

# Kinetics / Equilibrium

## Unit 7

Kinetics: the study of reaction rates and reaction mechanisms (or reaction pathways)

Collision Theory: for a chemical reaction to occur, reactant particles must come into contact (collide) with enough energy and in the proper orientation

Thermodynamics: the study of energy and entropy changes in chemical reactions

Heat of Reaction: often called the change in enthalpy,  $\Delta H$ , is the amount of heat released or absorbed in a chemical reaction (see Table I)

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} = H_P - H_R$$

Exothermic reaction:  $A + X \rightarrow AX + \text{energy}$  (bond formation is always exothermic)

Products have less PE than the reactants

Heat was released or given off to the surroundings

Heat of reaction is negative or  $\Delta H < 0$

Endothermic reaction:  $AX + \text{energy} \rightarrow A + X$  (bond breaking is always endothermic)

Products have more PE than the reactants

Heat was absorbed or gained from the surroundings

Heat of reaction is positive or  $\Delta H > 0$

Reactions tend to be spontaneous when they release heat (are exothermic or  $\Delta H < 0$ )

Entropy: the amount of disorder,  $\Delta S$

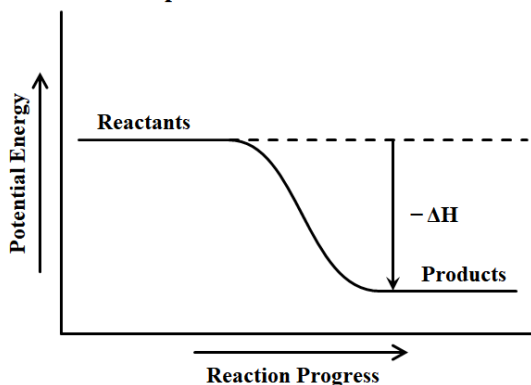
Reactions tend to be spontaneous when entropy increases ( $\Delta S > 0$ )

Potential Energy: chemical energy has to do with chemical bonds or PE

Potential energy diagrams give insights into reaction speed and whether the heat of reaction will be endothermic or exothermic

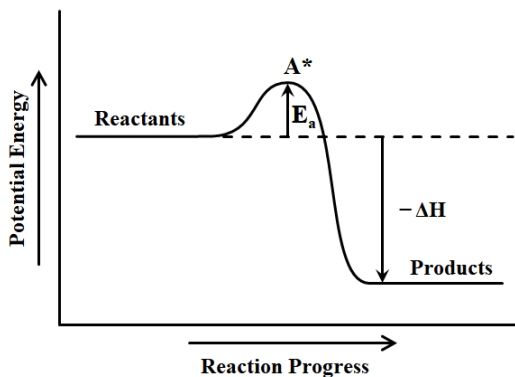
### Potential Energy Diagrams

Simplified Exothermic Reaction

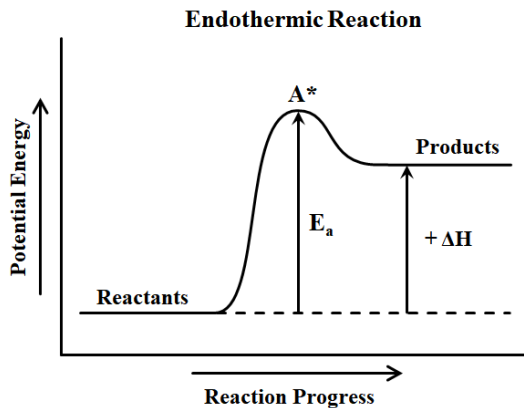


This simplified potential energy diagram shows that energy is released, but does not account for the fact that before new bonds can form, old bonds must be broken and bond breaking always requires energy (is always endothermic)

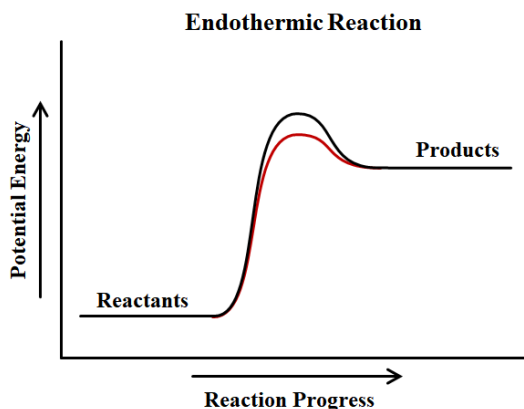
Exothermic Reaction



This modified potential energy diagram shows that energy is released, and also shows that the reactants must gain enough energy (activation energy,  $E_a$ ) to form an activated complex ( $A^*$ )



Notice that due to the nature of an endothermic reaction, the activation energy,  $E_a$ , is usually much higher than for exothermic reactions and that the  $\Delta H$  is now positive



The addition of a catalyst allows an alternate reaction pathway with a lower activation energy (see red line)

Because less energy is now needed to start the reaction, the reaction speed will increase

**Kinetics and Collision Theory:** for a chemical reaction to occur, reactant particles must come into contact (collide) with enough energy and in the proper orientation

There are two conditions for collision theory:

1. Sufficient energy to create an activated complex
2. Proper orientation

**Example question:** In terms of collision theory, explain why an increase in temperature causes a chemical reaction to increase in speed

As temperature increases, particles collide with more force which increases the chances of a collision with enough energy to create an activated complex and particles collide more often increasing the chances of a collision with proper orientation.

