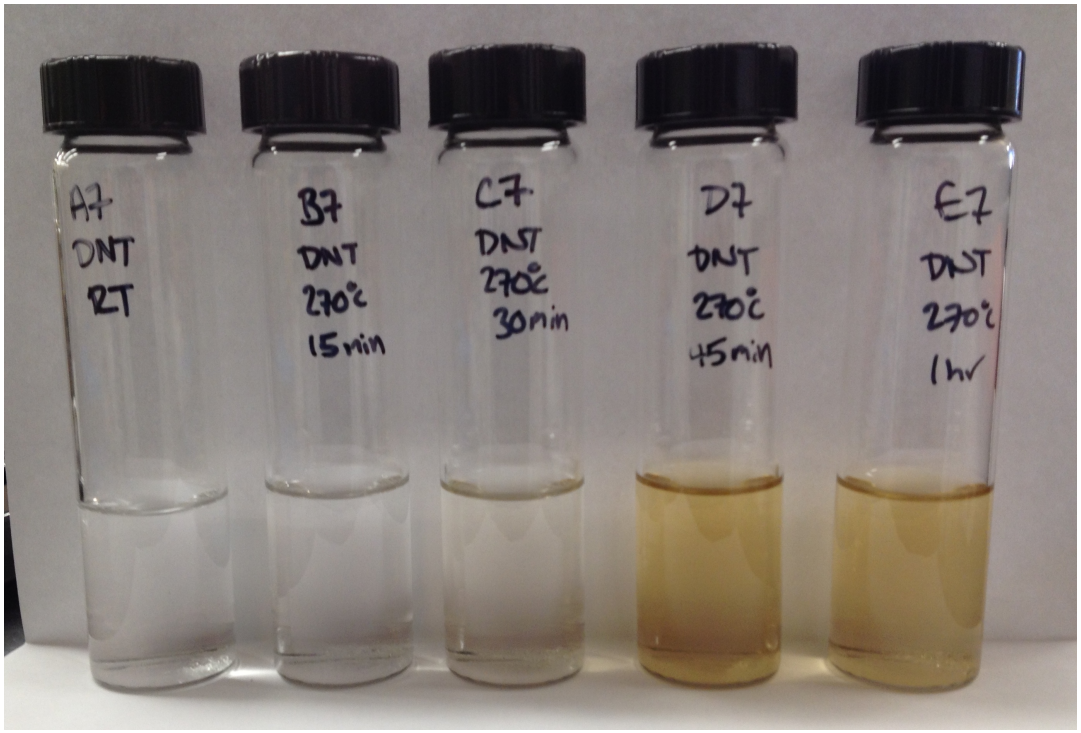
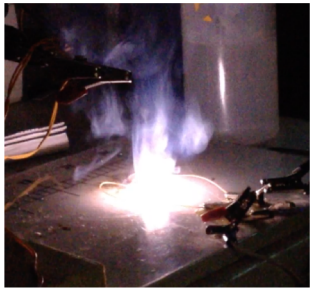
Chapter Fourteen:

Chemical Kinetics



Rate of Reaction = speed



Kinetics = study of how fast reactions take place

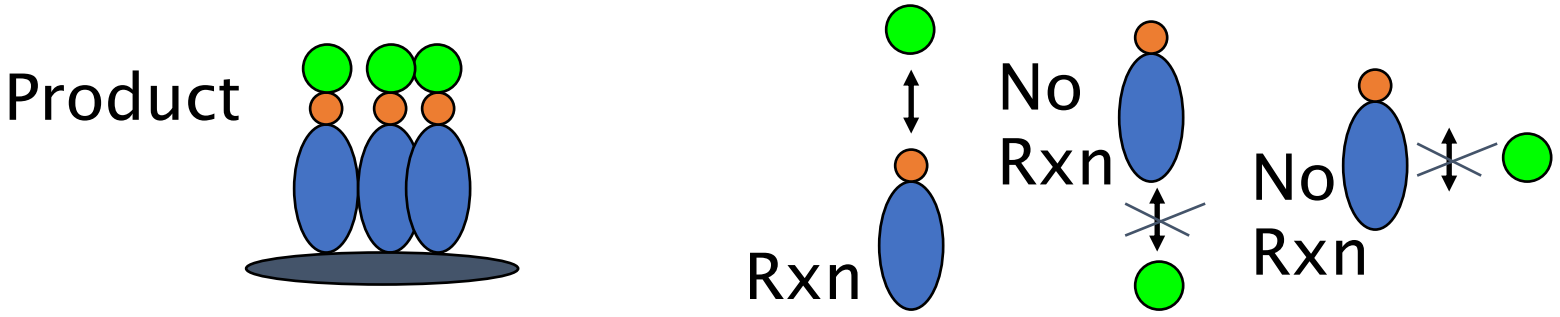
Collision Theory

Three things must happen for a reaction to occur:

1. Reacting molecules must collide

   Can increase the number of collisions with
   - increased reactant concentration
   - higher temps (= faster molecules)

