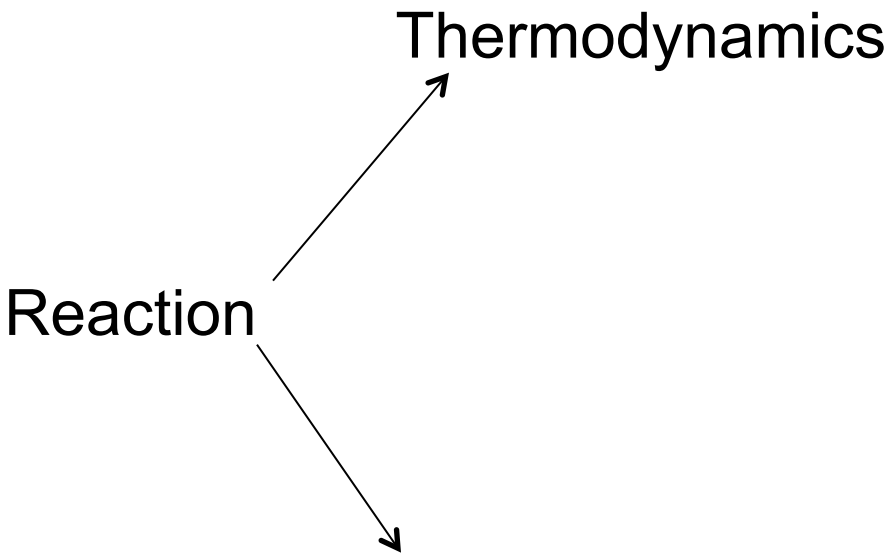
Unit 34.
Introduction to chemical equilibrium

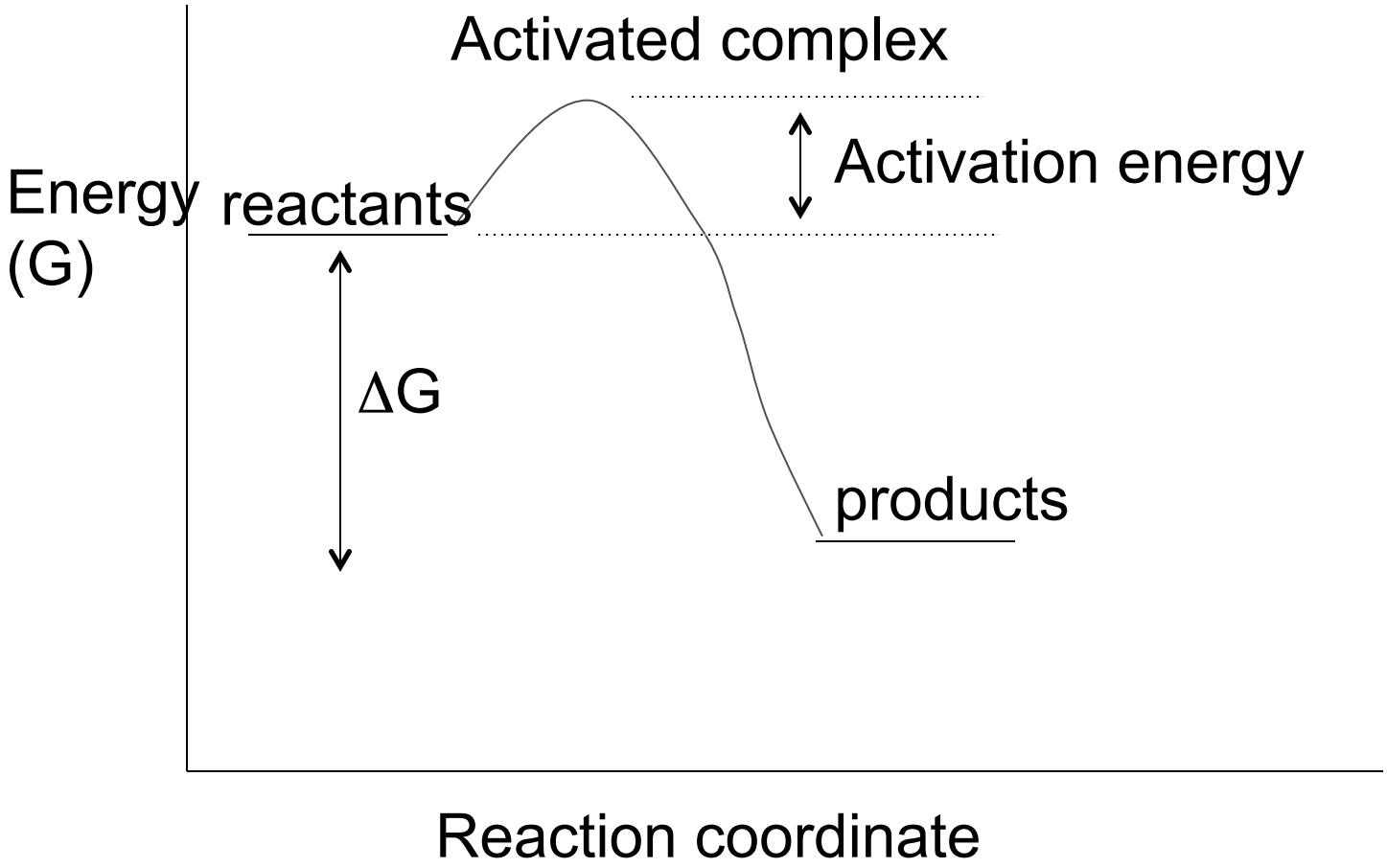
Why do reactions happen?



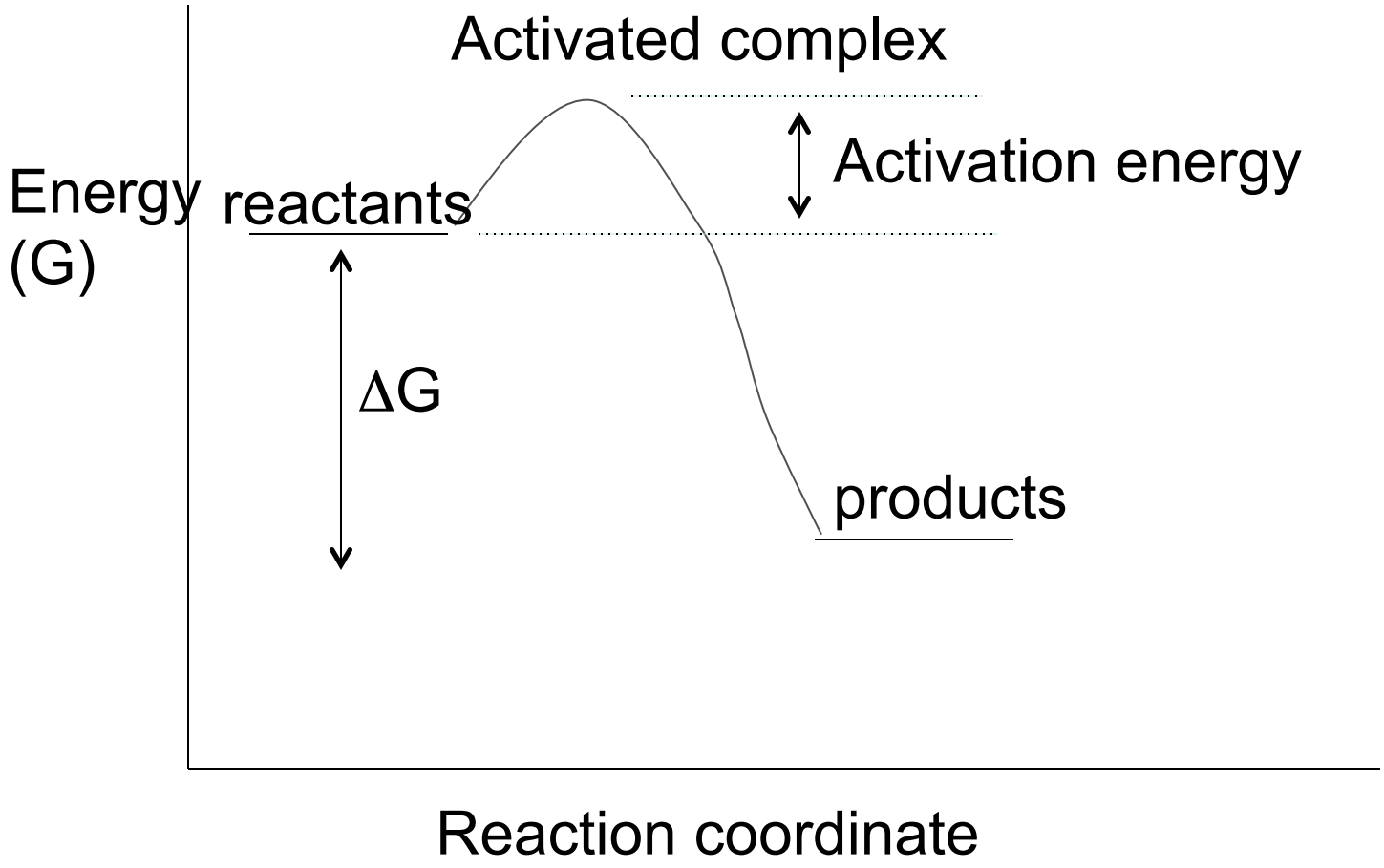
1. will it go (ΔG -)
2. How far will it go? ($\Delta G=0$)

1. By what route (mechanism)
2. How fast will it go (rate)

Charting the path of a reaction, One molecule at a time.



