

Chapter 14

Chemical Kinetics

Chemical kinetics: the area of chemistry dealing with the speeds or rates at which reactions occur.

Rates are affected by several factors:

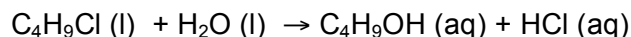
- *The concentrations of the reactants*: Most chemical reactions proceed faster if the concentration of one or more of the reactants is increased.
- *The temperature at which a reaction occurs*: The rates of chemical reactions increase as temperature is increased. Why do we refrigerate milk?
- *The presence of a catalyst*: A catalyst is a substance added to a reaction to increase its rate without being consumed in the reaction. The most common catalyst is *enzymes*.
- *The surface area of solid or liquid reactants or catalysts*: Reactions that involve solids often proceed faster as the surface area of the solid is increased. For example, a crushed aspirin will enter the bloodstream quicker.

I. Reaction rates

A. Speed of any event is measured by the change that occurs in any interval of time. The speed of a reaction (reaction rate) is expressed as the change in concentration of a reactant or product over a certain amount of time.

B. Units are usually Molarity / second (M/s)

C. Example: prepare a 0.100M solution butyl chloride in water and then measure the concentration at various intervals when it is involved in the following reaction:



average rate = (decrease in concentration butyl chloride)/ (change in time)

Since concentration of the reactant decreases over time, final concentration minus the initial will give a negative value. To account for this:

$$\text{Average Rate} = - \frac{\Delta [\text{C}_4\text{H}_9\text{Cl}]}{\Delta t}$$

D. Reaction Rates and Stoichiometry

We could also look at the rate of appearance of a product. As a product appears, its concentration increases. The rate of appearance is a positive quantity. We can also say the rate of appearance of a product is equal to the rate of disappearance of a reactant.

$$\text{Rate} = - \frac{\Delta [\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = + \frac{\Delta [\text{C}_4\text{H}_9\text{OH}]}{\Delta t}$$

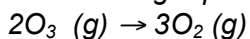
What happens when the stoichiometric relationships are not 1:1 in a reaction?

$2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ The rate of disappearance of HI is twice that than the rate of appearance of H_2 .

$$\text{Rate} = - \frac{\Delta[\text{HI}]}{2 \Delta T} = \frac{\Delta[\text{H}_2]}{\Delta T}$$

Example 1:

How is the rate of disappearance of ozone related to the rate of appearance of oxygen in the following equation?



$$\text{Rate} = - \frac{\Delta[\text{O}_3]}{2 \Delta T} = \frac{\Delta[\text{O}_2]}{3\Delta T}$$

If the rate of appearance of O_2 , $\Delta[\text{O}_2] / \Delta T$, is $6.0 \times 10^{-5} \text{ M/s}$ at a particular instant, what is the value of the rate of disappearance of O_3 , $\Delta[\text{O}_3] / \Delta T$, at this same time?

$$- \frac{\Delta[\text{O}_3]}{\Delta T} = \frac{2\Delta[\text{O}_2]}{3\Delta T} = \frac{2}{3} (6.0 \times 10^{-5} \text{ M/s}) = 4.0 \times 10^{-5} \text{ M/s}$$

II. The Dependence of Rate on Concentration

Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25°C

| Experiment Number | Initial [NH ₄ ⁺] (M) | Initial [NO ₂ ⁻] (M) | Observed initial rxn rate |
|-------------------|---|---|-----------------------------|
| 1 | 0.0100 | 0.200 | 5.4 x 10 ⁻⁷ M/s |
| 2 | 0.0200 | 0.200 | 10.8 x 10 ⁻⁷ M/s |
| 3 | 0.0400 | 0.200 | 21.5 x 10 ⁻⁷ M/s |
| 4 | 0.200 | 0.0202 | 10.8 x 10 ⁻⁷ M/s |
| 5 | 0.200 | 0.0404 | 21.6 x 10 ⁻⁷ M/s |

Notice, if we double the concentration [NH₄⁺] and keep [NO₂⁻] constant, the rate doubles. the same happens if we double [NO₂⁻] and keep [NH₄⁺] constant. We can express the overall concentration dependence as follows:

$$\text{Rate} = k [\text{NH}_4^+][\text{NO}_2^-]$$

Such an expression, which shows how the rate depends on the concentration of the reactants, is called the **rate law**. The constant k , is called the **rate constant**. Knowing the concentrations of reactants and the rate of a reaction with these concentrations, we can determine the rate constant.

$$5.4 \times 10^{-7} \text{ M/s} = k (0.0100\text{M})(0.200\text{M})$$

$$k = 2.7 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$$

No matter what concentrations are present in this reaction, the rate constant, k , is constant. We can then use the rate constant to determine the reaction rate for any given set of concentrations of [NH₄⁺] and [NO₂⁻].

