

Week 2

Intermolecular Dynamics and Intro to Rate Laws

2.1 Mean Free Path

4/4:

- The midterm will have some computational problems; the final will be nearly entirely conceptual.
- Reviews the conclusions of the derivation associated with Figure 1.3.
- The Maxwell-Boltzmann Distribution has been verified experimentally.
 - A furnace with a very small hole that allowed a beam of atoms (such as potassium) to emerge into an evacuated chamber. The beam passed through a pair of collimating slits and then through a velocity-selector.
 - In the second method, clocks the time it takes for molecules to travel a fixed distance. A very short pulse of molecules leaves the chopper and then spread out in space as they travel toward the detector.
 - Either way, we observe very good agreement with the M-B distribution.
- **Mean free path:** The average distance a molecule travels between collisions.
- **Collision cylinder:** The cylinder of radius d that encapsulates the trajectory of a particle of diameter d .

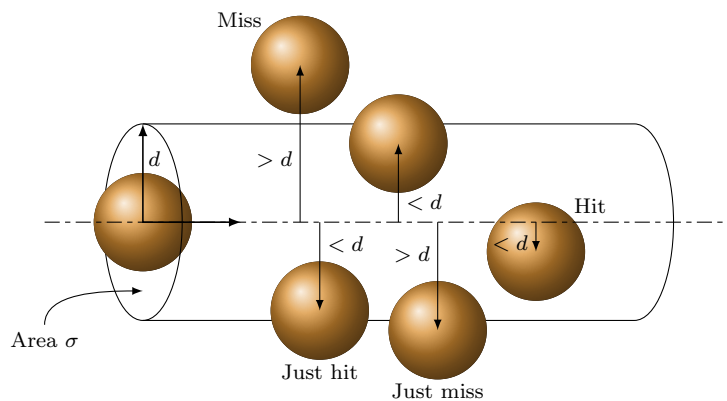


Figure 2.1: Collision cylinder.

- Particles whose center of mass lie within the collision cylinder collide with the original particle, and vice versa for particles whose center of mass lie outside the collision cylinder.
- Hard-sphere collision cross section πd^2 denoted by σ .
- Collision frequency in terms of cylinder parameters.
 - The number of collision in the time interval dt is

$$dN_{\text{coll}} = \rho \sigma \langle u \rangle dt$$

where $\rho = N/V$.

- The collision frequency z_A is

$$z_A = \frac{dN_{\text{coll}}}{dt} = \rho \sigma \langle u \rangle = \rho \sigma \sqrt{\frac{8k_B T}{\pi m}}$$

- Treat the motion of two bodies of masses m_1, m_2 moving with respect to each other by the motion of one body with a reduced mass $\mu = m_1 m_2 / (m_1 + m_2)$ moving with respect to the other one being fixed.
- If the masses of the two colliding molecules are the same, then $\mu = m/2$.
- Remember that $\langle u_r \rangle = \sqrt{2} \langle u \rangle$.
- Thus, the correct expression for z_A is

$$z_A = \rho \sigma \langle u_r \rangle = \sqrt{2} \rho \sigma \langle u \rangle$$

- The mean free path is temperature- and pressure-dependent.
 - The average distance traveled between collisions is given by

$$l = \frac{\langle u \rangle}{z_A} = \frac{\langle u \rangle}{\sqrt{2} \rho \sigma \langle u \rangle} = \frac{1}{\sqrt{2} \rho \sigma}$$

- If we replace $\rho = PN_A/RT$ by its ideal gas value, then we have

$$l = \frac{RT}{\sqrt{2} N_A \sigma P} = \frac{k_B T}{\sqrt{2} \sigma \rho}$$

- Now $k_B T$ has units of thermal energy, and we know from physics that $E = F \cdot l$ (energy is force times distance). Thus, $F \propto \sigma \rho$ by the above since $E = k_B T$ and $l = l$.

- The probability of a molecular collision.

