

Ch 13 Rates of Reaction (Chemical Kinetics)

Reaction Rates and Kinetics

- The reaction rate is how fast reactants are converted to products.
- Chemical kinetics is the study of reaction rates. Kinetics studies how reaction rates change under varying conditions, and what molecular events occur during chemical reactions.
- The rate is measured as an increase in molar concentration per unit time of a product, or as a decrease in molar concentration per unit time of a reactant.
- Reaction rates are affected by the concentrations of reactants, products, and catalysts, as well as by the areas of reacting surfaces, and by temperature.

Concentration of Reactants

- The rate is generally proportional to the concentration raised to an exponent: $\text{Rate} \propto [\text{A}]^n$
- Rate may be directly proportional to a reactant concentration: $[\text{A}]^1 = ?$
- Or the rate may be unaffected by a reactant: $[\text{A}]^0 = ?$
- The exponent can be negative or a fraction: $[\text{A}]^{-1/2} = ?$

Concentration of a Catalyst

- A catalyst is a substance which increases reaction rate without being consumed by reaction.
- A catalyst is not a reactant or product. So, it is not on either the left or right side of the reaction equation. It is usually written above the reaction arrow.
- The rate is proportional to the catalyst concentration raised to an exponent: $\text{Rate} \propto [\text{catalyst}]^n$

Temperature

- Increasing the temperature generally increases reaction rates by increasing both the energy and frequency of molecular collisions.

Surface Area of a Solid Reactant or Catalyst

- The reaction rate is proportional to the surface's concentration, which is expressed as the amount of surface area (m^2) per unit volume (cm^3). The overall units are in m^2/cm^3 .

Example 13.01 Expressing the Reaction Rate for $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

- The reaction's progress can be observed by formation of O_2 , and the average rate is $\frac{\Delta[\text{O}_2]}{\Delta t}$.
- The rate is usually not constant. To express an instantaneous rate (as Δt approaches 0), use a calculus derivative, so that rate = $\frac{d[\text{O}_2]}{dt}$.
- We can also express the reaction rate by its decomposition of N_2O_5 , so that the average rate is $-\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$. Note that there is a sign change. This is because N_2O_5 is consumed.
- The rate depends on substance chosen, because two N_2O_5 are consumed for each O_2 formed.

$$\left(\frac{\Delta[\text{O}_2]}{\Delta t}\right) \left(\frac{-2 \text{ molecules } \text{N}_2\text{O}_5}{1 \text{ molecule } \text{O}_2}\right) = \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} \quad \text{or} \quad \left(\frac{\Delta[\text{O}_2]}{\Delta t}\right) = \left(\frac{1 \text{ molecule } \text{O}_2}{-2 \text{ molecules } \text{N}_2\text{O}_5}\right) \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

Measurement of the Rate Requires an Indicator of the Concentration.

- The gas phase decomposition of N_2O_5 creates five moles of gas from two moles of gas. The moles created can be calculated from the pressure increase using the ideal gas law.
- NO_2 is reddish-brown, while N_2O_5 and O_2 are colorless. So, intensity of color (absorption of light) can also be used to indicate concentration.

Rate Law Equation

- The rate law relates the reaction rate to the concentrations of reactants and catalysts.
- For $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$, the equation is: $\text{rate} = k[\text{NO}_2][\text{F}_2]$.
- k is the rate constant, a proportionality constant relating rate to concentrations.
- For the general reaction $a\text{A} + b\text{B} \rightarrow d\text{D} + e\text{E}$ with catalyst C , the rate equals $k[\text{A}]^m[\text{B}]^n[\text{C}]^p$.

Exponents in the Rate Law

- The exponents are not usually the same as the stoichiometric coefficients.
- Exponents need to be determined experimentally.
- If the exponent is one for a reactant, the reaction is 1st order with respect to that reactant. An exponent of 2 is 2nd order, and so forth.
- The overall order of reaction is the sum of all exponents in the rate law. If m , n , and p are all 1 in the general rate law above, then overall order is 3rd ($1 + 1 + 1 = 3$).

