CHEM2100J
Chemistry
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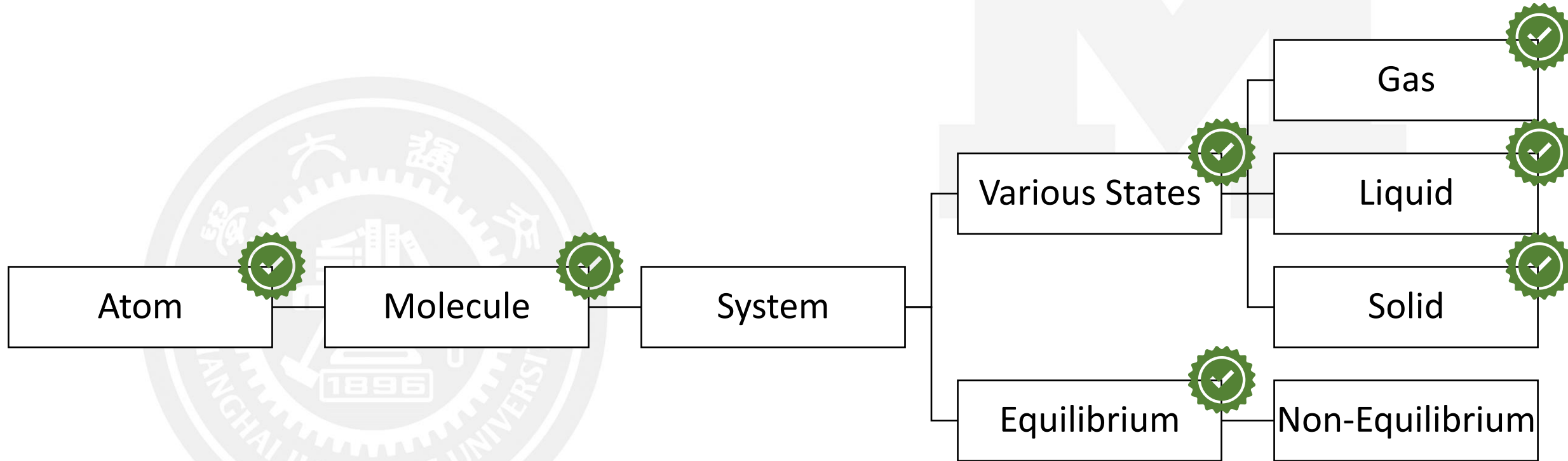
Chapter 14
Kinetics

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The Journey So Far

Thermodynamics vs Kinetics

Thermodynamics tells us *which way* a chemical reaction will go.

Kinetics tells us *how fast* a chemical reaction will go, as well as *how to control* the rate.

Reactions proceed at different rates.

Reaction Rates, Deriving the Laws

Chemical rates are **changes in concentration** over a **time interval**.

Rates can be either an **average** or **instantaneous**.

The advantage of an **average** rate is they are *easy to calculate*. The disadvantage is they tend to be very general and *not exact*.

The advantage of an **instantaneous** rate is it gives very specific *exact information*. The disadvantage is the time it takes time to *set up and make the calculation*.

Average Reaction Rates

Average change in molar concentration of **reactants**, **A**.

$$\Delta[A] = [A]_{t_2} - [A]_{t_1}$$

Divided by the time interval $\Delta t = t_2 - t_1$:

Average rate of ***consumption*** of **A**: $rate_{consumption,A} = -\dfrac{\Delta[A]}{\Delta t}$

Note: The "-" means reactants disappear/are consumed.

Average rate of ***formation*** of **products**, **B**: $rate_{formation,B} = \dfrac{\Delta[B]}{\Delta t}$

Hemoglobin (Hb) carries oxygen through our bodies by forming a complex with it: $Hb(aq) + O_2(aq) \rightleftharpoons HbO_2(aq)$. In a solution of hemoglobin exposed to oxygen, the concentration of hemoglobin fell from 1.2 nmol·L^{-1} to 0.80 nmol·L^{-1} in 0.10 μs. What was the average rate at which hemoglobin reacted with oxygen in that solution, in millimoles per liter per microsecond ?

$$rate_{consumption,A} = -\frac{\Delta[A]}{\Delta t}$$

$$rate_{consumption,Hb} = -\frac{\Delta[Hb]}{\Delta t} = -\frac{[Hb]_{t_2} - [Hb]_{t_1}}{\Delta t}$$

$$rate_{consumption,Hb} = -\frac{(0.80 \times 10^{-6} - 1.20 \times 10^{-6})\frac{\text{mmol}}{\text{L}}}{0.10 \text{ μs}} = 4.0 \times 10^{-7} \frac{\text{mmol}}{\text{L} \cdot \text{μs}}$$

Given the following balanced equation, if the rate of consumption for Cl_2 is 4.5×10^{-2} mol·L^{-1}·s^{-1}, then what is the rate of formation of NOCl?

$$2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$$

A. 4.5×10^{-2} mol·L^{-1}·s^{-1}

B. 2.25×10^{-2} mol·L^{-1}·s^{-1}

C. 9.0×10^{-2} mol·L^{-1}·s^{-1}

D. 4.5×10^{-1} mol·L^{-1}·s^{-1}

Unique Average Rate Based on Stoichiometry

To avoid confusion when reporting rates of a reaction, rates are always reported as the relationship of the *stoichiometric coefficients*. Thus, the rate is the same for the reaction, no matter for which species the rate is reported. This is known as the **unique rate** for a reaction.
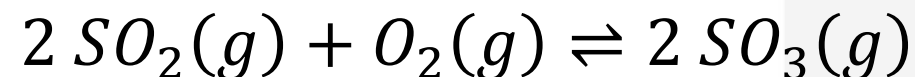
$$a\, A \rightleftharpoons B + cC$$

$$rate = -\frac{1}{a} \cdot \frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \cdot \frac{\Delta[C]}{\Delta t}$$

This means that the rate for the reaction can be different than the rate of consumption/formation for a certain species.

Short Quiz

Given the following balanced equation, determine the rate of reaction with respect to $[SO_2]$.

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

A. $rate = -\dfrac{\Delta[SO_2]}{2\Delta t}$

B. $rate = +\dfrac{\Delta[SO_2]}{2\Delta t}$
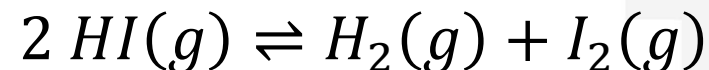
C. $rate = -\dfrac{\Delta[SO_2]}{\Delta t}$

D. $rate = +\dfrac{2\Delta[SO_2]}{\Delta t}$

Example

Suppose we are studying the reaction

$$2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

and find that in an interval of 100 s, the concentration of HI decreases from 4.00 mmol·L^{-1} to 3.50 mmol·L^{-1}. What is the average consumption rate of HI?

$$rate_{consumption,A} = -\frac{\Delta[A]}{\Delta t}$$
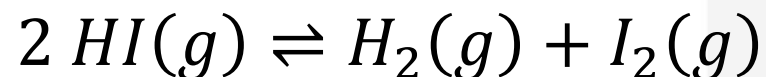
$$rate_{consumption,HI} = -\frac{\Delta[HI]}{\Delta t} = -\frac{[HI]_{t_2} - [HI]_{t_1}}{\Delta t}$$

$$rate_{consumption,HI} = -\frac{(3.50 - 4.00)\,\frac{\text{mmol}}{\text{L}}}{100\,\text{s}} = 5.0 \times 10^{-3}\,\frac{\text{mmol}}{\text{L} \cdot \text{s}}$$

Example

What is (a) the average rate of formation of H_2 in the same reaction and (b) the unique average rate, both over the same period?

$$2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

a)

$$rate_{formation,H_2} = \frac{1}{2} \cdot rate_{consumption,HI} = \frac{1}{2} \cdot \left(-\frac{[HI]_{t_2} - [HI]_{t_1}}{\Delta t} \right)$$

$$rate_{formation,H_2} = \frac{1}{2} \times 5.0 \times 10^{-3}\ \frac{\text{mmol}}{\text{L} \cdot \text{s}} = 2.5 \times 10^{-3}\ \frac{\text{mmol}}{\text{L} \cdot \text{s}}$$

b)

$$rate = -\frac{1}{2} \cdot \frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t} = \frac{1}{2} \times 5.0 \times 10^{-3}\ \frac{\text{mmol}}{\text{L} \cdot \text{s}} = 2.5 \times 10^{-3}\ \frac{\text{mmol}}{\text{L} \cdot \text{s}}$$

Instantaneous Rate of Reaction

Reactions slow down as reactants are used up.

An "instantaneous" rate is found by measuring two concentrations, *as close together in time* as possible.

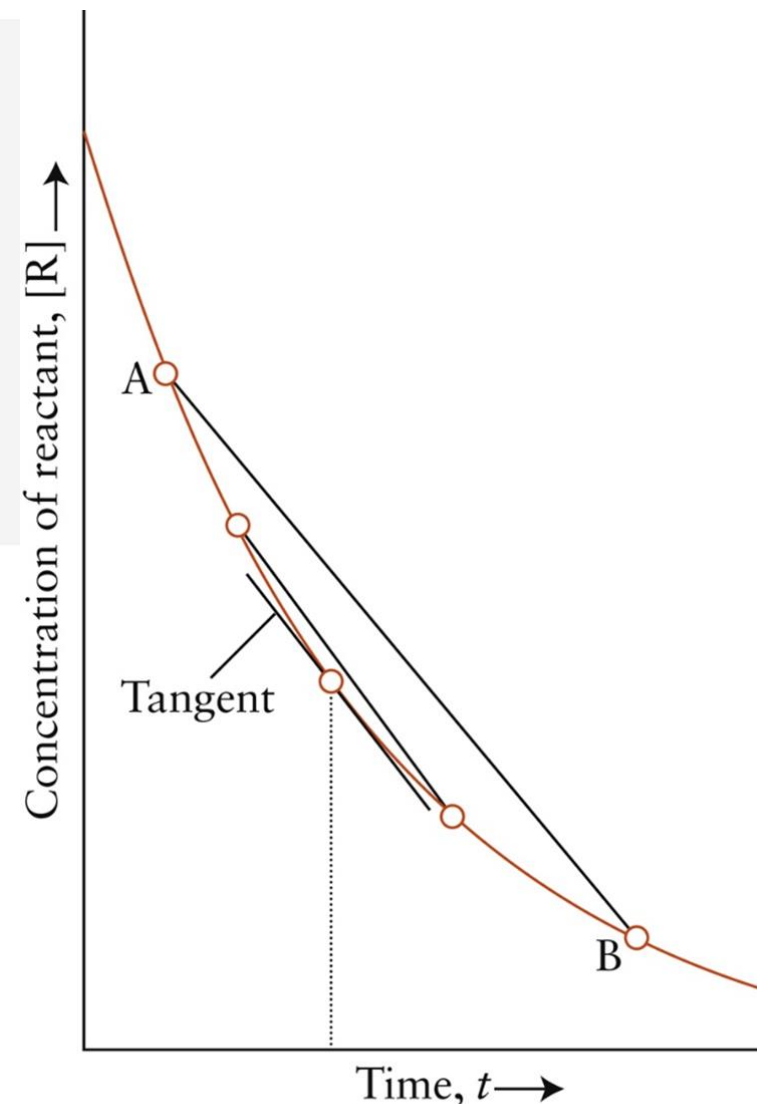A better method is to find the **slope of the tangent** that provides the *instantaneous rate*.

Figure 7A.4
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

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Though a computer can calculate tangent lines, we need to devise methods to **determine the equations for the development of concentration over time**, which are called **rate laws**.
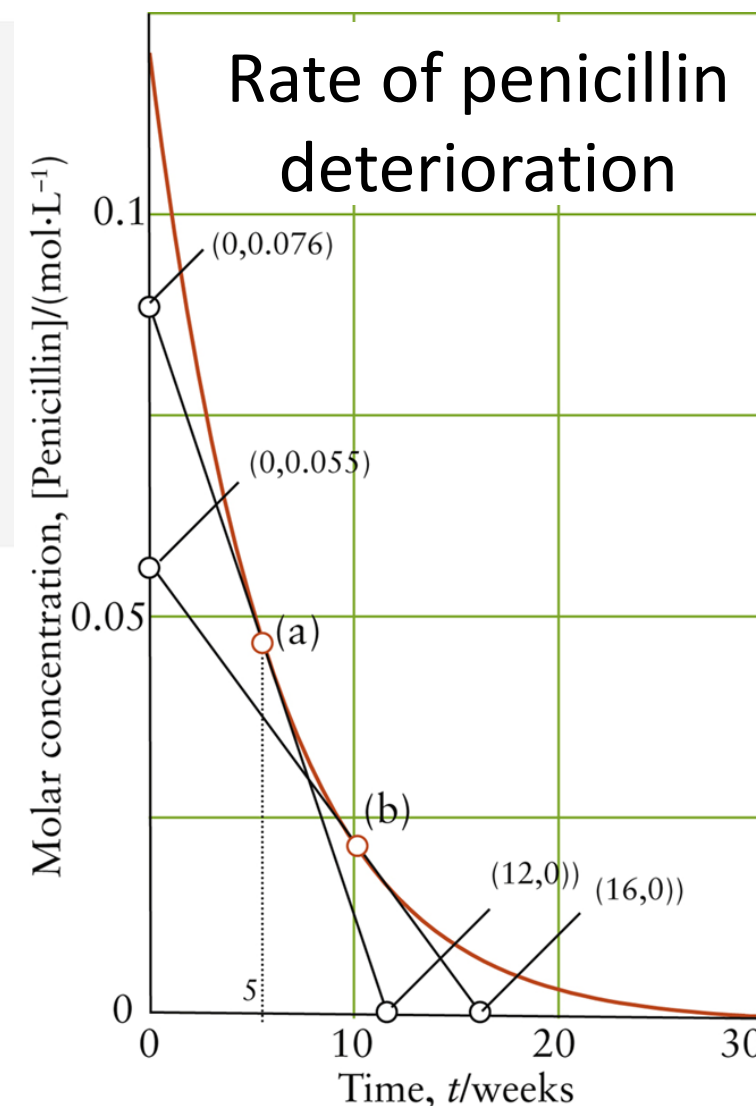

Rate of penicillin deterioration

Figure 7A.5
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman
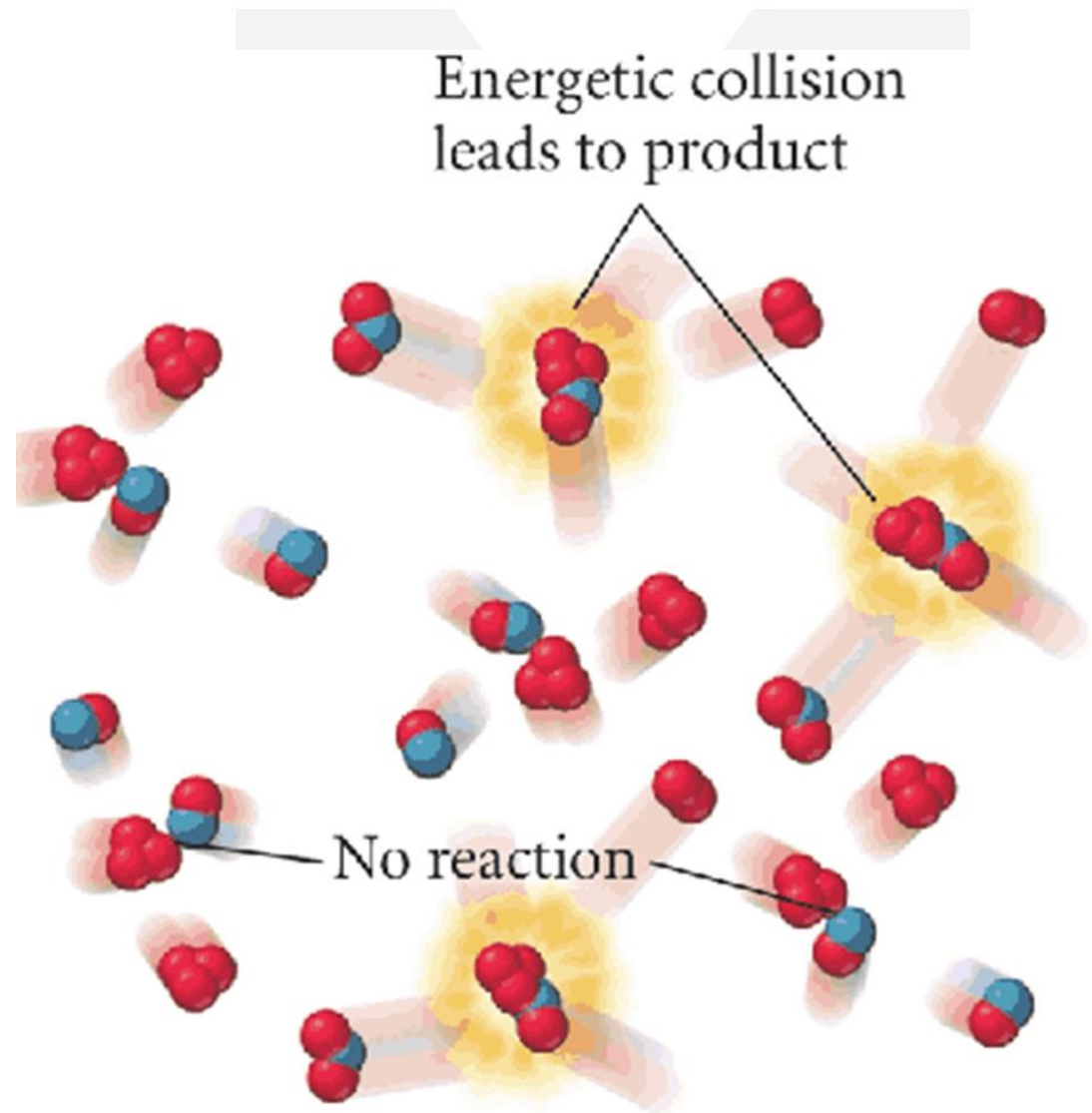
What Happens to Atoms During a Reaction?

