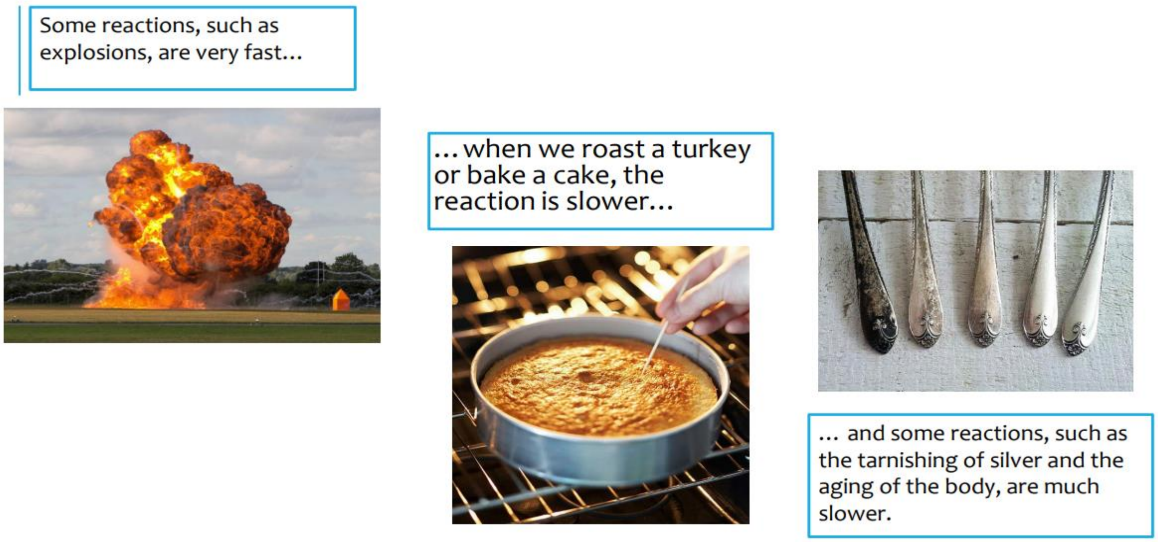
Rates of reactions and equilibrium

The Rates of Chemical Reactions

Chemical reactions require varying lengths of time for completion, depending upon the characteristics of the reactants and products and the conditions under which the reaction is taking place.

Reaction rate is the rate at which reactants change into products over time or The rate of a reaction is the speed at which a chemical reaction happens. Reaction rate is proportional to the number of effective collisions.



Reaction rate is a measure of how fast a reaction occurs. Some reactions are inherently fast, and some are slow: If a reaction has a low rate, that means the molecules combine at a slower speed than a reaction with a high rate. Some reactions take hundreds, maybe even thousands, of years while others can happen in less than one second. The rate of reaction also depends on the type of molecules that are combining. If there are low concentrations of an essential element or compound, the reaction will be slower.

Reactions occur at all different speeds.

some reactions need energy while other reactions produce energy.

There is another big idea for rates of reaction called collision theory. For a chemical reaction to take place, the molecules of the reactants must collide with each other. If you have more possible combinations, there is a higher chance that the molecules will complete the reaction. The reaction will happen faster which means the rate of that reaction will increase.

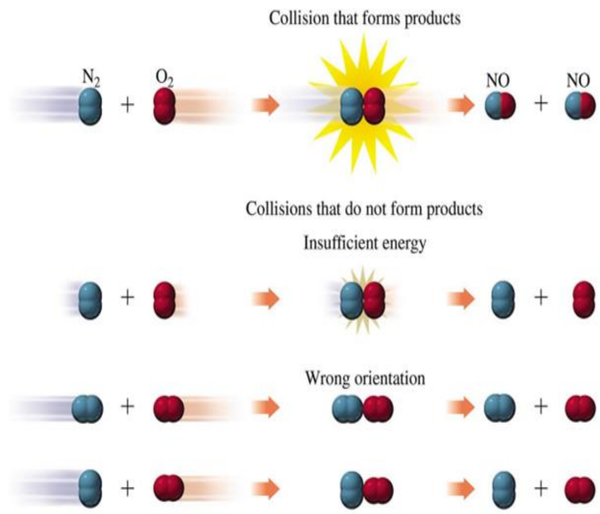
Collision Theory

The collision theory indicates that a reaction takes place only when molecules collide with the proper orientation and sufficient energy.