Example 13.03 Determine the Individual and Overall Orders of Reaction

- For $\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g})$, we have $\text{rate} = k[\text{NO}]^2[\text{H}_2]^1$
- The individual orders for each of the reactants are their individual exponents.
- The reaction is 2nd order with respect to NO .
- The reaction is 1st order with respect to H_2 .
- The overall order is the sum of the individual exponents. $1 + 2 = 3^{\text{rd}}$ order overall.

Determining a Rate Law ($\text{Rate} = k[\text{A}]^m$)

- The rate law must be determined experimentally, with initial rate experiments.
- Change concentration of one species, while keeping all others constant, to find its exponent.
- Divide the two rate laws for the two trials:
$$\left(\frac{\text{rate}_2}{\text{rate}_1}\right) = \frac{k[\text{A}]_2^m}{k[\text{A}]_1^m}$$
- The equation simplifies to this:
$$\left(\frac{\text{rate}_2}{\text{rate}_1}\right) = \left(\frac{[\text{A}]_2}{[\text{A}]_1}\right)^m$$
- If doubling concentration will double rate, then $(2) = (2)^m$, so $m = 1$ and $\text{rate} = k[\text{A}]^1$.
If doubling concentration will quadruple rate, then $(4) = (2)^m$, so $m = 2$ and $\text{rate} = k[\text{A}]^2$.
- Once the exponent has been determined, k can then be calculated by rearranging the rate law. The rearranged equation is $k = \frac{\text{rate}}{[\text{A}]^m}$.
- k is a function of temperature, and the relationship can be determined experimentally by performing rate experiments at different temperatures.

Example 13.04 Experimentally Determine the Exponents in the Rate Law

- We can use rate and concentration **data** to find the rate law for $\text{ClO}^{-1} + \text{I}^{-1} \rightarrow \text{IO}^{-1} + \text{Cl}^{-1}$
- $\left(\frac{\text{rate}_1}{\text{rate}_3}\right) = \left(\frac{[\text{ClO}^{-1}]_1}{[\text{ClO}^{-1}]_3}\right)^m \quad \left(\frac{1.84 \times 10^{-3} \text{ mol/L}\cdot\text{s}}{4.6 \times 10^{-4} \text{ mol/L}\cdot\text{s}}\right) = \left(\frac{0.0040 \text{ mol/L}}{0.0020 \text{ mol/L}}\right)^m \quad 4 = 2^m \quad m = 2$
- $\left(\frac{\text{rate}_2}{\text{rate}_3}\right) = \left(\frac{[\text{I}^{-1}]_2}{[\text{I}^{-1}]_3}\right)^n \quad \left(\frac{9.2 \times 10^{-4} \text{ mol/L}\cdot\text{s}}{4.6 \times 10^{-4} \text{ mol/L}\cdot\text{s}}\right) = \left(\frac{0.0040 \text{ mol/L}}{0.0020 \text{ mol/L}}\right)^n \quad 2 = 2^n \quad n = 1$
- Rate Law: $\text{Rate} = k[\text{ClO}^{-1}]^m[\text{I}^{-1}]^n = k[\text{ClO}^{-1}]^2[\text{I}^{-1}]^1$
- Rate Constant: $k = \frac{\text{Rate}}{([\text{ClO}^{-1}]^2[\text{I}^{-1}])} = \frac{(9.2 \times 10^{-4} \text{ mol/L}\cdot\text{s})}{(0.0020 \frac{\text{mol}}{\text{L}})^2 \times (0.0040 \frac{\text{mol}}{\text{L}})} = 5.75 \times 10^4 \frac{\text{L}^2}{\text{mol}^2\cdot\text{s}}$

