

Chemical Kinetics

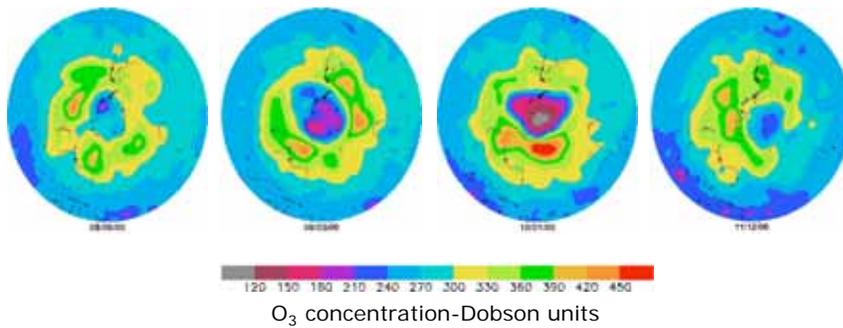
- Kinetics is a study of the rate at which a chemical reaction occurs.
- The study of kinetics may be done in steps:
 - ⇒ Determination of reaction mechanism
 - ⇒ Prediction of rate law
 - ⇒ Measurement of reaction rates
 - ⇒ Comparison of predicted and measured rates

Reaction Mechanisms

- Up to now, we have written chemical reactions as “net” reactions—a balanced chemical equation that shows the initial reactants and final products.
- A “reaction mechanism” shows the “elementary” reactions that must occur to produce the net reaction.
- An “elementary” reaction is a chemical reaction that actually takes place.

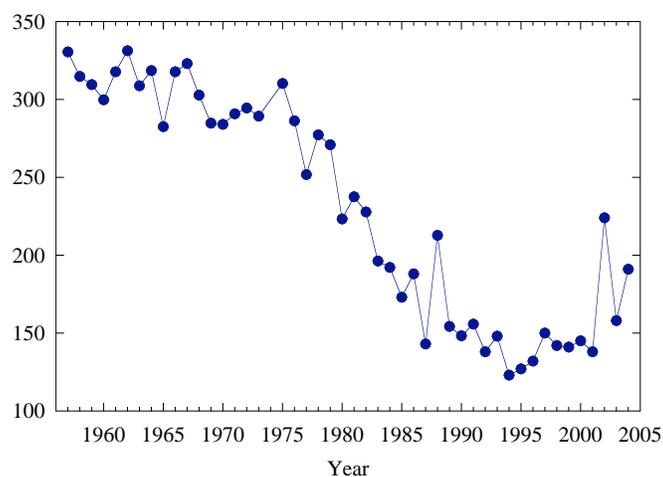
Reaction Mechanisms

- Every September since the early 80s, an "ozone hole" has developed over Antarctica which lasts until mid-November.



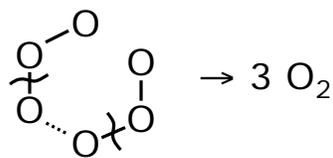
Reaction Mechanisms

Average Ozone Concentrations for October over Halley's Bay



Reaction Mechanisms

- The net reaction for this process is:
 $2 \text{O}_3(\text{g}) \rightarrow 3 \text{O}_2(\text{g})$
- If this reaction were an elementary reaction, then two ozone molecules would need to collide with each other in such a way to form a new O-O bond while breaking two other O-O bonds to form products:

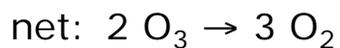
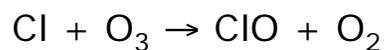
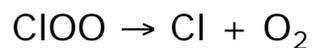
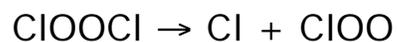
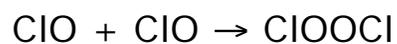
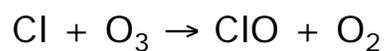


Reaction Mechanisms

- It is hard to imagine this process happening based on our current understanding of chemical principles.
- The net reaction must proceed via some other set of elementary reactions:

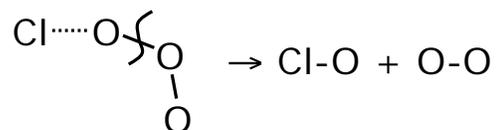
Reaction Mechanisms

- One possibility is:



Reaction Mechanisms

- In this mechanism, each elementary reaction makes sense chemically:



- The chlorine atom abstracts an oxygen atom from ozone leaving ClO and molecular oxygen.

