Chapter 14 – Chemical Kinetics

• 14.1 Factors that Affect Reaction Rates

- There are 4 factors that impact how fast a reaction will go:
    1. Physical state of the reactants
    2. Reactant concentrations
    3. Reaction temperature
    4. Adding a catalyst
- we will talk about these factors as we go through the chapter

• 14.2 Reaction Rates

- reaction rate = concentration change/time change
- the rate at which products are formed and reactants are consumed are connected
- general case: aA + bB → cC + dD

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

where $\Delta t = t_f - t_i$, [A] is the concentration of A (moles/L) and $\Delta[A] = [A]_f - [A]_i$

-- we loose reactants as products are formed which is why the rates of A & B are negative

- Example:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

Figure 12.1 & **Table 12.1** from *Chemistry* by McMurray & Fay

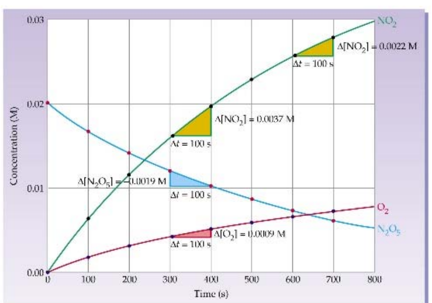


TABLE 12.1 Concentrations as a Function of Time at 55°C for the Reaction $2\ N_2O_5(g) \longrightarrow 4\ NO_2(g) + O_2(g)$

	Concentration (M)		
Time (s)	N_2O_5	NO_2	O_2
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

$$\text{rate of decomposition of } N_2O_5 = -\frac{\Delta[N_2O_5]}{\Delta t} = \frac{-(0.0101 - 0.0120)M}{(400-300)s} = 1.9\times10^{-5}\, M/s$$

$$\text{rate of formation of } O_2 = \frac{\Delta[O_2]}{\Delta t} = \frac{(0.00049 - 0.0040)M}{(400-300)s} = 9\times10^{-6}\, M/s$$

$$\text{rate of formation of } NO_2 = \frac{\Delta[NO_2]}{\Delta t} = \frac{(0.0197 - 0.0160)M}{(400-300)s} = 3.7\times10^{-5}\, M/s$$

- Example: What is the rate relationship between the production of O_2 and O_3?

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

$$-\frac{1}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t} \rightarrow -\frac{3}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t} \text{ or } \frac{\Delta[O_3]}{\Delta t} = -\frac{2}{3}\frac{\Delta[O_2]}{\Delta t}$$

-- the rate of O_2 production is 1.5 times faster than the ate of consumption of O_3

-- the rate of O_3 consumption is 2/3 times the production of O_2

- Example: The decomposition of N_2O_5 proceeds according to the equation:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

If the rate of decomposition of N_2O_5 at a particular instant is 4.2 x 10^{-7} M/s, what is the rate of production of NO_2 and O_2?

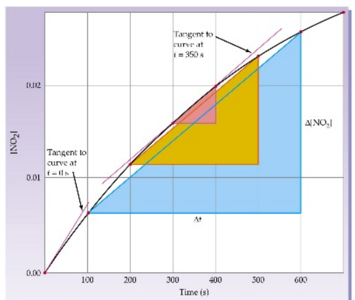
$$Rate = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

$$\frac{\Delta[NO_2]}{\Delta t} = \frac{4}{2}\frac{\Delta[N_2O_5]}{\Delta t} = 2\times 4.2\times 10^{7}\ M/s = 8.4\times 10^{7}\ M/s$$

$$\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = 2.1\times 10^{7}\ M/s$$

- But where does this rate come from?
  - -- a plot of concentration versus time

Figure 12.2 from *Chemistry* by McMurray & Fay



- we can use these plots to determine the concentration change over time
- average rate is found by taking the concentration change over a time interval
- instantaneous rate: is found by determining the slope of the line tangent to a particular time