A. Reaction Order

rate laws for most reactions have the general form

Rate = $k[\text{reactant 1}]^m[\text{reactant 2}]^n \dots$ where m and n are called **reaction orders** and their sum is the **overall reaction order**.

We can refer to reaction order *with respect to* a certain reactant. For example, in the expression Rate = $k [\text{NH}_4^+][\text{NO}_2^-]$, the reaction order is first order with respect to NH₄⁺ but is second overall.

The values of m and n are NOT related to the coefficients in the balanced equation, but are values that are determined experimentally. Given concentrations and reaction rates, the values for m and n can be found.

Example 2: IF ONE REACTANT IS INVOLVED (usually a decomposition reaction)

The initial rate of decomposition of acetaldehyde, CH₃CHO,

CH₃CHO (g) → CH₄ (g) + CO (g) was measured at a series of different concentrations with the following results:

| | | | | |
|---|-------|------|------|------|
| Concentration CH ₃ CHO (mol/L) | 0.10 | 0.20 | 0.30 | 0.40 |
| Rate (mol/L-s) | 0.085 | 0.34 | 0.76 | 1.4 |

Using this data, determine the order of the reaction; that is, determine the value of m in the equation

$$\text{rate} = k(\text{conc. CH}_3\text{CHO})^m$$

solution: *Write down the rate expression at two different concentrations:*

$$\text{rate}_2 = k(\text{conc}_2)^m$$

$$\text{rate}_1 = k(\text{conc}_1)^m$$

Dividing the first equation by the second :

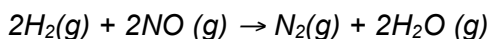
$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{(\text{conc}_2)^m}{(\text{conc}_1)^m}$$

substituting data:

$$\frac{0.34}{0.085} = \frac{(0.20)^m}{(0.10)^m}$$

Simplifying: 4 = 2^m Clearly, m=2.

Example 3: TWO REACTANTS



| | SERIES 1 | | | SERIES 2 | | |
|-------|-------------------|------|------|-------------------|------|------|
| | [H ₂] | [NO] | Rate | [H ₂] | [NO] | Rate |
| Exp 1 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| Exp 2 | 0.20 | 0.10 | 0.20 | 0.10 | 0.20 | 0.40 |
| Exp 3 | 0.30 | 0.10 | 0.30 | 0.10 | 0.30 | 0.90 |
| Exp 4 | 0.40 | 0.10 | 0.40 | 0.10 | 0.40 | 1.6 |

In the first series of experiments, we hold the initial concentration of NO constant and vary H₂. If you look at the data, it is clear the rate is directly proportional to the concentration of H₂. (When the concentration of H₂ doubles, the rate doubles). This means in the general expression:

$$\text{rate} = k[\text{H}_2]^m [\text{NO}]^n \quad m \text{ must equal } 1.$$

In the second series, [H₂] is held constant, while [NO] varies. It is apparent the rate is proportional to the square of [NO]. When [NO] is doubled (from 0.10 to 0.20) the rate increases by a factor of 2² = 4 (from 0.10 to 0.40). Therefore n = 2.

B. Summation:

1. If only one reactant is involved, find the ratio of the rates at two different concentrations and apply the relation

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{(\text{conc}_2)^m}{(\text{conc}_1)^m}$$

where m is the reaction order. Ordinarily m can be found by inspection. It is most often a whole number (0, 1, 2, 3..) but it can be a fraction (1/2, 3/2, ...).

2. If two reactants, A and B are involved.

- a. Find the ratio of rates at two points for which concentration B is constant but conc. A differs. Use the equation above to find the order with respect to A
- b. Repeat (a), this time varying conc B and keeping A constant. This leads to order with respect to B.