Reaction Mechanisms

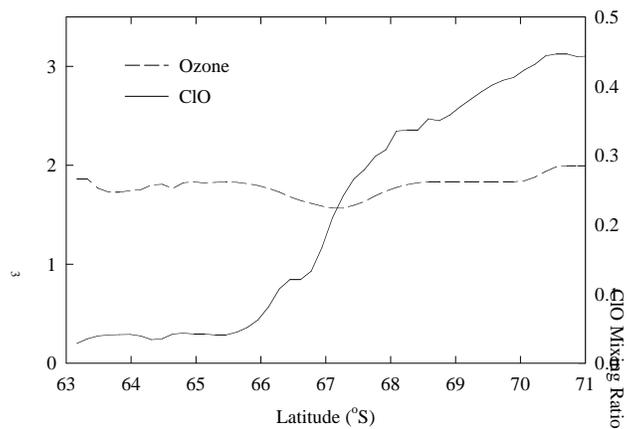
- Why does this chemistry occur over Antarctica producing an ozone hole?
 - ⇒ During the Antarctic winter, a polar vortex forms in which air from lower latitudes no longer enters the south polar region—the air mass within the polar vortex is trapped.
 - ⇒ There is no sunlight during winter, so no “photochemistry” takes place—reactions initiated by sunlight.

Reaction Mechanisms

- ⇒ During this period of darkness, molecules form, assisted by polar stratospheric clouds, containing chlorine atoms. These species absorb light and dissociate, but the absence of sunlight eliminates this process.
- ⇒ When the sun rises in mid-September, the chlorine containing species now dissociate to release a flood a chlorine atoms which react with ozone through the mechanism given.

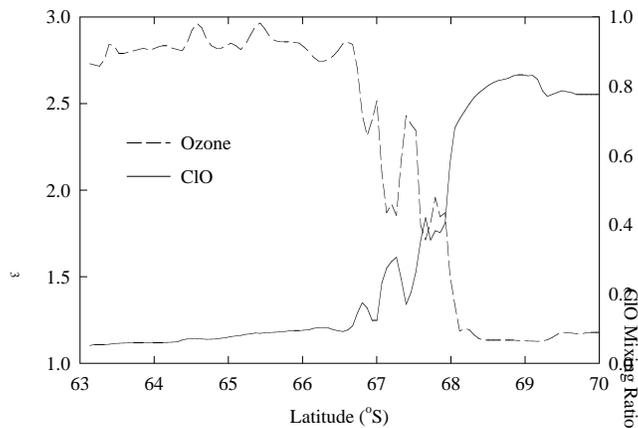
Reaction Mechanisms

Ozone and ClO Across the Polar Vortex Boundary--Aug. 1987



Reaction Mechanisms

Ozone and ClO Across the Polar Vortex Boundary--Sept. 1987



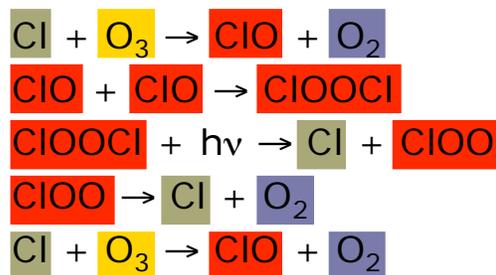
Reaction Mechanisms

- When we examine a reaction mechanism, we can identify the chemical species in one of four ways: reactants, intermediates, catalysts, or products.
- **Reactants** are necessary for the reaction to proceed and appear in the net reaction.
- **Intermediates** are species formed in the mechanism that undergo further reaction, but do not appear in the net reaction.