2. Molecules must have the correct orientation



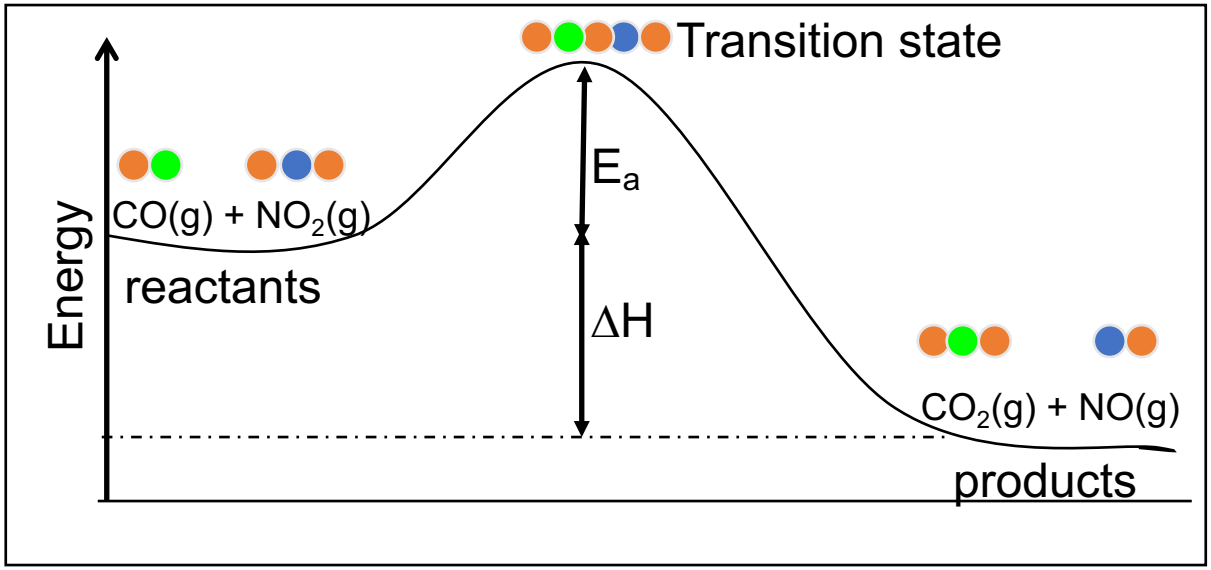
3. Activation Energy (E_a) must be exceeded

E_a = minimum energy required for a reaction to occur

Energy Diagrams: Activation Energy & Transition State

Given the following reaction:

$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$



Reactants: Original components before a reaction

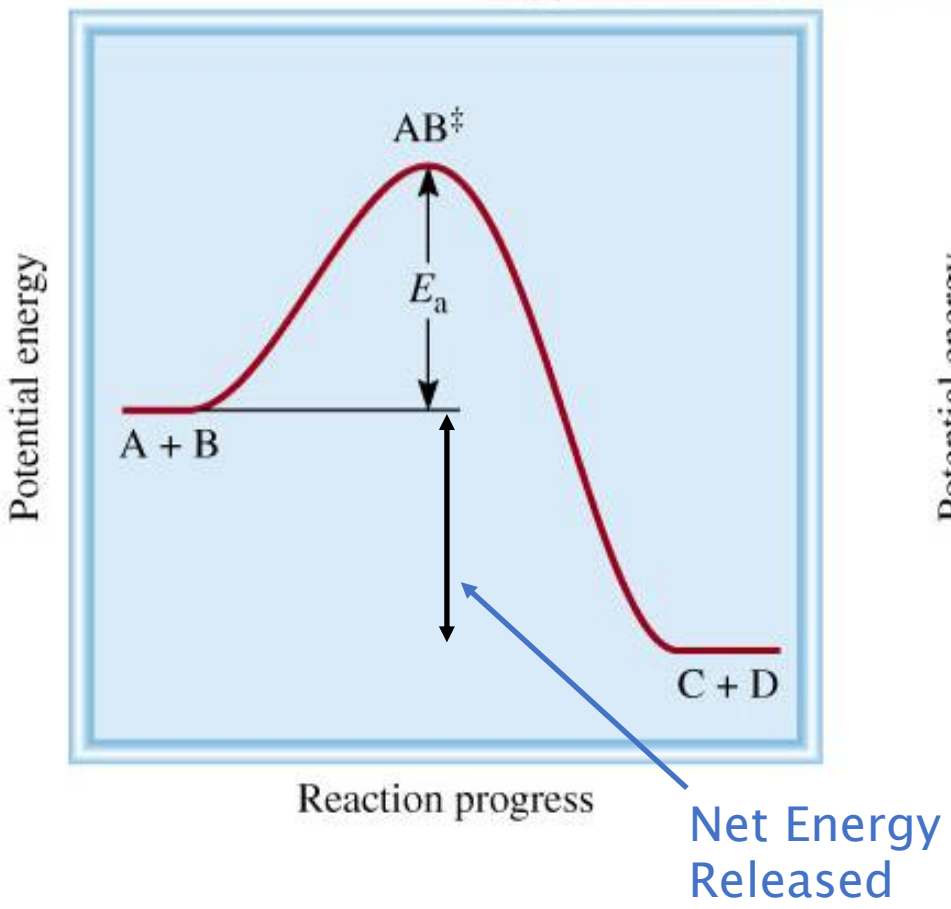
Products: New elements/compounds formed from reaction

Transition State (aka Activated Complex): Temporary & generally unstable combination of atoms formed from molecular collision. Will be transformed into products as the reaction proceeds.

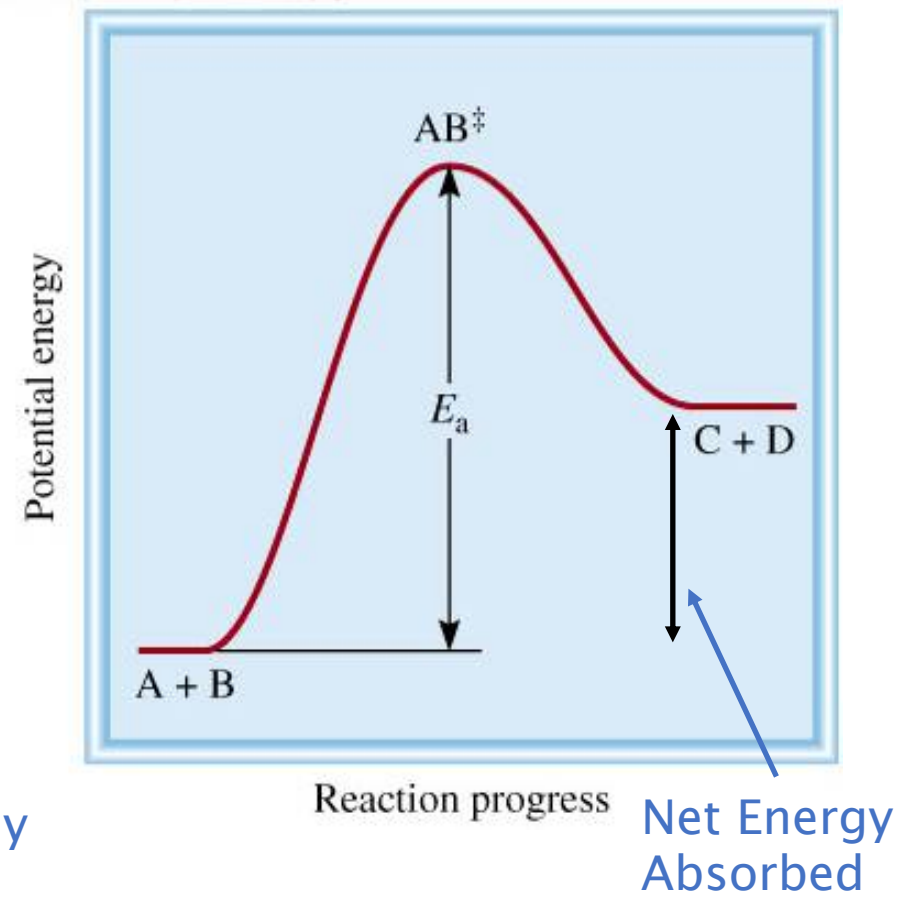
Energy Diagrams: Thermodynamics & Reaction Progress

