CHEMICAL KINETICS- TEMPERATURE AND RATES

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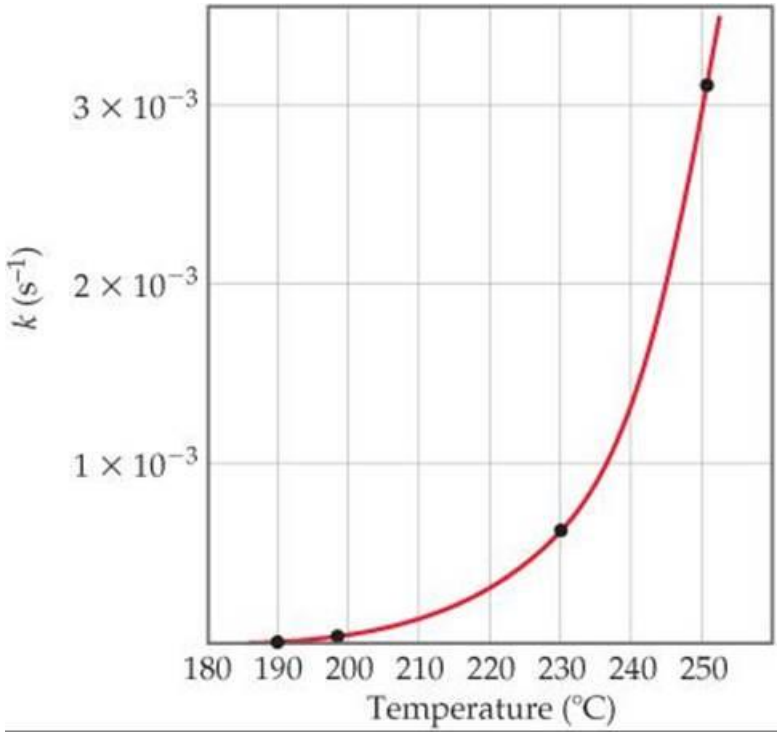
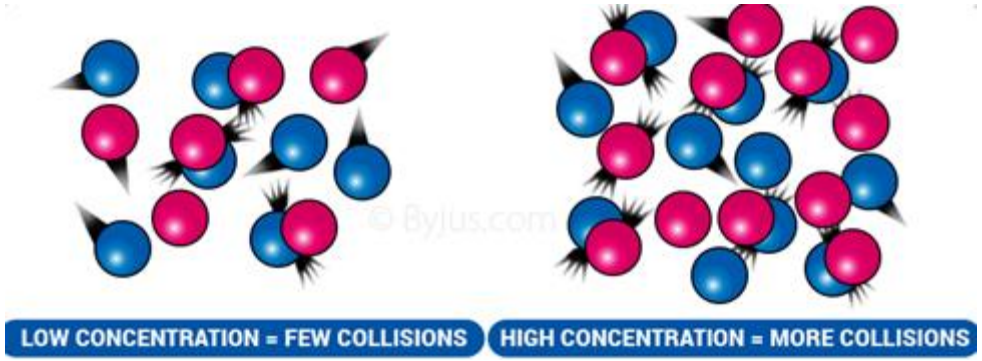
Temperature and Rate

- The rates of most chemical reactions increase as the temperature increases.
- This is because the rate constant increases as the temperature rises.