• 14.3 Concentration & Rate Laws

- rate law: relates the reaction rate with reactant concentration
  - -- In general: Rate = $k[A]^m[B]^n$ for aA + bB → products
    - --- where m and n are determined experimentally
    - --- k is called the rate constant
  - -- note the rate law is not related to the stoichiometry of the equation - other examples:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)} \qquad Rate = k[N_2O_5]$$

$$CHCl_{3(g)} + Cl_{2(g)} \rightarrow CCl_{4(g)} + HCl_{(g)} \qquad Rate = k[CHCl_3][Cl_2]^{1/2}$$

- reaction order: the power to which a reactant is raised in the rate law equation
  - -- rate = $k[O_2][NO]^2$
    - for O_2 this power is 1 so the rate has a 1st order dependence on $[O_2]$
    - for NO this power is 2 so the rate has a 2nd order dependence on [NO]
    - the overall reaction order is 1+2 = 3 or third order
  - -- in general, rate = $k[A]^m[B]^n$
    - rate dependence on A is mth order, rate dependence on B is nth order and overall reaction order is m+n

Experimental Determination of Rate Law

- Example: Determine the rate law, the rate constant and the reaction orders for each reactant and the overall reaction order using the data given below.

Experiment	$[A]_0$	$[B]_0$	Initial Rate $\left(\frac{M}{s}\right)$
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

-- comparing 1 & 2: doubling [B] has no effect on the rate therefore rate $\propto [B]^0$

-- comparing 1 & 3: double [A] quadruples the rate therefore rate $\propto [A]^2$

-- rate = $k[A]^2[B]^0 = k[A]^2$

$$k = \frac{4.0\times10^{-5}\,M/s}{(0.100M)^2} = 4.0\times10^{-3}M^{-1}s^{-1}$$

-- A is 2nd order and B is 0th order, with an overall reaction order of 2

• 14.4 The Change of Concentration with Time

- we can monitor the concentration change as a function of time
- First-Order Reactions

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

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = \int_o^t -kdt \rightarrow \ln[A]\,|_{[A]_0}^{[A]t} = -kdt\,|_0^t \rightarrow \ln[A]_t - \ln[A]_0 = -kt$$

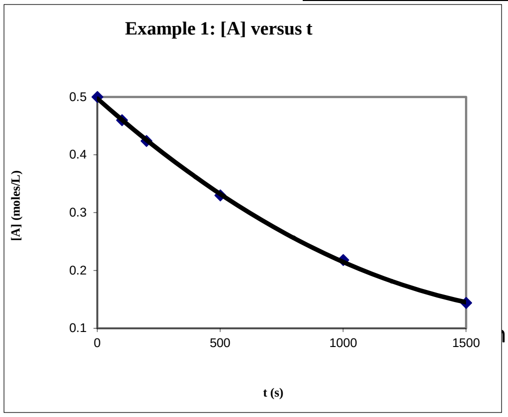
$$\therefore \ln[A]_t = -kt + \ln[A]_0$$

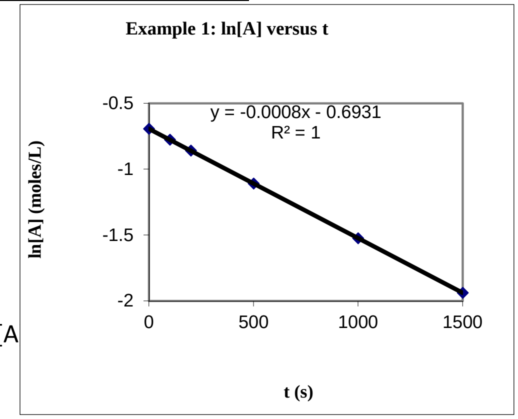
-- this is called the integrated rate law

-- in order to get a linear relationship so we can find the rate constant k, we use ln[A]

-- Example: Use the data below to determine if the reaction is first order and the rate law constant.