Reaction Mechanisms

- **Catalysts** are required to initiate the reaction. A catalyst does not appear in the net reaction and is regenerated in the reaction mechanism.
- **Products** are the final chemical species formed and appear in the net reaction.

Reaction Mechanisms



Reactants

Intermediates

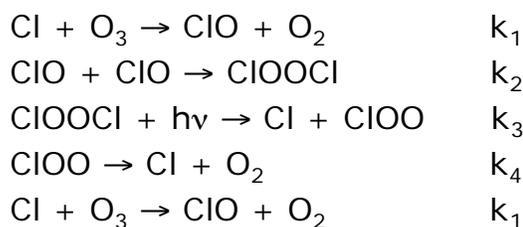
Products

Catalysts

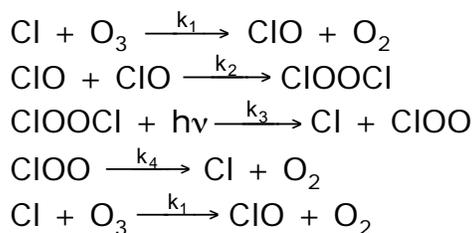
Reaction Mechanisms

- Each elementary reaction has a *rate coefficient* associated with it.
- The rate coefficient, given the symbol k , is a measure of how fast that specific elementary reaction occurs.
- k is often referred to as the *rate constant*, but this is a misnomer because k frequently changes with temperature or pressure.
- The rate coefficients are usually included in the reaction mechanism:

Reaction Mechanisms



Or



The Reaction Rate Law

- Based on the reaction mechanism, we can now derive a rate law.
- The rate law of a reaction expresses the speed of the reaction in terms of the concentrations of reactants and/or intermediates or catalysts and the rate coefficients of the elementary reactions.
- The overall rate law is given by:
rate = $K [A]^y[B]^z$
K is a collection of constants

The Reaction Rate Law

- The powers of concentrations in the rate law express the *order* of the reaction.

Example

If the rate law is

$$\text{rate} = K [A]^2[B]^1$$

the reaction is 2nd order in A, 1st order in B, and 3rd order overall.

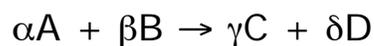
If the rate law is

$$\text{rate} = K [A]^3[B]^{1/2}$$

the reaction is 3rd order in A, 1/2 order in B, and 3 1/2 order overall.

The Reaction Rate Law

- The rate of a reaction is measured by monitoring the concentration of a chemical species as a function of time.

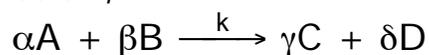


$$rate = -\frac{1}{\alpha} \frac{d[A]}{dt} = -\frac{1}{\beta} \frac{d[B]}{dt} = \frac{1}{\gamma} \frac{d[C]}{dt} = \frac{1}{\delta} \frac{d[D]}{dt}$$

- The rate is negative for reactants because the concentration is decreasing, positive for products because the concentration is increasing.

The Reaction Rate Law

- The rate law for a specific *elementary* reaction,



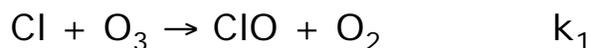
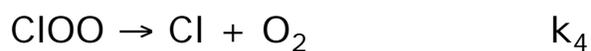
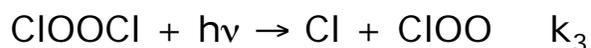
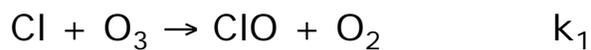
is given by:

$$rate = k[A]^\alpha[B]^\beta$$

- Note that the rate of a specific elementary reaction depends only on the concentration of reactants, not products.
- The overall rate law is derived by combining rate laws for each elementary reaction in the mechanism.

The Reaction Rate Law

Example: For the O₃ cycle over Antarctica, determine the rate law for the formation of oxygen.



