

## Summary and What's Next

Summary: Using **initial rates** from experimental data, we can find a rate law expression.  $\text{Rate} = k [\text{A}]^a [\text{B}]^b$  where  $a$  and  $b$  are the orders and  $k$  is the rate constant.

Now, we **extend** our ideas about *initial rates* into a way to **predict concentrations**. This requires calculus.

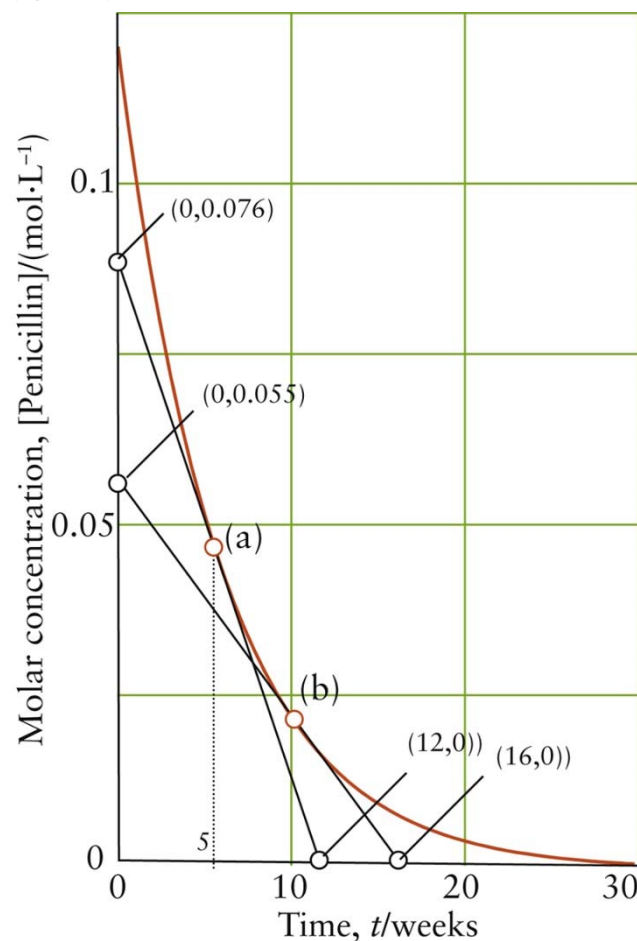


Figure 7A.5  
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One of the reasons to predict future concentrations might be to find out how much penicillin remains after 6 months. We'll have to find the slope of the tangent line in our rate expression to determine this.

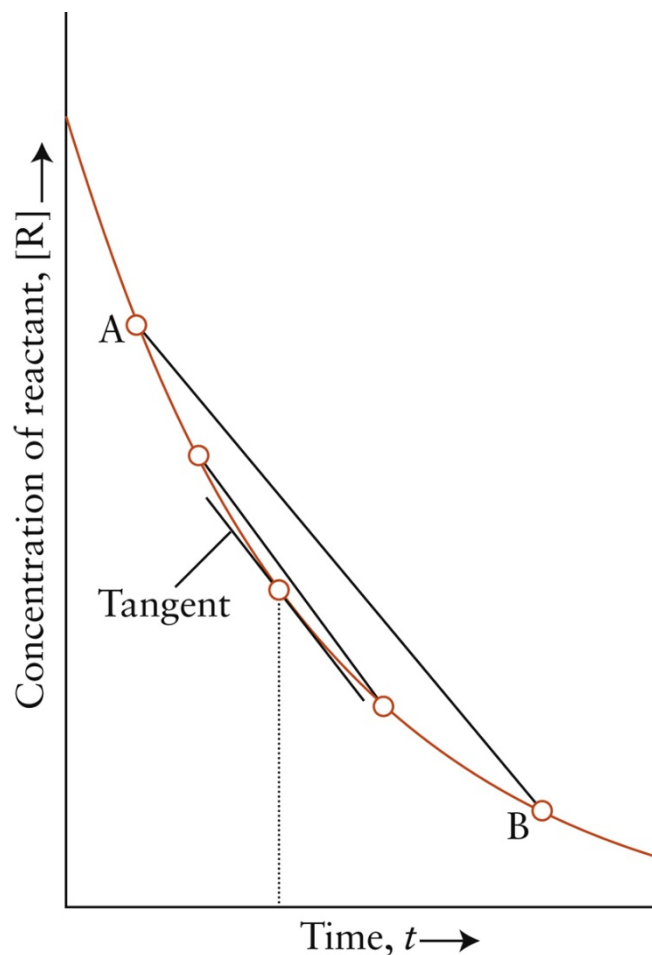


Figure 7A.4  
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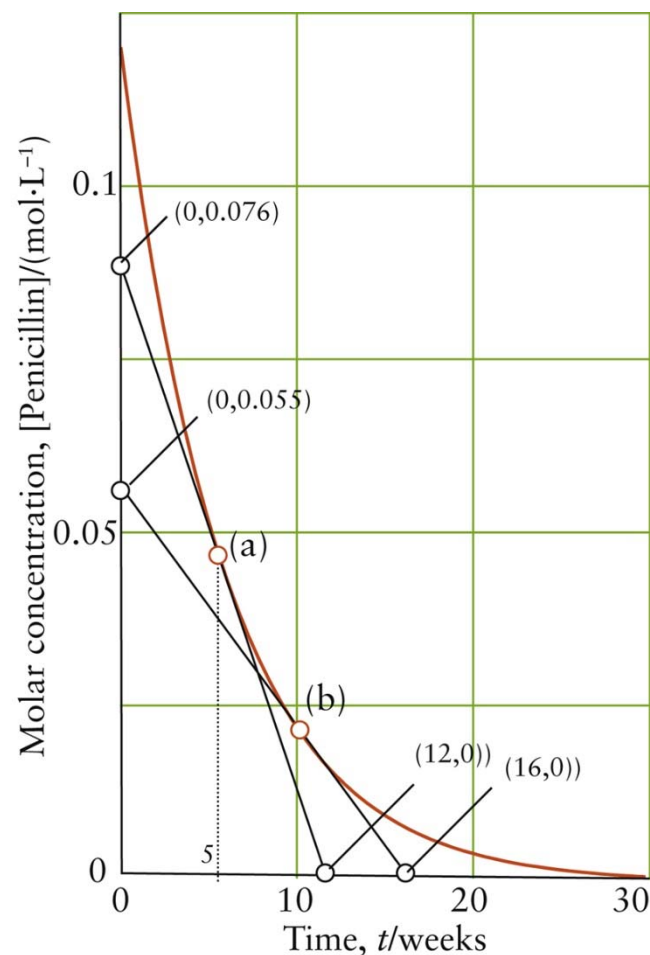