First Order Concentration -Time Equation

- A concentration-time equation gives concentration as a function of time.
- The equation can be derived from the rate law by using calculus.
- Concentration vs. Time can be found for 1st order where rate = $\frac{-d[\text{A}]}{dt} = k[\text{A}]^1$
- This rearranges to $\frac{d[\text{A}]}{[\text{A}]} = -k dt$
- Which integrates to $\ln[\text{A}] - \ln[\text{A}]_0 = -k(t) \quad \text{and} \quad \ln[\text{A}] = -k(t) + \ln[\text{A}]_0$
- And then rearranges to $\ln\left(\frac{[\text{A}]}{[\text{A}]_0}\right) = -kt \quad \text{and} \quad [\text{A}] = [\text{A}]_0(e^{-kt})$

First Order Half-Life

- The half-life is the time when the concentration of a reactant is half of its original value.
- At $t_{1/2}$, we have $[\text{A}]_{1/2} = (\frac{1}{2})[\text{A}]_0$.
- The half-life can be found from the concentration-time equation.
- For 1st order, we have $kt_{1/2} = -\ln\left(\frac{[\text{A}]_{1/2}}{[\text{A}]_0}\right) = -\ln\left(\frac{\frac{1}{2}[\text{A}]_0}{[\text{A}]_0}\right) = -\ln(\frac{1}{2}) = \ln(2) = 0.693$
- This rearranges to $t_{1/2} = \frac{0.693}{k}$ for 1st order.

Second Order Concentration-Time Equation

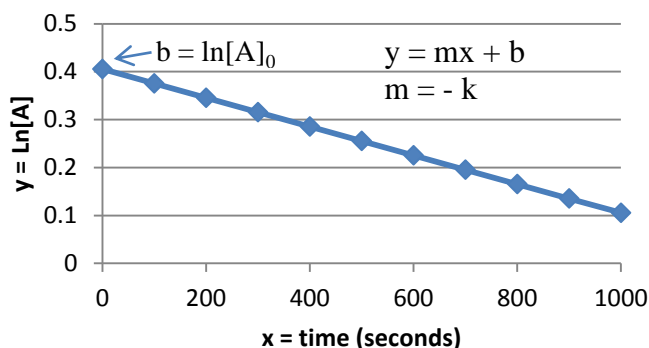
- Derive from rate law $\text{rate} = \frac{d[\text{A}]}{dt} = -k[\text{A}]^2$
- This rearranges to $-\frac{d[\text{A}]}{[\text{A}]^2} = (k)dt$
- Which integrates to $\frac{1}{[\text{A}]} - \frac{1}{[\text{A}]_0} = kt$
- And then rearranges to $\frac{1}{[\text{A}]} = kt + \frac{1}{[\text{A}]_0}$

Second Order Half-Life

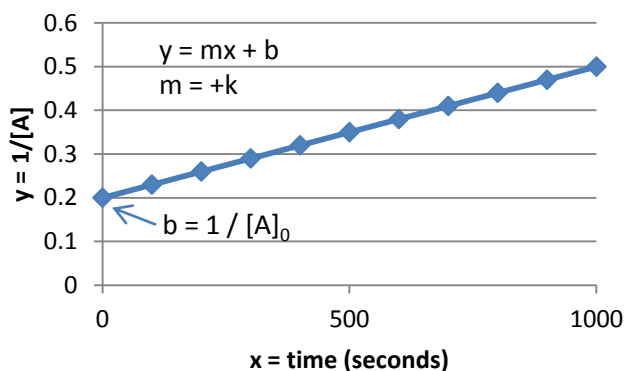
- Use conc-time equation $\frac{1}{[\text{A}]_{1/2}} = \frac{1}{(\frac{1}{2})[\text{A}]_0} = \frac{2}{[\text{A}]_0}$
- $kt_{1/2} = \frac{1}{[\text{A}]_{1/2}} - \frac{1}{[\text{A}]_0} = \frac{2}{[\text{A}]_0} - \frac{1}{[\text{A}]_0} = \frac{1}{[\text{A}]_0}$
- This rearranges to $t_{1/2} = \frac{1}{k[\text{A}]_0}$ for 2nd order
- Note that $t_{1/2}$ is now dependent on the original concentration (unlike 1st order).

