

## General Chemistry II

### Chapter 13 Lecture Notes

### Chemical Kinetics

**Chemical Kinetics** is concerned with reaction **rates**.

Typical reaction rate units are M/s, the change in concentration of a species per unit time.

There is a huge variation in possible reaction rates.

Increasing reaction rates is the goal of many industrial (and biological) processes.

In a simple reaction,  $A \rightarrow B$ , the number of A molecules or  $[A]$  decreases with time and the number of B molecules or  $[B]$  increases with time.

The reaction rate can be expressed in several useful forms,

$$\text{Rate} = -\Delta[A]/\Delta t \text{ or } \text{rate} = \Delta[B]/\Delta t$$

(Since is it desirable for rate values to be positive, the  $[A]$  equation has a negative sign.

Species may be monitored by pressure, pH, spectroscopically or otherwise.

#### The Oxidation of Formic Acid by Molecular Bromine.



The reaction may be followed by tracking the loss of bromine color spectroscopically using Beer's Law.

The average rate of the reaction can be calculated by measuring the bromine concentration and the time at two different stages of the reaction. The average rate will typically vary with the time interval and the stage of the reaction chosen. Since the reaction rate will decrease as the reactants are used up, a plot of the reaction rate vs. time will be a curve. The *average* rate of the reaction is not necessarily equal to the *instantaneous* rate of the reaction at any given time.

A sketch of  $\text{Br}_2(\text{M})$  vs. time will show steadily decreasing rate.

$$\text{Rate} = \Delta[\text{Br}_2]/\Delta t$$

Since  $[\text{Br}_2]$  is in mol/L and  $t$  is in seconds, the rate is expressed with units M/s.

The instantaneous rate at a given point of the reaction is more meaningful, since it is constant for a given reaction at a specified temperature and specified reactant concentrations.

To separate the factors influencing the rate of a reaction, one reactant concentration can be held constant by making it so high that it changes little during the reaction.

For the reaction between bromine and formaldehyde, keeping formaldehyde concentration constant, the rate of disappearance of bromine is proportional to  $[\text{Br}_2]$ .

$$\text{Therefore, } \text{rate} \propto [\text{Br}_2] \text{ or } \text{rate} = k[\text{Br}_2] \text{ or } k = \text{rate}/[\text{Br}_2]$$

$k$ , called the rate constant, therefore equals the reaction rate divided by the bromine concentration *at constant temperature and formaldehyde concentration*.

A sketch of reaction rate (M/s) vs. bromine concentration (M) will be linear. The slope of the line, the rate constant, expressed in  $s^{-1}$  therefore remains the same.

The experiment tells nothing about the reaction rate dependence on  $[HCOOH]$  or on temperature.

### Decomposition of Hydrogen Peroxide

Since one product of the reaction is a gas, the reaction rate can be tracked by measuring the pressure exerted by the evolved oxygen (at constant system volume).



If an expression involving the molar concentration of oxygen is desired, it can be derived from the measurable gas parameters, P, V, and T. the simplest experimental setup is to keep V and T constant and measure changing P.

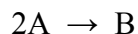
From  $PV = nRT$ , the molar concentration  $M(\text{mol/L})$  is equal to  $n/V = P/RT$ . A change in the concentration of oxygen  $\Delta M = \Delta P/RT$ . To measure  $\Delta M = \Delta[O_2]$  with respect to time,

$$\Delta[O_2]/dt = \Delta M/dt = d(\Delta P)dt \cdot 1/RT$$

Keep the temperature and volume constant and track the increase in oxygen pressure in a closed system. This can be converted to change in  $O_2$  concentration.

### Reaction Rates and Stoichiometry

How to express reaction rates when the stoichiometry of reactants is not one-to-one? For example:



In this reaction, the rate of disappearance of A is twice the rate of appearance of B.

If rate is written as  
rate =  $\Delta[B]/\Delta t$ ,

Then the rate of disappearance of A must be written as rate =  $-\frac{1}{2}\Delta[A]/\Delta t$

Note that the coefficient 2 appears in the denominator of the fraction. For  $3A$ , the rate coefficient would have been  $\frac{1}{3}$ , etc.

### The Rate Law

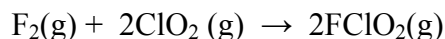
For the general expression of a chemical reaction,  $aA + bB \rightarrow cC + dD$ , the **rate law** is expressed as the rate law **constant, k**, times the **reactant** concentrations raised to the power of the order of each reactant.

$$\text{Rate} = k [\text{A}]^x [\text{B}]^y$$

It is tempting to assign  $x = a$ ,  $y = b$ , etc. for the reactant orders, but this is generally not possible. Reaction order often does not correlate to reactant coefficient. **Rate measurements** are needed to determine the values of  $x$  and  $y$ . The reaction is described as being first, second, etc. order in A and first, second etc. order in B. The overall reaction order is the sum of  $x + y + \dots$ . Reactant orders are typically 0, 1, 2, 3, or sometimes 0.5.

