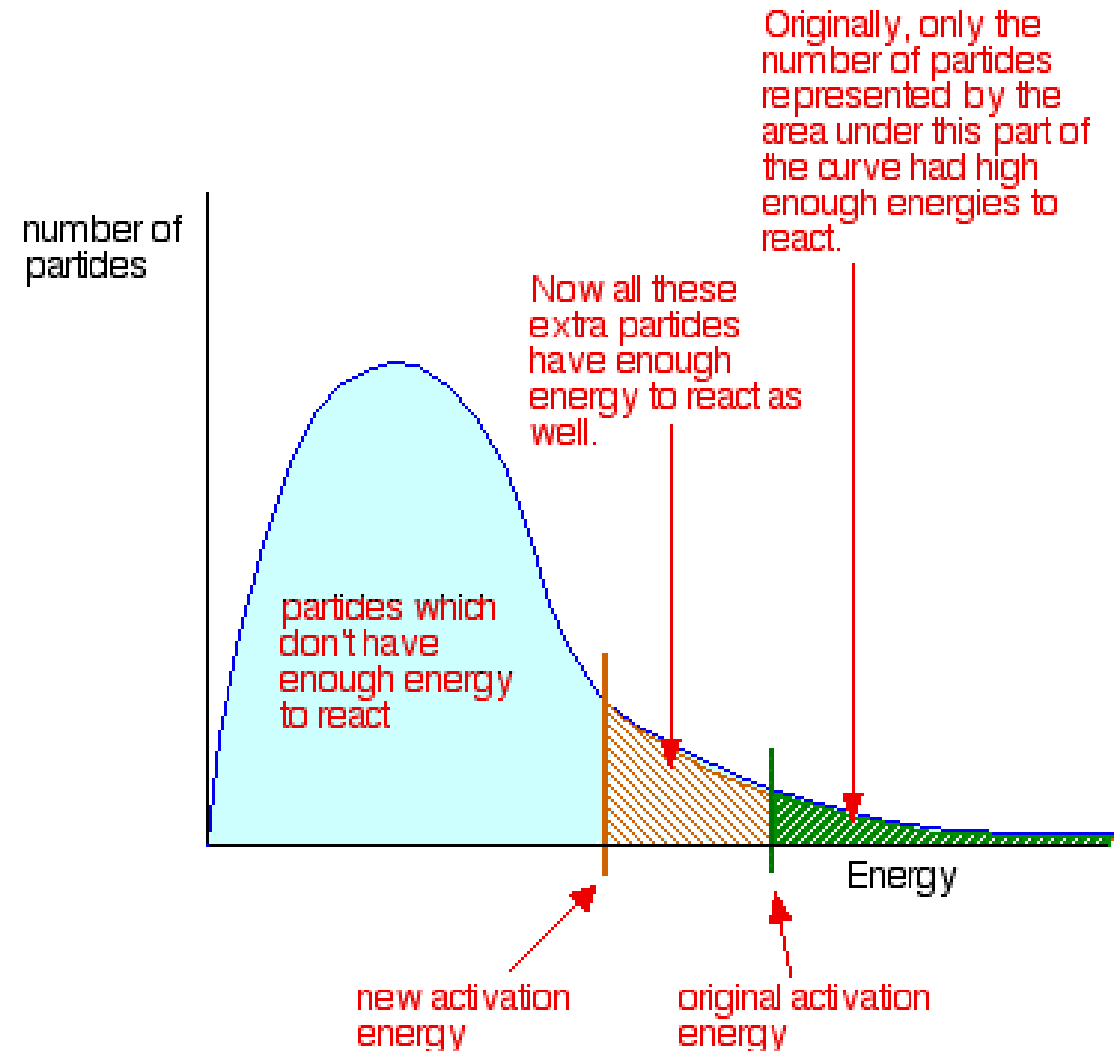
Surface area of Reactants

- What does changing the exposed surfaces of the reactants affect the rate of the reaction?

- **Answer**: If the surface area of a reactant is increased: **more particles are exposed to the other reactant.** there is a greater chance of particles colliding, which leads to more successful collisions per second

- Note: Gaseous state is different and Aqueous solutions are ultimate exposure!