Many collisions may occur, but only a few leads to the formation of product. For example,

$$N_2 + O_2 \longrightarrow 2NO$$

To form NO product, the collisions between N_2 and O_2 molecules must collide in a specific orientation and energy



Collision Theory Energy Requirements

1. For reactants to convert to products, an energy barrier called the activation energy, ***Ea,*** must be overcome.
2. Collisions that have the proper orientation and have at least the minimum ***Ea*** can convert to products.
3. The activation energy needed is related to the amount of energy needed to break bonds.

Activation Energy

Activation energy: the minimum amount of energy required to break the bonds between atoms of the reactants. The activation energy of a reaction must be supplied for the reaction to proceed. Each reaction has its own activation energy.

Activation energy is analogous to climbing a hill. To reach a destination on the other side, you must have the energy needed to climb to the top of the hill.
Once at the top, it's easy to run down the other side. The energy needed to get us from the starting point to the top of the hill would be the activation energy.

In the same way, a collision must provide enough energy to push the reactants to the top of the hill.

If the energy provided is less than the activation energy, the molecules simply bounce apart and no reaction occurs.

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Then the reactants may be converted to products.

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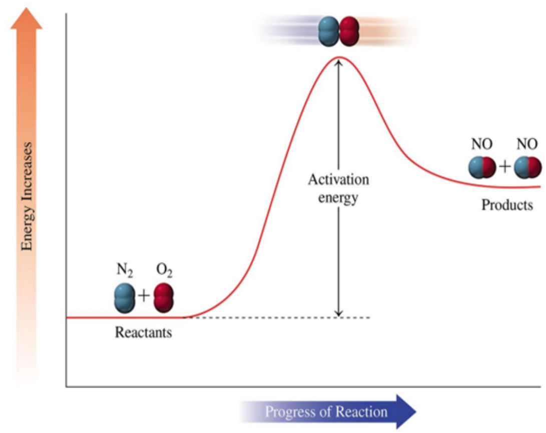


3 Conditions Required for a Reaction to Occur:

1. Collision The reactants must collide.
2. Orientation The reactants must align properly to break and form bonds.
3. Energy The collision must provide the energy of activation.

The rate of reaction is determined by measuring the amount of reactants used up, or the amount of product formed, in a certain period of time.

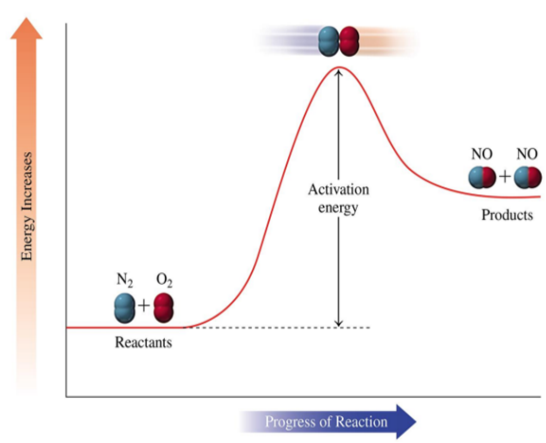
$$\text{rate of reaction} = \frac{\text{change in concentration of product or reaction}}{\text{change in time}}$$

Rates and Activation Energy

Reactions with low activation energy go faster than reactions with high activation energy.

Some reactions go very fast, while others go very slow.

For any reaction, the rate is affected by changes in temperature, concentration of the reactants and products, and the addition of catalysts.



Temperature

At higher temperatures, the kinetic energy of the reactants increases, making them move faster and therefore collide more often and it provides the collisions with more energy for activation.

Reactions almost always go faster at higher temperatures.

- *To cook food faster, we raise the temperature.*
- *When body temperature rises, the pulse rate, rate of breathing, and metabolic rate increase.*

We slow down a reaction by decreasing the temperature.

