# Chemical Kinetics

## Factors That Affect Reaction Rates

### Reaction Mechanism

**Definition:** A step by step, molecular level view of the pathway from reactants to products

### Reaction Rate

**Definition:** The speed at which a chemical reaction occurs

**Can be affected by**

1. **Physical State of the reactants**

**Homogeneous**

All reactants are liquids, or all reactants are gases

**Heterogenous**

Reactants are different phases

Limited by area of contact between reactants

2. **Reactant Concentrations**

Higher reactant concentrations tend to increase reaction rate

3. **Reactant Temperatures**

Increased temperature means increased average kinetic energy of particles and higher frequency of collisions amongst reactants. This generally increases the reaction rate.

4. **Presence of a catalyst**

Catalysts are agents that speed up reaction rates without themselves being used up

They affect the kinds of collisions that lead to reaction

## Reaction Rates

### Average Rates

By convention, rates are always expressed as positive values

**Average rate of disappearance**

Average rate at which the concentration of a reactant is decreasing

Average rate of disappearance of A =

**Average rate of appearance**

Average rate at which the concentration of a product is increasing

Average rate of appearance of B =

### Change of rate with time

It is typical for reaction rates to decrease as a reaction approaches equilibrium as the concentration of reactants decreases

### Instantaneous Rate

This is the rate of the reaction at a particular point in time

Instantaneous Rate at t=0 is called the **Initial Rate**

This can be found from the slope of the concentration curve vs. time

### Reaction Rates and Stoichiometry

When referring to “rate” it is implied that you are dividing the concentration rates of each reactant/product by its coefficient in the reaction equation to *normalize* it

In the reaction

The rate would be given by:

## Concentration and Rate Laws

### Rate Law

A **Rate Law** is an equation that shows how the rate of a reaction depends on the reactant concentrations

For the general reaction

The rate law generally has the form

Rate =

The constant **k** is called the **Rate Constant** and its magnitude changes with temperature.

### Reaction Orders: The Exponents in the Rate Law

Most reactions have rate laws of form

Where ***m*** and ***n*** are the ***reaction orders****.*

The ***Overall Reaction Order*** is the sum of all reaction orders.

*For any reaction, the rate law must be determined experimentally*.

### Magnitudes and Units of Rate Constants

General rule regarding reaction speed and rate constants

*Slow:* , *Fast:*

Units of Rate = (units of rate constant) (units of concentration)­Overall Reaction Order

Thus, if the overall reaction order is N, than

Units of Rate constant =

### Using Initial Rates to Determine Rate Laws

Rate of reaction depends on concentration, but rate constant does not.

Rate constant depends on temperature and catalysts

## The Change of Concentration with Time

### First Order Reactions

If we make the step infinitesimally small for we get

We can rearrange the equation to yield

Which upon integration yields the following expression (in 2 forms)

### Second Order Reactions

If we make the step infinitesimally small for we get

We can rearrange the equation to yield

Which upon integration yields the following expression

### Zero Order Reactions

For a zero order reaction the rate law is

In this case the rate is independent of concentration, which when integrated yields:

One example of a zero order reaction is when gas decomposes on the surface of a solid

### Half Life

The **half-life** of a reaction, , is the time required for the concentration of a reactant to reach half of its initial value.

The half life of a first order reaction is

Crucially, the half life is constant regardless of concentration in a first order reaction.

## Temperature and Rate

### The Collision Model

The collision model states that, as molecules must collide to react, the greater number of collisions per second, the greater number of reactions. According to the kinetic molecular theory of gases, increasing temperature increases molecular speeds, and thus collision frequency and energy.

### The Orientation Factor

In most reactions, a reaction will only occur if the molecules collide in the correct orientation.

For example, the reaction

Will only occur if the molecules collide in such a way as to bring the Cl atoms together.

### Activation Energy

**Activation Energy,** is the minimum amount of energy required to initiate a chemical reaction

Imagine the reactants and products as two different stable equilibriums, even if the products are lower energy than the products, a certain amount of energy must be supplied to get out of the potential well of the reactant system’s stable equilibrium and produce the products.

A molecule having an unstable arrangement that exists between the beginning and end state is called a **activated complex** or **transition state.**

The **Rate Constant** is generally inversely proportional to the activation energy.

For a collection of molecules in gas phase, the fraction of molecules that have kinetic energy greater than or equal to the activation energy is given by the following expression

### The Arrhenius Equation

The Arrhenius equation relates the reaction rate to

The fraction of molecules possessing energy or greater

The number of collisions per second

The fraction of collisions that have the appropriate orientation

The Arrhenius equation

In this equation **A** is referred to as the **frequency factor** and it is related to the frequency of collisions and the probability that collisions are favorably oriented for a reaction.