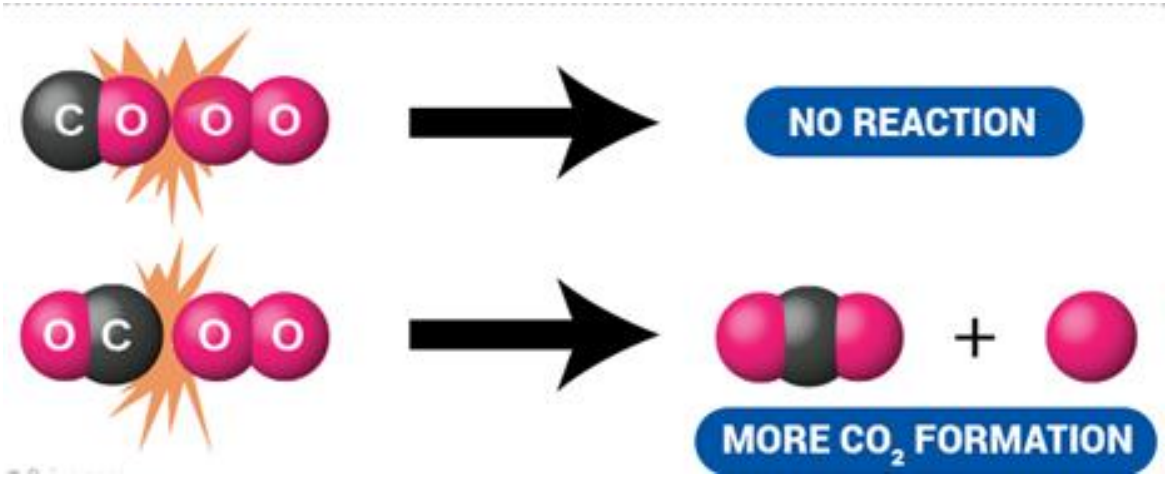
The Collision Model

- The central idea of the collision model is that molecules must collide to react.
- As reactant concentrations increase, the frequency of collisions also increases and thus rate of reaction increases.
- As temperature increases the molecular speed increases, thus molecules move faster and collide more frequently, and with more energy.
- Thus reaction rates increase.



The Orientation Factor

- In order for a collision between two molecules to be successful, i.e. form product, the molecules must be oriented in a certain way.
- The relative orientations of the molecules during collision determine whether the atoms are suitably positioned to form new bonds.