Figure 7A.5  
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Integrating the three rate laws will give us future concentrations.

rate = $k$	zeroth order
rate = $k[\text{N}_2\text{O}_5]$	first order
rate = $k[\text{NO}_2]^2$	second order

Integrating a zero-order rate law is easy. The rate constant,  $k$ , and initial value,  $[A]_0$ , is all we need because the reaction is proportional to time.

$$[A]_0 - [A] = kt \text{ or}$$

$[A] = [A]_0 - kt$ , where the slope is  $-k$  (slope is decreasing or the speed is slowing down).

Next, we'll look at first- and second-order reactions.

## First-Order Integrated Rate Laws

Start by using our first-order rate expression,  $\text{rate} = k[A]$ .

Our goal is to express the *rate* as *[A] changes over time*.

Rate of disappearance of A:  $-\frac{d[A]}{dt} = k[A]$

Divide both sides by [A] to keep the [A]'s together and move the  $dt$  so we can integrate the expression.

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

Now we integrate for concentration and for time.

## First-Order Integrated Rate Laws

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt$$

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

goes to:

$$\text{Noting that } \int \frac{d[A]}{[A]} = \ln x + \text{constant}$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = (\ln[A]_t + \text{constant}) - (\ln[A]_0 + \text{constant})$$

and

$$-k \int_0^t dt = -kt$$

$$\text{Noting that } \ln [A]_t - \ln [A]_0 = \ln \frac{[A]_t}{[A]_0}$$

Combining the two previous integrated expressions:

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad \text{or} \quad \ln [A]_t = \ln [A]_0 - kt \quad \text{or} \quad [A]_t = [A]_0 e^{-kt}$$

## Using the Integrated Rate Law to Calculate Concentrations.

Example 7B.1 What concentration of  $\text{N}_2\text{O}_5$  remains 10.0 min (600. s) after the start of its decomposition at 65 °C when its initial concentration was  $0.040 \text{ mol}\cdot\text{L}^{-1}$ ? See Table 7A.1 for the rate law.

$2 \text{ N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{ NO}_2(\text{g}) + \text{O}_2(\text{g})$ , Rate of =  $k[\text{N}_2\text{O}_5]$ , where  $k = 5.2 \times 10^{-3} \text{ s}^{-1}$ .

Using  $[\text{A}]_t = [\text{A}]_0 e^{-kt}$  we solve for  $[\text{N}_2\text{O}_5]_t = [\text{N}_2\text{O}_5]_0 e^{-kt}$

$$[\text{N}_2\text{O}_5]_t = 0.040 \text{ mol}\cdot\text{L}^{-1} e^{-5.2 \times 10^{-3} \text{ s}^{-1} \times 600. \text{ s}} = 0.0018 \text{ mol}\cdot\text{L}^{-1}$$

In 600. s, the concentration decreases  $0.040 \text{ mol}\cdot\text{L}^{-1}$  to  $0.0018 \text{ mol}\cdot\text{L}^{-1}$ .

## Using the Integrated Rate Law to Calculate a Time

Example 7B.2 A sample of  $\text{N}_2\text{O}_5$  is allowed to decompose by the following reaction:  $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ . Rate =  $k[\text{N}_2\text{O}_5]$ , where  $k = 5.2 \times 10^{-3} \text{ s}^{-1}$ . How long will it take for the concentration of  $\text{N}_2\text{O}_5$  to decrease from  $20. \text{ mmol}\cdot\text{L}^{-1}$  to  $2.0 \text{ mmol}\cdot\text{L}^{-1}$  at  $65^\circ\text{C}$ ?

Using  $\ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt$  we want to solve for  $t$ .

$$\ln \frac{2.0 \text{ mmol}\cdot\text{L}^{-1}}{20. \text{ mmol}\cdot\text{L}^{-1}} = - 5.2 \times 10^{-3} \text{ s}^{-1} t,$$

$$t = \ln \frac{2.0 \text{ mmol}\cdot\text{L}^{-1}}{20. \text{ mmol}\cdot\text{L}^{-1}} \times \frac{1}{- 5.2 \times 10^{-3} \text{ s}^{-1}} = 440 \text{ s}$$



# Half-Lives for First-Order Reactions

The half-life,  $t_{1/2}$ , is the **time** needed for its **concentration to fall to one-half** of its initial value.

There are many half-life processes, populations, chemical reactions, radioactive decay and others.