A zero order reactant means that the rate of the reaction is not influenced by the concentration of that particular reactant.

Example: An experimental determination of the order of the reaction between fluorine and chlorine dioxide gas was done by measuring the *initial* reaction rate for different *starting* concentrations of fluorine and chlorine dioxide.



The concentration of one gaseous reactant is held constant while the other is varied to find the rate order of each reactant. Experimentally it was found that, while keeping  $[\text{F}_2]$  constant and varying  $[\text{ClO}_2]$  (doubling, tripling, etc. the concentration), the reaction rate increased exactly in proportion to the change in  $[\text{ClO}_2]$ . This means that the reaction is first order in  $[\text{ClO}_2]$ , or that the reaction rate equals some constant times  $[\text{ClO}_2]$ . Similarly, when  $[\text{ClO}_2]$  is kept constant and  $[\text{F}_2]$  is varied, the reaction rate changes in the same ratio. The reaction is also first order in  $[\text{F}_2]$ . The overall reaction is **second** order, first order in each of the two reactants. The rate of this reaction is given by

$$\text{rate} = k[\text{ClO}_2] [\text{F}_2]$$

The units of rate are typically concentration/time, or in most cases, M/s.

For carrying out calculations, it is useful to know the value of  $k$ , which is invariant when temperature is constant.

$$k = \text{rate}/([\text{ClO}_2] [\text{F}_2])$$

In the case of a second order reaction, the units of  $k$  are M/s divided by  $\text{M}^2 = \text{M}^{-1} \cdot \text{s}^{-1}$ . In a first order reaction,  $k$  has units  $\text{M}/\text{s} \div \text{M} = \text{s}^{-1}$ . Higher order reactions give more complicated  $k$  values.

### **Relation Between Reactant Concentration and Time**

The mathematical relationships between reactant concentrations and time make possible the prediction of reaction times, per cent completion, half-lives, etc. The algebraic equations are different for **first** and for **second order** reactions.

### **First-Order Reactions**

The rate of a first-reaction depends only on the concentration of one reactant, A.

A → products

By definition, rate =  $-\Delta [A]/\Delta t$  and rate =  $k[A]$

Therefore,  $-\Delta [A]/\Delta t = k[A]$

$d[A]/dt = -kt$  (Instantaneous rate of change described by calculus.)

$\ln([A]/[A_0]) = -kt$  (Calculus solution to the equation by integration)

$\ln[A] - \ln[A_0] = -kt$  or

$\ln[A] = -kt + \ln[A_0]$

This is a useful equation for graphing since it is in the form  $y = mx + b$

Example: For a reaction with  $k = 5.50 \times 10^{-3} \text{ s}^{-1}$  at 45.0 °C, what will be the concentration of A remaining after 12.0 min if the initial concentration of A is 0.200 M?

$\ln[A] = -kt + \ln[A_0] = -5.50 \times 10^{-3} \text{ s}^{-1} (12.0 \text{ min} \times 60 \text{ s/1 min}) + \ln(0.200)$

$\ln[A] = -3.96 + -1.61 = -5.57$

$[A] = 3.81 \times 10^{-3} \text{ M}$ .

The half-life of a reaction is a useful parameter. The half-life of a first-order reaction is characteristic of the reaction and is *independent* of the starting concentration of A.

$t = (1/k) \cdot \ln [A_0]/[A]$

$t_{1/2} = 1/k \cdot \ln(1/0.5) = (1/k) \cdot \ln 2 = (1/k) \cdot 0.693 = 0.693/k$

$t_{1/2} = 0.693/k$  or  $k = 0.693 t_{1/2}$

## Second-Order Reactions

Second order reactions in A can be easily described mathematically. Second order in [A] and [B] and third order reactions will not be covered here.

For second order reactions in A:

A → products

rate =  $-\Delta [A]/\Delta t$ , but now rate =  $k[A]^2$

The graphable equation becomes:

$$1/[A] = 1/[A_0] + kt$$

again,  $y = mx + b$

The half-life equation can be obtained by substituting  $\frac{1}{2}[A_0] = [A]$

The half-life,  $t_{1/2}$  then becomes,  $t_{1/2} = (k[A_0])^{-1}$

This makes sense because a large rate constant leads to a faster reaction and short half-life. In second order reactions, half-life does depend on the initial  $[A]$  because a higher  $[A_0]$  means more frequent collisions between A molecules.