$A + B \rightarrow AB^{\ddagger} \rightarrow C + D$

Exothermic Reaction



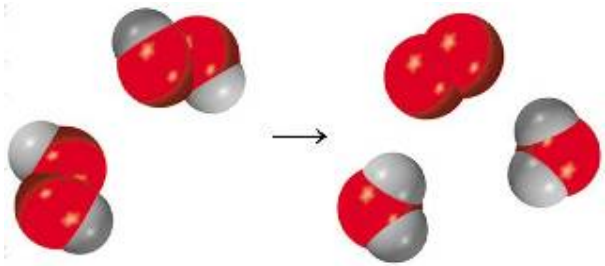
Endothermic Reaction



Reaction Rates

Kinetics:

- Study of rates of chemical reactions
- How fast does a reaction proceed?



Reaction Rate:

$$\text{Rate} = \frac{\Delta\text{Concentration}}{\Delta\text{Time}} = \frac{[\text{mol/L}]}{\Delta T} = \frac{M}{\text{sec}}$$

$2\ H_2O_2\ (l) \rightarrow 2\ H_2O\ (l) + O_2\ (g)$

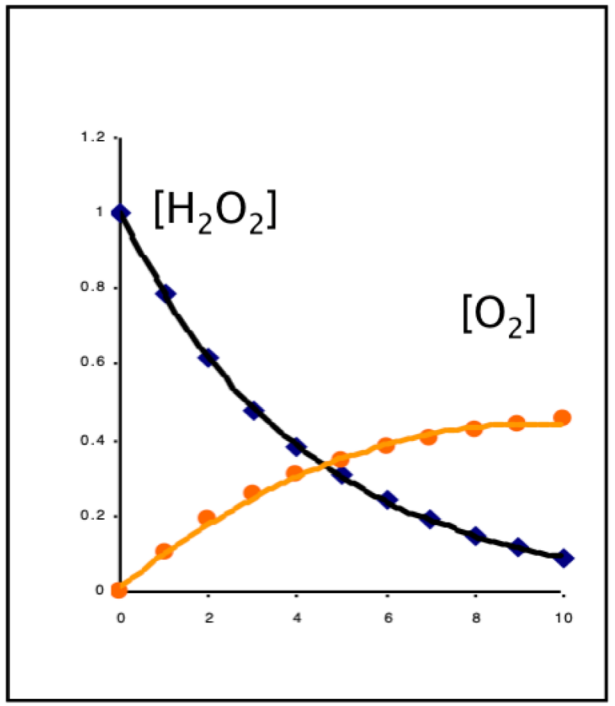
Rate of formation of product:

$\text{Rate} = +\Delta[O_2]/s$

Rate of disappearance of reactant:

$\text{Rate} = -\Delta[H_2O_2]/s$

(Use of negative makes rate positive, sometimes rate is written as negative)

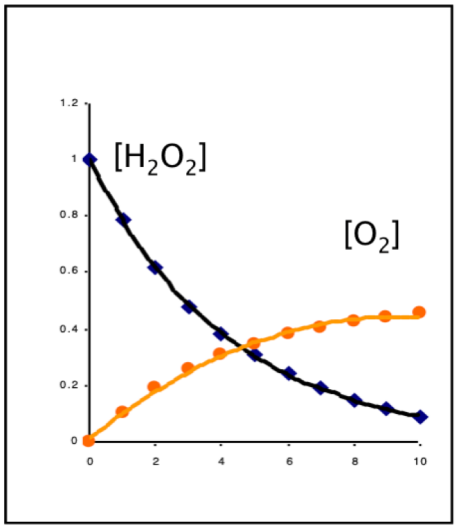


There is much variation in reaction rates

Linearity of Reaction Rates

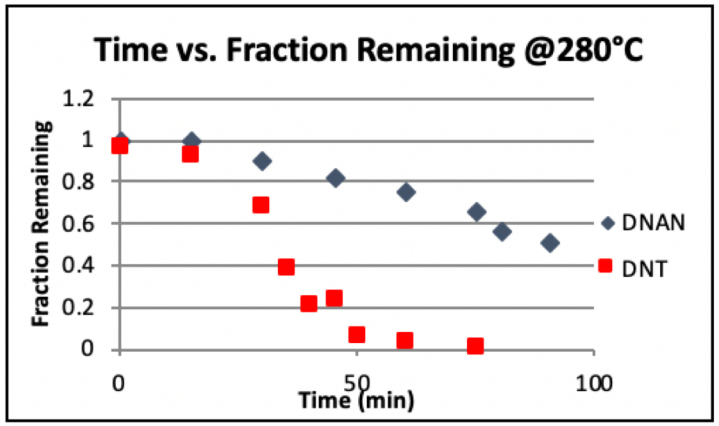
Reaction rates vary greatly

- Very fast; ex: burning
- Very slow; ex: disintegration of plastic in sunlight



Often not linear

- Rate is often faster at the beginning
- Rate is slowest at the end
- Some reactant often left over
- Especially pronounced for slow reactions



