

Chapter 14
Chemical Kinetics

- Thermodynamics tells us what can happen and how far towards completion a reaction will proceed.
- Kinetics tells us how fast the reaction will go.
- Study of rates of reactions and factors that affect these rates: concentration (Charcoal + LOx Video), temperature, pressure, catalysis, surface area, solvent, ionic environment, ...

14.1 Reaction Rates

- Rates vary from very low (geological processes) to very high (combustion of H₂)
- Must be able to measure rates to determine how to control them with concentration or temperature.
- Rate = $\Delta\text{conc}/\Delta\text{time}$ or $-\Delta\text{conc}/\Delta\text{time}$ so it will have a positive value

Rates and Stoichiometry

- Use reaction stoichiometry to specify reference points for rates. When reacting in ratios not equal to 1:1, one substance disappears or appears faster than the other.
- $5\text{Br}^- (\text{aq}) + \text{BrO}_3^- (\text{aq}) + 6\text{H}^+ (\text{aq}) \rightarrow 3\text{Br}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
- Br⁻ disappears 5 times as fast as BrO₃⁻
- $$\frac{-\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{-1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{-1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{+1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t}$$
- Can't measure change in H₂O because its concentration is so high, it stays constant.

Calculation of Rates

- $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2(\text{g})$ in CCl₄ solution
- Start with 2.330 M solution at 45°C, measure the concentration periodically.

Time(s)	[N ₂ O ₅] (M)
0	2.33
11100	2.08
19200	1.91
31600	1.67
52400	1.35
72000	1.11
112700	0.72
138900	0.55
188600	0.34

- Rate =
$$\frac{-1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{-1}{2} \frac{([\text{N}_2\text{O}_5]_2 - [\text{N}_2\text{O}_5]_1)}{(t_2 - t_1)}$$
- Rate during time period 52,400 to 72,000 sec, where the concentrations are measured to be 1.350 M and 1.110 M.

Calculation of Rates

- $\Delta t = 72,000 - 52,400 = 19,600 \text{ sec}$
- $-\Delta [\text{N}_2\text{O}_5] = -(1.110 \text{ M} - 1.350 \text{ M}) = 0.240 \text{ M}$
- $\text{Rate} = 1/2 \times 0.240 \text{ M}/19,600 \text{ s} = 6.12 \times 10^{-6} \text{ M/s}$
- Calculate the rate in terms of NO_2 and of O_2

Rates

- The rate changes as the reaction proceeds. Usually it gets smaller with time. The rates calculated were average rates for the particular time interval.
- Can get average rate and instantaneous rate from a graph of concentration vs. time

Initial Rates

- To get around the problem of the rate changing with time, we sometimes measure initial rates.
- If there is not much change in concentration, then $-\Delta C/\Delta t$ is a good approximation to the rate. We know concentration values much better at the beginning of the reaction than we do later.
- Examine initial rates for different concentrations. What is the relationship between initial rate and concentration?

14.2 The Dependence of Rate on Concentration

- Rates usually vary with concentrations of some or all reactants, possibly products, and possibly other substances (catalysts) that might be present.
- $2 \text{ g Na}_2\text{CO}_3 + 50 \text{ mL } 1 \text{ M, } 3 \text{ M, } 6 \text{ M HCl}$ in balloon; which reaction is fastest?

Rate and Concentration

- Why does rate generally decrease as the reaction proceeds?
 - concentration of reactants decreases
 - fewer molecules to collide, so collision frequency decreases
- Demo of collision frequency with gas_sim.exe (available on lrc_nts1)

Rate Law

- We describe the dependence of rate on concentration by an equation called the rate law:
- $\text{Rate} = k[\text{A}]^x[\text{B}]^y \dots$
- where x & y are not stoichiometric coefficients
- k , x , y must be determined experimentally
- k is the rate constant
- x, y are reaction orders for the individual species
- $x+y+\dots =$ overall reaction order (n)
- Units of $k = \text{M}^{-(n-1)}\text{s}^{-1}$ for an n th order reaction in solution
- Orders are usually positive or negative integers
- Each order tells us how the rate depends on that concentration; ***this order must be determined experimentally***; only occasionally does it match the coefficients from the balanced reaction equation

- $4V^{3+} + O_2 + 2H_2O \rightarrow 4VO^{2+} + 4H^+$
- Rate = $k[V^{3+}][O_2]/[H^+]$
- Rate = $k[V^{3+}][O_2][H^+]^{-1}$

$$\begin{array}{ccc|c} | & | & | & \\ 1 & 1 & -1 & \} \text{sum} = 1, \text{ so 1st order} \end{array}$$

- What are the individual and overall orders?
- $5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2(aq) + 2H_2O(l)$
- Rate = $k[Br^-][BrO_3^-][H^+]^2$
- 1,1,2 } overall = 4

How do we determine rate laws?