### Determining Activation Energy

Rearranging the Arrhenius equation yields the following relationship

This shows that the natural logarithm of the rate constant is linearly proportional to the reciprocal of temperature, with the slope being This can be used to solve for activation energy if data is collected for rate constant at multiple temperatures.

## Reaction Mechanisms

The **Reaction Mechanism** is the sequence of steps by which a reaction occurs.

### Elementary Reaction

**Elementary Reactions** are reactions that occur in a single step with no intermediate or transition states.

In an elementary reaction, the number of reactant molecules defines the **molecularity**.

**Molecularity**

Unimolecular – An elementary reaction with 1 reactant molecule

Bimolecular – An elementary reaction with 2 reactant molecules

Termolecular – An elementary reaction with 3 reactant molecules

It is very unlikely that more than 2 molecules collide in an elementary reaction, thus most reaction mechanisms are built of only **unimolecular** and **bimolecular** elementary reactions.

### Multistep Reactions

Mutistep reactions occur by N number of elementary reactions, and the chemical equations for the elementary reactions must add to give the overall process.

An **Intermediate** is a molecule that exists in an elementary process between the first and final reactions.

Intermediates can sometimes be stable and identified, but transition states cannot.

### Rate laws for Elementary Reactions

If a reaction is elementary, its rate laws is based directly on its molecularity.

Rate law for a **unimolecular** reaction

Rate law for a **bimolecular** reaction

### The Rate Determining Step for a Multistep Mechanism

The **Rate Determining Step** is the slowest step in a multistep mechanism.

If the rate determining step is not the first step, intermediate products build up.

### Mechanisms with a Slow Initial Step

Generally, if the first step is significantly slower than the others, the rate law of the overall reaction will equal the rate law of the first elementary reaction step.

### Mechanisms with a Fast Initial Step

In general, whenever a fast step precedes a slow one, we can solve for the concentration of an intermediate by assuming that an equilibrium is established in the fast step.

## Catalysis

A **Catalyst** is a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself.

### Homogeneous Catalysis

A catalyst present in the same phase as the reactants is a **homogeneous catalyst**

*As a general rule, a catalyst provides a different mechanism for the chemical reaction of lower overall activation energy.*

### Heterogeneous Catalysis

A **Heterogeneous Catalyst** is one that exists in a different phase as the reactants.

The initial step of heterogeneous catalysis is usually **adsorption**, which is the binding of molecules to a surface. This is because surface ions and atoms have unused bonding capacity, and thus are more reactive.

### Enzymes

An **Enzyme** is a biological catalyst.

The reaction on an enzyme catalyst occurs at one specific place called the **Active Site**.

Substances that react on an active site are called **substrates.**

# Chemical Equilibrium

## The Concept of Equilibrium

**Chemical equilibrium** occurs when the forward and reverse reactions proceed at equal rates

**Conditions for chemical equilibrium:**

The concentrations of reactants and products no longer change with time

Neither reactants nor products can escape from the system

A particular ratio of concentration terms equals a constant

## The Equilibrium Constant

The basis of the **Haber Process** is

**Law of mass action**: Suppose we have

The equilibrium is described by the **equilibrium-constant expression**

Where , the **equilibrium constant,** is the numerical value obtained when we substitute molar equilibrium concentrations into the equilibrium expression. The equilibrium constant is dependent on temperature.

***The equilibrium expression depends only on the stoichiometry of the reaction, not on its mechanism.***

### Evaluating

Multiple initial concentrations of both products and reactants are allowed to reach equilibrium at the same temperature, and from there the equilibrium constant can be empirically calculated

### Equilibrium Constants in Terms of Pressure,

The equilibrium constant in terms of pressure uses the partial pressures of gaseous products and reactants **(in atmospheres)** instead of concentrations.

Using the ideal gas equation we see that

Plugging this in for partial pressures and simplifying yields

Where is equal to the difference in moles from products to reactants in the balanced equation.

### Equilibrium Constants and Units

**Thermodynamic equilibrium constants** derived from activities have no units.

In reality, the units are

## Understanding and Working with Equilibrium Constants

### The Magnitude of Equilibrium Constants

In general

If K >> 1, Equilibrium “lies to the right”, products predominate

If K << 1, Equilibrium “lies to the left”, reactants predominate

### The Direction of the Chemical Equation and K

*The equilibrium expression for a reaction written in one direction is the reciprocal of the expression for the reaction written in the reverse direction.*

### Relating Chemical Equation Stoichiometry and Equilibrium Constants

*The concentrations of the substances in the equilibrium mixture will be the same no matter how you write the chemical equation, but the value of K c you calculate depends on how you write the reaction.*

If two reactions can be added to generate a third, the equilibrium constant of the third is the product of the equilibrium constants of the first 2

General Rules:

The equilibrium constant of a reaction in the reverse direction is the inverse (or reciprocal) of the equilibrium constant of the reaction in the forward direction:

The equilibrium constant of a reaction that has been multiplied by a number is equal to the original equilibrium constant raised to a power equal to that number.