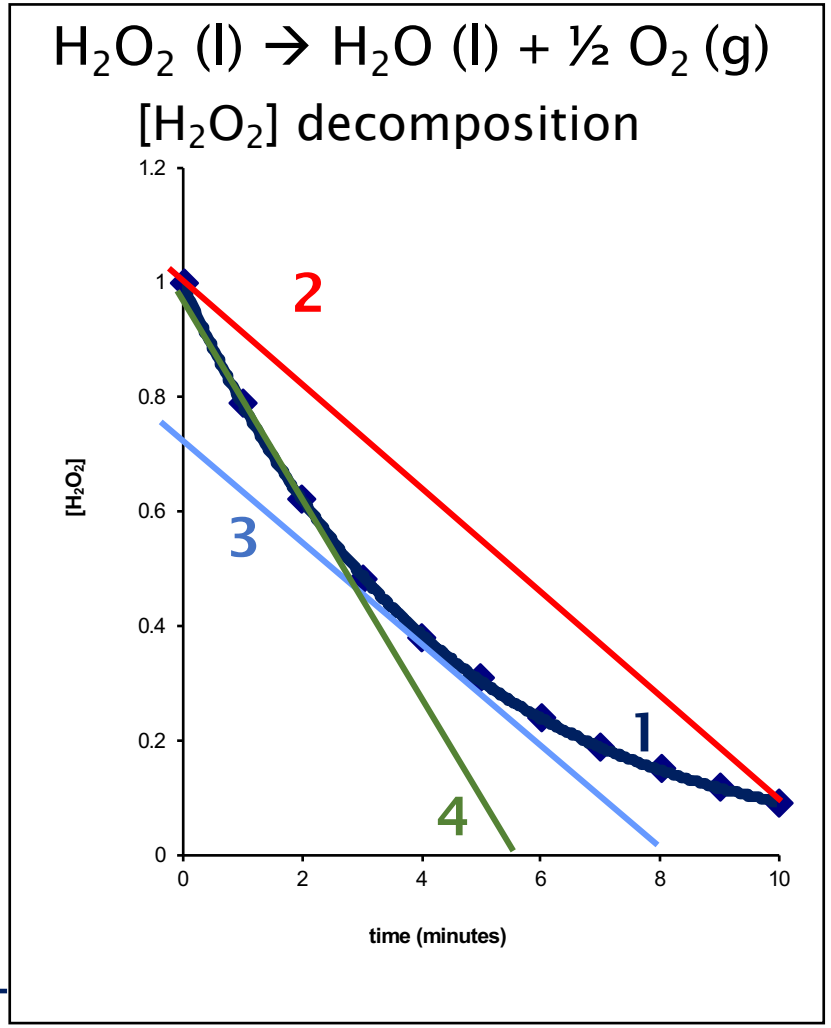
Average Rate of Reaction:

$$\text{Rate} = \frac{\text{Final Concentration} - \text{Initial Concentration}}{\text{Elapsed Time}}$$

Types of Reaction Rates

Reaction rate = ΔConcentration/Δtime = slope

1. Plot of original data
   - [Conc.] vs time
   - If curved = rate changes
     - Will reach equilibrium
   - If linear = rate is constant
     - Will run out of reactant
2. Average rate of reaction
3. Instantaneous rate
   - Tangent to curve 1
   - Can pick any time
4. Initial rate
   - t=0 to t=given time
   - Generally portion of curve 1 that is linear