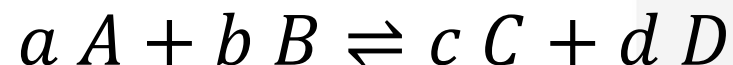|	
Collide into each other	Enough energy to break original bonds
Form new bonds	Product

$$rate = f(T, c)$$

Energetic collision leads to product

No reaction

The Rate Law

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

$$rate = f(T, c)$$

T: Temperature

c: Concentration

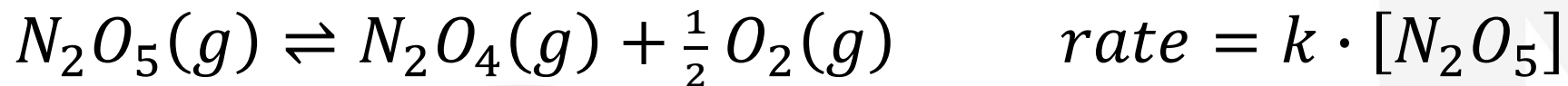General form of a rate law:

$$rate = k \cdot [A]^m [B]^n$$

Note: *m* and *n* are **not** the stoichiometric coefficients!

The Order of a Rate Law

We have two different rate laws for two different reactions.

$$N_2O_5(g) \rightleftharpoons N_2O_4(g) + \frac{1}{2}O_2(g) \qquad rate = k \cdot [N_2O_5]$$

$$2\,NO_2(g) \rightleftharpoons 2\,NO(g) + O_2(g) \qquad rate = [NO_2]^2$$

In the first reaction, the rate changes directly with changes in reactant concentrations ($[N_2O_5] \times 2 \rightarrow rate \times 2$).

In the second reaction, the rate changes by a squared factor with changes in reactant concentrations ($[NO_2] \times 2 \rightarrow rate \times 2^2 = rate \times 4$).

The Order of a Rate Law

$$rate = k$$

0th order

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$$

The concentration falls at a constant rate until the reactants are fully consumed.

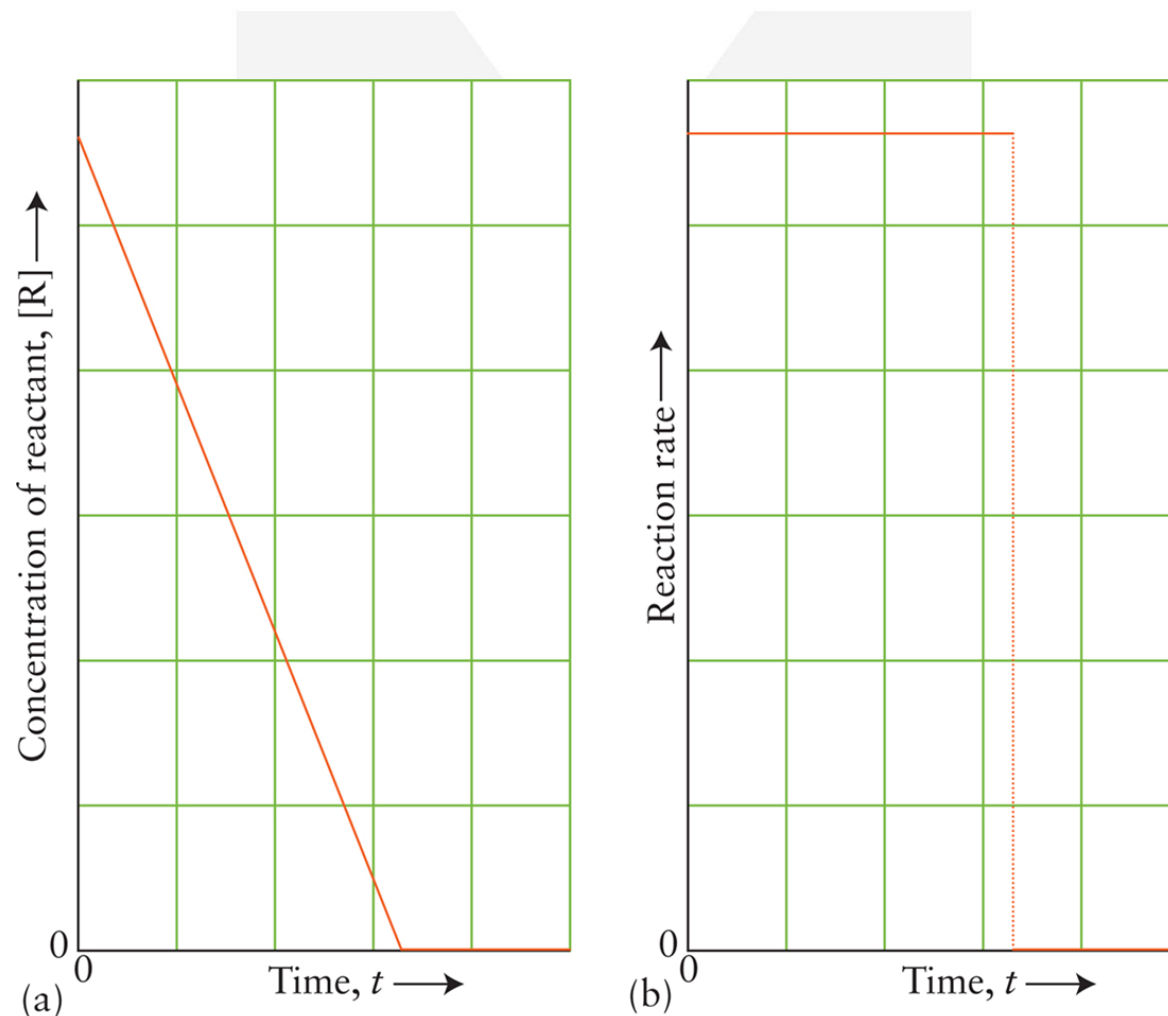The reaction rate is constant and falls abruptly to zero once the reactants are depleted.

(a)

(b)

Figure 7A.9
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

The Order of a Rate Law

$$rate = k \cdot [A]^m$$

k: Rate constant

$[A]$:   Concentration of substance A

m: Reaction **order**

$$rate = k \qquad \text{0th order}$$

$rate = k$	0th order
$rate = k \cdot [A]$	1st order
$rate = k \cdot [A]^2$	2nd order

Orders give us important insight as to **how** the reaction works. The overall order is 2 for a second order, and 1 or 0 for first and zero order, respectively. ost reactions are either first or second order.

In zero order cases, only a catalyts can control the rate.

Give the characteristic of a first-order reaction having only one reactant.

A. The rate of the reaction is not proportional to the concentration of the reactant.

B. The rate of the reaction is proportional to the square of the concentration of the reactant.

C. The rate of the reaction is proportional to the square root of the concentration of the reactant.

D. The rate of the reaction is directly proportional to the concentration of the reactant.

Short Quiz

Give the characteristic of a second-order reaction having only one reactant.

A. The rate of the reaction is not proportional to the concentration of the reactant.

B. The rate of the reaction is proportional to the square of the concentration of the reactant.

C. The rate of the reaction is proportional to the square root of the concentration of the reactant.

D. The rate of the reaction is proportional to the natural logarithm of the concentration of the reactant.

The Order of a Rate Law

In general, if $rate = k \cdot [A]^m [B]^n$, then the overall order is the sum of the exponents $m + n + \cdots$

Reaction	Rate Law	T / K	Rate constant k
$2\, N_2O(g) \rightleftharpoons 2\, N_2(g) + O_2(g)$	$rate = k[N_2O]$	1000	$0.76 \, \dfrac{1}{s}$
$H_2(g) + I_2(g) \rightleftharpoons 2\, HI(g)$	$rate = k[H_2][I_2]$	500	$4.3 \times 10^{-7} \, \dfrac{L}{mol \cdot s}$
$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2\, H_2O(l)$	$rate = k[H_3O^+][OH^-]$	298	$1.5 \times 10^{11} \, \dfrac{L}{mol \cdot s}$

Example

$$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$$
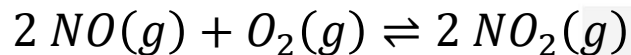
When the [NO] is doubled, the rate of the reaction increases by a factor of 4. When both [O_2] and [NO] concentrations are doubled, the rate increases by a factor of 8. What are (a) the reactant orders, (b) the overall order of the reaction (assuming only NO and O_2 are in the rate law), and (c) the units of k if the rate is expressed in moles per liter per second?

a) Reactant orders: $rate = k \cdot [A]^m[B]^n = k \cdot [NO]^m[O_2]^n$ $\qquad\qquad 4 \times rate = k \cdot [2 \times NO]^m[O_2]^n$

$$\frac{4 \times rate}{rate} = \frac{k \cdot [2 \times NO]^m[O_2]^n}{k \cdot [NO]^m[O_2]^n} = \frac{k \cdot 2^m \cdot [NO]^m\,[O_2]^n}{k \cdot [NO]^m[O_2]^n}$$

$$4 = 2^m \qquad\qquad m = \log_2(4) = \frac{\ln(4)}{\ln(2)} = 2$$

$$rate = k \cdot [NO]^m[O_2]^n \qquad\qquad 8 \times rate = k \cdot [2 \times NO]^m[2 \times O_2]^n$$

$$8 = 2^m \times 2^n = 2^2 \times 2^n = 4 \times 2^n \qquad\qquad 2 = 2^n \qquad\qquad n = \log_2(2) = \frac{\ln(2)}{\ln(2)} = 1$$

$$rate = k \cdot [NO]^2[O_2]^1$$

$$rate = k \cdot [NO]^2 [O_2]^1$$

b) Overall order: The overall order is the sum of all individual orders.

As determined in a), the reaction is 2nd order in regard to [NO] and 1st order in regard to [O_2]. Therefore, the overall order is $2 + 1 = 3$, so 3rd order.

c) The unit of the rate has to remain mol·L^{-1}·s^{-1}. Therefore, the unit of k must change accordingly:

Units:
$$\left[\frac{\text{mol}}{\text{L}\cdot\text{s}}\right] = [k] \cdot \left[\frac{\text{mol}}{\text{L}}\right]^2 \cdot \left[\frac{\text{mol}}{\text{L}}\right]^1$$

$$[k] = \left[\frac{\dfrac{\text{mol}}{\text{L}\cdot\text{s}}}{\dfrac{\text{mol}^2}{\text{L}^2}\cdot\dfrac{\text{mol}}{\text{L}}}\right] = \left[\frac{\text{L}^2}{\text{mol}^2\cdot\text{s}}\right]$$

The unit for k in this reaction is L^2·mol^{-2}·s^{-1}.
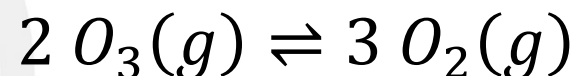
Negative Orders

Orders can also be negative:

$$[A]^{-1} = \frac{1}{[A]}$$

This means that [A] *slows down* and **reverses** the reaction!
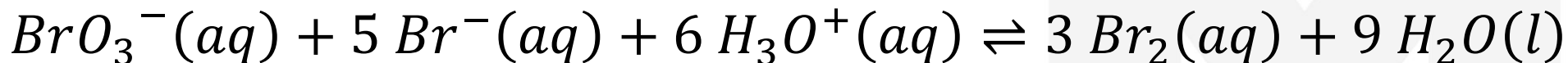
An example is the decomposition of ozone:

$$2\,O_3(g) \rightleftharpoons 3\,O_2(g)$$

The experimentally determined rate law is:

$$rate = k \cdot \frac{[O_3]^2}{[O_2]} = k \cdot [O_3]^2 [O_2]^{-1}$$

Determining Rate Laws Experimentally

Find (a) the orders, *m*, *n* and *o*; (b) the rate constant, *k*; and (c) the rate expression for the following reaction.

$$BrO_3^-(aq) + 5\ Br^-(aq) + 6\ H_3O^+(aq) \rightleftharpoons 3\ Br_2(aq) + 9\ H_2O(l)$$

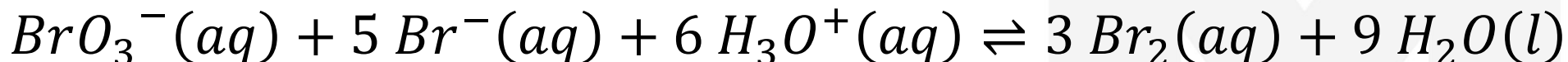| Experiment	$[BrO_3^-]_{initial}$ / mol·L⁻¹	$[Br^-]_{initial}$ / mol·L⁻¹	$[H_3O^-]_{initial}$ / mol·L⁻¹	$rate_{consumption,BrO_3^-\ initial}$ / mmol·L⁻¹·s⁻¹
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

Rates are measured experimentally.

$$rate = k \cdot [A]^m [B]^n [C]^o$$

Determining Rate Laws Experimentally

Find (a) the orders, m, n and o; (b) the rate constant, k; and (c) the rate expression for the following reaction.

$$BrO_3^-(aq) + 5\,Br^-(aq) + 6\,H_3O^+(aq) \rightleftharpoons 3\,Br_2(aq) + 9\,H_2O(l)$$

Experiment	$[BrO_3^-]_{initial}$ / mol·L⁻¹	$[Br^-]_{initial}$ / mol·L⁻¹	$[H_3O^-]_{initial}$ / mol·L⁻¹	$rate_{consumption,BrO_3^-\ initial}$ / mmol·L⁻¹·s⁻¹
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

In the last Example, **we were told** how much the rate changed, and from that we determined the order and rate expression. So, in this problem **we need to find** that for ourselves. We are given enough information to find k.

We need to find m, n, o, and k from:

$$rate = k \cdot [BrO_3^-]^m [Br^-]^n [H_3O^+]^o$$

If we double [BrO_3^-], how much does the rate increase?

Experiment	$[BrO_3^-]_{initial}$ / mol·L^{-1}	$[Br^-]_{initial}$ / mol·L^{-1}	$[H_3O^-]_{initial}$ / mol·L^{-1}	$rate_{consumption,BrO_3^- \, initial}$ / mmol·L^{-1}·s^{-1}
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

Looking at the difference between Experiment 1 and Experiment 2. The only concentration changing is bromate. Bromide and hydronium ion concentrations are held constant.