- *We refrigerate food to slow molding and decay.*
- *In some heart surgeries, the body temperature is decreased to 25°C (82°F) so the heart can be stopped and less O2 is required by the brain.*

Concentrations of Reactants

The rate of a reaction increases when the concentration of the reactants increases.

When there are more reacting molecules, more collisions that produce products can occur and so the reaction goes faster.

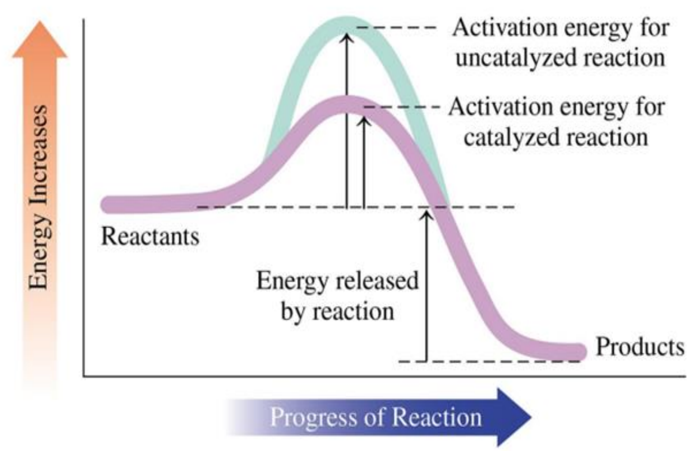
Example: A patient having difficulty breathing is given a breathing mixture with a higher oxygen content than the atmospheric concentration:

$$\mathbf{Hb} + \mathbf{O_2} \longrightarrow \mathbf{HbO_2}$$

More O_2 molecules in the lungs increases the rate of O_2 uptake into the body because there's more chances for O_2 to collide correctly with hemoglobin (Hb). (Hemoglobin is the taxi service for transferring oxygen through the blood.)

Catalysts

Another way to speed up a reaction is to lower the activation energy. A catalyst speeds up a reaction by providing an alternate pathway that has a lower activation energy. When activation energy is lowered, more collisions provide sufficient energy for reactants to form product. A catalyst is not a reactant or product. It interacts with the reactants but is not permanently changed or consumed during the reaction. Since catalysts are "recycled," small amounts are needed and last a long time.



In the manufacturing of margarine, H_2 is added to vegetable oils. Normally the reaction is very slow due to the high activation energy. However, when platinum (Pt) is used as a catalyst, the reaction proceeds rapidly.

In the body, biocatalysts called enzymes make most metabolic reactions proceed at rates necessary to support life.

Factors Affecting Reaction Rates

1. Temperature – increasing temperature increases reaction rates.
2. Surface Area – increasing surface area increases reaction rates.
3. Stirring – stirring increases reaction rates
4. Concentration – increased concentration increases reaction rates.
5. Catalysts – catalysts increase reaction rates. Catalysts work by DECREASING ACTIVATION ENERGY.
6. Light. Light of a particular wavelength may also speed up a reaction.
7. Pressure-Pressure affects the rate of reaction, especially when you look at gases. When you increase the pressure, the molecules have less space in which they can move. That greater **density** of molecules increases the number of collisions. When you decrease the pressure, molecules don't hit each other as often and the rate of reaction decreases. Generally, reaction rates
   for solids and liquids remain unaffected by increases in pressure.

Equilibrium

Basically, the term refers to what we might call a "balance of forces". When a chemical reaction takes place in a container which prevents the entry or escape of any of the substances involved in the reaction, the quantities of these components change as some are consumed and others are formed. Eventually this change will come to an end, after which the composition will remain unchanged as long as the system remains undisturbed. The system is then said to be in its *equilibrium state*, or more simply, "at equilibrium".

Reversible Reactions

When a reaction proceeds in both a forward and reverse direction, it is said to be reversible. A reversible reaction proceeds in both the forward and reverse directions.

That means there are 2 reaction rates:

- the rate of the forward reaction
- the rate of the reverse reaction

When molecules first begin to react, the rate of the forward reaction is faster than the reverse reaction. As reactants are consumed and products accumulate, the rate of the forward reaction decreases and the rate of the reverse reaction increases.

