

Rate Laws and Order of Reactions

chapter 6.3

Kinetics

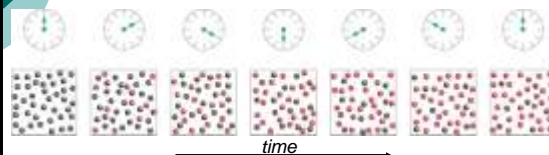
- Studies the rate at which a chemical process occurs.
- Besides information about the speed at which reactions occur, kinetics also sheds light on the **reaction mechanism** (exactly *how* the reaction occurs).

Reaction Rates



Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time. $\Delta[A]$ vs Δt

Reaction Rates



Reaction Rates



Time, t (s)	$[C_4H_9Cl]$ (M)
0.0	0.1000
50.0	0.0905
100.0	0.0820
150.0	0.0741
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
10,000	0

In this reaction, the concentration of butyl chloride, C_4H_9Cl , was measured at various times, t .

Reaction Rates



Time, t (s)	$[C_4H_9Cl]$ (M)	Average Rate M/s
0.0	0.1000	
50.0	0.0905	1.8×10^{-4}
100.0	0.0820	1.7×10^{-4}
150.0	0.0741	1.6×10^{-4}
200.0	0.0671	1.5×10^{-4}
300.0	0.0549	1.2×10^{-4}
400.0	0.0448	1.0×10^{-4}
500.0	0.0368	9.0×10^{-5}
800.0	0.0200	9.0×10^{-5}
10,000	0	

The **average rate** of the reaction over each interval is the change in concentration divided by the change in time:

$$\text{average rate} = \frac{\Delta [C_4H_9Cl]}{\Delta t}$$

$$\text{average rate} = \frac{\Delta [C_4H_9Cl]}{\Delta t} = \frac{0.1000 - 0.0905 \text{ M}}{50.0 - 0.0 \text{ s}}$$

Reaction Rates



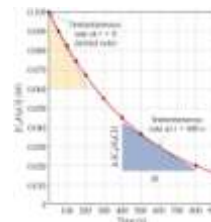
Time, min	[C ₄ H ₉ Cl], M	Average Rate (M/s)
0.00	0.1000	
50.0	0.0850	1.8×10^{-3}
100.0	0.0700	1.7×10^{-3}
150.0	0.0541	1.4×10^{-3}
200.0	0.0371	1.25×10^{-3}
250.0	0.0299	1.01×10^{-3}
300.0	0.0246	0.861×10^{-3}
350.0	0.0203	
400.0	0	

- Note that the average rate decreases as the reaction proceeds.
- This is because as the reaction goes forward, there are fewer collisions between reactant molecules.

Reaction Rates



- A plot of concentration vs. time for this reaction yields a curve like this.
- The slope of a line tangent to the curve at any point is the instantaneous rate at that time.

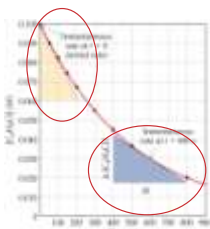


$$\frac{\Delta [A]}{\Delta t} \Rightarrow \frac{d[A]}{dt}$$

Reaction Rates



- The reaction slows down with time because the concentration of the reactants decreases.

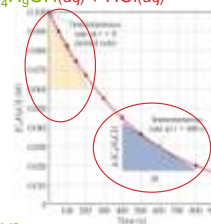


$$\frac{\Delta [A]}{\Delta t} \Rightarrow \frac{d[A]}{dt}$$

Reaction Rates and Stoichiometry



- In this reaction, the ratio of C₄H₉Cl to C₄H₉OH is 1:1.
- Thus, the rate of *disappearance* of C₄H₉Cl is the same as the rate of *appearance* of C₄H₉OH.



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

Reaction Rates and Stoichiometry

- What if the ratio is *not* 1:1?



- Only 1/2 HI is made for each H₂ used.

$$\text{rate} = -\frac{\Delta[\text{H}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}$$

Reaction Rates and Stoichiometry

- To generalize, for the reaction



$$\text{rate} = -\frac{1}{a} \frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b} \frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c} \frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d} \frac{\Delta[\text{D}]}{\Delta t}$$

Reactants (decrease) Products (increase)

Two Mathematical Expressions to Describe Reaction Rate



1. Rate; $-\Delta A / \Delta t = + \Delta B / \Delta t$
 - Determined from stoichiometry
 - Uses both reactants & products
2. Rate Law; $\text{rate} = k[A]^x$
 - Determined by experimental data- Stoichiometry of equation is irrelevant
 - Only reactants in rate law

Rate Law

The **rate law** expresses the relationship of the rate of a reaction to the rate constant and the **concentrations of the reactants raised to some powers**.



