

AP Chem
Kinetics
Topic #7

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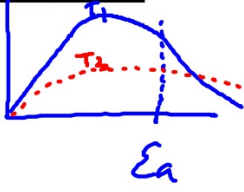
Schedule

Monday	Tuesday	Wed	Thur	Fri	Sat/Sun

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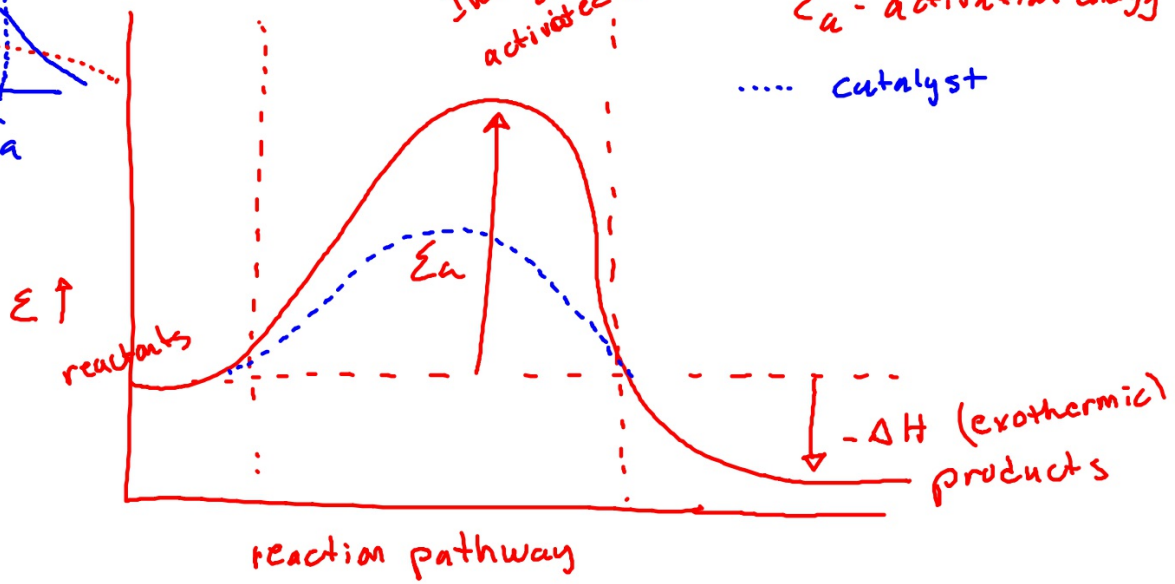
Introduction



Intermediate
or
activated complex

E_a - activation energy

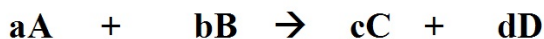
..... catalyst



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Formula Page

$$\text{rate} = \frac{\Delta[A]}{\Delta t}$$



$$\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Algebraic Method for Determining Rate Law Based on Data

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k_1 [\text{reactant}]^m [\text{reactant}]^n}{k_2 [\text{reactant}]^m [\text{reactant}]^n}$$

Order	Rate Law	Integrated Rate Law	Straight Line Plot
0	rate = k	$[A]_t = -kt + [A]_0$	$[A]_t$ vs. time
1	rate = k[A]	$\ln [A]_t = -kt + \ln [A]_0$	$\ln [A]_t$ vs. time
2	rate = k[A] ²	$1/[A]_t = kt + 1/[A]_0$	$1/[A]_t$ vs. time

$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

Activation Energy
slope = $-\frac{E_a}{R}$

Arrhenius Equation

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

activation energy based from two T

Half-Life

$$t_{1/2} = \frac{[A]_0}{2k}$$

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

$$t_{1/2} = \frac{1}{k[A]_0}$$

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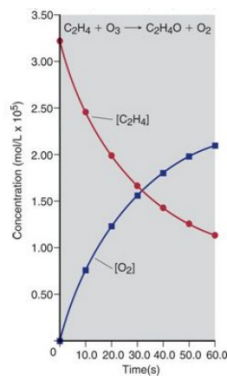
Reaction Rate

Meaning of the reaction rate



$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = +\frac{1}{c} \frac{\Delta[C]}{\Delta t} = +\frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

1. The reactant concentration decreases while the product concentration increases.
2. The change in reactant concentration is always negative, < 0 .
3. The change in product concentration is always positive, > 0 .
4. [] square bracket expresses the concentration in moles per liter ($\text{mol/L} = M$).



Note: Multiplying by the inverse of the coefficient sets ALL the changes in concentration over time equal to the overall rate of the reaction.

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Reaction Rate

- "rate" is equal to some measurable quantity changing with time.
- For a chemical reaction, we measure a change in concentration, molarity = mol/L = *M* vs. time, $\Delta[X]/\Delta t$ with a label of *M/s* or *M-s⁻¹*.
 - A decrease in reactant concentration or an increase in product concentration over change in time.
 - change is *negative* for reactants and *positive* for products
 - rate is not constant, it changes with time. Why?
- Let's take a look at the decomposition of NO₂.
 $2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g)$
 - What does the data initially tell us?
 - By studying the stoichiometry, we can conclude
 - a) O₂ forms at half the rate NO₂ decomposes
 - b) NO forms at the same rate as the decomposition of NO₂
 - c) NO appears twice as fast as O₂ appears

Time (s)	[NO ₂]	[NO]	[O ₂]
0	0.0100	0.0000	0.0000
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

$$\text{Initial Rate of Reaction} = \left| \frac{-\Delta[\text{NO}_2]}{\Delta t} \right|$$

$$\text{rate} = \frac{(0.0079 - 0.0100)M}{(50 - 0)s} = \left| -4.2 \times 10^{-5} M\text{-s}^{-1} \right| = 4.2 \times 10^{-5} M\text{-s}^{-1}$$

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Reaction Rate

$$\text{rate} = \frac{\Delta[A]}{\Delta t}$$

Even though the change in rate of consumption is a negative value and the rate of production is a positive value, these values are usually written as absolute values.

Kinetics Topic#7 Sample WS#1 - Reaction Rates

1. Consider the reaction, $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$. If the 0.879 moles of NO_2 were consumed over a specific time in a 3.50L container each second of the reaction, what are the rates of production for NO and O_2 in this experiment? (Ans: NO: $0.251\text{M}\cdot\text{s}^{-1}$, O_2 : $0.126\text{M}\cdot\text{s}^{-1}$)

Giv
mol = 0.879
V = 3.50L

NTK
 $[\text{NO}_2] = \frac{0.879}{3.50} = 0.251\text{M}$

unk
rate_{NO} =

rate_{NO₂} = $0.251\text{M}\cdot\text{s}^{-1}$

rate_{O₂} =

Solve:

$$0.251\text{M NO}_2 \times \frac{2\text{NO}}{2\text{NO}_2} = \boxed{0.251\text{M}\cdot\text{s}^{-1}}$$

$$0.251\text{M NO}_2 \times \frac{\text{O}_2}{2\text{NO}_2} = \boxed{0.126\text{M}\cdot\text{s}^{-1}}$$

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$$\text{rate} = \frac{\Delta[A]}{\Delta t}$$

Relative Reaction Rate Practice Problems

2. Write the relative rate terms for each of the species in the reaction: $4\text{PH}_3(\text{g}) \rightarrow \text{P}_4(\text{g}) + 6\text{H}_2(\text{g})$. In regards to the reaction, if, in a certain experiment, over a specific time period, 0.0048 mole of PH_3 is consumed in a 2.0L container each second of reaction, what are the rates of production of P_4 and H_2 in this experiment?
(Ans: P_4 : $6.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ and H_2 : $3.6 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$)

$$\begin{array}{l} \text{Giv} \\ 0.0048 \text{ moles } \text{PH}_3 \\ V = 2.0\text{L} \end{array}$$

$$\begin{array}{l} \text{NTR} \\ [\text{PH}_3] = \frac{0.0048}{2} = 0.0024 \text{ mol} \cdot \text{L}^{-1} \\ \text{rate } \text{PH}_3 = 0.0024 \text{ Mol} \cdot \text{s}^{-1} \end{array} \quad \begin{array}{l} \text{DnK} \\ [\text{P}_4] = \frac{6.0 \times 10^{-4} \text{ M}}{1} \\ [\text{H}_2] = \frac{3.6 \times 10^{-3} \text{ M}}{1} \end{array}$$

Solve:

$$\text{P}_4: 0.0024 \text{ mol} \cdot \text{L}^{-1} \times \frac{\text{P}_4}{4\text{PH}_3} = \boxed{6.0 \times 10^{-4} \text{ M} \cdot \text{s}^{-1}}$$

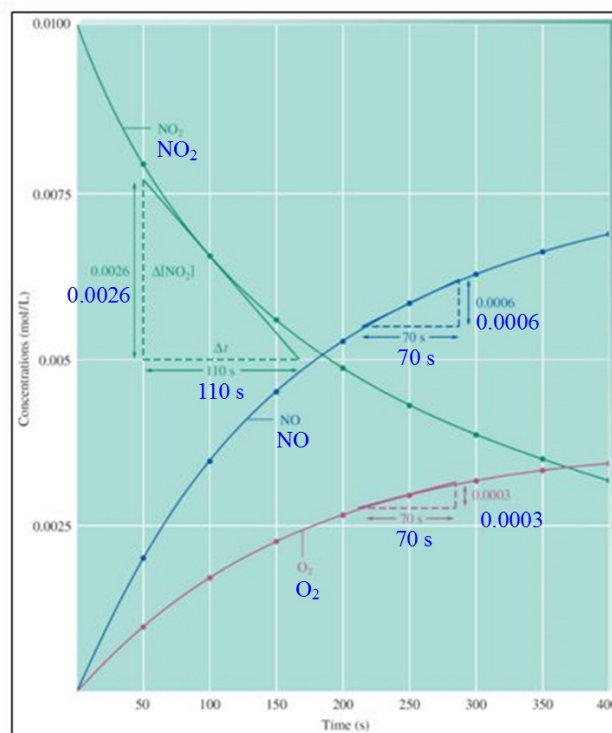
$$\text{H}_2: 0.0024 \text{ mol} \cdot \text{L}^{-1} \times \frac{6\text{H}_2}{4\text{PH}_3} = \boxed{3.6 \times 10^{-3} \text{ M} \cdot \text{s}^{-1}}$$

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Instantaneous Reaction Rate

- the rate at a specific time
- to calculate, draw a line tangential to the curve then calculate the slope of the tangential line.
- What is the instantaneous rate of the decomposition of NO_2 ?

$$\frac{\Delta y}{\Delta x} = \frac{0.0026}{110\text{s}} = 2.4 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}$$



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Instantaneous Reaction Rate

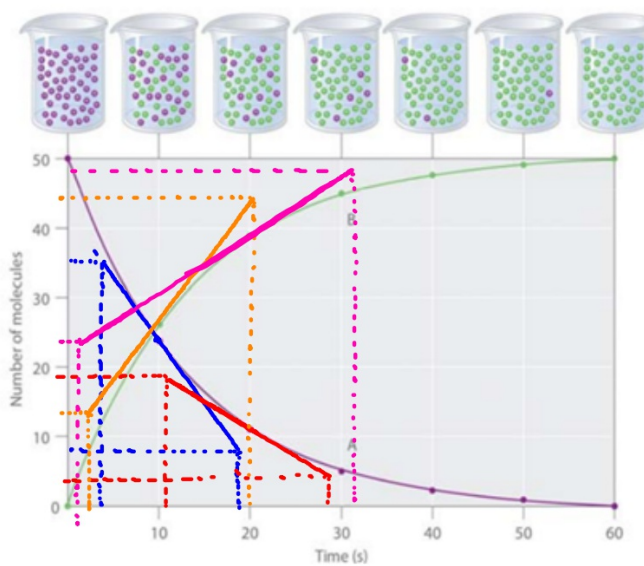
3. Using the diagram in the presentation, calculate the instantaneous rate:
- for the reactant, A, at 10s and at 20s.
 - for the product, B, at 10s and at 20s.
 - What has happened to this system at 60seconds?

a. $\frac{\Delta y}{\Delta x} = \frac{7-35}{19-3} = -1.75$ ●

$\frac{\Delta y}{\Delta x} = \frac{4-19}{28-11} = -0.88$ ✓ ●

b. $\frac{\Delta y}{\Delta x} = \frac{45-14}{20-2} = 1.72$ ●

$\frac{\Delta y}{\Delta x} = \frac{49-23}{31-1} = 0.87$ ✓ ●



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Reaction Rate - Factors

Kinetics is the study of the speed or rate of a reaction under specified conditions.