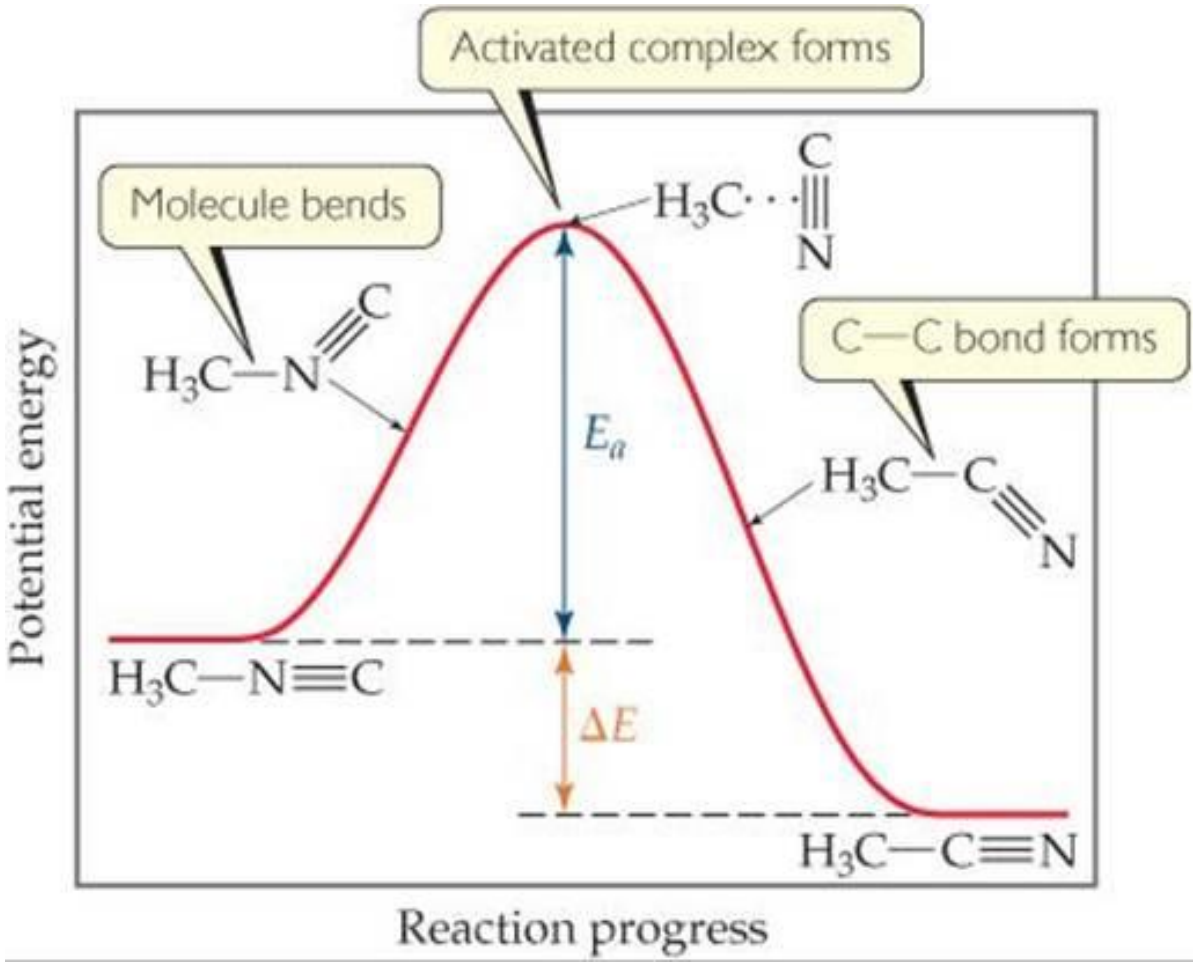


Activation Energy

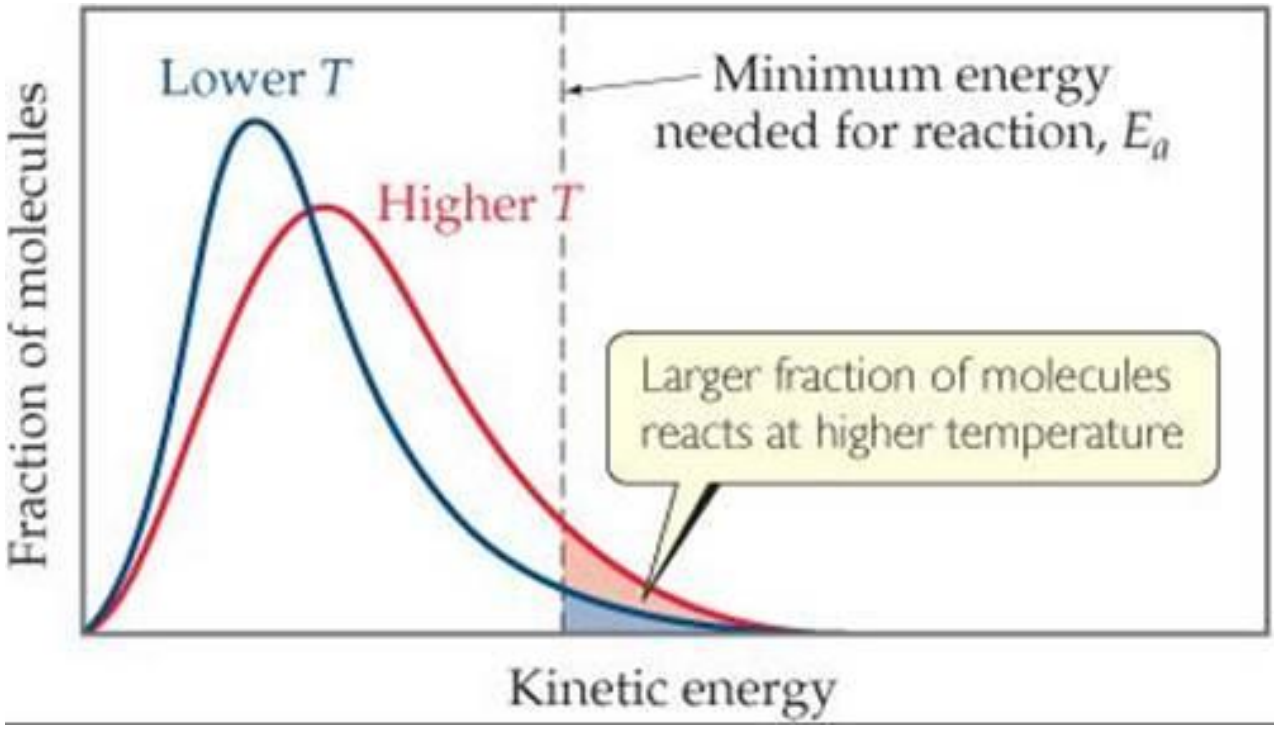
- In addition to the correct orientation of molecules, the collision must take place with a minimum amount of energy in order for bonds to break and new bonds to form.

- The minimum energy required to initiate a chemical reaction is called the activation energy, E_a, and its value varies from reaction to reaction.

- In general, the lower the value of E_a, the faster is the reaction.



*The **activated complex**, or **transition state**, is the molecule that has an arrangement of bonds that results in the molecule having the highest potential energy. It is highly unstable and cannot be isolated.*



The distribution of kinetic energies for two temperatures. At the higher temperature a much greater fraction of the molecules have kinetic energy greater than E_a, which leads to a greater rate of reaction.

The Arrhenius Equation

- Most reactions obey an equation based on:

a) The fraction of molecules possessing energy, E_a, or greater.

b) The number of collisions per second

c) The fraction of collisions that have the appropriate orientation.

These three factors are incorporated into the Arrhenius equation:

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

k = rate constant, E_a is the activation energy, R is the gas constant (8.314 J/mol-K), and T is the temperature (K).

