CHAPTER 17

Reaction Rates

17.1 Reaction Rates

- The change in concentration of a reactant or product in a specified amount of time.
- Must be determined experimentally
- They cannot be calculated from balanced equations or from stoichiometric caclulations

Average Reaction Rate

$$\text{Average Rate} = \frac{\Delta\text{quantity}}{\Delta\textit{time}} \qquad \text{Expressed in: } \frac{\text{mol}}{\text{L x s}}$$

Reaction rates must be positive, so the negative sign below is used when a reactant is consumed.

$$\text{Average Rate} = -\frac{\Delta\text{quantity}}{\Delta\textit{time}}$$

Calculating Average Reaction Rates

You are given initial and final concentrations of C_4H_9Cl and the time at which it occurred. What is the average reaction rate?

Known

$t_1 = 0.00$ s

$t_2 = 4.00$ s

$[C_4H_9Cl]$ at $t_1 = 0.220$-M

$[C_4H_9Cl]$ at $t_2 = 0.100$-M

$$\text{Average Rxn Rate} = -\frac{[C_4H_9Cl] \text{ at } t_2 - [C_4H_9Cl] \text{ at } t_1}{t_2 - t_1}$$

$$\text{Average Rxn Rate} = -\frac{0.100 \text{ mol/L} - 0.220 \text{ mol/L}}{4.00 \text{ s} - 0.00 \text{ s}}$$

$$\text{Average Rxn Rate} = -\frac{-0.120 \text{ mol/L}}{4.00 \text{ s}}$$

0.0300 mol/(L•s)

Collision Theory

Atoms, ions, and molecules must collide in order to react

Atoms, ions, and molecules can form a chemical bond when they collide, as long as the particles have enough kinetic energy and have the proper orientation.

Many atoms collide all the time, but never react because there is not enough energy or they do not collide with the proper orientation.

For a chemical reaction to occur

3 things required according to the Collision Theory

1. Atoms must collide
2. Atoms must collide with enough energy
3. Substances must collide with the correct orientation

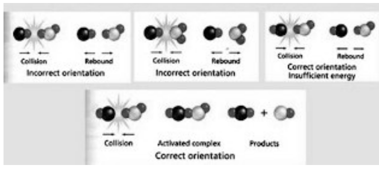
If the 3 things occur and a chemical reaction takes place

- There is a rearrangement of Atoms
- Bonds break in reactants
- Bonds form in products
- ΔH= Final Energy – Initial Energy

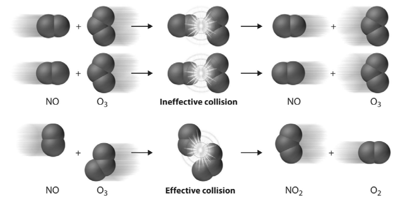
Orientation of colliding molecules

In order for the reactions to occur, molecules must collide with favorable orientations.

CO must collide with NO_2 properly



Effective Collisions

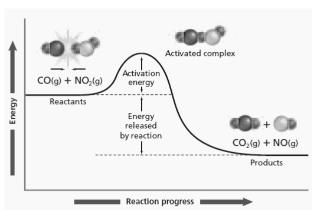


Favorable Orientations

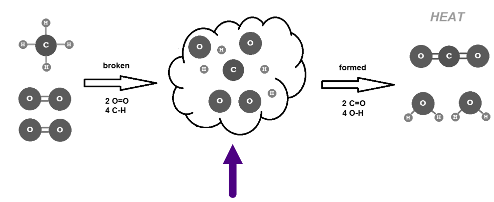
- The Nitrogen in the NO molecule must collide with the top Oxygen in the O_3 molecule or else the molecules will bounce off each other.

Activated Complex

- Forms only if the colliding particles have sufficient energy and are oriented properly.
- Lasts momentarily. *(10^{-13} second)*
- Unstable arrangement of atoms.



$CH_4 + 2O_2$ → $CO_2 + 2H_2O$



Activated Complex

Transition State

- Also called the Activated Complex.
- This is the first thing that must happen in order for a chemical reaction to occur.
- In this state, the activated complex can go back to the reactants or end with the formation of products.
- Has a great deal of energy!