Graphing Concentration-Time Equations

- For 1st order, use $\ln[A] = -k(t) + \ln[A]_0$ to create a straight line ($y = mx + b$).
- The plot is $\ln[A]$ versus t , where $\ln[A]_0$ is the y-intercept (b), and $-k$ is the slope (m).



- For 2nd order, use $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$ to create the straight line ($y = mx + b$).
- Plot is $\frac{1}{[A]}$ versus t , where $\frac{1}{[A]_0}$ is the y-intercept (b), and $+k$ is the slope (m).



Concentration-Time Equations for First-Order and Second-Order Reactions

Rate Law	Concentration-Time Equation ($y = mx + b$)	Linear Graphing Variables	Slope	y-Intercept	Half-Life	Units on k
Rate = $k[A]$	$\ln[A] = -kt + \ln[A]_0$	$\ln[A]$ vs. t	$-k$	$\ln[A]_0$	$\frac{-\ln(0.5)}{k}$	s^{-1}
Rate = $k[A]^2$	$\frac{1}{[A]} = +kt + \frac{1}{[A]_0}$	$\frac{1}{[A]}$ vs. t	$+k$	$\frac{1}{[A]_0}$	$+\frac{1}{k[A]_0}$	$\frac{L}{mol \cdot s}$

Effect of Temperature on Rate

Collision Theory

- For a reaction to occur and create products, the reactant molecules must collide. When they collide, they must possess more than the [activation energy](#) (E_a), and also have the proper orientation.
- According to Collision Theory, the rate constant (k) is the product of:
 - 1) the collision frequency (Z)
 - 2) the fraction (f) of molecules with more than E_a
 - 3) the fraction (p) of colliding molecules with the proper orientation
- The overall equation is: $k = Zfp$
- Z is proportional to molecular speed, which is $\sqrt{\frac{3RT}{M_M}}$ where M_M is the molar mass in kg/mole.
- R is the universal gas constant in units of energy per unit temperature: $R = 8.314 \text{ J}/(\text{K}\cdot\text{mol})$
- So, Z is proportional to $T^{1/2}$, but k actually increases much faster than that with T . That is, [k ≈ doubles](#) with each 10°C to 50°C rise in T .
- The dependence of k on T is related primarily to the activation energy (E_a).
$$f = e^{-(E_a/RT)} \text{ where } e \approx 2.718 \text{ or } \ln(f) = -E_a/RT.$$
- Compared with equation for Z , the equation for f results in a much larger increase in the value of k as T increases.
- p is a simple constant and it results from the molecular orientation during a collision. For example, in the [reaction](#) $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$, the C atom must strike the O_2 molecule in order for a reaction to happen. If the O atom in CO strikes the O_2 , there is no reaction. Only half of the collisions have the necessary orientation, and $p \approx 1/2$.

Transition State Theory

- Colliding reactant molecules form an activated complex during their transition into products.
- The activated complex (\ddagger) is an unstable molecular formation that can become products.
$$\text{O}=\text{N}\cdot + \text{Cl}-\text{Cl} \rightarrow [\text{O}=\text{N}\cdots\text{Cl}\cdots\text{Cl}\cdot]^\ddagger \rightarrow \text{O}=\text{N}-\text{Cl} + \text{Cl}\cdot$$
- In this activated complex, the reactant bonds (between Cl's) are partially broken, and the product bonds (between N and Cl) are partially formed.
- The activated complex can form when the molecules have their ground state E plus E_a .
- The enthalpy (or heat) of a reversible reaction can be found from the difference between the E_a 's for the forward and reverse reactions: $\Delta H_{\text{reaction}} = E_{a\text{fwd}} - E_{a\text{rev}}$
- For an endothermic reaction, ΔH is positive.
- For an [exothermic](#) reaction, ΔH is negative.