The change in rate and concentrations are:

$$\frac{rate_{Exp.2}}{rate_{Exp.1}} = \frac{k \cdot [BrO_3^-]^m_{Exp.2}[Br^-]^n_{Exp.2}[H_3O^+]^o_{Exp.2}}{k \cdot [BrO_3^-]^m_{Exp.1}[Br^-]^n_{Exp.1}[H_3O^+]^o_{Exp.1}}$$

$$\frac{rate_{Exp.2}}{rate_{Exp.1}} = \frac{[BrO_3^-]^m_{Exp.2}}{[BrO_3^-]^m_{Exp.1}}$$

$$\frac{2.4 \, \frac{mmol}{L \cdot s}}{1.2 \, \frac{mmol}{L \cdot s}} = \frac{\left(0.20 \, \frac{mol}{L}\right)^m}{\left(0.10 \, \frac{mol}{L}\right)^m} = \left(\frac{0.20 \, \frac{mol}{L}}{0.10 \, \frac{mol}{L}}\right)^m$$

$$2 = 2^m$$

$$m = \log_2(2) = \frac{\ln(2)}{\ln(2)} = 1$$

Therefore, we can write:

$$rate = k \cdot [BrO_3^-]^1[Br^-]^n[H_3O^+]^o$$

Determining Rate Laws Experimentally

The change in rate and concentrations are:

$$\frac{rate_{Exp.3}}{rate_{Exp.1}} = \frac{k \cdot [BrO_3^-]^1_{Exp.3}[Br^-]^n_{Exp.3}[H_3O^+]^o_{Exp.3}}{k \cdot [BrO_3^-]^1_{Exp.1}[Br^-]^n_{Exp.1}[H_3O^+]^o_{Exp.1}}$$

$$\frac{rate_{Exp.3}}{rate_{Exp.1}} = \frac{[Br^-]^n_{Exp.3}}{[Br^-]^n_{Exp.1}}$$

$$\frac{3.5 \frac{mmol}{L \cdot s}}{1.2 \frac{mmol}{L \cdot s}} = \frac{\left(0.30 \frac{mol}{L}\right)^n}{\left(0.10 \frac{mol}{L}\right)^n} = \left(\frac{0.30 \frac{mol}{L}}{0.10 \frac{mol}{L}}\right)^n$$

$$2.9 = 3^n$$

Experiment	$[BrO_3^-]_{initial}$ / mol·L⁻¹	$[Br^-]_{initial}$ / mol·L⁻¹	$[H_3O^-]_{initial}$ / mol·L⁻¹	$rate_{consumption,BrO_3^-\ initial}$ / mmol·L⁻¹·s⁻¹
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

Looking at the difference between Experiment 1 and Experiment 3. The only concentration changing is bromide, which triples.

$$n = \log_3(2.9) = \frac{\ln(2.9)}{\ln(3)} \approx 1$$

Therefore, we can write:

$$rate = k \cdot [BrO_3^-]^1[Br^-]^1[H_3O^+]^o$$

Determining Rate Laws Experimentally

The change in rate and concentrations are:

$$\frac{rate_{Exp.4}}{rate_{Exp.2}} = \frac{k \cdot [BrO_3^-]^1_{Exp.4}[Br^-]^1_{Exp.4}[H_3O^+]^o_{Exp.4}}{k \cdot [BrO_3^-]^1_{Exp.2}[Br^-]^1_{Exp.2}[H_3O^+]^o_{Exp.2}}$$

$$\frac{rate_{Exp.4}}{rate_{Exp.2}} = \frac{[H_3O^+]^o_{Exp.4}}{[H_3O^+]^o_{Exp.2}}$$

$$\frac{5.5 \frac{mmol}{L \cdot s}}{2.4 \frac{mmol}{L \cdot s}} = \frac{\left(0.15 \frac{mol}{L}\right)^o}{\left(0.10 \frac{mol}{L}\right)^o} = \left(\frac{0.15 \frac{mol}{L}}{0.10 \frac{mol}{L}}\right)^o$$

$$2.29 = 1.5^o$$

$$o = \log_{1.5}(2.29) = \frac{\ln(2.29)}{\ln(1.5)} = 2$$

Therefore, we can write:

$$rate = k \cdot [BrO_3^-]^1[Br^-]^1[H_3O^+]^2$$

Experiment	$[BrO_3^-]_{initial}$ / mol·L^{-1}	$[Br^-]_{initial}$ / mol·L^{-1}	$[H_3O^-]_{initial}$ / mol·L^{-1}	$rate_{consumption,BrO_3^-~initial}$ / mmol·L^{-1}·s^{-1}
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

Looking at the difference between Experiment 2 and Experiment 4. The only concentration changing is that of the hydronium ions.

The rate expression so far is:

$$rate = k \cdot [BrO_3{}^-]^1 [Br^-]^1 [H_3O^+]^2$$

The overall order is $1 + 1 + 2 = 4$. To find k, we use any experiment and insert the data to simply calculate k:

$$k = \frac{rate}{[BrO_3{}^-]^1 [Br^-]^1 [H_3O^+]^2}$$

Choosing the data from experiment 1:

$$k = \frac{1.2 \times 10^{-3} \frac{mol}{L \cdot s}}{\left(0.10 \frac{mol}{L}\right)^1 \left(0.10 \frac{mol}{L}\right)^1 \left(0.10 \frac{mol}{L}\right)^2} = 12 \frac{L^3}{mol^3 \cdot s}$$

The final rate expression is therefore:

$$rate = 12 \frac{L^3}{mol^3 \cdot s} \times [BrO_3{}^-]^1 [Br^-]^1 [H_3O^+]^2$$

Summary

Using **initial rates** from experimental data, we can find a rate law expression.

$$rate = k \cdot [A]^m [B]^n$$

where *m* and *n* are the orders and *k* is the rate constant.

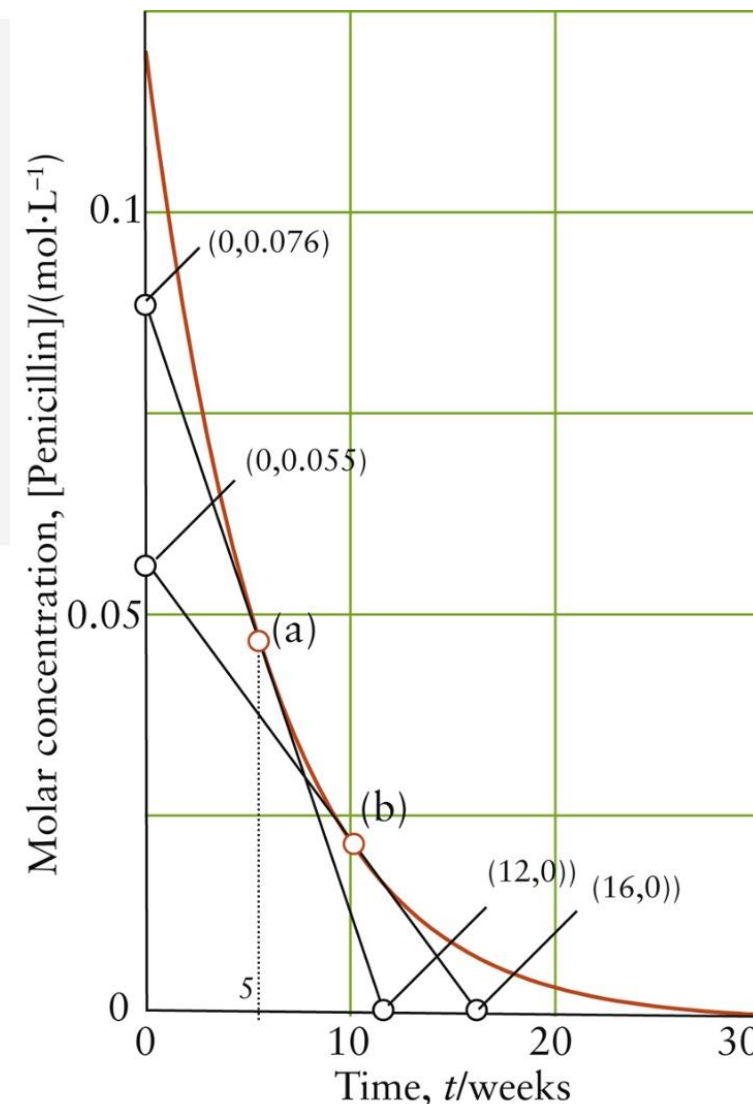Now, we **extend** our ideas about *initial rates* into a way to **predict concentrations**.

Figure 7A.5
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

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Predicting Concentrations

Integrating the three rate laws will give us future concentrations.

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.

0th order
$$rate = k$$

1st order
$$rate = k \cdot [A]$$

2nd order
$$rate = k \cdot [A]^2$$

$$rate = -\frac{\Delta[A]}{\Delta t} = -\frac{[A]_t - [A]_0}{t - 0} = \frac{[A]_0 - [A]_t}{t} = k$$

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

$$\boxed{[A]_t = [A]_0 - kt}$$

First-Order Integrated Rate Laws

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

0th order
$$rate = k$$

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

For infinitesimally small changes:
$$\frac{d[A]}{[A]} = -k \cdot dt$$

1st order
$$rate = k \cdot [A]$$

Integrating:

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

2nd order
$$rate = k \cdot [A]^2$$

$$\ln([A]_t + const.) - (\ln([A]_0 + const.)) = -kt$$

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \qquad \ln([A]_t) = \ln([A]_0) - kt$$
$$[A]_t = [A]_0 \cdot e^{-kt}$$

Calculating Concentrations

What concentration of N_2O_5 remains 10.0 min after the start of its decomposition at 65 °C when its initial concentration was 0.040 mol·L^{-1}?

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

$$rate = k \cdot [N_2O_5] \qquad k = 5.2 \times 10^{-3}\ \frac{1}{s}$$

$$[A]_t = [A]_0 \cdot e^{-kt}$$

$$[N_2O_5]_t = [N_2O_5]_0 \cdot e^{-kt} = 0.040\ \frac{mol}{L} \times e^{-5.2 \times 10^{-3}\frac{1}{s} \times 600\ s} = 0.0018\ \frac{mol}{L}$$

After 10.0 min, 0.0018 mol·L^{-1} N_2O_5 remain.

Calculating Concentrations

A sample of N$_2$O$_5$ is allowed to decompose. How long will it take for the concentration of N$_2$O$_5$ to decrease from 20 mmol·L^{-1} to 2.0 mmol·L^{-1} at 65 °C?

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

$$rate = k \cdot [N_2O_5] \qquad\qquad k = 5.2 \times 10^{-3}\ \frac{1}{s}$$

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt = \ln\left(\frac{[N_2O_5]_t}{[N_2O_5]_0}\right)$$

$$t = \frac{\ln\left(\frac{[N_2O_5]_t}{[N_2O_5]_0}\right)}{-k} = \frac{\ln\left(\frac{2.0\ \frac{\text{mmol}}{\text{L}}}{20\ \frac{\text{mmol}}{\text{L}}}\right)}{-5.2 \times 10^{-3}\ \frac{1}{s}} = 440\ s$$
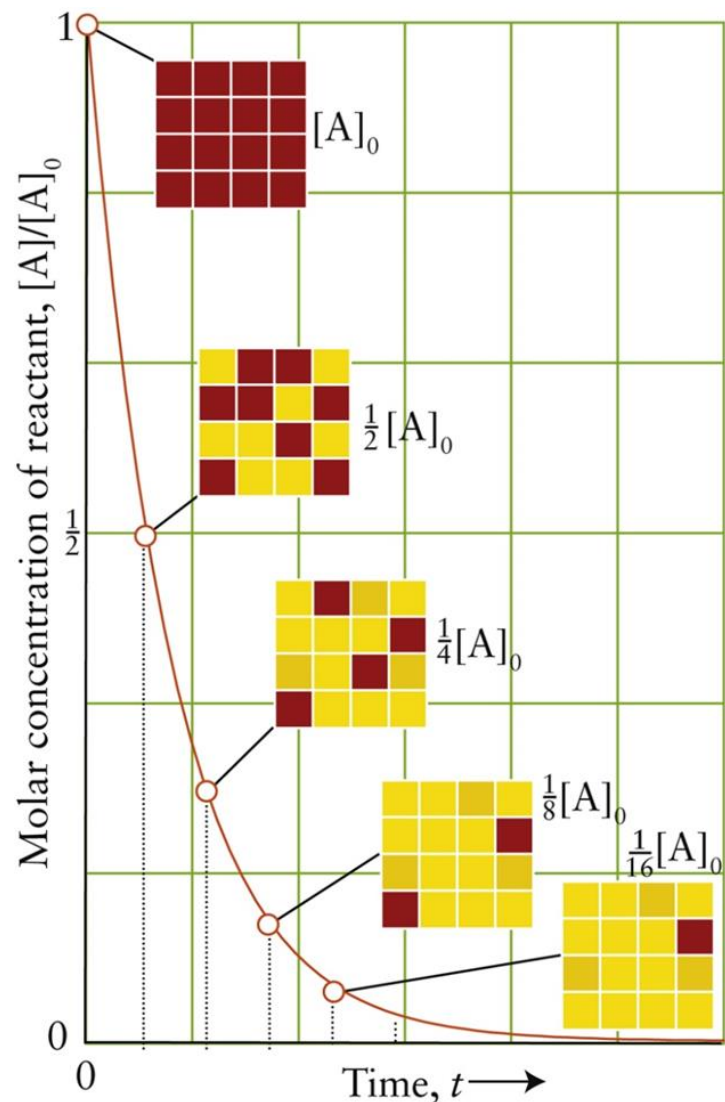
Figure 7B.4
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

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

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

The **higher the value of *k***, the *more rapid* the consumption of a reactant.

If *k* is very large, for instance with certain **radioactive decay** reactions, it would be considered to decay faster.

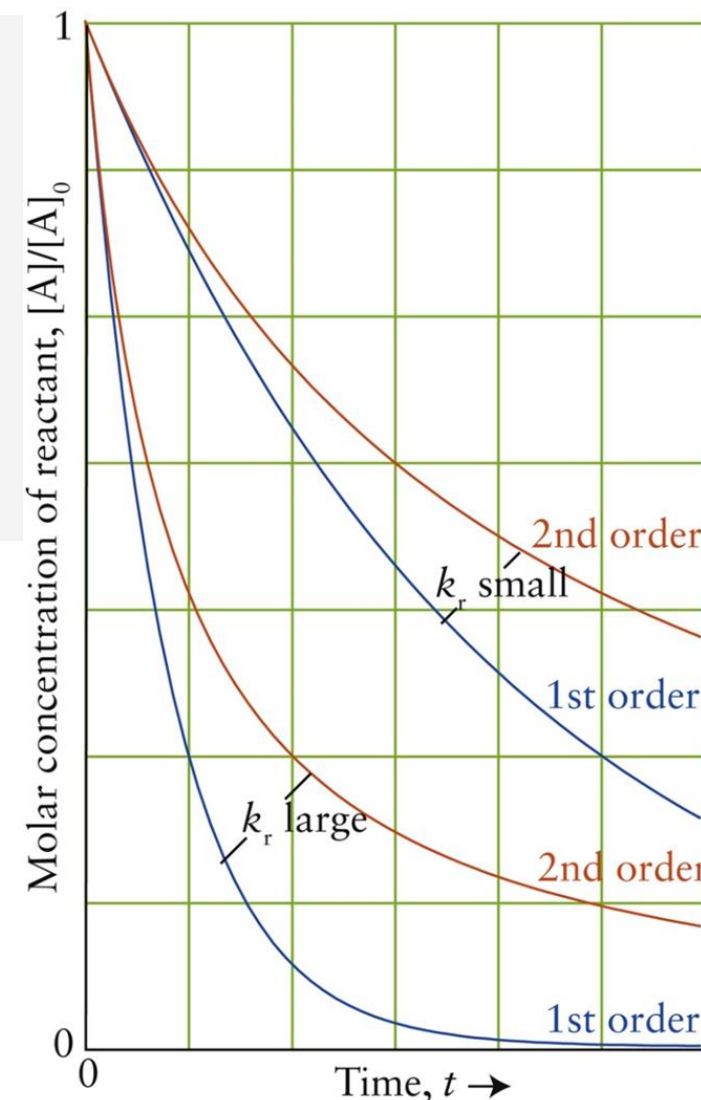High values of *k* in a **population decay** means the population is dying quickly.