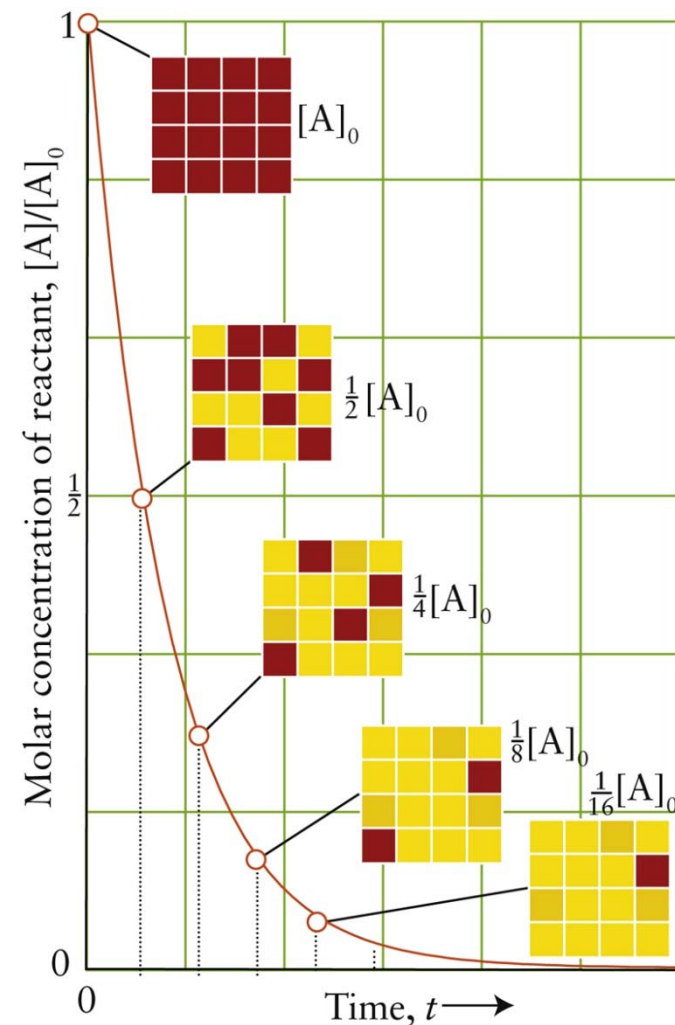


Figure 7B.4

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## Half-Lives for First-Order Reactions: Meaning of $k$

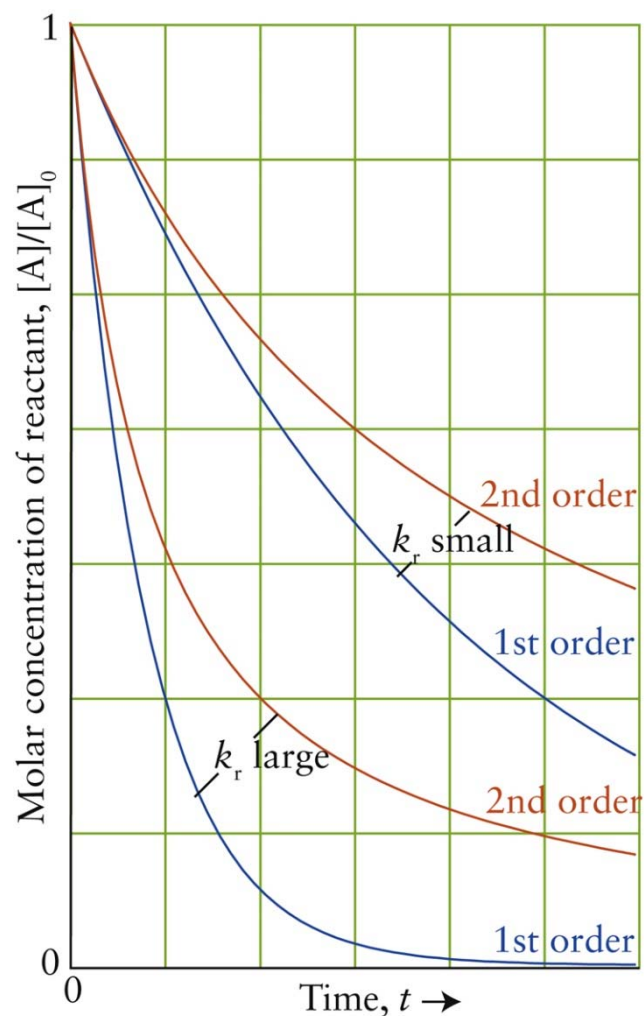


Figure 7B.5  
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The **higher the value of  $k$** , the *more rapid* the consumption of a reactant.

If  $k$  is very large, for instance with **radioactive decay**, it would be considered hotter.

High values of  $k$  in a **population decay** means the population is dying quickly.

## Finding $t_{1/2}$

In a first order process,  $\ln \frac{[A]_t}{[A]_0} = -kt$  for  $t$  or  $t_{1/2}$ .

We arbitrarily pick  $[A]_t = 1$ .  $[A]_0 = 2$  represents half of the material disappearing (starting at 2 and going to 1), so this goes to  $\ln \frac{1}{2} = -kt_{1/2}$

Now, rearrange the “-” and get  $\ln 2 = kt_{1/2}$

Solve for  $t_{1/2}$ ,  $t_{1/2} = \frac{\ln 2}{k}$

Example 7B.4 In 1989 a teenager in Ohio was poisoned by breathing vapors from spilled mercury. The mercury level in his urine, which is proportional to its concentration in his body, was found to be  $1.54 \text{ mg}\cdot\text{L}^{-1}$ . Mercury(II) is eliminated from the body by a first-order process that has a half-life of 6 days (6d). What would be the concentration of mercury(II) in the patient's urine in milligrams per liter after 30d if therapeutic measures were not taken ?

To find a future concentration, use the first-order decay formula  $[A]_t = [A]_0 e^{-kt}$ . However, we're missing both  $[A]_t$  and  $k$ , so we also need to use the half-life formula for finding  $k$ ,  $t_{1/2} = \frac{\ln 2}{k}$  or  $k = \frac{\ln 2}{t_{1/2}}$

Substituting  $k$  into  $[A]_t = [A]_0 e^{-kt}$  and solving  $[A]_t = [A]_0 e^{-\frac{\ln 2}{t_{1/2}} t}$

$$[A]_t = 1.54 \text{ mg}\cdot\text{L}^{-1} e^{\frac{-\ln 2}{6\text{d}} \times 30\text{d}} = 0.05 \text{ mg}\cdot\text{L}^{-1}$$

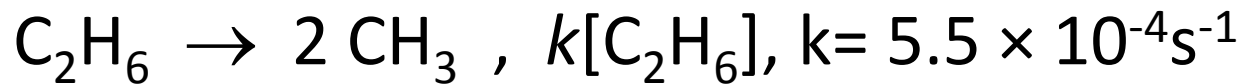
Self-test 7B.5B Calculate (a) the number of half-lives and (b) the time required for the concentration of  $\text{C}_2\text{H}_6$  to fall to one-sixteenth of its initial value as it dissociates into  $\text{CH}_3$  radicals at 973 K.



