

Chemical Kinetics

- Kinetics is the study of how fast chemical reactions occur.

There are 4 important factors which affect rates of reactions:

- reactant concentration
 - temperature
 - action of catalysts
 - surface area
- Our goal is to understand chemical reactions at the molecular level.

Reaction Rate

- Speed of a reaction is measured by the change in concentration with time.

by Dan Reid

Reaction Rate

- For the reaction “ $A \rightleftharpoons B$ ” there are two ways of measuring rate:
 - (1) the speed at which the reactants disappear
 - (2) the speed at which the products appear
- Reactions are reversible, so as products accumulate they can begin to turn back into reactants.
- Early on the rate will depend on only the amount of reactants present. We want to measure the reactants as soon as they are mixed.
- The most useful (and general) way of measuring the rate of the reaction is in terms of change in concentration per unit time...

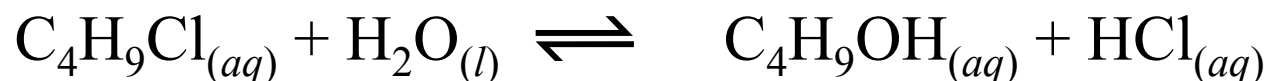
$$\text{Rate} = \Delta[A]/\Delta t$$

Most Common Units... $\text{Rate} = \text{M/s}$

(Remember...Molarity (M) = moles/Liter)

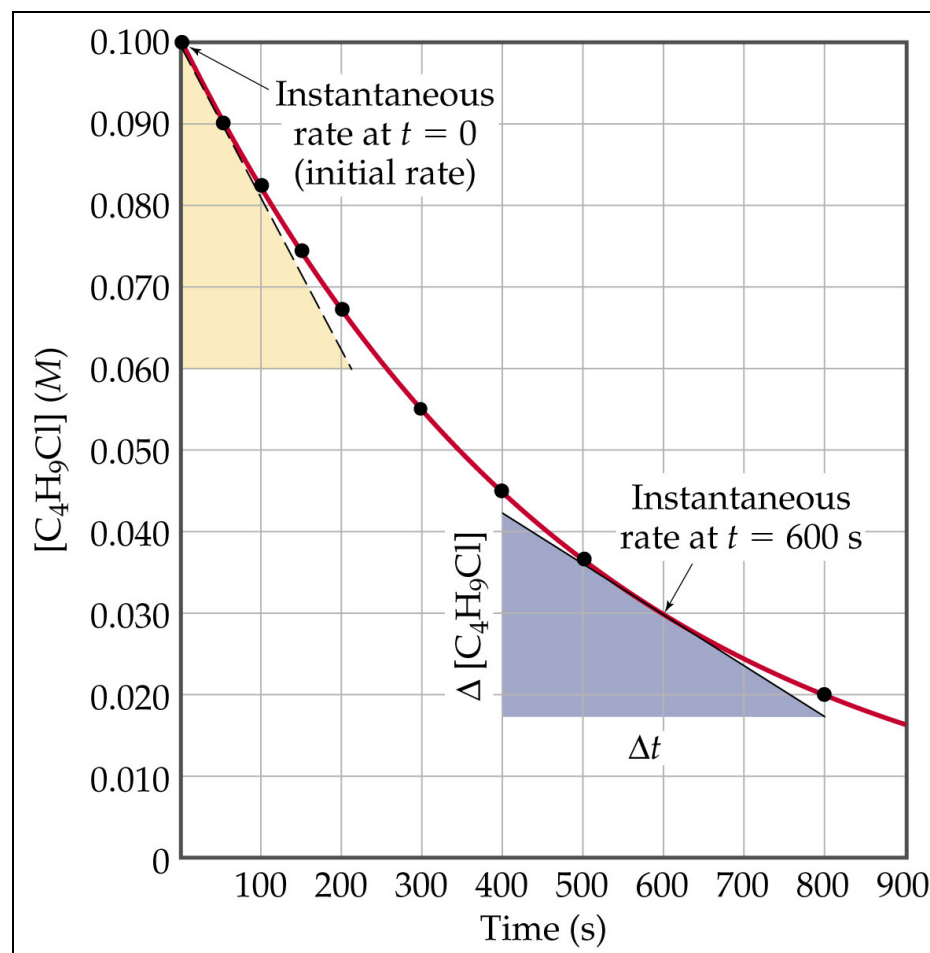
Reaction Rate

- Here's an example of a reaction...



- We can plot $[\text{C}_4\text{H}_9\text{Cl}]$ versus time...

- The average rate of a reaction decreases with time.
- The rate at any instant in time (instantaneous rate) is the slope of the tangent to the curve.
- Instantaneous rate is different from average rate, so when we refer to the rate of a reaction, we will be assuming it's the instantaneous rate unless otherwise told.



Reaction Rate

- Here's another way of looking at reaction rates...



- Notice that for every 1 mole of O_2 that appears, 4 x as many moles of NO_2 will also appear. In the meantime, twice as many moles of N_2O_5 will be disappearing as moles of O_2 forming.

- Changes in concentrations of the reactants and/or products is inversely proportional to their stoichiometric proportions.

- This means that the rate of the reaction could be written like this...

$$\text{Rate} = -\frac{1}{2} \Delta [\text{N}_2\text{O}_5]/\Delta t = \frac{1}{4} \Delta [\text{NO}_2]/\Delta t = \Delta [\text{O}_2]/\Delta t$$

* (Notice the negative sign on the rate of $[\text{N}_2\text{O}_5]$ reminds us that it is disappearing.)

- In general, for a reaction that looks like this... $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

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

Rate Law

- In general, rates of reactions increase as concentrations increase since there are more collisions occurring between reactants.
- The overall concentration dependence of reaction rate is given in a **rate law** or rate expression.
- Here's what a general rate law for a reaction will look like...

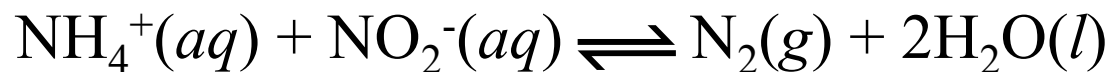
$$\text{Rate} = k [A]^m [B]^n$$

- [A] & [B] represent the reactants.
- The exponents m and n are called “**reaction orders**”.
- The proportionality constant k is called the **rate constant**.
- The **overall reaction order** is the sum of the reaction orders.
- The overall “order of reaction” is therefore...

$$m + n + \dots$$

Rate Law Example

- Consider the following reaction:



- Let's say that the following observations from several experiments were made...
 - as $[\text{NH}_4^+]$ doubles the rate doubles with $[\text{NO}_2^-]$ constant.
 - as $[\text{NO}_2^-]$ doubles the rate doubles with $[\text{NH}_4^+]$ constant.
- The rate of this reaction would be expressed as....