Figure 7B.5
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

In a first order process:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \qquad\qquad \ln\left(\frac{[A]_{t_{1/2}}}{[A]_0}\right) = -kt_{1/2}$$

The half-time is the time needed for the concentration to fall to one-half of its initial value:

$$\ln\left(\frac{\frac{1}{2}[A]_o}{[A]_0}\right) = -kt_{1/2}$$

$$\ln\left(\frac{1}{2}\right) = -kt_{1/2}$$

Rearranging:

$$\ln(2) = kt_{1/2}$$

$$\boxed{t_{1/2} = \frac{\ln(2)}{k}}$$

Example

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

$$[A]_t = [A]_0 \cdot e^{-kt}$$

$$t_{1/2} = \frac{\ln(2)}{k} \qquad k = \frac{\ln(2)}{t_{1/2}}$$

$$[A]_t = [A]_0 \cdot e^{-\frac{\ln(2)}{t_{1/2}} \cdot t} = 1.54 \frac{mg}{L} \times e^{-\frac{\ln(2)}{6\,d} \times 30\,d} = 0.05 \frac{mg}{L}$$

Second-Order Integrated Rate Laws

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

0th order

$$rate = k$$

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

For infinitesimally small changes:

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

1st order

$$rate = k \cdot [A]$$

Integrating:

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

2nd order

$$rate = k \cdot [A]^2$$

$$\left(-\frac{1}{[A]_t} + cons. \right) - \left(-\frac{1}{[A]_0} + cons. \right) = -kt$$

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

Rate Law Summary

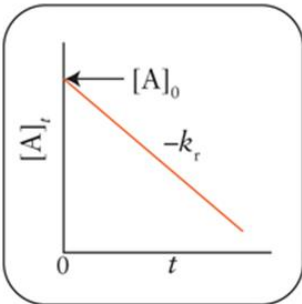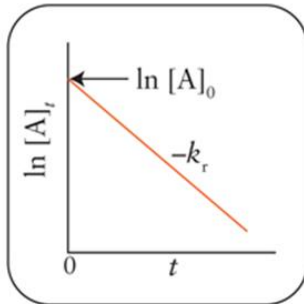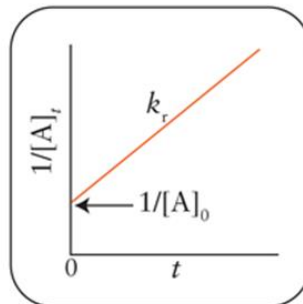**TABLE 7B.1   Integrated Rate Laws, Rate Law Plots, and Half-Lives**

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

Table 7B.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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Short Quiz

Which of the following represents the integrated rate law for a first-order reaction?

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

B. $\dfrac{1}{[A]_t} - \dfrac{1}{[A]_0} = kt$

C. $[A]_0 - [A]_t = kt$

D. $A \cdot e^{-\frac{E_a}{RT}} = k$

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 that all but <u>the simplest reactions are the outcome of several</u>, 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:

$$2\,O_3(g) \rightleftharpoons 3\,O_2(g)$$
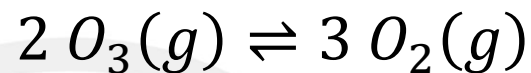
We could imagine the reaction taking place two different ways:

One-step mechanism:

Two O_3 molecules collide and rearrange into three O_2 molecules:
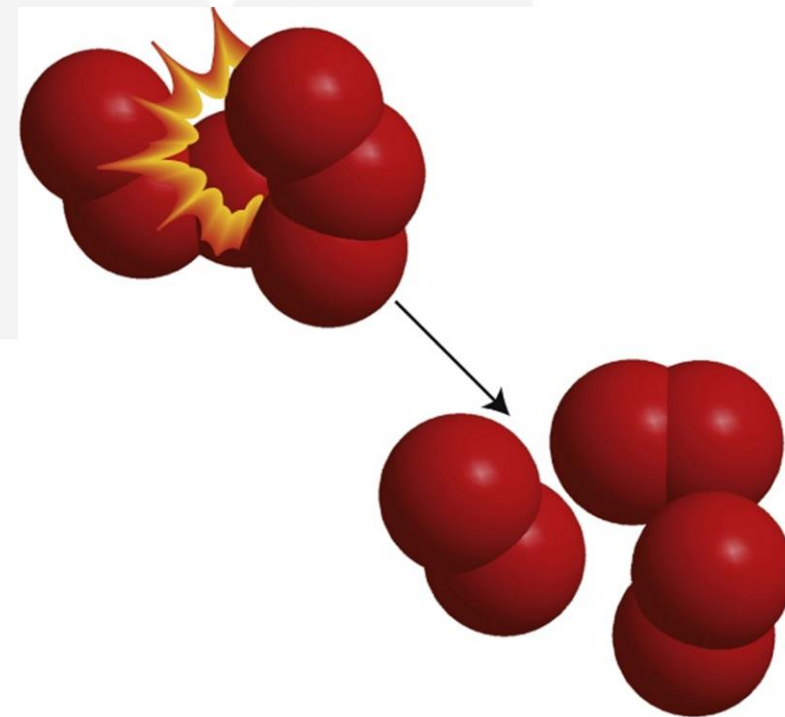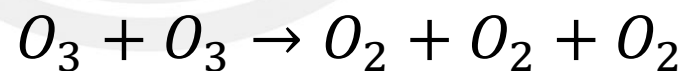
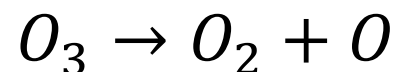$$O_3 + O_3 \rightarrow O_2 + O_2 + O_2$$

Figure 7C.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

Choosing the Right Mechanism

Two-step mechanism:

1. O_3 dissociates

$$O_3 \rightarrow O_2 + O$$

2. the O attacks another O_3 molecule making two more O_2

$$O_3 + O \rightarrow O_2 + O_2$$

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

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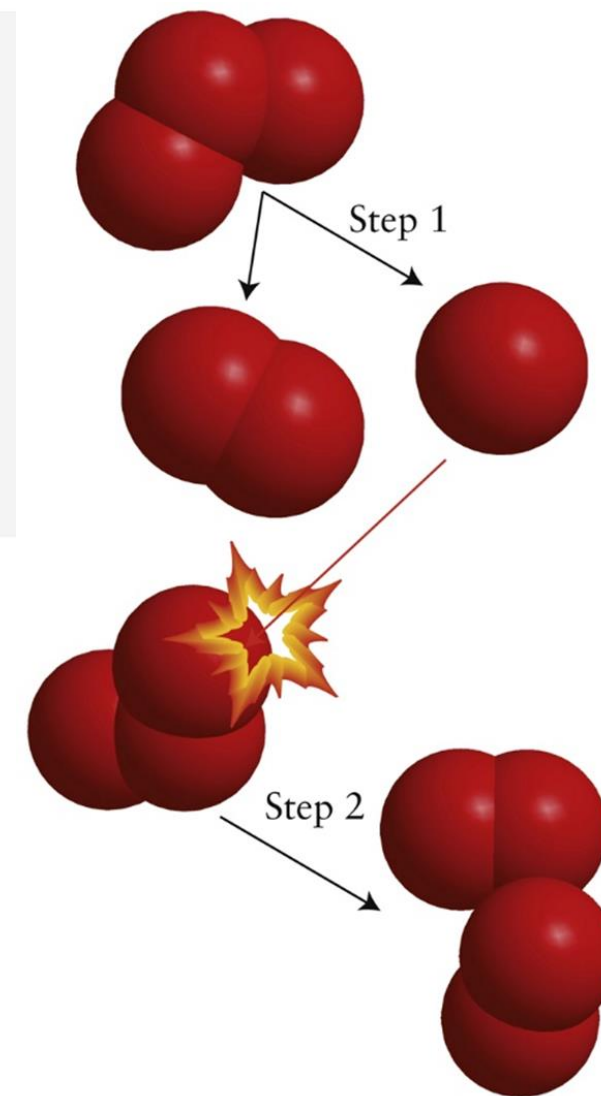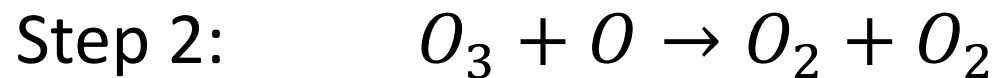

Figure 7C.2
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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A Note on Good Practice

Step 1: $O_3 \rightarrow O_2 + O$

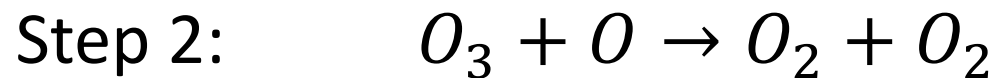Step 2: $O_3 + O \rightarrow O_2 + O_2$

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 they do **not use stoichiometric coefficients**. Instead, the formula is written as many times as required.

Step 1: $O_3 \rightarrow O_2 + O$

Step 2: $O_3 + O \rightarrow O_2 + O_2$
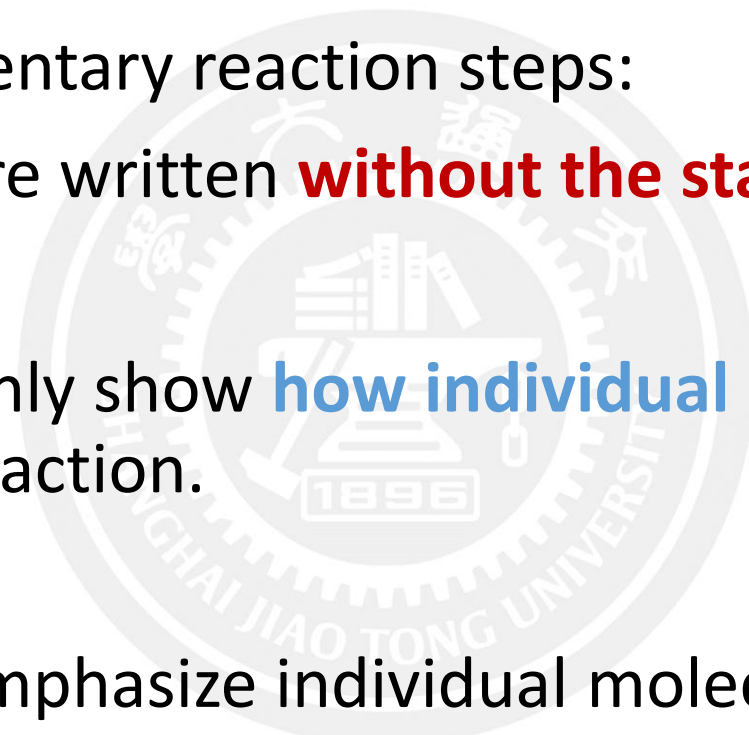
Step 1 is a unimolecular reaction because only one reactant molecule participates.

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.

What are the molecularities of the following reactions?

a) $C_2H_5Br + OH^- \rightarrow C_2H_5Br + OH^-$
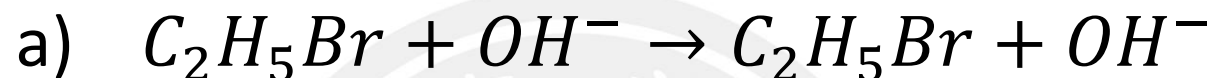
A bimolecular reaction, so the molecularity is 2.

b) $Br_2 \rightarrow Br + Br$

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:
$$O_3 + O_3 \rightarrow O_2 + O_2 + O_2$$

Or a two-step mechanism

Step 1: $O_3 \rightarrow O_2 + O$
Step 2: $O_3 + O \rightarrow O_2 + O_2$

The Rate Laws of Elementary Reactions
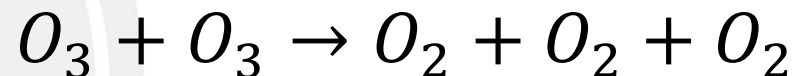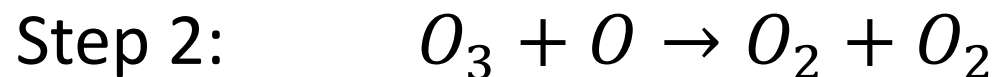
We may still be incorrect because some other mechanism may also lead to the same rate law.

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

The Proof of a Mechanism

Reconstruction of the overall rate law from a mechanism:

- Writing the rate law for each of the elementary reactions.

- Combining them into an overall rate law.

The Proof of a Mechanism

Molecularity	Elementary reaction	Rate law
1	$A \rightarrow products$	$rate = k \cdot [A]$
2	$A + A \rightarrow products$	$rate = k \cdot [A]^2$
	$A + B \rightarrow products$	$rate = k \cdot [A][B]$
3	$A + A + A \rightarrow products$	$rate = k \cdot [A]^3$
	$A + A + B \rightarrow products$	$rate = k \cdot [A]^2[B]$
	$A + B + C \rightarrow products$	$rate = k \cdot [A][B][C]$

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

- Unimolecular means one component is necessary to proceed the reaction

- Bimolecular means two components are required

- Trimolecular means three components are necessary
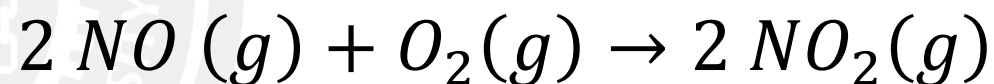
Example of a Proof

Reconstruction of the overall rate law from a mechanism:

- Writing the rate law for each of the elementary reactions.

- Combining them into an overall rate law.

The overall rate law has been determined experimentally:

$$2\, NO\,(g) + O_2(g) \rightarrow 2\, NO_2(g)$$

$$rate_{formation, NO_2} = k \cdot [NO]^2 [O_2]$$

This rate law is our target equation.

Example of a Proof

$$rate_{formation,NO_2} = k \cdot [NO]^2[O_2]$$ This rate law is our target equation.

The following reaction mechanism has been proposed:

$$NO + NO \rightarrow N_2O_2 \qquad rate_{formation,N_2O_2} = k_1 \cdot [NO]^2$$

$$N_2O_2 \rightarrow NO + NO \qquad rate_{consumption,N_2O_2} = k_{-1} \cdot [N_2O_2]$$

Step 1 is a fast bimolecular dimerization. **Note:** The reverse reaction is also shown as a reference for later. The index -1 indicates the reversal of the first reaction.

$$O_2 + N_2O_2 \rightarrow NO_2 + NO_2 \qquad rate_{consumption,N_2O_2} = k_2 \cdot [N_2O_2][O_2]$$

Step 2 is a slow bimolecular reaction in which an O2 molecule collides with the dimer N2O2. **Note:** The reverse reaction of this step is too slow to include.

We need to combine or steps to reach the overall rate law:
$$rate_{formation,NO_2} = k \cdot [NO]^2[O_2]$$

Step 1:
$$NO + NO \rightarrow N_2O_2 \qquad rate_{formation,N_2O_2} = k_1 \cdot [NO]^2$$
$$N_2O_2 \rightarrow NO + NO \qquad rate_{consumption,N_2O_2} = k_{-1} \cdot [N_2O_2]$$

Step 2:
$$O_2 + N_2O_2 \rightarrow NO_2 + NO_2 \ rate_{consumption,N_2O_2} = k_2 \cdot [N_2O_2][O_2]$$

We notice that NO_2 is the molecule we want to find the rate law for and it is a product in step 2, so we write:

$$rate_{formation,NO_2} = 2 \cdot rate_{consumption,N_2O_2} = 2k_2 \cdot [N_2O_2][O_2]$$

The factor 2 stems from the two molecules of NO_2 produced in step 2.