## Activation Energy and Temperature Dependence of Rate Constants

### The Collision Theory of Chemical Kinetics

Common sense dictates that a reaction between two particles can occur only if they collide (usually in a gas or liquid). Therefore expect that a reaction rate is *proportional* to the rate of collision or the number of collisions per second.

The percentage of *successful* collisions in chemical systems varies greatly.

In some systems, almost every collision results in chemical change. (Instantaneous rxn)

In other systems, collisions rarely produce chemical change. (A slow rxn)

Therefore, the reaction rate is not the same as the *collision* rate but is often directly proportional to it.

Chemical reactions occur when the energy of collision is enough to break reactant bands and form product bonds. If there is not enough kinetic energy in colliding species, reactant bonds will not *break* and new, *product* bonds will not form.

It stands to reason that higher temperatures (which increase the frequency of collisions and increase the energy of collisions) will increase all or most reaction rates.

The kinetic energy of the colliding particles must equal or exceed a certain minimum value in order for a reaction to proceed. This minimum energy is called the **Activation Energy,  $E_a$** . If a collision has enough energy to break some reactant bonds, an **Activated Complex** may form. This is an intermediate state, higher in energy than the reactants that may lead to products or may lead back to the original reactants. The products that form may be lower in energy than the reactants (exergonic or exothermic reaction) or may be higher in energy than the reactants (endergonic or endothermic reaction).

Two Sketches of Activated Complex Curves:

### The Arrhenius Equation

The Arrhenius Equation relates the rate constant  $k$  to the activation energy,  $R$  the gas law constant and  $T$  the absolute temperature.

$$k = A \text{ times } e \text{ raised to the power } -E_{act}/RT$$

$A$  is not the reactant species  $A$ , but a dimensionless constant called the collision frequency or frequency factor.  $E_{\text{act}}$ , the reaction activation energy is given in J/mol or kJ/mol,  $R$  is equivalent to the gas law constant but is expressed as  $8.314 \text{ J} \cdot (\text{mol} \cdot \text{K})^{-1}$ , and  $T$  is in kelvins. (Remember that  $1/T$  will be in  $\text{K}^{-1}$ .)

To adapt the equation to graphing, take the natural log of both sides. The equation becomes

$$\ln k = \ln A - E_{\text{act}}/RT \quad \text{or} \quad \ln k = (-E_{\text{act}}/R)(1/T) + \ln A,$$

again corresponding to  $y = mx + b$ .

This form of the equation shows that  $\ln k$  varies as minus  $T^{-1}$ .  
Does this make sense?

For using the Arrhenius Equation algebraically to compare rate constant value at different temperatures, write two equations for different temperatures and therefore different  $k$  values.

$$\ln k_1 = \ln A - E_{\text{act}}/RT_1 \quad \text{and} \quad \ln k_2 = \ln A - E_{\text{act}}/RT_2$$

$$\ln k_1 - \ln k_2 = -E_{\text{act}}/RT_1 + E_{\text{act}}/RT_2$$

$$\ln (k_1/k_2) = E_{\text{act}}/R(1/T_2 - 1/T_1) \quad \text{useful for solving for } T_1 \text{ or } T_2, \text{ and}$$

$$\ln (k_1/k_2) = E_{\text{act}}/R(T_1 - T_2)(T_1 \cdot T_2) \quad \text{useful when both } T\text{s are known.}$$

Example: The rate constant for a first-order reaction is  $4.50 \times 10^{-4} \text{ s}^{-1}$  at  $25.0^\circ \text{C}$ . What is its rate constant at  $50.0^\circ \text{C}$  if the activation energy is  $35.6 \text{ kJ/mol}$ ? Note that the collision frequency  $A$ , being the same, has cancelled out of the equation.

$$\ln (k_1/k_2) = E_{\text{act}}/R(T_1 - T_2)(T_1 \cdot T_2) \quad T_1 = 298.2 \text{ K}, \quad T_2 = 323.2 \text{ K}$$

$$\ln k_1 = E_{\text{act}}/R(T_1 - T_2)(T_1 \cdot T_2) + \ln k_2$$

$$\ln (k_2) = \ln k_1 - E_{\text{act}}/R(T_1 - T_2)(T_1 \cdot T_2)$$

$$= -7.71 - 35.6 \text{ kJ/mol}/(8.314 \text{ J} \cdot \text{mol} \cdot \text{K})^{-1} \cdot 1000 \text{ J/kJ} \cdot (-2.589 \times 10^{-4} \text{ K}^{-1})$$

$$= -7.71 + 1.11 = -6.60$$

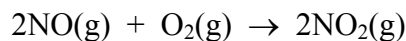
$$k = 1.36 \times 10^{-3} \text{ s}^{-1}$$

The Arrhenius equation can also be used to solve algebraically for  $E_{\text{act}}$ , for either  $k$  or for either  $T$ .