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

- The reaction is said to be “first order” with respect to $[\text{NH}_4^+]$ and “first order” with respect to $[\text{NO}_2^-]$.
- But the overall order of the reaction is said to be “second order.”
- Reaction rates come from experiment data, not stoichiometry!

Order of Reactions

- A reaction is **zero order** in a reactant if the change in concentration of that reactant produces no effect.
- A reaction is **1st order** if doubling the concentration causes the rate to double.
- A reaction is **2nd order** if doubling the concentration causes a quadruple increase in rate.
 - 3rd order**...doubling concentration leads to 2^3 (or 8 times) the rate.
- Note-- The rate constant, k , does not depend on concentration!
- Once we have determined the rate law and the rate constant, we can use them to calculate initial reaction rates under any set of initial concentrations. (See Practice Problems for examples.)

Change of Concentration with Time

- Our Goal: to convert the rate law into a convenient equation to give concentrations as a function of time...(the book has the derivation, and it involves calculus, so we will skip to the conclusion)...

For 1st order reactions: $\ln[A]_t = -kt + \ln[A]_0$

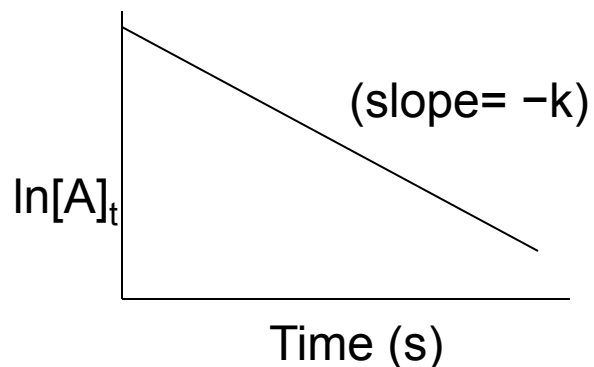
where $[A]_t$ = concentration of $[A]$ after some time, t

k = reaction rate constant in units of s^{-1}

t = time in seconds

$[A]_0$ = initial concentration of A

- This equation has the general form for a straight line, $y=mx+b$, so a plot of $\ln[A]_t$ vs. t is a straight line with slope $(-k)$ and intercept $\ln[A]_0$.



Change of Concentration with Time

For 2nd order reactions: $1/[A]_t = kt + 1/[A]_0$

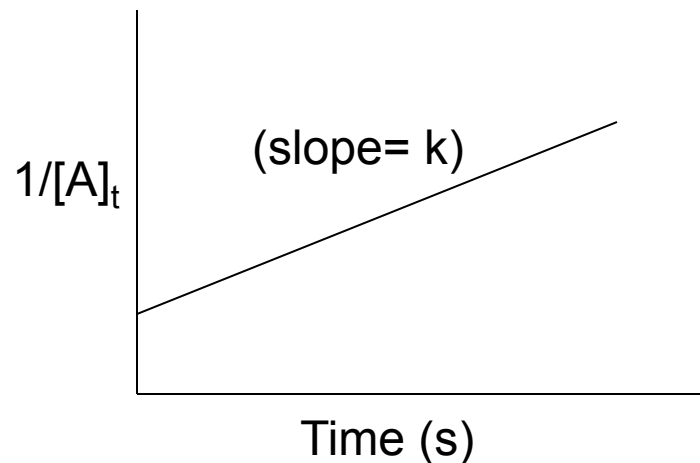
where $[A]_t$ = concentration of $[A]$ after some time, t

k = reaction rate constant in units of $M^{-1}s^{-1}$

t = time in seconds

$[A]_0$ = initial concentration of A

- This equation has the general form for a straight line, $y=mx+b$, so a plot of $1/[A]_t$ vs. t is a straight line with slope (k) and intercept of $1/[A]_0$.



Change of Concentration with Time

For Zero order reactions:

$$\text{Rate} = k[A]^0 = k$$

Rate does not change with concentration.

$$\text{So... } [A]_t = -kt + [A]_0$$

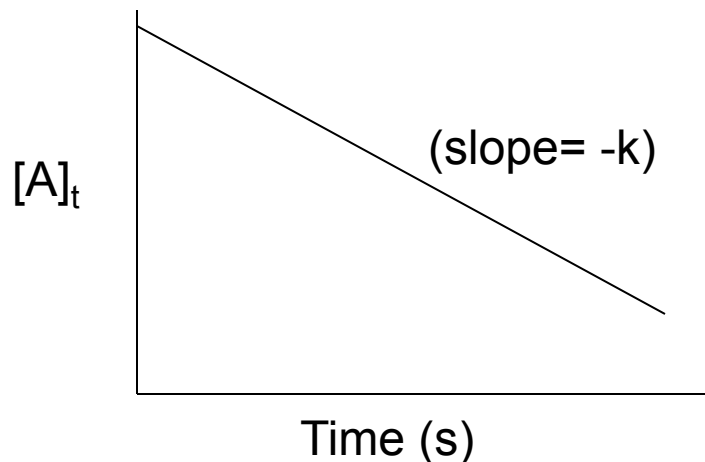
where $[A]_t$ = concentration of $[A]$ after some time, t

k = reaction rate constant in units of M/s

t = time in seconds

$[A]_0$ = initial concentration of A

- This equation has the general form for a straight line, $y=mx+b$, so a plot of $[A]_t$ vs. t is a straight line with slope $(-k)$ and intercept $[A]_0$.