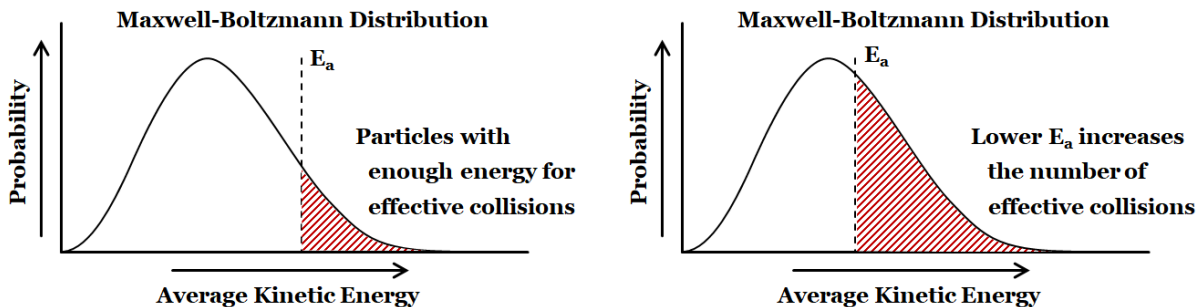
Five factors affecting rate of reaction:

1. Nature of the reactants
  - Mg is a more active metal than Cu (see Table J)
  - if fewer and smaller bond rearrangements are required, reaction speed increases
  - ions react fast because opposites attract and almost any angle is auspicious
  - if the first step in a mechanism requires bond breaking, the reaction will be slower
2. Concentration of the reactants
  - higher concentrations increase the number of collisions
  - higher gas pressure increases the number of collisions (only works for gases)
3. Temperature: near STP, each  $10^\circ\text{C}$  increase doubles the reaction rate (Arrhenius' Law)
  - higher temperatures increase both
    - force so more collisions have enough activation energy
    - speed so collisions occur more often

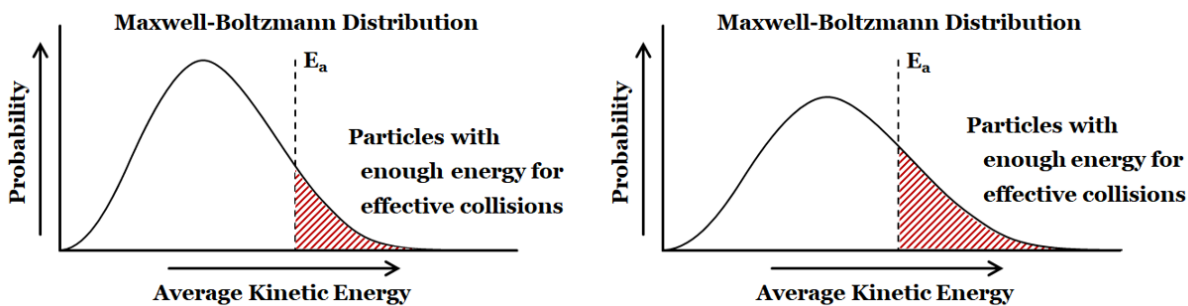
4. Surface area
  - more surface area increases the number of exposed particles that can collide
5. Catalysts
  - catalysts provide an alternate reaction path that has a lower activation energy ( $E_a$ )
  - inhibitors prevent faster pathways and result in paths with higher  $E_a$

Maxwell-Boltzmann Distributions and  $E_a$ :

Effect of a catalyst on  $E_a$ :



Effect of increase in temperature:



Enthalpy ( $\Delta H$ ) and Entropy ( $\Delta S$ )

Heat of Reaction (or Enthalpy,  $\Delta H$ ) see Table I

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

$\Delta H$  negative ( $\Delta H < 0$ ) is an exothermic reaction

$\Delta H$  positive ( $\Delta H > 0$ ) is an endothermic reaction

See the note at the bottom of Table I:

The  $\Delta H$  values are based on molar quantities represented in the equations