The Arrhenius Equation

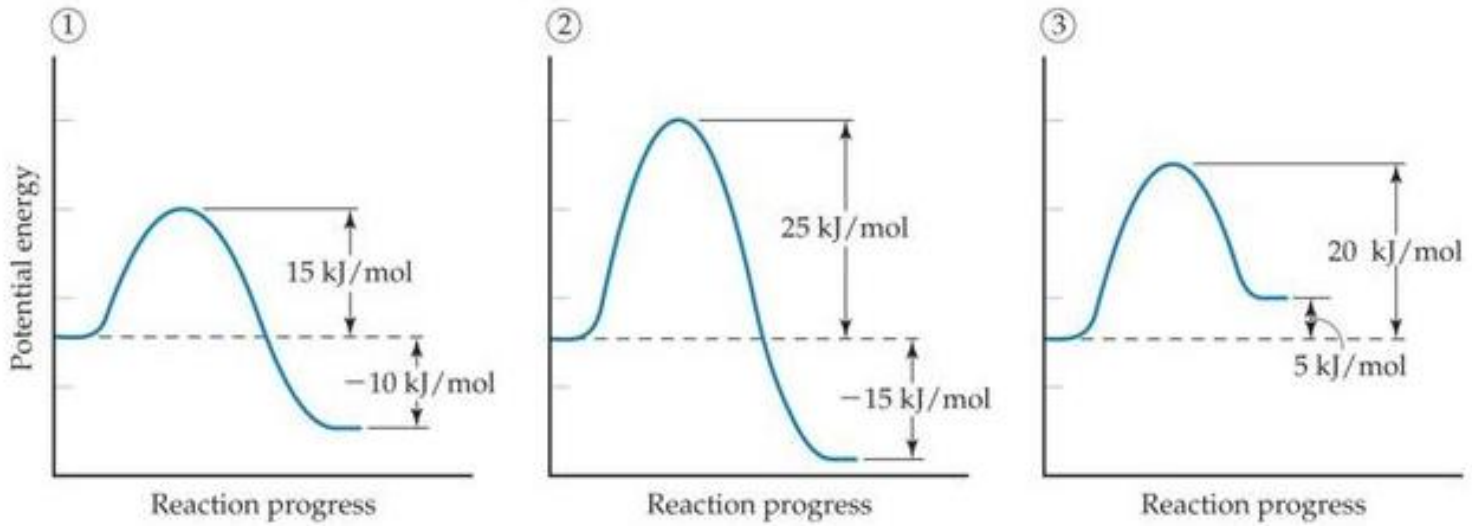
$$k = Ae^{-E_a/RT}$$

- *A* is the frequency factor.
- This factor is related to the frequency of collisions and the probability that the collisions are favourably oriented for reaction.
- As magnitude of E_a increases, *k* decreases because the fraction of molecules that possess the required energy is smaller.
- *Thus reaction rates decrease as E_a increases.*

- Sample Exercise:

Consider a series of reactions having these energy profiles:

Rank the reactions from slowest to fastest assuming that they have nearly the same value for the frequency factor *A*.



Ans: 2 < 3 < 1.

- Practice exercise:

Rank the reverse reactions from sample exercise in the previous slide from slowest to fastest.

Ans: 2 < 1 < 3

Determining the Activation Energy

- Manipulating the Arrhenius equation enables us to calculate the E_a of a reaction:

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

y = mx + c

- Thus a graph of ln *k* versus 1/*T* will yield a straight line with a slope equal to $-E_a/R$ and a y intercept equal to ln *A*.
- We can also use this equation to determine the E_a of a reaction in a nongraphical way if we know the rate constant of a reaction at two or more temperatures:

- $\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

- The above equation provides a convenient way to calculate a rate constant k_1 at some temperature T_1 when we know the activation energy and the rate constant k_2 at some temperature T_2.

- Sample exercise: the following table shows the rate constants for the rearrangement of methyl isonitrile at various temperatures:

Temperature (°C)	k (s^{-1})
189.7	2.52×10^{-5}
198.9	5.25×10^{-5}
230.3	6.30×10^{-4}
251.2	3.16×10^{-3}

Provided the E_a = 160 kJ/mol, calculate the rate constant when T = 430.0 K

Ans: $1.0 \times 10^{-6}\ s^{-1}$

Reaction Mechanisms

- The steps by which a reaction occurs is called the reaction mechanism.

- A ***reaction mechanism*** describes the order in which bonds are broken and formed and the changes in relative positions of the atoms in the course of the reaction.

- Reactions that occur in a single step or single event are said to be ***elementary reactions***.

- The number of molecules that participate as reactants in an elementary reaction defines the molecularity of the reaction.

- If the elementary reaction involves a single reactant molecule, the reaction is said to be *unimolecular*.