The Reaction Rate Law

Example (con't.):

Oxygen is formed in reactions 1 (repeated in last step of mechanism) and 4. We write a rate for each of these reactions and sum them to get a total rate of oxygen formation:

$$\begin{aligned} \frac{d[\text{O}_2]}{dt} &= k_1[\text{Cl}][\text{O}_3] + k_4[\text{ClOO}] + k_1[\text{Cl}][\text{O}_3] \\ &= 2k_1[\text{Cl}][\text{O}_3] + k_4[\text{ClOO}] \end{aligned}$$

The Reaction Rate Law

Example (con't.):

Note that oxygen is a product in each of these elementary reactions, so the sign of each term is positive.

$$\begin{aligned}\frac{d[\text{O}_2]}{dt} &= k_1[\text{Cl}][\text{O}_3] + k_4[\text{ClOO}] + k_1[\text{Cl}][\text{O}_3] \\ &= 2k_1[\text{Cl}][\text{O}_3] + k_4[\text{ClOO}]\end{aligned}$$

The Reaction Rate Law

Example (con't.):

Let's assume that reaction 4 occurs much faster than reaction 1, *i.e.*, as soon as the ClOO intermediate is formed, it immediately decomposes to Cl and O₂, but the Cl + O₃ reaction takes more time to proceed. In this case, reaction 1 is called the "rate-limiting" step because it determines the overall rate at which the net reaction can occur.

The Reaction Rate Law

Example (con't.):

This simplifies the rate law:

$$\frac{d[\text{O}_2]}{dt} = 2k_1[\text{Cl}][\text{O}_3] + k_4[\text{ClOO}] \cong 2k_1[\text{Cl}][\text{O}_3]$$

This rate law predicts that the formation of oxygen depends only on the concentration of atomic chlorine and ozone.

As [Cl] increases, the rate of oxygen formation from the reaction of ozone increases.

Experimental Determination of Rate Law

- If we measure the rate of a reaction under different concentration conditions, we can determine the order of the reaction.
- Experimentally, we design the measurements to change only one variable at a time:

Experimental Determination of Rate Law

Example:

For the reaction $A + B \rightarrow C + D$, the following data were measured:

	[A]	[B]	rate
#1	1.0 M	1.0 M	25.0 M s ⁻¹
#2	0.5 M	2.0 M	12.5 M s ⁻¹
#3	0.5 M	1.0 M	6.25 M s ⁻¹
#4	1.0 M	2.0 M	50.0 M s ⁻¹

Determine the rate law for this reaction.

Experimental Determination of Rate Law

Example (con't.):

We need to find K, y, and z in:

$$\text{rate} = K [A]^y [B]^z$$

Compare #1 and #3: [A] is halved and the rate decreases by a factor of 4

$$\Rightarrow y = 2$$

Compare #1 and #4: [B] is doubled and the rate increases by a factor of 2

$$\Rightarrow z = 1$$

Experimental Determination of Rate Law

Example (con't.):

We need to find K, y, and z in:

$$\text{rate} = K [A]^y[B]^z$$

We can take any run and determine the value of the constant K:

$$12.5 \text{ M s}^{-1} = K [0.5 \text{ M}]^2[2.0 \text{ M}]$$

$$\Rightarrow K = 25 \text{ M}^{-2} \text{ s}^{-1}$$

Rate law is:

$$\text{rate} = 25 \text{ M}^{-2}\text{s}^{-1} [A]^2[B]$$

Experimental Determination of Rate Law

- If a reaction is 1st order in some reactant A, the rate can be expressed as

$$\frac{d[A]}{dt} = -k[A]$$

- Rearrangement and integration of this expression yields:

$$[A(t)] = [A]_0 \exp\{-k \cdot t\}$$

where $[A]_0$ is the initial concentration of A at $t = 0$.

Experimental Determination of Rate Law

- If we take the natural log of both side of this expression, we get
$$\ln[A(t)] = \ln[A]_o - k \cdot t$$
- If we now plot $\ln[A(t)]$ *versus* time, we get a straight line with a slope equal to $-k$.