Part (a) needs two pieces of information: the total time and the half-life. We can get the half-life by using  $t_{1/2} = \frac{\ln 2}{k}$  but part (b) is the total time.

$$t_{1/2} = \frac{\ln 2}{k}, \quad \frac{\ln 2}{5.5 \times 10^{-4} \text{s}^{-1}} = 1300 \text{s}$$

Self-test 7B.5B Calculate (a) the number of half-lives and (b) the time required for the concentration of  $\text{C}_2\text{H}_6$  to fall to one-sixteenth of its initial value as it dissociates into  $\text{CH}_3$  radicals at 973 K.



Part (b) is to find the total time by solve for time,  $t$ ,

$$\ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt$$

Solving for  $t$ ,  $t = \ln \frac{[\text{A}]_t}{[\text{A}]_0} \times \frac{1}{-k}$ ,  $t = \ln \frac{0.0625}{1} \times \frac{-1}{5.5 \times 10^{-4} \text{s}^{-1}} = 5000 \text{ s}.$

Number of half-lives  $\frac{\text{Total time}}{t_{1/2}}$ ,  $\frac{5000 \text{ s}}{1300 \text{ s}} = 3.8$  or 4 half-lives

## Second-Order Integrated Rate Laws

The integrated rate law for second-order reactions

$$A = k[A]^2$$

Rate of disappearance of:  $A = -\frac{d[A]}{dt} = k[A]^2$

Divide both sides by  $[A]^2$  to keep the  $[A]$ 's together and move the  $dt$  so we can integrate the expression.

$$\frac{d[A]}{[A]^2} = -k dt \quad \text{Now we integrate both sides.}$$

$$\int_{[A_0]}^{[A]} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

## Second-Order Integrated Rate Laws

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

Noting that  $\int \frac{d[A]}{[A]^2} = -\frac{1}{[A]} + \text{constant}$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = \left( -\frac{1}{[A]_t} + \text{constant} \right) - \left( -\frac{1}{[A]_0} + \text{constant} \right)$$

$$-k \int_0^t dt = -kt$$

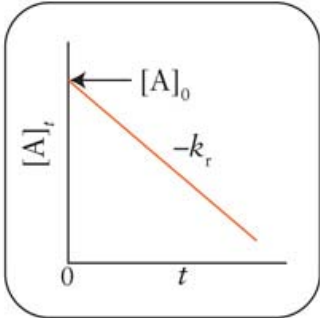
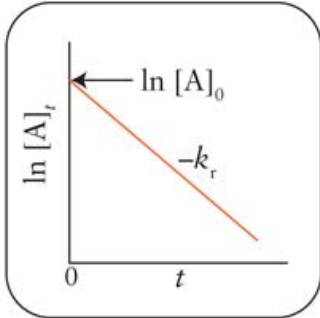
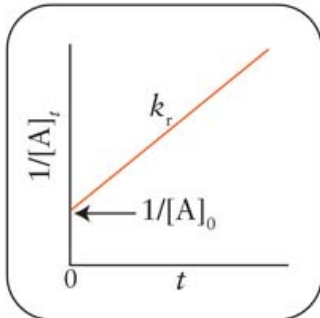
Combining the two integrated expressions:  $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$

Note the “+”  $k$ .



# Rate Law Summary

**TABLE 7B.1** Integrated Rate Laws, Rate Law Plots, and Half-Lives

	Order of reaction		
	0	1	2
Rate law	$\text{Rate} = k_r$	$\text{Rate} = k_r[A]$	$\text{Rate} = k_r[A]^2$
Integrated rate law	$[A]_t = -k_r t + [A]_0$	$[A]_t = [A]_0 e^{-k_r t}$	$[A]_t = \frac{[A]_0}{1 + k_r t [A]_0}$ $\frac{1}{[A]_t} = \frac{1}{[A]_0} + k_r t$
Plot to determine order			
Slope of the line plotted	$-k_r$	$-k_r$	$k_r$
Half-life	$t_{1/2} = \frac{[A]_0}{2k_r}$ <p>(not used)</p>	$t_{1/2} = \frac{\ln 2}{k_r} \approx \frac{0.693}{k_r}$	$t_{1/2} = \frac{1}{k_r [A]_0}$ <p>(not used)</p>

**Table 7B.1**

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# Reaction Mechanisms

Rate laws are a window into the molecular level events taking place during a chemical reaction.

- What molecular events convert ozone into oxygen?
- What turns a mixture of fuel and air into carbon dioxide and water when it ignites in an engine ?

## Reaction Mechanisms

We **cannot** write a *rate law* from a *chemical equation*.

- The reason is all but the simplest reactions are the outcome of several, and sometimes many, steps called **elementary reactions**.

**Elementary reactions** describe a distinct event, often a collision of particles.

Understanding how reactions takes place requires us to propose a **reaction mechanism**, a **sequence of elementary reactions**.

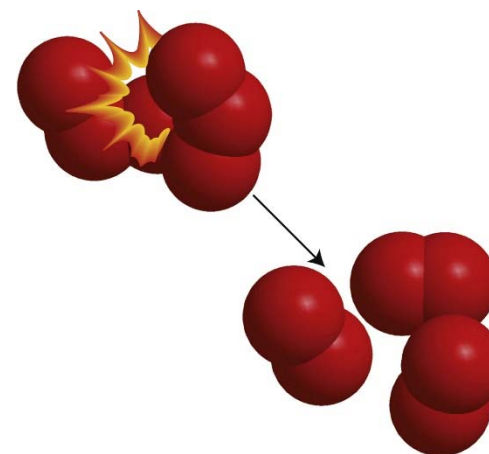
## Choosing the Right Mechanism

Although several different mechanisms might be proposed for a reaction, rate measurements can eliminate some of them for the decomposition of ozone,  $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$ .