Example of a Proof

Step 1:

$$NO + NO \rightarrow N_2O_2 \qquad\qquad rate_{formation,N_2O_2} = k_1 \cdot [NO]^2$$

$$N_2O_2 \rightarrow NO + NO \qquad\qquad rate_{consumption,N_2O_2} = k_{-1} \cdot [N_2O_2]$$

Step 2:

$$O_2 + N_2O_2 \rightarrow NO_2 + NO_2 \qquad rate_{consumption,N_2O_2} = k_2 \cdot [N_2O_2][O_2]$$

$$rate_{formation,NO_2} = 2k_2 \cdot [N_2O_2][O_2]$$

Unfortunately, this rate law is not complete yet, because it contains N_2O_2, which is an **intermediate**. This means that N_2O_2 is formed in one step and consumed in the other. We therefore need to determine an expression for the overall formation of N_2O_2:

$$total\ rate_{formation,N_2O_2} = k_1 \cdot [NO]^2 - k_{-1} \cdot [N_2O_2] - k_2 \cdot [N_2O_2][O_2]$$

Remember that intermediates never appear in overall rate laws.

Example of a Proof

$$total\ rate_{formation,N_2O_2} = k_1 \cdot [NO]^2 - k_{-1} \cdot [N_2O_2] - k_2 \cdot [N_2O_2][O_2]$$

We now apply the steady-state approximation, which assumes that the concentration of intermediates will always stay very low. In other words: As soon as an intermediate is formed, it is immediately consumed.

$$0 = k_1 \cdot [NO]^2 - k_{-1} \cdot [N_2O_2] - k_2 \cdot [N_2O_2][O_2]$$

$$0 = k_1 \cdot [NO]^2 - (k_{-1} + k_2 \cdot [O_2])[N_2O_2]$$

$$(k_{-1} + k_2 \cdot [O_2])[N_2O_2] = k_1 \cdot [NO]^2$$

$$[N_2O_2] = \frac{k_1 \cdot [NO]^2}{(k_{-1} + k_2 \cdot [O_2])}$$

Example of a Proof

$$rate_{formation,NO_2} = 2k_2 \cdot [N_2O_2][O_2]$$

Substituting $[N_2O_2] = \frac{k_1 \cdot [NO]^2}{(k_{-1} + k_2 \cdot [O_2])}$:

$$rate_{formation,NO_2} = 2k_2 \cdot \frac{k_1 \cdot [NO]^2}{k_{-1} + k_2 \cdot [O_2]}[O_2]$$

As step 2 is much slower than step 1, we can approximate $k_{-1} + k_2 \cdot [O_2] \approx k_{-1}$:

$$rate_{formation,NO_2} = \frac{2k_2 k_1 \cdot [NO]^2}{k_{-1}}[O_2] = \left(\frac{2k_2 k_1}{k_{-1}}\right)[NO]^2[O_2]$$

$$rate_{formation,NO_2} = \left(\frac{2k_2 k_1}{k_{-1}}\right)[NO]^2[O_2] = k \cdot [NO]^2[O_2]$$

Rate-Determining Step

In our last example, we had a slow step:

Step 2:
$$O_2 + N_2O_2 \rightarrow NO_2 + NO_2$$

The <u>slowest step</u> governs the rate of all the other steps, so it is called the **rate-determining step**.

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

Reactants Intermediates Products
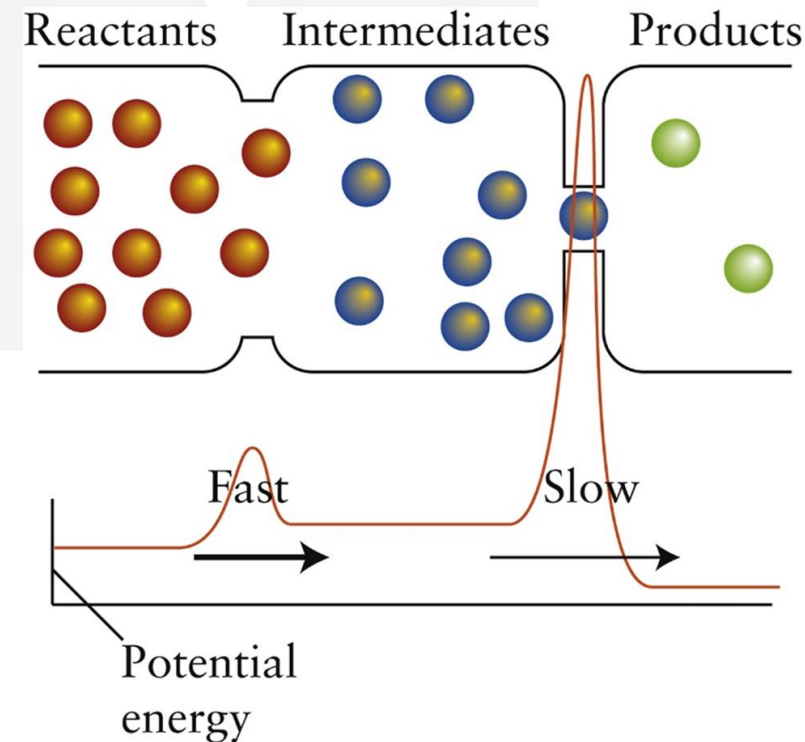
Fast   Slow

Potential energy

Figure 7C.3
Atkins, *Chemical Principles: The Quest for Insight*, 7e
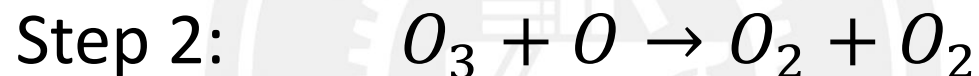W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

The following rate law has been determined for the decomposition of ozone:

$$2\,O_3(g) \rightarrow 3\,O_2(g) \qquad rate_{decomposition,O_3} = k \cdot \frac{[O_3]^2}{[O_2]}$$

The following two-step mechanism has been proposed:

Step 1: $\qquad O_3 \rightarrow O_2 + O$

Step 2: $\qquad O_3 + O \rightarrow O_2 + O_2$

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

The following rate law has been determined for the decomposition of ozone:

$$2\,O_3(g) \rightarrow 3\,O_2(g) \qquad rate_{decomposition,O_3} = k \cdot \frac{[O_3]^2}{[O_2]}$$

The following two-step mechanism has been proposed:

Step 1: $\qquad O_3 \rightarrow O_2 + O \qquad\qquad rate_{decomposition,O_3} = k_1 \cdot [O_3]$

$\qquad\qquad O_2 + O \rightarrow O_3 \qquad\qquad rate_{formation,O_3} = k_{-1} \cdot [O_2][O]$

Step 2: $\qquad O_3 + O \rightarrow O_2 + O_2 \qquad rate_{decomposition,O_3} = k_2 \cdot [O_3][O]$

This is the slow step, and the reverse reaction is ignored.

$$rate_{decomposition,O_3} = k_1 \cdot [O_3] - k_{-1} \cdot [O_2][O] + k_2 \cdot [O_3][O]$$

$$rate_{decomposition, O_3} = k_1 \cdot [O_3] - k_{-1} \cdot [O_2][O] + k_2 \cdot [O_3][O]$$

We see that O is an intermediate and apply the steady-state approximation:

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

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

Substituting:

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

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

$$rate_{decomposition,O_3} = \frac{k_1 \cdot [O_3](k_{-1} \cdot [O_2] + k_2 \cdot [O_3])}{k_{-1} \cdot [O_2] + k_2 \cdot [O_3]} - \frac{k_{-1} \cdot [O_2] \cdot k_1 \cdot [O_3]}{k_{-1} \cdot [O_2] + k_2 \cdot [O_3]} + \frac{k_2 \cdot [O_3] \cdot k_1 \cdot [O_3]}{k_{-1} \cdot [O_2] + k_2 \cdot [O_3]}$$

$$rate_{decomposition,O_3} = \frac{k_1 k_{-1} \cdot [O_3][O_2] + k_1 k_2 \cdot [O_3]^2 - k_1 k_{-1} \cdot [O_3][O_2] + k_1 k_2 \cdot [O_3]^2}{k_{-1} \cdot [O_2] + k_2 \cdot [O_3]}$$

$$rate_{decomposition,O_3} = \frac{2 k_1 k_2 \cdot [O_3]^2}{k_{-1} \cdot [O_2] + k_2 \cdot [O_3]}$$

As step 2 is much slower than step 1, we can approximate $k_{-1} \cdot [O_2] + k_2 \cdot [O_3] \approx k_{-1} \cdot [O_2]$:

$$rate_{decomposition,O_3} = \frac{2 k_1 k_2 \cdot [O_3]^2}{k_{-1} \cdot [O_2]} = \left(\frac{2 k_1 k_2}{k_{-1}}\right) \frac{[O_3]^2}{[O_2]} = k \cdot \frac{[O_3]^2}{[O_2]}$$
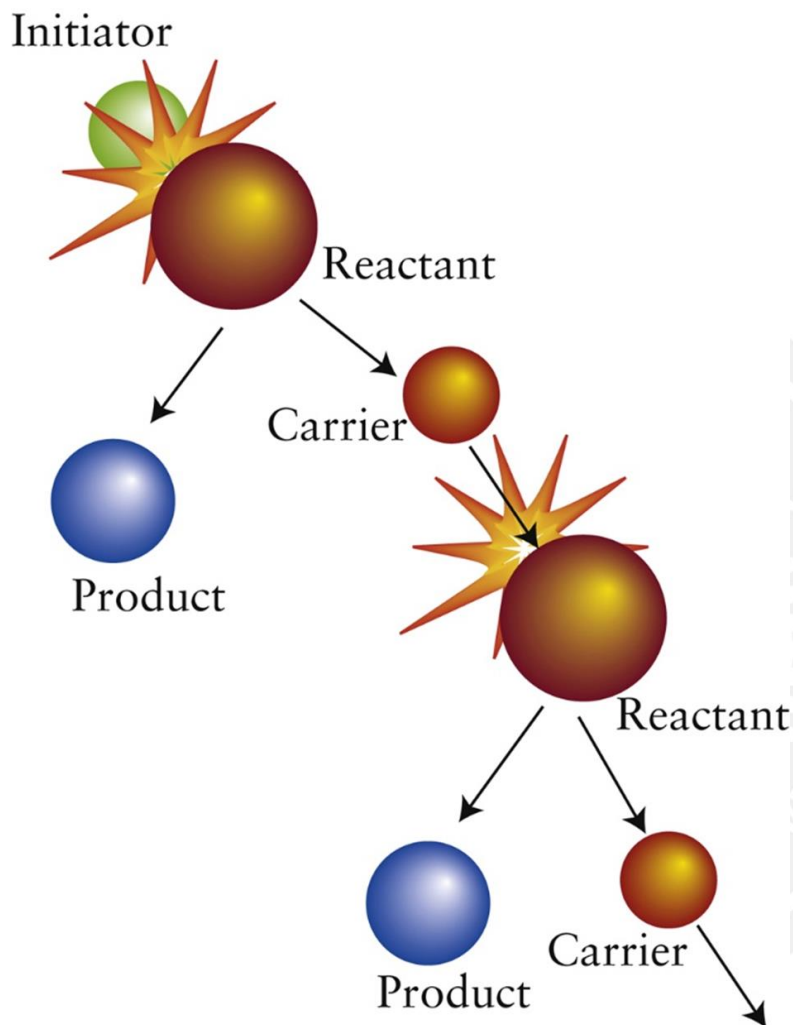
Chain Reactions

Figure 7C.6
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

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

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

Radical chain reactions have radical intermediates.
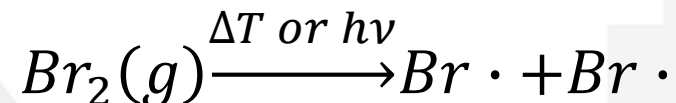
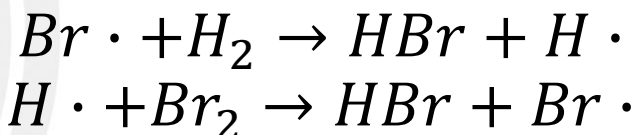The rate laws are very complex and not derived here.

Formation of HBr in the reaction takes place by a chain reaction:
$$H_2(g) + Br_2(g) \rightarrow 2\ HBr(g)$$
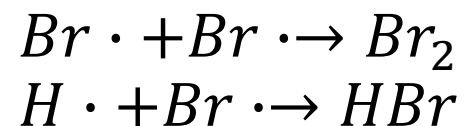
The first step is called **initiation** and produces chain carriers H· and Br·. *ΔT* is heat, *hν* is light.

$$Br_2(g) \xrightarrow{\Delta T\ or\ h\nu} Br \cdot + Br \cdot$$

The second step, **propagation**, creates more chain carriers, in this case radicals.
$$Br \cdot + H_2 \rightarrow HBr + H \cdot$$
$$H \cdot + Br_2 \rightarrow HBr + Br \cdot$$

The final step, **termination**, occurs when two chain carriers combine to form products.
$$Br \cdot + Br \cdot \rightarrow Br_2$$
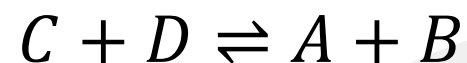$$H \cdot + Br \cdot \rightarrow HBr$$

Rates and Equilibrium

The equilibrium constant for an elementary reaction is equal to the forward and reverse rate constants of the reaction. We can show $K = \frac{k_1}{k_{-1}} \cdot \frac{k_2}{k_{-2}} \cdot \cdots$
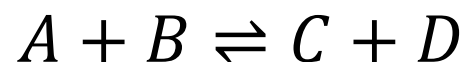
$$A + B \rightleftharpoons C + D \qquad\qquad rate = k_1 \cdot [A][B]$$
$$C + D \rightleftharpoons A + B \qquad\qquad rate = k_{-1} \cdot [C][D]$$

At equilibrium:

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

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

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

The Rate Law: Temperature

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$
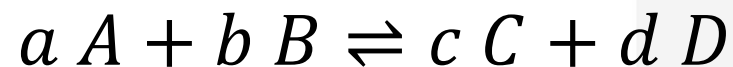
$$rate = f(\textbf{\textcolor{red}{T}}, c)$$

T: Temperature

c: Concentration

General form of a rate law:

$$rate = \textbf{\textcolor{red}{k}} \cdot [A]^m [B]^n$$

Note: *m* and *n* are **not** the stoichiometric coefficients!

Models of Reactions

Reaction	Rate law	T / K	k / L·mol^{-1}·s^{-1}
$H_2 + I_2 \rightleftharpoons 2\,HI$	$k \cdot [H_2][I_2]$	500	4.3×10^{-7}
		600	4.4×10^{-4}
		700	6.3×10^{-2}

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

They also vary with temperature.

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

Effects of Temperature

We've seen how rates depend on concentrations.

Rates also depend on temperature. An ***increase of 10 ℃*** 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.

Arrhenius Equation

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

$$k = A \cdot e^{-\frac{E_a}{RT}}$$

The two constants, *A* and *E*$_a$, are known as the Arrhenius parameters for the reaction and are found experimentally.

A is called the **pre-exponential factor**.

E$_a$ is the **activation energy**.