Eventually, the rates of the forward and reverse reactions become equal, the reactants form products at the same rate that the products form reactants.

At equilibrium:

The rate of the forward reaction is equal to the rate of the reverse reaction. No further changes occur in the concentrations of reactants and products, even though the two reactions continue at equal but opposite rates. When a chemical reaction reaches a state where the concentrations of reactants and products remain constant, a chemical equilibrium has been established.

The Equilibrium Constant (K_{eq})

The position of equilibrium is a constant for a reaction at a specific temperature. The relative amount of reactants and products is the same. At equilibrium, the concentrations of the reactants and products are constant.

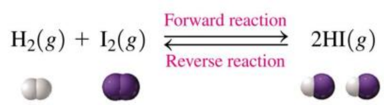
At equilibrium, the concentrations can be used to set up a relationship between the reactants and the products.

$$aA + bB \rightarrow cC + dD$$

Equilibrium constant expression for a reversible chemical reaction

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \underbrace{\frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}}_{\text{Equilibrium constant expression}} \quad \text{Coefficients}$$

Write the equilibrium constant expression:



$$K_c = \frac{HI^2}{H^2 I^2}$$

In an experiment, the molar concentrations for the reactants and products at equilibrium were found to be: $[H_2] = 0.10M$ $[I_2] = 0.20M$ $[HI] = 1.04M$. What is the value for the equilibrium constant?

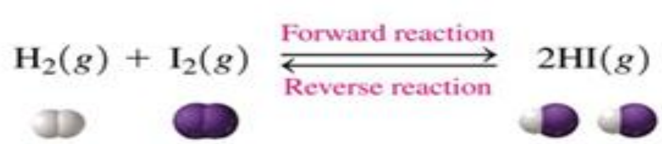


TABLE 10.2 Equilibrium Constant for $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 427 °C

Experiment	Concentrations at Equilibrium			Equilibrium Constant
	$[H_2]$	$[I_2]$	$[HI]$	$K_c = \frac{[HI]^2}{[H_2][I_2]}$
1	0.10 M	0.20 M	1.04 M	$K_c = \frac{[1.04]^2}{[0.10][0.20]} = 54$
2	0.20 M	0.20 M	1.47 M	$K_c = \frac{[1.47]^2}{[0.20][0.20]} = 54$
3	0.30 M	0.17 M	1.66 M	$K_c = \frac{[1.66]^2}{[0.30][0.17]} = 54$

The experiment is repeated with different starting amounts of reactants and once again, measured the concentrations at equilibrium. The equilibrium constant is calculated for each experiment and is found to have the same value for each. **A reaction at a specific temperature can have only one value for the equilibrium constant**. The units in the equilibrium constant expression are ignored. K_c has no units.

The decomposition of dinitrogen tetroxide forms nitrogen dioxide:

$$N_2O_4 \rightleftharpoons 2NO_2$$

What is the numerical value for K_c at 100°C if a reaction mixture at equilibrium contains 0.45M N_2O_4 and 0.31M NO_2?

The values of Kc can be large or small. The size of the equilibrium constant (Kc) depends on whether equilibrium is reached with more products than reactants, or more reactants than products. However, the size of an equilibrium constant does not affect how fast equilibrium is reached.

Equilibrium with a Large K_c

When a reaction has a large K_c, it means that the forward reaction produced a large amount of products when equilibrium was reached. Equilibrium mixtures contain more products than reactants.

Equilibrium with a Small K_c

When a reaction has a small K_c, the equilibrium mixture contains a high concentration of reactants and a low concentration of products.

A few reactions have equilibrium constants close to 1 which means they have about equal concentrations of reactants and products.

