Chapter 14 Chemical Kinetics

Kinetics

•Studies the rate at which a chemical process occurs.

•Besides information about the speed at which reactions occur, kinetics also sheds light on the reaction mechanism (exactly *how* the reaction occurs).

## Factors That Affect Reaction Rates:

•Physical State of the Reactants

>In order to react, molecules must come in contact with each other.

The more homogeneous the mixture of reactants, the faster the molecules can react. Factors That Affect Reaction Rates

•Concentration of Reactants

 $\triangleright$  As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.

Factors That Affect Reaction Rates

•Temperature

At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy. Factors That Affect Reaction Rates

•Presence of a Catalyst

Catalysts speed up reactions by changing the mechanism of the reaction.

Catalysts are not consumed during the course of the reaction.

# Reaction Rates

Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time.

In this reaction, the concentration of butyl chloride,  $C_4H_9Cl$ , was measured at various times.

The average rate of the reaction over each interval is the change in concentration divided by the change in time:

•Note that the average rate decreases as the reaction proceeds.

•This is because as the reaction goes forward, there are fewer collisions between reactant molecules.

•A plot of concentration vs. time for this reaction yields a curve like this.

•The slope of a line tangent to the curve at any point is the instantaneous rate at that time.

•All reactions slow down over time.

•Therefore, the best indicator of the rate of a reaction is the instantaneous rate near the beginning.

**Reaction Rates and Stoichiometry** 

•In this reaction, the ratio of  $C_4H_9Cl$  to  $C_4H_9OH$  is 1:1.

•Thus, the rate of disappearance of  $C_4H_9Cl$  is the same as the rate of appearance of  $C_4H_9OH$ .

•What if the ratio is *not* 1:1?

•To generalize, then, for the reaction

Concentration and Rate

One can gain information about the rate of a reaction by seeing how the rate changes with changes in concentration.

Comparing Experiments 1 and 2, when  $[NH_4^+]$  doubles, the initial rate doubles. Likewise, comparing Experiments 5 and 6, when  $[NO_2^-]$  doubles, the initial rate doubles.

•This means Rate  $\propto [NH_4^+]$ Rate  $\propto [NO_2^-]$ Rate  $\propto [NH^+] [NO_2^-]$ or Rate  $= k [NH_4^+] [NO_2^-]$ 

•This equation is called the rate law, and *k* is the rate constant.

# Rate Law

•A rate law shows the relationship between the reaction rate and the concentrations of reactants.

•The exponents tell the order of the reaction with respect to each reactant.

•This reaction is

First-order in [NH<sub>4</sub><sup>+</sup>] First-order in [NO<sub>2</sub><sup>-</sup>]

•The overall reaction order can be found by adding the exponents on the reactants in the rate law.

•This reaction is second-order overall.

```
•For a general reaction:

aA + bB \rightarrow cC + dD

Rate law has the form

Rate =k [A]^{m}[B]^{n}

where k is the rate constant and is dependent on temperature.
```

If we know the rate law and the rate for a set of reaction conditions we can calculate the value of k.

Unit for k depends on the overall order of the reaction.

For example for a second order reaction

To calculate the rate constant: Rate law

Rate =  $k [A]^m [B]^n$ Rate =  $k[NH_4] [NO_2]$ 

For experiment 1:  $5.4X10^{-7}$  M/s = k (0.0100M)(0.200M)

$$k = 5.4X10^{-7} M/s$$

$$= 2.7 \text{X} 10^{-4} / \text{Ms}$$

Exponents in the rate law

The exponent in the rate law indicates how the rate is affected by the concentration of each reactant.

In the first order reactions:

If the concentration is raised to the first power the rate doubles when the concentration doubles the rate doubles and triples when the concentration triples.

Doubling and tripling other reactants would also do the same.

Second order reaction:

If the rate is second order doubling its concentration increases the rate by a factor of  $2^2 = 4$ 

Tripling its concentration increases the rate by a factor of  $3^2 = 9$  and so forth

### •For Zero order reactions:

If a reaction is zero order in a particular reactant, changing its concentration will have no effect on the rate as long as long as the reactant is present.

It is because any concentration raised to zero is one

Examples of rate laws

•Although the exponents in the rate law are the same as the coefficients in the balanced reaction, this is not necessarily the case.

•The values of these exponents must be determined experimentally.

•Most reaction orders are 0, 1 or 2.However we may encounter reaction orders in fraction.

•The rate of the reaction depends on the concentration but the k does not.

•k is dependent only on temperature.