Experimental Determination of Rate Law

- If a reaction is 2nd oder in some reactant A, the rate can be expressed as

$$\frac{d[A]}{dt} = -k [A]^2$$

- Rearrangement and integration of this expression yields:

$$\frac{1}{[A(t)]} = \frac{1}{[A]_o} + k \cdot t$$

Experimental Determination of Rate Law

- If we now plot $1/[A(t)]$ *versus* time, we get a straight line with a slope equal to k .
- One way of determining if a reaction is 1st or 2nd order is to plot the natural log of the measured concentration *versus* time or the inverse of the measured concentration *versus* time—which ever plot results in a straight line indicates the order of the reaction for that species.

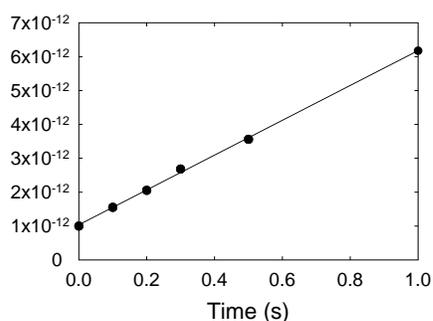
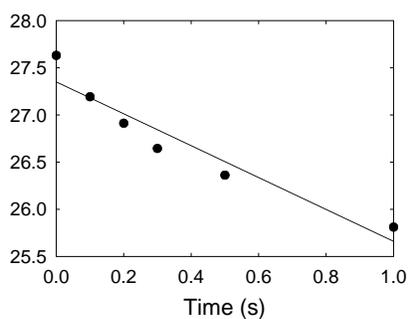
Experimental Determination of Rate Law

Example: For the reaction $\text{ClO} + \text{ClO} \rightarrow \text{ClOOCl}$, the following data were obtained:

<u>[ClO] (molecule cm⁻³)</u>	<u>time (s)</u>
1.00 x 10 ¹²	0.0
6.45 x 10 ¹¹	0.1
4.87 x 10 ¹¹	0.2
3.73 x 10 ¹¹	0.3
2.81 x 10 ¹¹	0.5
1.62 x 10 ¹¹	1.0

Experimental Determination of Rate Law

Example: For the reaction $\text{ClO} + \text{ClO} \rightarrow \text{ClOOCl}$, the following data were obtained:



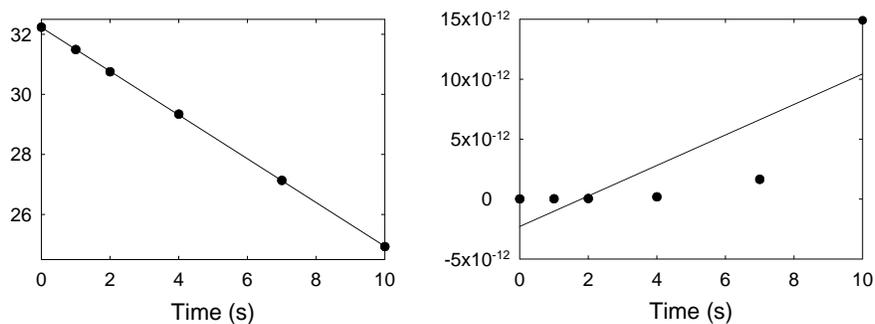
Experimental Determination of Rate Law

Example: For the reaction $\text{Cl} + \text{H}_2\text{CO} \rightarrow \text{HCl} + \text{HCO}$, the following data were obtained:

<u>[Cl] (molecule cm⁻³)</u>	<u>time (μs)</u>
1.00 x 10 ¹⁴	0.0
4.75 x 10 ¹³	1.0
2.27 x 10 ¹³	2.0
5.52 x 10 ¹²	4.0
6.09 x 10 ¹¹	7.0
6.71 x 10 ¹⁰	10.0

Experimental Determination of Rate Law

Example: For the reaction $\text{Cl} + \text{H}_2\text{CO} \rightarrow \text{HCl} + \text{HCO}$, the following data were obtained:



Experimental Determination of Rate Law

Example: For the reaction $\text{CH}_3\text{CHO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$ at 1000 K, the following data were obtained:

