

Kinetics

5.1 Reaction Rates

The kinetics of a chemical reaction is defined as the rate at which an amount of reactions is converted to products per unit of time. The rates of change of reactant and the product contains are determined by the stoichiometry in the balanced chemical equation.

Rates for reactants are generally shown to be negative and rates for products are generally shown to be positive.

The units for reaction rate are $\frac{M}{time}$.

According to collision theory, the rate of a reaction is influenced by anything that affects the number or force of collisions:

- Reactant concentrations
- Temperature
- Surface area
- Catalysts

Reactant Concentrations

Increased concentration of aqueous species = increased collisions = increased reaction rate

Decreased volume of gases = increased collisions = increased reaction rate

As concentration increases, the frequency with which the reactant molecules collide increases, leading to increased rates.

Temperature

Increased temperature = increased collisions = increased reaction rate

As temperature increases, reactant molecules move more rapidly, collide more often AND with more force, leading to increased rates.

Surface Area

Increased surface area = increased collisions = increased reaction rate

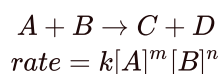
As surface area increases (fine powder vs. solid chunk), reactant molecules collide more frequently, leading to increased rates.

5.2 Introduction to Rate Law

Experimental methods can be used to monitor the amounts of reactants and/or products of a reaction and to determine the rate of the reaction.

The rate law expresses the rate of a reaction is proportional to the concentration of each reactant raised to a power. The power of each reactant in the rate law is the order of the reaction with respect to that reactant. The sum of the powers of the reactant concentrations in the rate law is the overall order of the reaction.

The proportionality constant in the rate law is called the rate constant. The value of this constant is temperature dependent and the units reflect the overall order. Comparing initial rates of a reaction is a method to determine the order with respect to each reactant.



rate = rate of disappearance of reactants (in $\frac{M}{time}$)

k = rate constant (temperature specific)

[A] = concentration of reactant A

[B] = concentration of reactant B

m = reactant order of A

n = reactant order of B

OVERALL REACTION ORDER	GENERAL RATE LAW	RATE CONSTANT UNITS
0	$rate = k$	$mole\ L^{-1}\ s^{-1}$ (or $M s^{-1}$)
1	$rate = k[A]$	s^{-1}
2	$rate = k[A]^2$ OR $rate = k[A][B]$	$L\ mol^{-1}\ s^{-1}$ (or $M^{-1} s^{-1}$)

OVERALL REACTION ORDER	GENERAL RATE LAW	RATE CONSTANT UNITS
3	$rate = k[A]^2[B]$	$L^2 \text{ mol}^{-2} \text{ s}^{-1}$ (or $M^{-2} \text{ s}^{-1}$)

Shortcuts

CONCENTRATION	RATE	ORDER
x	no change	0
x	x	1
x	x^2	2

5.3 Concentration Changes Over Time

5.7 Introduction to Reaction Mechanisms

A reaction mechanism consists of a series of elementary reactions, or steps, that occur in sequence. The components may include reactants, intermediates, products, and catalysts. The elementary steps when combined should align with the overall balanced equation of a chemical reaction. A reaction intermediate is produced by some elementary steps and consumed by others, such that it is present only while a reaction is occurring. A catalyst is consumed by some reaction steps then reformed by others. Experimental detection of a reaction intermediate is a common way to build evidence in support of one reaction mechanism over an alternative mechanism.

Will not be assessed on collection of data pertaining to detection of a reaction intermediate

For a mechanism to be plausible, the sum of the elementary steps must lead to the final, overall reaction with the correct stoichiometry and the mechanism must agree with an experimentally determined rate law expression.

5.8 Reaction Mechanism and Rate Law

For reaction mechanism in which each elementary step is irreversible, or in which the first step is rate limiting, **the rate law of the reaction is determined by the molecularity of the slowest elementary step (i.e., the rate limiting step).**

Will not be assessed on collection of data pertaining to detection of a reaction intermediate

A rate law expression cannot be determined from an overall, balanced equation. It can, however, be determined from an elementary step in a mechanism.

Unimolecularity:

Bimolecularity:

Termolecular:

5.9 Steady-State Approximation

If the first elementary reaction is not rate limiting, approximations (such as steady state) must be made to determine a rate law expression.

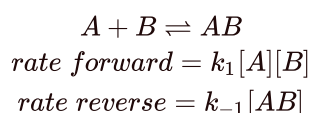
The presence of an intermediate complicates writing rate law expressions. We do not want them in our expression. If the first step is a fast equilibrium, we can use the first step to substitute an intermediate with reactants, catalysts, or even products.

What is Equilibrium?

Some reactions are reversible, denoted by double arrows (\rightleftharpoons). At equilibrium, the rate of the forward reaction is equal to the reverse reaction (*rate forward* = *rate reverse*).

Using Equilibrium in our Rate Law Expressions

We can calculate a rate law for both sides of our equilibrium equation. (Assume that AB is an intermediate.)



Rate forward = rate reverse, therefore:

$$k_1[A][B] = k_{-1}[AB]$$

Solve for the intermediate:

$$\frac{k_1}{k_{-1}}[A][B] = [AB]$$

Substitute $\frac{k_1}{k_{-1}}[A][B]$ into the slow rate determining step in order to not list the intermediate ($[AB]$). The rates can be combined together into k' or k_{obs} , which is the observed rate constant and is a combination of rate constants from the steps in a mechanism.

5.10 Multistep Reaction Energy Profile

Knowledge of the energetics of each elementary reaction in a mechanism allows for the construction of an energy profile for a multistep reaction.

The introduction of a catalyst makes it so that it is at least a 2 step reaction. The slow step is the reaction with the highest activation energy. Endo/exothermic elementary reactions do not determine the overall reaction.

By looking at a reaction profile, you can see how many steps there are based on the number of hills (representing activation energy).

5.11 Catalysis

In order for a catalyst to increase the rate of a reaction, the addition of the catalyst must increase the number of effective collisions and/or provide a reaction path with a lower activation energy relative to the original reaction coordinate. In a reaction mechanism continuing a catalyst, the next concentration of the catalyst is constant. However, the catalyst will frequently be consumed in the rate determining step of the reaction, only to be regenerated in a subsequent step in the mechanism.

A catalyst increases the rate constant via:

- Formation of a more stable activated complex
- Increased collision frequency
- Improved orientation effects

Homogeneous catalysis reaction is the same phase as the catalyst. For example, if this is an acid catalyzed reaction, all species are aqueous. The catalyst can then be used in the intermediate and form covalent bonds.

Heterogeneous catalysis is when the reaction is a different phase than the catalyst. The catalyst can be absorbed in the beginning of the reaction and desorbed at the end of the reaction. An example is a catalytic converter.

Some catalysts involve covalent bonding between the catalyst and the reactant(s). An example is an acid-base catalysis, in which a reactant or intermediate neither gains or loses a proton. This introduces a new reaction intermediate and new elementary reactions involving that intermediate.

In surface catalysis, a reaction or intermediate binds to, or forms a covalent bond with, the surface. This introduces elementary reactions involving these new bound reaction intermediate(s).