Chemical Kinetics (chpt. 6)

- Is the study of ways to change the rate (speed) of reactions
- Involves research of reaction times and changes in the concentration of reactants and products
- Also involves the development of theories & models to explain and predict observed rates of reaction

Rate of Reaction (6.1)

- Reaction rate = a measure of how fast a reactant is used up or how fast a product is formed
- The rate of reaction shows how the concentration of a product or a reactant changes over time

\[ r = \frac{\Delta c}{\Delta t} \]

where \( \Delta c \) = the change in concentration and \( \Delta t \) = time elapsed

Graphical Representation:
\[ A + B \rightarrow AB \]

Notice that if we follow the changes in the [reactant], we would get a negative rate. Since this is not realistic, we use the **absolute value** of \( \Delta c \) when calculating rate.

Notice also that the rate of a reaction changes most rapidly at the start of the reaction.

**Finding the Average Rate of a reaction**

|r| Take the slope of the secant line

**Finding the Instantaneous Rate**

|r| Take the slope of the tangent line

**Ex 1:** What is the average rate of production of ammonia in the following system, between 1.0 min and 4.0 min, if the \([\text{NH}_3(g)]\) is 3.5 mol/L after 1.0 min and 6.2 mol/L after 4.0 min?

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \]
Ex 2: What is the rate of consumption of each of the reactants in the following system when the rate of production of ammonia is $4.0 \times 10^{-3}$ mol(L.min)?

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Measuring Reaction Rates
- Method used to measure a reaction rate will depend on the kinds of substances & the type of reaction
  a) Reactions that produce gas $\rightarrow$ examine changes in pressure or volume (using water displacement)
  b) Reactions that produce ions $\rightarrow$ measure changes in conductivity
  c) Reactions that change colour $\rightarrow$ measure changes in colour intensity using a spectrophotometer

ASSIGN: Do pg. 365 – 366 # 7 – 11

Factors Affecting Reaction Rates (6.2)
- The chemical nature of the reactants
- The concentration of the reactants
- The temperature of the reacting system
- The availability of catalysts
- The ability of the reactants to come in contact with each other (Surface Area)

Chemical nature of reactants
- Some substances naturally react faster than others (Na in air vs gold in air)
- In general the fewer bonds are broken, the faster the reaction takes place

Concentration of Reactants
- The rates of reactions generally increase as the [reactants] is increased
- In systems with more than one reactant, the rate may vary with the concentration of one or two of the reactants

Temperature of the System
- Generally, if the temperature of a reacting system is increased, the rate of the reaction will increase
- If the temperature of the reaction is decreased, the rate of the reaction will decrease

Availability of Catalysts
- A catalyst is a substance that increases the rate of a chemical reaction, but is not consumed during the reaction.
- The catalyst may take part in the reaction, but it must be regenerated during the reaction
- Enzymes = biological catalysts

The ability of the reactants to meet (Surface Area)
- When the reactants are in different phases (i.e a gas and a liquid or solid), the reaction that occurs = heterogeneous reaction
- In such reactions, reactants are only able to come in contact with each other, when they meet at the interface between the two phases. The size of this area of contact determines the rate of the reaction.
- The area of contact can be increased by decreasing the size of the reactant particles
The Rate Laws and Order of Reaction (6.3)

- Analysis of empirical (experimental) evidence shows that there is a mathematical relationship between reaction rate and the various factors that affect it.
- Empirical evidence suggest that the rate of a reaction is exponentially proportional to the product of the initial concentrations of the reactants ➔ The RATE LAW

THE RATE LAW:
In a reaction \(ax + by \rightarrow \text{products}\), the rate, \(r\), will always be proportional to the product of the initial concentrations of the reactants, where these concentrations are raised to some exponential values.

\[
r \propto [X]^m[Y]^n
\]

\(m \text{ and } n\) can only be determined experimentally

Rate Law Equation (Rate Law)
\[
r = k[X]^m[Y]^n
\]

\(k\) = a rate constant, it must be determined experimentally and is only valid for a specific reaction at a specific temperature

Orders of Reaction
These are the exponents in the rate law. The overall order of the reaction is the sum of the individual orders of reaction for each reactant.

For example: The Rate Law Equation for the reaction, \(2\text{NO}_2(g) + \text{F}_2(g) \rightarrow 2\text{NO}_2\text{F}(g)\) is:

\[
r = [\text{NO}_2]^1[\text{F}_2]^1
\]

Notice that the exponents in the rate law equation are not the same as the coefficients in the balanced chemical equation.