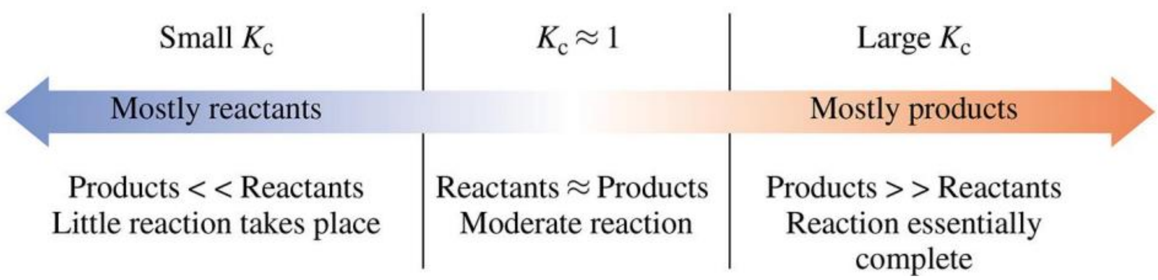


Table 1: Examples of Reactions with Large and Small K_c Values

Reactants		Products	K_c	Equilibrium Mixture Contains
$2CO(g) + O_2(g)$	$\rightleftharpoons$	$2CO_2(g)$	2×10^{11}	Mostly products
$2H_2(g) + S_2(g)$	$\rightleftharpoons$	$2H_2S(g)$	1.1×10^{7}	Mostly products
$N_2(g) + 3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$	1.6×10^{2}	Mostly products
$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g) + Cl_2(g)$	1.2×10^{-2}	Mostly reactants
$N_2(g) + O_2(g)$	$\rightleftharpoons$	$2NO(g)$	2×10^{-9}	Mostly reactants

Types of Equilibria

1. Physical equilibrium – when a physical change does not go to completion.
2. Chemical equilibrium – when a chemical change does not go to completion.

3. Homogeneous equilibria – − reactants and products are in the same physical state.
4. Heterogeneous equilibria – − reactants and products are not all in the same physical state.

Factors Affecting Chemical Equilibrium

LeChatlier's Principle – when a change is introduced to a system in equilibrium, the equilibrium shifts in the direction that relieves the change. Equilibrium means equal rate of formation of products and reactants, NOT an equal amount of product and reactants.

a. Temperature – if you add heat (endothermic), the equilibrium will shift in the direction that removes heat (exothermic).
b. Pressure – if you increase pressure, the equilibrium will shift in the direction that decreases pressure.
c. Concentration – if you increase concentration, the equilibrium will shift in the direction that decreases concentration.

Changing Concentrations

When the concentration of a product or reactant is changed, the system increases the forward or reverse reaction to re-establish equilibrium.

When reactant is added, the concentration of reactants increases, and the forward rate will increase to make more products to balance.

When reactant is removed, the concentration of reactants decreases, and the reverse rate will increase to replace the lost reactant.

When product is added, the concentration of products increases, and the reverse rate will increase to make more reactants to balance.

When product is removed, the concentration of products decreases, and the forward rate will increase to replace the lost reactant.

Effect of a Catalyst on Equilibrium

When a catalyst is added to a reaction, the activation energy is lowered, therefore speeding up the reaction. As a result, both the forward and reverse reactions increase, but the same ratios of products and reactants are attained. Therefore, catalysts do not affect equilibrium.

Effect of Volume Change on Equilibrium

If there is a change in volume of a gas mixture, there will also be a change in the concentrations of those gases.

$$2CO(g) + O_2\,(g) \rightleftharpoons 2CO_2\,(g)$$

Decrease the volume, all the concentrations will increase. With less room for each molecule, the system will shift toward producing the side with fewer moles.

Increase the volume, all the concentrations will decrease. The system is free to move toward producing the side with more moles.

If there are the same number of moles on both sides, changing volume will have no effect.

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

Effect of Temperature Change on Equilibrium

1. Heat as a reactant or a product in a reaction. Endothermic reactions

$$N_2\,(g) + O_2\,(g) + \text{heat} \rightleftharpoons 2NO(g)$$

Increase temperature – shifts right to remove the heat Decrease temperature – shifts left to remove the heat.

2. Heat as a reactant or a product in a reaction. Exothermic reactions

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) + \text{heat}$$

Increase temperature – shift left to remove the heat Decrease temperature – shifts right to add heat.