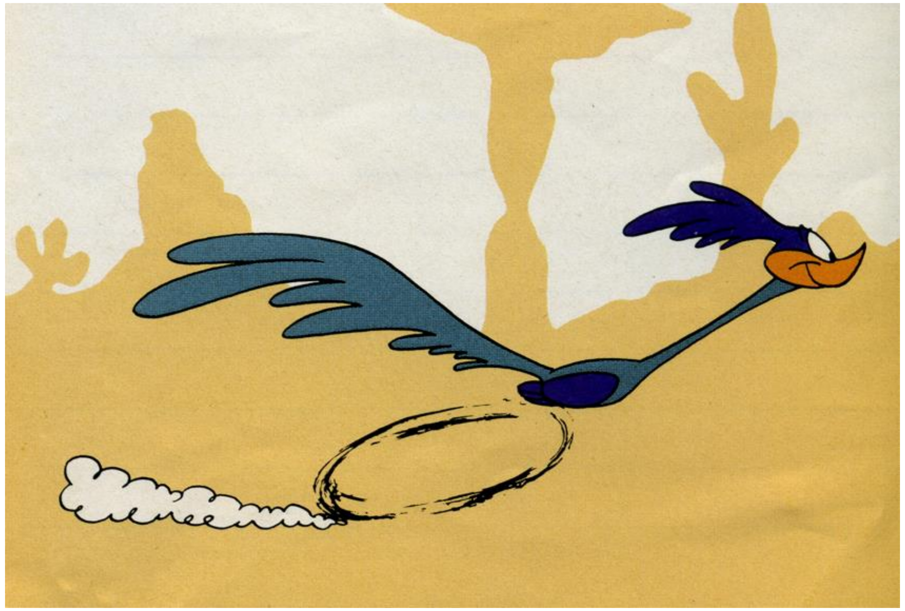
Reaction Rates and Chemical Equilibrium

Chapter 10

Earlier we looked at chemical reactions and determined the amounts of substances that react and the products that form.

$$\mathrm{NaCl}(s) \xrightarrow[\text{Dissociation}]{\mathrm{H_2O}} \mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq)$$

Now we are interested in how *fast* a reaction goes.



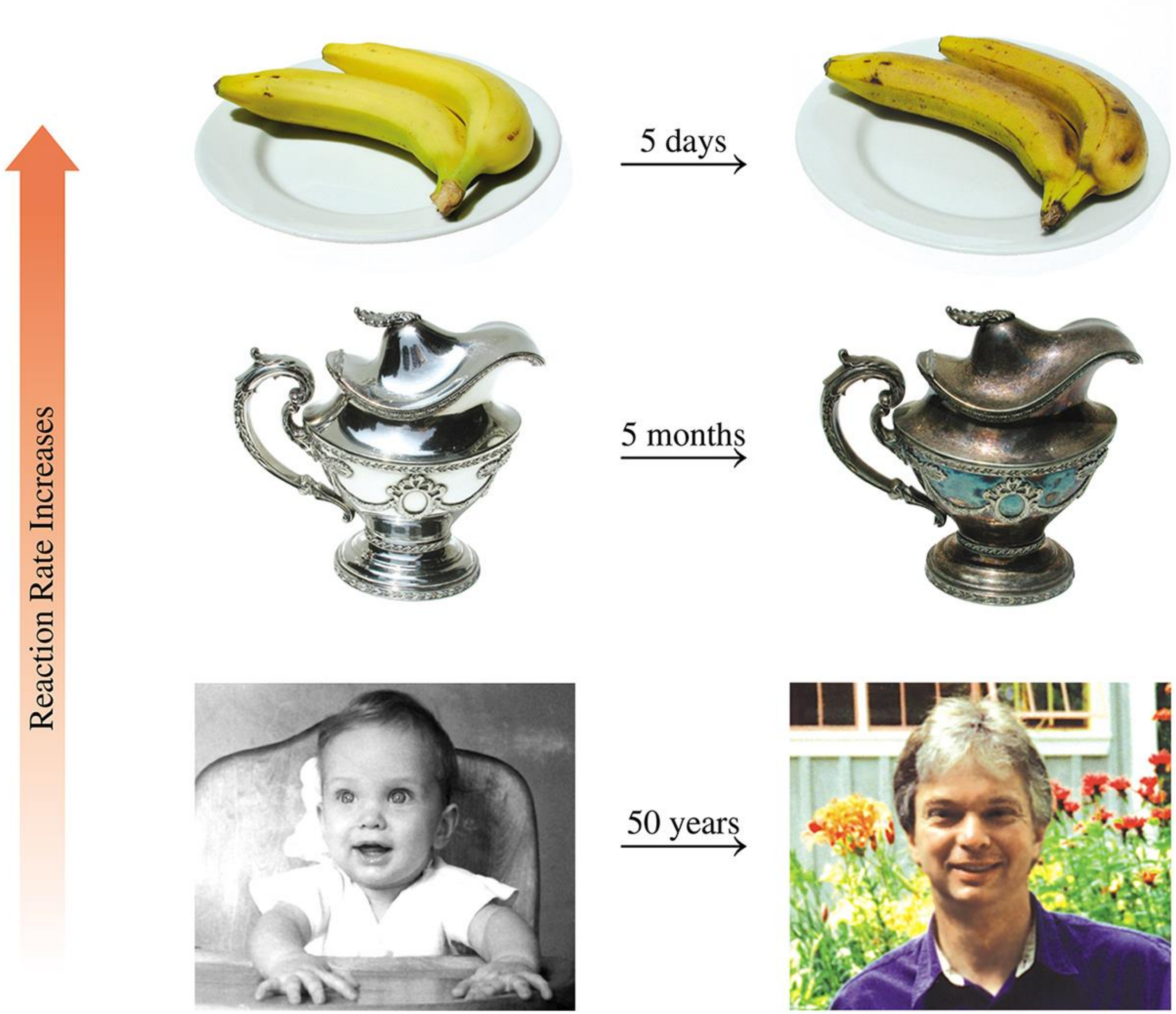
If we know how fast a medication acts on the body, we can adjust the time over which the medication is taken.