Activation Energy

- The minimum energy that particles must have in order to react.
- Even if molecules collide with a favorable orientation, they still need a sufficient amount of energy to react.
- It is the point that reactants must cross to form products.
- High activation energy (E_a) reactions will not occur easily & often
- Low activation energy (E_a) reactions will occur easily & often

Exothermic

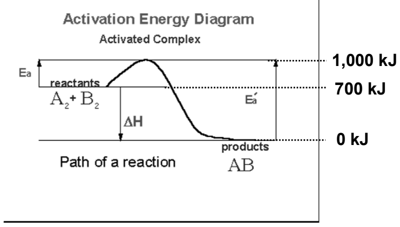
A + B → C + D + Energy

- Energy Stored in bonds of A + B
- Reactions occur easily
- Bonds in A + B were broken when activation energy was met.
- When C + D formed, energy was released.

Exothermic Reaction

The ΔH is not changed by the activation energy.

The ΔH is the difference between the energy stored in the reactants and the energy stored in the products.



Endothermic

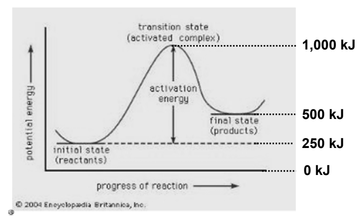
A + B + Energy → C + D

- No energy Stored in bonds of A + B
- Require a lot of energy to react
- Bonds in A + B were broken when activation energy was met.
- When C + D formed, the excess energy was stored in their bonds.

Endothermic Reaction

The ΔH is not changed by the activation energy.

The ΔH is the difference between the energy stored in the reactants and the energy stored in the products.



The influence of spontaneity on Reaction Rates

- Spontaneous reactions occur when the change in free energy is negative
- The spontaneity of a reaction does not necessarily give you the rate of the reaction.
- The rate of a chemical reaction is controlled by other factors.

FACTORS AFFECTING REACTION RATES

Depends of the reactive nature of the elements

Remember, some substances are more reactive than others based on their electron arrangement

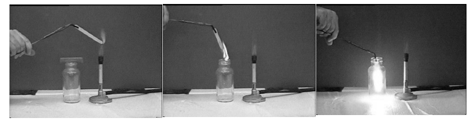
FACTORS AFFECTING REACTION RATES

These Increase collisions and/or kinetic energy

- Temperature
- Concentration
- Particle Size
- Catalysts

Concentration

- Higher concentration increases collision rate.
- This speeds up reaction rate.
- Magnesium in 6-*M* HCl vs. Magnesium in 1-*M* HCl.
  - > High concentration = more dissolved particles
- Flame in air vs. flame in pure oxygen.



Surface Area

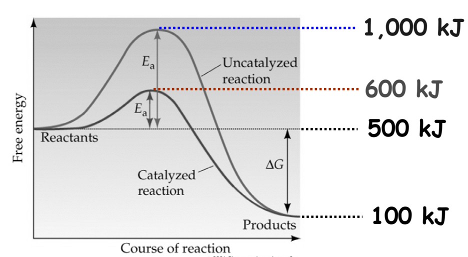
- **Smaller particles increase surface area, which increases reaction rate.**
- **Large particles have a lot of atoms inside, which are unable to react since they are not exposed to other reactants.**
- **How to increase surface area?**
  - > **Grinding substance into a powder.**
  - > **Dissolving substances.**

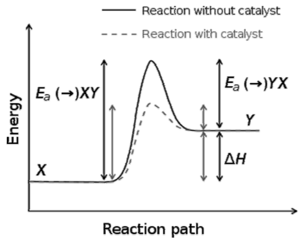
Temperature

- Raising temperature usually speeds up the reaction and lowering the temperature usually slows it down.
- Increasing temperature causes more collisions between particles and raises their kinetic energy.

Catalysts

- Are used when increasing temperature and concentration is not an option.
- Lowers activation energy and increases the rate of a reaction without being used up itself.
- The faster rate allows reactions to occur with less energy.
- Enzymes break down protein.
- **Catalysts <u>DO NOT</u> change ΔH.**





Inhibitors

- **a substance that interferes with the action of a catalyst.** *(Preservatives, medications)*
- **React with the catalyst or change the catalyst.**
- **The catalyst is then used up or different.**

CHAPTER 18

Chemical Equilibriuim

Reversible Reactions

A reaction that can occur in both the forward and reverse direction.

These are really two reactions.

The double arrow indicates a reaction is reversible.

- $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ *Forward Reaction*
- $N_2(g) + 3H_2(g) \leftarrow 2NH_3(g)$ *Reverse Reaction*
- $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Reversible Reactions

The forward and reverse reactions can occur simultaneously

The rate of the forward and reverse reactions depends on the concentration of the substances.