$[\text{CH}_3\text{CHO}]_0$	$\frac{d[\text{CH}_4]}{dt}$
1.0×10^{14}	$1.47 \times 10^{12} \text{ s}^{-1}$
1.0×10^{13}	$4.65 \times 10^{10} \text{ s}^{-1}$
2.0×10^{12}	$4.16 \times 10^9 \text{ s}^{-1}$
5.0×10^{11}	$5.20 \times 10^8 \text{ s}^{-1}$

Experimental Determination of Rate Law

Example: For the reaction $\text{CH}_3\text{CHO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$ at 1000 K:

Part I. Determine the rate law for the formation of CH_4 .

$$\text{rate} = K [\text{CH}_3\text{CHO}]^y$$

$$\ln(\text{rate}) = \ln(K) + y \ln[\text{CH}_3\text{CHO}]$$

plot $\ln(\text{rate})$ *versus* $\ln[\text{CH}_3\text{CHO}]$

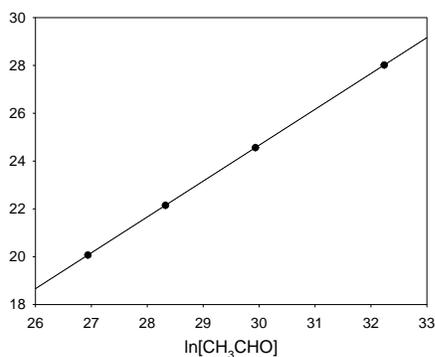
$$\text{slope} = y$$

$$\text{y-int} = \ln(K)$$

Experimental Determination of Rate Law

Example: For the reaction $\text{CH}_3\text{CHO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$ at 1000 K:

plot $\ln(\text{rate})$ *versus* $\ln[\text{CH}_3\text{CHO}]$



$$\text{Slope} = 1.50$$

$$\text{Y-int} = -20.33$$

Experimental Determination of Rate Law

Example: For the reaction $\text{CH}_3\text{CHO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$ at 1000 K:

Part I. Determine the rate law for the formation of CH_4 .

$$\text{rate} = K [\text{CH}_3\text{CHO}]^y$$

$$y = 1.50$$

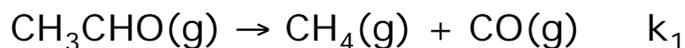
$$\ln(K) = -20.33 \quad \Rightarrow K = 1.48 \times 10^{-9}$$

$$\text{rate} = 1.48 \times 10^{-9} [\text{CH}_3\text{CHO}]^{3/2}$$

Experimental Determination of Rate Law

Example (con't.): For the reaction $\text{CH}_3\text{CHO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$ at 1000 K:

Part II. If we assume the reaction



is an elementary reaction, does this mechanism predict the correct rate law?

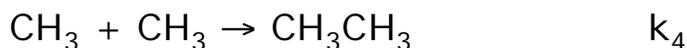
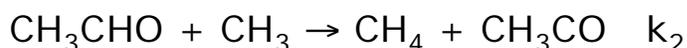
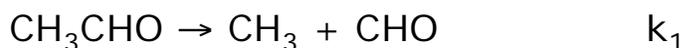
$$\frac{d[\text{CH}_4]}{dt} = k_1 [\text{CH}_3\text{CHO}]$$

This is not the measured rate law!

Experimental Determination of Rate Law

Example (con't.): For the reaction $\text{CH}_3\text{CHO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$ at 1000 K:

Part II. A reaction mechanism that correctly predicts the measured rate law is:



$$\frac{d[\text{CH}_4]}{dt} = k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

Experimental Determination of Rate Law

- A reaction mechanism can not be proven correct, it can only be proven incorrect
- If a proposed mechanism correctly predicts the observed rate law, it is possibly the "true" mechanism, but there may be other proposed mechanisms that also correctly predict the observed behavior.