Time (s)	[A]	ln[A]
0	0.5	-0.69315
100	0.46	-0.77653
200	0.424	-0.85802
500	0.33	-1.10866
1000	0.218	-1.52326
1500	0.144	-1.93794





- half-life is the amount of time required for the original concentration of reactant to be reduced by half

$$\ln\frac{[A]_t}{[A]_0} = -kt \rightarrow \ln\frac{\frac{1}{2}[A]_0}{[A]_0} = -kt_{1/2} \rightarrow \ln\frac{1}{2} = -kt_{1/2} \rightarrow -0.693 = -kt_{1/2} \rightarrow t_{1/2} = 0.693/k$$

- Second-Order Reactions

$$rate = k[A]^2 = \frac{-\Delta[A]}{\Delta t} \rightarrow \frac{\Delta[A]}{[A]^2} = -k\Delta t$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = \int_{o}^{t} -kdt \rightarrow \frac{-1}{[A]}\Big|_{[A]_0}^{[A]t} = -kdt\,\Big|_0^t \rightarrow \frac{-1}{[A]_t} + \frac{-1}{[A]_0} = -kt$$

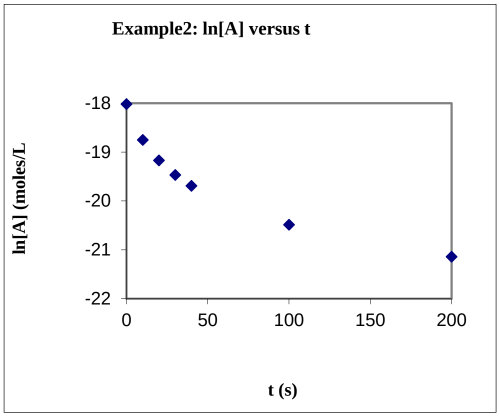
$$\therefore \frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

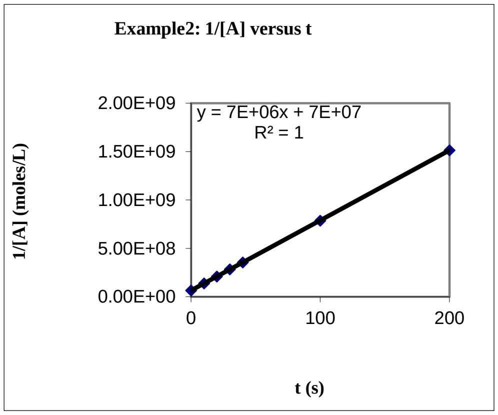
-- in this case in order to get a linear relationship to determine k, we use the inverse

-- Example: Use given the data below determine whether the rate law is first or second order and find the rate constant using the data below.

Time (s)	[A]	ln[A]	1/[A]
0	1.50×10^{-8}	-18.015	6.667×10^{7}
10	7.19×10^{-9}	-18.751	1.391×10^{8}
20	4.74×10^{-9}	-19.167	2.110×10^{8}
30	3.52×10^{-9}	-19.465	2.841×10^{8}
40	2.81×10^{-9}	-19.690	3.559×10^{8}
100	1.27×10^{-9}	-20.484	7.874×10^{8}
200	6.60×10^{-9}	-21.139	1.515×10^{9}

Since the inverse relationship is linear this reaction must be second order





- Zeroth-Order Reactions

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

$$\int_{[A]_0}^{[A]_t} d[A] = \int_{o}^{t} -kdt \rightarrow [A]\Big|_{[A]_0}^{[A]t} = -kdt\,\Big|_0^t \rightarrow [A]_t - [A]_0 = -kt$$

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

-- for this order we need only plot concentration of versus time to get a linear relationship