Both *A* and *E*$_a$ are **nearly independent of temperature** but have values that depend on the reaction being studied.
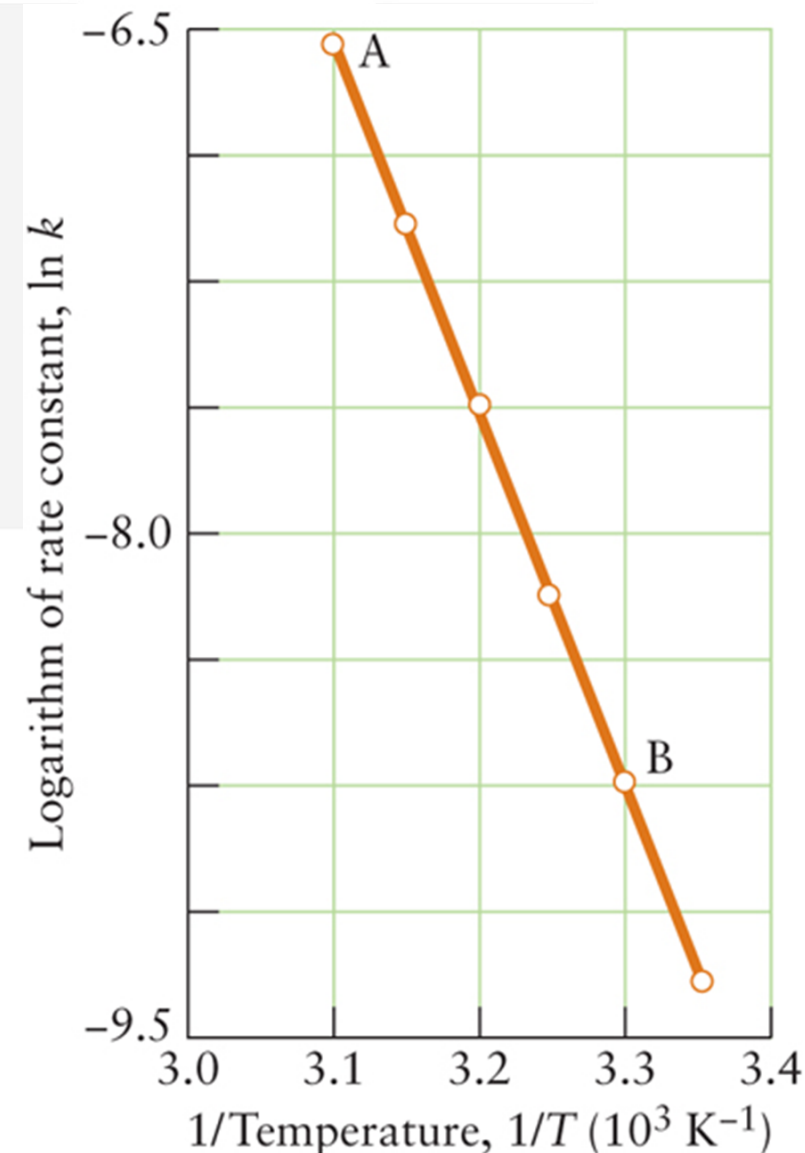
The rate constant for the second-order reaction between bromoethane and hydroxide ions in water, was measured at several temperatures, with the results shown here.
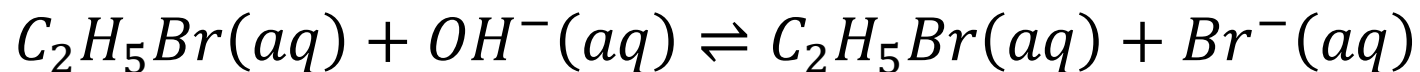
$$C_2H_5Br(aq) + OH^-(aq) \rightleftharpoons C_2H_5Br(aq) + Br^-(aq)$$

The first step is to make a table to find (1) the temperature in Kelvin; (2) $1/T$; (3) ln k; and (4) the slope either by graph or spreadsheet (=LINEST(Values)).

T / °C	T / K	$T^{-1} \times 10^3$ / K^{-1}	$k \times 10^{-3}$ / L·mol^{-1}·s^{-1}	ln(k)	slope
25	298	3.36	8.80×10^{-5}	-9.34	
30	303	3.30	1.60×10^{-4}	-8.74	
35	308	3.25	2.80×10^{-4}	-8.18	-1.07×10^{-4}
40	313	3,19	5.00×10^{-4}	-7.60	
45	318	3.14	8.50×10^{-4}	-7.07	
50	323	3.10	1.40×10^{-3}	-6.57	

The first step is to make a table to find (1) the temperature in Kelvin; (2) 1/T; (3) ln k; and (4) the slope either by graph or spreadsheet (=LINEST(Values)).

T / °C	T / K	$T^{-1} \times 10^3$ / K^{-1}	$k \times 10^{-3}$ / L·mol^{-1}·s^{-1}	ln(k)	slope / K
25	298	3.36	8.80×10^{-5}	-9.34	
30	303	3.30	1.60×10^{-4}	-8.74	
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45	318	3.14	8.50×10^{-4}	-7.07	
50	323	3.10	1.40×10^{-3}	-6.57	

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

By plotting ln(k) against T^{-1}, slope $= -\frac{E_a}{R}$. Therefore:

$$E_a = -R \cdot slope = -8.314 \ \frac{\text{J}}{\text{mol} \cdot \text{K}} \times -1.07 \times 10^4 \ K = 89 \ \frac{\text{kJ}}{\text{mol}}$$

Arrhenius Behaviour

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

E_a and temperatures are closely tied to each other.

A low E_a, for example 10 kJ·mol⁻¹, will have a low slope and is not so strongly dependent on temperature.

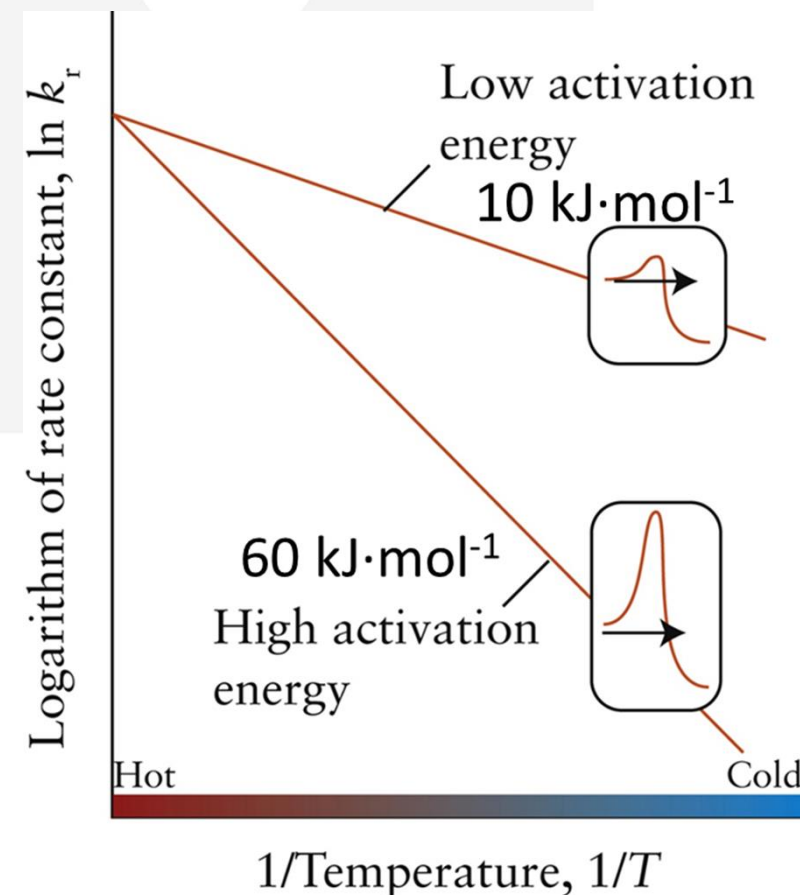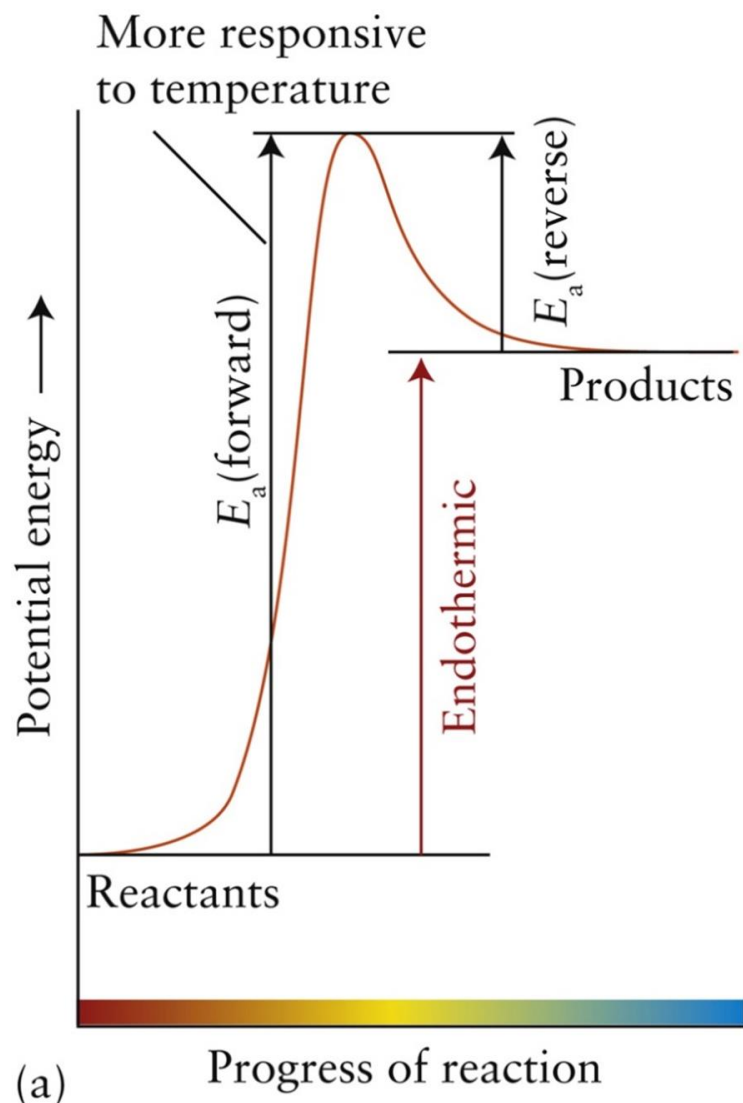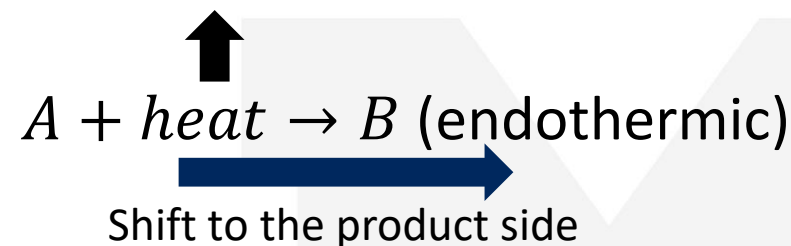A high E_a, say above 60 kJ·mol⁻¹, produces a steep slope and more temperature-dependent reactions.

Figure 7D.3
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W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

More responsive to temperature

E_a (forward)

E_a (reverse)

Potential energy ⟶

Endothermic

Products

Reactants

Progress of reaction

(a)

Figure 7D.6a
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

$$A + heat \rightarrow B \text{ (endothermic)}$$

Shift to the product side

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad K = \frac{k_1}{k_{-1}}$$

E_a is the minimum kinetic energy required to activate a successful collision.

For **endothermic reactions**, since **E_a forward is large**, it is sensitive to increases in temperature. Raising the temperature will **increase K**, the equilibrium constant, and is exactly what Le Chatelier's principle predicts.
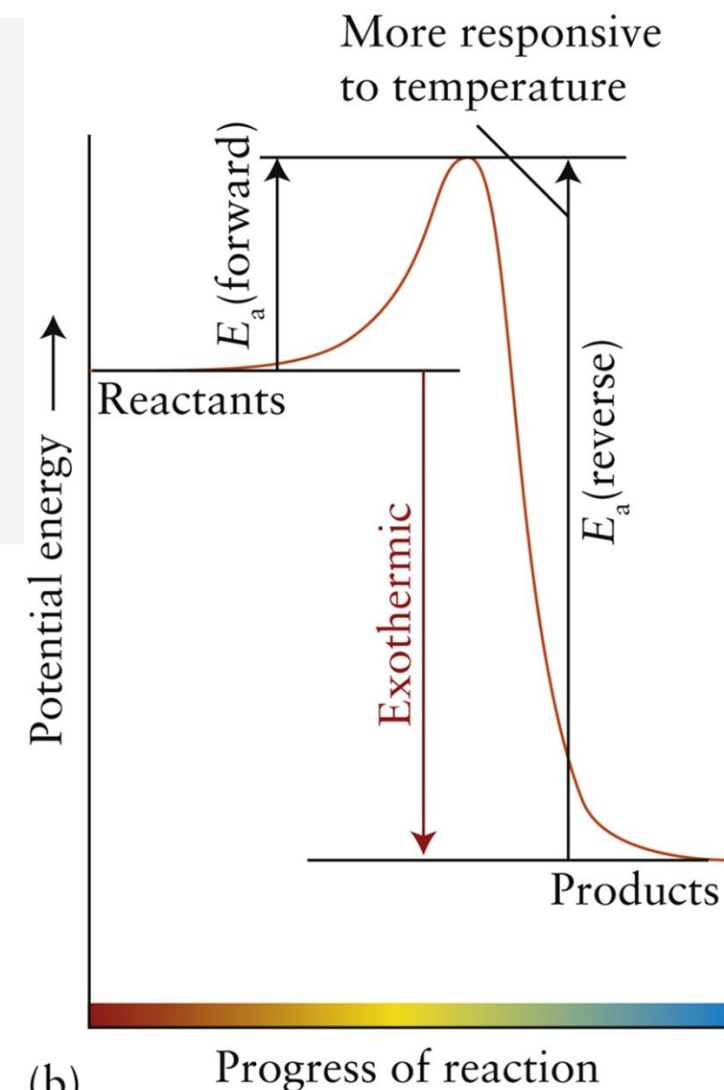
$A \rightarrow B + heat$ (exothermic)
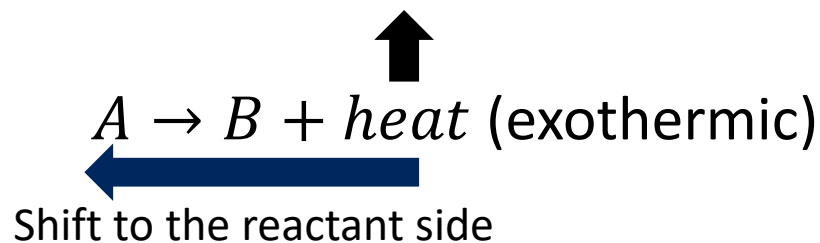
Shift to the reactant side

$$A \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} B \qquad K = \frac{k_1}{k_{-1}}$$

E_a is the minimum kinetic energy required to activate a successful collision.

For **exothermic reactions**, since E_a **forward is small**, it is insensitive to increases in temperature. Raising the temperature will **decrease *K***, the equilibrium constant, and is exactly what Le Chatelier's principle predicts

More responsive to temperature

E_a (forward)

Reactants

Potential energy

Exothermic

E_a (reverse)

Products

Progress of reaction

(b)

Figure 7D.6b
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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Two-Point Arrhenius Equation

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

At two different temperatures with two different rate constants:

$$\ln\left(k_{T_2}\right) - \ln\left(k_{T_1}\right) = \ln(A) - \frac{E_a}{RT_2} - \left(\ln(A) - \frac{E_a}{RT_1}\right) = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

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

Example

The hydrolysis of sucrose is a part of the digestive process. To investigate how strongly the rate depends on our body temperature, calculate the rate constant for the hydrolysis of sucrose at 35.0 °C, given that k = 1.0 mL·mol^{-1}·s^{-1} at 37.0 °C (normal body temperature) and that the activation energy of the reaction is 108 kJ·mol^{-1}.

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

$$k_{T_2} = k_{T_1} \cdot e^{-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$k_{35.0\,°C} = 1.0\,\frac{\text{mL}}{\text{mol}\cdot\text{s}} \times e^{-\frac{108\times10^3\,\frac{\text{J}}{\text{mol}}}{8.314\,\frac{\text{J}}{\text{mol·K}}}\left(\frac{1}{(35.0+273.15)\text{K}} - \frac{1}{(37.0+273.15)\text{K}}\right)} = 0.76\,\frac{\text{mL}}{\text{mol}\cdot\text{s}}$$

The high activation energy indicates that the reaction is temperature sensitive.

Collision Theory

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

The Arrhenius equation can help us build a model of chemical reactions at the molecular level.