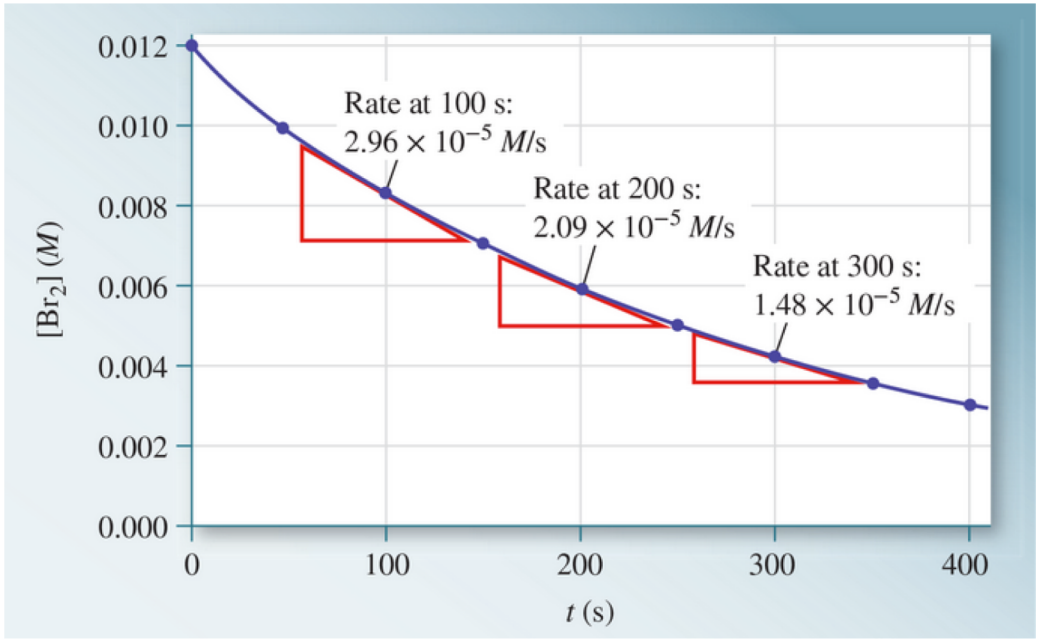
Instantaneous Rate

$Br_2\ (aq) + HCOOH\ (aq) \rightarrow 2\ Br^-\ (aq) + 2H^+\ (aq) + CO_2\ (g)$

Brown color of Br_2 disappears as reaction progresses

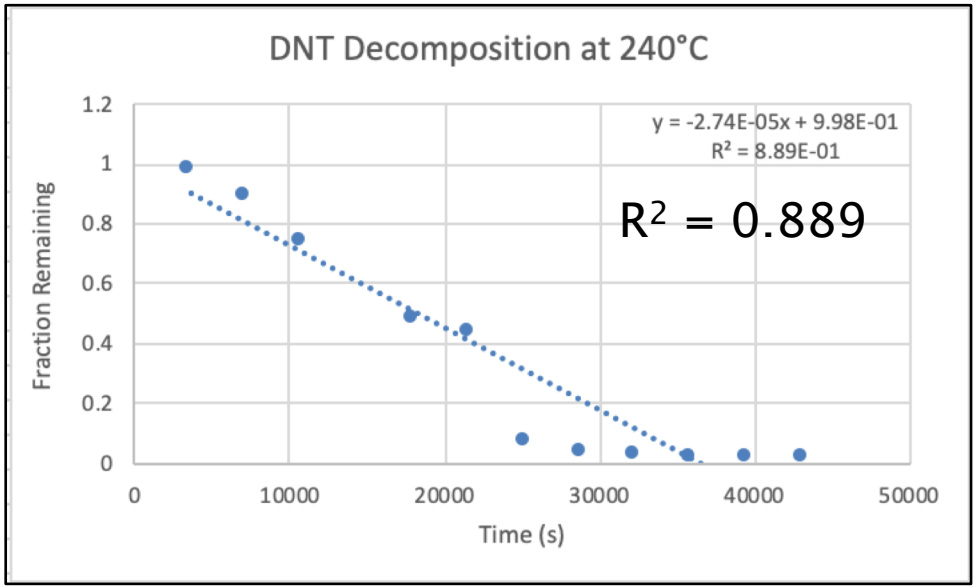
To Find Instantaneous Rate:

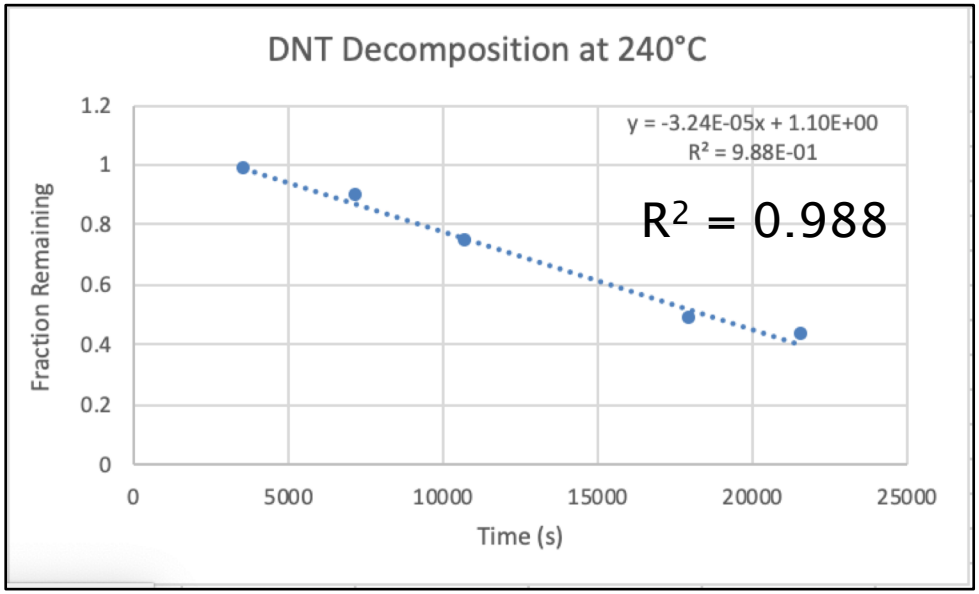
- Select time
- Draw line tangent to curve at that time
- Find slope of the tangent line
- Units of [conc.]/time



Initial Rate

Portion of original data where curve is linear





Stoichiometry & Reaction Rate

When writing rates based on different reactants or products, think about what is happening

Br_2 (aq) + HCOOH (aq) → 2 Br^- (aq) + 2H^+ (aq) + CO_2 (g)

Rate at which Br_2 disappears: X M/s

In terms of Br_2:

What is the rate of formation of Br^- ? 2X M/s

What is the rate of disappearance of HCOOH? X M/s

Rate at which Br^- forms: Z M/s

In terms of Br^-:

What is the rate of disappearance of Br_2? ½ Z M/s

What is the rate of formation of CO_2? ½ Z M/s

This method works for zero order & instantaneous rates, not for more complex rates.

Stoichiometry & Reaction Rate

1. The rate of decomposition of N_2O_5 at a particular instant in a reaction vessel is 4.2×10^{-7} M/s. What is the rate of appearance of (a) NO_2 and (b) O_2?

$$2\ N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

(a) 8.4×10^{-7} M/s

(b) 2.1×10^{-7} M/s

2. Consider the reaction:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

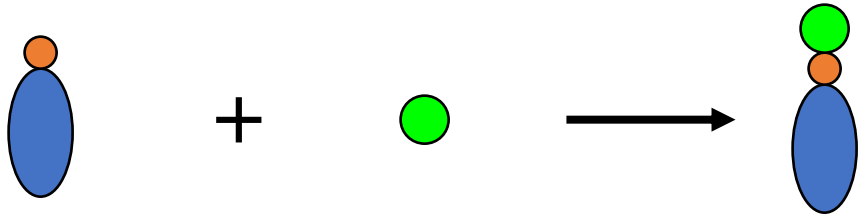
Suppose that at a particular moment during the reaction hydrogen is reacting at the rate of 0.074M/s. (a) At what rate is ammonia being formed? (b) At what rate is nitrogen reacting?

(a) 0.049 M/s

(b) -0.025 M/s

Factors Affecting Reaction Rates

Increasing # collisions increases rate

Reaction: 

1. Increase concentration of reactant

More particles in same volume = greater chance of collision

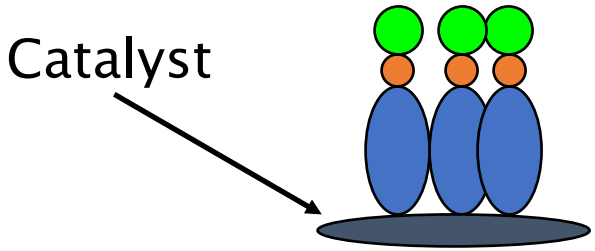
2. Increase temperature

Particles move faster – more likely to collide with enough E_A

3. Add a catalyst

Catalyst: chemical that does not change the amount of overall product or reactants, only the rate of the reaction

- fix molecular orientation
- alter transition state; lower E_a
- increase desired surface area