The equilibrium constant for a net reaction made up by adding two or more reactions is the product of the equilibrium constants for the individual reactions:

### Heterogeneous Equilibria

*Whenever a pure solid or a pure liquid is involved in a heterogeneous equilibrium, its concentration is not included in the equilibrium expression.*

## Calculating Equilibrium Constants

### How to Determine Concentrations of Unknown Species in an Equilibrium Mixture

Tabulate all known initial and equilibrium concentrations of the species that appear in the equilibrium expression.

For those species for which initial and equilibrium concentrations are known, calculate the change in concentration that occurs as the system reaches equilibrium.

Use the stoichiometry of the reaction (that is, the coefficients in the balanced chemical equation) to calculate the changes in concentration for all other species in the equilibrium expression.

Use initial concentrations from step 1 and changes in concentration from step 3 to calculate any equilibrium concentrations not tabulated in step 1.

Determine the value of the equilibrium constant.

### Applications of Equilibrium Constants

K indicates the extent to which a reaction proceeds, but also allows us to:

Predict the direction in which a reaction mixture achieves equilibrium.

Calculate equilibrium concentrations of reactants and products.

### Predicting the Direction of Reaction

The **Reactant Quotient, Q,** is a number obtained by substituting reactant

and product concentrations or partial pressures at any point during a reaction

into an equilibrium expression.

Comparing the initial reactant quotient to the equilibrium constant allows us to predict which direction a reaction will travel to reach equilibrium.

For a given **Q** and **K**:

**Q < K:** The concentration of products is too small and that of reactants too large. The reaction achieves equilibrium by forming more products; it proceeds from left to right.

**Q = K:** The reaction quotient equals the equilibrium constant only if the system is equilibrium.

**Q > K:** The concentration of products is too large and that of reactants too small. The reaction achieves equilibrium by forming more reactants; it proceeds from right to left.

### Calculating Equilibrium Concentrations

## Le Chatelier’s Principle

**If a system at equilibrium is disturbed by a change in temperature, pressure, or a component concentration, the system will shift its equilibrium position so as to counteract the effect of the disturbance.**

**Concentration:**

**Pressure:** At constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.

**Temperature:** If the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the “excess reagent”, namely, heat.

### Change in Reactant or Product Concentration

*If a chemical system is already at equilibrium and the concentration of any substance in the mixture is increased (either reactant or product),* ***the system reacts to consume some of that substance****. Conversely, if the concentration of a substance is decreased, the system reacts to produce some of that substance.*

Crucially, equilibrium constant **does not change**.

### Effects of Volume and Pressure Changes

*At constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.*

Pressure/Volume changes **do not** change the value of K **at constant temperature.**

### Effect of Temperature Changes

*When the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the excess reactant (or product), namely heat.*

### The Effect of Catalysts

*A catalyst increases the rate at which equilibrium is achieved.*

# Acid Base Equilibria

## Acid Base Equilibria

### Arrhenius Acids and Bases

Arrhenius definitions:

Acid: A substance that, when dissolved in water, increases the concentration of ions.

Base: A substance that, when dissolved in water, increases the concentration of ions.

### Bronsted-Lowry Acids and Bases

Bronsted-Lowry definitions:

Acid: A substance that donates a proton to another substance

Base: A substance that accepts a proton.

### The Ion in Water

is a bare proton and is thus very reactive with sources of electron density (especially the nonbonding electrons on water molecules)

### Proton-Transfer Reactions

*The transfer of a proton always involves both an acid (donor) and a base (acceptor).*

To be a BL acid, a molecule or ion must have a hydrogen atom it can lose as an ion, to be a BL base, an ion or molecule must have a nonbonding pair of electrons it can use to bind the Ion.

A substance that can act as both an acid and a base (depending on the reaction) is called **amphiprotic.**

An amphiprotic substance acts as a base when combined with something more strongly acidic than itself and as an acid when combined with something more strongly basic than itself.

### Conjugate Acid-Base Pairs

A **Conjugate acid-base pair** is an acid base pair that differ only in the presence or absence of a proton.

### Relative Strengths of Acids and Bases

Acids which donate their protons more easily, have conjugate bases that accept protons less easily.

In other words,

*The stronger an acid, the weaker its conjugate base, and the stronger a base, the weaker its conjugate acid.*

*In every acid–base reaction, equilibrium favors transfer of the proton from the stronger acid to the stronger base to form the weaker acid and the weaker base.*

## The Autoionization of Water

**Autoionization** in water is when a water molecule donates a proton to another water molecule.

### The Ion Product of Water

The **Ion-Product Constant** for water is

And

## The pH Scale

Normal human blood has a pH of between 7.35 and 7.45

### pOH and Other “p” Scales

### Measuring pH

pH meters measure voltage with electrodes in an aqueous solution to measure pH.

