

Chemical Reactions have two very important characteristics:

- 1) Position of Equilibrium (thermodynamics)
- 2) Reaction Rates (kinetics)

A spontaneous reaction, $\Delta G < 0$, does not mean the reaction will be fast.

Thermodynamics:

- 1) indicates relative stability of products and reactants and the equilibrium position
(the concentration of products relative to the concentration of reactants at equilibrium)
- 2) independent of path between reactants and products
- 3) indicates why a reaction occurs $\Delta G = \Delta H - T\Delta S$

Kinetics:

- 1) study of reaction rates and reaction mechanism (reaction steps)
- 2) depends on the path between reactants and products
=> Kinetics tells you how a reaction occurs (the mechanism) and how fast.

Consider the change in concentration as a function of time: Initially only reactants are present and only the forward reaction occurs. As products are produced the reverse reaction occurs until equilibrium is reached. See Figure 6.2, 6.3 and 6.4 pg 192-194 text.

At equilibrium: the forward rate = the reverse rate. When can we ignore the reverse reaction?

- 1) When reactants are first put together. In this case, the forward reaction dominates and we can ignore the reverse reaction,
- 2) When the reaction goes to completion, that is when $K \gg 1$ (many reactions go to completion), we can only measure the forward rate and therefore we can ignore the reverse rate.

See Figure 15.1 pg 705 text. This Figure shows that at a given point (time, concentration) the forward rate corresponds to the change in concentration with respect to change in time.

$$\text{For the reaction: } A \rightarrow \text{products} \quad \text{Rate} = -d[A]/dt = k[A]^n$$

In this equation, k is the rate constant and n is the order of the reaction with respect to A. The rate constant, k, and the reaction order, n, are determined from experiment.

The integrated rate law allows us to determine the concentration of the reactants or products at any time during the course of a reaction.

	Zero Order	First Order	Second Order
Rate Law	Rate = k	Rate = k [A]	Rate = k[A] ²
Integrated Rate Law	[A] = -k t + [A] ₀	ln [A] = -k t + ln [A] ₀	1/[A] = k t + 1/[A] ₀
Straight Line Plot	[A] versus t	ln [A] versus t	1/[A] versus t
Rate Constant, k	slope = -k	slope = -k	slope = k
Half-life	t _{1/2} = [A] ₀ /2k	t _{1/2} = 0.693/k	t _{1/2} = 1/k[A] ₀

The rates of chemical reactions range from instantaneous to very slow. **Many reactions involve a series of elementary steps (the reaction mechanism).** It is possible to understand the large range in reaction rates in terms of the reaction mechanisms and the nature of elementary processes. For a given reaction there can be more than one possible mechanism leading from reactants to products. We must test the proposed mechanisms experimentally to see which mechanism occurs.

Reaction Mechanisms:

- 1) **Elementary reactions are single step reactions, the rate law is written directly from the reaction stoichiometry (See examples in Table below*).**
- 2) **The overall reaction is the sum of elementary steps.**
For the overall reaction the rate law must be determined from experiment.

Elementary Step	Molecularity	Rate Law
A → products	Unimolecular	Rate = k [A]
2A → products	Bimolecular	Rate = k [A] ²
A + B → products	Bimolecular	Rate = k [A][B]
2A + B → products	Termolecular	Rate = k [A] ² [B]
A + B + C → products	Termolecular	Rate = k [A][B][C]

*Reference: Chemical Principles, S. S. Zumdahl

How do we write the rate law for a reaction when we do NOT know the reaction mechanism? Remember that a chemical reaction may occur in a series of elementary steps.

Consider Example 15.7 pg 731 text. Overall Reaction: $\text{Cl}_2 + \text{CHCl}_3 \rightarrow \text{HCl} + \text{CCl}_4$

This is the overall reaction which may involve several elementary steps.

What is the rate law?

$$\text{Rate} = k [\text{Cl}_2]^n [\text{CHCl}_3]^m$$

How do we determine the variables n and m ? To determine n and m , we must measure the rate as a function of concentration. To determine m , we measure the rate as a function of $[\text{CHCl}_3]$. When we change $[\text{CHCl}_3]$, we must keep $[\text{Cl}_2]$ constant. To determine n , we measure the rate as a function of $[\text{Cl}_2]$. When we change $[\text{Cl}_2]$, we must keep $[\text{CHCl}_3]$ constant.