- Remember that thermodynamic favorability is important but DOES NOT imply a fast reaction.

For example, the changing of graphite into diamond is thermodynamically favorable but occurs so slowly that we cannot see any change, even in a lifetime. Why? The activation energy (E_a) is so high that the reaction doesn't proceed.

Factors Affecting Reaction Rate

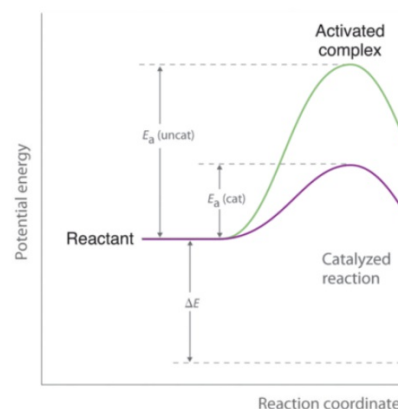
- Nature of reactants
 - physical state matters (consider gasoline (*l*) vs gasoline (*g*))
 - chemical identity - What exactly is reacting?
 - ions of opposite charge react quickly
 - the more bonds a reacting species has, the slower the reaction rate (more energy needed separate)
 - stronger bonds, more energy needed to break (slower reaction rate)
 - sodium reacts faster with water than calcium
- Concentration - With more particles present, more collisions occur and the faster the reaction proceeds, so the greater the rate.
- Temperature - "Heat 'em up and Speed 'em up." Faster particles result in more collisions with enough energy to react.
 - An increase in T produces more collisions that can overcome the needed activation energy.
 - Generally, a 10°C increase in T will result double the reaction rate.

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Reaction Rate - Factors

Factors Affecting Reaction Rate

- Surface area of reactants - greater the surface area allows a reaction to occur at more places.
 - Reactions occur at the boundary (interface) between the two phases (except in solutions and gases). In other words, at the exposed surfaces.
 - More surface area leads to a greater chance of correct collisions between particles hence a faster reaction rate. Ex. coal dust is explosive while coal is not. Aqueous solutions are the ULTIMATE exposure!
- Addition of an inert gas DOES NOT affect rate or equilibrium of a reaction. Not part of the mechanism.
- Catalysis is the increase in the rate of reaction due to a substance called a catalyst.
 - A catalyst is not consumed during the reaction.
 - Enzymes are biological catalysts that are affected by heat and pH. Lose effectiveness at high T and pH change.
 - Changes the reaction pathway, lowering the E_a for the reaction.
 - Usually, the catalyst participates in the slowest step (rate determining step).
 - Homogeneous catalyst - same phase as the reactants.
 - Heterogeneous catalyst - different phase as the reactants. Appear in rate law because their concentration does affect the rate of the reaction.



Reaction Rate - Factors

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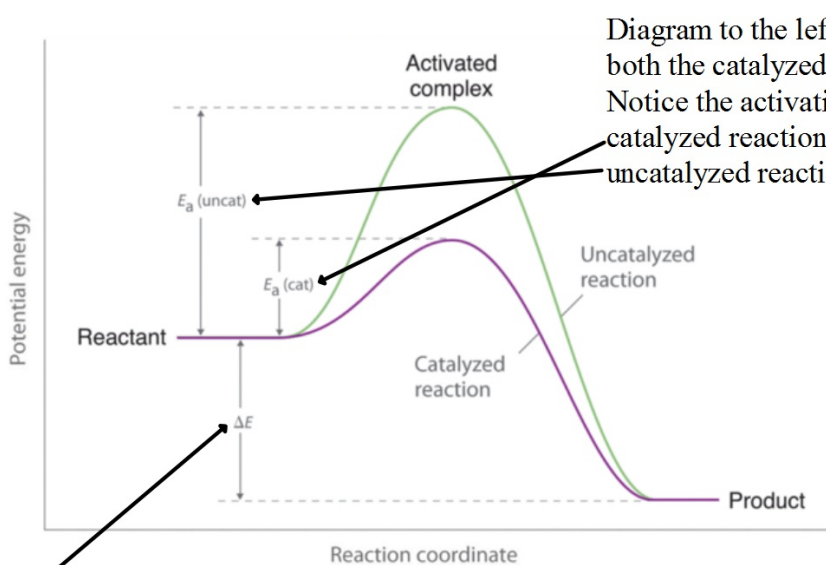


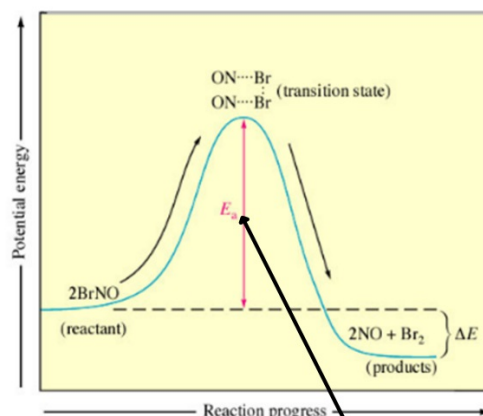
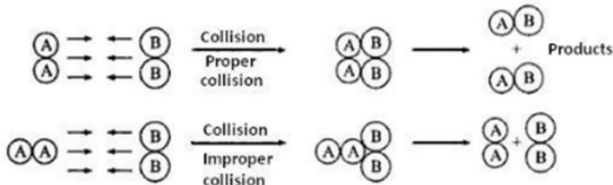
Diagram to the left illustrates a reaction for both the catalyzed and uncatalyzed reaction. Notice the activation energy, E_a , for the catalyzed reaction is lower than the uncatalyzed reaction.

Also, the addition of a catalyst DOES NOT affect the energy change between the reactants and products.

Reaction Rate - Collision Theory

Collision Theory of Reaction Rates

- Particles need to collide in order to react with only a percentage of the collisions actually leading to a change. Successful collisions have enough energy (E_a) at collision to break bonds and start the process of forming new bonds.
- Essential Components of a Collision Theory
 - Particles must collide
 - Usually, only two particles collide at a time
 - Proper orientation of colliding particles
 - Collision must have enough energy to overcome E_a .
 - An activated complex (transition state) is created at the peak of the E_a .



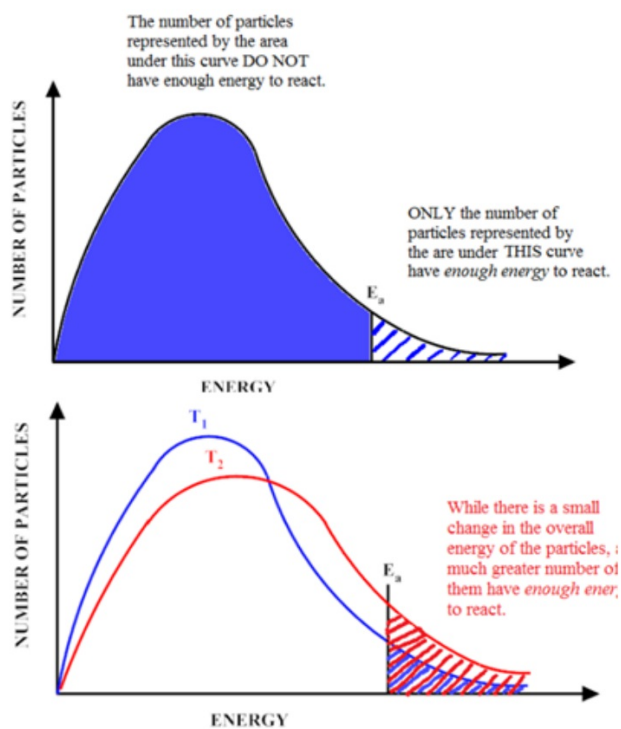
activation energy for the reaction, E_a

Reaction Rate - Collision Theory

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Maxwell-Boltzmann Distribution of E_a

- plots number of particles vs. energy of particles (KE directly related to T)
- a certain percentage of particles will have enough energy to conquer the E_a of the reaction.
- An increase in T from T_1 to T_2 will result in more particles with enough energy to react



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Determining Rate Law

Rate Law (or Expression) (or Differential Rate Law)

- Measure *initial reaction rates* immediately after mixing of products
 - Many reactions form an equilibrium after a given amount of time where **forward rate** is equal to **reverse rate**, so for kinetics we look at the reaction immediately after mixing of the reactants.
 - Only reactants are in rate law
- The rate law is the relation between reaction rate and the initial concentrations of the reactants.
- The rate law CAN ONLY be determined from experimental data.
 - So, to find the exact relation between rate and concentration, experiments must be conducted and data collected. A subsequent interpretation of the data can yield the rate law for the reaction.

General reaction: $aA + bB \rightarrow xX$

Rate Law Skeleton

$$\text{Rate} = k[A]^m[B]^n$$

where

k is the rate constant

$[A]$ = molar concentration of reactant A

$[B]$ = molar concentration of reactant B

m = order of reaction for reactant A

n = order of reaction for reactant B

*we call the exponents "orders" and they can be zero, a whole number, or a fraction. These orders are derived from experimental data

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Determining Rate Law
The Rate Constant, k

- T dependent
- You will be asked to determine the value and units of k
- General rule for determining the unit for k :

add the orders of the reactants subtract 1, take the inverse and add s to the denominator

• Example: rate = $k[A]^2[B]$ the label for k is $L^2 \cdot mol^{-2} \cdot s^{-1}$

reaction order 3

$$L^2 \cdot mol^{-2} \cdot s^{-1}$$

Orders

- m and n are *reactant* orders
- the sum of m and n is the *reaction* order
- From the above rate law, the reactant order with respect to A is 2, B is 1, and the reaction order is 3.

Rate Law Skeleton

$$\text{Rate} = k[A]^m[B]^n$$

$$1 = s^{-1}$$

How to determine the reactant order:

- zero order - a change in concentration of a reactant has NO effect on rate.
- first order - rate is directly proportional to increase in concentration of reactant: double reactant concentration doubles reaction rate. Very common! Nuclear decay reactions are first order. General form of rate law; Rate = $k[A]^1 = k[A]$
- second order - rate quadruples when reactant concentration is doubled or rate increases by a factor of 9 when reactant concentration is tripled. Common especially in gas phase reactions. General form of rate law; Rate = $k[A]^2$ or Rate = $k[A]^1[B]^1$ (or $k[A][B]$)
- fractional orders - rare but do exist, use mathematical equation to calculate this form of reactant order.

$$2^x = 2 \quad x=1$$

$$2^x = 4 \quad x=2$$

$$3^x = 9 \quad x=2$$

Determining Rate Law

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Rate Law Skeleton

$$\text{Rate} = k[A]^m[B]^n$$

Reactants - Doubled, Rate - Does Not Change

$$2^m = 1$$

$$m = 0$$

(zero order)

Reactants - Doubled, Rate - Doubles

$$2^m = 2$$

$$m = 1$$

(first order)

Reactants - Doubled, Rate - Quadruples

$$2^m = 4$$

$$m = 2$$

(second order)

Reactants - Tripled, Rate - Increases by a Factor of Nine

$$3^m = 9$$

$$m = 2$$

(second order)

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Determining Rate Law - Table Logic

Method 1: Table Logic

After selecting two trials where one of the reactants is held constant, ask yourself

- (1) Did the rate double when the concentration of the other reactant was doubled? Yes, then the reaction order for this reactant is 1.
- (2) Did the rate quadruple when the concentration of the other reactant was doubled? Yes, then the reaction order for this reactant is 2.
- (3) Did the rate increase by a factor of eight when the concentration of the other reactant was doubled? Yes, then the reaction order for this reactant is 3.
- (4) Did the rate remain constant when the concentration of the other reactant was doubled? Yes, then the reaction order for this reactant is 0.

