

Kinetics

Kinetics – the study of reaction rates (how fast a reaction occurs).

Rate of Reaction:

- How fast the reactants disappear and the products appear.
- Reaction rates have to be determined experimentally.
- **Rate = $\frac{\Delta[\text{product or reactant}]}{\Delta \text{time}}$**
- Note that since reactant concentrations decrease with time, a rate expression involving a reactant will have a negative sign.
- **Average rate of reaction** - the rate of reaction over time t is an average.
- **Instantaneous rate of reaction** – the rate of reaction at a given time.
- **Initial rate of reaction** – the instantaneous rate at the beginning of the reaction.
- If the graph is plotted of concentration v's time, the instantaneous rate of reaction can be found from the slope of the tangent line at the required time. For products, the rate will be equal to the slope, for reactants the rate will be the negative of the slope. (see P558, figure 13.4).

The Rate Law:

- Relates the rate of reaction to the concentrations of reactants.
- Is determined experimentally.
- Although reactions can be reversible, they are usually studied under conditions where the reverse reaction is unfavorable and can be considered negligible.

Differential Rate Law:

- Expresses how the rate depends on concentration.

For the reaction: $A + B \rightarrow C + D$ **rate = $k [A]^m[B]^n$**

- **k** is the **rate constant** and depends on the particular reaction, the temperature, and the presence of a catalyst.
- **m and n** have to be calculated from experimental data.
- Product concentrations do not appear in the rate law expression since the reaction is studied under conditions which do not favor the reverse reaction.

Reaction Order:

- The exponents, m and n give the **order** of the reaction.
- m is the order of the reaction with respect to reactant A and n is the order of the reaction with respect to reactant B.
- The **overall order** of reaction is the sum of the exponents m + n.

Determining the Rate Law:

Method of Initial Rates:

- Several experiments are carried out using different initial concentrations and the initial rate is determined for each run.
- The results are compared to see how the initial rates depend on initial concentrations and the form of the rate law is determined.

Summary of effects of order on initial rate:

- When the concentration of a particular reactant is doubled while all other reactant concentrations are held constant, the effect on the rate depends on the order of the reactant being doubled.
- **Zero order** for the reactant = **no effect** on rate.
- **First order** for the reactant = the **rate doubles**
- **Second order** for the reactant = the **rate quadruples**.
- **Third order** for the reactant = the **rate increases eightfold**.

Units for k:

- The units for k depend on the overall order of the reaction.

Overall reaction order	Units for k
0	M s^{-1}
1	s^{-1}
2	$\text{M}^{-1} \text{s}^{-1}$
3	$\text{M}^{-2} \text{s}^{-1}$

Integrated Rate Law:

- Describes the concentration of a reactant as a function of time.

1. First-Order Reactions (a single reactant yields products):

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

- $[A]_t = [A]$ at a time t
- $[A]_0 = [A]$ at time = 0
- For a first order reaction, a plot of $\ln [A]$ v's time will result in a straight line.
- The slope of the line is $-k$

Half-life ($t_{1/2}$)

- The time required for one half of the original reactant to be consumed.

$$t_{1/2} = \frac{0.693}{k}$$

- For a first-order reaction, the half-life is a constant; it only depends on k, not on the concentration.

2. Zero order reactions:

$$[A]_t = -kt + [A]_0$$

- The rates of reaction are independent of concentrations.
- A plot of concentration v's time will result in a straight line with a negative slope.
- Rate of reaction = $k = -\text{slope}$.

Half-life:

$$t_{1/2} = \frac{[A]_0}{2k}$$

3. Second-order reactions:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

- A graph of $1/[A]$ v's time gives a straight line.
- k = slope
- intercept ($t=0$) is $1/[A]_0$

Half-life:

$$t_{1/2} = \frac{1}{k[A]_0}$$

- the half-life depends on the initial concentration and the rate constant k .

Summary

	ORDER		
	ZERO	FIRST	SECOND
Rate Law	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated Rate Law	$[A]_t = -kt + [A]_0$	$\ln \frac{[A]_t}{[A]_0} = -kt$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
Plot needed for a straight line	$[A]$ v's t	$\ln[A]$ v's t	$1/[A]$ v's t
Relationship of k to slope of straight line	Slope = $-k$	Slope = $-k$	Slope = k
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Theories:

1. Collision theory.

- Particles must collide before they can react together.
- Any action that increases the number of collisions will increase the rate of reaction. Ex: increases in temperature or concentration.
- Some collisions are ineffective- only a small fraction of colliding molecules actually react.
- **Activation energy (E_a)** is the minimum energy which must be provided by the collisions in order for the reaction to take place.
- The energy of the collision must exceed the activation energy.
- The orientation of the reactants also affects the reaction rate; the relative orientation of the reactants must allow formation of the necessary new bonds.

Arrhenius Equation:

- Accounts for the effect of temperature on the rate constant k .

$$k = Ae^{-E_a/RT}$$

- **A** is the **frequency factor** and is a product of the collision frequency (Z) and the probability factor (p). ie: it takes into account the frequency of the collisions and the orientations necessary for an effective collision.
- **E_a** is the activation energy.
- **R** = 8.3145 J mol⁻¹K⁻¹
- **T** = Kelvin temperature

2. Transition state theory:

- The **transition state** is the highest energy state in the reaction.
- The configuration of molecules is the transition between reactants and products- molecules may go on to form either products or reactants.
- The species present in the transition state are called the **activated complex**.
- The transition state is very unstable.

Reaction Profiles (energy profiles):

- Potential energy v's the progress of the reaction.
- See textbook examples and examples in class.

Reaction Mechanisms:

- A series of simple steps that lead from the reactants to the products.
- Plausible reaction mechanisms must account for the experimentally determined rate law.
- The sum of the elementary steps must give the overall balanced equation for the reaction.

Elementary reactions (steps):

- A single stage in the overall reaction.
- A reaction whose rate law can be written from its molecularity.

Molecularity – the number of species that must collide to produce the reaction in that step.

Unimolecular reactions – 1 molecule dissociates.

Bimolecular reactions – 2 molecules collide effectively.

Termolecular reactions – require the collision of 3 species simultaneously (rare).

Rate Determining Step:

- The slowest step in the sequence.

Catalysis:

- **Catalysts** speed up a reaction without being consumed in the reaction themselves.
- Allow the reaction to occur with a lower activation energy by changing the mechanism of the reaction.

Homogeneous catalysts:

- Are present in the same phase as the reacting molecules.

Heterogeneous catalysts:

- Exist in a different phase to the reactants – usually as a solid.
- Usually involve four basic steps:

1. Adsorption and activation of the reactant molecules. (Adsorption is the collection of one substance on the surface of another, absorption is the penetration of one substance by another).
2. Migration of the adsorbed reactants along the surface.
3. Reaction of the adsorbed substances.
4. Desorption (escape) of the products.

Enzymes:

- Large molecules (usually proteins) which catalyze specific reactions in living organisms.
- **Induced-fit model:** The substrate (reacting substance) attaches to the enzyme at the active site to form an enzyme-substrate complex. The complex decomposes to form products and the enzyme is regenerated.
- Reaction rates are influenced by concentrations, acidity, and temperature.