- Method 1: Measure initial rates for various concentration of species.

- $2N_2O_5 \rightarrow 4NO_2 + O_2(g)$
- | $[N_2O_5]$ | $[NO_2]$ | $[O_2]$ | Rate |
|------------|----------|---------|-----------------------|
| 2.21 | 2.00 | 1.00 | 1.14×10^{-5} |
| 2.21 | 1.00 | 1.00 | 1.13×10^{-5} |
| 2.21 | 1.00 | 2.00 | 1.12×10^{-5} |
| 2.21 | 0.00 | 0.00 | 1.13×10^{-5} |

- The rate is constant when we change $[NO_2]$ and $[O_2]$, so orders are 0 (not in rate law)

- Thus, Rate = $k[N_2O_5]^n$

$$n = 0, \text{ Rate} = k$$

$$n = 1, \text{ Rate} = k[N_2O_5]$$

$$n = 2, \text{ Rate} = k[N_2O_5]^2$$

- Since k should have a constant value, calculate $k = \text{Rate}$, $k = \text{Rate}/[N_2O_5]$, and $k = \text{Rate}/[N_2O_5]^2$, then see which is constant

- Data in table indicate that $n = 1$

$[N_2O_5]$	Rate	Rate/ $[N_2O_5]$
2.00	1.05E-05	5.25E-06
1.79	9.67E-06	5.40E-06
1.51	7.83E-06	5.19E-06
1.23	6.31E-06	5.13E-06
0.92	4.81E-06	5.23E-06

- The reaction is first order and follows first order kinetics.

- Compare two rates

- $\text{Rate}_1/\text{Rate}_2 = ([N_2O_5]_1/[N_2O_5]_2)^n$

- Vary concentration by 2, then $\text{Rate}_1/\text{Rate}_2 = 2^n$

- $n = 0$, ratio = 1

- $n = 1$, ratio = 2

- $n = 2$, ratio = 4

- Determine the rate law for

- $2O_3(g) \rightarrow 3O_2(g)$

- [O₃] Rate
- 0.00600 M 5.03 x 10⁻⁷ M/s
- 0.00300 M 1.28 x 10⁻⁷
- 0.00150 M 3.08 x 10⁻⁸
- Rate = k[O₃]²
- k = 5.03 x 10⁻⁷/(0.00600)² = 0.0140 M⁻¹ s⁻¹
- From 2nd and 3rd expts, k = 0.0142, 0.0137

14.3 The Change of Concentration with Time

- How do we determine rate laws?
- Method 2: Determine the order graphically by measuring concentration at various times during the reaction. Must convert the rate law (rate–concentration) to an equation relating concentration to time.
 - $-\Delta[A]/\Delta t = k[A]^n$
 - n = 0, $-\Delta[A]/\Delta t = k$
 - $[A] = [A]_0 - kt$
 - Example: $\text{Mg} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2$
 - If $\Delta[\text{H}_2]/\Delta t = k$, a graph of $[\text{H}_2]$ vs. time should be linear.

 - n = 1, $-\Delta[A]/\Delta t = k[A]$
 - $\ln [A] = \ln [A]_0 - kt$
 - $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2(\text{g})$
 - If n = 1, a graph of $\ln [\text{N}_2\text{O}_5]$ vs. time should be linear.