In construction, substances are added to cement to make it dry faster.

Some reactions, such as explosions, are very fast…

… when we roast a turkey or bake a cake, the reaction is slower…

… and some reactions, such as the tarnishing of silver and the aging of the body, are much slower.



Reactions occur at all different speeds.

In this chapter we will see that some reactions need energy while other reactions produce energy.

We will also look at the effect of changing the concentrations of reactants and products on the rate (speed) of reaction.

EQUILIBRIUM

Up to now, we have considered a reaction as proceeding in the forward direction from reactants to products (left to right).

However, in many reactions, a reverse reaction also takes place as products collide to reform the reactants.

$$H_2(g) + I_2(g) \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftarrows}} 2HI(g)$$

When the forward and reverse reactions occur at the same rate, the overall amounts of reactants and products stays the same. When this balance is reached, we say that the reaction has reached **equilibrium**.

EQUILIBRIUM

Equilibrium: The rate of the forward reaction and the rate of the reverse reaction are equal.

$$H_2(g) + I_2(g) \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftarrows}} 2HI(g)$$

At equilibrium, both reactants and products are present.

- Some reaction mixtures contain mostly reactants and form only a few products at equilibrium.
- Some reaction mixtures contain mostly products and remain mostly reactants at equilibrium.

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10.5 – Changing Equilibrium Conditions: Le Châtelier's Principle

10.1 Rates of Reactions

Describe how temperature, concentration, and catalysts affect the rate of a reaction.

Collision Theory

For a chemical reaction to take place, the molecules of the reactants must come in contact with each other.

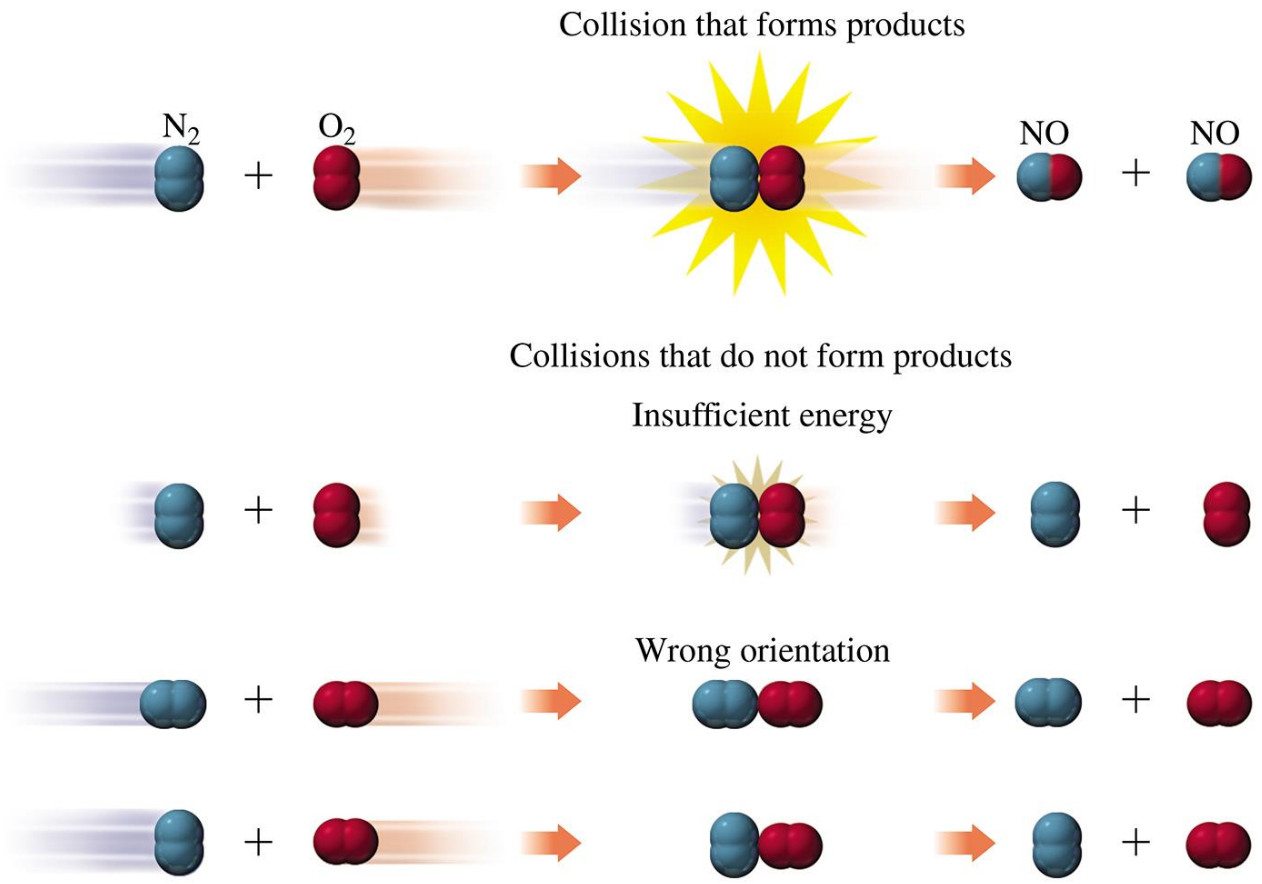
The **collision theory** indicates that a reaction takes place only when molecules collide with the *proper orientation* and *sufficient energy*

Collision Theory

Many collisions may occur, but only a few actually lead to the formation of product.