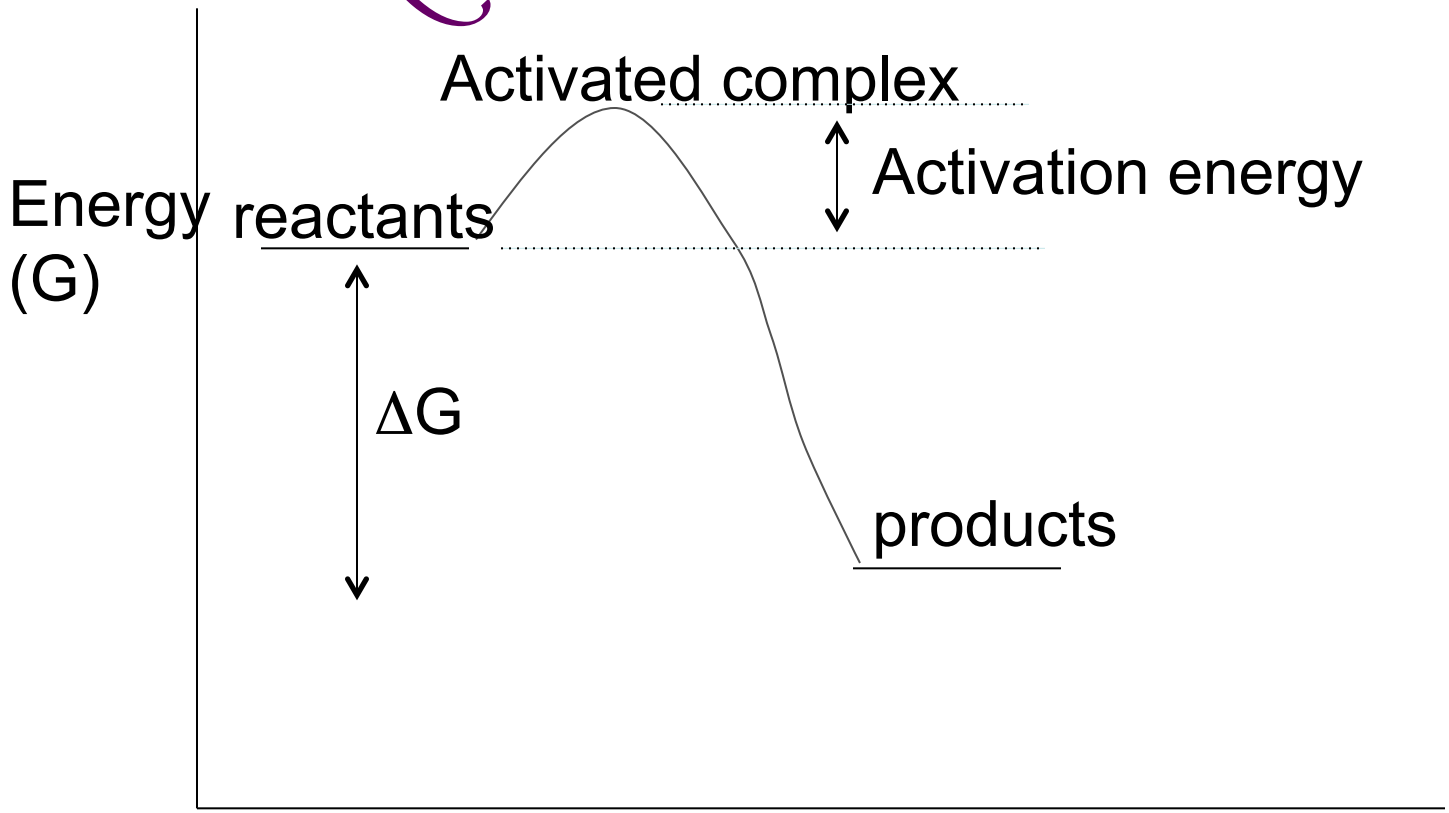
Reaction coordinate.



NO_2 CO O—N---O----C—O NO CO_2

Reactants activated complex products

Reaction coordinate.



NO_2 CO O—N---O----C—O NO CO_2

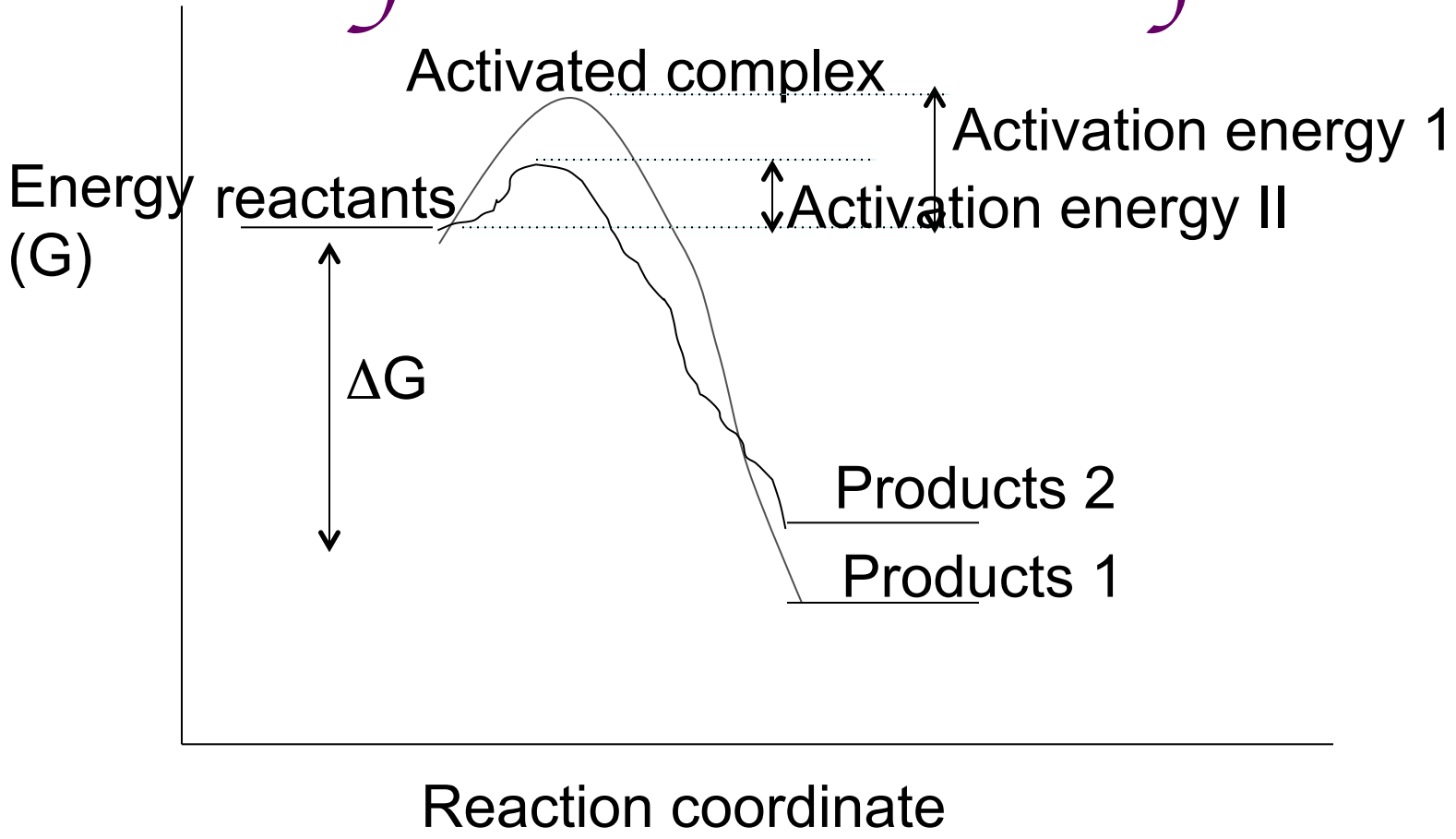
Reactants activated complex products

For a reaction to happen: 1. species much collide

2. Must collide with enough E

3. Must be oriented right.

Thermodynamic vs. kinetic product.



Kinetic product: smaller hill to climb, higher E product
- not enough E, Kinetic product.