 - n = 2, $-\Delta[A]/\Delta t = k[A]^2$
 - $1/[A] = 1/[A]_0 + kt$
 - $2\text{UO}_2^+ + 4\text{H}^+ \rightarrow \text{U}^{4+} + \text{UO}_2^{2+} + 2\text{H}_2\text{O}$
 - If n = 2, a graph of $1/[\text{UO}_2^+]$ vs. time should be linear.
- Summary:

n = 0	$-\Delta[A]/\Delta t = k$	$[A] = [A]_0 - kt$
n = 1	$-\Delta[A]/\Delta t = k[A]$	$\ln [A] = \ln [A]_0 - kt$
n = 2	$-\Delta[A]/\Delta t = k[A]^2$	$1/[A] = 1/[A]_0 + kt$
- Graph $[A]$ vs. t, $\ln [A]$ vs. t, and $1/[A]$ vs. t and see which graph is linear.

- How do we determine rate laws?
- Method 3: Measure half-life (time to consume half of the current reactant — reduce its concentration to 1/2)
 - n = 0, $t_{1/2} = [A]_0/2k$
 - $t_{1/2}$ decreases as the reaction proceeds
 - n = 1, $t_{1/2} = \ln 2/k = 0.693/k$
 - $t_{1/2}$ is constant throughout the reaction
 - n = 2, $t_{1/2} = 1/k[A]_0$
 - $t_{1/2}$ increases as the reaction proceeds

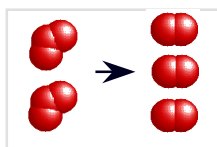
- Use these equations to calculate k or $t_{1/2}$ from one another.
- Often used for radioactivity — see Chapter 21
- How do we determine rate laws?
- Method 4: If the rate depends on the concentration of more than one substance, design the experiment so only one concentration changes appreciably. Vary one concentration at a time and measure the rate. Compare one variable at a time.
- For example, compare the ratio of rates for variation of concentration by factors of 2, one variable concentration at a time.
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- Derive the rate law and value of k for the reaction, $F_2 + 2ClO_2 \rightarrow 2FCIO_2$
- | $[F_2]_0$ | $[ClO_2]_0$ | Rate (M/s) |
|-----------|-------------|------------|
| 0.100 | 0.0100 | 0.0012 |
| 0.100 | 0.0400 | 0.0048 |
| 0.200 | 0.0100 | 0.0024 |

14.4 Temperature and Rate

- N_2 and O_2 coexist in air, but combine at high temperatures (in auto engines) to form NO_x
- Rates generally increase with increasing T
- $2Cr^{3+} + 6Mn^{3+} + 7H_2O \rightarrow CrO_4^{2-} + 6Mn^{2+} + 14H^+$

Rates and Temperature

- k also increases with temperature, causing the increase in rate
- $2NO_2 \rightarrow 2NO + O_2$ Rate = $k[NO_2]^2$
- Often k increases $\sim \times 2$ for $10^\circ C$ T increase
- Make a list of all the things that must happen to the reacting molecules for a chemical reaction to occur. Consider the following reaction as an example:
- $2O_3(g) \rightarrow 3O_2(g)$

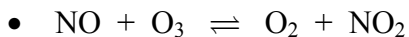


Why does k increase with T ?

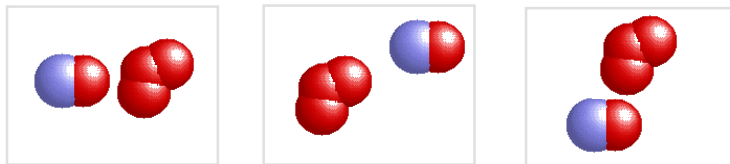
- Collision Theory:
- For reaction to occur,
 1. molecules must collide; more collisions \rightarrow higher rate
 2. colliding molecules must be oriented properly to react
 3. properly oriented colliding molecules must have sufficient energy (which explains the T dependence)
- The average kinetic energy of molecules increases with temperature.

Collision Theory

- Not all collisions lead to products.

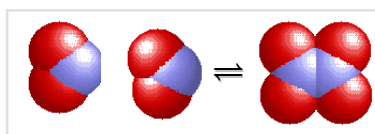


- Which collisions are likely to be effective?



Effective Collisions

- Consider the reaction of NO_2 to form N_2O_4



- Draw pictures of some ineffective and effective collisions

Average Kinetic Energy

- The number of molecules with sufficient kinetic energy to react increases as the temperature increases
- Not all molecules have the same kinetic energy.

Activation Energy

- Why don't all properly-oriented collisions lead to products?
- There must be sufficient energy to break reactant bonds.
- The activation energy, E_a , is the minimum energy required to initiate a chemical reaction.
- Thus, there is always an energy barrier that must be overcome for reaction to occur.