- Elementary reactions involving the collision of two reactant molecules are said to be *bimolecular*.

- Elementary reactions involving the simultaneous collision of three molecules are *termolecular*.

Multistep Mechanisms

- For example, below 225 °C, the reaction

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

Appears to proceed in two elementary reactions, each of which is bimolecular.

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)$$

$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$$

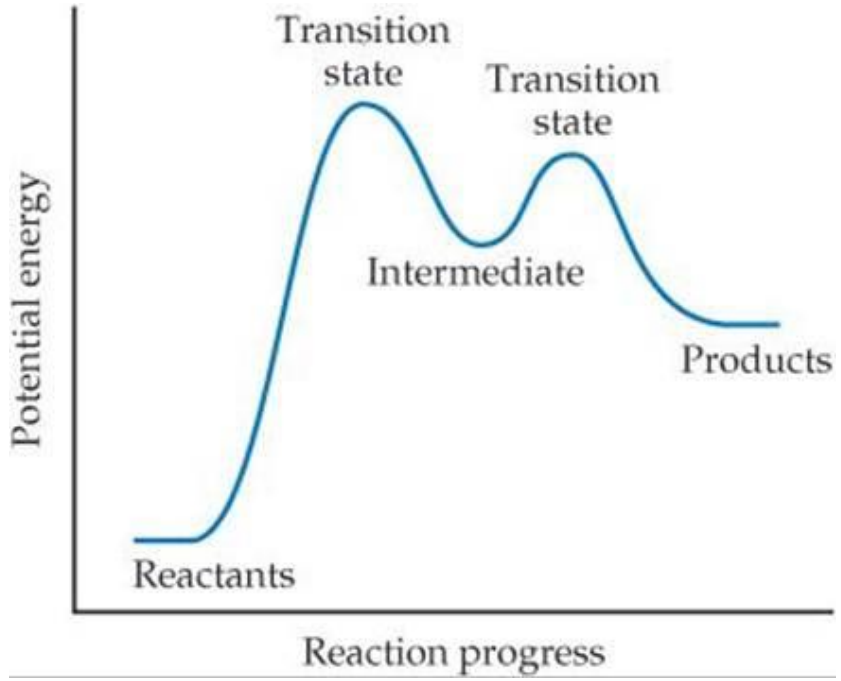
Thus, we say the reaction occurs by a two-step mechanism.

The sum of the two elementary reactions is:

$$2NO_2(g) + \cancel{NO_3}(g) + CO(g) \longrightarrow NO_2(g) + \cancel{NO_3}(g) + NO(g) + CO_2(g)$$

Which simplifies to the net equation above.

- *The chemical equations for the elementary reactions in a multistep mechanism must always add to give the chemical equation of the overall process.*
- Because NO_3 is neither a reactant nor a product of the reaction – it is formed in one elementary reaction and consumed in the next – it is called an ***intermediate***.
- Unlike transition states, intermediates are sometimes stable enough to be identified and isolated.



- Sample exercise:

It has been proposed that the conversion of ozone into O_2 proceeds by a two-step mechanism:

$O_3(g) \longrightarrow O_2(g) + O(g)$

$O_3(g) + O(g) \longrightarrow 2O_2(g)$

a) Describe the molecularity of each elementary reaction in this mechanism.

b) Write the equation for the overall reaction.

c) Identify the intermediate(s).

- Practice exercise:

For the reaction

$Mo(CO)_6 + P(CH_3)_3 \longrightarrow Mo(CO)_5P(CH_3)_3 + CO$

The proposed mechanism is:

$Mo(CO)_6 \longrightarrow Mo(CO)_5 + CO$

$Mo(CO)_5 + P(CH_3)_3 \longrightarrow Mo(CO)_5P(CH_3)_3$

a) Is the proposed mechanism consistent with the equation for the overall reaction?

b) What is the molecularity of each step of the mechanism?

c) Identify the intermediate(s)

Rate Laws for Elementary Reactions

- If a reaction is elementary, its rate law is based directly on its molecularity.
- For example, for the unimolecular reaction: A $\longrightarrow$ products, Rate = k[A].
- For the bimolecular elementary steps, the rate law is second order

A + B $\longrightarrow$ products Rate = k[A][B]

- Sample exercise:

1. If the following reaction occurs in a single elementary reaction, predict its rate law:

$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

2. Consider the following reaction: $2NO(g) + Br_2(g) \longrightarrow 2NOBr(g)$.

a) Write the rate law for the reaction, assuming it involves a single elementary reaction.

b) Is a single-step mechanism likely for this reaction?