Specifically, our model must account for the **temperature dependence** of rate constants, as well as the **energy of activation**.
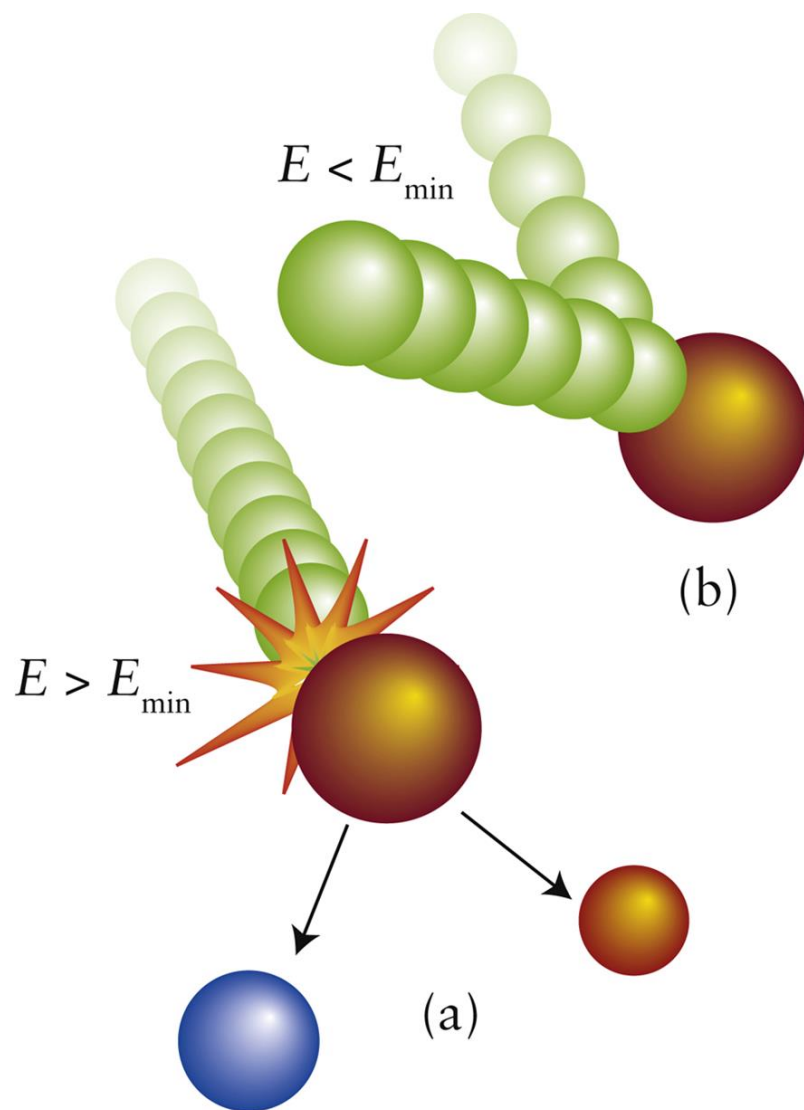
Collision Theory

$E < E_{min}$

(b)

$E > E_{min}$

(a)

Figure 7D.4
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

Hard spheres like billiard balls collide.

If they collide too slowly, nothing will happen.

They need a minimum energy (speed) called E_{min} to react.
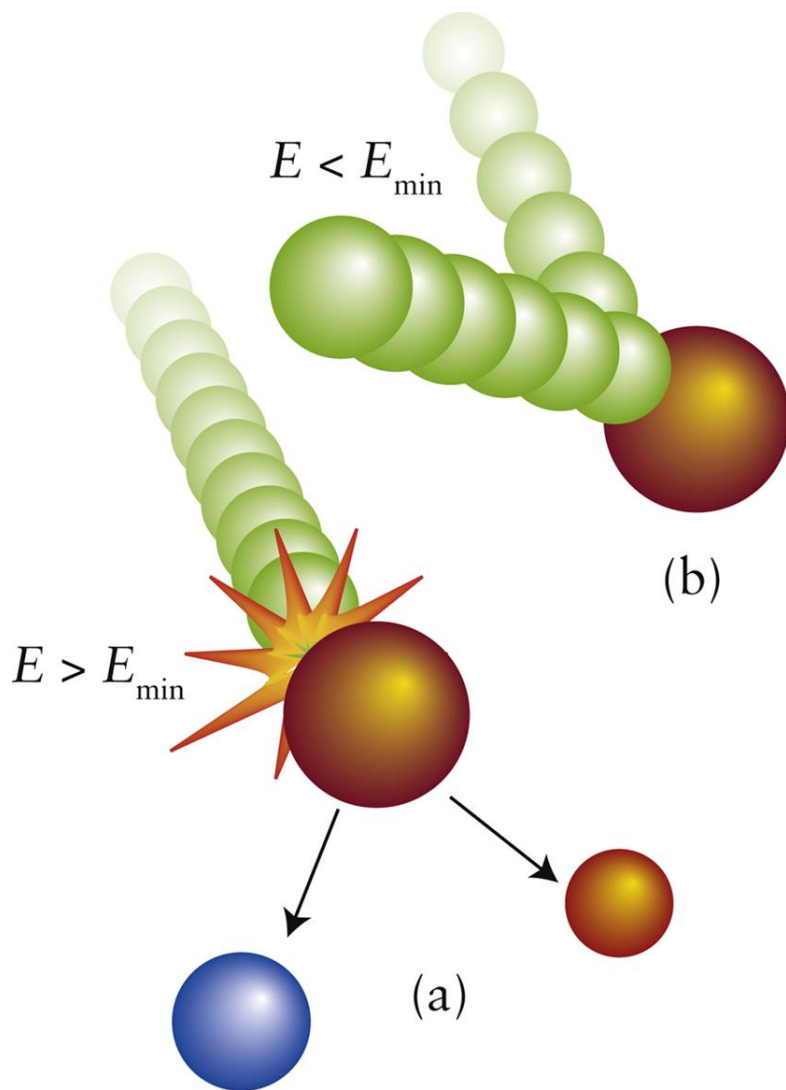
Collision Theory
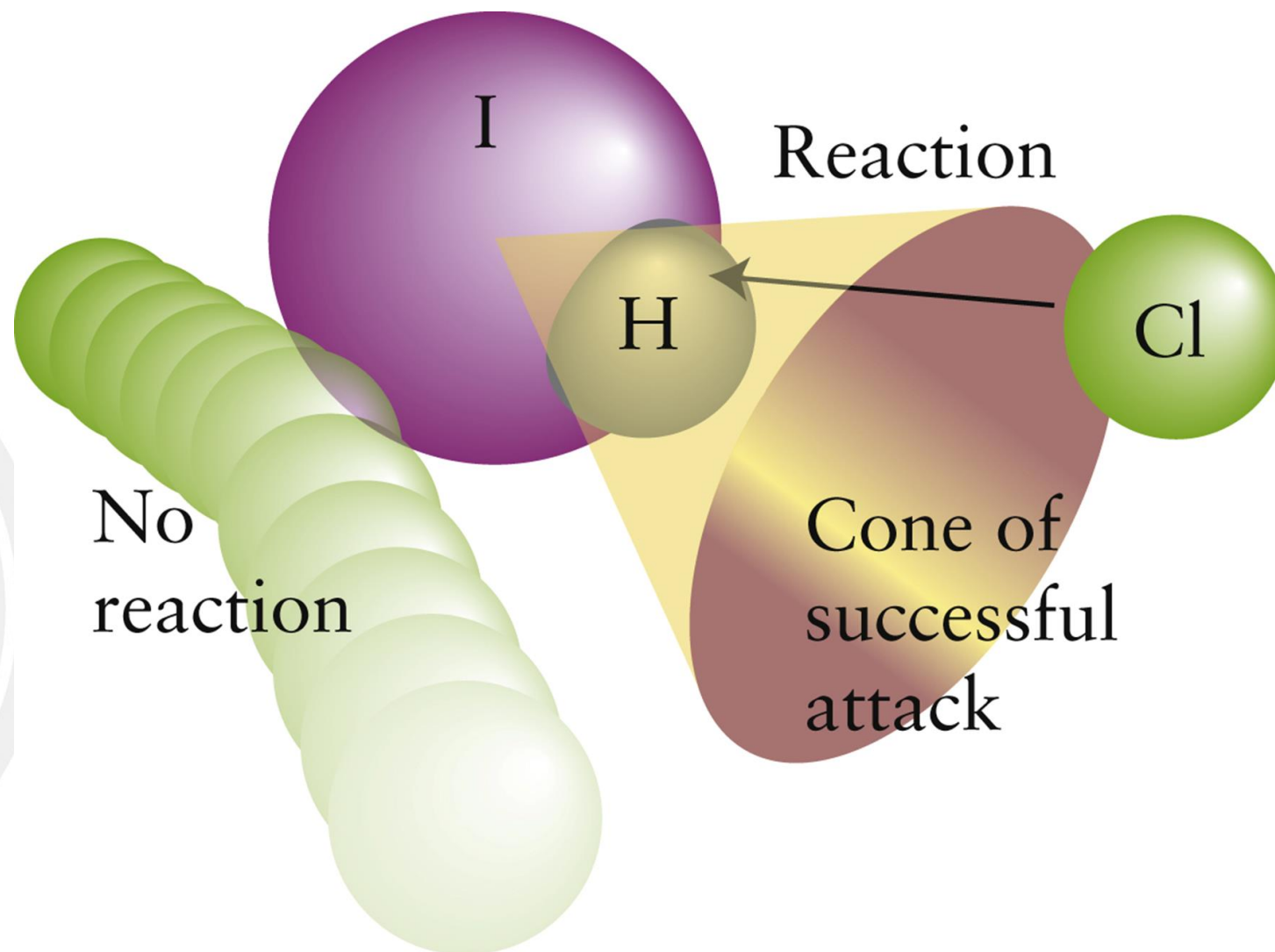
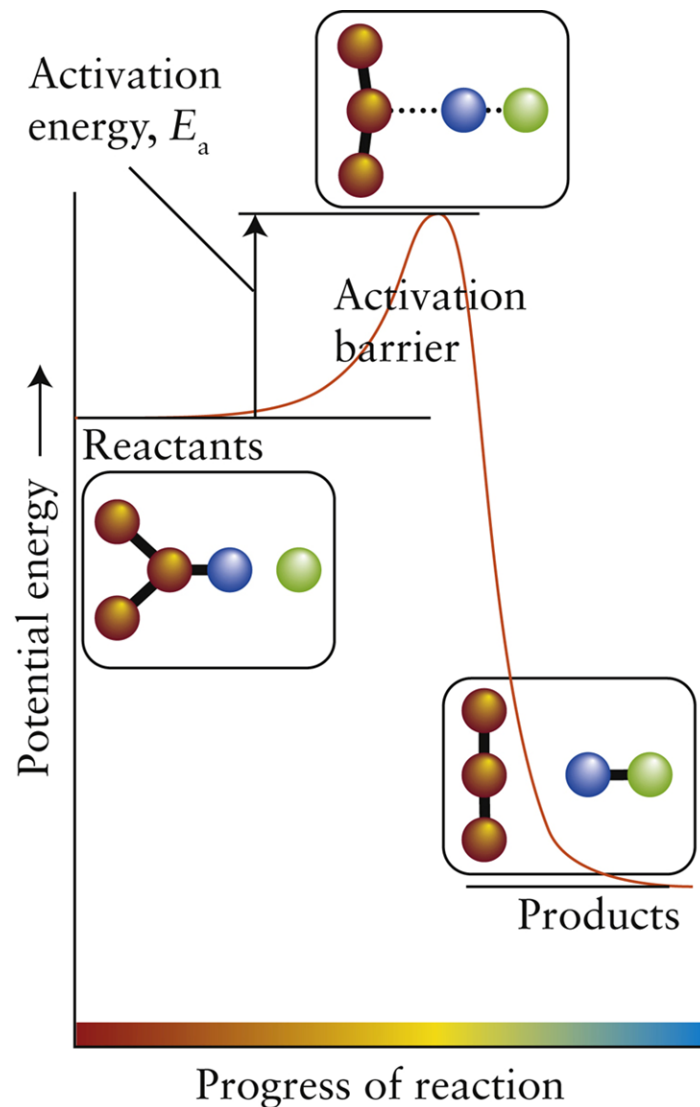$E < E_{min}$

$E > E_{min}$

(b)

(a)

Figure 7D.4
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$$rate = f_{collision} \cdot p_{success}$$

Rate = collision frequency × successful rate

Previously:
$$rate = f(\boldsymbol{T}, \boldsymbol{c}) = k \cdot [A]^m [B]^n$$

T: Temperature

c: Concentration

A higher concentration increases the chances for collisions and therefore $f_{collision}$.

A higher temperature increases the energy of the reactants, thus increasing the chances for a successful reaction (increasing $p_{success}$).

81

Steric Requirement

Improving the model depends on how easily the molecules line up for a collision.

Figure 7D.7
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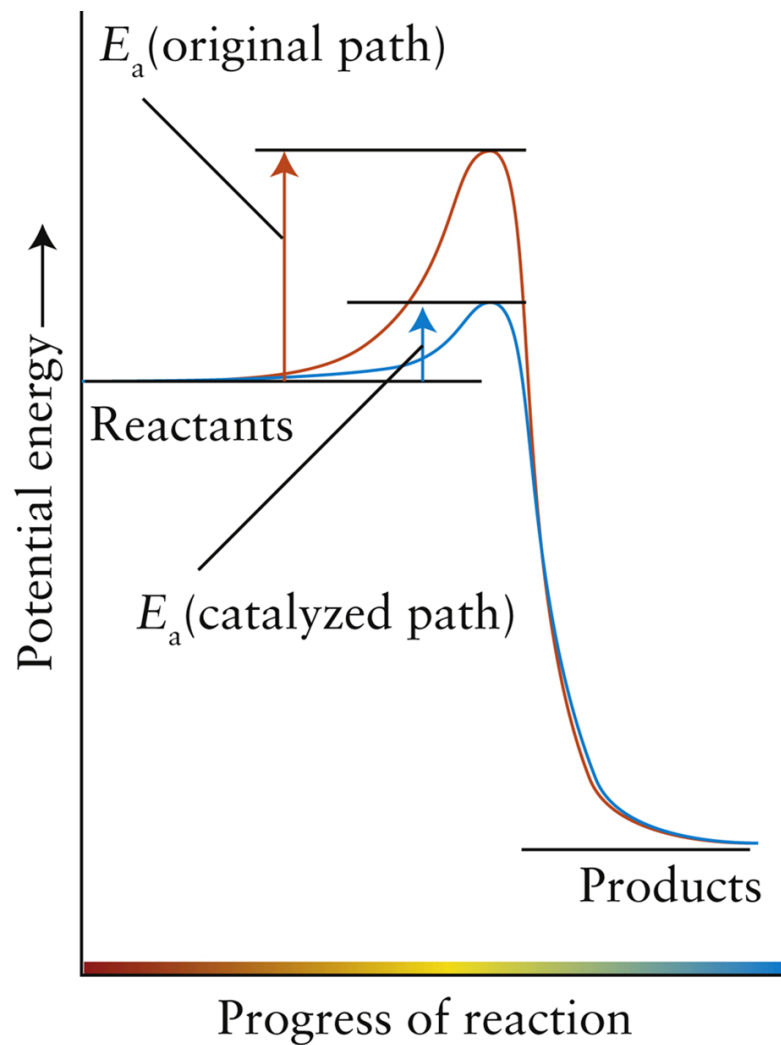
Transition State Theory

Figure 7D.9
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In a reaction profile, the different stages leading up to the activated complex are shown.

As the molecules meet, repulsive forces increase the energy, so the molecule must have enough E_{min} to overcome this opposing force.

As the molecules climb to the top of the E_a, the reaction can go either way.

Accelerating Reactions

We have seen how rates increase by increasing both the concentration of reactants and temperature. But there are other ways.

Catalysis

A catalyst increases the rate, without being consumed.

The name comes from the Greek word καταλύειν meaning "'to annul", "to untie", or "to pick up". In many cases, only a small amount of catalyst is necessary because it acts over and over again (and is not consumed).
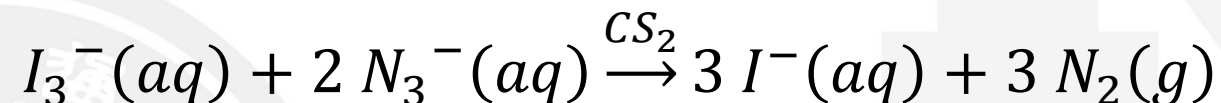
Catalysts

Figure 7E.2
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Catalysts provide a new reaction pathway.