Half-Life

- **Half-life** is the time taken for the concentration of a reactant to drop to half its original value.
- For a first order process, half life, $t_{1/2}$ is the time taken for $[A]_0$ to reach $\frac{1}{2}[A]_0$...(see the book for the next equation's derivation.)

$$t_{1/2} = \frac{-\ln(1/2)}{k} = \frac{0.693}{k} \quad \text{where } k = \text{the rate constant} \underline{\hspace{2cm}}$$

- For a 2nd order reaction, half-life depends on the reactant concentrations... $t_{1/2} = 1/k[A]_0$
- For Zero order reactions... $t_{1/2} = [A]_0 / 2k$

Collision Model

- Most reactions speed up as temperature increases.
 - Example: food spoils when not refrigerated.
- Since the rate law equation has no temperature term in it, the rate constant, k , must depend on temperature.
- The **collision model** assumes that in order for molecules to react they must collide.
 - The greater the number of collisions the faster the rate.
 - The more molecules present, the greater the probability of collisions and the faster the rate.
 - The higher the temperature, the more energy available to the molecules and the faster the rate.
 - Complication: not all collisions lead to products. In fact, only a small fraction of collisions lead to product.

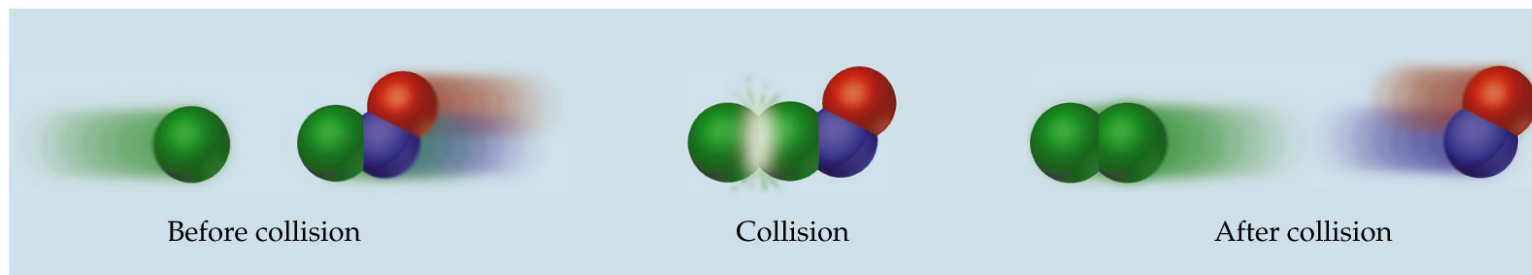
The Orientation Factor

- In order for reaction to occur the reactant molecules must collide in the correct orientation and with enough energy to form products.

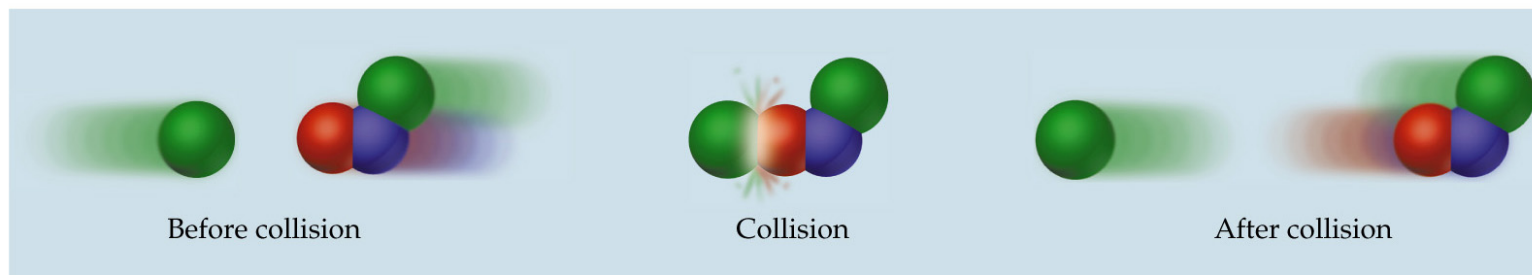
- For Example:



- There are two possible ways that Cl atoms and NOCl molecules can collide; one is effective and one is not.



(a) Effective collision



(b) Ineffective collision

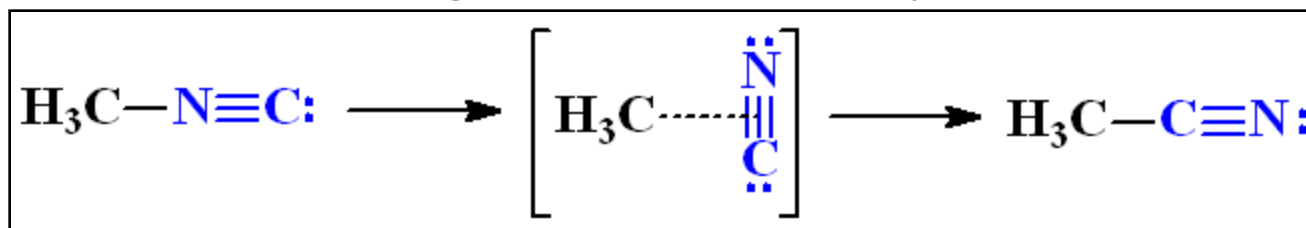
Activation Energy

- Arrhenius: molecules must possess a minimum amount of energy to react. Why?
 - In order to form products, bonds must be broken in the reactants. Bond breakage requires energy.
 - Molecules moving too slowly, with too little kinetic energy, don't react when they collide.
- Activation energy, E_a , is the minimum energy required to initiate a chemical reaction.
 - E_a will vary with the reaction.

Next we will look at an example of E_a .