Example: Ponder the following experimental data for the reaction $A + B \rightarrow \text{Product}$

$\text{rate} = k[A]^0[B]$

Experiment Number	Initial Rate mol/(L•hr)	Initial concentration [A] ₀	Initial concentration [B] ₀
1	0.50×10^{-2}	0.50	0.20
2	0.50×10^{-2}	0.75	0.20
3	0.50×10^{-2}	1.00	0.20
4	1.00×10^{-2}	0.50	0.40
5	1.50×10^{-2}	0.50	0.60

$2^m = 1$
 $m = 0$

$2^n = 2$
 $n = 1$

$\text{rate} = k[B]$

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Determining Rate Law - Table Logic

Method 1: Table Logic

Example: Ponder the following experimental data for the reaction $A + B \rightarrow \text{Product}$

Experiment Number	Initial Rate mol/(L·hr)	Initial concentration [A] ₀	Initial concentration [B] ₀
1	0.50×10^{-2}	0.50	0.20
2	0.50×10^{-2}	0.75	0.20
3	0.50×10^{-2}	1.00	0.20
4	1.00×10^{-2}	0.50	0.40
5	1.50×10^{-2}	0.50	0.60

$$\frac{\text{mol}}{\text{L} \cdot \text{s}} = k \left(\frac{\text{mol}}{\text{L}} \right) \left(\frac{\text{mol}}{\text{L}} \right)$$

$$\text{L} \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$$

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

$$\text{L}^0 \cdot \text{mol}^{-0} \cdot \text{hr}^{-1}$$

Using a data table of experimental data and logic to determine:

a) rate law

$$\text{rate} = k [A]^m [B]^n$$

$$\text{rate} = k [B]$$

b) reactant order

$$A = \text{zero}$$

$$B = \text{one}$$

c) reaction order

$$0 + 1 = 1$$

e) units for k

$$\text{s}^{-1}$$

$$\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

$$1 - 1 = 0$$

d) value of k

$$\text{rate} = k [B]$$

$$0.50 \times 10^{-2} = k (0.20)$$

$$\frac{0.5 \times 10^{-2}}{0.20} = k$$

$$k = 0.025 \text{hr}^{-1} \text{L}^x \cdot \text{mol}^{-x} \cdot \text{s}^{-1} \text{power}(x)$$

$$x \cdot 1 = 1$$

$$\text{L}^1 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

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Determining Rate Law - Algebraic

Method 2: "Ugly Algebraic Method"

Example: Ponder the following experimental data for the reaction $A + B \rightarrow \text{Product}$

Experiment Number	Initial Rate mol/(L•hr)	Initial concentration [A] ₀	Initial concentration [B] ₀
1	0.50×10^{-2}	0.50	0.20
2	0.50×10^{-2}	0.75	0.20
3	0.50×10^{-2}	1.00	0.20
4	1.00×10^{-2}	0.50	0.40
5	1.50×10^{-2}	0.50	0.60

$\frac{1}{2} = \left(\frac{1}{2}\right)^n$
 $n = 1$

Using a data table of experimental data and algebra to determine:

a) rate law

$rate = k[A]^m[B]^n$
#1
#4

$$\frac{rate_1}{rate_2} = \frac{k_1 [reactant]^m [reactant]^n}{k_2 [reactant]^m [reactant]^n} \text{ becomes } \frac{0.50 \times 10^{-2}}{1.00 \times 10^{-2}} = \frac{k_1 [0.50]^m [0.20]^n}{k_2 [0.50]^m [0.40]^n}$$

b) reactant order

A - 0
B - 1

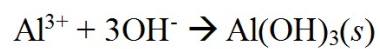
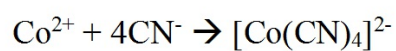
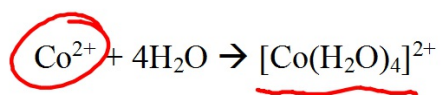
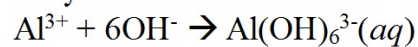
Commence canceling like terms!

c) reaction order

1

$$\frac{0.50 \times 10^{-2}}{1.00 \times 10^{-2}} = \frac{k_1 [0.50]^m [0.20]^n}{k_2 [0.50]^m [0.40]^n} \text{ becomes } \frac{0.50}{1.00} = \frac{[0.20]^n}{[0.40]^n} \text{ which simplifies to } \frac{1}{2} = \left[\frac{1}{2}\right]^n \therefore n = 1$$

Determining Rate Law**Ligands**OH⁻Cl⁻H₂O (neutral, do not affect charge on cation)NH₃ (neutral, do not affect charge on cation)SCN⁻CN⁻**Kinetics**
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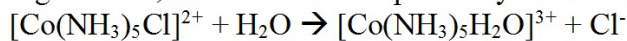
yet if we add more OH⁻

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Determining Rate Law

Rate Law Practice Problems

4. In the following reaction, a Co-Cl bond is replaced by a Co-OH₂ bond.



$$\text{Initial rate} = k \{ [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \}^m$$

Using the data below, find the value of m in the rate expression and calculate the value of k .

Exp	Initial Concentration of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$	Initial Rate (mol/L-min)
1	1.0×10^{-3}	1.3×10^{-7}
2	2.0×10^{-3}	2.6×10^{-7}
3	3.0×10^{-3}	3.9×10^{-7}

Ans: $m = 1, k = 1.3 \times 10^{-4} \text{ min}^{-1}$

Table Logic

Use Exp #1 & #2

$[\text{x}]$ is doubled, and this doubles the initial rate

$$2^x = 2 \text{ so } m = 1 \quad \text{rate} = k \{ [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \}^m$$

Use Exp #1

$$1.3 \times 10^{-7} = k (1.0 \times 10^{-3})^1$$

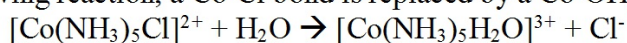
$$k = \frac{1.3 \times 10^{-7}}{1.0 \times 10^{-3}} = 1.3 \times 10^{-4} \text{ min}^{-1}$$

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Determining Rate Law

Rate Law Practice Problems

4. In the following reaction, a Co-Cl bond is replaced by a Co-OH₂ bond.



$$\text{Initial rate} = k\{[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}\}^m$$

Using the data below, find the value of m in the rate expression and calculate the value of k .

Exp	Initial Concentration of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$	Initial Rate (mol/L-min)
1	1.0×10^{-3}	1.3×10^{-7}
2	2.0×10^{-3}	2.6×10^{-7}
3	3.0×10^{-3}	3.9×10^{-7}

Ans: $m = 1, k = 1.3 \times 10^{-4} \text{ min}^{-1}$

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k_1 \{[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}\}^m}{k_2 \{[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}\}^m}$$

$$\frac{1.3 \times 10^{-7}}{2.6 \times 10^{-7}} = \frac{k_1 (1.0 \times 10^{-3})^m}{k_2 (2.0 \times 10^{-3})^m}$$

$$\text{so } \frac{1.3}{2.6} = \left(\frac{1.0}{2.0}\right)^m$$

$$0.5 = 0.5^m$$

$$1 = m$$

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k_1 [\text{reactant}]^m [\text{reactant}]^n}{k_2 [\text{reactant}]^m [\text{reactant}]^n} \text{ becomes } \frac{0.50 \times 10^{-2}}{1.00 \times 10^{-2}} = \frac{k_1 [0.50]^m [0.20]^n}{k_2 [0.50]^m [0.40]^n}$$

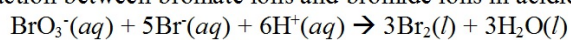
Commence canceling like terms!

$$\frac{0.50 \times 10^{-2}}{1.00 \times 10^{-2}} = \frac{k_1 [0.50]^m [0.20]^n}{k_2 [0.50]^m [0.40]^n} \text{ becomes } \frac{0.50}{1.00} = \frac{[0.20]^n}{[0.40]^n} \text{ which simplifies to } \frac{1}{2} = \left[\frac{1}{2}\right]^n \therefore n=1$$

Kinetics
Topic#7

Determining Rate Law

5. (OYO) The reaction between bromate ions and bromide ions in acidic aqueous solution is given by the equation



The table below gives the results of four experiments. Using these data, determine the orders for all three reactants, the overall reaction order, and the value of the rate constant with proper units.

Experiment	Initial [BrO ₃ ⁻]	Initial [Br ⁻]	Initial [H ⁺]	Measured Initial Rate (mol/L-s)
1	0.10	0.10	0.10	8.0x10 ⁻⁴
2	0.20	0.10	0.10	1.6x10 ⁻³
3	0.20	0.20	0.10	3.2x10 ⁻³
4	0.10	0.10	0.20	3.2x10 ⁻³

Ans: rate = $k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$, overall = 4, $k = 8.0 \text{ L}^3/\text{mol}^3\text{-s}$ (or $\text{L}^3 \text{ mol}^{-3} \text{ s}^{-1}$)

Kinetics
Topic#7

Determining Rate Law

HW Questions

5. At 40°C, $\text{H}_2\text{O}_2(l)$ will decompose according to the following reaction:

$2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$. The following data were collected for the concentration of H_2O_2 at various times.

Time (s)	$[\text{H}_2\text{O}_2]$ (mol/L)
0	1.000
2.16×10^4	0.500
4.32×10^4	0.250

- a. Calculate the average rate of decomposition of H_2O_2 between 0 and 2.16×10^4 s. Use this rate to calculate the average rate of production of $\text{O}_2(g)$ over the same period. (Ans: $1.16 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$)
- b. What are these rates for the time period 2.16×10^4 s to 4.32×10^4 s? (Ans: $2.31 \times 10^{-5} \text{ mol/L}\cdot\text{s}$, $1.16 \times 10^{-5} \text{ mol/L}\cdot\text{s}$)

Kinetics
Topic#7

Determining Rate Law

HW Questions

2. If a reaction is second order in B and the concentration of B increased from $0.0850M$ to $0.2975M$, what should happen to the rate?

3. For each of the following rate equations, describe what would happen to the rate if the concentration of reactant A was tripled and the concentration of reactant B is halved.

- a. Rate = $k[A][B]$ (Ans: 1.5 times)
- b. Rate = $k[A]^2[B]$ (Ans: 4.5 times)
- c. Rate = $k[A]^2[B]^2$ (Ans: 2.25 times)
- d. Rate = $k[A][B]^3$ (Ans: 0.375 times)

Kinetics
Topic#7

Determining Rate Law

WS#2

7. The reaction $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ was studied at 904°C , and the data in the table were collected.

	<u>Initial [NO] mol•L⁻¹</u>	<u>Initial [H₂] mol•L⁻¹</u>	<u>Initial Rate N₂ mol•L⁻¹•s⁻¹</u>
Experiment 1	0.420	0.122	0.136
Experiment 2	0.210	0.122	0.0339
Experiment 3	0.210	0.244	0.0678
Experiment 4	0.105	0.488	0.0339

- Determine the order of the reaction for each reactant. (Ans: NO is 2 and H₂ is 1)
- Write the rate equation for the reaction. (Ans: rate = $k[\text{NO}]^2[\text{H}_2]$)
- Calculate the rate constant at 904°C . (Ans: $6.32 \text{ L}^2\text{-mol}^{-2}\text{-s}^{-1}$)
- Find the rate of appearance of N₂ at the instant when $[\text{NO}] = 0.350\text{M}$ and $[\text{H}_2] = 0.205\text{M}$. (Ans: $0.159 \text{ mol-L}^{-1}\text{-s}^{-1}$)

Kinetics
Topic#7

Determining Rate Law

WS#2

7. The reaction $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ was studied at 904°C , and the data in the table were collected.