The Rate-Determining Step for a Multistep Mechanism

- If a mechanism occurs by two or more elementary steps, often one step is slower than the others.
- The slow step limits the overall rate of reaction, and is known as the rate-determining step (or rate-limiting step).
- Consider the reaction below for which the first-step in the multistep mechanism is the rate determining step:

Step 1: $NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g)$ (slow)

Step 2: $NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g)$ (fast)

Overall: $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

- $k_2 >> k_1$
- Thus the rate of the overall reaction depends on the rate of step 1.
- Step 1 is a bimolecular process that has the rate law:

$$\text{Rate} = k_1[NO_2]^2$$

- Sample exercise:

The decomposition of nitrous oxide, N_2O, is believed to occur by a two-step mechanism:

$N_2O(g) \longrightarrow N_2(g) + O(g)$ (slow)

$N_2O(g) + O(g) \longrightarrow N_2(g) + O_2(g)$ (fast)

a) Write the equation for the overall reaction.

b) Write the rate law for the overall reaction.

- Practice exercise:

Ozone reacts with nitrogen dioxide to produce dinitrogen pentoxide and oxygen:

$$O_3(g) + 2NO_2(g) \longrightarrow N_2O_5(g) + O_2(g)$$

The reaction is believed to occur in two steps:

$$O_3(g) + NO_2(g) \longrightarrow NO_3(g) + O_2(g)$$

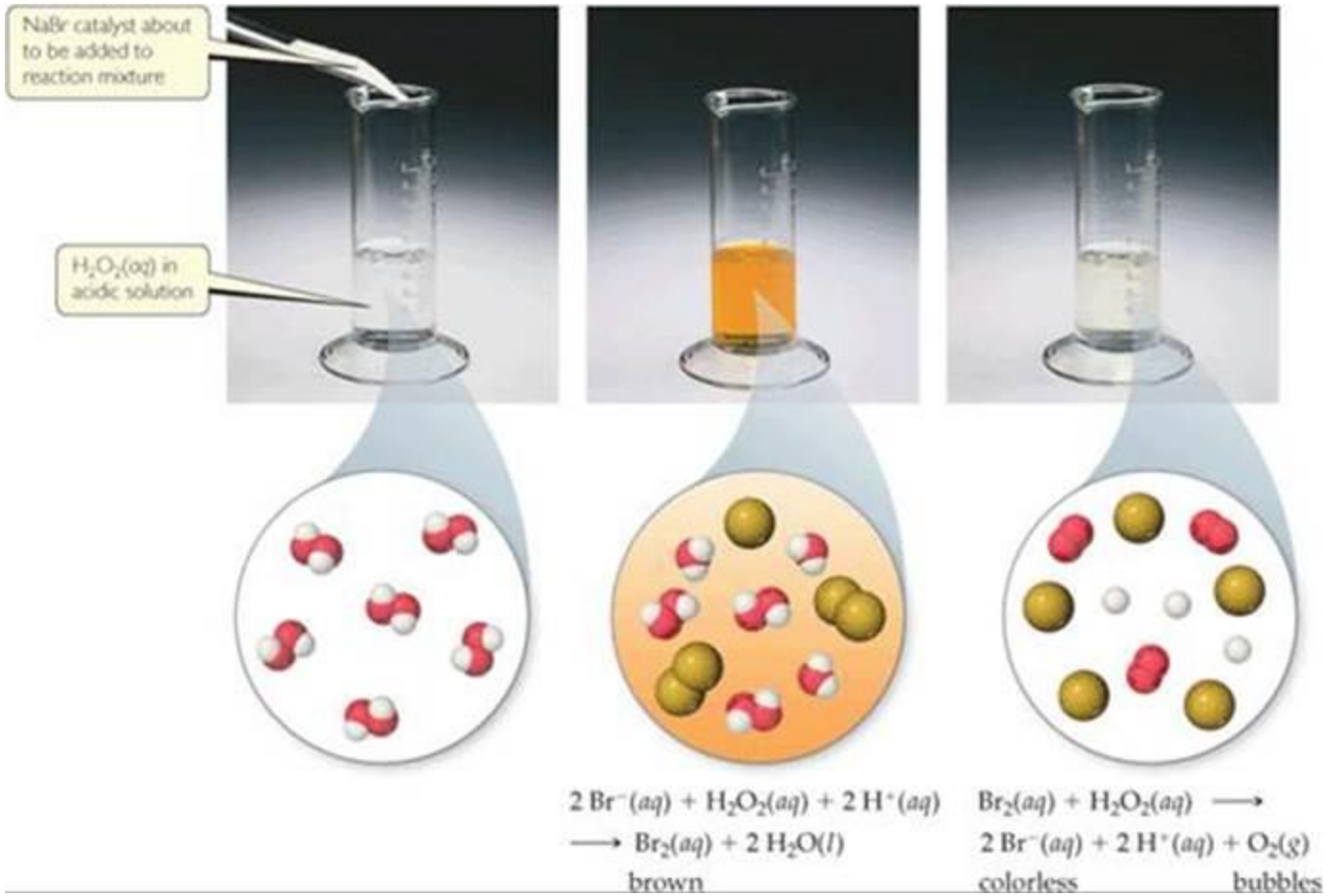
$$NO_3(g) + NO_2(g) \longrightarrow N_2O_5(g)$$