For example, $N_2 + O_2 \rightarrow 2NO$

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



Activation Energy

Even when a collision has the proper orientation, there still must be sufficient energy to break the bonds of the reactants.

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

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, its 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.

Then the reactants may be converted to products.

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

Activation Energy

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

Then the reactants may be converted to products.

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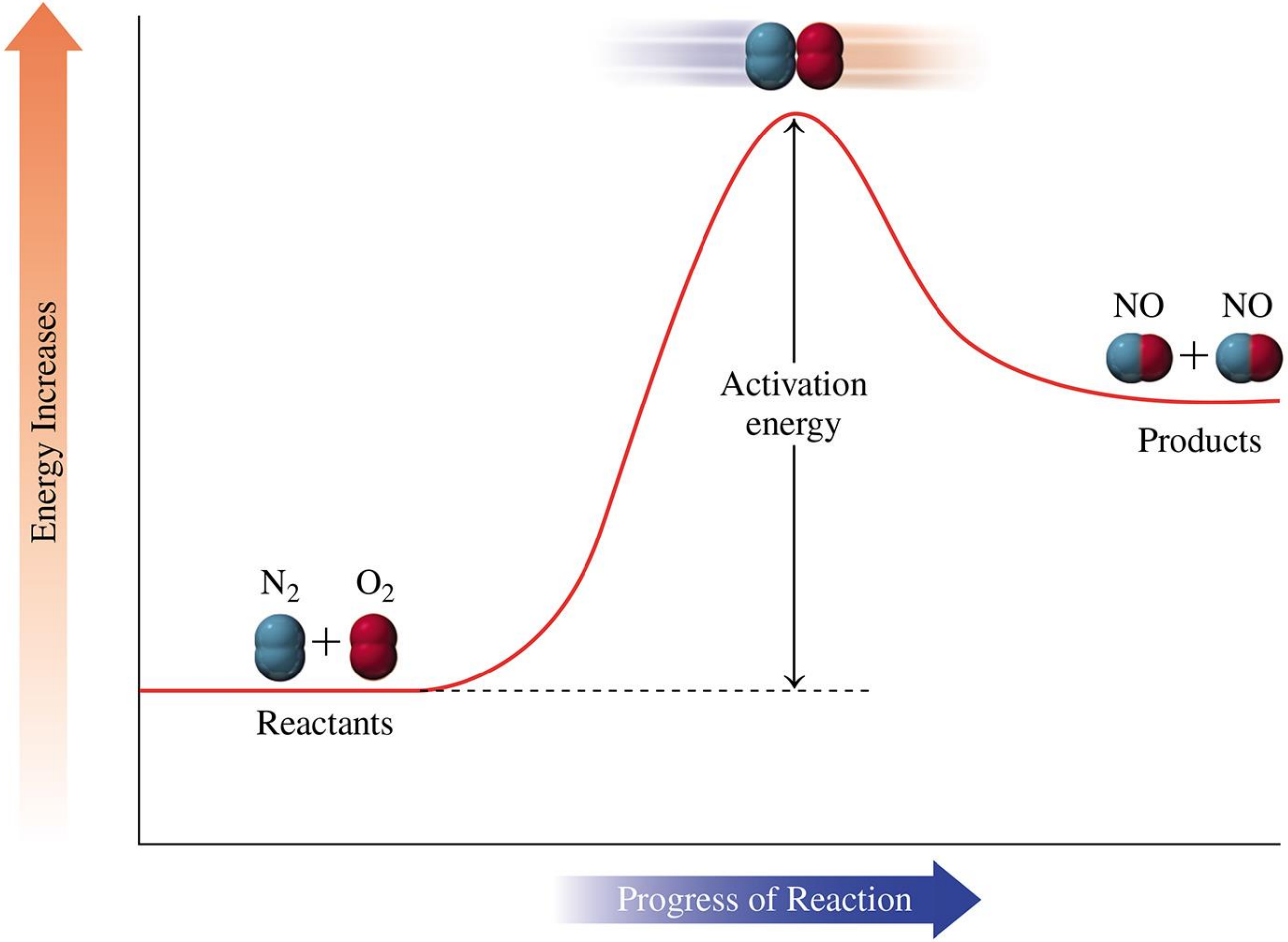


3 Conditions Required for a Reaction to Occur:

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.

Rates of Reactions

The **rate of reaction** is determined by measuring the amount of a 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 of Reactions - Pizza

Describing the rate of reaction:

When you eat a pizza, you begin with a whole pizza. As time goes by, there are fewer slices of pizza left.

If we know how long it took to eat the pizza, we could determine the rate at which the pizza was consumed.

Let's assume four slices are eaten every 8 minutes. That gives a rate of ½ slice per minute. After 16 minutes, all 8 slices are gone.