The other of reaction with respect to \(\text{NO}_2\) is 1
The other of reaction with respect to \(\text{F}_2\) is 1
The overall order of reaction is 2 (1 + 1)

Rate law & Concentrations
The rate depends on initial reactant concentrations raised to various exponents:

- If the order of a reactant is zero, this means the rate does not depend on this reactant
- If the order of a reactant is 1, then doubling the initial concentration will also double the rate (\(2^1\)); if the concentration is multiplied by 3, then the rate will also multiply by 3 (\(3^1\))
- If the rate order of a reactant is 2, then doubling the initial concentration will multiply the rate by 4 (\(2^2\)); if the initial concentration is tripled, then the rate will multiply by 9 (\(3^2\))

See summary table 1, pg. 374

Examples:
1) The decomposition of dinitrogen pentoxide, \(2\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \text{O}_2(g)\) is first order with respect to \(\text{N}_2\text{O}_5\). If the initial rate of consumption is \(2.1 \times 10^{-4}\) mol/(L.min) when the initial concentration of \(\text{N}_2\text{O}_5\) is 0.40 mol/L, predict what the rate would be if another experiment were performed in which the initial concentration of \(\text{N}_2\text{O}_5\) is 0.80 mol/L.

\[
r = [\text{N}_2\text{O}_5]^1
\]
2) Mixing an acidic solution containing iodate, IO$_3^-$ (aq), ions with another solution containing I$^-$ (aq) ions begins a reaction that proceeds, in several steps, to finally produce molecular iodine as one of the products as shown in the following reaction.

\[
\text{IO}_3^-(aq) + 5 \text{I}^-(aq) + 6 \text{H}^+(aq) \rightarrow 3 \text{I}_2(aq) + 3\text{H}_2\text{O}(l)
\]

The data in Table 3 are obtained for rate of production of iodine (I$_2$):

a) What is the rate equation for this reaction?

b) What will the rate reaction be when [IO$_3^-$] = 0.20 mmol/L, [I$^-$] = 0.40 mmol/L, and [H$^+$] = 0.10 mmol/L
Theories Regarding Rates of Reactions (6.4)

**The Collision Theory:**

A. Postulates

1. Reacting molecules must collide with each other or no reaction takes place
2. Collision must result in new bond formation, the breaking of existing bonds or both
3. Only collisions between particles with sufficient kinetic energy to bring about changes in bonding are beneficial
4. There is an energy barrier known as the threshold or activation energy ($E_a$). $E_a$ is the minimum kinetic energy to break bonds and cause a reaction. Only those particles with kinetic energies greater than $E_a$ can react. For a given temperature, the lower the value of $E_a$, the faster the reaction takes place (see KE curve below)

5. The shapes and orientation of molecules help to determine if a molecular collision will result in a reaction. Even if the molecules possess the activation energy associated with a given reaction, the orientation of the molecules may not be proper. (see illustration below)

\[
\text{Rate of rxn} = \text{the frequency of collision} \times \text{the fraction of those collisions that are effective}
\]
B. Explanations (6.5)

1. *Increase in temperature*
   - If the temperature is increased, the kinetic energy is increased and the particles move faster and collide more often.
   - A greater number of particles have greater energies than $E_a$ and are able to react when they collide.
   - Therefore the rate of the reaction is faster.

2. *Increase in concentration*
   - If the concentration is increased, the number of particles is increased and so the number particles with kinetic energy greater than $E_a$ is increased.
   - The number of collisions would also increase ➔ faster rate.

3. *Use of a catalyst*
   - The number of particles is not changed.
   - The kinetic energy is not changed.
   - The number of collisions remains the same.
   - The rate of the reaction increases because a catalyst lowers the $E_a$, therefore more particles would then have kinetic energy greater than $E_a$.

4. *Surface area*
   - The greater the surface area, the greater the chance of collision.
   - Therefore the greater the surface area, the faster the rate.
**Formation of the activated-complex (6.4)**

*Postulates:*

**a.** As reacting particles approach each other, old bonds begin to weak and new bonds begin to form between the reacting particles. As this occurs, particles slow down, thus their kinetic energy is converted to potential energy. When the potential energy reaches a maximum, an **activated complex** is formed.

The **activated complex** is a high energy, unstable, short-lived group of reactant particles that is considered to have bonds that are in the process of being broken to form products.

The minimum energy required to form the activated complex is called the activated energy ($E_a$).

**b.** Only those particles with sufficient kinetic energy to convert to sufficient potential energy to form the activated complex, can react.

*N.B*

Once the reacting system reaches the activated complex stage it may reverse to the reactants or may continue to form the products.

**c.** The potential energy associated with the activated complex is greater than the potential energy of both the reactants and products.