- **14.5 Temperature & Rate**

- Arrhenius equation, $k = Ae^{-E_a/RT}$

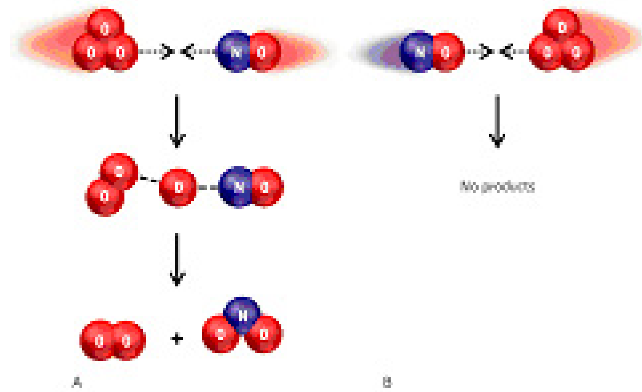
-- k is the rate constant

-- A is the frequency factor

--- product of collision frequency between reacting species and orientation factor

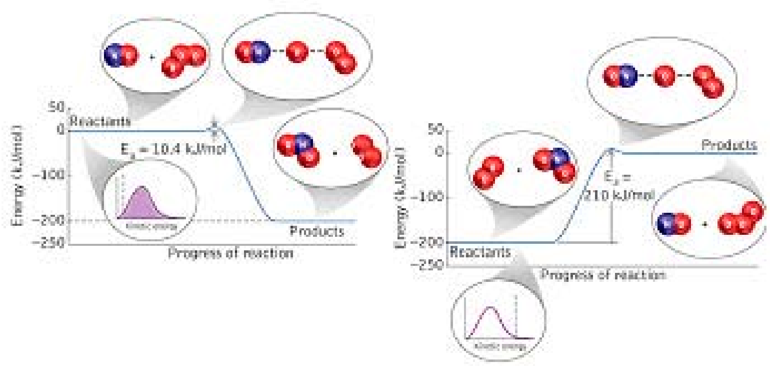
--- not all collisions generate products - some collisions are in the wrong orientation

Figure 14.16 from *Chemistry*: *The Science in Context*



-- E_a, the activation energy: amount of E which must be overcome to generate products

Figure 14.17 from *Chemistry*: *The Science in Context*

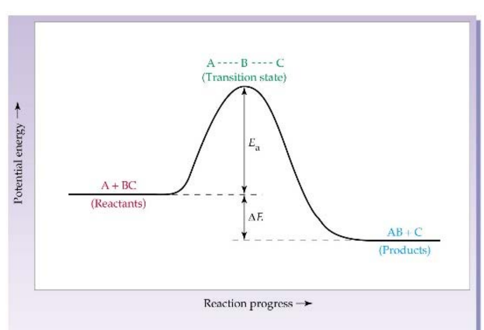


-- R is the gas law constant in Joules, R = 8.314 J/mol*K

-- T is the temperature in K

- transition state is the activated complex formed in the course of a reaction

Figure 12.14 from *Chemistry* by McMurray & Fay



Using the Arrhenius Equation

- if we take the ln of $k = Ae^{-E_a/RT}$ we get $\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$

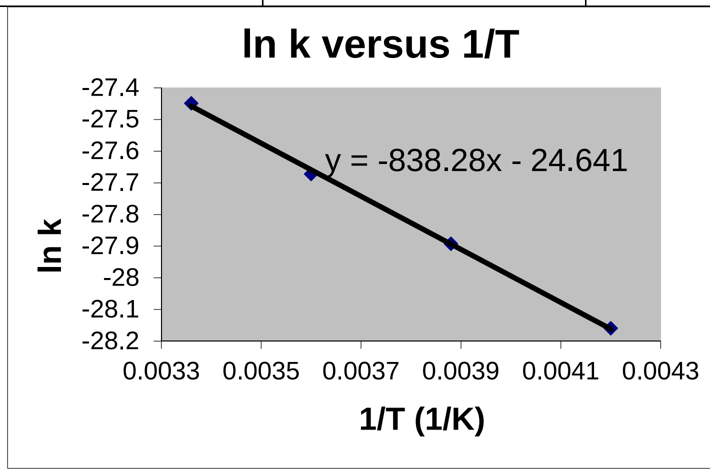
- if we plot ln k versus 1/T we can use the slope and R to get $E_a \rightarrow E_a$ = -slope*R

- Example: Find the activation energy of for the $Br + O_3 \rightarrow BrO + O_2$ given the data below.