4. Improve Mixing

More interactions = greater chance of effective collision

Rate Laws:

Show Impact of Reactant Concentration on Rate

Rate Law Format: For the reaction A + B + C … → Products

Rate Law: Rate = $k[A]^m[B]^n[C]^p$…

Based on initial concentrations and rate

Variables required in Rate Law:

k = rate constant

m = order of reaction in reactant A

n = order of reaction in reactant B

p = order of reaction in reactant C

other letters as needed for additional reactants

Overall Order of Reaction = sum of the orders of reaction for each reactant

Overall Order = m + n + p

Rate Laws account for non-linearity of reactions

Rate Laws con't

Properties of Rate Laws:

- Orders do not need to be positive integers
  - Ex: if concentration does not impact rate, order is zero
- Orders must be found <u>experimentally</u>
- Catalyst concentrations are included
- Rate Laws hold only for a specific temperature
- Rate Laws do **NOT** come from the balanced equation!

Not squared!

Example:

$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$ Rate = $k[H_2][NO]^2$

Rate Constant, k

- Depends on reaction, temperature, and catalyst
- Also found experimentally

Determining Rate Laws: Isolation Method

Conduct a series of experiments

- Change the concentration of just one reactant each time
- Measure the impact on the rate from each reactant
- Use the ratios of the rates to determine m, n, etc.
- Rearrange the Rate Law & plug in values to solve for k.

Example: For the reaction A + B → Products Rate = $k[A]^m[B]^n$

Conduct 3 experiments:

1. Use [A] & [B], measure Rate 1
2. Use $[A]_2$ & [B], measure Rate 2
3. Use [A] & $[B]_2$, measure Rate 3

To determine m, divide $\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{k[A]^m[B]^n}{k[A]_2^m[B]^n} = \frac{[A]^m}{[A]_2^m}$

To determine n, divide $\frac{\text{Rate 1}}{\text{Rate 3}} = \frac{k[A]^m[B]^n}{k[A]^m[B]_2^n} = \frac{[B]^n}{[B]_2^n}$

To determine k, solve $k = \frac{\text{Rate}}{[A]^m[B]^n}$

When reporting Rate Laws, use the numbers for k, m, & n

Determining Rate Laws: Isolation Method

A set of experiments was run to study the rate of the reaction:

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

The following data was obtained:

Expt #	$[BrO_3^-]$	$[Br^-]$	$[H^+]$	Rate (M/s)
1	0.10	0.10	0.10	-1.2×10^{-3}
2	0.20	0.10	0.10	-2.4×10^{-3}
3	0.20	0.30	0.10	-7.4×10^{-3}
4	0.20	0.10	0.15	-5.4×10^{-3}

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

Determining Rate Laws: Order of Reactants

$Rate = k[BrO_3^-]^m[Br^-]^n[H^+]^p$

Expt #	$[BrO_3^-]$	$[Br^-]$	$[H^+]$	Rate (M/s)
1	0.10	0.10	0.10	-1.2×10^{-3}
2	0.20	0.10	0.10	-2.4×10^{-3}
3	0.20	0.30	0.10	-7.4×10^{-3}
4	0.20	0.10	0.15	-5.4×10^{-3}

Order of reaction in BrO_3^- (m):

Order of reaction in Br^- (n):

Order of reaction in H^+ (p):

Determining Rate Laws: k & Rate Law

Expt #	$[BrO_3^-]$	$[Br^-]$	$[H^+]$	Rate (M/s)
1	0.10	0.10	0.10	-1.2×10^{-3}
2	0.20	0.10	0.10	-2.4×10^{-3}
3	0.20	0.30	0.10	-7.4×10^{-3}
4	0.20	0.10	0.15	-5.4×10^{-3}

$Rate = k[BrO_3^-]^m[Br^-]^n[H^+]^p$

m = 1

n = 1

p = 2

k: Solve using data from each experiment (4X!) & <u>average</u>

$$k = \frac{Rate}{[BrO_3^-]^1[Br^-]^1[H^+]^2}$$

Rate Law =

Rate Laws can be used to determine the initial speed of a reaction with given concentrations of reactants.

For the reaction:

BrO_3^- (aq) + $5Br^-$ (aq) + $6H^+$ (aq) → $3Br_2$ (aq) + $3H_2O$ (l)

we determined that the Rate Law was:

$Rate = -12M^{-3}s^{-1}[BrO_3^-][Br^-][H^+]^2$

If we start with the following concentrations:

$[BrO_3^-] = 0.4M$

$[Br^-] = 0.8M$

$[H^+] = 0.2M$

How fast will the initial reaction proceed?

$$Rate = -12M^{-3}s^{-1} \times [0.4M] \times [0.8M] \times [0.2M]^2$$
$$= 0.15\ M^{-3}s^{-1}\ M^4$$
$$= 0.15\ Ms^{-1}$$