Rate Coefficients

- The rate coefficient, k , of an elementary reaction is a measure of how fast that reaction occurs.
- For a 1st order reaction, the expression relating the concentration of reactant A and the rate coefficient is:

$$[A(t)] = [A]_o \exp\{-kt\}$$

- This can be manipulated to the form:

$$\ln([A(t)]/[A]_o) = -kt$$

Rate Coefficients

- The half-life of a reaction is the time required for the reactants to be reduced to 1/2 their initial concentration:

$$[A(t_{1/2})] = \frac{1}{2} [A]_o$$

- If we substitute these values into the 1st order expression, we get

$$\ln\left(\frac{1/2[A]_o}{[A]_o}\right) = -kt_{1/2} \quad \Rightarrow \quad \ln\left(\frac{1}{2}\right) = -kt_{1/2}$$

$$\ln(1) - \ln(2) = -kt_{1/2} \quad \Rightarrow \quad t_{1/2} = \frac{\ln(2)}{k}$$

Rate Coefficients

- Examples of 1st order kinetics include radioactive decay—the half-life of a radioisotope is the time it takes for the amount of that isotope to be decreased by a factor of two.
- Because 1st order half-lives are constant (half-life does not depend on concentration of isotope) this can be used to date materials containing radioactive elements.

Rate Coefficients

- The half-life of a 2nd order reaction is given by:

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

- For second order kinetics, the half-life depends on the initial concentration of the reactant, so the half-life get longer as the concentration decreases.

Temperature Dependence of Rate Coefficients

- The value of the rate coefficient, k , *usually* changes with temperature.
- The *Arrhenius Equation* expresses the temperature dependence of the rate coefficient:

$$k(T) = A \exp\{-E_a/RT\}$$

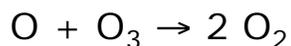
where

A is called the pre-exponential factor or frequency factor

E_a is the activation energy

Temperature Dependence of Rate Coefficients

- For the reaction:



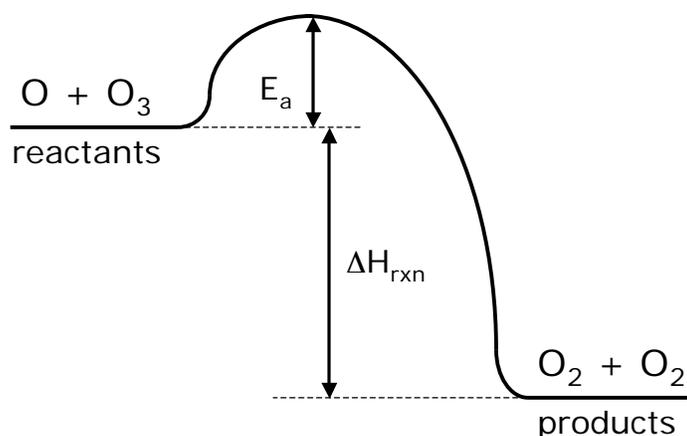
the rate coefficient has an Arrhenius expression of

$$k(T) = 8.0 \times 10^{-12} \exp\{-17.1 \text{ kJ}/RT\}$$

in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

- The reaction has an activation barrier of 17.1 kJ mol^{-1} —this means that the reactants must collide with at least that much energy in order to proceed to products.

Temperature Dependence of Rate Coefficients



Temperature Dependence of Rate Coefficients

- The $\text{O} + \text{O}_3 \rightarrow 2 \text{O}_2$ reaction is very exothermic:

$$\Delta H_{\text{rxn}}^{\circ} = -391.9 \text{ kJ mol}^{-1}$$

but at room temperature, the rate coefficient is only

$$8.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

- This is very slow, indicating that only one in every 40,000 collisions between O and O_3 results in reaction. The inefficiency of reaction is due to the large activation barrier.