III. The Change in Concentration with Time

In reactions, most likely, one would be interested in knowing how much reactant is left after a certain period of time. The mathematics to do this involves calculus and is quite complex. We will look at first and second order reactions as well as half-life.

A. First Order Reaction

For the reaction $A \rightarrow \text{products}$, the rate is as follows:

$$\text{Rate} = - \frac{\Delta[A]}{\Delta t} = k[A]$$

using calculus, this equation can be transformed into an equation that relates the conc. A at the start of the reaction, $[A_0]$, to its concentration at any other time t , $[A_t]$:

$$\ln[A_t] - \ln[A_0] = -kt \quad \text{or} \quad \ln\left(\frac{[A_t]}{[A_0]}\right) = -kt \quad (1)$$

$$\ln[A_t] = -kt + \ln[A_0] \quad (2)$$

This equation has the form for the general equation of a straight line, $y=mx+b$. Thus, for a first order reaction, a graph of $\ln[A_t]$ vs time gives a straight line with the slope of $-k$ and a y -intercept of $\ln[A_0]$

For a first order reaction, equation (1) or (2) can be used to determine

- the concentration of a reactant at any time after the reaction has started
- the time required for a given fraction of a sample to react
- the time required for a certain reactant to reach a certain level.

Example4:

The first-order rate constant for the decomposition of a certain insecticide in water at 12°C is 1.45 per year. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of $5.0 \times 10^{-7} \text{ g/cm}^3$ of water. Assume the effective temperature of the lake is 12°C. (a) What is the concentration of the insecticide June 1 of the following year? (b) How long will it take for the concentration of the insecticide to drop to $3.0 \times 10^{-7} \text{ g/cm}^3$?

B. Half-Life

The half-life of a reaction ($t_{1/2}$) is the amount of time required for the concentration of the reactant to drop to one-half its initial value. $[A_{t_{1/2}}] = 1/2 [A_0]$ We can determine the half-life of a first order reaction by substituting $[A_{t_{1/2}}]$ into equation (1).

$$\ln (1/2[A_0]/[A_0]) = -kt_{1/2}$$

$$\ln 1/2 = -kt_{1/2}$$

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

Notice that half-life is independent of the initial concentration. For example, pick any point in a reaction, one half life from that point is where the concentration of the reactant is 1/2. *In a first-order reaction, the concentration of the reactant decreases by 1/2 in each series of regularly spaced time intervals, namely $t_{1/2}$*

C. Second-Order Reactions

A second order reaction is one where one reactant is raised to the second power or two reactants each raised to the first power. We will discuss the simpler relationship.

$$\text{Rate} = k[A]^2$$

Relying on calculus, the law can be used to derive the following:

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

Again, this has the form of a straight line. If the reaction is second order, the plot of $1/[A_t]$ vs t will yield a straight line with a slope equal to k and a y intercept equal to $1/[A_0]$. One way to distinguish between a first order and a second order reaction is to graph both $\ln[A_t]$ and $1/[A_t]$ vs t . If the $\ln [A_t]$ plot is linear, the reaction is first order; if the $1/[A_t]$ plot is linear, the reaction is second order. The half-life of a second order reaction is given by:

$$t_{1/2} = 1/k[A_0]$$

Notice, in a second order reaction, the half-life is dependent on the initial concentration of the reactant.

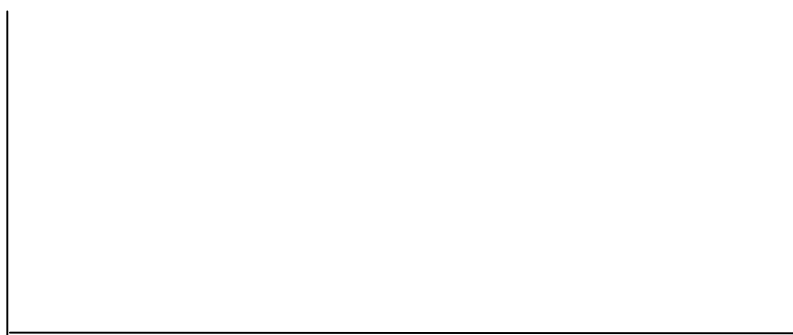
IV. Temperature and Rate

A. Collision Model

The collision model of chemical kinetics state: *molecules must collide to react*. The greater the number of collisions occurring per second, the greater the reaction rate. Increasing concentration as well as temperature will increase the number of collisions. For most reactions, though, only a small fraction of collisions lead to a reaction. What keeps a reaction from happening more quickly?