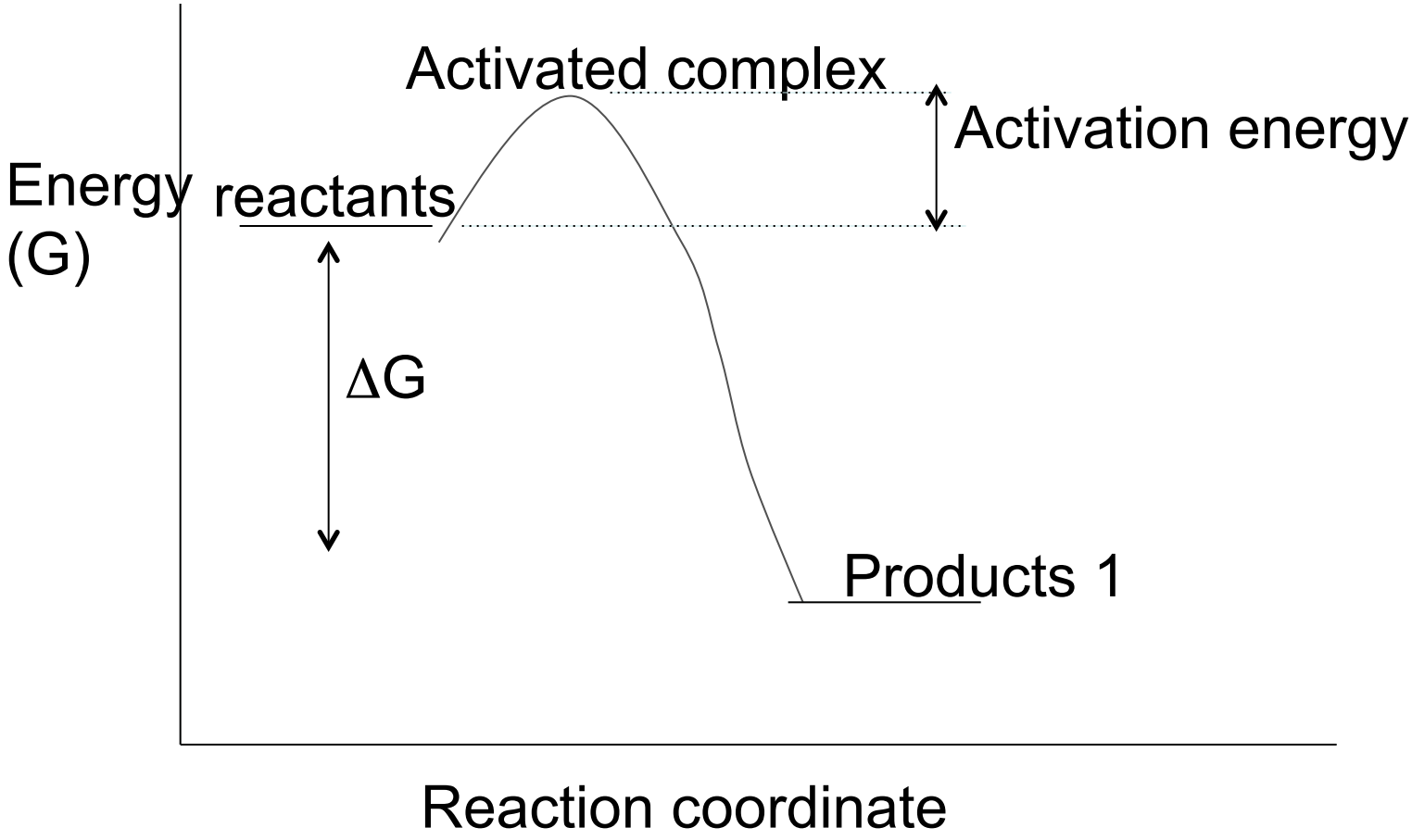
Thermodynamic product: Higher hill to climb, lower E product.
Plenty of E, thermodynamic product.

Thermodynamics: it can happen
Kinetics: When?

Chemical kinetics How fast will it go?

The more activated complexes formed, the faster the reaction.

1. Increase collision frequency (higher concentration)
2. Increase collision energy (higher T).



Chemical kinetics: Concentration

Back to our example:

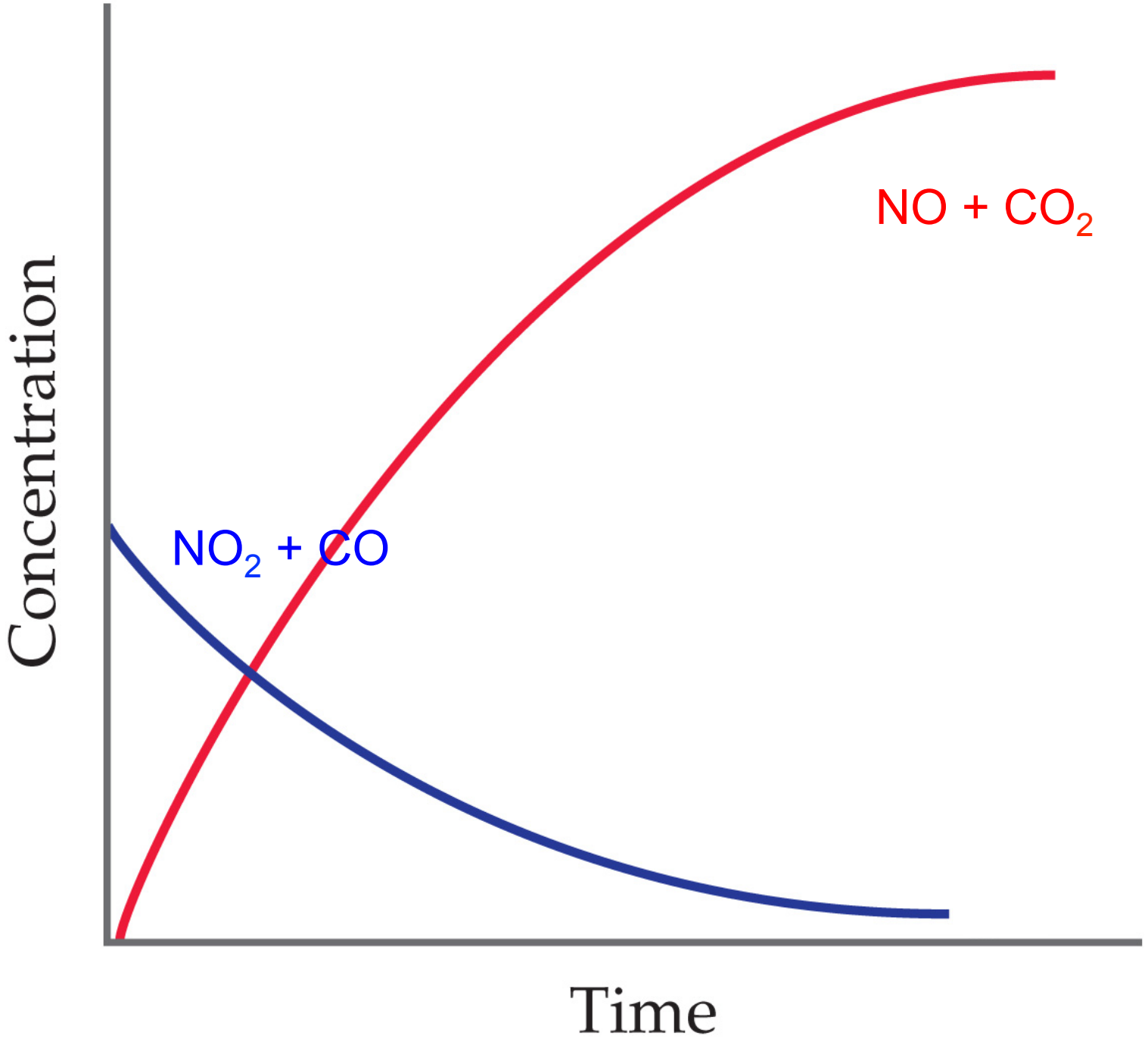
$NO_2 + CO \rightarrow NO + CO_2$

The rate depends on number of collisions of the "right type"
More reactants, more collisions so:

Rate is proportional to $[NO_2]$ AND [CO]
(brackets mean concentration)