At first, there cannot be a reverse reaction

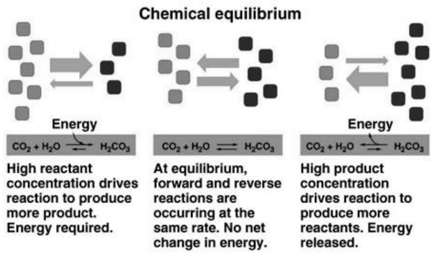
- $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ *Forward Reaction*
- $N_2(g) + 3H_2(g) \leftarrow 2NH_3(g)$ *Reverse Reaction*
- $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$

Chemical Equilibrium

The state in which the forward and reverse reactions balance each other because they take place at equal rates

Rate $_{\text{forward rxn}}$ = Rate $_{\text{reverse rxn}}$

This does not mean that the concentrations of the products equals the concentrations of the reactants



Dynamic Nature of Equilibrium

- The fact that the rates of forward and reverse reactions are the same in a chemical equilibrium does not mean that the concentrations of the components on both sides of the chemical equation are the same
- At equilibrium the concentrations of reactants and products remain constant. Equilibrium simply means that the rate of reactants forming products equals the rate of the products forming reactants.

Law of Chemical Equilibrium

- If reactants are not completely consumed, then not all of the products can be produced as shown in balanced equation.
- At equilibrium, a chemical system reaches a state in which a ratio of reactant and product concentration has a constant value.
- The ratio is called the **equilibrium constant**.

Equilibrium Contstant

- **The numerical value of the ratio of product concentration compared to the reactant concentration.**
- **Occurs only had a specified temperature.**
- **If the $K_{eq} > 1$, then more products exist at equilibrium.**
- **If the $K_{eq} < 1$, then more reactants exist at equilibrium.**
- **A K_{eq} of 5 versus a K_{eq} of 1/5.** ***What does this mean?***

EQUILIBRIUM CONSTANTS

- **Relate the amounts of reactants to products at equilibrium**
- **Equilibrium formula**

$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

Coefficient

moles of substance

Equilibrium Constant

aA + bB <=> cC + dD

$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

Products / **Reactants**

Remember, the coefficients give you the ratio of the reactants and products.

Example Problem #1

$H_{2\,(g)} + I_{2\,(g)} <=> 2HI_{(g)}$

3 mol/L of HI are at equilibrium with 1.5 mol/L of H_2 and I_2, what is the equilibrium constant?

K_{eq} = [ ] = [ ] =

Expression Calculation

Example Problem #2

$N_{2\,(g)} + 3H_{2\,(g)} <=> 2NH_{3\,(g)}$

$[N_2]$ = 0.5 mol/L, $[H_2]$ = 0.2 mol/L, $[NH_3]$ = 0.02 mol/L

K_{eq} = [ ] = [ ] =

Expression Calculation

Homogeneous vs. Heterogeneous

Homogeneous Equilibrium: when all reactants and products are in the same physical state

Heterogeneous Equilibrium: when the reactants and products of a reaction are in more than one physical state.

EQUILIBRIUM CONSTANTS

Only includes gases and aqueous solutions!

Do not use liquids or solids when using the equilibrium constant.

Example Problem #3

$2KClO_{3\,(s)} <=> 2KCl_{(s)} + 3O_{2\,(g)}$

$[O_2]$ = 0.1 mol/L

K_{eq} = [ ] = [ ] =

Expression Calculation

Example Problem #4

$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$

Calculate the K_{eq} if a 4.0-L flask contains 0.176 mol N_2, 0.048 mol H_2, and 0.0136 mol NH_3. *Hint: you must first find the molarity...*

K_{eq} = [ ] = [ ] =

Expression Calculation

When does Equilibrium Constant (K) change?

- Not if concentration changes.
- Not if pressure changes.
- Only if temperature changes.

<u>When Forward is Exothermic</u>:
- Increase Temp, K decreases
- Decrease Temp, K increases

<u>When Forward is Endothermic</u>:
- Increase Temp, K increases
- Decrease Temp, K decreases

In reversible reactions, one of the reactions is always spontaneous and the other is always nonspontaneous

If A + B release enough energy, C + D will react and make this reaction reversible...

$$A + B \rightleftharpoons C + D + \text{Heat}$$

Calculating Equilibrium Concentrations

- Knowing the equilibrium constant can help to determine the concentrations of a reactant or product at equilibrium.

$$CO(g) + 3H_2 \rightleftharpoons CH_4(g) + H_2O(g)$$

- At 1200 K, the K_{eq} for the reaction is 3.933.