## Reaction Mechanisms

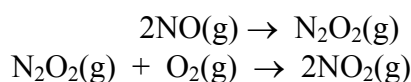
Observing the overall course of a reaction and measuring its rate usually tells little about the **reaction mechanism**. A reaction mechanism is a series of **elementary reactions** or **elementary steps** that lead from reactants to products. To be reasonable, the sum of the elementary steps must add up to the overall reaction.

Example: the reaction of nitrogen oxide (NO) and oxygen gas does not proceed in one step as shown by the overall equation

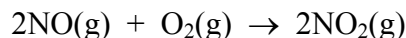


First, three-body (*termolecular*) collisions are extremely unlikely and rare. Second,  $\text{N}_2\text{O}_2$  (an *intermediate*) is detected during the reaction.

The two postulated (and plausible) elementary steps are :



The add up to the overall observed reaction:

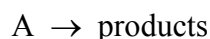


The intermediate  $\text{N}_2\text{O}_2$  is not present in the final product.

Both elementary steps above are bimolecular; they involve the collision of two molecules. Bimolecular and unimolecular reactions (when a single molecule breaks into two or more particles) are by far the most common examples of molecularity.

### Rate Laws and Elementary Steps

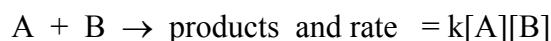
Knowing or postulating the elementary steps can lead to an expression of the rate law of a reaction. For the simple unimolecular reaction where a reactant A changes spontaneously to products,



the elementary step predicts a unimolecular mechanism. That means that A decomposes without regard to anything else present in the system. The rate depends only on the concentration of A (obviously, the more A is present, the faster the reaction proceeds).

$$\text{Rate} = k[\text{A}]$$

For a bimolecular elementary reaction involving two different molecules, A and B:



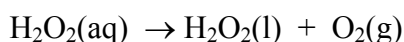
If a reaction proceeds by the collision of two A molecules,  
 $2\text{A} \rightarrow \text{products}$

$$\text{then, Rate} = k[\text{A}][\text{A}] \quad \text{or} \quad \text{Rate} = k[\text{A}]^2$$

When a chemical reaction proceeds by more than one elementary step and the different elementary steps have different rate laws, the rate law for the overall process is the one for the slowest reaction (the bottleneck), called the *rate-determining step*.

### Hydrogen Peroxide Decomposition

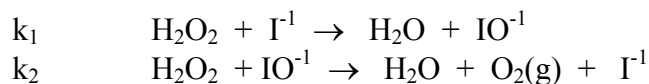
The uncatalyzed decomposition of hydrogen peroxide is very slow, especially in the dark. Drugstore 3% hydrogen peroxide lasts for years in brown bottles. Many substances, including the ubiquitous enzyme catalase in the body, hasten (catalyze) the breakdown of hydrogen peroxide to water and oxygen. Iodide ion effectively promotes the reaction. What is the rate law of the overall reaction



Experimentally the rate is found to be proportional both to hydrogen peroxide and iodide concentration and first order with respect to both.

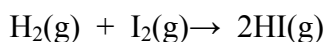
$$\text{Rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$$

The experimental observations can be explained by the following two elementary steps:



The observed rate law,  $\text{Rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$ , can be explained if the first elementary step is the rate-determining step. Since all the iodide ion is recovered at the end of the reaction, it fits the definition of a catalyst, a substance that speeds up a chemical reaction without itself being consumed in the process.

### The Hydrogen Iodide Reaction



A logical assumption would be that the rate law is first order with respect to both hydrogen gas and iodine vapor. In fact, just that rate law was found experimentally. It was assumed the only elementary step was the simple collision of a  $\text{H}_2$  molecule with an  $\text{I}_2$  molecule.

$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$

The reaction, however, does not take place so simply. First of all, the reaction rate is greatly increased by UV radiation in the reaction vessel. The first elementary step is the UV-induced **fast** dissociation of  $\text{I}_2$  into two highly reactive I atoms. Then the *rate-determining* step is the rare termolecular collision of two I atoms with one  $\text{H}_2$  molecule to produce two HI molecules. Why does this reaction appear to be second order, first order in both  $\text{H}_2$  and  $\text{I}_2$ ?