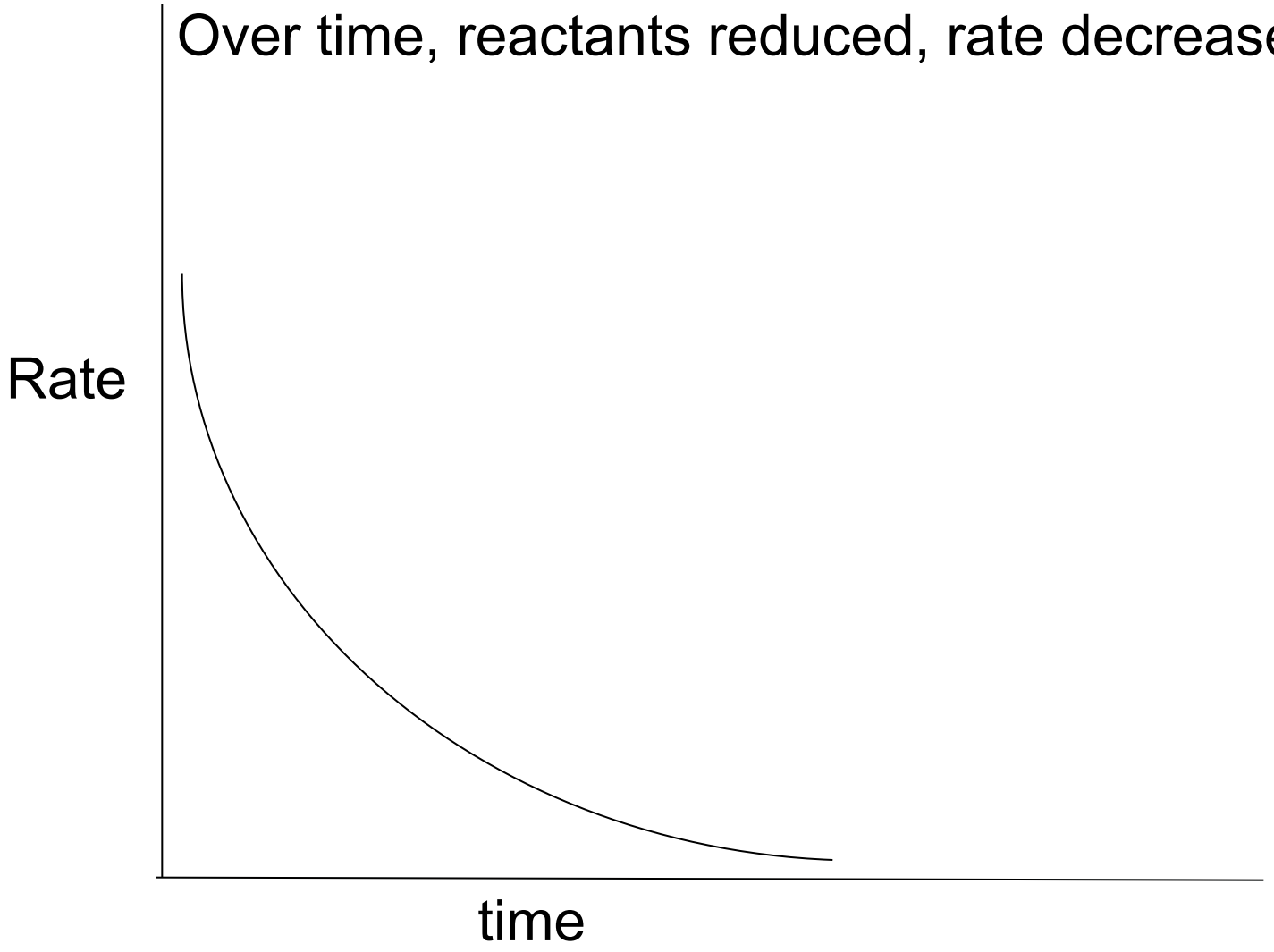
So rate = $k[NO_2][CO]$ where k is *rate constant.*

This is a rate equation. What is rate?:
Rate = change in amount/time (amount can be react. or prod.)

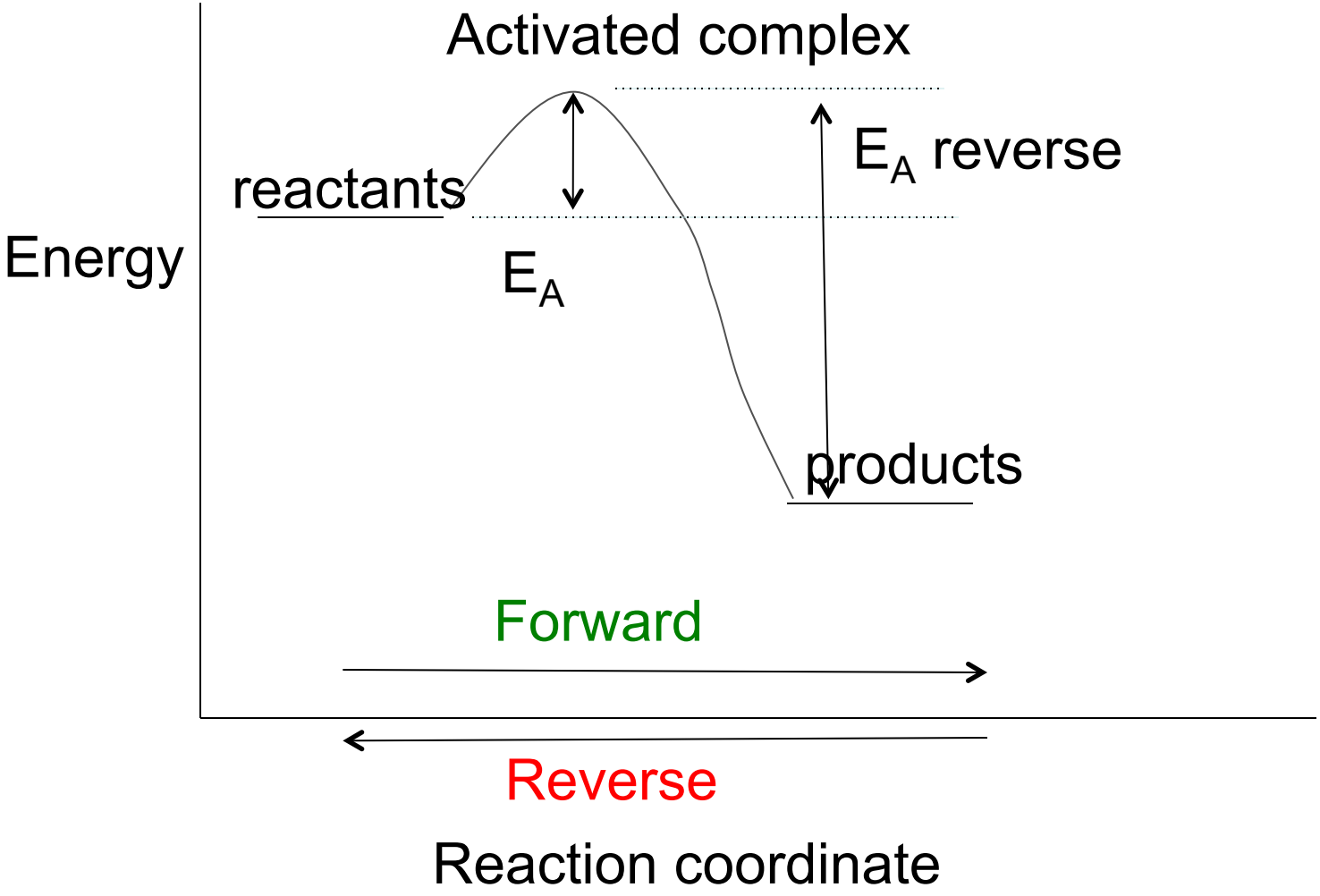


Rate over time:

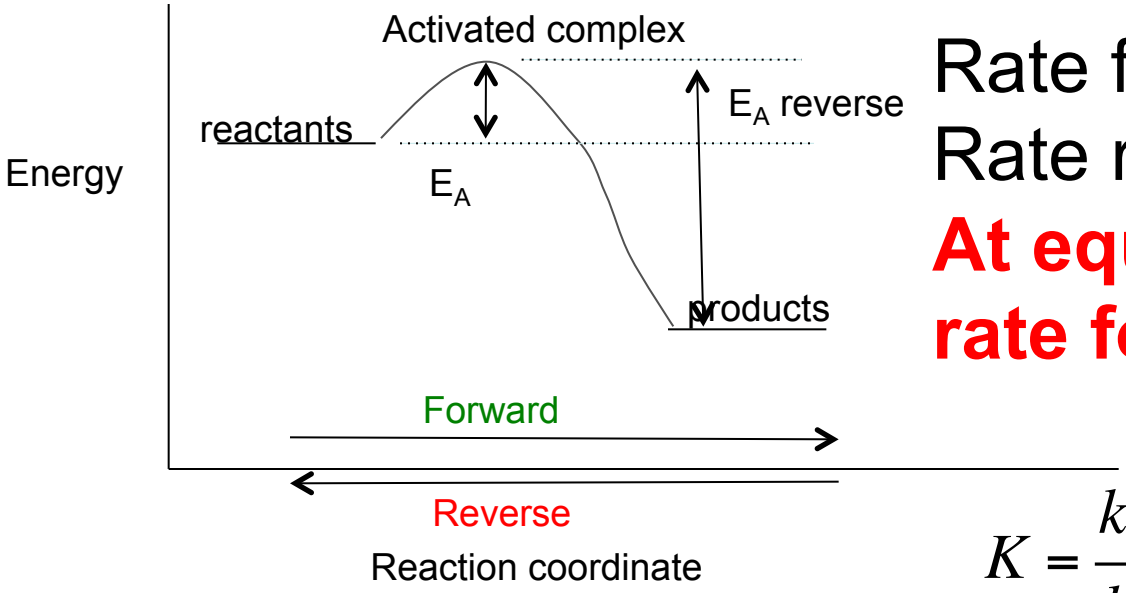
Over time, reactants reduced, rate decreases.



Charting the path of a reaction, Both backwards and forwards.



Charting the path of a reaction, Both backwards and forwards.



Rate forward $=k_f[\text{reactants}]$

Rate reverse $= k_r[\text{products}]$

At equilibrium ($\Delta G=0$)

rate forward = rate reverse.