A catalyst lowers the activation energy, thereby allowing more reactant molecules to cross the barrier and form products.

Catalysts in Rate Laws

Catalysts **do not** appear in the balanced equation for a reaction, but their concentrations do appear in the rate law.

The reaction between the triiodide ion and the azide ion is very slow unless a CS_2 catalyst is added.

$$I_3{}^-(aq) + 2\,N_3{}^-(aq) \xrightarrow{CS_2} 3\,I^-(aq) + 3\,N_2(g)$$

Step 1: $\qquad CS_2 + N_3{}^- \rightarrow S_2CN_3{}^-$ (slow)

Step 2: $\qquad 2\,S_2CN_3{}^- + I_3{}^- \rightarrow 2\,CS_2 + 3\,I^- + 3\,N_2$ (fast)

The rate law derived is:

$$rate_{consumption, I_3{}^-} = k \cdot [CS_2][N_3{}^-]$$

Notice that the rate law is 1st order in the catalyst, **carbon disulfide**, but 0th order in triiodide ion, which appears only in the fast step following the slow step.

Homogeneous Catalyst

Homogeneous catalysts are in the **same phase** as the reactants.

Hydrogen peroxide can be stored safely for months, but adding a catalyst, Br_2, causes rapid decomposition:

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

(a)   (b)
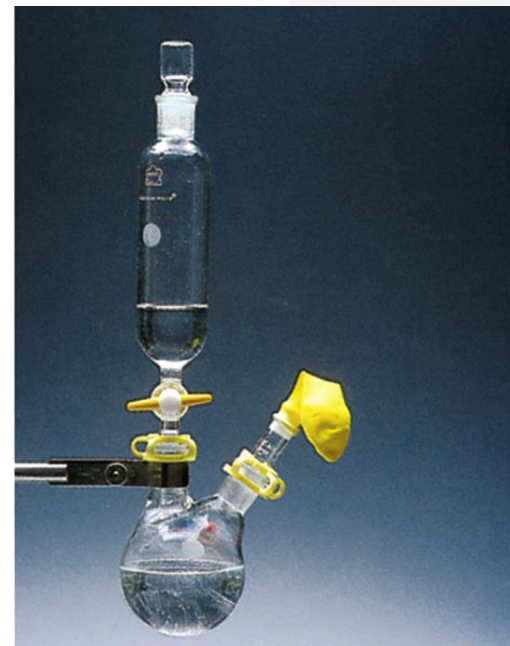
Figure 7E.1
Atkins, *Chemical Principles: The Quest for Insight,* 7e
W. H. Freeman photos by Ken Karp

Heterogeneous Catalyst

Heterogeneous catalysts are in a **different phase** than the reactants.

Common heterogeneous catalysts are finely-divided or porous solids that have a large surface area.

A common one is the iron catalyst used in the Haber process for ammonia. Another catalyst is finely-divided vanadium pentoxide, V_2O_5, which is used in the "contact process" for the production of sulfuric acid.

$$2\,SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2\,SO_3(g)$$
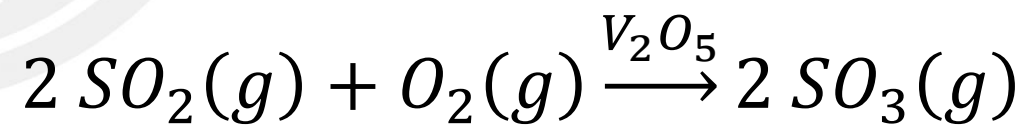
How Does a Catalyst Lower the E_a?

Catalysts grab and hold onto reactants.

Once held, catalysts position reactants so they react with minimal steric hindrance.

Railroad rails provide a train the path of least resistance, so rails are like a catalysts, positioning the train so it can travel with the least amount of energy expended.

Shown is a reaction between ethene, $H_2C=CH_2$, and hydrogen on a Pt metal catalytic surface.

The ethene and hydrogen **stick** to the metal surface (adsorption).

The **metal dissociates the hydrogen**.

The ethene molecule meets two hydrogen atoms to form bonds making H_3C-CH_3; ethane is formed and escapes from the surface.
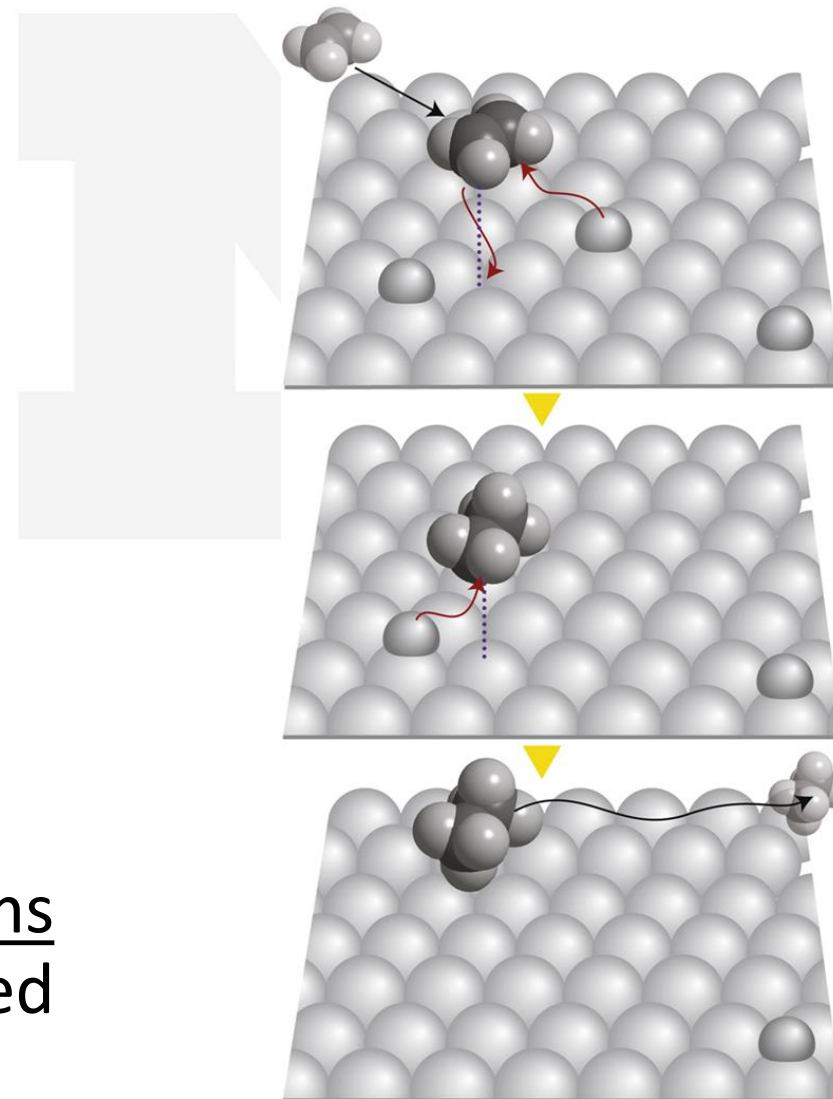
Figure 7E.3
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Poisoned Catalysts

Catalysts can be poisoned, or inactivated.

A common cause of poisoning is the adsorption of a molecule to the catalyst that seals the surface.

Heavy metals, especially *lead,* are very potent poisons for heterogeneous catalysts, which is why *lead-free gasoline* must be used in engines fitted with catalytic converters.
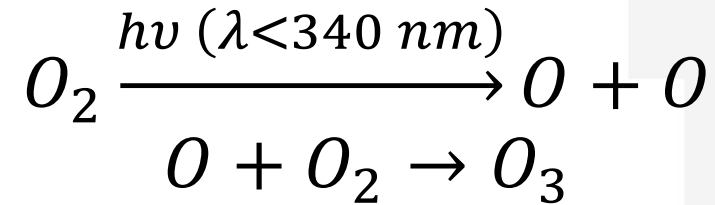
Ozone

Every year the Sun bombards our planet with enough energy to destroy all life.

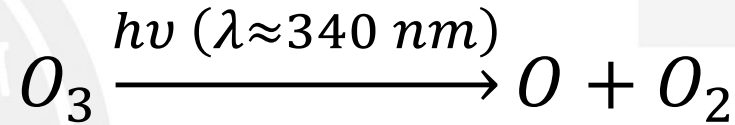Ozone in the stratosphere protects us from that onslaught.

Chemicals used as coolants and propellants, such as chlorofluorocarbons (CFCs), and the nitrogen oxides in jet exhausts, have been found to create holes in Earth's protective ozone layer.

Because CFCs act as catalysts, they can cause large changes in the vast reaches of the stratosphere.

Ozone forms in two steps:

$$O_2 \xrightarrow{hv \ (\lambda < 340 \ nm)} O + O$$
$$O + O_2 \rightarrow O_3$$

The protection stems from:

$$O_3 \xrightarrow{hv \ (\lambda \approx 340 \ nm)} O + O_2$$

Ozone absorbing UV light.

Susan Solomon and James Anderson showed that CFCs containing chlorine atoms catalysed the destruction of stratospheric ozone.

CFCs are not water soluble, so they do not precipitate with rain, but are light and airborne enough to reach the stratosphere.

At one time CFCs emanated from everyday objects, such as cans of hair spray, refrigerators, and air conditioners.

$$Cl \cdot + O_3 \rightarrow ClO \cdot + O_2$$

$$ClO \cdot + O \rightarrow Cl \cdot + O_2$$
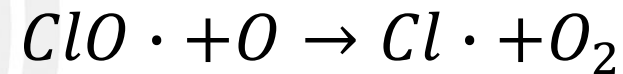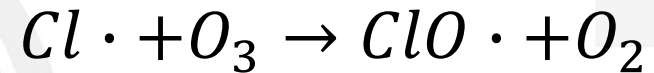
Most nations signed the Montreal Protocol of 1987 which required the more dangerous CFCs to be phased out by 1996.

Current data show that the levels of compounds that deplete ozone are gradually beginning to decrease.

Living Catalysts: Enzymes

Living cells contain thousands of different kinds of catalysts.

Many **catalysts are proteins called enzymes**, with a slot-like active site, where the reaction takes place.

However, unlike an ordinary lock, a protein molecule distorts slightly as the substrate molecule approaches, and its ability to undergo the correct distortion also determines whether the "key" will fit.
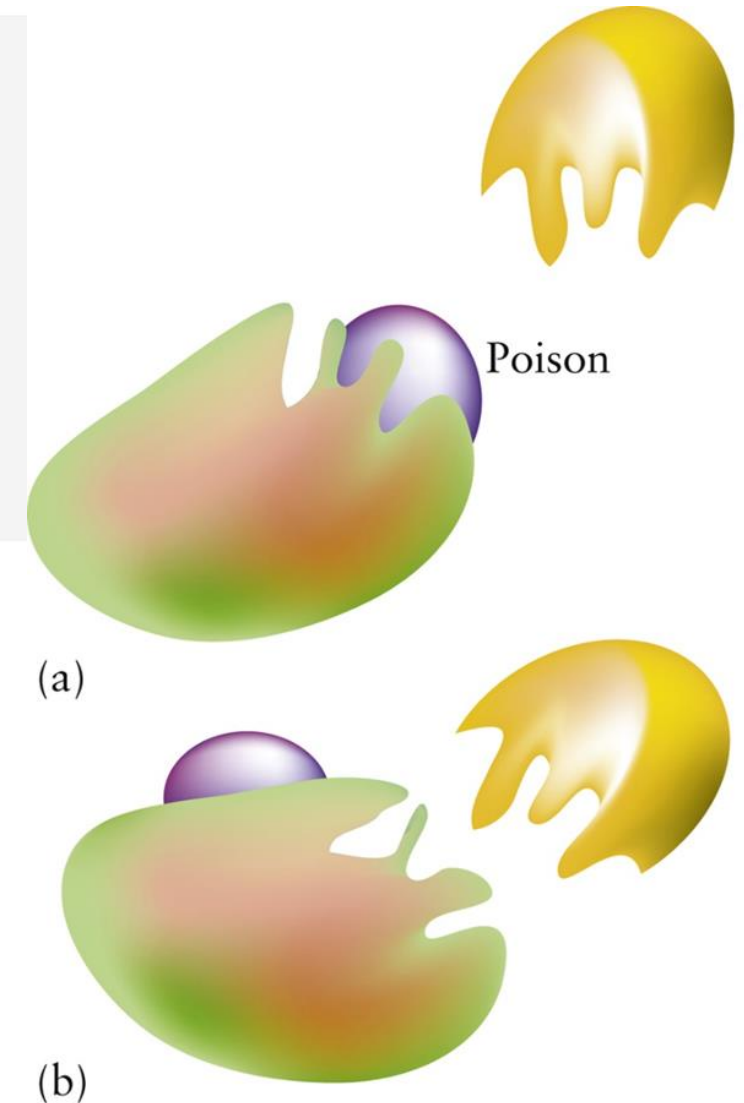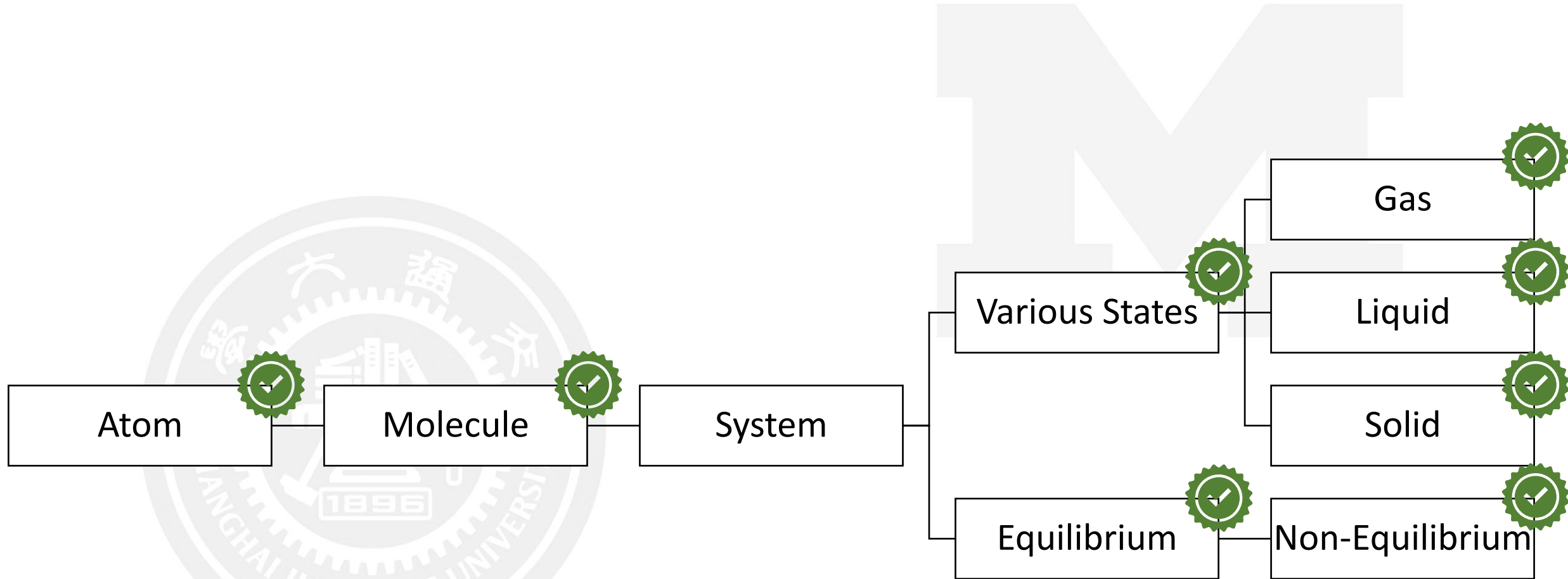
Poison

(a)

(b)

Figure 7E.9
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The Journey So Far…

Atom — Molecule — System

Various States
- Gas
- Liquid
- Solid

Equilibrium — Non-Equilibrium

…Was Just the Beginning!