Effect of Surface Area 2

If we break up this 'lump' into smaller pieces the number of particles has not changed but the there are now more 'surface' particles.

There is now a greater surface area with more exposed particles so more collisions can occur, hence faster reaction.

Larger surface area = faster reaction.

Factors that influence Reaction Rates

Catalysis

- What does adding a **Catalysis** do to the rate of the reaction?

  - A **catalyst** is a substance that can be added to a reaction to increase the reaction rate without getting consumed in the process.

  - Catalysts function by lowering the activation energy of an **elementary step** in a **reaction mechanism**, and by providing a new and faster reaction mechanism.


number of particles

Originally, only the number of particles represented by the area under this part of the curve had high enough energies to react.

Now all these extra particles have enough energy to react as well.

particles which don't have enough energy to react

Energy

new activation energy

original activation energy

Rate Laws

Rate Laws: Mathematical expression that shows how the **rate of reaction** depends on the **concentration of the reactants [ ]**

- Typically, reaction **rates** decrease with time because reactant concentrations decrease as reactants are converted to products

Two types of Rate Laws

- **Two different approaches are needed to solve**

1. **Differential rate law** expresses the reaction rate in terms of changes in the concentration of one or more reactants, $\Delta [R]$, over a specific time interval, Δt

2. **Integrated rate law** describes the reaction rate in terms of the initial concentration, $[R]_0$, and the measured concentration of one or more reactants, $[R]$, after a given amount of time.
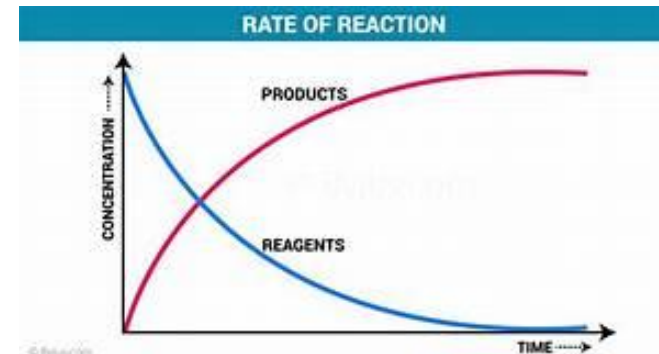
Differential Rate Law vs. **Integrated Rate Law**

- **Differential Rate Law** gives the rate of a chemical reaction as a function of the **change in concentration of one or more reactants** during a particular time period whereas **Integrated rate law** gives the rate of a chemical reaction as a function of the **initial concentration** of one or more reactants after a specific period of time.

In Summary:

- You use the **differential rate law** to calculate how fast a reaction is going (reaction rate) at specific reaction concentrations.

- You use the **integrated rate law** when you want to find out how long (time) it takes to get from one reactant concentration to another concentration.

  - this is the one you use to calculate half lives (original concentration to half of what you started with).

Differential Rate law
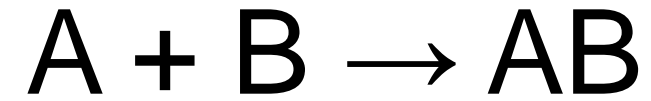
$$A + B \rightarrow AB$$

- Mathematical expression that shows how the **rate of reaction** depends on the **concentration of the reactants [ ]**

Rate Law Constant.
Specific to each different chemical rxn.
Units vary!

How quickly the reactants will disappear over time

Order of reactants
Compares the concentration of reactant consumed over a given amount of time

$$Rate = K \, [A]^M [B]^N$$

Rate of Reaction
Units: Molarity/s

Concentrations
Units: M or Mol/L

Orders

$$\text{Rate} = K\,[A]^M[B]^N$$

- The **order of reaction** determines the relationship between the rate of **reaction** and the concentration of reactants or products. It is the power to which a concentration **[ ]** is raised in the rate law equation.

  - Orders (M, N) can be zero, whole numbers or fractions

  - Must be determined by experimentation

- **Zero order: (M=0)** The change in [reactant] has no effect on the rate.

- **First order: (M=1)** Rate is directly proportional to [reactant]. Doubling [reactant], doubles rate.