So:

$$K = \frac{k_f}{k_r} = \frac{[\text{products}]}{[\text{reactants}]}$$

For example:

$$NO_2 + CO \rightarrow NO + CO_2$$

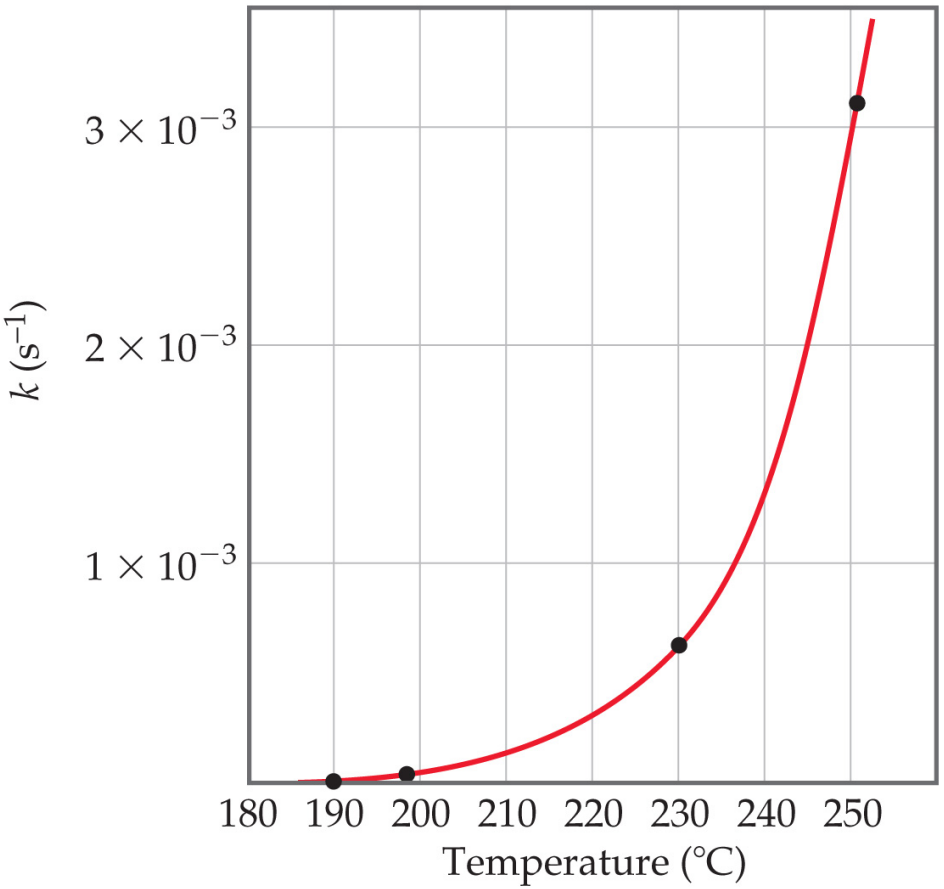
$$K = \frac{k_f}{k_r} = \frac{[NO][CO_2]}{[NO_2][CO]}$$

K is called an equilibrium constant

Factors That Affect Reaction Rates

- Temperature
  - At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy.

Temperature and Rate



Generally, as temperature increases, so does the reaction rate.

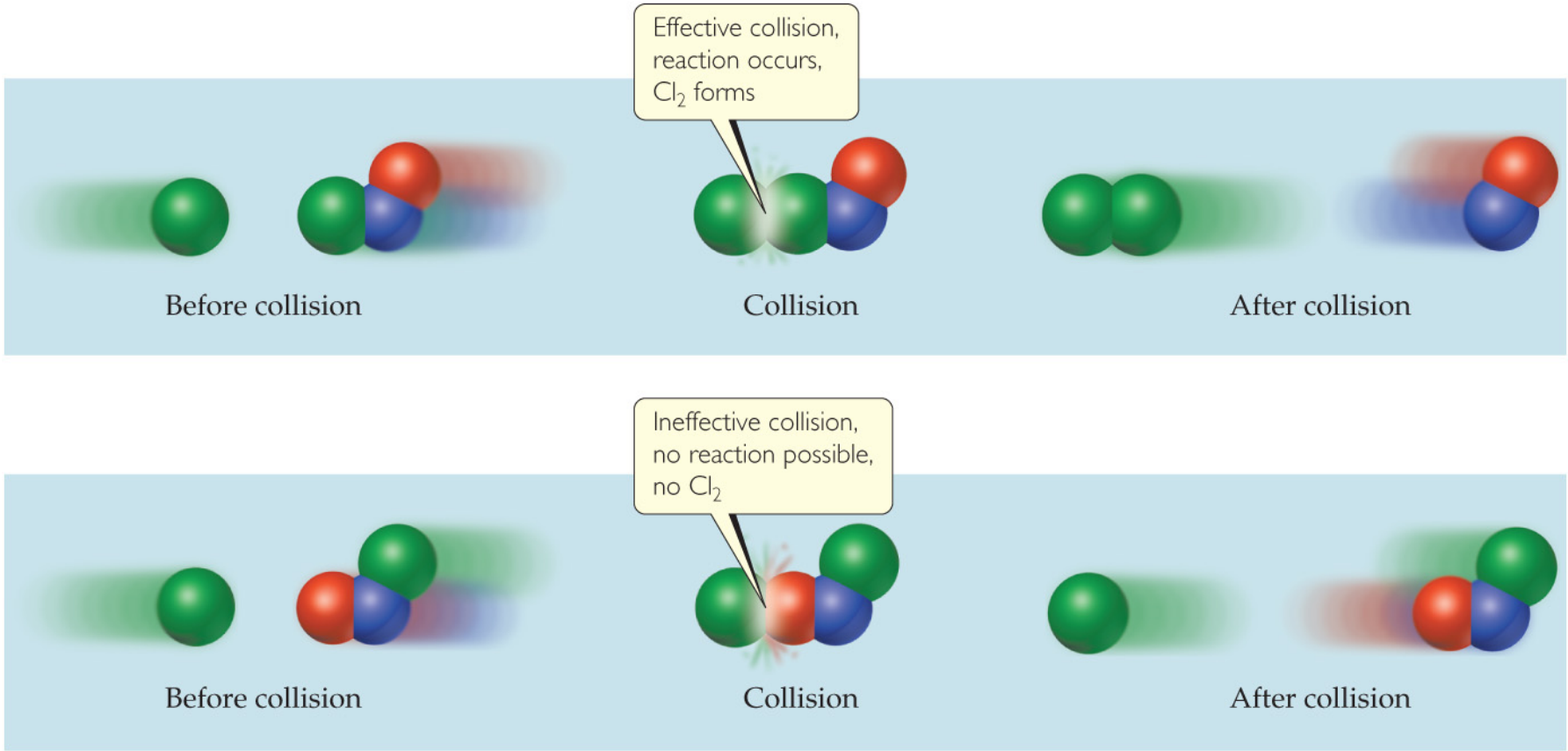
This is because *k* is temperature-dependent.

The Collision Model

- In a chemical reaction, bonds are broken and new bonds are formed.
- Molecules can only react if they collide with each other.

The Collision Model

Furthermore, molecules must collide with the correct **orientation** and with enough **energy** to cause bond breakage and formation.