### Experimental Support for Reaction Mechanisms



Oxygen-18 labeling of hydrolyzing water to show that the carbonyl C-O single bond breaks and the oxygen atom adjacent to the ester carbonyl group ends up in the parent alcohol, not the carboxylic acid.

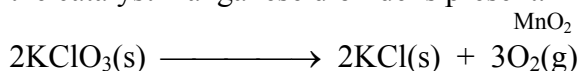
Using O-18 labeled water and carbon dioxide, it can be shown that the evolved O<sub>2</sub> is derived exclusively from water and not from CO<sub>2</sub>. The CO<sub>2</sub> oxygen atoms are all incorporated into the glucose.

## Catalysis

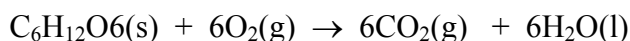
A catalyst is a substance that increases a reaction rate without itself being consumed in the reaction. In principle, all of a catalyst can be recovered unchanged at the end of a reaction.

In writing a chemical equation, the catalyst is not shown as a reactant or a product, but is written above the arrow.

Example: The decomposition of potassium chlorate when heated is thousands of times more rapid when the catalyst manganese dioxide is present.



Example: The burning of glucose to produce carbon dioxide and water takes place at a much lower temperature in the body in the presence of biological catalysts called *enzymes*. The energy released during air combustion is exactly the same but the reaction takes place at a flame temperature.



The energy released or absorbed by a chemical reaction is exactly the same whether a catalyst is present or not.

A catalyst serves to lower the **Activation Energy** of a reaction, allowing the bonds to break and reform with much less input of energy.

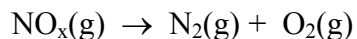
Three main types of catalysis are Heterogeneous Catalysis, Homogeneous Catalysis and enzyme Catalysis.

## HETEROGENEOUS CATALYSIS

Heterogeneous two-phase) Catalysis is widely used in industrial manufacture of chemicals. The catalyst is usually in the solid phase and the reactants are either gaseous or liquid. The gas or liquid molecules bond temporarily to the atoms at the surface of the catalyst, which allows their internal bonds to break more rapidly or at a lower temperature.

### **Catalytic Converter**

In the automobile catalytic converter a Cu or Cr oxide surface catalyzes the *rapid* decomposition of toxic and smog-producing nitrogen oxides in the exhaust to harmless nitrogen and oxygen gas.

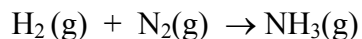


If the nitrogen oxides were allowed to escape to the urban air, they would persist for days, causing environmental and health effects.

A precious metal catalyst (Pt, Rh, Pd, etc.) converts CO and O<sub>2</sub> in the exhaust stream to CO<sub>2</sub>. In the atmosphere, CO would be slowly oxidized to CO<sub>2</sub> anyway but its presence in city air is associated with heart disease and other problems.

### The Haber Synthesis of Ammonia

Probably the most important industrial process converts nitrogen gas and hydrogen to ammonia for use in fertilizer. The reaction is exothermic (energetically favorable) but it is very slow.

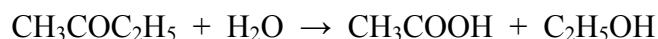


H<sub>2</sub> molecules adhere readily to the surface of an iron metal catalyst and dissociate readily into H atoms which allows them to react with nitrogen gas. The reaction proceeds much more rapidly at 500 °C than it would without the catalyst and makes the reaction an economically process.

### Homogeneous Catalysis

Homogeneous implies that the reaction takes place in solution, with the *soluble* catalyst also in solution.

The classic example is the catalysis of ester hydrolysis by hydrogen ion.



Without H<sup>+</sup> the process is very slow and the rate depends only on ester concentration.

$$\text{Rate} = k [\text{CH}_3\text{COC}_2\text{H}_5]$$

With H<sup>+</sup>, it is much more rapid and the catalyzed reaction is second order, that is first order with respect to both ester and hydrogen ion concentration.

$$\text{Rate} = k_c [\text{CH}_3\text{COC}_2\text{H}_5] [\text{H}^{+}]$$

By the definition of catalysis,  $k_c > k$

### Enzyme Catalysis

Enzymes are biological catalysts, always or almost always protein in nature that speed up many biological reactions. Enzymes have an **active site**, where the **substrate** attaches in order for its bonds to be weakened. Life as we know it would not exist without enzymes to speed up otherwise sluggish reactions. Enzymes are very substrate specific, since their active sites will only accept a substrate of the right size, shape and charge distribution.

Low temperatures slow down enzyme-catalyzed reactions because collision rates are lowered. High temperatures also slow down enzyme-catalyzed reaction rates because high temperatures denature (damage) proteins.