- **Second order: (M=2**) Rate is quadrupled when [reactant] is doubled, etc…

Orders

$$\textcolor{red}{\textbf{Rate}} = \textbf{K } \textcolor{blue}{\textbf{[A]}}^{\textcolor{green}{\textbf{M}}}\textcolor{blue}{\textbf{[B]}}^{\textcolor{green}{\textbf{N}}}$$

Overall reaction order = add the individual reactants orders together and get a sum

- Example:

   Rate = **K [A]^{M}[B]^{N}[C]^{P}**

   M = 0, N = 1, P=2

   Rate = **K [A]^{0}[B]^{1}[C]^{2}**

   Write rate expression as:

   Rate = **K [B][C]^{2}**

   Overall reaction order = 3   (add up exponents: 0+1+2)

Example 1

C + D → E

Trial	[C]	[D]	Rate M/s
1	1.36	2.472	10.688
2	0.340	2.472	0.668
3	0.340	0.412	0.668

$$Rate = k[C]^m [D]^n$$

$$Rate = k[C]^2 [D]^0$$
$$Rate = k[C]^2$$

Overall Rxn Order is 2nd

Order of reactants

[C] =
D Constant
$$\left(\frac{1.36}{0.340}\right)^m = \left(\frac{10.688}{0.668}\right)$$

$$4^m = 16$$

$$m = 2 \quad 2^{nd} \text{ order reactant}$$

[D] =
C Constant
$$\left(\frac{2.472}{0.412}\right)^n = \left(\frac{0.688}{0.668}\right)$$

$$6^n = 1$$

$$n = 0 \quad \text{zero order reactant}$$

Example 2

$$Rate = k[NO]^m [Cl_2]^n$$

2 NO + Cl$_2$ → 2NOCl			
Trial	[NO] M	[Cl$_2$] N	Rate M/s
1	1.32	.363	1.598
2	2.64	.736	12.784
3	2.64	.363	6.392

$$Rate = k[NO]^2 [Cl_2]$$

Overall Rxn Order is 3rd

Solve for rate constant - K

1.598 M/s = K [1.32 M]^2 [0.363 M]

K = 2.53 M^{-2} S^{-1}

Order of reactants

[NO] = Cl$_2$ Constant

$$\left(\frac{2.64}{1.32} \right)^m = \left(\frac{6.393}{1.598} \right)$$

$$2^m = 4$$

m = 2 2nd order reactant

[Cl$_2$] = NO Constant

$$\left(\frac{.736}{.363} \right)^n = \left(\frac{12.784}{6.393} \right)$$

$$2^n = 2$$

n = 1 1st order reactant

Example 3- NSMI Chemical Kinetics   p. 12 exercise 3

$$\text{Rate} = k[BrO_3^-]^m [Br^-]^n[H^+]^P$$

Order of reactants

$[BrO_3^-]$

$$\left(\frac{0.20}{0.10}\right)^m = \left(\frac{16.0\times10^{-4}}{8.0\times10^{-4}}\right)$$

$$2^m = 2$$

$m = 1$ 1st order reactant

$$\boxed{\begin{array}{l}\text{Rate} = k[BrO_3^-] [Br^-] [H^+]^2 \\ \text{Overall Rxn Order is } 4^{th}\end{array}}$$

$[Br^-]$

$$\left(\frac{0.20}{0.10}\right)^n = \left(\frac{3.2\times10^{-3}}{1.6\times10^{-3}}\right)$$

$$2^n = 2$$

$n = 1$ 1st order reactant

$[H^+]$

$$\left(\frac{0.20}{0.10}\right)^P = \left(\frac{32\times10^{-3}}{8.0\times10^{-3}}\right)$$

$$2^P = 4$$

$P = 2$ 2nd order reactant

Example 3- NSMI Chemical Kinetics p. 11 exercise 3

Solve for Rate Constant K?