We could imagine the reaction taking place two different ways:

### One-step mechanism:

- Two  $\text{O}_3$  molecules collide and rearrange into three  $\text{O}_2$  molecules:



or

Figure 7C.1  
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## Choosing the Right Mechanism

**Two-step mechanism:** *First step*,  $\text{O}_3$  dissociates. *Second step*, the O attacks another  $\text{O}_3$  molecule making two more  $\text{O}_2$ :

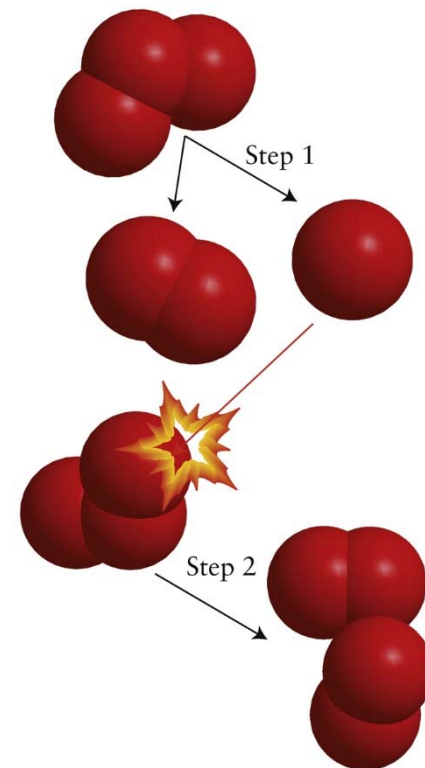
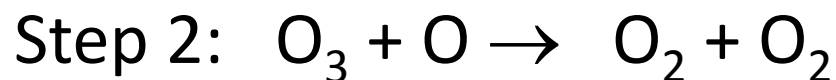
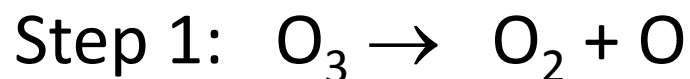
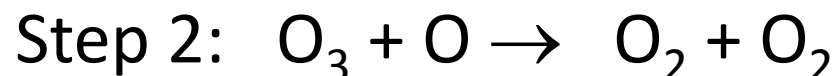
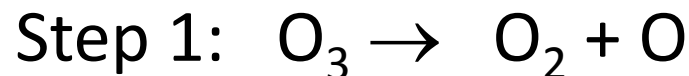


Figure 7C.2  
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The **free O atom** is a reaction **intermediate**, (it is produced in one step but is used up in a later step) a species that plays a role in a reaction but **does not appear in the chemical equation.**

The two equations for the elementary reactions add together to give the equation for the overall reaction.

## Molecularity: The Number of Reactant Molecules

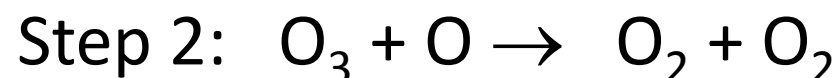
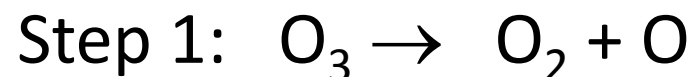


Step 1 is a **unimolecular** reaction because only one reactant molecule participates.

Step 2 is another elementary reaction called a **bimolecular** reaction because two reactants come together.

The **molecularity** of a unimolecular reaction is 1 and that of a bimolecular reaction is 2.

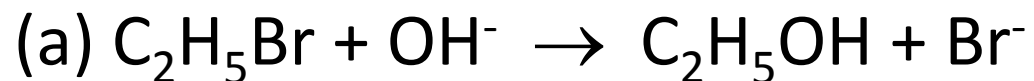
## A Note on Good Practice



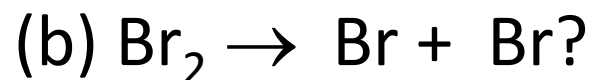
Elementary reaction steps:

1. are written **without the state symbols**.
2. only show **how individual** atoms and or molecules take part in the reaction.
3. emphasize individual molecules, so do **not use stoichiometric coefficients** (that is write the formula as many times as required).

# Molecularity



A bimolecular reaction, so the molecularity is 2.



A unimolecular reaction, so the molecularity is 1.



## The Rate Laws of Elementary Reactions

To verify a mechanism, it must agree with experimental data.

Once we perform experiments, we calculate the rate law, then we proceed as follows:

Either a one-step mechanism:  $\text{O}_3 + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 + \text{O}_2$

Or a two-step mechanism

Step 1:  $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$

Step 2:  $\text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2$

[our answer is coming shortly]

## The Rate Laws of Elementary Reactions

We may still be incorrect because some other mechanism may also lead to the same rate law.

Kinetic information can **only support** a proposed mechanism; it can never prove that a mechanism is correct.

## The Proof of a Mechanism from Elementary Reactions

Reconstruction of the overall rate law from a mechanism, starts by

- writing the rate law for each of the elementary reactions;
- combine them into an overall rate law.

# The Proof of a Mechanism from Elementary Reactions

**Exponents** are related to the **number of reactants** in the elementary reaction.

**TABLE 7C.1** The Rate Laws of Elementary Reactions

Molecularity	Elementary reaction		Rate law*
1	$A \longrightarrow$	products	$\text{rate} = k_r[A]$
2	$A + B \longrightarrow$	products	$\text{rate} = k_r[A][B]$
	$A + A \longrightarrow$	products	$\text{rate} = k_r[A]^2$
	$A + B + C \longrightarrow$	products	$\text{rate} = k_r[A][B][C]$
3	$A + A + B \longrightarrow$	products	$\text{rate} = k_r[A]^2[B]$
	$A + A + A \longrightarrow$	products	$\text{rate} = k_r[A]^3$

\* When it is necessary to distinguish the steps in a mechanism, replace  $k_r$  by  $k_1$ ,  $k_2$ , etc.