Rate at Which Pizza Slices Are Eaten

Slices Eaten	0	4 slices	6 slices	8 slices
Time (min)	0	8 min	12 min	16 min

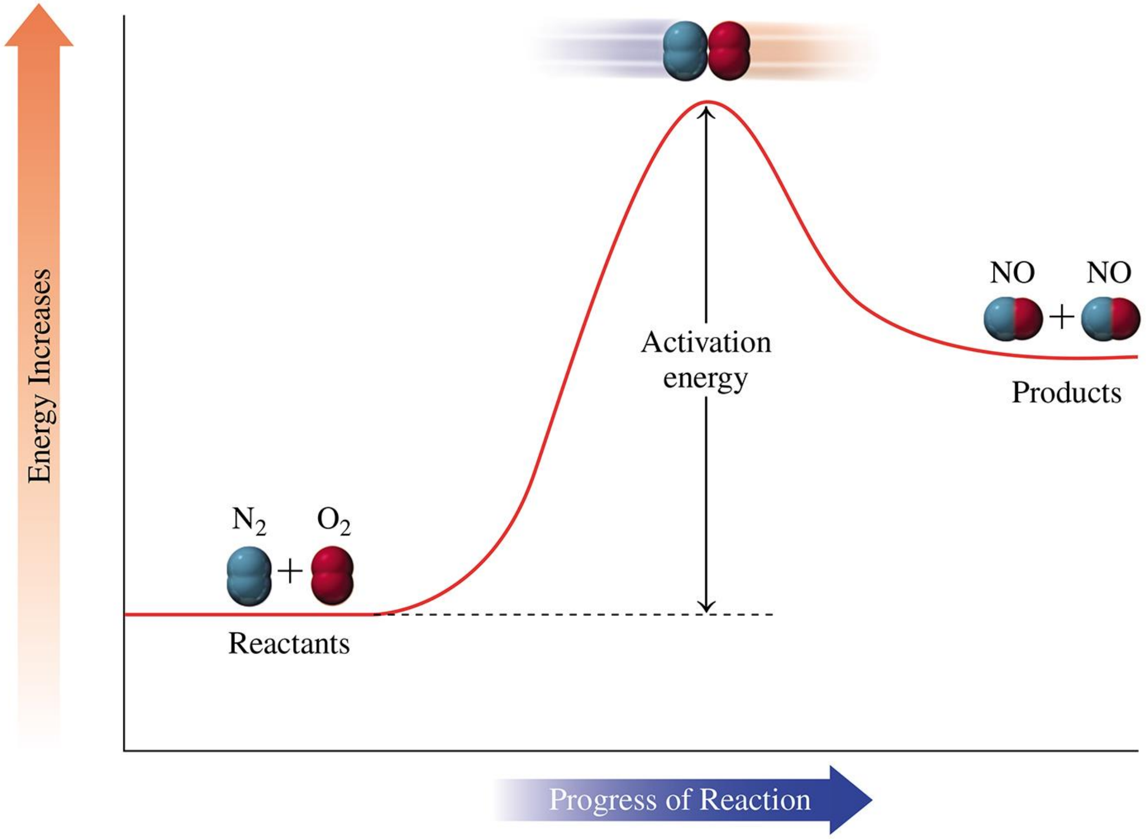
$$\text{Rate} = \frac{4\ \text{slices}}{8\ \text{min}} = \frac{1\ \text{slice}}{2\ \text{min}} = \frac{\frac{1}{2}\ \text{slice}}{1\ \text{min}}$$

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 sow.

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 increase, 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 O_2 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 collision 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:

$Hb + O_2 \rightarrow HbO_2$

More O_2 molecules in the lungs increases the rate of O_2 uptake into the body because there's more changes for O_2 to collide correctly with hemoglobin (Hb).

- (Hemoglobin is the taxi service for transferring oxygen through the blood.)

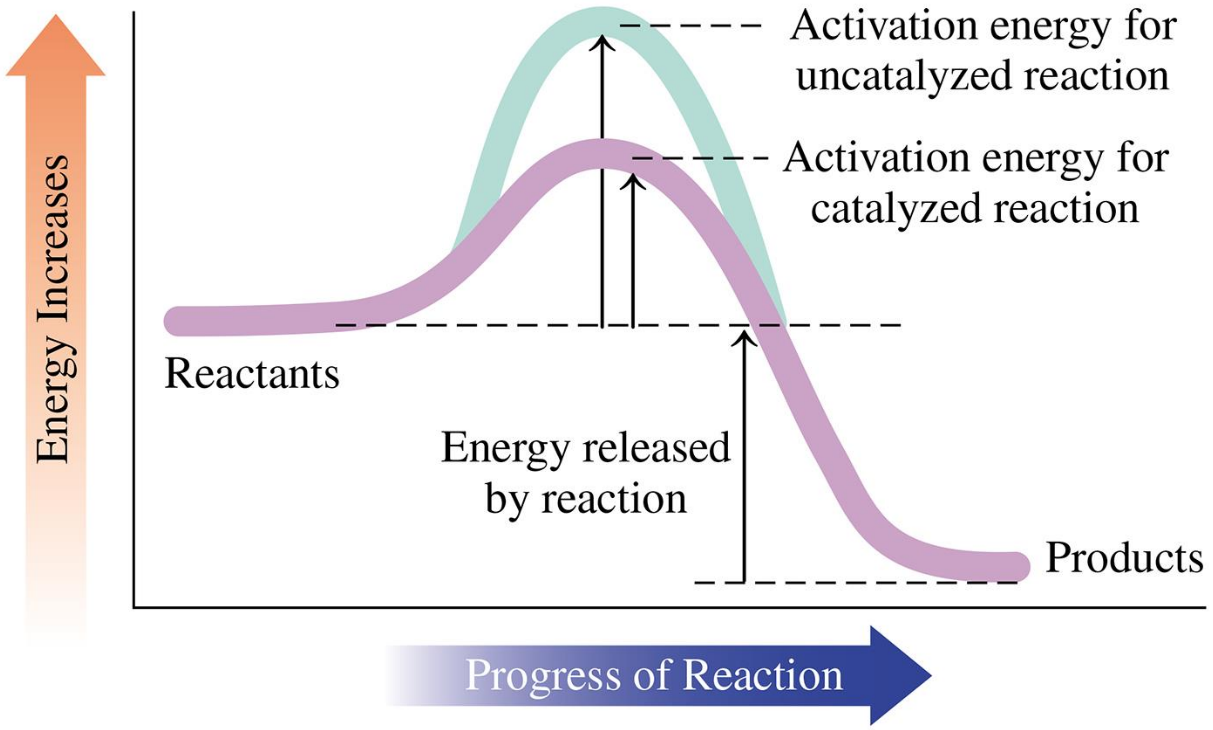
Catalysts

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.