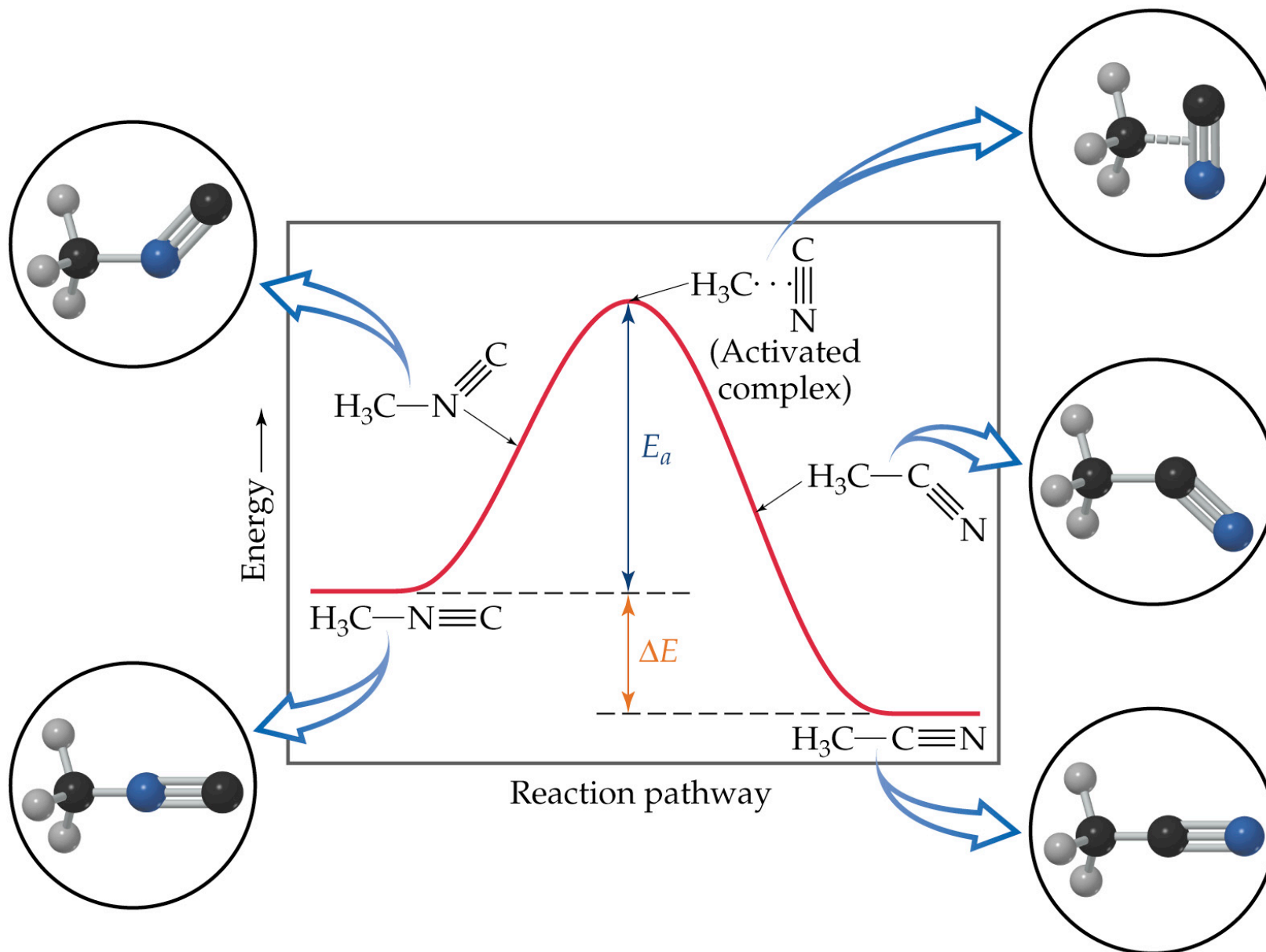
Activation Energy

- Consider the rearrangement of methyl isonitrile:



- In $\text{H}_3\text{C}-\text{N}\equiv\text{C}$, the $\text{C}-\text{N}\equiv\text{C}$ bond bends until the $\text{C}-\text{N}$ bond breaks and the $\text{N}\equiv\text{C}$ portion is perpendicular to the H_3C portion. This structure is called the **activated complex** or **transition state**.
- The energy required for the above twist and break is the **activation energy**, E_a .
- Once the $\text{C}-\text{N}$ bond is broken, the $\text{N}\equiv\text{C}$ portion can continue to rotate forming a $\text{C}-\text{C}\equiv\text{N}$ bond.

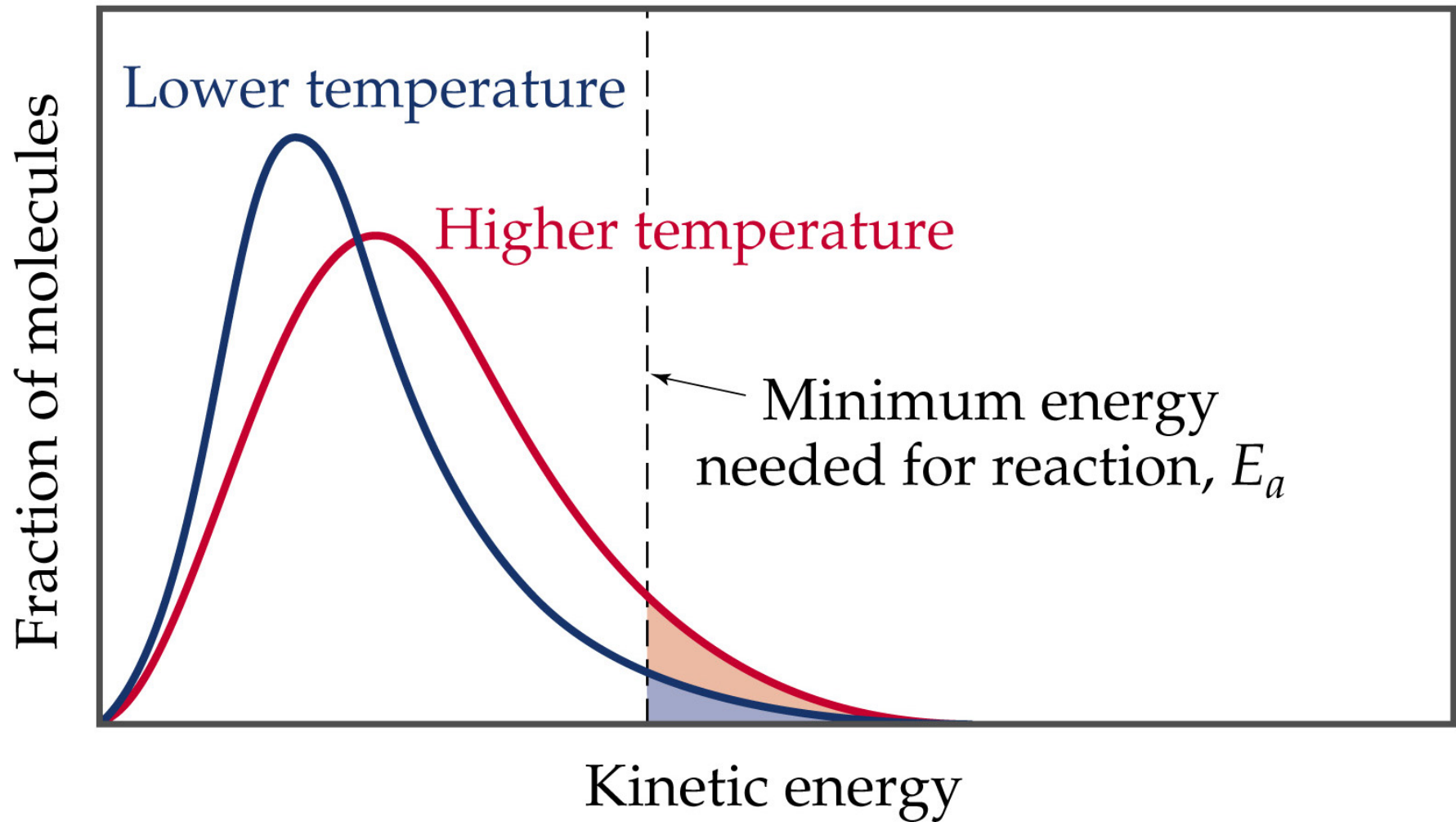
* Here's what the reaction looks like in terms of a graph of the energies that are involved in the process...