Types of Reactions Based on Rate: Zero Order

Change in concentration over time IS linear

Rate Law for A→ Product: rate = k $[A]^0$ = k

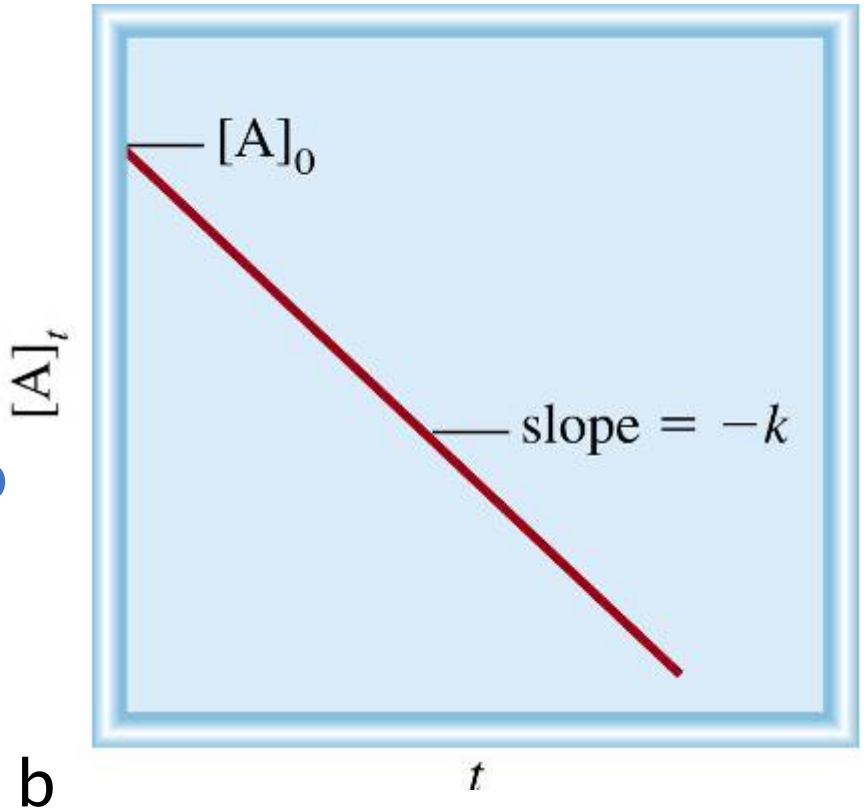
Units of k: k = rate = M/s

Linear Rate Equation:

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

Eventually [A] will go to zero (all reactant will be used up)

Note that this equation is in the form y = mx + b, where b is the y-intercept (i.e. the initial concentration of A).



Types of Reactions Based on Rate: First Order

Change in concentration over time is NOT linear

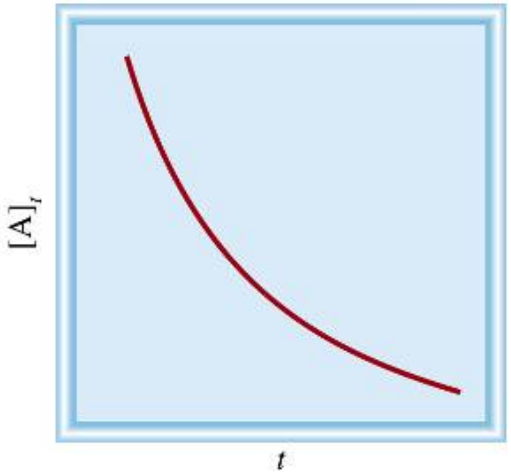
Change in the natural log (ln) of concentration over time IS linear.

Rate Law for A→ Product: $\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$

Units of k: $k = \text{rate}/[A] = (M/s)/M = 1/s = s^{-1}$

[A] vs. time is Nonlinear

$[A] = [A]_0 e^{(-kt)}$

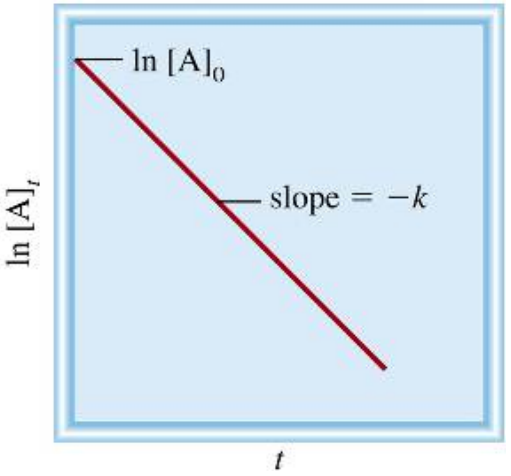


$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

$[A]_t$ = [A] at time *t*
$[A]_0$= [A] at *t*=0

ln [A] vs time is Linear:

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



Types of Reactions Based on Rate: Second Order

Change in concentration over time is NOT linear

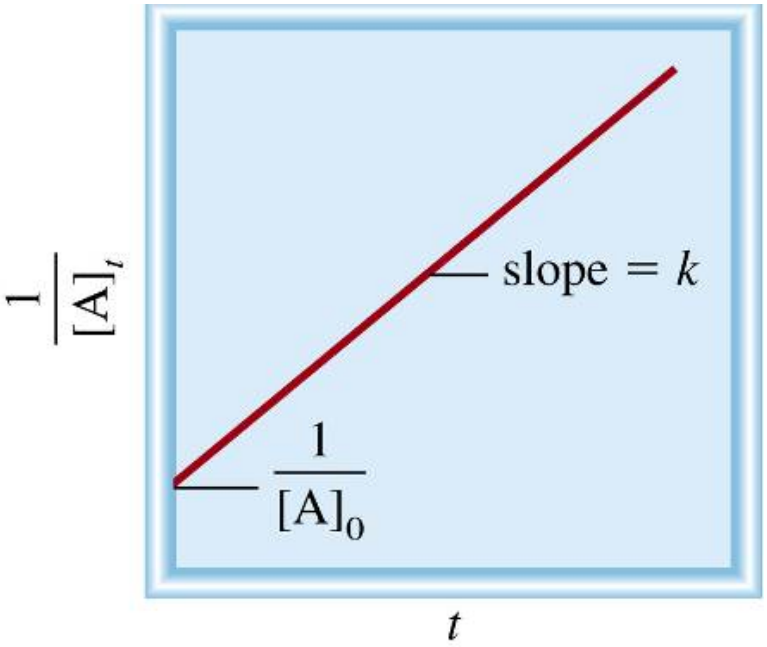
Change in the inverse of concentration (1/[A]) over time IS linear.