**Table 7C.1**

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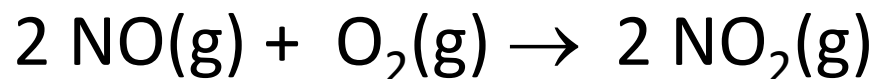
- Unimolecular means one component is necessary to make the reaction proceed;
- Bimolecular means two components, and so on.

## Example of a Proof

Reconstructing the overall rate law from a mechanism, starts by:

- writing the rate law for each of the elementary reactions;
- combining them into an overall rate law.

This overall rate law has been determined experimentally:



Rate of formation of  $\text{NO}_2 = k[\text{NO}]^2[\text{O}_2]$  (The rate is our target equation.)

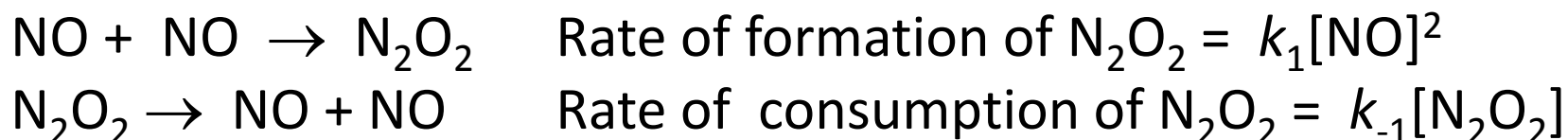
The following mechanism has been proposed.



## Example of a Proof

Rate of formation of  $\text{NO}_2 = k[\text{NO}]^2[\text{O}_2]$  (The rate is our target eq.)

Proposed:



Step 1: A fast bimolecular dimerization; note the reverse is also shown as a reference for later on, also note that -1 means reverse.

Next:



Step 2: A slow bimolecular reaction in which an  $\text{O}_2$  molecule collides with the dimer.

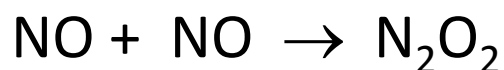
The reverse of Step 2 is too slow to include.

## Example of a Proof

We want to combine our steps to get Rate of formation of

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

Step 1:

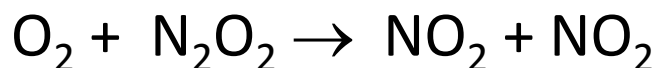


$$\text{Rate of formation of } \text{N}_2\text{O}_2 = k_1[\text{NO}]^2$$



$$\text{Rate of consumption of } \text{N}_2\text{O}_2 = k_{-1}[\text{N}_2\text{O}_2]$$

Step 2:

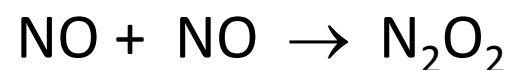


$$\text{Rate of consumption of } \text{N}_2\text{O}_2 = k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

We start by noticing in Step 2,  $\text{NO}_2$  is a product, which is the molecule we are writing the proof for, so we start by writing Rate of formation of  $\text{NO}_2 = 2k_2[\text{N}_2\text{O}_2][\text{O}_2]$ .

The 2 comes from the 2  $\text{NO}_2$  that are produced for each  $\text{N}_2\text{O}_2$ . This keeps the rates the same.

Step 1:

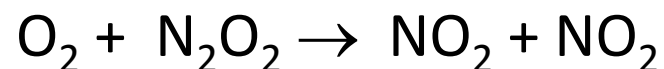


$$\text{Rate of formation of } \text{N}_2\text{O}_2 = k_1[\text{NO}]^2$$



$$\text{Rate of consumption of } \text{N}_2\text{O}_2 = k_{-1}[\text{N}_2\text{O}_2]$$

Step 2:



$$\text{Rate of consumption of } \text{N}_2\text{O}_2 = k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

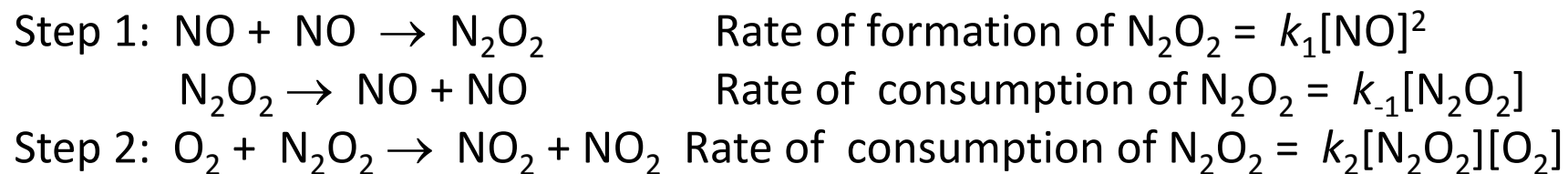
However, the Rate of formation of  $\text{NO}_2 = 2k_2[\text{N}_2\text{O}_2][\text{O}_2]$  is still not complete because it contains  $\text{N}_2\text{O}_2$  which is an **intermediate**, and intermediates do not appear in overall rate laws.