B. Activation Energy

Arrhenius: suggested molecules must possess a certain minimum amount of energy in order to react. According to the collision model, this energy must come from the kinetic energy of collisions. the minimum energy required is called **activation energy, E_a** .



- For reactions to occur, not only do we need sufficient energy to overcome the activation energy, but the atoms must be suitably oriented.
- In general, for any process, $\Delta H = E_a - E_a'$

1. Activated Complex: Intermediate step. Bonds are breaking and new bonds are forming.

2. Exothermic vs Endothermic reaction:

If the forward reaction is exothermic ($\Delta H < 0$), E_a is smaller than E_a' .

If the forward reaction is endothermic ($\Delta H > 0$), the activation energy for the forward reaction, E_a , is larger than the reverse reaction, E_a' .

C. Catalyst

Catalyst increases reaction rate without being consumed in a reaction. This happens because a catalyst provides an alternative path for the reaction with lower activation energy.

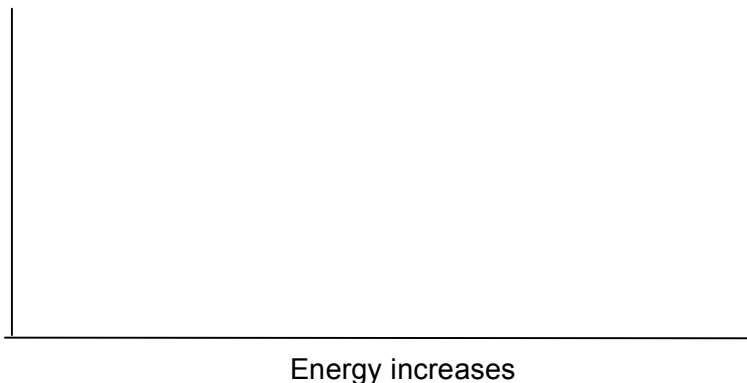
Even though the activation energy is lowered, ΔH remains the same.



D. Effect of Temperature on Reaction Rate.

In general increase in temperature increases rate. Rate is approximately doubled when T increases by 10°C.

Since increasing temperature does not affect concentration that much, rate expressions must reflect temperature increases through the rate constant. Therefore, the rate constants we've used previously, are very temperature dependent.



Relation between K and T

Arrhenius: found that most reaction-rate data obeyed the equation:

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

where k is the rate constant, E_a , the activation energy, R the gas constant (8.314 J/mol-K), T is the temperature and A is constant as temp varies. A, called the **frequency factor**, is related to the frequency of collisions and the probability that the collisions are favorably oriented for the reaction. The equation can also be rearranged as follows:

$$\ln k = \frac{-E_a}{RT} + \ln A$$

Graphing this equation, $\ln k$ vs $1/T$ should yield a straight line. The activation energy can be obtained from the slope of the line.

$(-E_a/R)$

We can use a variation of the Arrhenius equation to obtain a relation between rate constants k_2 and k_1 at two different temperatures, T_2 and T_1 . The "two point" equation we use is as follows:

$$\begin{aligned} K_1 \text{ at } T_1 \ln k_1 &= \frac{-E_a}{RT_1} + \ln A \\ K_2 \text{ at } T_2 \ln k_2 &= \frac{-E_a}{RT_2} + \ln A \end{aligned}$$

Subtracting $\ln k_2$ from $\ln k_1$ for change in temperature

$$\ln \left(\frac{k_1}{k_2} \right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3)$$

to avoid the use of negative logs, T_2 is always the higher temperature.

Why do we care??? We can determine the activation energy needed for a reaction to go.

Example: What must the value of E_a for a reaction if the rate constant is to double when the temperature increases from 15 to 25°C?

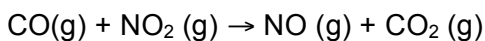
Other examples: page 512 Sample 14.8

V. Reaction Mechanisms

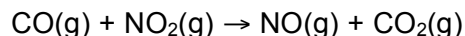
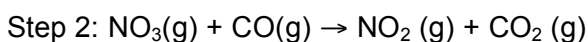
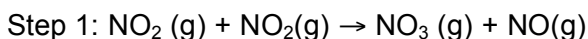
A reaction mechanism is a description of the path, or sequence of steps by which a reaction occurs.