Rate = $k[BrO_3^-]$ $[Br^-]$ $[H^+]^2$

8.0×10^{-4} M/s = k [.10 M] [.10 M] [.10M]^2

$K = 8$ M^{-3} s^{-1}

Differential Rate Laws

Differential Rate Law:

- By looking at data, at specific conditions, we should be able to express

1. The effect of the concentration of **one** reactant on the reaction

2. The effect of the concentration of **all** reactants on the reaction

Possibilities include:

- **No effect -** not likely but possible

- **Direct effect** - 2x the concentration, the rxn happens twice as fast – most likely

- **Exponential effect** - 2x the concentration, 4x the rate – not likely but possible
  - There are other in-between possibilities we need to be aware off

Integrated rate law

- **Integrated rate law**: gives you the amount of time (t) it takes to get from an initial concentration of a reactant to some other concentration.

- Each equation can be derived by integrating the differential rate law. You get a different equation depending on the **order** (exponent) of the reactant in the differential rate law.

- In summary, you use the **differential rate law** to calculate how fast a reaction is going (reaction rate) at specific reaction concentrations.

- You use the **integrated rate law** when you want to find out how long (time) it takes to get from one reactant concentration to another concentration.

Integrated rate law
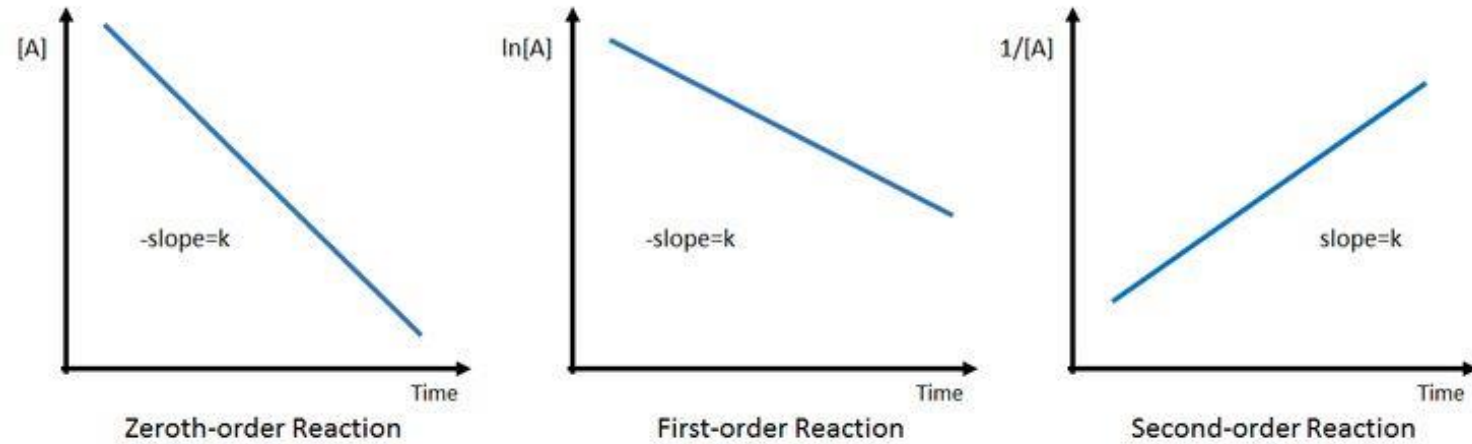
Order	Rate Law	Integrated Rate Law	Plot for straight line	Half life
0	Rate = k	$[A] = -kt + [A_o]$	$[A]$ vs t	$t_{1/2} = [A_o]/2k$
1	Rate = $[A]$	$Ln [A] = -kt + ln[A_o]$	$ln [A]$ vs t	$t_{1/2} = 0.693/k$
2	Rate = $[A]^2$ or $[A][B]$	$1/[A] = kt + 1/[A_o]$	$1/[A]$ vs t	$t_{1/2} = 1/k[A_o]$
		$y = mx + b$		

- [Ao] is the inital concentration,
- [A] is the concentration at time t
- t is the time it takes for the reactant to get from [Ao] to [A].

Integrated rate law

To pick the correct integrated rate law to use is done in several ways.