Activation Energy

- The change in energy, ΔE , for the reaction is the difference in energy between CH_3NC and CH_3CN .
- The activation energy, E_a , is the difference in energy between reactants, CH_3NC , and the transition state.
- The rate depends on E_a . If the “hill” is taller, the reaction rate is slower. If the “hill” is shorter the rate is faster.
- Notice that if a forward reaction is exothermic... ($\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$), then the reverse reaction is endothermic... ($\text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{NC}$).
- The methyl isonitrile molecule needs to gain enough energy to overcome the activation energy barrier.
- From kinetic molecular theory, we know that as temperature increases, the total kinetic energy increases and the number of molecules with energy greater than E_a increases.
- So as long as the temperature is high enough, the reaction can make it “over the hill” and proceed.

Temperature vs. Energy of Activation



Reaction Mechanisms

- Up until now, we have only been concerned with the reactants and products. Now we will examine what path the reactants took in order to become the products.
- The **reaction mechanism** gives the path of the reaction.
- Mechanisms provide a very detailed picture of which bonds are broken and formed during the course of a reaction.

Elementary Steps & Molecularity

- **Elementary step**: any process that occurs in a single step.
- **Molecularity**: the number of molecules present in an elementary step.
 - **Unimolecular**: one molecule in the elementary step,
 - **Bimolecular**: two molecules in the elementary step, and
 - **Termolecular**: three molecules in the elementary step.

(It is uncommon to see termolecular processes...statistically improbable for an effective collision to occur.)

Rate Laws of Elementary Steps

- Since this process occurs in one single step, the stoichiometry can be used to determine the rate law!
- Law of Mass Action: The rate of a simple (one step) reaction is directly proportional to the concentration of the reacting substances.

TABLE 14.3 Elementary Steps and Their Rate Laws

Molecularity	Elementary Step	Rate Law
<i>Unimolecular</i>	$A \longrightarrow \text{products}$	$\text{Rate} = k[A]$
<i>Bimolecular</i>	$A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^2$
<i>Bimolecular</i>	$A + B \longrightarrow \text{products}$	$\text{Rate} = k[A][B]$
<i>Termolecular</i>	$A + A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^3$
<i>Termolecular</i>	$A + A + B \longrightarrow \text{products}$	$\text{Rate} = k[A]^2[B]$
<i>Termolecular</i>	$A + B + C \longrightarrow \text{products}$	$\text{Rate} = k[A][B][C]$

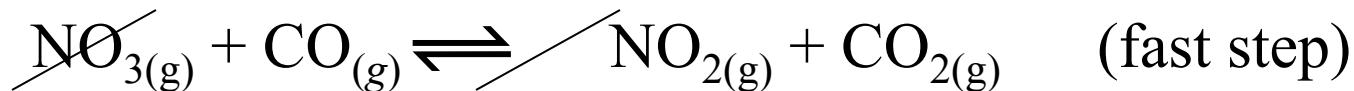
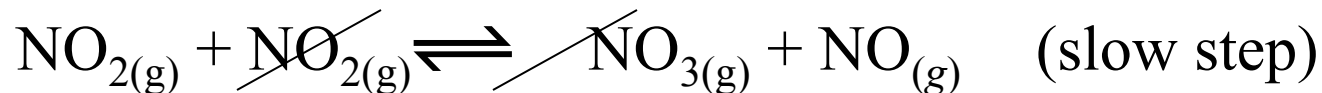
- Notice that the coefficients become the exponents.

Rate Laws for Multistep Mechanisms

- Most reactions proceed through more than one step:



- A proposed mechanism is as follows...



- Notice that if we add the above steps, we get the overall reaction:



- If a reaction proceeds via several elementary steps, then the elementary steps must add to give the balanced chemical equation.
- **Intermediate:** a species which appears in an elementary step which is not a reactant or product. They are formed in one elementary step and consumed in another...Our Example: $\text{NO}_{3(g)}$

Rate Laws for Multistep Mechanisms

- Often one step is much slower than the others. The slow step limits the overall reaction rate.
- This is called the **rate-determining step** of the reaction.
- This step governs the overall rate law for the overall reaction.
- In our previous example, the theoretical rate law is therefore...

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

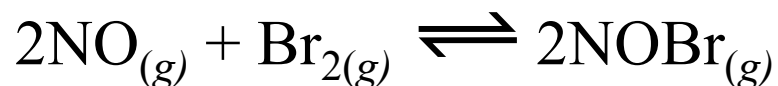
- The experimentally determined rate law is...

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

- This supports, (but does not prove), our mechanism.

Rate Laws for Multistep Mechanisms

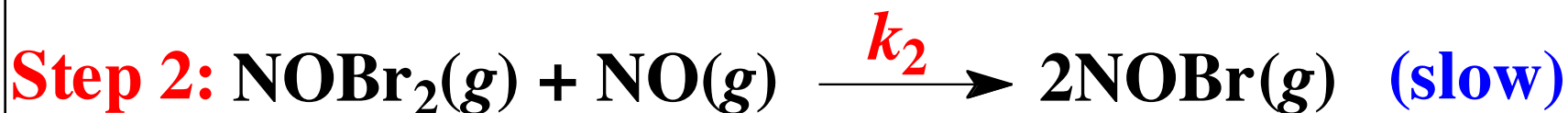
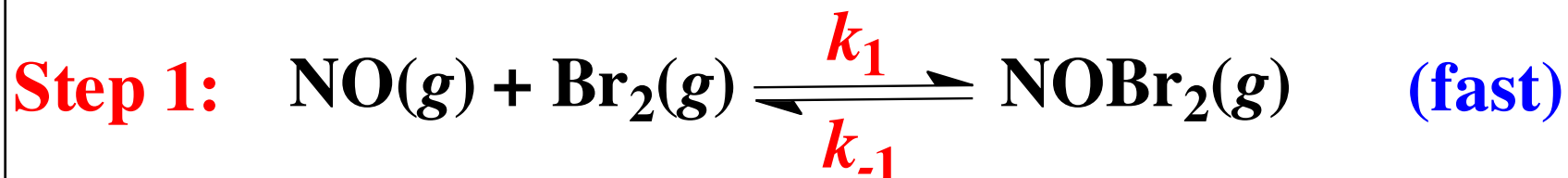
- Let's look at another example...