Other indicators use substances which change color based on pH.

## Strong Acids and Bases

**Strong Acids and Bases** are **Strong Electrolytes.** That is, they dissociate completely into ions in an aqueous solution.

### Strong Acids

Strong acids are generally considered to dissolve entirely in water and thus their reactions lie entirely to the right.

|  |  |
| --- | --- |
| HCl | Hydrochloric Acid |
| HBr | Hydrobromic Acid |
| HI | Hydroiodic Acid |
| HNO3 | Nitric Acid |
| HClO3 | Chloric Acid |
| HCLO4 | Perchloric Acid |
| H­2SO4 | Sulfuric Acid |

### Strong Bases

Most common strong bases are ionic hydroxides of alkali metals and heavier alkaline earth metals like Sr(OH)2

## Weak Acids

Weak acids do not fully dissociate into ions in solution, and thus, the equilibrium point must be accounted for when calculating the pH.

or

is the **acid-dissociation constant** for acid HA.

*The larger the value of K a, the stronger the acid.*

### Calculating from pH

Use pH to calculate hydrogen ion concentration, then use the balanced equation to calculate the other concentrations and plug into the acid-dissociation constant

### Percent Ionization

If autoionization is considered negligible.

Percent Ionization =

### Using to Calculate pH

*As a general rule, if x is more than about 5% of the initial concentration value, it is better to use the quadratic formula.*

### Polyprotic Acids

A **Polyprotic Acid** is an acid which has more than one ionizable H atom.

It is always easier to remove the first proton from a polyprotic acid than to remove the second.

The differences in magnitude between the first, second, …nth proton removal from a polyprotic acid are usually so large that it is appropriate to estimate the acid as monoprotic with .

## Weak Bases

K\_b is the **base-dissociation constant,** and *it always refers to the equilibrium in which a base reacts with H2O to form the corresponding conjugate acid and .*

**Amines** are weak bases.

### Types of Weak Bases

Two main types of weak bases include:

* Neutral substances that have an atom with a nonbonding pair of electrons that can accept a proton.
* Anions of weak acids (conjugate bases)

### Relationship Between and

For a reversible acid base reaction, the and values associated with the forward and reverse reaction satisfy the equation:

In other words, in general:

*The product of the acid-dissociation constant for an acid and the base-dissociation constant for its conjugate base equals the ion-product constant for water*

Letting

@ 25 C

## Acid-Base Properties of Salt Solutions

### An Anion’s Ability to React with Water

If adding a proton to the anion of a dissolved salt creates a strong acid, it will not appreciably affect the pH of the solution. If, however, it forms a weak acid when a proton is added, then the anion will produce ions in water and therefore is a weak base.

### A Cation’s Ability to React with Water

One mechanism in which the cation of a salt can affect pH is similar to the case for bases. If the cation has a conjugate base which is not strong, it can be considered a weak acid, and increase pH by donating protons to water to create hydronium molecules.

Another mechanism involves strongly charged ions like which, upon becoming hydrated, can weaken the bonds between the oxygen and hydrogen atoms on their hydrating water molecules so much that a proton is transferred from the hydrating water molecules to solvent molecules.

### Combined Effect of Cation and Anion in Solution

Use ur hed

## Acid-Base Behavior and Chemical Structure

### Factor that Affect Acid Strength

* **H-A Bond Polarity:**
  + Molecules containing bonds in which H is slightly positive will produce acids in solution.
  + Molecules containing bonds in which H is slightly positive will produce bases in solution.
* **H-A Bond Strength:**
  + As the H-A bond strength decreases, the stronger the acid.
* **Conjugate Base Stability:**
  + The greater the stability of the conjugate base, the stronger the acid.

### Binary Acids

Generally for binary acids HA in the same group, bond strength is the most important factor.

For binary acids in the same period, bond polarity is the dominating factor.

### Oxyacids

An **Oxyacid** is an acid in which OH groups and possibly additional oxygen atoms are bound to a central atom.

Consider a molecule in which an atom Y is bonded to an OH group.

*Generally, as the electronegativity of Y increases, so does the acidity of the substance.*

And

*the strength of an acid increases as additional electronegative atoms bond to the central atom Y*

### Carboxylic Acids

Acids containing COOH (carboxyl groups)

### Lewis Acids and Bases

Definitions:

Acid: An electron-pair acceptor

Base: An electron-pair donor

Allows for treatment of a wider range of reactions as acid-base reactions.

**ALL**

**Arrhenius** are **Bronsted Lowry**

**Bronsted Lowry** are **Lewis**