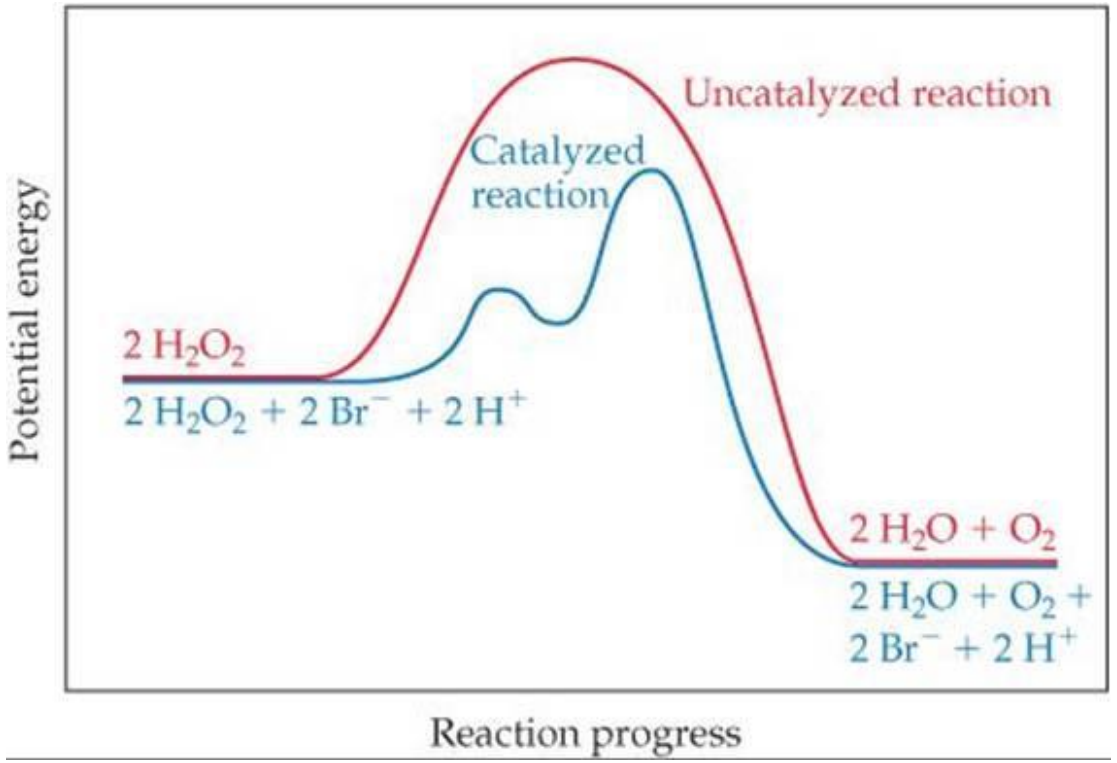
The experimental rate law is rate = $k[O_3][NO_2]$. What can you say about the relative rates of the two steps of the mechanism?