During a reaction, a catalyst is not changed or comsumed.



Catalysts - examples

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 that Increase Reaction Rate

Increase temperature - more collisions possible, and more collisions that have the required activation energy.

Increase reactant concentration – More collisions.

Add a catalyst – Lowers energy of activation.

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10.2 Chemical Equilibrium

Use the concept of reversible reactions to explain chemical equilibrium.

Reversible Reactions

In earlier chapters, we considered the *forward reaction* in an equation and assumed that all of the reactants were converted to products.

However, most of the time, reactants are not completely converted to products because a *reverse reaction* takes place in which products collide to form the reactants.

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

Reversible Reactions

We have looked at reversible processes already:

A **reversible reaction** proceeds in both the forward and reverse directions.

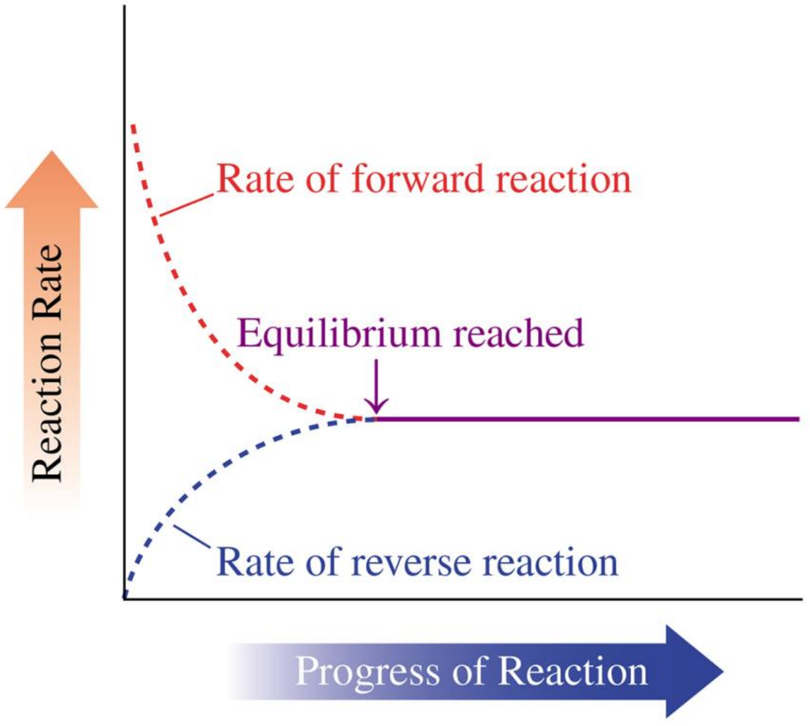
That means there are 2 reaction rates:

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

Reversible Reactions

When molecules first begin to react, they 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.



Equilibrium

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

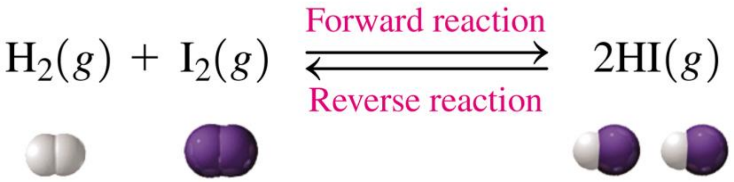
At equilibrium:

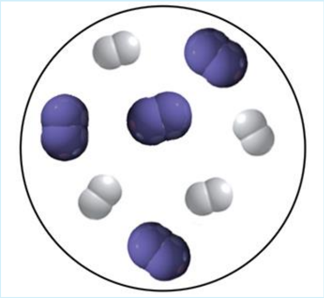
The rate of the forward reaction is equal to the rate of the reverse reaction.

No further changes occur in the concentrations of reactants and products, even though the two reactions continue at equal but opposite rates.

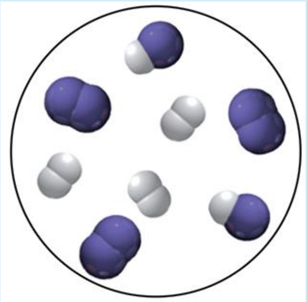
Equilibrium - example

The process as the reaction of H_2 and I_2 proceeds to equilibrium:

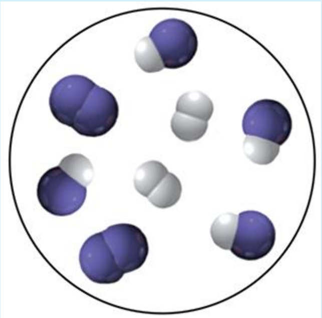




Initially only the reactants, H_2 and I_2, are present.



Soon, a few molecules of HI are produced by the forward reaction.



With more time, additional HI molecules are produced.

As the concentration of HI increase, more HI molecules collide and react in the reverse direction.

As HI builds up, the rate of the reverse reaction increases, while the rate of the forward reaction decreases (not as much H2 and I2 to react as often).

Eventually the rates become equal, which means the reaction has reached equilibrium.