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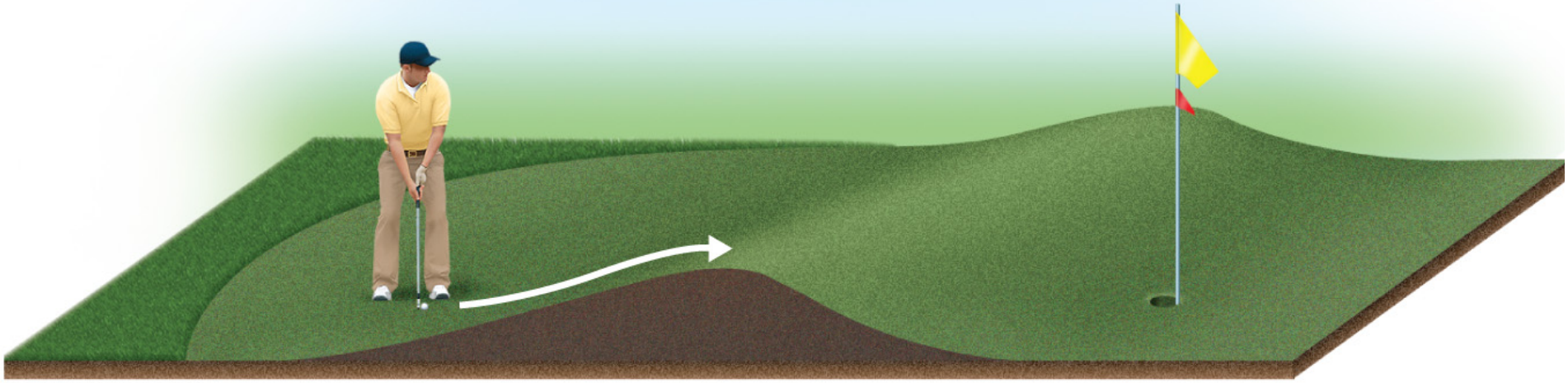
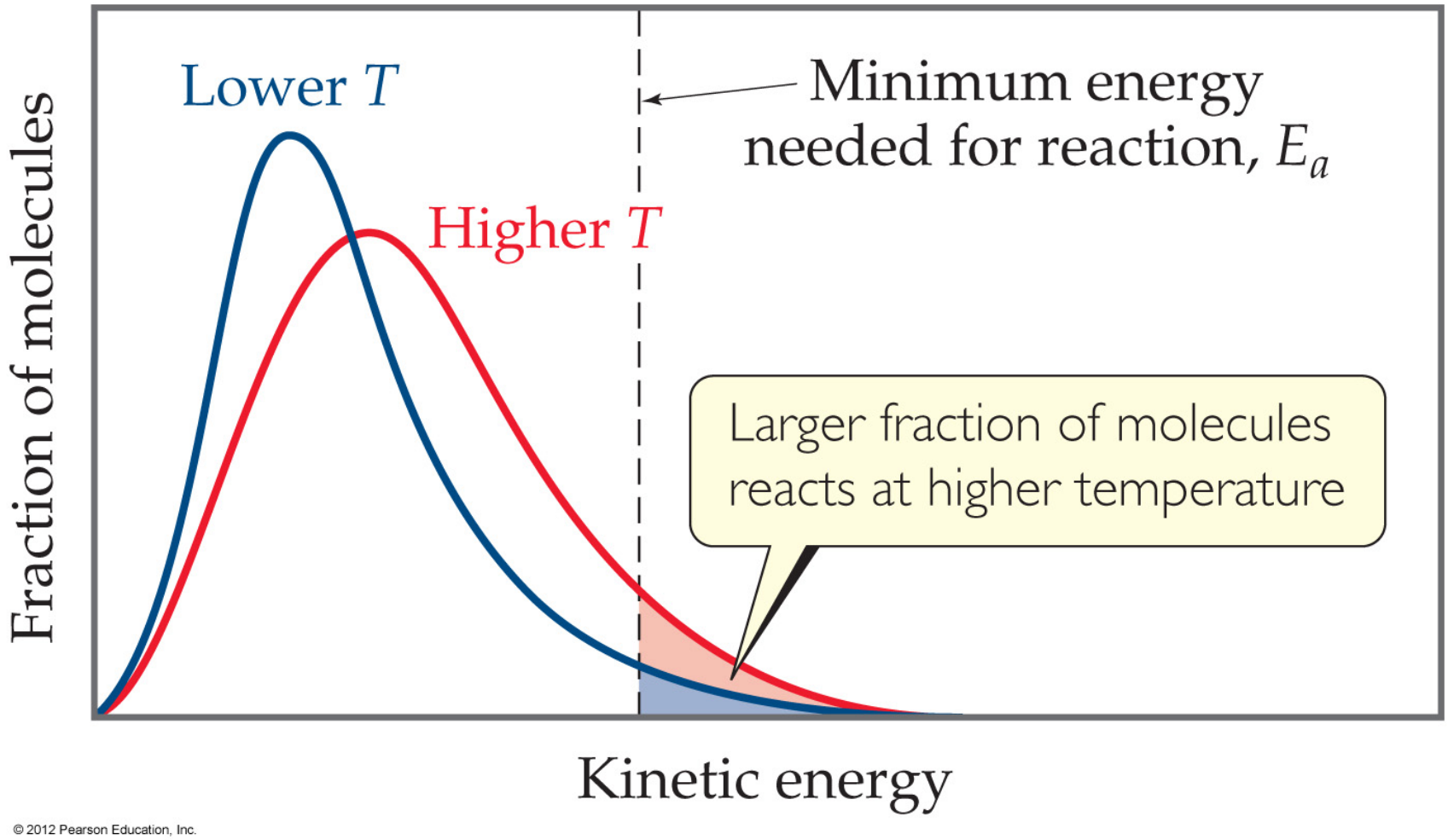
Activation Energy

- the **activation energy**, E_a.
- Hit the ball hard enough, or it doesn't go over the hill
- A bogey for you.

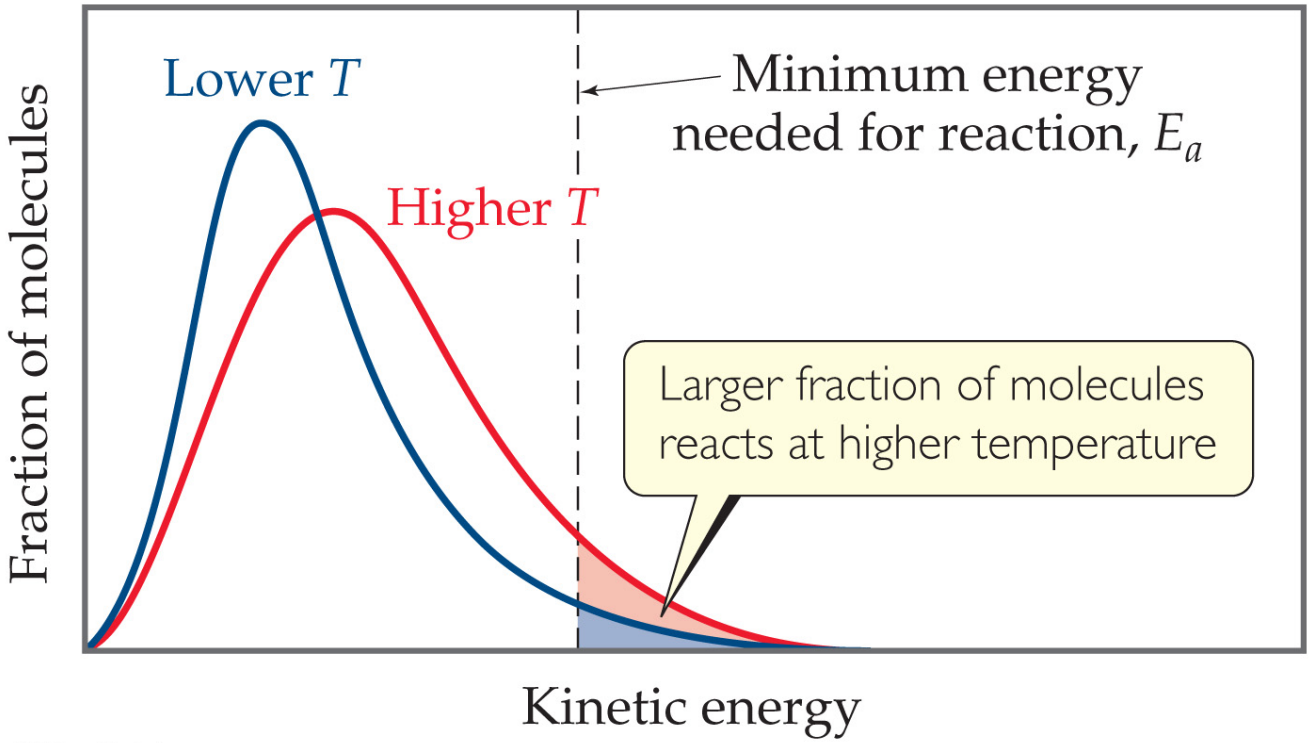


Temperature and kinetic E.



- Higher T, more K.E. More molecules with enough E to climb E_A barrier.

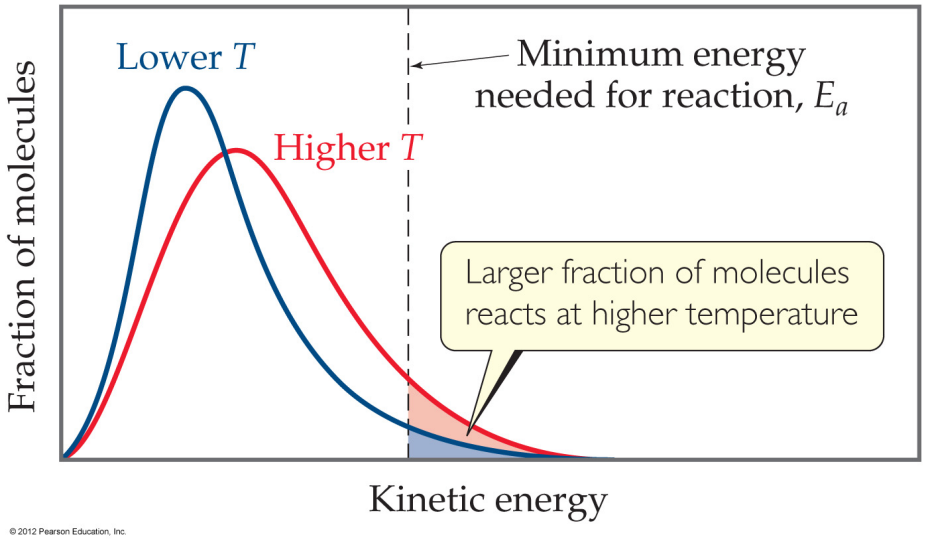
Maxwell–Boltzmann Distributions



- As the temperature increases, the curve flattens and broadens.
- Thus, at higher temperatures, a larger population of molecules has higher energy.