**d.** If the products of a reaction have a higher potential energy (hence lower K.E), than the reactants, it is an **ENDOTHERMIC REACTION** (see diagram below).

The difference in potential energy between the products and reactants == enthalpy of the reaction ($\Delta H$)

**e.** If the products of a reaction have a lower potential energy (hence higher K.E), than the reactants, it is an **EXOTHERMIC REACTION** (see diagram below)
**Reaction Mechanisms (6.4)**

- A reaction mechanism is a series of reactions that produce a net equation/reaction.
- Most chemical reactions involve more than one step (therefore a reaction mechanism)
- A reaction mechanism is *step-wise*, meaning that the product of one reaction is the reactant in the next reaction
- Each reaction in the mechanism will involve collisions between no more than two or three particles
- Each step is known as an *elementary step*.
- The reaction mechanism can be considered to be the pathway that the reaction takes

EX: Nitrogen monoxide is a pollutant in automobile exhaust. The mechanism whereby nitrogen monoxide reacts to form nitrogen dioxide is believed to consist of several steps:

Step 1: \(2 \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_2(g)\)

Step 2: \(\text{N}_2\text{O}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)\)

If we add these steps, we get:

\[
2 \text{NO}_2(g) + 2\text{N}_2\text{O}_2(g) + 2\text{O}_2(g) \rightarrow 2\text{N}_2\text{O}_2(g) + 4\text{NO}_2(g)
\]

Which leads to the following overall equation after common particles are canceled.

\[
2 \text{NO}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)
\]

**NOTE:**
- Notice that that \(\text{N}_2\text{O}_2(g)\) cancels out and does not appear in the overall equation. It was produced in the first reaction and used up in the second one
- Species such as \(\text{N}_2\text{O}_2(g)\) are called *reaction intermediates*, these particles are very short-lived and are usually difficult to isolate

**Which reaction will determine the rate of the overall reaction?**

- In a reaction mechanism, each reaction occurs at its own rate; some will occur at a faster rate than others.
- The reaction in the mechanism that occurs at the *slowest rate* is called the RATE DETERMINING STEP (RDS). It controls the rate of the entire process
- The overall reaction cannot occur at a faster rate than the slowest step (like water pouring through a funnel – the size of the opening at the bottom determines how fast the water can exit, not how fast water is poured in).
- The RDS is not necessarily the first step in the reaction mechanism, but can occur at any point in the mechanism

⇒ What factor about the rate determining step would make it the slowest?
Given the following reaction:

\[ 4 \text{HBr}_\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{H}_2\text{O}_\text{(l)} + 2 \text{Br}_2\text{(g)} \]

⇒ According to collision theory, what would have to happen in order for this reaction to occur in one step?

⇒ What is the probability of that happening?

A suggested mechanism for this reaction is:

*N.B: Each equation in the reaction mechanism must be balanced!*

- a. \( \text{HBr} + \text{O}_2 \rightarrow \text{HOBr} \) (slow)
- b. \( \text{HOBr} + \text{HBr} \rightarrow 2\text{HOBr} \) (fast)
- c. \( 2\text{HOBr} + 2\text{HBr} \rightarrow 2\text{H}_2\text{O} + 2\text{Br}_2 \) (fast)

Overall reaction:

\[ 4 \text{HBr}_\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{H}_2\text{O}_\text{(l)} + 2 \text{Br}_2\text{(g)} \]

⇒ The rate experimentally determined rate law for the above reaction is: \( r = k [\text{HBr}]^1[\text{O}_2]^1 \)
⇒ Notice that the reactants in the rate law are those in the RDS
⇒ Notice also, that the coefficients of the reactants in the RDS are the same as the exponents in the rate law

**CONCLUSION:**
In general, if the experimentally rate equation is \( r = k [X]^m[Y]^n \), then the rate determining steps must be \( mX + nY \rightarrow \) products or reaction intermediates

**Rules for writing Reaction Mechanisms**
- Each step must be elementary, involving no more than three reactant molecules (usually 1 or 2)
- The slowest step (RDS) must be consistent with the rate equation
- The elementary steps must add up to the overall equation

**Using the rate law to determine the RDS**

EX. Consider the decomposition of dinitrogen pentoxide : \( 2\text{N}_2\text{O}_5\text{(g)} \rightarrow 2\text{N}_2\text{O}_4\text{(g)} + \text{O}_2\text{(g)} \)

a) What would the rate equation be if the reaction occurred in a single step?

b) If the actual experimentally derived rate equation is: \( r = k [\text{N}_2\text{O}_5]^1 \); what is the RDS?

c) Given the rate law above, suggest a possible mechanism and indicate the slowest step.