Arrhenius Equation $k = Ae^{-(Ea/RT)}$

- A is called the frequency factor.
It is nearly constant, and it is equivalent to Z times p (from Collision Theory)
- The exponential portion is equivalent to f, where $f = e^{-(Ea/RT)}$ as seen previously.
- Graph a linear equation by taking the ln of both sides: $\ln(k) = \ln(A) - \left(\frac{Ea}{R}\right)\left(\frac{1}{T}\right)$
- A straight line results with $y = \ln(k)$ and $x = (1/T)$.
- The y-intercept (b) is $\ln(A)$ and the slope (m) is $-\left(\frac{Ea}{R}\right)$.
- Subtract equations at two different temperatures to solve for Ea (or for k at different T).
$$\ln(k_2) - \ln(k_1) = \ln\left(\frac{k_2}{k_1}\right) = \left(\frac{Ea}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Elementary Reactions

- An elementary reaction is a single molecular event which results in a reaction.
It is either a single collision of two molecules or a single molecule breaking into smaller pieces.
- A reaction mechanism is a series of molecular events (steps) which combine in a sequence to create the net chemical equation. Each step is an elementary reaction.
- The net reaction $\text{NO}_{2(g)} + \text{CO}_{(g)} \rightarrow \text{NO}_{(g)} + \text{CO}_{2(g)}$ has two steps in its mechanism.
(1) $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ is followed by (2) $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$.
- $\text{NO}_{3(g)}$ is a reaction intermediate. It is produced in one elementary reaction and is consumed in a subsequent elementary reaction. A reaction intermediate does not appear in the net chemical equation because it cancels out when the steps are added together.
- The sum of the two steps is $\text{NO}_2 + \text{NO}_2 + \text{NO}_3 + \text{CO} \rightarrow \text{NO}_3 + \text{NO} + \text{NO}_2 + \text{CO}_2$
- After cancelling the duplicated molecules, the sum reduces to the net chemical equation.

Molecularity is the number of reactant molecules involved in an elementary reaction.

- Unimolecular reaction (decomposition or rearrangement): $\text{O}_3^* \rightarrow \text{O}_2 + \text{O}$
- Bimolecular reaction (collision): $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$

Rate Equation for an Elementary Reaction

- The rate is directly proportional to the concentrations of reactants for an elementary reaction.
- For $\text{A} \rightarrow \text{B} + \text{C}$, rate = $k[\text{A}]$
- For $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$, rate = $k[\text{A}][\text{B}]$

Rate Law for a Net Chemical Equation

- The rate of the net chemical equation is determined by its slowest elementary reaction (step).
- The overall rate for the net chemical equation is the same as the rate for the slowest step.
- The slowest elementary reaction is called the “rate-determining step”.
- (1) $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$ (slow, with rate constant k_1)
- (2) $\text{F} + \text{NO}_2 \rightarrow \text{NO}_2\text{F}$ (fast, with k_2)
- Net: $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$ Rate = $k_1[\text{NO}_2][\text{F}_2]$

Mechanisms with an Initial Fast (Equilibrium) Step (Refer to [Example 12.14](#))