A single step reaction mechanism:

The reaction between CO and NO₂ at high temperatures (above 600 K)



Research shows that at low temperatures, this reaction occurs in two steps:



Net equation: Simplifying by eliminating substances that are on both sides of the equation. The substances eliminated (in this case NO₃) is the **intermediate**.

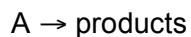
Rate Laws in Reaction Mechanisms

We stressed that rate laws must be determined experimentally. They cannot be derived from the balanced equations. The reason: Every reaction is actually made of one or more steps and the rate laws and relative speed of these steps will determine the overall rate law. the overall rate law cannot exceed the rate of the slowest elementary step. (**rate determining step**) We can therefore determine the rate law from the reaction mechanism.

Before we do this, we need to understand the types of elementary steps:

The number of molecules that participate as reactants in an elementary step defines the **molecularity** of the step.

Unimolecular: a single molecule is involved as a reactant:



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

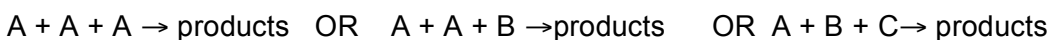
Bimolecular: elementary step involving collision of two reactant molecules



$$\text{rate} = k[A][B]$$

$$\text{rate} = k[A]^2$$

Termolecular: elementary step involving simultaneous collision of three molecules. These are rarely encountered



$$\text{Rate} = k[A]^3$$

$$\text{Rate} = k[A]^2[B]$$

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

To Determine the overall rate law based on the reaction mechanism:

1. Locate the slow step in the mechanism. The rate of the overall reaction will be the rate of that step.



Step 2 is much faster than step 1, that is $k_2 \gg k_1$ if you were given rate constants

2. Write the rate expression for the slow step. To do this, note the exponent of a reactant in the rate expression for a step is its coefficient in the equation for that step. NOTE THIS IS A DIFFERENT PROCEDURE THAN WE USED TRYING TO FIND THE RATE EXPRESSION STRAIGHT FROM THE OVERALL EQUATION.

$$\text{Rate} = k_1[\text{NO}_2]^2 \quad (\text{notice it is bimolecular})$$

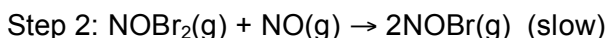
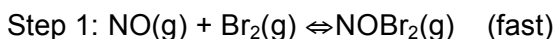
This is the rate law that is observed experimentally. If we had attempted to derive a rate law from the overall Net equation, the rate law would be

$$\text{Rate} = k[\text{NO}_2][\text{CO}]$$

however, this does not agree with experimental observations.

3. If the rate expression contains an unstable intermediate, the term for that species must be eliminated. Frequently, this is done by working with the equilibrium constant for the fast step in the mechanism. This usually happens when the initial step in a reaction mechanism is fast.

Example:





$$\text{Rate of the slow step} = k_2[\text{NOBr}_2][\text{NO}]$$

But NOBr_2 is an intermediate and can't be a part of the overall rate expression. Intermediates are usually unstable molecules that have a low unknown concentration. Fortunately, with some *assumptions* we can express the concentration of NOBr_2 in terms of the concentrations of NO and Br_2 . After NOBr_2 is formed, it can do one of two things: (1) react with NO to give NOBr or (2) fall back apart to NO and Br_2 . Since formation of NOBr is a slow process it is more probable for NOBr_2 to fall back apart as the reverse of step 1: We can then assume the first step achieves an equilibrium with its forward and reverse reactions.

$$\begin{array}{ccc} k_1[\text{NO}][\text{Br}_2] & = & k_{-1}[\text{NOBr}_2] \\ \text{rate forward} & & \text{rate reverse} \end{array}$$

Solving for $[\text{NOBr}_2]$, we have:

$$[\text{NOBr}_2] = k_1/k_{-1}[\text{NO}][\text{Br}_2]$$

Substituting the relationship into the rate law for the rate-determining step, we have,

$$\text{Rate} = k_2(k_1/k_{-1}) [\text{NO}][\text{Br}_2][\text{NO}] = k[\text{NO}]^2[\text{Br}_2]$$