Catalysis

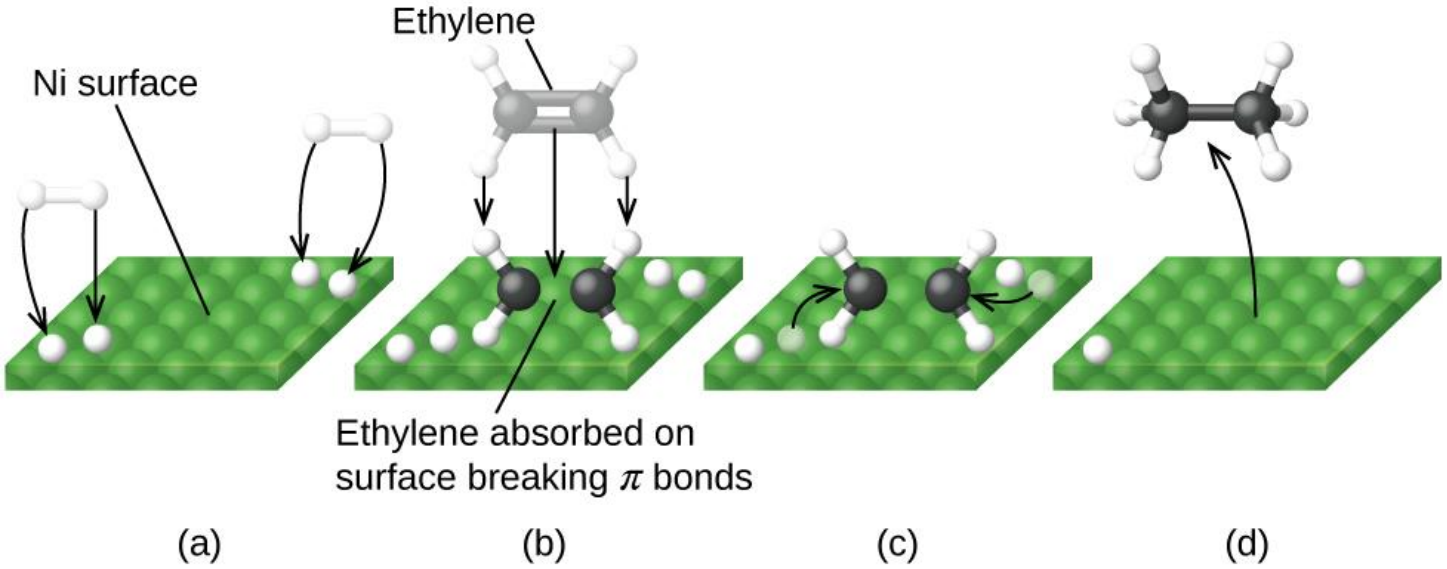
- A catalyst is a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself.
- A catalyst that is present in the same phase as the reactants in a reaction mixture is called a ***homogeneous catalyst***.
- As a general rule, a catalyst lowers the overall activation energy for a chemical reaction.
- It does this by providing a different mechanism for the reaction that requires less energy.

- A heterogeneous catalyst is one that exists in a phase different from the phase of the reactant molecules.
- Usually as a solid in contact with gaseous or liquid reactants.



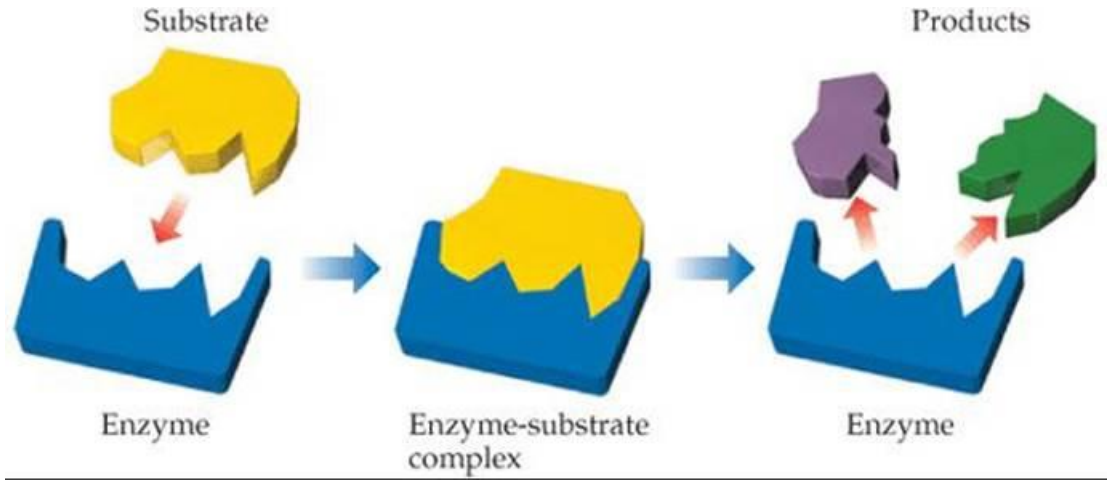


Consider for example the energy profiles for the uncatalysed and bromide-catalysed decomposition of H_2O_2.



For example, in the Ni catalysed hydrogenation of ethylene to form ethane.

The initial step in heterogeneous catalysis is usually adsorption of reactants. Adsorption refers to the binding of molecules to the surface, whereas absorption refers to the uptake of molecules into the interior of a substance.

Enzymes

- Enzymes are biological catalysts.
- The reaction that an enzyme catalyses takes place at a specific location in the enzyme called an ***active site***.
- The substances that react at this site are called ***substrates***.
- The specificity of enzymes is described by the ***lock-and-key model***.