T (K)	k (cm^3/molecule*s)
238	5.9×10^{-13}
258	7.7×10^{-13}
278	9.6×10^{-13}
298	1.2×10^{-12}

-- we need to make a plot of ln k versus 1/T

T (K)	1/T	k (cm^3/molecule*s)	ln(k)
238	0.00420	5.9×10^{-13}	-28.1587
258	0.00388	7.7×10^{-13}	-27.8924
278	0.00360	9.6×10^{-13}	-27.6718
298	0.00336	1.2×10^{-12}	-27.4487

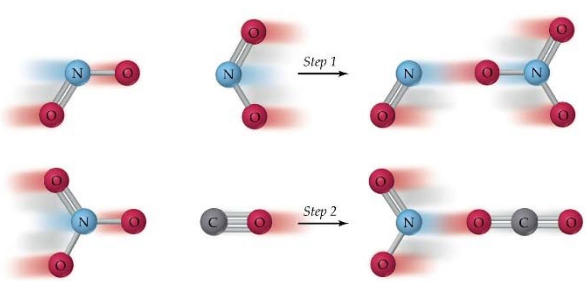


-- E_z = -slope * R = -(-838.28K)*8.314 J/mol*K = 6969.5 J/mol or 6.7 kJ/mol

- **14.6 Reaction Mechanisms**
  - reaction mechanism: the way in which electrons move during a chemical reaction
    - -- how bonds are broken in reactants and reformed to products
  - intermediate: species that is both produced and consumed in the course of a reaction – doesn't partake in the rate law
  - elementary steps: a step which takes place during a reaction
    - -- the stoichiometry of these steps may be used to get reactant order
    - -- molecularity: the number of reacting particles in an elementary step
    - -- overall sum of these steps leads to the overall reaction
  - Example: NO_2 + CO:

$$\begin{array}{lll} step1: & NO_2 + NO_2 \rightarrow NO + NO_3 & elementary \\ step2: & NO_3 + CO \rightarrow NO_2 + CO_2 & elementary \\ \hline & NO_2 + CO \rightarrow NO + CO_2 & overall \end{array}$$

Figure 12.10 from *Chemistry* by McMurray & Fay



-- intermediate - NO_3

-- molecularity of both elementary steps - bimolecular

Rate Laws and Reaction Mechanisms

Molecularity	**Elementary step**	**Rate Law**
Unimolecular	A $\rightarrow$ products	Rate = k[A]
Bimolecular	A + A $\rightarrow$ products	Rate = $k[A]^2$
Bimolecular	A + B $\rightarrow$ products	Rate = [A][B]
Termolecular	A + A + A $\rightarrow$ products	Rate = $k[A]^3$
Termolecular	A + A + B $\rightarrow$ products	Rate = $k[A]^2[B]$
Termolecular	A + B + C $\rightarrow$ products	Rate = k[A][B][C]

- Example: Determine the molecularity and rate law for each of the elementary steps.

$$H_2 + NO \rightarrow N + H_2O$$
$$N + NO \rightarrow N_2 + O$$
$$H_2 + O \rightarrow H_2O$$

Solution:

$$rate = k[H_2][NO]$$
$$rate = k[N][NO]$$
$$rate = k[H_2][O]$$

all the steps are bimolecular

Rate Laws for Overall Reactions

-rate-determining step: is the slowest elementary step which thereby limits the reaction rate

-- just like a relay race - if 3/4 runners are fast than the rate of the race is determined the slowest runner

$$step1: \quad 2NO_2 \xrightarrow{k_1} NO + NO_3 \qquad (slow) \quad rate = k_1[NO_2]^2$$
$$step2: \quad NO_3 \xrightarrow{k_2} NO + O_2 \qquad (fast)$$

- What if we go backwards with the above reaction? How do we handle that?

$$step1: \quad NO + O_2 \xrightarrow{k_1} NO_3 \qquad (fast)$$
$$step2: \quad NO + NO_3 \xrightarrow{k_2} 2NO_2 \quad (slow)$$