Temperature Dependence of Rate Coefficients

- To determine the activation barrier of a reaction, we must measure the rate coefficient at a number of different temperatures:

$$k(T) = A \exp\{-E_a/RT\}$$

$$\ln(k) = \ln(A) - E_a/RT$$

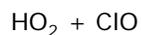
- If we plot $\ln(k)$ vs $1/T$, the graph has:

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

$$\text{y-int} = \ln(A)$$

Temperature Dependence of Rate Coefficients

Arrhenius plot for the reaction:



$$\text{slope} = 312.1$$

$$\text{y-int} = -26.58$$

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

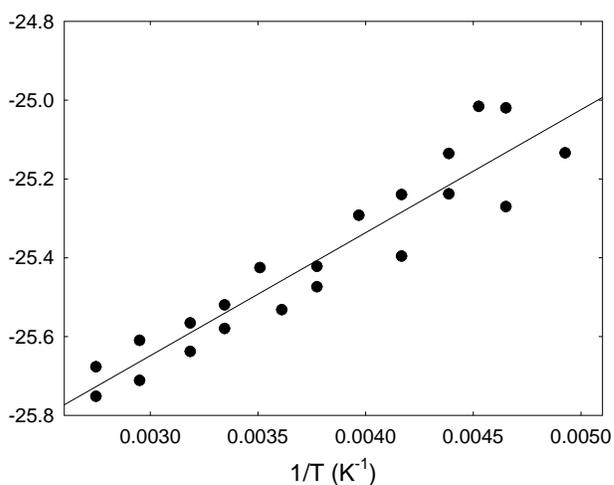
$$= -(8.314)(312.1)$$

$$= -2.59 \text{ kJ mol}^{-1}$$

$$A = \exp\{\text{y-int}\}$$

$$= \exp\{-26.82\}$$

$$= 2.9 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$



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Catalysts and Rate Coefficients

- A catalyst is a species that participates in a reaction, is regenerated in the reaction mechanism, and has the effect of increasing the net rate of reaction relative to the absence of the catalyst.

Catalysts and Rate Coefficients

- Catalytic destruction of ozone:
The reaction $O + O_3 \rightarrow 2 O_2$ occurs naturally in the stratosphere, but the rate coefficient at stratospheric temperatures is
$$k(220 \text{ K}) = 7.0 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$
This is very slow and does not account for very much ozone loss in the "natural" stratosphere.

Catalysts and Rate Coefficients

There is a catalytic reaction mechanism involving chlorine atoms that accomplishes the same thing chemically:

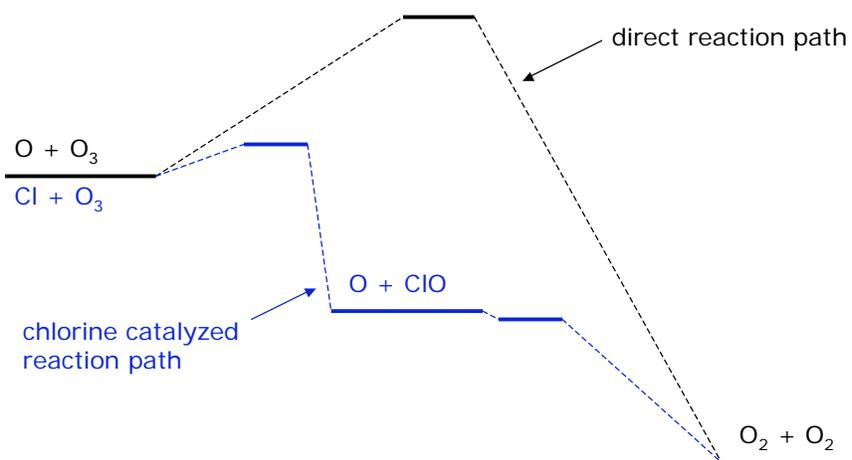


The rate coefficients for these two reactions are:

$$k_1(T) = 2.9 \times 10^{-11} \exp\{-2.16 \text{ kJ/RT}\}$$

$$k_2(T) = 3.0 \times 10^{-11} \exp\{+0.58 \text{ kJ/RT}\}$$

Catalysts and Rate Coefficients



Catalysts and Rate Coefficients

- This chlorine catalytic cycle has the same net reaction as the $O + O_3$ reaction, but forms products about 200 times faster than the direct $O + O_3$ reaction.
- This is due to the much smaller activation barrier in the catalytic mechanism—it is much easier for O_3 to react with chlorine atoms than with oxygen atoms, so the overall process is faster.