Maxwell–Boltzmann Distributions

- as the temperature increases, so does the fraction of molecules that can overcome the activation-energy barrier.



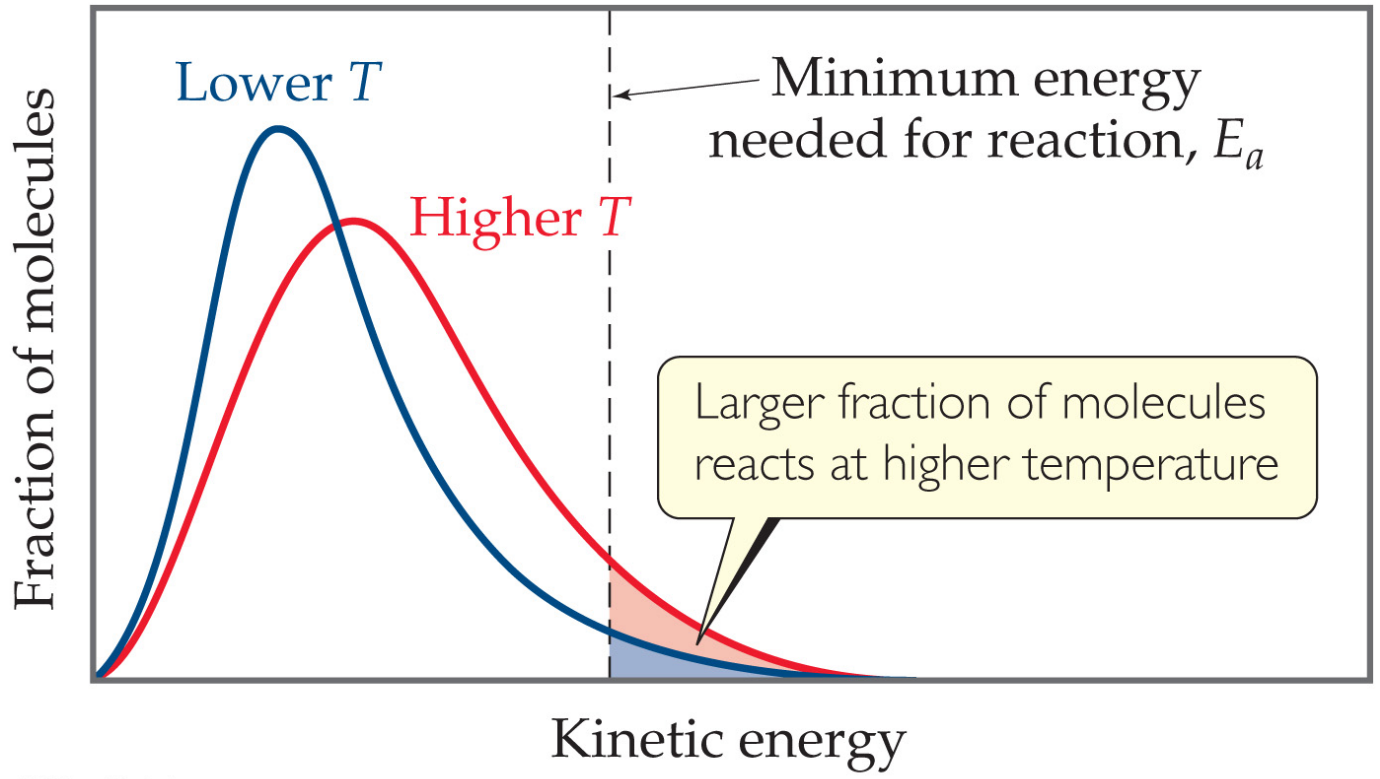
- reaction rate increases.

Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression

$$f = e^{-E_a/RT}$$

Where R is the gas constant and T is the Kelvin temperature.



Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between k and E_a:

$$k = Ae^{-E_a/RT}$$

$$\text{Rate} = Ae^{-E_a/RT}[\text{reactants}]$$

For our example: $\text{Rate} = Ae^{-E_a/RT}[NO_2][CO]$

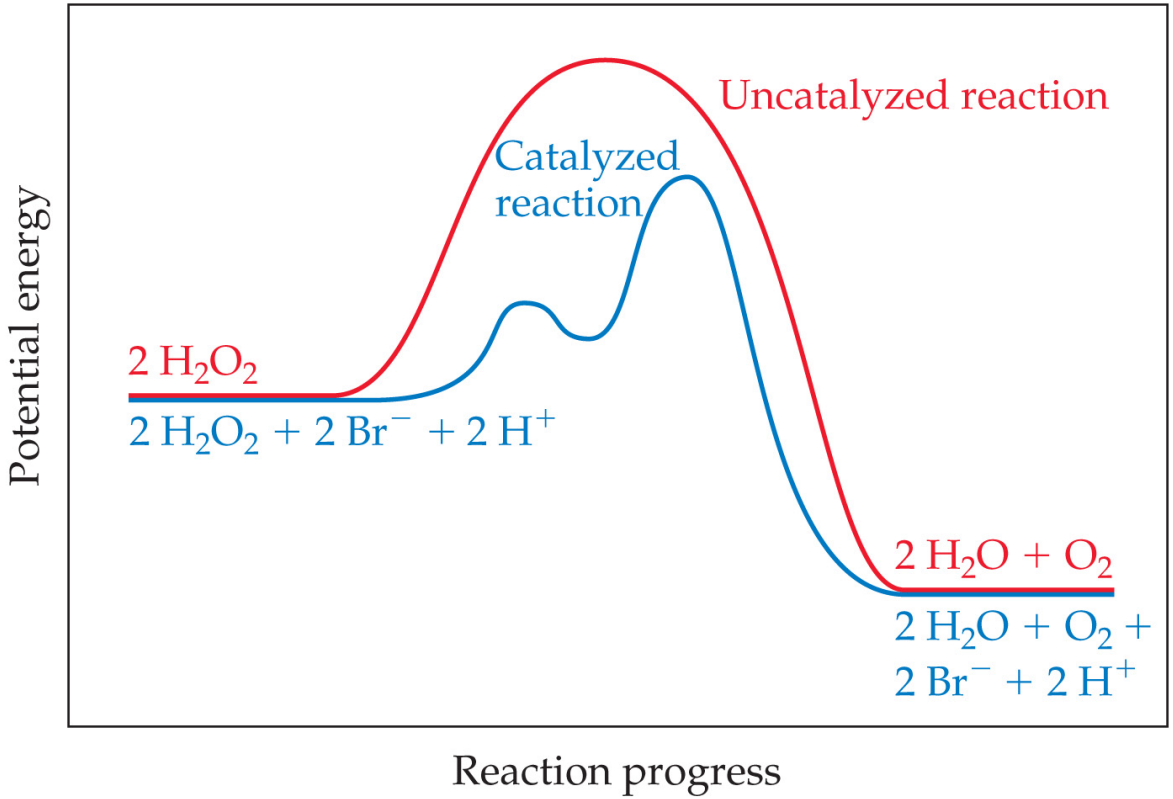
where A is the **frequency factor**, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

Factors That Affect Reaction Rates

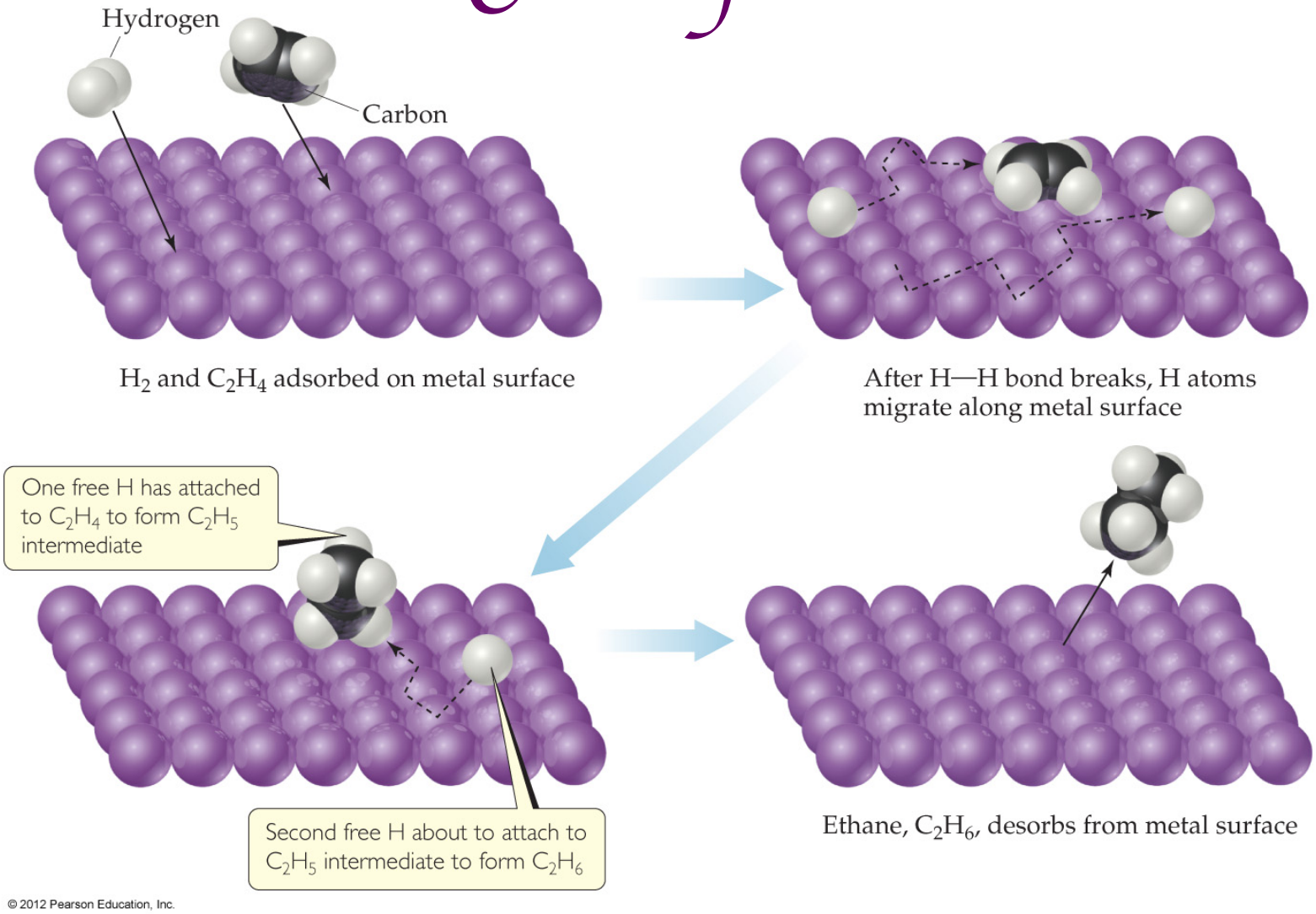
- Presence of a catalyst.
  - Catalysts speed up reactions by changing the mechanism of the reaction.
  - Catalysts are not consumed during the course of the reaction.