Time (s)	[O] (atoms/cm ³)
0	5.0×10^9
1.0×10^{-2}	1.9×10^9
2.0×10^{-2}	6.8×10^8
3.0×10^{-2}	2.5×10^8

a. What is the order of the reaction with respect to oxygen atoms?

b. The reaction is known to be first order with respect to NO_2 . Determine the overall rate law and the value of the rate constant.

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Topic#7

Determining Rate Law

4. The data below were collected for the reaction at 327°C: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$

Experiment	Initial $[\text{H}_2]$ (mol/L)	Initial $[\text{I}_2]$ (mol/L)	Initial Rate (mol-L ⁻¹ -s ⁻¹)
1	0.113	0.110	3.01x10 ⁻⁴
2	0.220	0.330	1.76x10 ⁻³
3	0.550	0.110	1.47x10 ⁻³

- What is the reaction order in terms H_2 ? (Ans: 1st order for H_2)
- What is the reaction order in terms I_2 ? (Ans: 1st order for I_2)
- What is the overall reaction order of this reaction? (Ans: 2nd order for reaction)
- Determine the rate law for this reaction. (Ans: rate = $k[\text{H}_2][\text{I}_2]$)
- Calculate the value of k for this reaction and express the answer with the correct units.
(Ans: $k = 0.0242\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)

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Types of Rate Law

Two Types of Rate Law: Differentiated and Integrated

- Differentiated - data table contains concentration and initial rates
 - solve for k using table logic or algebraic methods
- Integrated - data table contains concentration and time
 - use graphical methods to determine the order of a given reactant
 - solve for k using the integrated rate law (shown below)

Order	Rate Law	Integrated Rate Law	Straight Line Plot
0	rate = k	$[A]_t = -kt + [A]_0$	$[A]_t$ vs. time
1	rate = $k[A]$	$\ln [A]_t = -kt + \ln [A]_0$	$\ln [A]_t$ vs. time
2	rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$1/[A]_t$ vs. time

$y = mx + b$

Table 1
Graphs for Integrated Rate Laws

Integrated Rate Law

Integrated Rate Law (Concentration-Time Data)

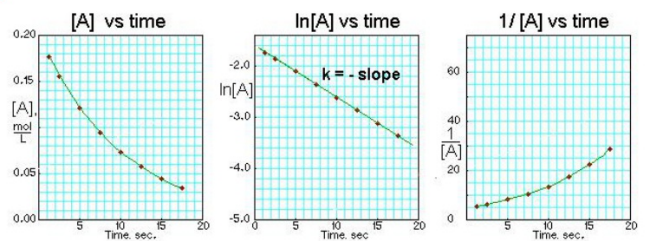
- Used to determine time it takes for a reactant to arrive at a specific concentration.
- Always plot concentration (y -axis) vs time (x -axis)
- Plot three graphs
 - 1st: concentration vs. time: $[A]$ vs time
 - straight line: zero order for reactant
 - 2nd: $\ln(\text{concentration})$ vs time: $\ln[A]$ vs. time
 - straight line: first order for reactant
 - 3rd: $1/[\text{concentration}]$ vs time: $1/[A]$ vs. time
 - straight line: second order for reactant
- You are in search of linear data!

**Kinetics
Topic#7**

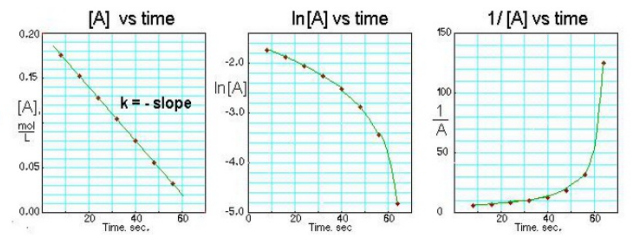
Integrated Rate Law

[A] vs time - straight line: zero order for reactant
 ln[A] vs. time - straight line: first order for reactant
 1/[A] vs. time - straight line: second order for reactant

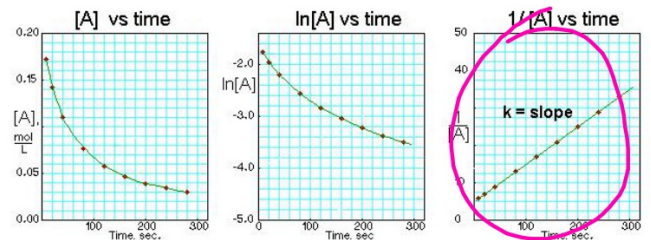
(a) 1st



(b) 0



(c) 2nd



Identify the following graphs as either zero order, first order, or second order.

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Integrated Rate Law

You can solve for either time or concentration by remembering the equation for a line; $y = mx + b$.

	y	=	mx	+	b
zero order:	$[A]_t$	=	$-kt$	+	$[A]_0$
first order:	$\ln[A]_t$	=	$-kt$	+	$\ln[A]_0$
second order:	$1/[A]_t$	=	kt	+	$1/[A]_0$

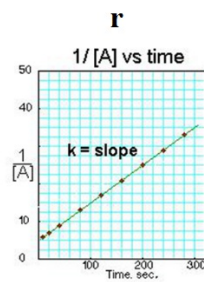
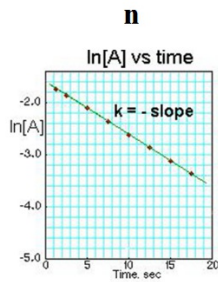
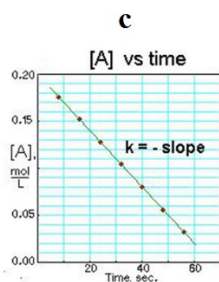
where,

$[A]_0$ is the initial concentration of the reactant

$|\text{slope}| = k$ since the rate constant is NEVER negative

If asked to write the rate law from a graph it is simply: $\text{Rate} = k[A]^{\text{order}}$ determined from graphs

If you set the graphs in order of y-axis; concentration, natural log of concentration, and reciprocal of concentration, the graph that produces a straight line will be the order for the reactant. This follows alphabetically which leads to **c** is 0, **n** is 1st, **r** is 2nd orders respectively.

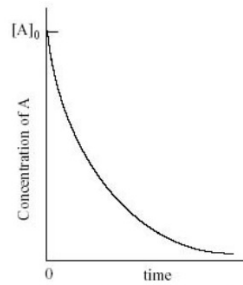


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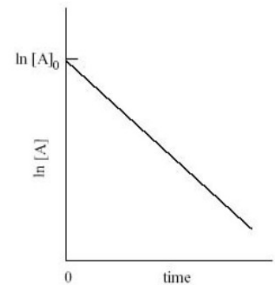
Integrated Rate Law - 1st Order Reactions

First order integrated rate law: $\ln[A]_t = -kt + \ln[A]_0$
 Straight line graph $\ln[A]$ vs t ,
 Slope = $-k$,
 Half-life: $t_{1/2} = 0.693/k$

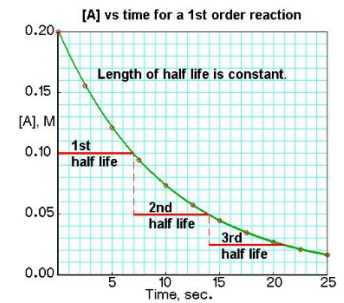
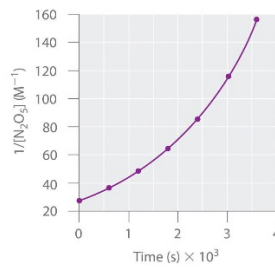
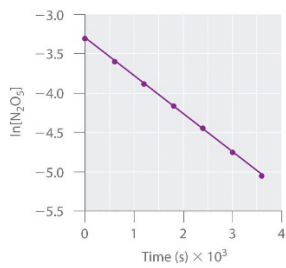
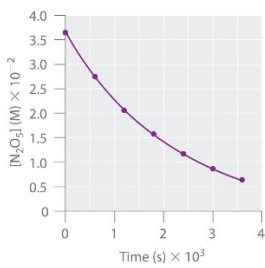
First Order



Graph of $[A]_0$ vs. time
Curved Plot



Graph of $\ln[A]_0$ vs. time
 k - negative slope

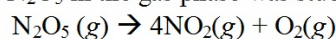


Kinetics
Topic#7

Integrated Rate Law - 1st Order Reactions

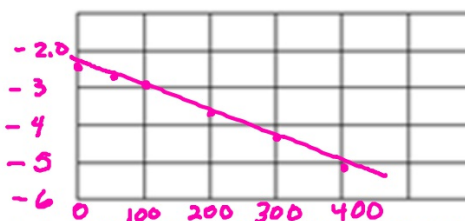
Kinetics Sample WS#2 - Integrated Rate Law

1. The decomposition of N₂O₅ in the gas phase was studied at constant temperature.



The following data were collected:

[N ₂ O ₅]	Time (s)	ln[N ₂ O ₅]
0.1000	0	-2.303
0.0707	50	-2.649
0.0500	100	-2.996
0.0250	200	-3.689
0.0125	300	-4.382
0.00625	400	-5.075



First order integrated rate law:

$$\ln[A] = -kt + \ln[A]_0$$

graph $\ln[A]$ vs t ,

slope = $-k$, half-life = $0.693/k$

$$\ln[N_2O_5]_t = -kt + \ln[N_2O_5]_0$$

(a) Verify the rate law is first order in [N₂O₅] and write the rate law. Graph $\ln [N_2O_5]$ vs time and label graph properly.

• 1st order

$$\text{rate} = k [N_2O_5]$$

(b) Calculate the value of k . (use integrated rate law and slope method)

$$\ln [A]_t = -kt + \ln [A]_0$$

$$-5.075 = -k(400) + (-2.303) = \underline{6.93 \times 10^{-3} \text{ s}^{-1}}$$

$$k = - \left(\frac{\Delta Y}{\Delta X} \right) = \frac{-5.075 - (-2.303)}{400 - 0} = - \left(\frac{-2.772}{400} \right) = \underline{0.00693 \text{ s}^{-1}}$$

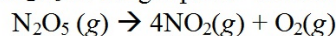
Ans: rate = $k[N_2O_5]$, $k =$ -slope of graph $\ln[N_2O_5]$ vs. time = $6.93 \times 10^{-3} \text{ s}^{-1}$; 0.0177M; 0.00156M; 606s; 100s

Kinetics
Topic#7

Integrated Rate Law - 1st Order Reactions

Kinetics Sample WS#2 - Integrated Rate Law

1. The decomposition of N₂O₅ in the gas phase was studied at constant temperature.



The following data were collected:

[N ₂ O ₅]	Time (s)	ln[N ₂ O ₅]
0.1000	0	
0.0707	50	
0.0500	100	
0.0250	200	
0.0125	300	
0.00625	400	

First order integrated rate law:

$$\ln[A] = -kt + \ln[A]_0$$

graph $\ln[A]$ vs t ,

slope = $-k$, half-life = $0.693/k$

$$\ln[\text{N}_2\text{O}_5]_t = -kt + \ln[\text{N}_2\text{O}_5]_0$$

(e) At what time is the concentration of N₂O₅(g) equal to 0.00150M? Explain how you know your answer is correct.

$$\ln[\text{N}_2\text{O}_5]_t = -kt + \ln[\text{N}_2\text{O}_5]_0$$

$$\ln(0.00150) = -(0.00693)t + (-2.303)$$

$$\frac{-6.502 + 2.303}{-0.00693} = t = 606 \text{ s}$$

(c) Determine the concentration of N₂O₅(g) at 150s.