- Sometimes the rate law from the rate-determining step contains an intermediate. However, intermediate concentrations are usually very small and difficult to measure. The intermediate can sometimes be removed from the equation, though, if its formation is in a prior step that reaches equilibrium quickly.
- Net: $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ Net Rate = $k[\text{N}_2\text{O}_5(\text{g})]$
 - (1) $\text{N}_2\text{O}_5(\text{g}) \rightleftharpoons \text{NO}_2(\text{g}) + \text{NO}_3(\text{g})$ (fast, stays at eqm, with rate constants k_{1F} and k_{1R})
 - (2) $\text{NO}_2(\text{g}) + \text{NO}_3(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ (slow, with rate constant k_2)
 - (3) $\text{NO}_3(\text{g}) + \text{NO}(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ (fast, with rate constant k_3)
- Rate-determining (slow) step gives us rate = $k_2[\text{NO}_2(\text{g})][\text{NO}_3(\text{g})]$. $\text{NO}_3(\text{g})$ is the intermediate that we want to remove from the equation.
- Since equation (1) is at equilibrium, we know that its forward rate equals its reverse rate.
$$(k_{1F})[\text{N}_2\text{O}_5(\text{g})] = (k_{1R})[\text{NO}_2(\text{g})][\text{NO}_3(\text{g})] \quad \text{and} \quad [\text{NO}_3(\text{g})] = \frac{k_{1F}[\text{N}_2\text{O}_5(\text{g})]}{k_{1R}[\text{NO}_2(\text{g})]}$$
- Rate = $k_2[\text{NO}_2(\text{g})][\text{NO}_3(\text{g})] = k_2[\text{NO}_2(\text{g})] \times \frac{k_{1F}[\text{N}_2\text{O}_5(\text{g})]}{k_{1R}[\text{NO}_2(\text{g})]} = \left(\frac{k_2 k_{1F}}{k_{1R}}\right) \frac{[\text{NO}_2(\text{g})][\text{N}_2\text{O}_5(\text{g})]}{[\text{NO}_2(\text{g})]} = \left(\frac{k_2 k_{1F}}{k_{1R}}\right) [\text{N}_2\text{O}_5(\text{g})]$
- Rate = $k_{\text{overall}}[\text{N}_2\text{O}_5(\text{g})]$ where $k_{\text{overall}} = \left(\frac{k_2 k_{1F}}{k_{1R}}\right)$

Catalysis

- A catalyst increases the reaction rate without being consumed. It is used in one elementary reaction, usually the first step in the mechanism, but is then regenerated in a subsequent mechanism step.
- The catalyst provides an alternate pathway for a reaction. The alternate pathway has a [lower \$E_a\$](#) than the uncatalyzed reaction.
- Industrial H_2SO_4 Production: $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ (with $\text{NO}(\text{g})$ as the catalyst)
Alternate, catalyzed pathway: (1) $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, then (2) $\text{NO}_2 + \text{SO}_2 \rightarrow \text{NO} + \text{SO}_3$
- Decomposition of O_3 (ozone) in the stratospheric ozone layer occurs due to free radicals of residual chlorine atoms from chlorofluorocarbon refrigerants like CCl_2F_2 (R-12).
 - (1) $\text{Cl}\cdot(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{ClO}\cdot(\text{g}) + \text{O}_2(\text{g})$
 - (2) $\text{ClO}\cdot(\text{g}) + \text{O}(\text{g}) \rightarrow \text{Cl}\cdot(\text{g}) + \text{O}_2(\text{g})$Net: $\text{O}_3(\text{g}) + \text{O}(\text{g}) \rightarrow 2\text{O}_2(\text{g})$

There is no $\text{Cl}\cdot$ in the net equation. $\text{Cl}\cdot$ is a catalyst. It is regenerated and is not consumed.
- If the catalyst and all reactants are in the same phase (gas or liquid solution), then the reaction has homogeneous catalysis. The ozone decomposition above has homogeneous catalysis because all of the molecules involved are in the gas phase.
- Industrial reactions typically use a solid catalyst with fluid reactants, which is heterogeneous catalysis. Gases bind to surface by chemisorption (chemically bonded to the catalyst surface) in order to convert to products at that surface. Review the sequence of the [catalytic hydrogenation](#) reaction.
- Enzymes are large protein molecules, with specific 3D geometries, and they are biological catalysts. They convert a Substrate into Products ($\text{E} + \text{S} \rightarrow \text{ES} \rightarrow \text{E} + \text{P}$) by first combining together with the substrate in a [lock-and-key](#) mechanism.