- The experimentally determined rate law is...

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

- Consider the following mechanism...



- The rate law is based on **Step 2**:

$$\text{Rate} = k_2[\text{NOBr}_2][\text{NO}]$$

Rate Laws for Multistep Mechanisms

- But we have a problem... This rate law depends on the concentration of an intermediate species.
- Intermediates are usually unstable and have low/ unknown concentrations. We need to find a way to remove this term from our rate law.
- So we have to express $[\text{NOBr}_2]$ in terms of NO and Br_2 by assuming there is an equilibrium in **step 1**.
- In a dynamic equilibrium, the forward rate equals the reverse rate. Therefore, by definition of equilibrium we get:

$$k_1[\text{NO}][\text{Br}_2] = k_{-1}[\text{NOBr}_2]$$

Rearranging...

$$[\text{NOBr}_2] = (k_1/k_{-1})[\text{NO}][\text{Br}_2]$$

Rate Laws for Multistep Mechanisms

- Now we substitute $[\text{NOBr}_2] = \frac{k_1}{k_{-1}}[\text{NO}][\text{Br}_2]$ into our previous rate law...

$$\text{Rate} = k_2[\text{NOBr}_2][\text{NO}]$$

And we get...

$$\text{Rate} = (k_2k_1/k_{-1})[\text{NO}][\text{Br}_2][\text{NO}]$$

Combining terms...

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

- This matches the experimentally determined rate law equation, so this supports, (but does not prove) our reaction mechanism.

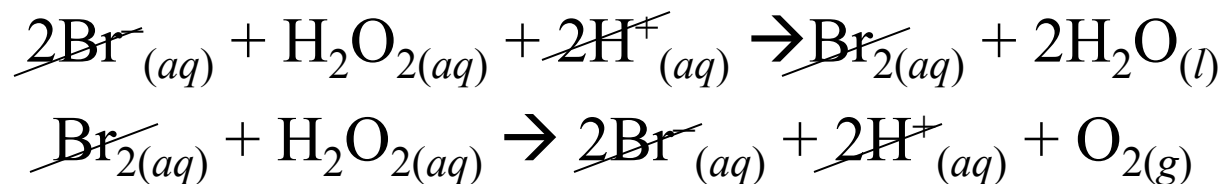
Catalysts

- A **catalyst** is a substance that changes the rate of a chemical reaction without itself undergoing a permanent chemical change in the process.
- There are two types of catalyst: Heterogeneous--one that is present in a different phase as the reacting molecules. Homogeneous-- one that is present in the same phase as the reacting molecules.

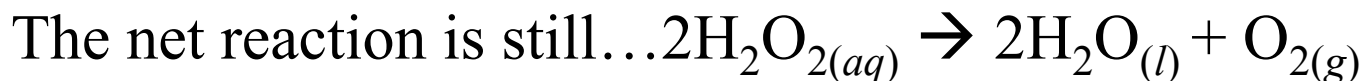
Example: Hydrogen peroxide decomposes very slowly in the absence of a catalyst:



In the presence of bromide ions, the decomposition occurs rapidly in an acidic environment:



Br^- is a homogeneous catalyst because it is regenerated at the end of the reaction.