Rate Law for A→ Product: $\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$

Units of k: $k = \text{rate}/[A]^2 = (M/s)/M^2 = 1/Ms = M^{-1}s^{-1}$

The linear equation is:

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



Predicting Reaction Order Graphically

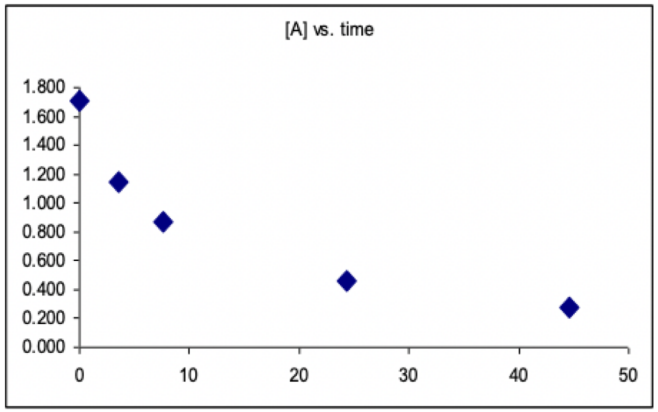
For the reaction A → Products:

1. Calculate ln[A] and 1/[A]
2. Make 3 graphs: [A], ln[A], and 1/[A] vs. time
3. The graph with the best straight line is the reaction order

	Zero	First	Second
time, s	[A] M	ln [A]	1/[A]
0	1.710	0.536	0.585
4	1.150	0.140	0.870
8	0.870	-0.139	1.149
24	0.460	-0.777	2.174
45	0.280	-1.273	3.571

Predicting Reaction Order Graphically

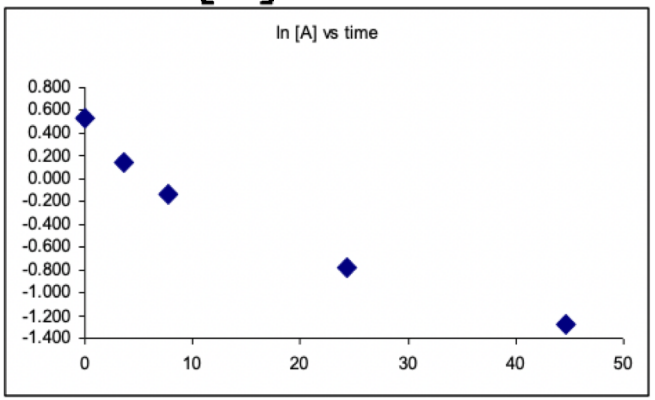
[A] vs. time



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

Not linear, so not Zero Order

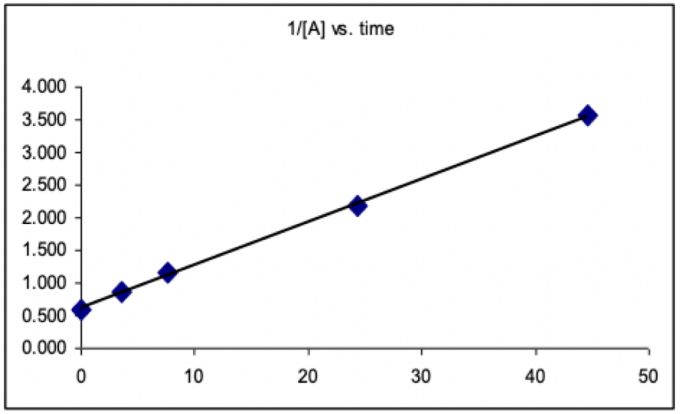
ln[A] vs. time



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

Not linear, so not First Order

1/[A] vs. time



$1/[A] = kt + 1/[A]_0$

Linear, so reaction is

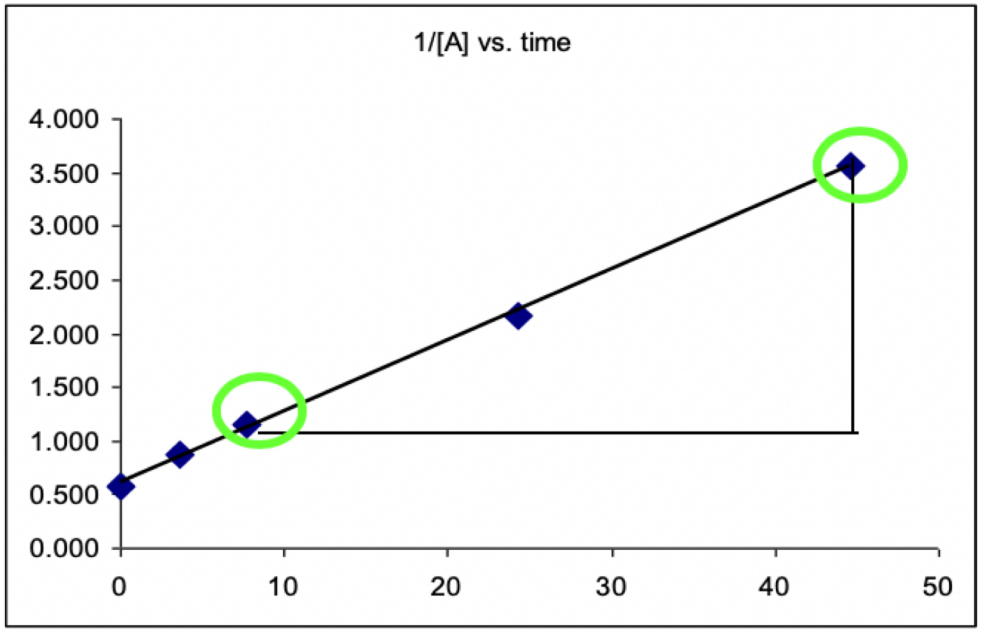
<u>Second Order</u>

Using a Graph to Find Rate Constant, k

Equation of the line is: $y = mx + b$

$1/[A] = kt + 1/[A]_0$

k = m = slope!



$k = m = (y - y_1)/(x - x_1)$

$= (3.57 - 1.15)/(45 - 8)$

$= 0.066\ M^{-1}s^{-1}$

$$\frac{1}{[A]} = 0.066t + \frac{1}{[A]_0}$$

Using Line Equations to Find Information

1. For the first order reaction: $2\ N_2O_5 \rightarrow 2\ N_2O_4 + O_2$ at 45°C, $k = 6.22 \times 10^{-4}\ s^{-1}$. If $[N_2O_5] = 0.100M$:

a.) How long does it take for the concentration to drop to 0.010M?

A: $3.70 \times 10^3 s$

b.) What is the concentration after one hour?

A: 0.0107M

2. The decomposition of sulfuryl chloride (SO_2Cl_2) is first order in SO_2Cl_2. The rate constant for the decomposition at 660K is $4.5 \times 10^{-2}\ s^{-1}$.

a.) If we begin with an initial SO_2Cl_2 pressure or 450 torr, what is the pressure of this substance after 60.s? A: 30. torr

b.) At what time will the pressure of SO_2Cl_2 decline to 1/10 its initial value? A: 51s