Note: **The variables, n and m , can be positive, negative, an integer or a fraction.**

For this reaction, experimental data indicate: $n = \frac{1}{2}$ and $m = 1$.

Thus, the experimental rate law is: $\text{Rate} = k [\text{Cl}_2]^{\frac{1}{2}} [\text{CHCl}_3]$

The reaction is first order with respect to CHCl_3 , and half order with respect to Cl_2 .

The **overall order** = $n + m$. For this reaction, the overall order = $\frac{1}{2} + 1 = 1.5$.

Now a mechanism for this reaction can be proposed and the rate law is derived from the mechanism. Derive the rate law from the mechanism given in example 15.7, pg 731 to show the derived rate law is the same as the experimental rate law.

General Process:

- 1) For a given overall reaction, the rate law is determined from experimental data.
- 2) A mechanism is proposed (generally more than one mechanism is possible).
- 3) Derive the rate law from the proposed mechanism (the derived rate law must be the same as the observed rate law).
- 4) Do experiments to test the proposed mechanism.

For a mechanism to be acceptable, the sum of the elementary steps must give the overall balanced equation for the reaction, and the mechanism must give a rate law that agrees with the experimentally determined rate law.

If the mechanism for an overall reaction involves several steps, and there is one step that is much slower than the others, the rate of the overall reaction is assumed to be equal to the rate of the slow step (the rate determining step).

Intermediates are often short lived and are therefore more difficult to measure. Derive the rate law in terms of measurable quantities => eliminate all intermediates in the rate law.

Some mechanisms do not have a slow step. In this case, the steady state approximation can be used to derive the rate law. The central feature of this method is the assumption that the concentration of any intermediate remains small and constant as the reaction proceeds (see text, Section 15.7). Note: the steady state approximation will not be covered in class and you are not required to learn how to derive rate laws using the steady state approximation.

What factors determine the magnitude of reaction rates? Generally collision rates are much larger than reaction rates. Why? In the atmosphere, at 27°C and 1 atm, N_2 and O_2 collide at a rate of ~ 4 billion collisions/sec but these collisions are not reactive. Why not? Why is there such a large range in reaction rates? Reaction rates depend on temperature (for example, refrigeration slows down food spoilage). In elementary processes energy may be transferred between molecules, bonds may be broken or formed, and electrons may be transferred. In a bimolecular elementary reaction in which bonds are broken and other bonds are formed, there may be an orientation requirement and a minimum energy requirement for a collision to be reactive. As a result, the observed rate constant is often less than the collision rate constant (that is, not every collision is reactive).

Arrhenius proposed that the minimum energy requirement (the activation energy, E_a) must be overcome to produce a chemical reaction.

Arrhenius equation: $k = A e^{-E_a/RT}$

where A is a factor, reflecting collision frequency and molecular orientation, and $e^{-E_a/RT}$ represents the fraction of collisions with sufficient energy to react (see text, pg 737, Figure 15.12, where the shaded blue area is equal to $e^{-E_a/RT}$, which increases as the temperature increases). Taking the natural logarithm of the Arrhenius equation yields the following equation.

$$\ln k = \ln A - E_a/RT$$

A plot of $\ln k$ versus $1/T$ yields a straight line with the slope equal to $-E_a/R$ and the intercept equals $\ln A$. If you measure the rate constant at two temperatures, you can calculate the activation energy using the following equation (see text pg. 739).

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

A marked change in temperature or the addition of a catalyst may change the mechanism. Adding a catalyst can speed up a reaction by providing a different pathway with a lower activation energy. A catalyst does not affect the energy of the reactants relative to the products (ΔE for the reaction is the same). A catalyst may increase the rate at which equilibrium is attained but a catalyst has no effect on the equilibrium constant. Why not? See text, pg 741, Figure 15.15. Compare ΔE for the catalyzed and uncatalyzed reaction. In cases where a reaction proceeds by two or more mechanisms simultaneously, the reaction proceeds by the fastest mechanism available to it.