- **Given order of reaction, concentration values , and time**– use indicated integrated Rate law

- **Given values – but not order**. You determine order from k and use correct integrated rate law

  - Units of K

    - $K = M^{1-n} t^{-1}$ n = overall order of Rxn

    - n = 0 $M^{1-0} t^{-1} = M t^{-1}$

    - n = 1 $M^{1-1} t^{-1} = t^{-1}$

    - n = 2 $M^{1-2} t^{-1} = M^{-1} t^{-1}$

- **Data table** – no order of reaction: use graphing computer and determine which plot gives you a straight line (look at regression if necessary)

Integrated rate law - Example

- The initial concentration of a reactant is zero order is 2.5 . Calculate the final concentration of the reactant after 80. seconds, if the rate constant is 3.4 x 10^{-3} M/S

Soln:

Integrated Rate Law for zero order:

$[A_F]$ = -kt + $[A_0]$

    = (-3.4 x 10-3 M/s) (80. sec) + 2.5 M

$[A_F]$ = 2.23 M

Integrated rate law - Example

- The initial concentration of 1.58M for the 2nd order reaction. It takes 12.3 mins for the concentration to decrease to 0.75 M. Calculate the rate constant k.

Soln:

$1/[A_F] = kt + 1/[A_0]$

$1/(0.75 \text{ M}) = k (12.3 \text{ mins}) + 1/(1.58 \text{ M})$

$0.700 \text{ M}^{-1} = k (12.30 \text{ mins})$

$k = 5.69 \times 10^{-2} \text{ M}^{-1} \text{ mins}^{-1}$

Integrated rate law - Example

- The initial concentration of reactant, if it took 4.7 mins to reach final concentration of 0.15 M. k= 2.5×10^{-2} $M^{-1}S^{-1}$

Soln:
Don't know order of reaction but determine it from the
Rate constant k
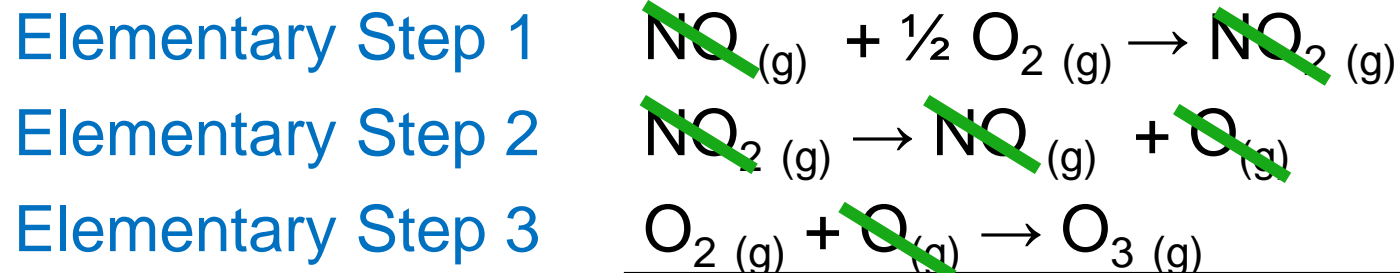
$n = 2$ M^{1-2} t^{-1} = M^{-1} t^{-1} Matches given k unit

Change mins into seconds = 282 secs

$1/[A_F]$ = $kt + 1/[A_0]$

$1/(0.15\ M)$ = 2.5×10^{-2} $M^{-1}S^{-1}$ (282 secs) + $1/[A_o]$)

$5.965 = 1 / [A_O]$

$[A_O] = 0.168$ M

Reaction Mechanisms

- Chemists often write chemical equations for reactions as a single step, which shows only a reaction's net result. However, most chemical reactions occur over a series of **elementary reactions**. The **reaction mechanism** is the step-by-step process by which reactants actually become products.