Starting with Step 1 where  $\text{N}_2\text{O}_2$  is formed, we want to rewrite all the steps without  $\text{N}_2\text{O}_2$ .

$$\text{Formation } [\text{N}_2\text{O}_2] = k_1[\text{NO}]^2 - k_{-1}[\text{N}_2\text{O}_2] - k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

("-" if being removed in that step)





$$\text{Formation } [\text{N}_2\text{O}_2] = k_1[\text{NO}]^2 - k_{-1}[\text{N}_2\text{O}_2] - k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

Apply the steady-state approximation—that intermediates remain at low concentration.

$$0 = k_1[\text{NO}]^2 - k_{-1}[\text{N}_2\text{O}_2] - k_2[\text{N}_2\text{O}_2][\text{O}_2], \text{ rearrange without } [\text{N}_2\text{O}_2].$$

$$k_1[\text{NO}]^2 - (k_{-1} + k_2 [\text{O}_2]) [\text{N}_2\text{O}_2] = 0$$

$$\text{Move } k_1 \text{ over } k_1[\text{NO}]^2 = (k_{-1} + k_2 [\text{O}_2]) [\text{N}_2\text{O}_2]$$

$$\text{Isolate } [\text{N}_2\text{O}_2] = \frac{k_1[\text{NO}]^2}{(k_{-1} + k_2 [\text{O}_2])}$$

## Example of a Proof

We can substitute this  $[N_2O_2] = \frac{k_1[NO]^2}{k_{-1} + k_2[O_2]}$  back into our first expression for Rate of formation of  $NO_2 = 2k_2[N_2O_2][O_2]$

Rate of formation of  $NO_2 = 2k_2 \frac{k_1[NO]^2}{k_{-1} + k_2[O_2]} [O_2]$ . At first glance, this does not appear to be equal to our proposed rate expression. However, Step 2 is a slow step, which means the rate to the reaction is much faster in Step 1. Thus, we can ignore the  $k_2$  term when we are solving for  $[N_2O_2]$ . This goes to

Rate of formation of  $NO_2 = \frac{2k_1k_2[NO]^2[O_2]}{k_{-1}}$  where  $k = \frac{2k_1k_2}{k_{-1}}$ . So, our final  $k[NO]^2[O_2]$  rate expression does agree with each elementary reaction, which is a third-order rate law.

## Rate-Determining Step

In our last example, we had a slow step.

Step 2:  $\text{O}_2 + \text{N}_2\text{O}_2 \rightarrow \text{NO}_2 + \text{NO}_2$  the slowest step governs the rate of all the other steps, so is called the **rate-determining step**.

Rate-determining steps (RDS) are like a ferry crossing a river—your journey is limited by how fast you can get across the river.

Steps that follow the rate-determining step are neglected in the overall rate law from the mechanism.

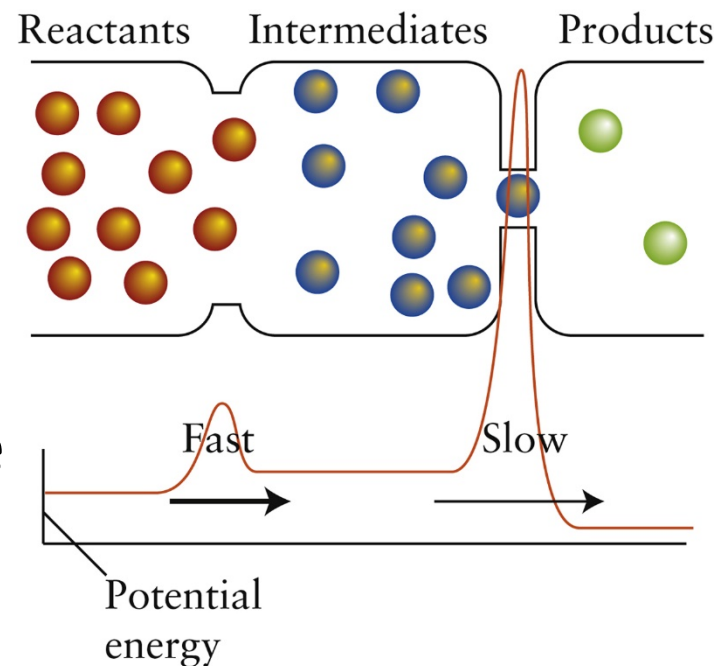


Figure 7C.3  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
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Example 7C.1 the following rate law has been determined for the decomposition of ozone,  $2 \text{O}_3(\text{g}) \rightarrow 3 \text{O}_2(\text{g})$ , Rate of decomposition of  $\text{O}_3 = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$  The following two-step mechanism has been proposed:

Step 1:  $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$

Step 2:  $\text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2$  This is the slow step, so the reverse step is ignored.

Measurements of the elementary reactions show that the slow step is the forward reaction in the second step. Its reverse is so slow that it can be ignored. Derive the rate law implied by the mechanism, and confirm that it matches the observed rate law.

Example 7C.1 the following rate law has been determined for the decomposition of ozone,  $2 \text{O}_3(\text{g}) \rightarrow 3 \text{O}_2(\text{g})$ , Rate of decomposition of  $\text{O}_3 = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$  The following two-step mechanism has been proposed:

Step 1:  $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$

Step 2:  $\text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2$  This is the slow step, so the reverse step is ignored.

Next, write the rate law for the net rate of decomposition of  $\text{O}_3$ :

Rate of decomposition of  $\text{O}_3 = k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}] + k_2[\text{O}_3][\text{O}]$  (For decomposition, “+” is adding.)

Use steady state approximation and set to 0, so we can get rid of the intermediates.

Rate of decomposition of  $O_3 = k_1[O_3] - k_{-1}[O_2][O] + k_2[O_3][O]$

The intermediate is O, so we consider the net forming of [O].

$$0 = k_1[O_3] - k_{-1}[O_2][O] - k_2[O_3][O]$$

Bring [O] out by itself.

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]}$$

Substitute back into Rate of decomposition of

$$O_3 = k_1[O_3] - k_{-1}[O_2][O] + k_2[O_3][O]$$

Net rate  $O_3 = k_1[O_3] - \frac{k_{-1}[O_2]k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} + \frac{k_2[O_3]k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]}$  make the denominators the same.

$$\frac{k_1[O_3](k_{-1}[O_2] + k_2[O_3])}{k_{-1}[O_2] + k_2[O_3]} - \frac{k_{-1}[O_2]k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} + \frac{k_2[O_3]k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} \text{ combine}$$

$$\frac{k_{-1}[O_2]k_1[O_3] + k_2[O_3]k_1[O_3] - k_{-1}[O_2]k_1[O_3] + k_2[O_3]k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} =$$

(1<sup>st</sup> and 3<sup>rd</sup> terms cancel)  $\frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}$

Rate of decomposition of  $O_3 = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}$

We had a slow step:

Forward:  $O_3 + O \rightarrow O_2 + O_2$  Rate of consumption of

$O_3 = k_2[O_3][O]$  slowest step

So,  $k_2[\text{O}_3][\text{O}]$  is slower than any other step. We can disregard the  $k_2[\text{O}_3]$  because it has the  $[\text{O}]$ .