Catalysts

- Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.
- Catalysts change the mechanism by which the process occurs.

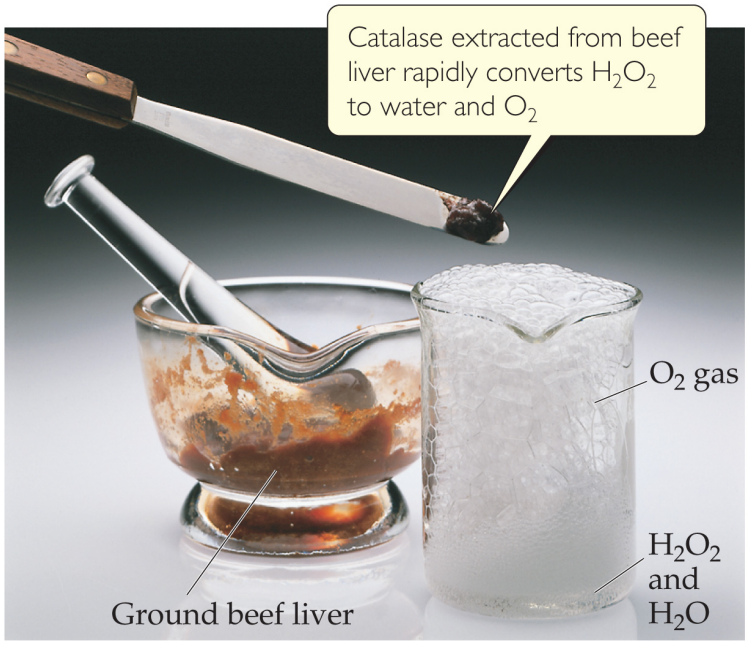


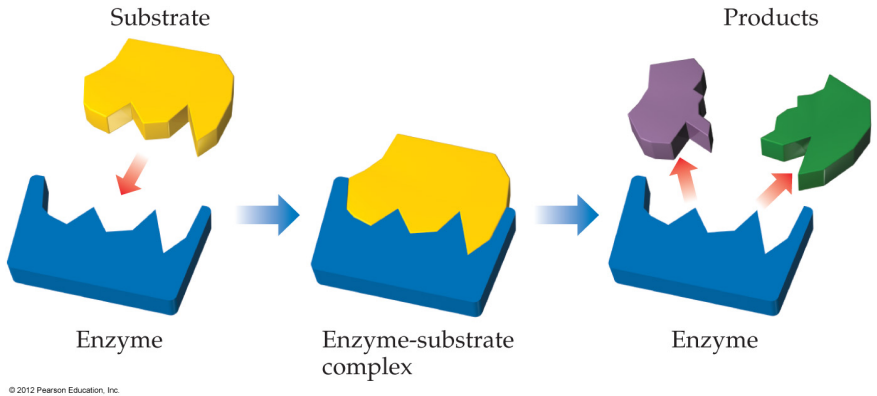
Catalysts



One way a catalyst can speed up a reaction is by holding the reactants together and helping bonds to break.

Enzymes





- Enzymes are catalysts in biological systems.
- The substrate fits into the active site of the enzyme much like a key fits into a lock.

Unit 35 A quick tour of equilibrium

- An example of a reaction:

$2NO + O_2 \rightleftharpoons 2NO_2$

If the system is in *dynamic equilibrium*

Rate forward = rate reverse

Therefore no change over time

$$\Delta G = 0$$

$$K = \frac{k_f}{k_r} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

A quick tour of equilibrium, Q

- But what if the reaction is NOT at equilibrium?
  - Its handy to define a measure of how far you are from Equilibrium.

The ***Reaction Quotient Q***

$$\Delta G = 0$$

$$Q = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[NO_2]^2}{[NO]^2[O_2]} \text{ at any point, equilibrium or not.}$$

If Q = K, system at equilibrium

If Q > K, too much product, reaction heads backward.

If Q < K, too much reactant, reaction heads forward.

Lechatelier's principle

- Perturbations from equilibrium, what happens?
  - Take a system at equilibrium, do something to it that takes it away from equilibirium, what will it do?

It will change in a way that brings it back to equilibrium. **Lechatelier's principle. Everything is moving toward equilibrium where** $\Delta G = 0$

Example: Change concentration. Start at equilbrium:

$2NO + O_2 \rightleftharpoons 2NO_2$

Add more oxygen, get more product.

Add more NO_2, get more reactants.

Example problem

Example 1: For the following reaction, the concentrations in $molL^{-1}$ are: PCl_5, 3 M, PCl_3, 2 M, $Cl_2$1 M at equilibrium. Now add 1 mole Cl_2 per liter. What are the final concentrations?

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
equil	3		2		1
start	3		2		2
Change	+x		-x		-x
End	3+x		2-x		2-x

Example problem

Example 1: PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
equil		3		2		1
start		3		2		2
Change		+x		-x		-x
End		3+x		2-x		2-x
		3.75		1.25		1.25

$$K = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{[2][1]}{3} = \frac{2}{3}$$

$$K = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{[2-x][2-x]}{[3+x]} = \frac{2}{3}$$

Solve for x:

x = 0.75 (trial and error)

Example problem

Example 2: $2SO_2 + O_2 \rightleftharpoons 2SO_3$

equil	1	5	5
start	2	5	5
Change	-2x	-x	+2x
End	2-2x	5-x	5+2x

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[5]^2}{1^2[5]} = 5$$

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[5+2x]^2}{[2-2x]^2[5-x]} =$$

Solve for x:

x = 0.4 (trial and error)

Change in Temperature

Direction depends on whether the reaction is:

endo

exothermic.

Endothermic ($\Delta H+$) heat is required. Increase T, reactions moves to *products* (sucks in heat)

Exothermic ($\Delta H-$) , heat is given off, Increase T, reaction moves to *reactants (again to suck in heat)*

Change in volume/pressure

An increase in P, or decrease in V, causes equilibrium to shift to side that takes up less Volume (less gas, more liquid/solid).

Example:

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

Increase P, move to products (less gas to compensate for higher P)

Increase V, move to reactants (more gas to occupy expanded space).

Catalyst. Does NOTHING to equilibrium, just makes reaction faster

Examples

$CO(g) + 2H_2(g) \rightleftharpoons 2CH_3OH(g)$ $\Delta H = -18$ kJ

Increase P

Increase T

More CO

$2NO(g) + Cl_2(g) \rightleftharpoons 2NOH(g)$ $\Delta H = -77$ kJ

Increase T

Remove NO

Increase T

Examples

$CO(g) + 2H_2(g) \rightleftharpoons 2CH_3OH(g)$ $\Delta H = -18$ kJ

Increase P To products

Increase T toward reactants

More CO Toward products

$2NO(g) + Cl_2(g) \rightleftharpoons 2NOH(g)$ $\Delta H = -77$ kJ

Increase T Toward reactants

Remove NO Toward reactants

Examples

$2C(s) + O_2(g) \rightleftharpoons 2CO(g) \quad \Delta H = -220\ kJ$

Add more C(s)

Increase P

Examples

$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ $\Delta H = -220$ kJ

Add more C(s) Toward Products

Increase P Toward reactants