Does your calculated answer make sense? Justify your answer.

$$\ln[\text{N}_2\text{O}_5]_{150} = -(0.00693)(150) + (-2.303)$$

$$e^{\ln[\text{N}_2\text{O}_5]_{150}} = e^{-3.3425}$$

$$[\text{N}_2\text{O}_5]_{150} = e^{-3.3425} = 0.0353 \text{ M}$$

(d) Determine the concentration of N₂O₅(g) at

600s. Does your calculated answer make sense?

Justify your answer.

$$\ln[\text{N}_2\text{O}_5]_{600} = -(0.00693)(600) - 2.303$$

$$= e^{-6.461} = 0.00156 \text{ M}$$

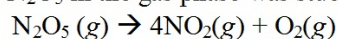
Ans: rate = $k[\text{N}_2\text{O}_5]$, $k = -\text{slope of graph } \ln[\text{N}_2\text{O}_5] \text{ vs. time} = 6.93 \times 10^{-3} \text{ s}^{-1}$; 0.0177M; 0.00156M; 606s; 100s

Kinetics
Topic#7

Integrated Rate Law - 1st Order Reactions

Kinetics Sample WS#2 - Integrated Rate Law

1. The decomposition of N_2O_5 in the gas phase was studied at constant temperature.



The following data were collected:

$[\text{N}_2\text{O}_5]$	Time (s)	$\ln[\text{N}_2\text{O}_5]$
0.1000	0	
0.0707	50	
0.0500	100	
0.0250	200	
0.0125	300	
0.00625	400	

First order integrated rate law:

$$\ln[A] = -kt + \ln[A]_0$$

graph $\ln[A]$ vs t ,

slope = $-k$, half-life = $0.693/k$

$$\ln[\text{N}_2\text{O}_5]_t = -kt + \ln[\text{N}_2\text{O}_5]_0$$

(f) What is the half-life of the reaction?

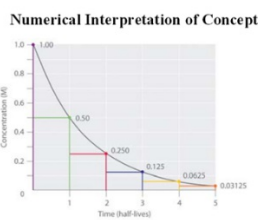
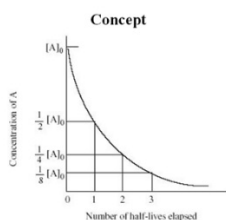
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.00693} = 100\text{s}$$

Ans: rate = $k[\text{N}_2\text{O}_5]$, k = -slope of graph $\ln[\text{N}_2\text{O}_5]$ vs. time = $6.93 \times 10^{-3} \text{ s}^{-1}$; $0.0177M$; $0.00156M$; 606s ; 100s

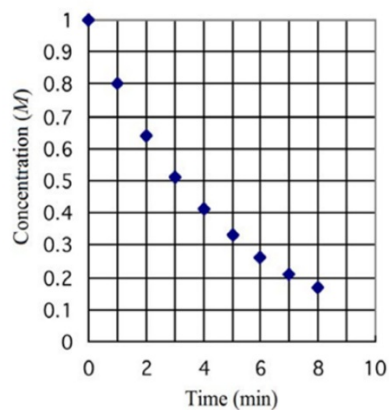
Kinetics
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Integrated Rate Law - Half-Life

Half-life is the time required for one half of one of the reactants to disappear. You will need to be able to analyze this verbally, graphically, and algebraically. You only need to do this for 1st order reactions. MEMORIZE!



The data points plotted on the graph pictured right represent concentration-time data collected for the radioactive decay of Element Q. Your task is to **supply the graph with an appropriate title** and answer the following questions:

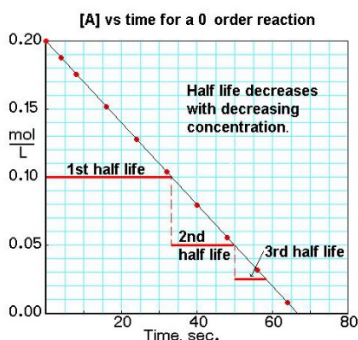


Half-Life Practice Problems

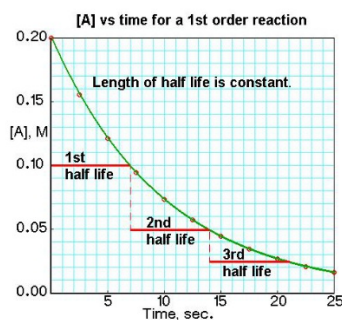
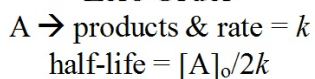
1. While you may at a glance be unable to determine the order of reaction, you can definitely determine the order it is NOT! So, which order is *not* the order for this reaction?
2. What is the half-life of Element Q? *3 minutes*
3. What is the molar concentration of Element Q after a second half-life has elapsed? *0.250*
4. At what time has 75% of the original sample decayed? *6 minutes*

Kinetics Topic#7

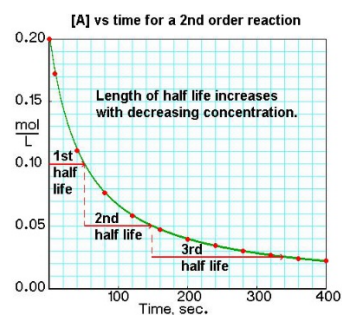
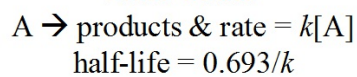
Integrated Rate Law - Half-Life



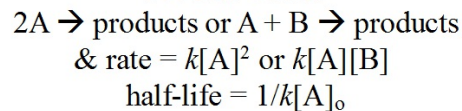
Zero Order



First Order



Second Order



5. What is alike about each graph?
6. What is different about each graph?
7. What is the significance of the lengths of the horizontal red lines associated with each half-life

Notice that, for first order reactions, the half-life is *independent of the initial concentration of reactant*, which is a unique aspect to first order reactions.

Integrated Rate Law - 1st Order Reactions**Kinetics
Topic#7**

First order integrated rate law:

$$\ln[A] = -kt + \ln[A]_0$$

graph $\ln[A]$ vs t , slope = $-k$, half-life = $0.693/k$

$$\ln[N_2O_5]_t = -kt + \ln[N_2O_5]_0$$

2. A certain first order reaction has a half-life of 20.0 minutes.

a) Calculate the rate constant for this reaction.

$$\ln[A]_t = -kt + \ln[A]_0 \text{ or } k = \frac{0.693}{t_{1/2}}$$
$$k = 0.0347 \text{ min}^{-1}$$

b) How much time is required for this reaction to be 75% complete?

$$\ln(0.5) = -k(20) - 0$$

(Ans: $3.47 \times 10^{-2} \text{ min}^{-1}$, 40 minutes)

(b) 75% is 2 half-lives

$$\downarrow t_{1/2} = 2(20) = 40 \text{ minutes}$$

3. A certain first-order reaction is 45% complete in 65s. Determine the rate constant and half-life for this process. ($9.2 \times 10^{-3} \text{ s}^{-1}$, 75.4s)

$$\ln(0.55) = -k(65) + 0$$
$$\frac{-0.5978}{65} = -k, k = 9.2 \times 10^{-3} \text{ s}^{-1}$$
$$t_{1/2} = \frac{0.693}{9.2 \times 10^{-3}} = 75.3 \text{ s}$$

Integrated Rate Law - 1st Order Reactions**Kinetics
Topic#7**

First order integrated rate law:

$$\ln[A] = -kt + \ln[A]_0$$

graph $\ln[A]$ vs t , slope = $-k$, half-life = $0.693/k$

$$\ln[N_2O_5]_t = -kt + \ln[N_2O_5]_0$$

4. (OYO) The rate constant for the first order transformation of cyclopropane to propene is $5.40 \times 10^{-2} \text{ hr}^{-1}$. Calculate the half-life of this reaction. What fraction of the cyclopropane remains after 51.2hrs? What fraction remains after 18.0hrs?

(Ans: 12.8hrs, 0.063, 0.38)

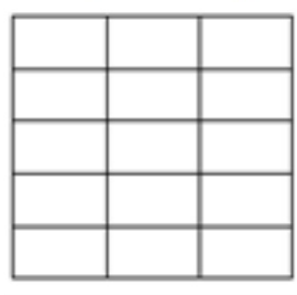
Integrated Rate Law - 1st Order Reactions**Kinetics
Topic#7**

$$\ln[\text{N}_2\text{O}_5]_t = -kt + \ln[\text{N}_2\text{O}_5]_0$$

Graphing Data Practice Problem

5. (OYO) For the reaction of $(\text{CH}_3)_3\text{CBr}$ with OH^- , $(\text{CH}_3)_3\text{CBr} + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{COH} + \text{Br}^-$, the following data were obtained in the laboratory.

<u>Time (s)</u>	<u>$[(\text{CH}_3)_3\text{CBr}]$</u>	<u>$\ln[(\text{CH}_3)_3\text{CBr}]$</u>
0	0.100	
30.0	0.074	
60.0	0.055	
90.0	0.041	



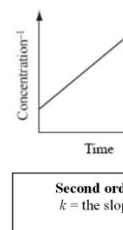
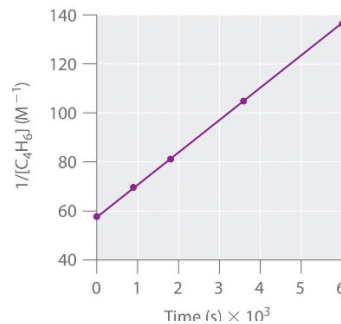
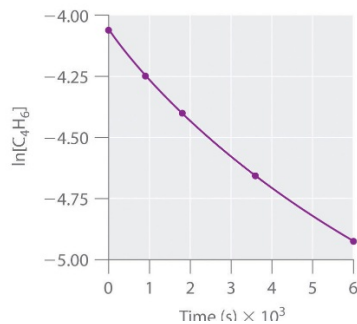
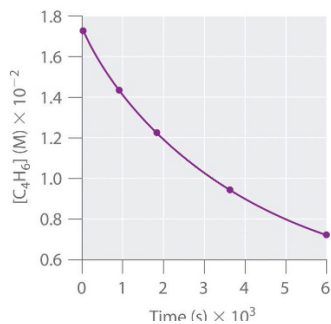
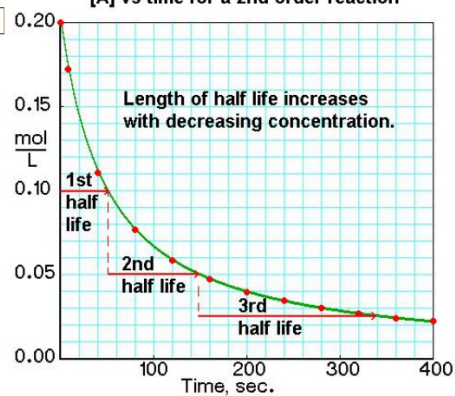
- (a) Determine the order of this reaction. Sketch your graph.
- (b) Determine the value of the rate constant and include proper units. (Ans: $9.9 \times 10^{-3} \text{ s}^{-1}$)
- (c) What is the half-life of this reaction? (Ans: 70s)
- (d) At what time is the concentration of $(\text{CH}_3)_3\text{CBr}$ equal to $[0.086]$? Justify your answer. (Ans: 15.0s)
- (e) At what time is the concentration of $(\text{CH}_3)_3\text{CBr}$ equal to $[0.025]$? Justify your answer. (Ans: 140s)
- (f) What is the concentration of $(\text{CH}_3)_3\text{CBr}$ after 2 minutes? Justify your answer. (Ans: $0.0304M$)

Kinetics Topic#7

Integrated Rate Law - 2nd Order Reactions

Second order integrated rate law: $1/[A]$
 Straight Line Graph $1/[A]$ vs t
 Slope = k
 Half-life: $t_{1/2} = 1/k[A]_0$

[A] vs time for a 2nd order reaction

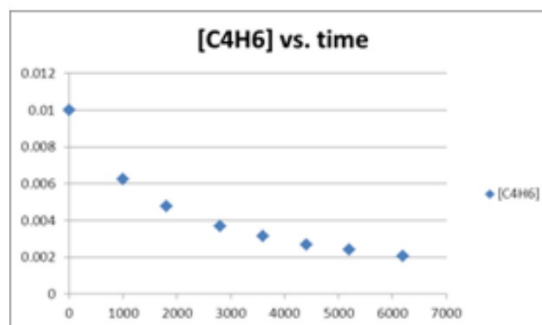


Kinetics
Topic#7

Integrated Rate Law - 2nd Order Reactions

6. Butadiene reacts to form a dimer according to the equation $2\text{C}_4\text{H}_6(\text{g}) \rightarrow \text{C}_8\text{H}_{12}(\text{g})$. The following data were collected for this reaction at a given temperature.