A minus sign indicates an exothermic reaction

**Example: what is the heat of formation of 1.0 mole of  $\text{NO}_2(\text{g})$ ?**



$\Delta H$  for  $2 \text{NO}_2(\text{g}) = +66.4 \text{ kJ}$

$\therefore \Delta H$  for 1 mole  $\text{NO}_2(\text{g}) = +33.2 \text{ kJ}$

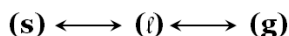
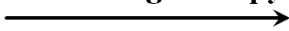
Helpful hints about Table I:

- 101.3 kPa and 298 K are room temperature and pressure
- the first 7 equations are  $\Delta H_{\text{combustion}}$
- the next 11 equations are  $\Delta H_{\text{formation}}$
- the first 6 equations are  $\Delta H_{\text{solvation}}$
- the last equation is  $\Delta H$  for a net ionic reaction
- the  $\Delta H$  for the reverse reaction for the one shown is  $-\Delta H_{\text{shown}}$
- use Table I when asked to find:
  - energy change
  - heat change
  - change in PE
  - heat of reaction
  - $\Delta H$

Entropy changes ( $\Delta S$ ): amount of disorder

Entropy is related to phase changes [for phase,  $(\text{aq}) \approx (\ell)$ ]

**increasing entropy**



**decreasing entropy**

**Examples: Predict the change in entropy for the following reactions**



Entropy is related to the number of particles (if phase changes are no help)  
an increase in the total number of moles = an increase in the entropy

**Example: Predict the change in entropy for the following reaction**



Spontaneous Reactions

Spontaneous reactions proceed without outside intervention (but do require  $E_a$ )

Conditions that tend toward spontaneity

- exothermic reactions ( $-\Delta H$ )
- when entropy is increased ( $+\Delta S$ )

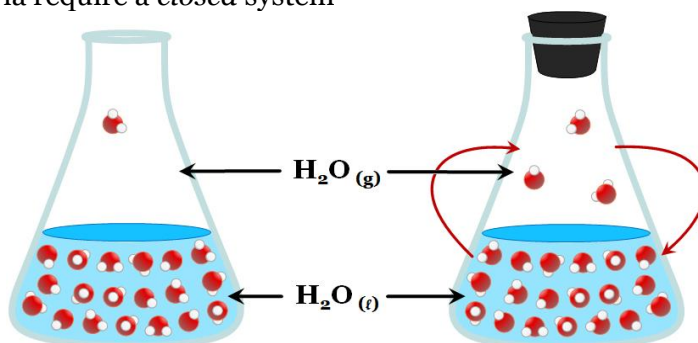
If  $\Delta H$  is - and  $\Delta S$  is +, the reaction *must* be spontaneous

Equilibrium: a state in which a process and its reverse are occurring at *equal rates* so that no *net change* is taking place

Equal rates does *not* mean the same thing as equal amounts or equal concentrations

Most equilibria are dynamic, *not* static

Dynamic equilibria require a *closed system*

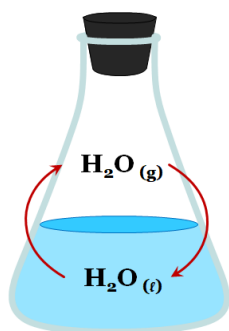


In this open system,  $\text{H}_2\text{O (g)}$  can escape so the rate of condensation will always be less than the rate of evaporation

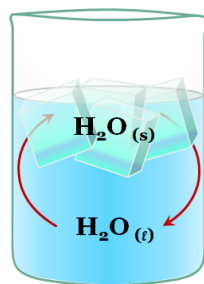
In this closed system,  $\text{H}_2\text{O (g)}$  builds up until the rate of condensation is equal to the rate of evaporation

Three types of chemical equilibria:

1. Phase equilibria (physical changes occur)

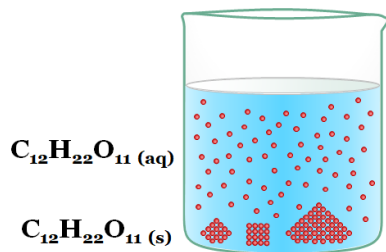


a. liquid  $\rightleftharpoons$  gas  
 $\text{H}_2\text{O (l)} \rightleftharpoons \text{H}_2\text{O (g)}$



b. solid  $\rightleftharpoons$  liquid  
 $\text{H}_2\text{O (s)} \rightleftharpoons \text{H}_2\text{O (l)}$

2. Solution equilibria (physical changes occur)



a. solid  $\rightleftharpoons$  aqueous  
 $\text{C}_{12}\text{H}_{22}\text{O}_{11} \text{ (s)} \rightleftharpoons \text{C}_{12}\text{H}_{22}\text{O}_{11} \text{ (aq)}$



b. gas  $\rightleftharpoons$  aqueous  
 $\text{CO}_2 \text{ (g)} \rightleftharpoons \text{CO}_2 \text{ (aq)}$