Example Problem

- **At 1200 K, the K_{eq} for the reaction is 3.933.**
- **The known concentrations are:**
  - **> CO = 0.850-*M*, H_2 = 1.333-*M*, H_2O = 0.286-*M***

$$CO(g) + 3H_2 \rightleftharpoons CH_4(g) + H_2O(g) \qquad K_{eq} = \frac{[CH_4]\,[H_2O]}{[CO]\,[H_2]^3}$$

$$[CH_4] = \frac{[CO]\,[H_2]^3}{[H_2O]} \times K_{eq} = \frac{[0.850]\,[1.333]^3}{[0.286]} \times 3.933 = 27.7\text{-}M$$

18.2 Le Chatelier's principle

- **If a stress is applied to a system in a dynamic equilibrium, the system changes to relieve the stress**
- **A stress takes a reaction at equilibrium out of equilibrium, so the reaction must adjust to get back to equilibrium.**
- **A stress is any kind of change in a system at equilibrium that upsets the equilibrium.**

Equilibrium Shifts and K_{eq}

- **Even if there is an equilibrium shift, the K_{eq} for a given reaction remains constant.**
- **Stresses do not change K_{eq}, they simply change the amounts of substances.**
- **The purpose of equilibrium shifts is to get back to equilibrium.**

FACTORS AFFECTING EQUILIBRIUM

These factors can cause SHIFTS:

- Changes in concentration (Amount)
- Changes in Temperature
- Changes in Volume/Pressure (Gases only)

Changes in Concentration

- **Adding reactant at equilibrium & it will temporarily shift the reaction toward the products.**
  - > **After the shift, the reverse reaction increses until it is back to equilibrium.**
- **Removing reactant at equilibrium will temporarily shift the reaction toward the reactants.**
  - > **After the shift, the forward reaction increases unitl it is back to equilibrium**

$$2A(g) + B(g) \rightleftharpoons 3C(g) + 4D(g) + \text{Heat}$$

	Shift	Production
Add B	$\rightleftharpoons$	
Remove A	$\rightleftharpoons$	
Add C	$\rightleftharpoons$	
Remove D	$\rightleftharpoons$	

Changes in Temperature

- **Increase Temperature at equilibrium & the reaction will shift in the direction that <u>absorbs heat</u>. (Endothermic)**
- **Removing heat will shift it toward the side that <u>releases heat</u>. (Exothermic)**

$$2A(g) + B(g) \rightleftharpoons 3C(g) + 4D(g) + \text{Heat}$$

- Increase temperature
- Lower the temperature

Changes in Pressure/Volume

NO gases = NO SHIFT

- **Affects only gases at Equilibria.**
- **Add pressure and the rxn shifts toward the side with the fewest gas molecules.**
- **Reduce pressure and it shifts to the side with more gas molecules.**

2A(g) + B(g) $\rightleftharpoons$ 3C(g) + 4D(g) + Heat

- Raise the pressure
- Decrease Pressure

Test Question

Which will cause the Equilibrium shifts to the right?

2A(g) + B(g) $\rightleftharpoons$ 3C(g) + 4D(g) + Heat

A. Removing substance B
B. Decreasing Temperature
C. Increasing Pressure
D. Increasing Temperature.

What happens if?

$2SO_2 + O_2 \leftrightarrow 2SO_3$ + Heat

- The reaction is reversed?
- You increase temperature?
- You decrease the temperature
- Add a catalyst?
- Decrease particle size of reactant?
- Increase the concentration of O_2?

What happens at equilibrium if?

$2H_2 + O_2 \Leftrightarrow 2H_2O$ + Heat

- You add hydrogen?
- You lower the pressure?
- You raise the pressure?
- You increase temperature?
- You lower the temperature?
- You remove oxygen?

2A(g) + B(g) $\rightleftharpoons$ 3C(g) + 4D(g) + Heat

- Add B
- Remove A
- Raise the pressure
- Increase temperature
- Decrease Pressure
- Lower the temperature
- Add C
- Remove D
- Name 5 ways to increase D
- Name 5 ways to decrease C