Even though the concentrations remain constant at equilibrium, the forward and reverse reactions continue to occur.

Practice

Before equilibrium is reached, the concentrations of the reactants and products *change or don't change.*

Initially, reactants placed in a container have a *faster or slower rate* of reaction than the rate of reaction of the products.

At equilibrium, the rate of the forward reaction is *equal or not equal* to the rate of the reverse reaction.

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10.3 Equilibrium Constants

Calculate the equilibrium constant for a reversible reaction given the concentrations of reactants and products at equilibrium.

At equilibrium, the concentrations of the reactants and products are constant.

Ski Lift

Early in the morning, skiers at the bottom of the mountain begin to ride the ski lift up to the slopes. After the skiers reach the top of the mountain, they ski down.

Eventually, the number of people riding the lift becomes equal to the number of people skiing down the mountain. There is no further change in the number of skiers on the slopes; the system is at equilibrium.

Equilibrium Constant Expression

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

$$aA + bB \rightleftharpoons cC + dD$$

Equilibrium constant expression for a reversible chemical reaction:

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Coefficients

Equilibrium
constant expression

Equilibrium Constant Expression

Write the equilibrium constant expression:

$$H_2(g) + I_2(g) \xrightleftharpoons[\text{Reverse reaction}]{\text{Forward reaction}} 2HI(g)$$

Practice

Write the equilibrium constant expression:

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

Calculating Equilibrium Constants

The **equilibrium constant, Kc,** is the numerical value obtained by substituting experimentally measured molar concentrations at equilibrium into the equilibrium constant expression.

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[\text{C}]^c\,[\text{D}]^d}{[\text{A}]^a\,[\text{B}]^b}$$

Coefficients

Equilibrium
constant expression

Calculating Equilibrium Constants

$$H_2(g) + I_2(g) \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftarrows}} 2HI(g)$$

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 value for the equilibrium constant?

Calculating Equilibrium Constants

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.

$$H_2(g) + I_2(g) \underset{\text{Reverse reaction}}{\overset{\text{Forward reaction}}{\rightleftharpoons}} 2HI(g)$$

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

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

Practice

The decomposition of dinitrogen tetroxide forms nitrogen dioxide:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

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

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10.4 Using Equilibrium Constants

Use an equilibrium constant to predict the extend of reaction and to calculate equilibrium concentrations.

Equilibrium Constants

The values of K_c can be large or small.

The size of the equilibrium constant (K_c) 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.

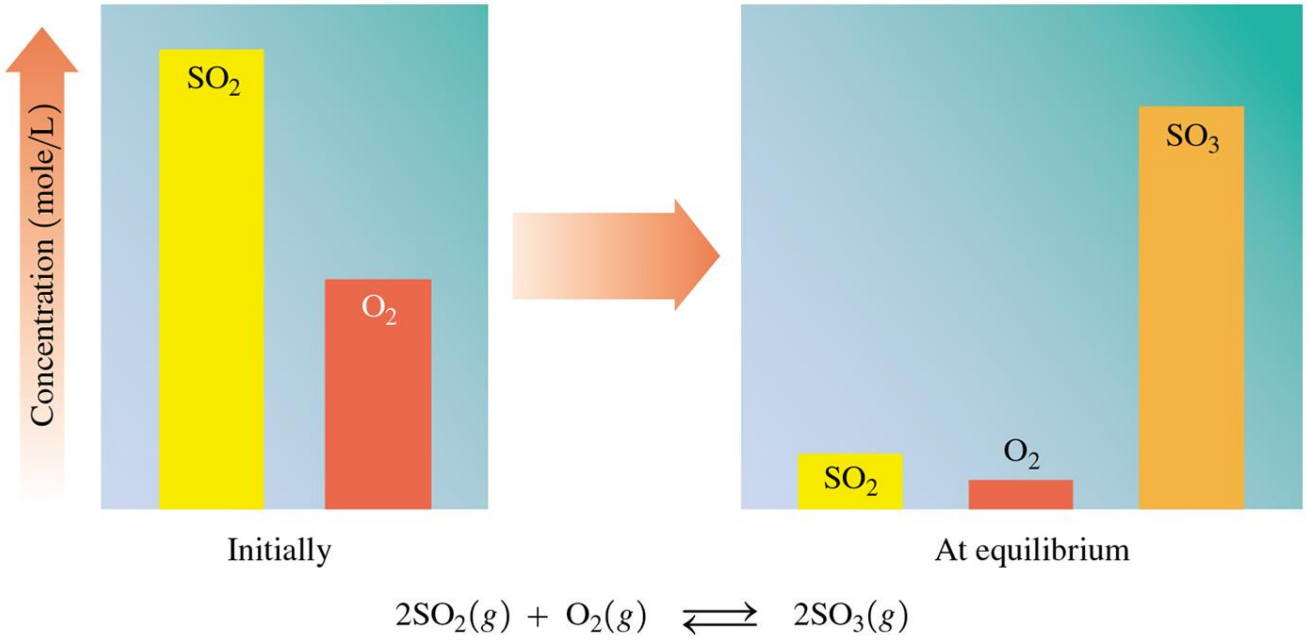
Equilibrium with a Large K_c

When a reaction has a large Kc, it means that the forward reaction produced a large amount of products when equilibrium was reached.

The equilibrium mixtures contains more products than reactants.