<u>[C₄H₆]</u>	<u>Time(+/- 1s)</u>	<u>ln[C₄H₆]</u>	<u>1/[C₄H₆]</u>
0.01000	0		
0.00625	1000		
0.00476	1800		
0.00370	2800		
0.00313	3600		
0.00270	4400		
0.00241	5200		
0.00208	6200		



- Determine the order of this reaction and write the rate law. Justify your answer. Sketch a graph as part of your explanation.
- Determine the value of the rate constant for this reaction.
- Determine the half-life for the reaction under the conditions of this experiment.

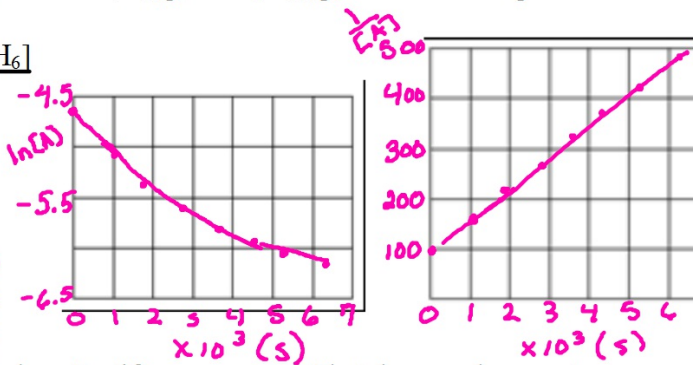
Ans: 2nd order, rate = $k[\text{C}_4\text{H}_6]^2$, $k = 6.14 \times 10^{-2} \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $t_{1/2} = 1630 \text{s}$

Kinetics
Topic#7

Integrated Rate Law - 2nd Order Reactions

6. Butadiene reacts to form a dimer according to the equation $2C_4H_6(g) \rightarrow C_8H_{12}(g)$. The following data were collected for this reaction at a given temperature.

$[C_4H_6]$	Time(+/- 1s)	$\ln[C_4H_6]$	$1/[C_4H_6]$
0.01000	0	-4.605	100
0.00625	1000	-5.036	160
0.00476	1800	-5.348	210
0.00370	2800	-5.599	270
0.00313	3600	-5.766	319
0.00270	4400	-5.915	370
0.00241	5200	-6.028	415
0.00208	6200	-6.175	481



a) Determine the order of this reaction and write the rate law. Justify your answer. Sketch a graph as part of your explanation.

rate = $k[C_4H_6]^2$ 2nd order
 The graph of $\frac{1}{[A]}$ vs. t produces a straight line, so this is a second order reaction.

b) Determine the value of the rate constant for this reaction.

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{(0.00208)} = k(6200) + \frac{1}{(0.01)}$$

$$k = \frac{\frac{1}{(2.08 \times 10^{-3})} - \frac{1}{(0.01)}}{6200}$$

$$k = \frac{480.77 - 100}{6200}$$

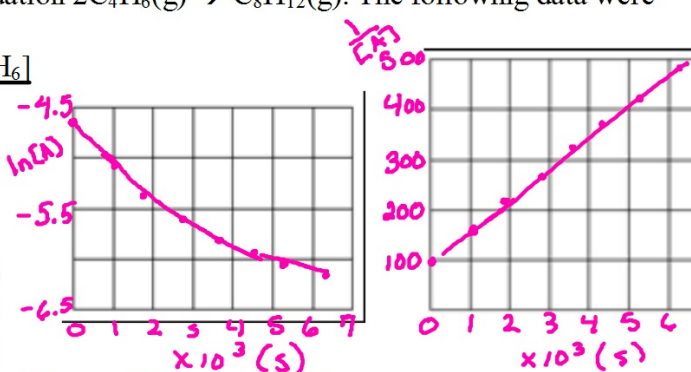
$$k = \frac{6.14 \times 10^{-2}}{L \cdot mol^{-1} \cdot s^{-1}}$$

Kinetics
Topic#7

Integrated Rate Law - 2nd Order Reactions

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0.00241	5200	-6.028	415
0.00208	6200	-6.175	481



c) Determine the half-life for the reaction under the conditions of this experiment.

$[A]_0 = 0.01$
 $[A]_{1/2} = 0.005$

$$\frac{1}{[A]_{1/2}} = k t_{1/2} + \frac{1}{[A]_0}$$

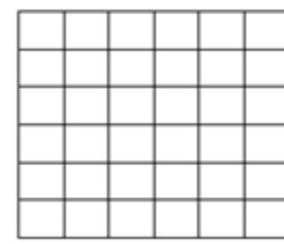
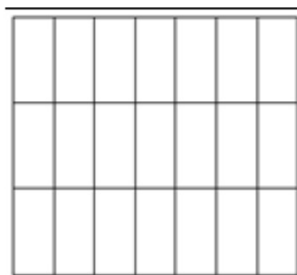
$$\left(\frac{1}{0.005} - \frac{1}{0.01} \right) = t_{1/2} \cdot k = \frac{200 - 100}{6.14 \times 10^{-2}} = 1630 \text{ s}$$

Kinetics
Topic#7

Integrated Rate Law - 2nd Order Reactions

7. (OYO) The rate of the reaction $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$ depends on the concentration of nitrogen dioxide below 225°C . At a temperature below 225°C , the following data were collected:

Time	$[\text{NO}_2](\text{mol/L})$	$\ln[\text{NO}_2]$	$1/[\text{NO}_2]$
0	0.500		
1.20×10^3	0.444		
3.00×10^3	0.381		
4.50×10^3	0.340		
9.00×10^3	0.250		
1.80×10^4	0.174		



a. Determine rate law. (Ans: rate = $k[\text{NO}_2]^2$)

c. What is the value of the rate constant, k ?
(Ans: $k = 2.08 \times 10^{-4} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)

b. Determine the integrated rate law.
(Ans: $1/[\text{NO}_2]_t = kt + 1/[\text{NO}_2]_0$)

d. Calculate $[\text{NO}_2]$ at $2.70 \times 10^4 \text{ s}$ after the start of the reaction. (Ans: 0.131 M)

Kinetics
Topic#7

Integrated Rate Law Zero Order Reactions

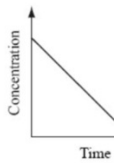
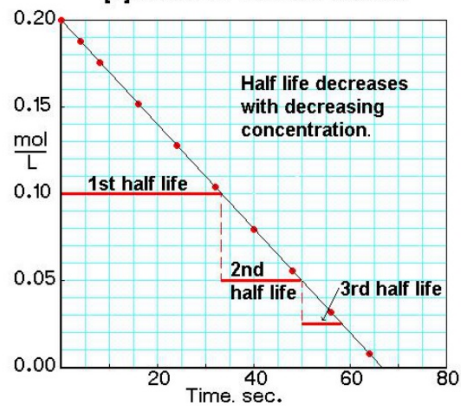
Zero order integrated rate law: $[A] = -kt + [A]_0$

Straight Line Graph: $[A]$ vs t

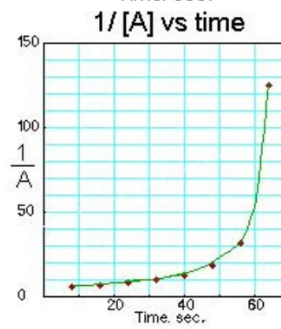
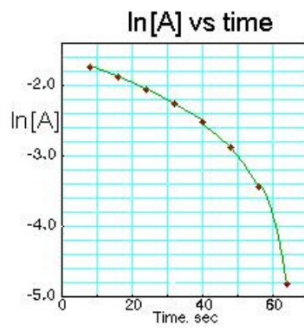
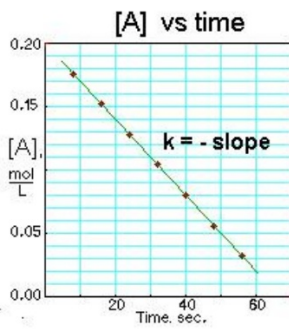
Slope = $-k$,

Half-life: $t_{1/2} = [A]_0/2k$

[A] vs time for a 0 order reaction



Zero or
 $k = \text{negative}$



Kinetics
Topic#7

Integrated Rate Law

Graphing Calculator Tutorial Set up your calculator so that *time* is always in L1.
Use L2, L3 and L4 to display the *y*-variables. Remember the list for what is placed on the *y*-axis is alphabetical (concentration, natural log of concentration and reciprocal concentration).

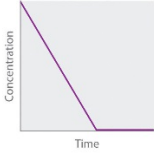
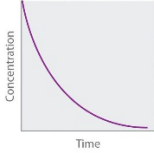

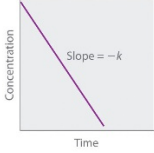

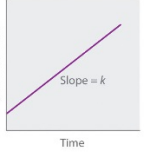
L1 = time (<i>x</i> -variable throughout!)		
L2 = concentration	[A]	straight line infers zero order
L3 = ln concentration	ln [A]	straight line infers first order
L4 = reciprocal concentration	1/[A]	straight line infers second order

Use this system to set up the data given in the following exercise:

We are going to perform 3 linear regressions to determine the order of the reactant. They will be L1,L2; L1,L3; L1,L4. Next, we will determine which regression has the best *r*-value [linear regression correlation coefficient in big people language!] We will also paste the best regression equation $Y=$ so that we can easily do other calculations commonly required on AP Chemistry Exam problems.

Kinetics Topic#7

Integrated Rate Law

	Zeroth Order	First Order	Second Order																								
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$																								
Concentration vs. time																											
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$																								
Straight-line plot to determine rate constant																											
Relative rate vs. concentration	<table border="1"> <thead> <tr> <th>[A], M</th> <th>Rate, M/s</th> </tr> </thead> <tbody> <tr><td>1</td><td>1</td></tr> <tr><td>2</td><td>1</td></tr> <tr><td>3</td><td>1</td></tr> </tbody> </table>	[A], M	Rate, M/s	1	1	2	1	3	1	<table border="1"> <thead> <tr> <th>[A], M</th> <th>Rate, M/s</th> </tr> </thead> <tbody> <tr><td>1</td><td>1</td></tr> <tr><td>2</td><td>2</td></tr> <tr><td>3</td><td>3</td></tr> </tbody> </table>	[A], M	Rate, M/s	1	1	2	2	3	3	<table border="1"> <thead> <tr> <th>[A], M</th> <th>Rate, M/s</th> </tr> </thead> <tbody> <tr><td>1</td><td>1</td></tr> <tr><td>2</td><td>4</td></tr> <tr><td>3</td><td>9</td></tr> </tbody> </table>	[A], M	Rate, M/s	1	1	2	4	3	9
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Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$																								
Units of k, rate constant	M/s	1/s	$M^{-1} \cdot s^{-1}$																								

Kinetics
Topic#7

Integrated Rate Law

Integrated Rate Law Summary

Note $k = |\text{slope}|$ for any linearized graph.