Mechanisms
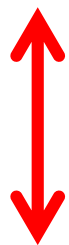
Overall Reaction:	$3/2 \ O_{2 \ (g)} \rightarrow O_{3 \ (g)}$

Elementary Step 1 $NO_{(g)} + \frac{1}{2} O_{2 \ (g)} \rightarrow NO_{2 \ (g)}$

Elementary Step 2 $NO_{2 \ (g)} \rightarrow NO_{(g)} + O_{(g)}$

Elementary Step 3 $O_{2 \ (g)} + O_{(g)} \rightarrow O_{3 \ (g)}$

A **mechanism** for a reaction is a collection of elementary processes (also called **elementary steps** or elementary reactions) that explains how the overall reaction proceeds

Reaction Mechanisms

- A **mechanism** represents the sequence of bond-making and bond-breaking steps that occur during the conversion of reactants to products

- A **mechanism** for a reaction is a collection of elementary processes (also called **elementary steps** or elementary reactions) that explains how the overall reaction proceeds.
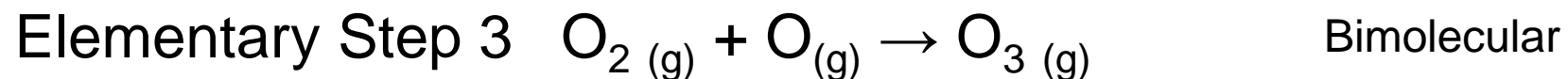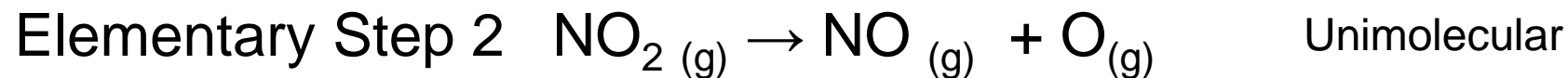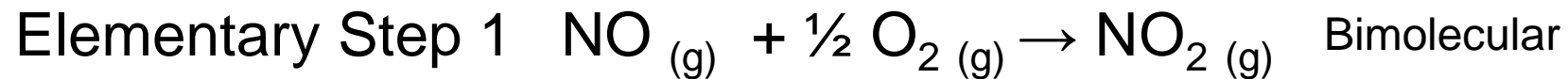
- **elementary steps**. The steps themselves are characterized by their "molecularity".

  - **Molecularity** – describes the number of molecules that participate in an atomic rearrangement.

Mechanism - Element Steps

- **Molecularity** – describes the number of molecules that participate in an atomic rearrangement

- **Molecularity** can be described as unimolecular, bimolecular, or termolecular. There are no known elementary reactions involving four or more molecules

  - Unimolecular – involves one reactant

  - Bimolecular- involves a collision between two reactant molecules

  - Termolecular collision between 3 reactant molecules (very rare, Why?)
    - Collision Theory

Elementary Step 1 $NO_{(g)} + ½ O_{2\,(g)} \rightarrow NO_{2\,(g)}$ Bimolecular

Elementary Step 2 $NO_{2\,(g)} \rightarrow NO_{(g)} + O_{(g)}$ Unimolecular

Elementary Step 3 $O_{2\,(g)} + O_{(g)} \rightarrow O_{3\,(g)}$ Bimolecular
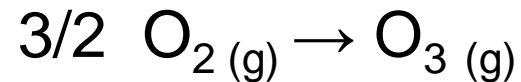
Mechanism - Element Steps

- In a mechanism, elementary steps proceed at various speeds.

  - The slowest step is the **rate-determining step (RDS)**.

  - The order for that elementary process (**RDS**) is the order for the overall reaction

    - but the concentrations of reactants in that step must be expressed in terms of the concentrations of the reactants.

      - Means – no **intermediates** in rate expression

- The **rate-determining step** is like the narrowest point in the hourglass; it is the "bottleneck" point of the reaction that determines how quickly reactants can become products

Mechanism – Intermediates & Catalyst

- **Intermediates** – produced in one step but consumed in another

- **Catalyst** – goes in as a reactant, comes out unharmed product and **DOES NOT** show up in the final overall rxn

Overall Reaction: $\quad$ $3/2$ $O_{2\,(g)} \rightarrow O_{3\,(g)}$

Elementary Step 1 $\quad$ $NO_{(g)} + \frac{1}{2} O_{2\,(g)} \rightarrow NO_{2\,(g)}$

Elementary Step 2 $\quad$ $NO_{2\,(g)} \rightarrow NO_{(g)} + O_{(g)}$

Elementary Step 3 $\quad$ $O_{2\,(g)} + O_{(g)} \rightarrow O_{3\,(g)}$

$\overline{}$

$3/2$ $O_{2\,(g)} \rightarrow O_{3\,(g)}$

$NO_{(g)}$ is a **homogeneous catalyst** – same phase as reacting molecules

Heterogeneous catalyst – different phase as reacting molecules

Mechanism – Rate Expression Elementary Steps

- **Rate expression for elementary steps**–cannot be predicated from overall stoichiometry.