$2SO_2 + O_2 \rightleftharpoons 2SO_3$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\text{mostly products}}{\text{few reactants}} = 3.4 \text{ x } 10^2$$

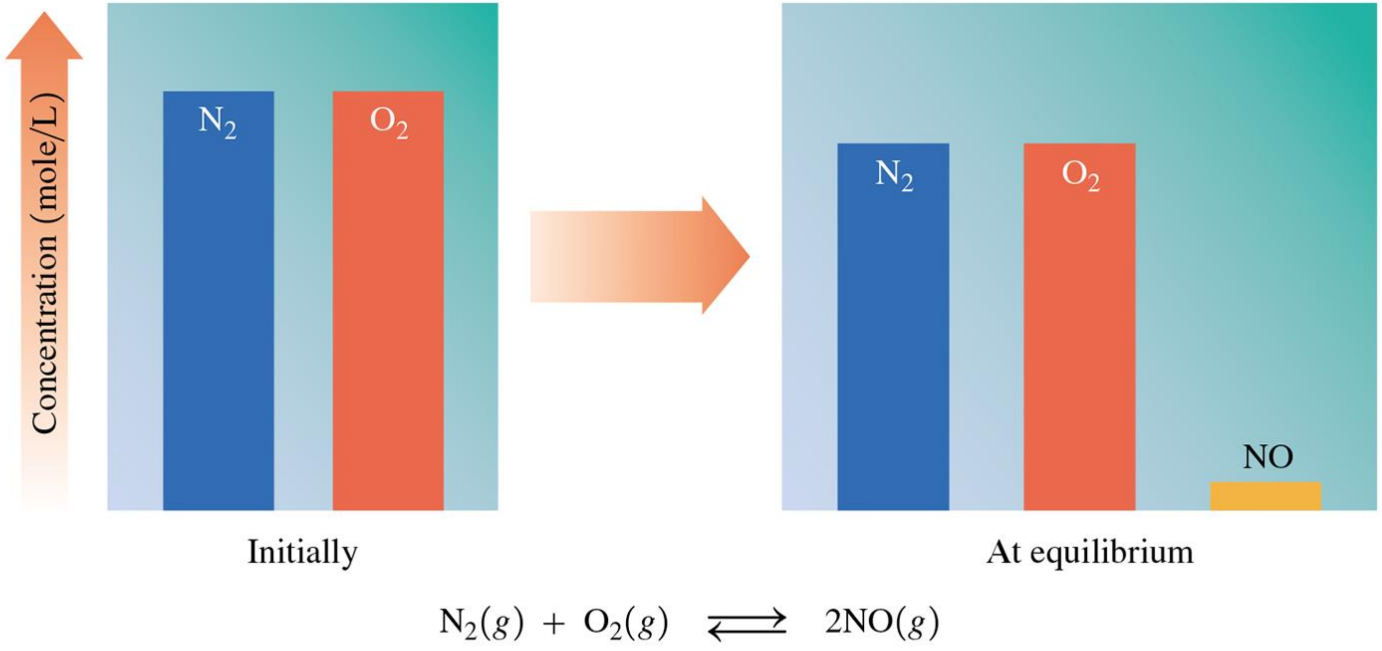


Equilibrium with a Small K_c

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

$N_2 + O_2 \rightleftharpoons 2NO$

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = \frac{\text{few products}}{\text{mostly reactants}} = 2 \text{ x } 10^{-9}$$



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

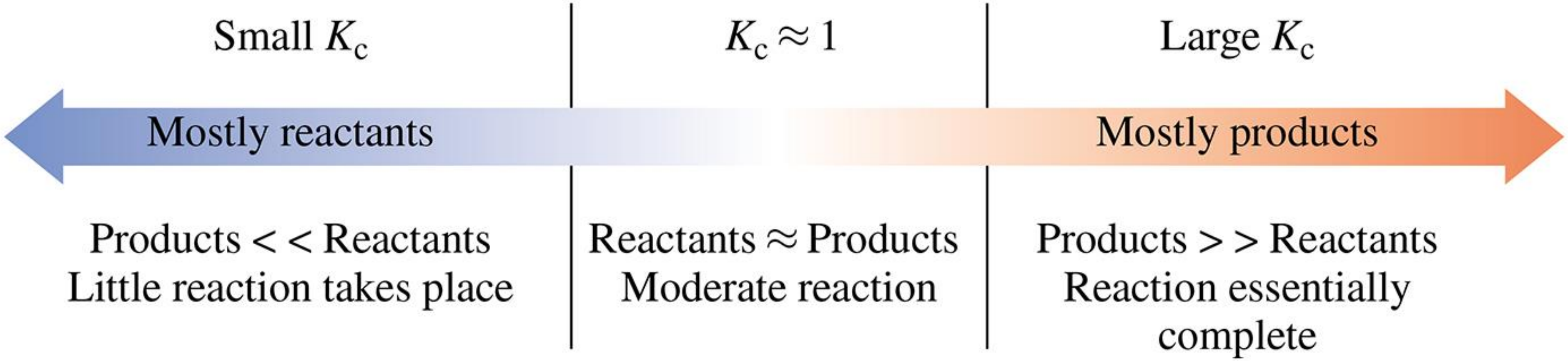


TABLE 10.3 Examples of Reactions with Large and Small K_c Values

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

Calculating Concentrations at Equilibrium

When we know the numerical value of the equilibrium constant and all the equilibrium concentrations except one, we can calculate the unknown concentration.

For the reaction of carbon dioxide and hydrogen, the equilibrium concentrations are 0.25M CO2, 0.80M H2, and 0.50M H2O. What is the equilibrium concentration of CO?

$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ $\qquad K_c = 0.11$

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10.5 Changing Equilibrium Conditions: Le Châtelier's Principle

Use Le Châtelier's Principle to describe the changes made in equilibrium concentrations when reactions conditions change.