•Work with printouts

First order reactions

•The first order reaction is one whose rate depends on the concentration of a single reactant raised to the first power

reactant  $A \rightarrow$  product Rate= $\frac{-\Delta[A]}{\Delta t} = k [A]$ 

This form of rate law which expresses how rate depends upon concentration is called differential rate law.

#### •That gives

 $- \ln [A]_{t} - \ln [A]_{o} = k(t-0)$ -  $\ln [A]_{t} - \ln [A]_{o} = kt$ -  $\ln [A]_{t}/[A]_{o} = kt$   $\ln a - \ln b = \ln a/b$  $\ln [A]_{t}/[A]_{o} = -kt$  $\ln [A]_{t} - \ln [A]_{o} = -kt$  $\ln [A]_{t} = -kt + \ln [A]_{o}$ 

## Integrated Rate Laws

Using calculus to integrate the rate law for a first-order process we get:

Manipulating this equation produces...

#### First-Order Processes

Therefore, if a reaction is first-order, a plot of  $\ln [A]_t$  vs. *t* will yield a straight line, and the slope of the line will be *-k*.

Consider the process in which methyl isonitrile is converted to acetonitrile. This data was collected for this reaction at 198.9°C.

•When ln *P* is plotted as a function of time, a straight line results.

•Therefore, ≻The process is first-order. >k is the negative slope:  $5.1 \times 10^{-5} \text{ s}^{-1}$ .

•How to get the natural log value on your calculator LN will give the natural log value. Pressing LN will show In (key in the value) and press enter

Second-Order Processes

•A second order reaction is one whose rate depends upon the reactant concentration raised to the second power or the concentrations of two different reactants each raised to the first power.

•A  $\rightarrow$  products or

•A+ B  $\rightarrow$  products that are second order in just one reactant A

Rate = 
$$\underline{-\Delta[A]} = k [A]^2$$
  
•  $\Delta t$ 

•

Similarly, integrating the rate law for a process that is second-order in reactant A. we get

So if a process is second-order in A, a plot of 1/[A] vs. t will yield a straight line, and the slope of that line is k.

# Half-Life

•Half-life is defined as the time required for one-half of a reactant to react. •Because [A] at  $t_{1/2}$  is one-half of the original [A],  $[A]_t = 1/2 [A]_0.$ 

For a first-order process, this becomes

•The half life of a first order reaction remains the same throughout the reaction.

•The concentration of the reactant keeps becoming half of the previous value after every half life.

•In the first order reaction, the concentration of reactant decreases by  $\frac{1}{2}$  in each of a series of regularly spaced time intervals, namely  $t_{1/2}$ 

•The concept of a first order reaction is widely used in describing radioactive decay, a first order process.

Half-Life For a second-order process,

•As seen in the equation the half life of a second order reaction depends on the initial concentration of the reactants. The lower the concentration the higher the half life.

Temperature and Rate

•Generally, as temperature increases, so does the reaction rate.

•This is because *k* is temperature dependent.

The Collision Model

•In a chemical reaction, bonds are broken and new bonds are formed.

•Molecules can only react if they collide with each other.

The Collision Model

Furthermore, molecules must collide with the correct orientation and with enough energy to cause bond breakage and formation.

## Activation Energy

•In other words, there is a minimum amount of energy required for reaction: the activation energy,  $E_a$ .

•Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.

•This is a reaction where methyl isonitrile is rearranging to acetonitrile

•This reaction passes through an intermediate state in which the N C is sitting sideways.

•

**Reaction Coordinate Diagrams** 

It is helpful to visualize energy changes throughout a process on a reaction coordinate diagram like this one for the rearrangement of methyl isonitrile.

It shows the energy of the reactants and products (and, therefore,  $\Delta E$ ).

•The high point on the diagram is the transition state.

•Temperature is defined as a measure of the average kinetic energy of the molecules in a sample.

•

Maxwell–Boltzmann Distributions

•As the temperature increases, the curve flattens and broadens.

•Thus at higher temperatures, a larger population of molecules has higher energy.

•If the dotted line represents the activation energy, as the temperature increases, so does the fraction of molecules that can overcome the activation energy barrier.

This fraction of molecules can be found through the expression

where *R* is the gas constant (8.314J/mol-K) and *T* is the Kelvin temperature.  $E_a$  is the minimum energy needed for reaction.

•Arrhenious noted that the increase in reaction rate is not linear with increase in temperature in most reactions.