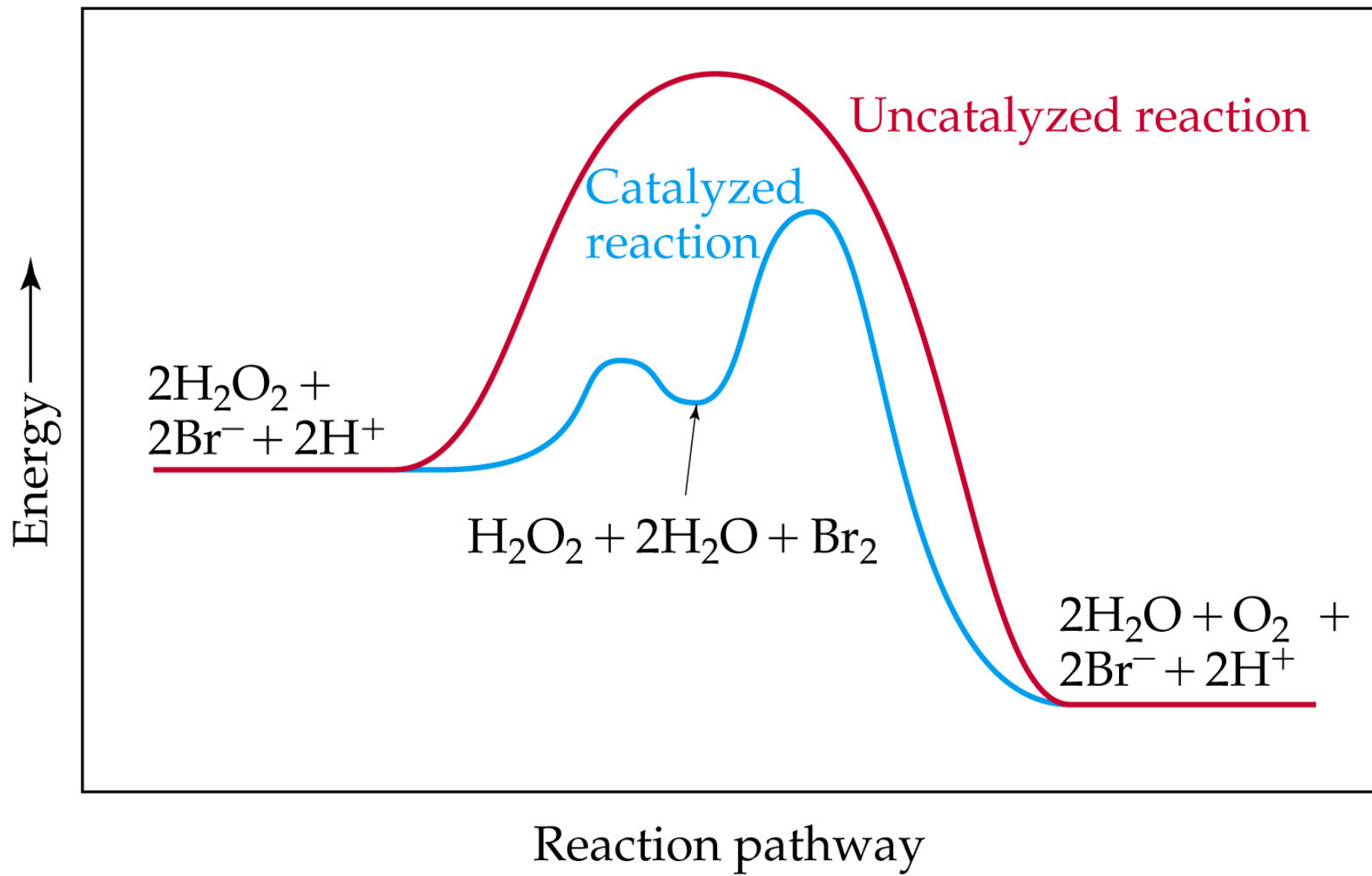


Catalysts and Reaction Rates

How do catalysts increase reaction rates?

- In general, catalysts operate by lowering the overall activation energy, E_a , for a reaction... (It lowers the “hill”.)
- However, catalysts can operate by increasing the number of effective collisions.
- A catalyst usually provides a completely different mechanism for the reaction.
- In the preceding peroxide decomposition example, in the absence of a catalyst, H_2O_2 decomposes directly to water and oxygen.
- In the presence of Br^- , $\text{Br}_{2(aq)}$ is generated as an **intermediate**.
- When a catalyst adds an intermediate, the activation energies for *both* steps must be lower than the activation energy for the uncatalyzed reaction.

Catalysts and Reaction Rates



Heterogeneous Catalysts

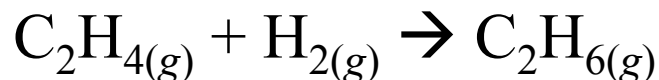
- Often we encounter a situation involving a solid catalyst in contact with gaseous reactants and gaseous products... (Example: catalytic converters in cars).
 - Many industrial catalysts are heterogeneous.

How do they do their job?

- The first step is **adsorption** (the binding of reactant molecules to the catalyst surface).
- Adsorption occurs due to the high reactivity of atoms or ions on the surface of the solid.
- Molecules are adsorbed onto **active sites** on the catalyst surface.
- The number of active sites on a given amount of catalyst depends on several factors such as:
 - The nature of the catalyst.
 - How the catalyst was prepared.
 - How the catalyst was treated prior to use.

Heterogeneous Catalysts

Example:

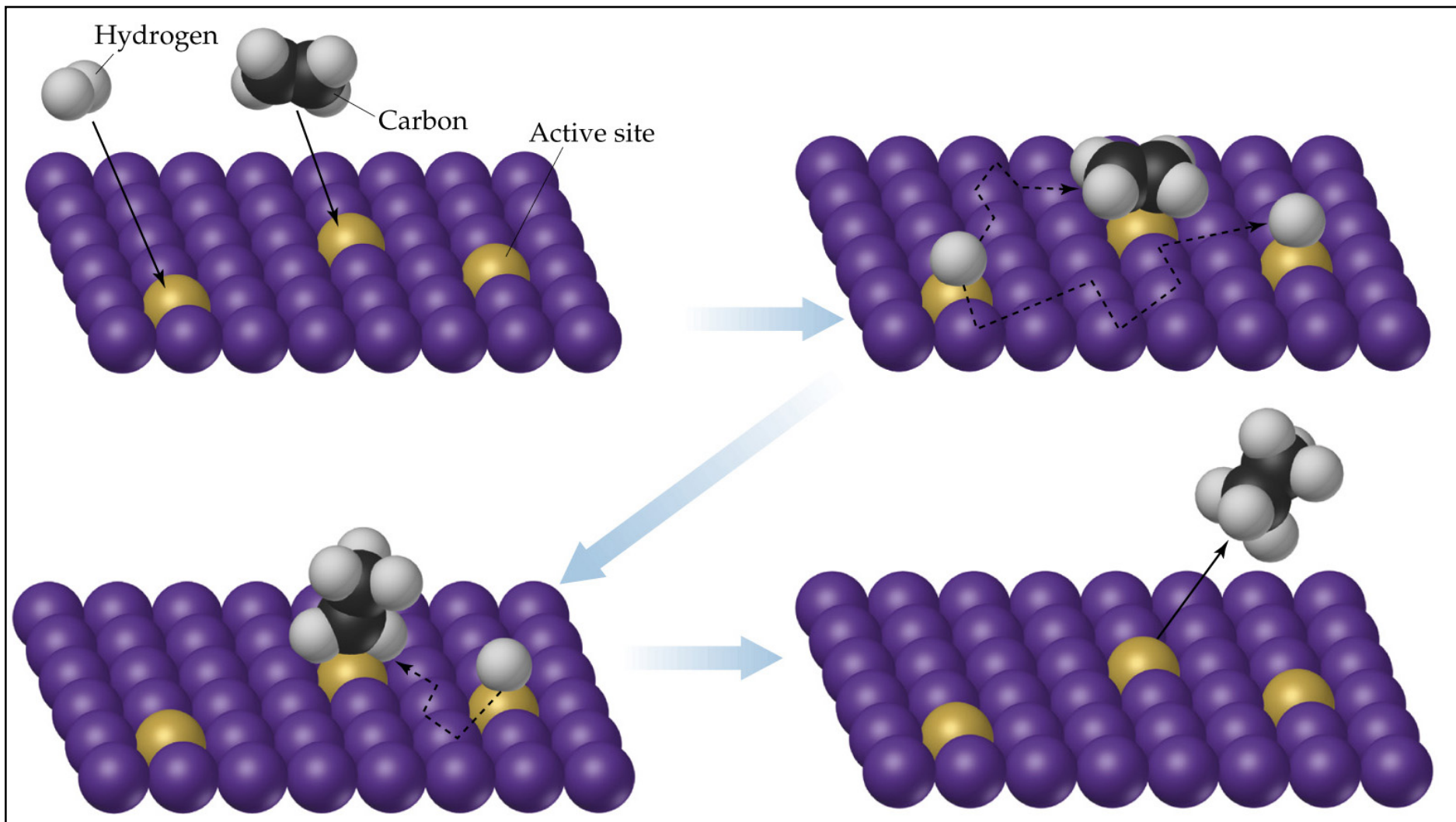


- In the presence of a metal catalyst (Ni, Pt or Pd) the reaction occurs quickly at room temperature.