	ORDER		
	Zero	First	Second
Rate law:	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Units of rate constant:	$M \text{ time}^{-1}$ or M/time	time^{-1} or $1/\text{time}$	$M^{-1} \text{ time}^{-1}$ or $\frac{1}{M \cdot \text{time}}$
Integrated rate law:	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Relationship of rate constant to slope of straight line:	Slope = $-k$	Slope = $-k$	Slope = k
Plot needed to give a straight line:	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Half-life:	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Integrated Rate Law**Kinetics**
Topic#7

Starter

1. A first-order reaction is 75% complete in 320.s.
- What are the first and second half-lives for this reaction? (Ans: 160s (both))
 - How long does it take for 90.0% completion? (Ans: 532s)

2. Consider the following initial rate data for the decomposition of compound AB to give A and B:

$[AB]_0(M)$	Initial Rate (M/s)
0.200	3.20×10^{-3}
0.400	1.28×10^{-2}
0.600	2.88×10^{-2}

Determine the half-life for the decomposition reaction initially having 1.0M AB present. (Ans: 12.5s)

3. For the reaction $A \rightarrow$ products, successive half-lives are observed to be 10.0, 20.0, and 40.0 minutes for an experiment in which $[A]_0 = 0.10M$. Calculate the concentration of A at the following times:
- 80.0min (Ans: $1.1 \times 10^{-2}M$)
 - 30.0min (Ans: $0.025M$)

Kinetics
Topic#7

Reaction Mechanisms

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

1. Must be determined by experiment!
2. Must agree with overall stoichiometry!
3. Must agree with the experimentally determined rate law!

Vocabulary:

elementary step: individual step in a mechanism

molecularity: describes the number of molecules that participate in atomic rearrangement.

unimolecular: decomposition or one molecule colliding with a background molecule or solvent

bimolecular: two particles colliding

termolecular: three particles colliding (almost NEVER happens!)

rate determining step: slowest step

intermediate: produced in one step and then consumed in the next step

catalyst: enters and exits the reaction unchanged

Kinetics
Topic#7

Reaction Stoichiometry

The rate expression cannot be predicted from overall stoichiometry.

The rate expression of an elementary step is predicted from the stoichiometry of the elementary step as per the table below.

Elementary Step	Molecularity	Rate Expression
$A \rightarrow \text{products}$	unimolecular	$\text{rate} = k[A]$
$A + B \rightarrow \text{products}$	bimolecular	$\text{rate} = k[A][B]$
$A + A \rightarrow \text{products}$	bimolecular	$\text{rate} = k[A]^2$
$A + B + C \rightarrow \text{products}$	termolecular	$\text{rate} = k[A][B][C]$

The Physical Significance of Rate Expressions for Elementary Steps

- the more molecules the more collisions, the faster the rate
- the faster the molecules are moving, the more likely they will collide, the faster the rate

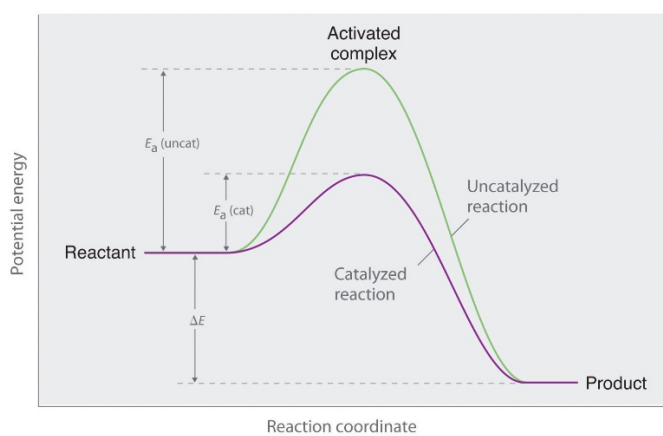
Molecularity and Order

- an **elementary step** is a reaction whose rate law can be written from its molecularity
- NOT true of the overall reaction order!

Reaction Mechanisms

Reaction Mechanisms and Rate Expressions

1. Determined through experimentation and MUST agree with experimental rate law.
2. Slowest elementary step is rate determining step.
3. The rate of the overall reaction is limited by, and is exactly equal to, the combined rates of all elementary steps **up to and including the slowest step in the mechanism.**
4. Intermediates are produced then consumed.
5. A catalyst goes in as a reactant and leaves as an unadulterated product and does not show up in the overall reaction.



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Reaction Mechanisms

Reaction Mechanisms

- 1) Sum of elementary steps must give the overall balanced equation for the reaction.
- 2) The mechanism must agree with the experimentally determined rate law.

Rate law from a mechanism

- 1) Use reactants up until the slow step.
- 2) Do not include catalysts or intermediates
 - an intermediate is a species produce in one elementary step and used immediately in the next step.
 - a catalyst enters the reaction and exits the reaction unchanged.

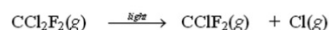
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Catalyzed reaction

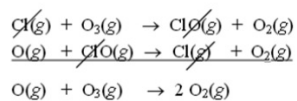
Catalysis is the increase in the rate of reaction due to a catalyst. A catalyst is not consumed. They function by lowering the activation energy (E_a) of an elementary step in a reaction allowing for the formation of the activated complex (intermediate) at lower energy.

- How? Alter mechanism
- Important classes of catalysts: acid-base, surface, and enzyme.
- Overall ΔE is not changed.
- Homogeneous Catalysts - same phase as reacting particles.
- Heterogeneous catalysts - different phase as reacting particles.
 - adsorption - collection on the surface of a solid
 - gaseous reactants adsorbed on the surface of a solid

Freons or chlorofluorocarbons [CFC's] were used until recently as refrigerants and as propellants in aerosol cans. Freon-12 (CCl_2F_2) is relatively inert and thus remains in the environment for a long time. Eventually they migrate upward into the upper atmosphere and are decomposed by high-energy light. Among the decomposition products are chlorine atoms:



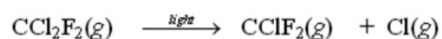
These chlorine atoms can catalyze the decomposition of ozone by forming a new reaction intermediate, thus thinning the atmospheric ozone layer that protects Earth from harmful UV rays :



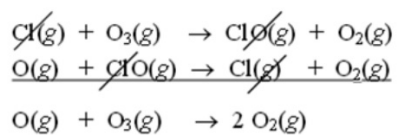
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Catalyzed reaction

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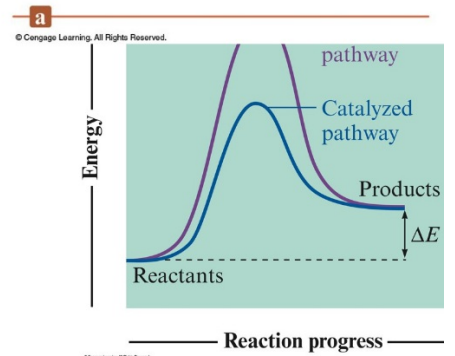
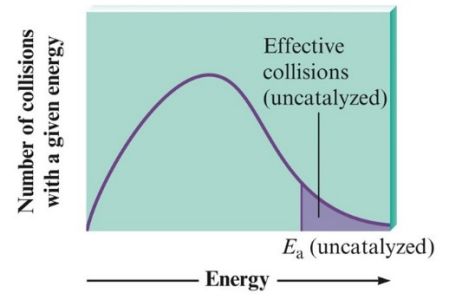
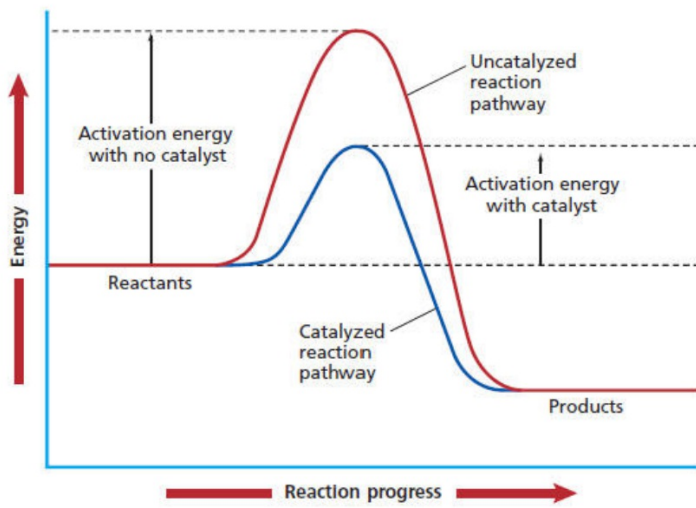


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Catalyzed reaction

Kinetics Topic#7

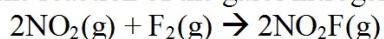


Kinetics
Topic#7

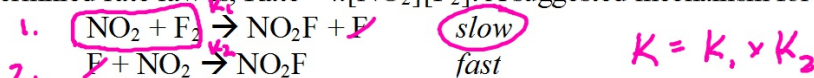
Reaction Mechanisms

Kinetics Sample WS#3 - Mechanisms

1. The balanced equation for the reaction of the gases nitrogen dioxide and fluorine is



The experimentally determined rate law is, $\text{Rate} = k[\text{NO}_2][\text{F}_2]$. A suggested mechanism for the reaction is



a. Is this an acceptable mechanism? That is, does it satisfy the two requirements? Justify your answer.

① Does the rate law based on the mechanism resemble the experimentally determined rate law? $\text{rate} = k[\text{NO}_2][\text{F}_2]$ yes

② Does the overall reaction based on the mechanism resemble the balanced equation? $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$ yes

b. What is F in this mechanism?

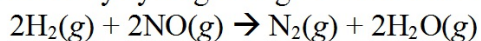
intermediate

yes, this is an acceptable mechanism.

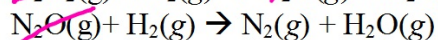
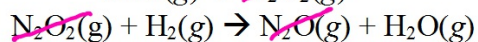
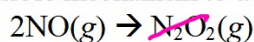
Kinetics
Topic#7

Reaction Mechanisms

2. Nitrogen oxide is reduced by hydrogen to give water and nitrogen,



and one possible mechanism to account for this reaction is



a. What is the molecularity of each of the three steps? Show that the sum of these elementary steps yields the net reaction.

b;
b;
b;



$$\text{rate} = k [\text{NO}]^2 [\text{H}_2]$$

$$\text{slow} \rightarrow \text{rate} = k [\text{NO}]^2$$

$$\text{slow} \rightarrow \text{rate} = k [\text{NO}]^2 [\text{H}_2]^2$$

b. What are $\text{N}_2\text{O}_2(\text{g})$ and $\text{N}_2\text{O}(\text{g})$ in the above mechanism?

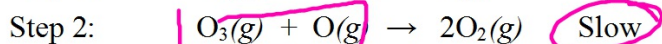
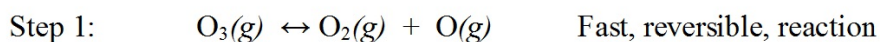
N_2O_2 - intermediate
 N_2O

Kinetics
Topic#7

Reaction Mechanisms

WS#4: Question#1

1. The decomposition of ozone in the upper atmosphere to dioxygen occurs by a two-step mechanism. The first step is a fast reversible step and the second is a slow reaction between an oxygen atom and an ozone molecule:



$$K_1 = \frac{[O_2][O]}{[O_3]}$$

$$[O] = \frac{K_1 [O_3]}{[O_2]}$$

- a. Which is the rate determining step?
- b. Write the rate equation for the rate-determining step. $rate = k[O_2][O]$
- c. Write the rate equation for the overall reaction.

For step 1 you need both the rate law for the forward and reverse reactions:

forward: $rate_f = k[O_3]$

reverse: $rate_r = k^{-1}[O_2][O]$

since $rate_f = rate_r$ set the above rate equations equal to each other and solve for the intermediate, $[O]$

$$k[O_3] = k^{-1}[O_2][O] \text{ so } [O] = \frac{k[O_3]}{k^{-1}[O_2]} \text{ substitute}$$

$$rate = k_2 [O_3] [O]$$

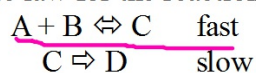
$$rate = k_2 [O_3] \times k_1 \frac{[O_3]}{[O_2]}$$

$$rate = K \frac{[O_3]^2}{[O_2]}$$

Kinetics
Topic#7

Reaction Mechanisms

Assume a reaction occurs by the mechanism given below.
What is the rate law for the reaction?