3. Chemical equilibria (chemical changes occur)

Example:  $\text{N}_2 \text{ (g)} + 3 \text{H}_2 \text{ (g)} \rightleftharpoons 2 \text{NH}_3 \text{ (g)}$  (the Haber process for fixing nitrogen)

Under pressure, the  $\text{NH}_3 \text{ (g)}$  will form  $\text{NH}_3 \text{ (l)}$  which shifts the equilibrium to the right

Le Châtelier's Principle: a stress on a system in equilibrium causes a shift that will act to partially relieve that stress

The equilibrium system must be a *closed* system

Stresses that can cause an equilibrium to shift:

- Temperature (T)
- Concentration [ ]
- Pressure (P) which affects *gases only*

Le Châtelier also noted that changes in volume can cause an equilibrium to shift, but changes in volume can be expressed as changes in [ ] for solutions and as changes in P for gases

Temperature and equilibrium: write the reaction with heat as a reactant or a product

Example:  $A + \text{heat} \rightleftharpoons C + D$

Increase in T: will add more reactant and causes the equilibrium to shift to the right

- A will decrease
- C will increase
- D will increase

Decrease in T: will remove some reactant and causes the equilibrium to shift to the left

- A will increase
- C will decrease
- D will decrease

Example:  $A + B \rightleftharpoons \text{heat} + C$

Increase in T: will add more product and causes the equilibrium to shift to the left

- A will increase
- B will increase
- C will decrease

Decrease in T: will remove some product and causes the equilibrium to shift to the right

- A will decrease
- B will decrease
- C will increase

Concentration and equilibrium:

Example:  $A_{(aq)} + B_{(aq)} \rightleftharpoons C_{(s)}$

Increase in [A]: causes the equilibrium to shift to the right

- [B] will decrease
- amount of  $C_{(s)}$  will increase (but not the concentration)

Increase the amount of  $C_{(s)}$ : no equilibrium shift will occur

Pressure changes and equilibrium: effective only for reactions that contain a gas

Example:  $A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)}$

Increase in pressure of A: causes the equilibrium to shift to the right

- B will decrease
- C will increase

Decrease the total pressure (increase the volume): will shift the equilibrium to the left

- A and B will increase
- C will decrease

Example:  $A_{(g)} + B_{(g)} \rightleftharpoons 2 C_{(g)}$

Increase in pressure of A: causes the equilibrium to shift to the right

- B will decrease
- C will increase

Increase the total pressure by decreasing the volume: no equilibrium shift will occur

Catalysts and equilibrium: catalysts lower the activation energy ( $E_a$ ) for both the forward and the reverse rates; since both rates are faster, there is no shift in the equilibrium

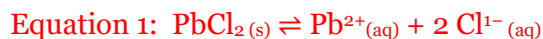
Common Ion Effect: increasing the concentration of one of the dissolved component ions in a reversible reaction will cause a shift in the reaction by Le Châtelier's principle even if the concentration of only one ion in the equation changes

Example: lead(II) chloride

Table F lists  $\text{PbCl}_2$  as insoluble, but the solubility is actually  $0.45 \text{ g PbCl}_2 / 100 \text{ g H}_2\text{O}$

This amount of lead is 3350 ppm and safe water contains less than 15 ppm

Using Le Châtelier's principle to our advantage:



Notice that  $\text{Cl}^{-}(\text{aq})$  appears in both equations, a *common ion*

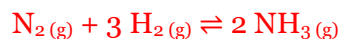
Table G shows  $38 \text{ g NaCl} / 100 \text{ g H}_2\text{O}$  or 6.5 moles  $\text{Cl}^{-}$  per liter

Better tables show  $35.8 \text{ g} / 100 \text{ g}$  which is 5.4 moles  $\text{Cl}^{-}$  per liter of solution

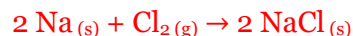
By Le Châtelier's principle, this would reduce the  $\text{Pb}^{2+}$  to 0.010 ppm  
(but the water is now far too salty to drink)

## Reversible Reactions and Completion Reactions

Le Châtelier's principle requires a *reversible* reaction



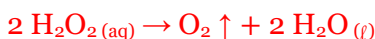
Reactions that go to completion:



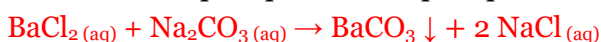
- are irreversible (only go one way)
- go 100% to products (react completely)
- have a driving force

Factors that drive reactions to completion:

- formation of a gas – the gas escapes and the reaction cannot reverse



- formation of a precipitate – the precipitate removes ions and the reaction cannot reverse



- formation of a molecule ( $\text{H}_2\text{O}$ ) – the molecule removes ions and the reaction cannot reverse