•Arrhenius observed that most reaction rates depend on the following three factors

A. Fraction of molecules possessing Ea or greater

B. number of collisions per second

C. fraction of molecules having the correct orientation

### Arrhenius Equation

Taking the natural logarithm of both sides, the equation becomes  $\ln k = -E_a$  ( ) + ln A

## **Reaction Mechanisms**

The sequence of events that describes the actual process by which reactants become products is called the reaction mechanism.

•Reactions may occur all at once or through several discrete steps.

•Each of these processes is known as an elementary reaction or elementary process. Rate laws for elementary reactions

•The rate law of an elementary reaction is directly based on its molecularity or concentration.

The molecularity of a process tells how many molecules are involved in the process.

•In a multistep reaction each step will have its own rate constant and activation energy.

•The slowest step determines the overall rate.

Multistep Mechanisms

•In a multistep process, one of the steps will be slower than all others.

•The overall reaction cannot occur faster than this slowest, rate-determining step.

•A balanced chemical reaction itself could have a multi step mechanism Slow Initial Step

•The rate law for this reaction is found experimentally to be

Rate =  $k [NO_2]^2$ 

•CO is necessary for this reaction to occur, but the *rate* of the reaction does not depend on its concentration.

•This suggests the reaction occurs in two steps. Slow Initial Step

•A proposed mechanism for this reaction is Step 1:  $NO_2 + NO_2 \longrightarrow NO_3 + NO$  (slow) Step 2:  $NO_3 + CO \longrightarrow NO_2 + CO_2$  (fast)

•The NO<sub>3</sub> intermediate is consumed in the second step.

•As CO is not involved in the slow, rate-determining step, it does not appear in the rate law.

•Since step 1 is the slow rate determining step the rate law is going to be Rate =  $[NO_2]^2$ 

Practice exercise

Ozone reacts with NO<sub>2</sub> to give dinitrogen pentoxide and oxygen:

 $O_3(g) + 2NO_2(g) \rightarrow N_2O_5(g) + O_2(g)$ 

The reaction occurs in the following two steps:

 $O_3(g) + NO_2(g) \rightarrow NO_3(g) + O_2(g)$ 

 $NO_3(g) + NO_2(g) \rightarrow N_2O_5(g)$ 

The experimental rate law is

Rate =  $[O_3][NO_2]$ 

What can you sat about the relative rate of the two steps of the mechanism?

•How many elementary reactions are there in the mechanism?

•How many intermediates?

•Which step is rate limiting?

•Which is the fastest step?

•Exo or endothermic?

Problems

•How many elementary reactions are there in the mechanism?

•How many intermediates?

•Which step is rate limiting?

•Which is the fastest step?

•Exo or endothermic?

Fast Initial Step

•Experimentally the rate law for this reaction is found to be Rate =  $k [NO]^2 [Br_2]$  Because *ter* molecular processes are rare, this rate law suggests a two-step mechanism.
Fast Initial Step
A proposed mechanism is

Fast Initial Step

•NOBr<sub>2</sub> can react two ways:

► With NO to form NOBr

By decomposition to reform NO and Br<sub>2</sub>

•The reactants and products of the first step are in equilibrium with each other.

•Therefore, Rate<sub>f</sub> = Rate<sub>r</sub> Fast Initial Step

•Because Rate<sub>f</sub> = Rate<sub>r</sub>,  $k_1$  [NO] [Br<sub>2</sub>] =  $k_{-1}$  [NOBr<sub>2</sub>] Pay attention to the fact that the reverse k is k-1

•Solving for [NOBr<sub>2</sub>] gives us

Fast Initial Step From before Rate =  $k_2$  [NOBr<sub>2</sub>] [NO] From the previous equation:

Substituting this expression for  $[NOBr_2]$  in the rate law for the rate-determining step gives

•Write down the rate law for the overall reaction.

Catalysts

•Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.

•Catalysts change the mechanism by which the process occurs.

•Homogeneous catalysts  $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ NaBr in an acidic solution acts as a catalyst for this reaction

 $2Br^{-}(aq) + \underline{H_2O_2(aq)} + 2H^{+}(aq) \rightarrow Br_2(aq) + \underline{2H_2O(l)}$ 

 $Br_2(aq) + \underline{H_2O_2(aq)} \rightarrow 2Br^{-}(aq) + 2H^{+}(aq) + \underline{O_2(g)}$ 

Heterogeneous Catalyst

One way a catalyst can speed up a reaction is by holding the reactants together and helping bonds to break.

The reactants are adsorbed on the surface of the catalyst.

Enzymes

•Enzymes are catalysts in biological systems.

•The substrate fits into the active site of the enzyme much like a key fits into a lock.