- a) Rate = $k[A][B][C]$
- b) Rate = $k[A]^2$
- c) Rate = $k[A][B]$
- d) Rate = $k[A][B]/[D]$
- e) Rate = $k[A]$

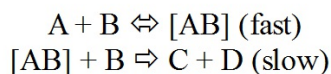
$$K_1 = \frac{[C]}{[A][B]} \quad K_1 [A][B] = [C]$$

$$\text{rate} = k_2 [C] \rightarrow \text{rate} = K [A][B]$$

$$K_1 = \frac{[AB]}{[A][B]} \quad K_1 [A][B] = [AB]$$

From the 1990 FRQ

(c) Write the rate law expression that would result if the reaction proceeded by the mechanism shown below.



$$\text{rate}_2 = k_2 [AB][B]$$

$$\begin{array}{l} \text{rate} = k_2 (K_1 [A][B]) [B] \\ \text{rate} = K [A][B]^2 \end{array}$$

Kinetics
Topic#7

Activation Energy

Determining Activation Energy

1. A graph of $\ln k$ vs. $1/T$ will produce a straight line graph with a negative slope.
2. The slope of the line is equal to the negative of the activation energy (E_a) divided by R (8.3145 J/K-mol).
3. Slope = $\Delta \ln k / \Delta (1/T)$
4. So, $E_a = -R(\text{slope})$

Kinetics
Topic#7

Activation Energy

3. The reaction $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}(\text{g}) + \text{O}_2(\text{g})$ was studied at several temperatures, and the following values of k were obtained:

k (s^{-1})	T ($^{\circ}\text{C}$)	T (K)	Activation Energy
2.0×10^{-5}	20	293	slope = $-\frac{E_a}{R}$
7.3×10^{-5}	30	303	
2.7×10^{-4}	40	313	
9.1×10^{-4}	50	323	
2.9×10^{-3}	60	333	

Calculate the value of E_a for this reaction.

(Ans: 1.0×10^5 J/mol)

Arrhenius Equation

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$R = 8.31$ 4.10×10^{-4}

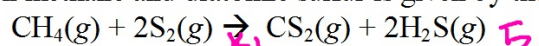
$$\ln \left(\frac{2.9 \times 10^{-3}}{2.0 \times 10^{-5}} \right) = \frac{E_a}{8.31} \left(\frac{1}{293} - \frac{1}{333} \right)$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\frac{(\ln(145)) 8.31}{4.10 \times 10^{-4}} = E_a = 1.01 \times 10^5 \text{ J}$$

Reaction Stoichiometry**Kinetics**
Topic#7

4. The gas-phase reaction between methane and diatomic sulfur is given by the equation



At 550°C the rate constant for this reaction is 1.1 L/mol-s, and at 625°C the rate constant is 6.4 L/mol-s. Using these values, calculate E_a for this reaction. (Ans: 1.4×10^5 J/mol)

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
$$\frac{8.31 \left(\ln\left(\frac{6.4}{1.1}\right)\right)}{\left(\frac{1}{823} - \frac{1}{898}\right)} = \frac{E_a}{(1.015 \times 10^{-4})} = 1.45 \times 10^5 \text{ J/mol}$$

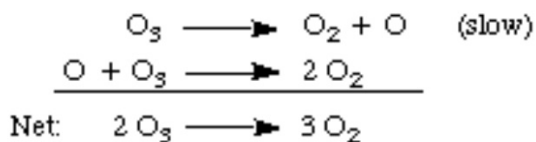
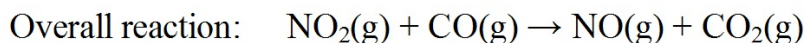
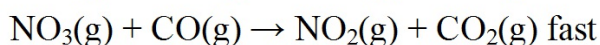
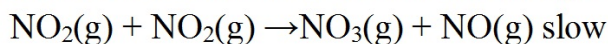
Reaction Mechanisms

Reaction Mechanisms

- 1) Sum of elementary steps must give the overall balanced equation for the reaction.
- 2) The mechanism must agree with the experimentally determined rate law.

Rate law from a mechanism

- 1) Use reactants up until the slow step.
- 2) Do not include catalysts or intermediates
 - an intermediate is a species produce in one elementary step and used immediately in the next step.
 - a catalyst enters the reaction and exits the reaction unchanged.



Collision Model

- 1) Reactants collide with enough energy
- 2) Correct orientation

Activated complex (transition state)

- species located at the top of PE "hill"

Temperature - increase in T more than doubles effective collisions

- number of effective collisions *exponentially* increases

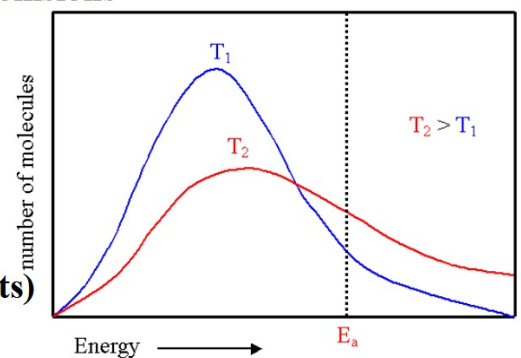
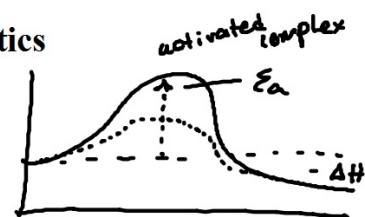
Molecular orientation

Activation energy

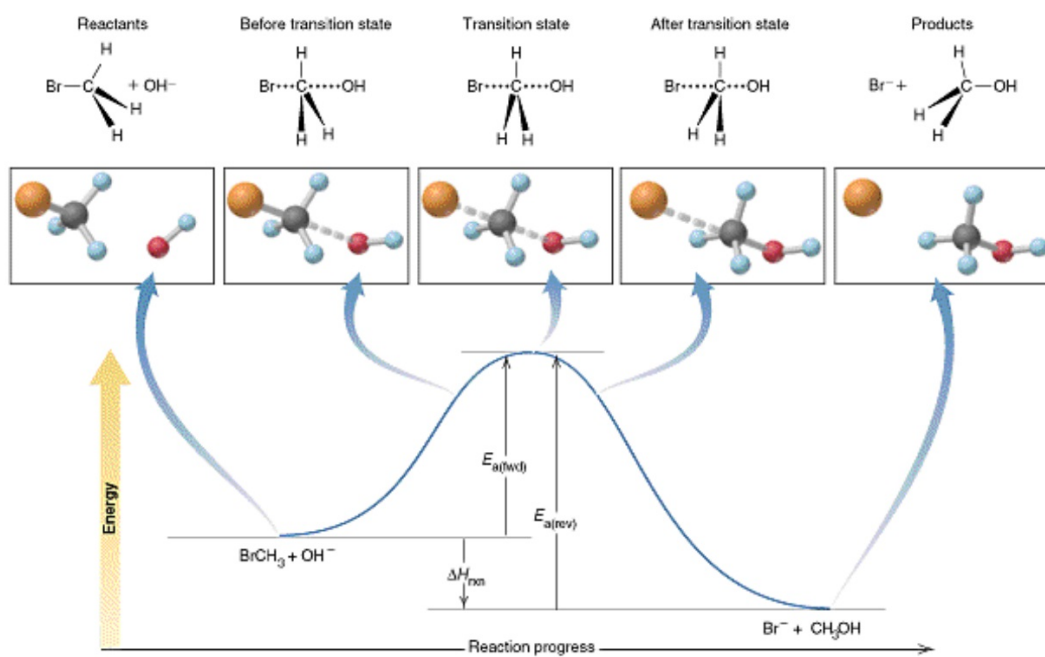
Catalysts

- 1) Decreases activation energy for the reaction
- 2) Homogeneous catalyst (same state as the reactants)
- 3) Heterogeneous catalyst (different state than reactants)

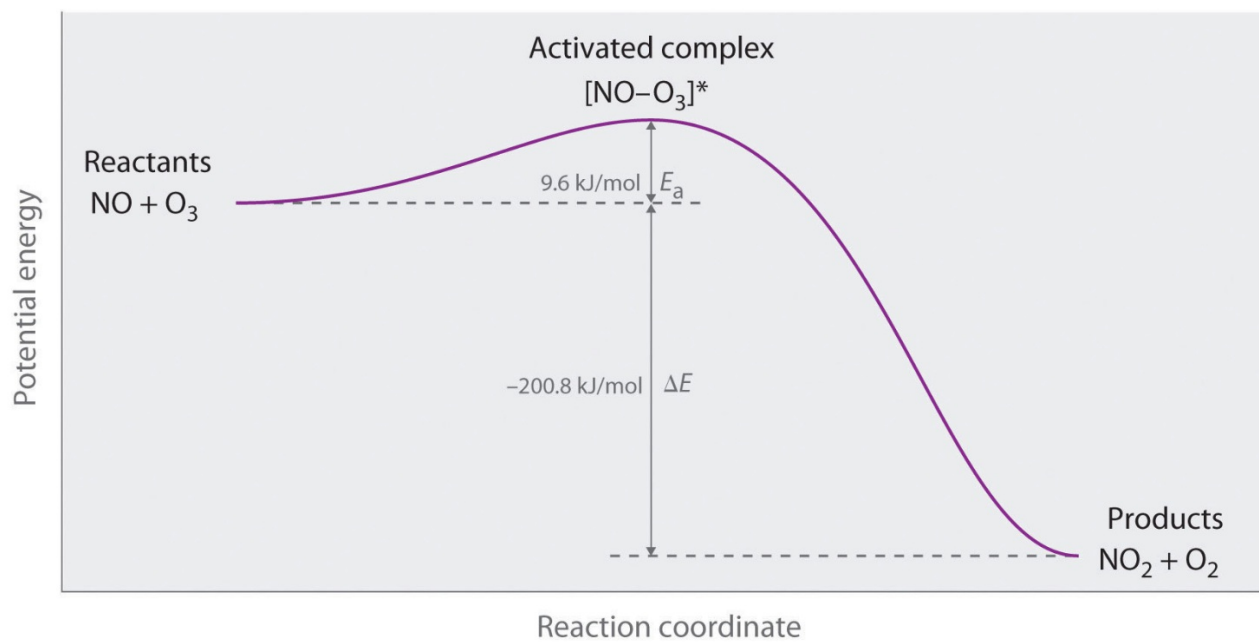
A Model for Chemical Kinetics



A Model for Chemical Kinetics

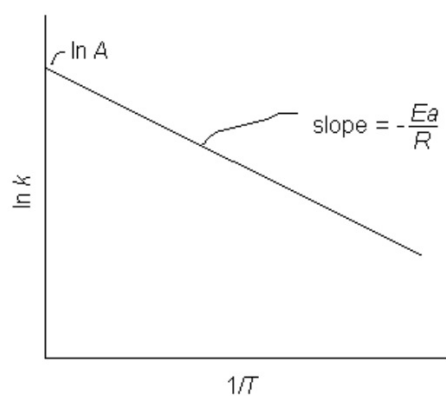


A Model for Chemical Kinetics



Determining Activation Energy, E_a

Natural log of k versus Reciprocal Temperature



Arrhenius equation

$$k = Ae^{-E_a/RT}$$

More Common form:

$$\ln(k) = \frac{-E_a}{R} (1/T) + \ln(A)$$

$$R = 8.3145 \text{ J/K-mol}$$

$$\text{slope} = \frac{\Delta \ln(k)}{\Delta (1/T)}$$

and

$$\text{slope} = \frac{-E_a}{R}$$