Here are the steps...

- First, the ethylene and hydrogen molecules are adsorbed onto active sites on the metal surface.
 - Second, the H–H bond breaks and the H atoms migrate about the metal surface and runs into a C₂H₄ molecule on the surface.
 - Third, when an H atom collides with a C₂H₄ molecule on the surface, the C–C π-bond breaks and a C–H σ-bond forms.
 - Lastly, When C₂H₆ forms it desorbs from the surface.
- When ethylene and hydrogen are adsorbed onto a surface, less energy is required to break the bonds.
 - The E_a for the reaction is lowered, thus the reaction rate increases.

Heterogeneous Catalysts



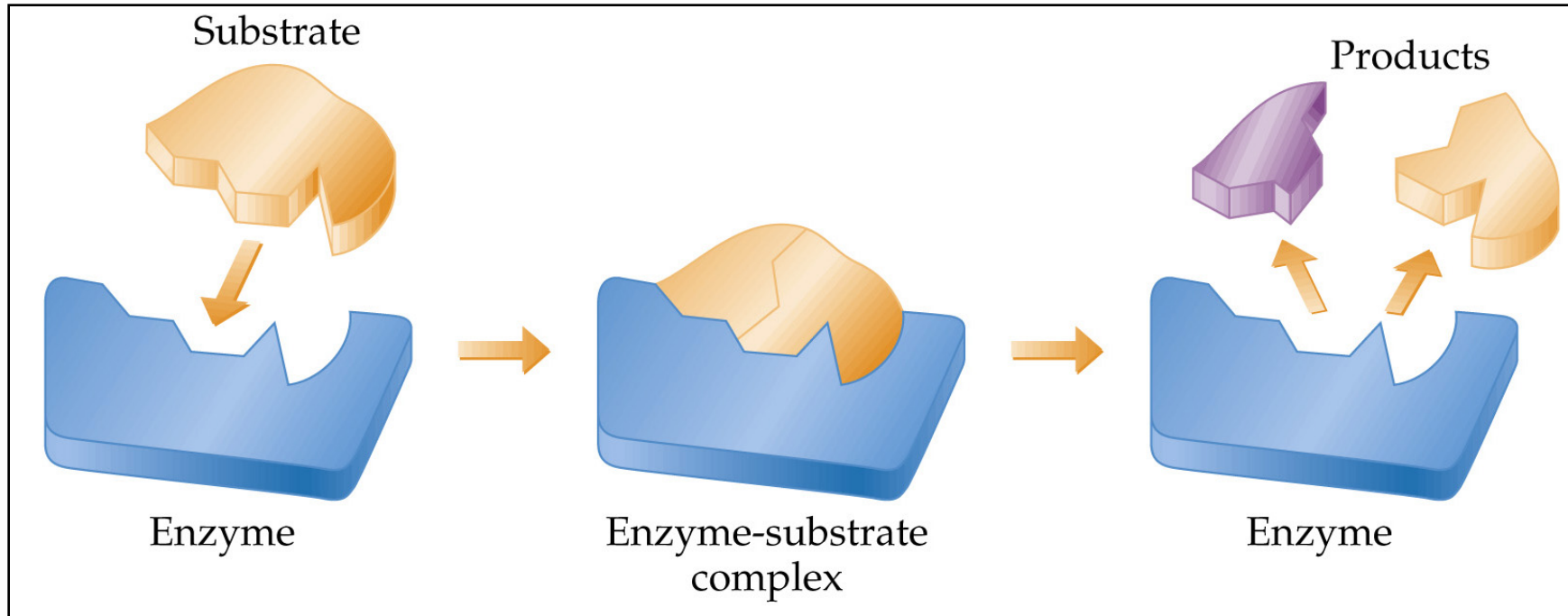
Enzyme Catalysts

- **Enzymes** are biological catalysts. There may be as many as 30,000 enzymes in the human body. (Ex: Lactase)
- Most enzymes are protein molecules with large molecular masses (10,000 to 10^6 amu).
- Enzymes have very specific shapes.
- Most enzymes catalyze very specific reactions.
- The substances that undergo reaction at the active site on enzymes are called **substrates**.
- A substrate locks into an enzyme and a fast reaction occurs. The products then move away from the enzyme.

Enzyme Catalysts

- Only substrates that fit into the enzyme lock can be involved in the reaction.
- If a molecule binds tightly to an enzyme so that another substrate cannot displace it, then the active site is blocked and the catalyst is inhibited (**enzyme inhibitors**).
- Many poisons act by binding to the active site blocking the binding of substrates. The binding can also lead to changes in the enzyme.
- Enzymes are extremely efficient catalysts.
- The number of individual catalytic events occurring at an active site per unit time is called the *turnover number*.
- Large turnover numbers correspond to very low E_a values. For enzymes, turnover numbers are very large $\approx 10^3$ to 10^7 /sec

Enzyme Catalysts



Another example...Nitrogen gas cannot be used in the soil for plants or animals. Nitrogen compounds, NH_3 , NO_2^- , and NO_3^- are used in the soil. The conversion between N_2 and NH_3 is a process with a high activation energy (the $\text{N}\equiv\text{N}$ triple bond needs to be broken). Nitrogenase, an enzyme in bacteria that lives in root nodules of legumes such as clover and alfalfa, catalyses the reduction of nitrogen to ammonia. It lowers the E_a , and the reaction proceeds.

Arrhenius Equation

- This is how the rate constant of a chemical reaction varies with respect to temperature and other variables.

$$\ln(k) = - E_a/R(1/T) + \ln(A)$$

where... k= rate constant

E_a = Activation Energy (in kJ/mole)

R = Gas Constant

T = Kelvin temperature

A = “Frequency Factor” -- a constant indicating how many collisions have the correct orientation to lead to products.

Plot of Arrhenius Equation