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

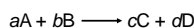


k is the Rate Law Constant

x and y are determined experimentally, and do **not** depend on stoichiometric coefficients from balanced equation

Rate Law

The **rate law** expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.



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

Reaction Order

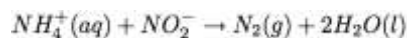
reaction is **xth order** in A
 reaction is **yth order** in B
 reaction is **(x+y)th order overall**

- Reaction order tells how quickly rate will increase when concentration increases

13.2

Concentration and Rate

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.100	0.20	5.4×10^{-7}
2	0.200	0.20	10.8×10^{-7}
3	0.400	0.20	21.5×10^{-7}
4	0.600	0.20	32.5×10^{-7}
5	0.30	0.200	10.8×10^{-7}
6	0.30	0.400	21.6×10^{-7}
7	0.30	0.600	32.4×10^{-7}
8	0.30	0.800	43.2×10^{-7}



Compare Experiments 1 and 2:
 when $[NH_4^+]$ **doubles**, the initial rate **doubles**.

Concentration and Rate

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.100	0.20	5.4×10^{-7}
2	0.200	0.20	10.8×10^{-7}
3	0.400	0.20	21.5×10^{-7}
4	0.600	0.20	32.5×10^{-7}
5	0.30	0.200	10.8×10^{-7}
6	0.30	0.400	21.6×10^{-7}
7	0.30	0.600	32.4×10^{-7}
8	0.30	0.800	43.2×10^{-7}



Likewise, compare Experiments 5 and 6:
 when $[NO_2^-]$ **doubles**, the initial rate **doubles**.

Concentration and Rate

$$\text{rate} \propto [NH_4^+]$$

$$\text{rate} \propto [NO_2^-]$$

$$\text{rate} \propto [NH_4^+][NO_2^-]$$

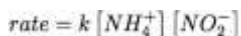
$$\text{rate} = k [NH_4^+][NO_2^-]$$

This equation is called the **rate law**, and **k** is the **rate constant**.



Rate Laws

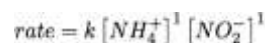
- A rate law shows the relationship between the reaction rate and the concentrations of reactants.
 - For gas-phase reactants use P_A instead of $[A]$.
- k is a constant that has a specific value for each reaction.
- The value of k is determined experimentally.



"Constant" is relative here-
 k is unique for each rxn
 k changes with T

Rate Laws

- Exponents tell the **order** of the reaction with respect to each reactant.
- This reaction is
 First-order in $[\text{NH}_4^+]$
 First-order in $[\text{NO}_2^-]$
- The **overall reaction order** can be found by adding the exponents on the reactants in the rate law.
- This reaction is **second-order overall**.

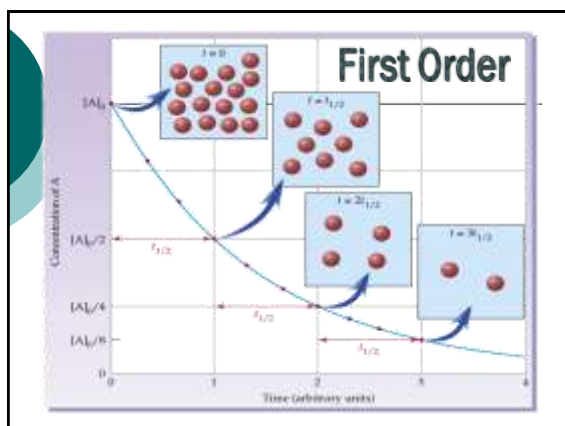


Reaction Order

- Rxns are classified as either zero-order, first-order, second-order, or mixed order (higher order) rxns.
 The rate of chemical rxns and the size of the rate constant (k) is dependent on the "order" of the rxn
- **Zero-Order Rxns**
 (Order = 0) have a constant rate. This rate is independent of the conc of the reactants. The rate law is: $\text{rate} = k$, with k having the units of M/sec.

Reaction Order

- **First-Order Reactions**
 - (order = 1) has a rate proportional to the conc of one of the reactants. A common example of a first-order reaction is the phenomenon of radioactive decay. The rate law is:
 - $\text{rate} = k[\text{A}]^1$ (or B instead of A), with k having the units of sec^{-1}



Reaction Order

- **Second-Order Reactions**
 - (order = 2) has a rate proportional to the conc of the square of a single reactant or the product of the conc of two reactants.
 - $\text{rate} = k[\text{A}]^2$ (or substitute B for A or k multiplied by the concentration of A, $[\text{A}]$, times the concentration of B, $[\text{B}]$), with the units of the rate constant $\text{M}^{-1}\text{sec}^{-1}$

Reaction Order

- Mixed Order Rxns
 - Mixed-order reactions have a fractional order for their rate:
 - e.g., rate = $k[A]^{1/3}$