Therefore, Rate of decomposition of  $\text{O}_3 = \frac{2k_1k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2]}$

And making  $k = \frac{2k_1k_2}{k_{-1}}$  our final Rate of decomposition of  $\text{O}_3 = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$  which agrees with experimental data.



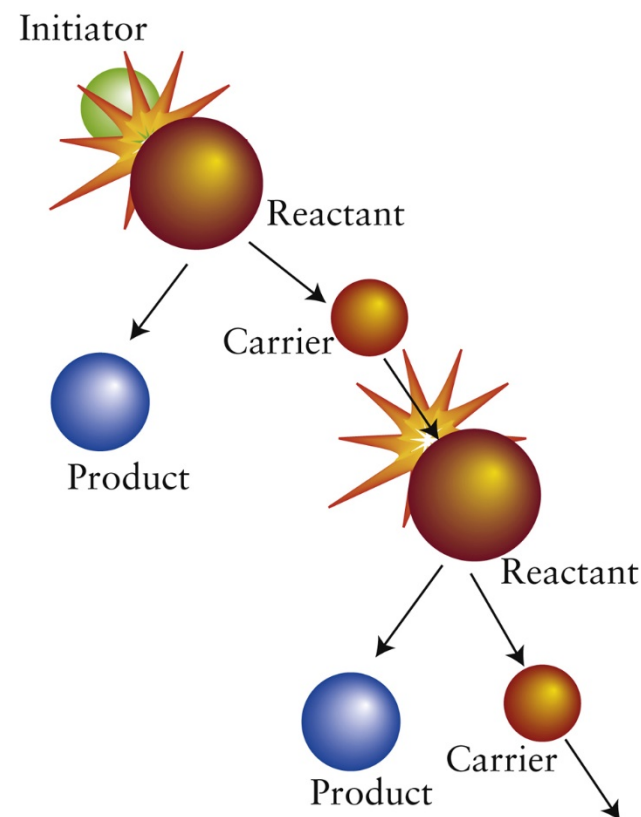
## Chain Reactions

Chain reactions have highly reactive intermediates that produce more highly reactive intermediates...and so on.

These reaction intermediates are called a **chain carrier**.

Radical chain reactions have radical intermediates.

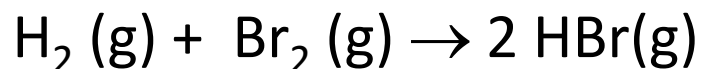
The rate laws are very complex and not derived here.



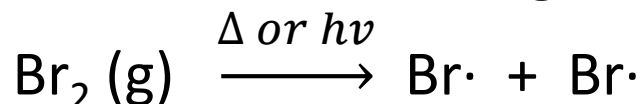
**Figure 7C.6**  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
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## Chain Reactions: Initiation, Propagation, Termination.

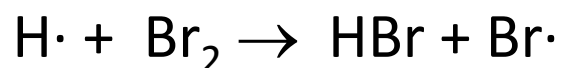
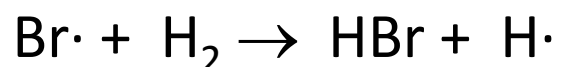
Formation of HBr in the reaction takes place by a chain reaction.



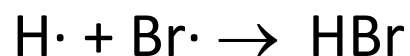
The first step is called **initiation** and produces chain carriers  $\text{H}\cdot$  and  $\text{Br}\cdot$ .  $\Delta$  is heat,  $h\nu$  is light.



The second step, **propagation**, creates more chain carriers, in this case radicals.



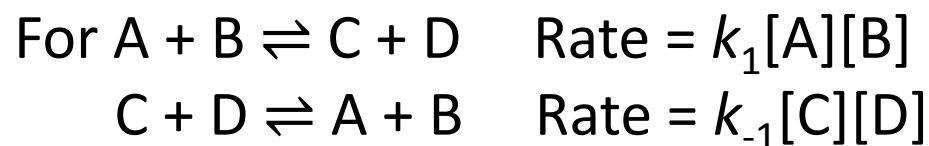
The final step, **termination**, occurs when two chain carriers combine to form products.



## Rates and Equilibrium

The equilibrium constant for an elementary reaction is equal to the forward and reverse rate constants of the reaction. We can

$$\text{show } K = \frac{k_1}{k_{-1}} \times \frac{k_2}{k_{-2}} \dots$$



$$k_1[A][B] = k_{-1}[C][D]$$

$$\text{or } \frac{k_1}{k_{-1}} = \frac{[C][D]}{[A][B]}$$

$$K = \frac{k_1}{k_{-1}}$$

So for multiple steps, we get  $K = \frac{k_1}{k_{-1}} \times \frac{k_2}{k_{-2}} \dots$

## Models of Reactions

Some rate constants vary; some are large, others are small.

They also vary with temperature.

Reaction	Rate law	Temp (K)	Rate constant $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
$\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$	$k[\text{H}_2][\text{I}_2]$	500	$4.3 \times 10^{-7}$
		600	$4.4 \times 10^{-4}$
		700	$6.3 \times 10^{-2}$

In this section we look at factors that affect rate constants.

## Models of Reactions: Effects of Temperature

We've seen how rates depend on concentrations.

Rates also depend on temperature. An *increase of 10 °C* from room temperature typically *doubles the rate* of organic reactions.

One of the reasons why we put food in the refrigerator is to keep it from spoiling.

## Models of Reactions: Effects of Temperature

Rates almost always increase with temperature.



Figure 7D.1  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman photo by Ken Karp

magnesium in cold water

magnesium in hot water

An indicator shows pH of the solution