-- *when a fast step preceeds the slow step we assume the fast step is in eq or reversible*

$$step1: \quad NO + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3 \quad (fast)$$
$$step2: \quad NO + NO_3 \xrightarrow{k_2} 2NO_2 \quad (slow)$$

-- we can then write the rate of step1 as rate =$k_1[NO][O_2]$ = $k_{-1}[NO_3]$solving for $[NO_3]$,

$$[NO_3] = \frac{k_1}{k_{-1}}[NO][O_2]$$

-- the rate for step2: rate = $k_2[NO][NO_3]$, we can plug in the relationship from step1 into this equation:

$$rate = k_2[NO]\frac{k_1}{k_{-1}}[NO][O_2] = k_2\frac{k_1}{k_{-1}}[NO]^2[O_2]$$

- Example: The rate laws for the thermal and photochemical decomposition of NO_2 are different. Which of the following mechanisms are possible for thermal and photochemical rates given the information below?

Thermal rate = $k[NO_2]^2$

Photochemical rate = $k[NO_2]$

a.) b.) c.)

$$NO_2 \xrightarrow{slow} NO + O$$
$$O + NO_2 \xrightarrow{fast} NO + O_2$$

$$NO_2 + NO_2 \xrightarrow{fast} N_2O_4$$
$$N_2O_4 \xrightarrow{slow} NO + NO_3$$
$$NO_3 \xrightarrow{fast} NO + O_2$$

$$NO_2 + NO_2 \xrightarrow{slow} NO + NO_3$$
$$NO_3 \xrightarrow{fast} NO + O_2$$

a.) rate = k[NO_2] which is consist with the photochemical rate

b.) fast step before slow so we assume eq:

$$NO_2 + NO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_4 \qquad k_1[NO_2]^2 = k_{-1}[N_2O_4] \rightarrow [N_2O_4] = \frac{k_1}{k_{-1}}[NO_2]^2$$

$$N_2O_4 \xrightarrow{k_2} NO + NO_3 \qquad rate = k_2[N_2O_4] = k_2\frac{k_1}{k_{-1}}[NO_2]^2$$

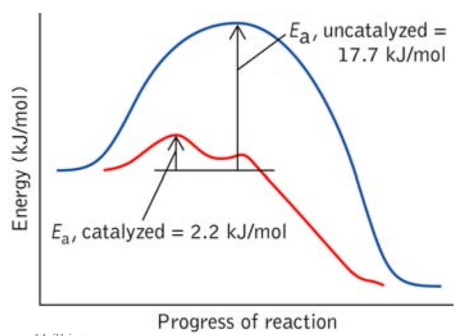
therefore this mechanism is consistent with the thermal rate

c.) rate = k[NO_2]^2 which is also consistent with the thermal rate

- **14.7 Catalysis**

- How can we change the rate of a chemical reaction? we can use a catalyst
- defn: a species that lowers the activation energy of a chemical reaction and does not undergo any permanent chemical change
- it is not present in the overall reaction expression
- it is not present in the rate law
- it must be consumed and produced in the elementary steps
    -- Catalysis of ozone by Cl

Figure 14.21 *Chemistry*: *The Science in Context*



14_21.jpg

Uncatalyzed mechanism - blue line in the figure

$$step1: \quad O_3 \xrightarrow{hv} O_2 + O$$
$$step2: \quad O + O_3 \longrightarrow 2O_2$$
$$2O_3 \longrightarrow 3O_2$$

E_a = 17.7 kJ/mol

Cl Catalyzed mechanism - red line

$$step1: \quad Cl + O_3 \longrightarrow O_2 + ClO$$
$$step2: \quad ClO + O_3 \longrightarrow Cl + 2O_2$$
$$2O_3 \longrightarrow 3O_2$$

E_a = 2.2 kJ/mol

Types of Catalysts

-- homogeneous catalyst: is one that exists in the same phase as the reactants

-- heterogeneous catalyst: is one that is not in the same phase as the reactants