We have seen that when a reaction reaches equilibrium, the rates of the forward and reverse reactions are equal and the concentrations remain constant.

Now we will look at what happens to a system at equilibrium when changes occur in reaction conditions, such as changes sin concentration, volume, and temperature.

Le Châtelier's Principle

When we alter any of the conditions of a system at equilibrium, the rates of the forward and reverse reactions will no longer be equal.

- We say that *stress* is placed on the equilibrium.

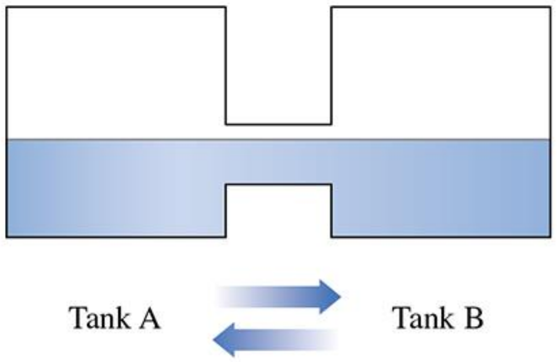
Then the system responds by *changing the rate* of the forward or reverse reaction in the direction that relieves the stress to reestablish equilibrium.

Le Châtelier's Principle: When a stress (change in conditions) is placed on a reaction at equilibrium, the equilibrium will shift in the direction that relieves the stress.

Le Châtelier's Principle - example

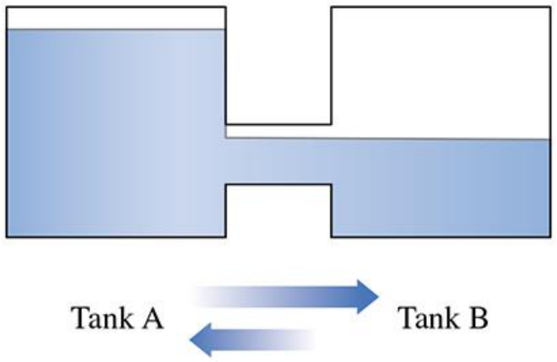
Two water tanks are connected by a pipe. When the water levels in the tanks are equal, water flows in the forward direction from Tank A to Tank B at the same rate as it flows in the reverse direction from Tank B to A.

At equilibrium, the water levels are equal.



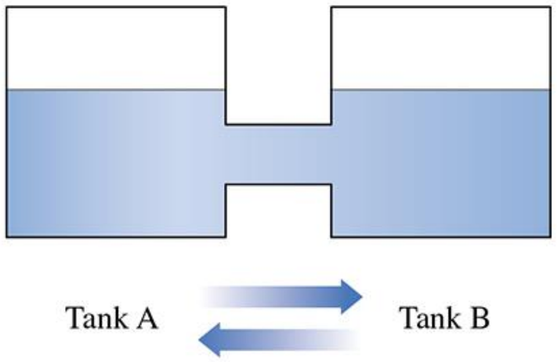
Suppose we add more water to tank A. ith a higher level of water in A, more water flows in the forward direction (A to B) than in the reverse direction (B to A).

Water added to tank A increases the rate of the forward direction.



Eventually equilibrium is reached as the levels in both tanks become equal, but higher than before.

Equilibrium is reached again when the water levels are equal.



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 Concentration Changes on Equilibrium

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

Add H_2:

Remove H_2:

Add HI:

Remove HI:

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 effect 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.

$$2CO(g) + O_2(g) \quad 2CO_2(g)$$

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.

Effect of Volume Change on Equilibrium

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

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

FYI: Oxygen-Hemoglobin Equilibrium

The transport of oxygen involves an equilibrium between hemoglobin (Hb), oxygen, and oxyhemoglobin (HbO_2):

$Hb(aq) + O_2(g) \rightleftharpoons HbO_2(aq)$ $\qquad$ $K_c = \frac{[HbO_2]}{[Hb][O_2]}$

When the O_2 level is high in the lungs, the reaction shift toward the products. HbO_2 then carries O_2 along the blood stream to the tissues.

In the tissues, where O_2 concentration is low, the reverse reaction releases the oxygen from the hemoglobin.

Effect of Temperature Change on Equilibrium

We can think of 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

Effect of Temperature Change on Equilibrium

We can think of 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

TABLE 10.5 Effects of Condition Changes on Equilibrium

Condition	Change (Stress)	Shift in the Direction of
Concentration	Add a reactant	Products (forward reaction)
	Remove a reactant	Reactants (reverse reaction)
	Add a product	Reactants (reverse reaction)
	Remove a product	Products (forward reaction)
Volume (container)	Decrease volume	Fewer moles of gas
	Increase volume	More moles of gas
Temperature	**Endothermic reaction**	
	Increase T	Products (forward reaction to remove heat)
	Decrease T	Reactants (reverse reaction to add heat)
	Exothermic reaction	
	Increase T	Reactants (reverse reaction to remove heat)
	Decrease T	Products (forward reaction to add heat)
Catalyst	Increases rates equally	No effect

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REACTION RATES AND CHEMICAL EQUILIBRIUM

involves

- **Reaction Rates**
  - are affected by
    - **Concentrations of Reactants**
    - **Temperature**
    - **Catalyst**
- **Reversible Reactions**
  - when equal in rate give
    - **Equilibrium Constant Expression**
      - is written as
        - $K_c = \dfrac{\text{Products}}{\text{Reactants}}$
          - **Small K_c Has Mostly Reactants**
          - **Large K_c Has Mostly Products**
- **Le Châtelier's Principle**
  - indicates that equilibrium adjusts for changes in
    - **Concentration, Temperature, and Volume**