- Coefficients of the reactants in an elementary step of a reaction indicates that reactant's order

  - NOT true for the overall reaction order

- **IN ELEMENTARY STEPS ONLY, COFFICIENTS ARE THE EXPONETS ON RATE LAW**

TABLE 12.3	Elementary Reactions and their Rate Laws	
Molecularity	**Elementary Reaction**	**Rate Law**
*Uni*molecular	A $\longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	A + A $\longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	A + B $\longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	A + A + A $\longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	A + A + B $\longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	A + B + C $\longrightarrow$ products	Rate $= k[A][B][C]$

Reaction Mechanism

Two Requirements for an acceptable Mechanisms

√ 1. The elementary steps sum to give the correct overall balanced equation

√ 2. The mechanism agrees with the experimentally determined rate law

NO_2 + CO → NO + CO_2 Given Rate = $k[NO_2]^2$

Step 1 NO_2 + NO_2 → NO + NO_3 Slow   Rate Determining Step

Step 2 NO_3 + CO → NO_2 + CO_2 Fast

Rate Elementary Step1 = $k [NO_2]^2$

Remember in Elementary steps coefficients become exponents
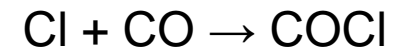
Reaction Mechanism - Example

- Elementary Step Rate expression cannot have an Intermediate in it

- Find overall Rate expression, Molecularity of each step, over reaction equation?

$Cl_2 \rightarrow 2Cl$ Fast

$Cl + CO \rightarrow COCl$ Fast

$COCl + Cl_2 \rightarrow COCl_2 + Cl$ **Slow**

$2Cl \rightarrow Cl_2$ Fast

Slow Step: determines Rate Expression

Rate = k [COCl][Cl$_2$]

[COCl] is an intermediate
$Cl + CO \rightarrow COCl$
Sub in
Rate = k[Cl][CO][Cl$_2$]
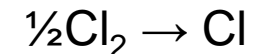
[Cl] is an intermediate
$\frac{1}{2}Cl_2 \rightarrow Cl$
Sub in
Rate = k[Cl$_2$]$^{\frac{1}{2}}$[CO][Cl$_2$]

Rate = k[Cl$_2$]$^{2/3}$ [CO]
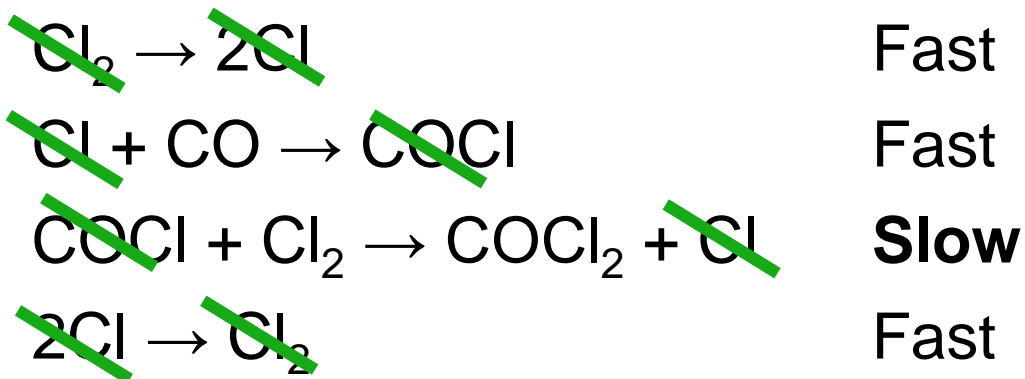
- **Activation Energy** - The difference in energy between the reactants and the transition state that is the energy barrier the reactants must overcome to achieve a chemical reaction.