Activation Energy

- The energy barrier is called the activation energy, E_a . This is the difference between the transition state energy and the average reactant energy.
- Related to the energy change of the reaction:
 - $\Delta H = E_{a,f} - E_{a,r}$
 - $\text{O}_3 + \text{NO} \rightleftharpoons \text{O}_2 + \text{NO}_2$
 - $\Delta H = -199.8 \text{ kJ/mol}$, $E_{a,f} = 10.7 \text{ kJ/mol}$
 - What is $E_{a,r}$?

Arrhenius Equation

- Relates k to T and E_a and is used to calculate E_a
- $k = A e^{-E_a/RT}$
- A is frequency factor, T in Kelvins, $R = 8.314 \text{ J/mol K}$
- Measured experimentally by measuring k at different temperatures

- $\ln k = \ln A - E_a/RT$
- Graph $\ln k$ vs. $1/T$

14.5 Reaction Mechanisms

- Mechanism is a detailed pathway for a reaction
- Proposed mechanism must be consistent with the rate law and other experimental evidence
- Consider two possible mechanisms for the reaction
- $\text{CH}_3\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Cl}^-$

S_N1 Mechanism

- Substitution reactions can occur with several different mechanisms. One possibility, called the S_N1 mechanism, involves the breaking of the bond to the leaving group before making a bond to the entering group. An intermediate of lower coordination number is formed.

S_N2 Mechanism

- Substitution reactions can occur with several different mechanisms. One possibility, called the S_N2 mechanism, involves the simultaneous bonding of both the entering and the leaving group to the central atom.

Mechanisms

- Usually have several mechanisms consistent with a given rate law
- Mechanism identifies the elementary reactions (one-step reactions) that combine to make up the overall reaction.
- Elementary steps must add up to give the balanced chemical equation.
- Molecularity: number of reactant molecules in an elementary reaction
- unimolecular, bimolecular, termolecular (more is rare)
- Overall reaction may be elementary:
- $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$ Rate = $k[\text{CH}_3\text{NC}]$
- For an elementary reaction, orders = coefficients
- $\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2$ Rate = $k[\text{O}_3][\text{NO}]$
- This reaction may be elementary.

Multistep Mechanisms

- Many rate laws are more complex, so the overall reaction cannot be an elementary reaction. These have multistep mechanisms.
- One step in multistep mechanism is slower than the others — called the rate-determining step.
- $\text{Tl}^{3+} + 2\text{Fe}^{2+} \rightarrow \text{Tl}^+ + 2\text{Fe}^{3+}$
- Rate = $k[\text{Tl}^{3+}][\text{Fe}^{2+}]^2/[\text{Fe}^{3+}]$
- $\text{Tl}^{3+} + \text{Fe}^{2+} \rightleftharpoons \text{Tl}^{2+} + \text{Fe}^{3+}$ fast
- $\text{Tl}^{2+} + \text{Fe}^{2+} \rightarrow \text{Tl}^+ + \text{Fe}^{3+}$ slow (rate det.)
- Intermediate: substance produced in one step and consumed in a later step (Tl^{2+})

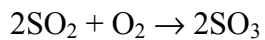
- $\text{S}_2\text{O}_8^{2-} + \text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}^+$ slow
- $\text{I}^+ + \text{I}^- \rightarrow \text{I}_2$ fast
- Which step is rate determining? What is the intermediate?

Catalysis

- Catalyst: substance that changes the rate of reaction but is not permanently changed itself
- Metals catalyze many reactions of gases; called heterogeneous catalysis
- Mechanism: absorption, reaction, desorption
- Catalyst changes the reaction mechanism and lowers the activation energy

Homogeneous Catalysis

- In homogeneous catalysis, everything is in solution (or in gas phase)
- $\text{NO} + \text{O}_2 \rightarrow \text{NO}_3$
- $\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$
- $\text{NO}_2 + \text{SO}_2 \rightarrow \text{NO} + \text{SO}_3$
- $\text{NO}_2 + \text{SO}_2 \rightarrow \text{NO} + \text{SO}_3$



Enzymes as Catalysts

- Enzymes have cavities that just fit the reacting molecules and act to bring the reactants together in the proper orientation.