- The probability that one molecule will suffer a collision is $\sigma \rho dx$.
 - This should make intuitive sense as σ is the area inside which a molecule must be to collide with some particle, ρ is the density (related to the number of particles likely to be within that area), and dx tells us over how much space we're moving.
 - σdx is a volume.
- Let $n(x)$ be the number of molecules that travel a distance x without a collision.
- Then the number of molecules that undergo a collision between $x, x + dx$ is

$$\begin{aligned} n(x) - n(x + dx) &= \sigma \rho n(x) dx \\ \frac{n(x + dx) - n(x)}{dx} &= -\sigma \rho n(x) \\ \frac{dn}{dx} &= -\sigma \rho n \end{aligned}$$

2.2 Collision Frequency and Gas-Phase Reaction Rate

4/6:

- Submit homework in paper next Monday.
- Picking up with the probability of a molecular collision from last time.
 - Solving the differential equation gives

$$n(x) = n_0 e^{-\sigma \rho x} = n_0 e^{-x/l}$$

where l is the mean free path.

- Note that the $\sqrt{2}$ arises from treating every other molecule as static, so we don't need it in this case?
- The number of molecules that collide in the interval $x, x + dx$ is $n(x) - n(x + dx)$.
- The probability that one of the initial n_0 molecules will collide in this interval is

$$p(x) dx = \frac{n(x) - n(x + dx)}{n_0} = -\frac{1}{n_0} \frac{dn}{dx} dx = \frac{1}{l} e^{-x/l} dx$$

- Discussion of Figure 27.12.
 - Figure 27.12 does not graph the above equation.
 - Rather, it graphs the accumulated (integrated) probability from 0 to x . We call this function $P(x)$.

$$P(x) = \int_0^x p(x') dx'$$

- Collision frequency of one particular molecule per unit volume.
 - z_A is the collision frequency of one particular molecule.
 - Z_{AA} is the total collision frequency per unit volume.
 - We have

$$Z_{AA} = \frac{1}{2} \rho z_a$$

- Multiplying by the number density should make intuitive sense.
 - We divide by two to avoid counting a collision between a pair of similar molecules as two distinct collisions.
- It follows that

$$Z_{AA} = \frac{1}{2} \sigma \langle u_r \rangle \rho^2 = \frac{\sigma \langle u \rangle \rho^2}{\sqrt{2}}$$

- In a gas consisting of two types of molecules, say A and B , then the collision frequency per unit volume is

$$Z_{AB} = \sigma_{AB} \langle u_r \rangle \rho_A \rho_B$$

where

$$\sigma_{AB} = \pi \left(\frac{d_A + d_B}{2} \right)^2 \quad \langle u_r \rangle = \sqrt{\frac{8k_B T}{\pi \mu}} \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

- There is no $1/2$ coefficient here because there are also AA and BB collisions.
 - Indeed, Z_{AB} is not the *total* collision frequency but just the collision frequency of A - B collisions.
- The rate of a gas-phase chemical reaction depends on the rate of collisions.
 - The rate of collisions is not just the total frequency of collisions.

- The relative energy of the two colliding molecules exceeds a certain critical value. This does not show up directly in the equation for Z_{AB} .
- The number of collisions per unit time per unit are with the wall by molecules whose speeds are in the range $u, u + du$ and whose direction lies within the solid angle $\sin \theta d\theta d\phi$ is approximately $u^3 e^{-mu^2/2k_B T}$.
- We can account for the fact that the molecules collide with each other rather than with a stationary wall by replacing m with the reduced mass $\mu = m_A m_B / (m_A + m_B)$.
- The collision frequency per unit volume between molecules A and B in which they collide with a relative speed between $u, u + du$.

■ We have that $dZ_{AB} \propto u_r^3 e^{-\mu u_r^2/2k_B T} du_r$. Thus, if A is a proportionality constant, then

$$dZ_{AB} = A u_r^3 e^{-\mu u_r^2/2k_B T} du_r$$

■ It follows since $Z_{AB} = \sigma_{AB} \langle u_r \rangle \rho_A \rho_B$ and $\langle u_r \rangle = \sqrt{8k_B T / \pi \mu}$ that

$$\begin{aligned} \sigma_{AB} \rho_A \rho_B \sqrt{\frac{8k_B T}{\pi \mu}} &= A \int_0^\infty u_r^3 e^{-\mu u_r^2/2k_B T} du_r \\ &= 2A \left(\frac{k_B T}{\mu} \right)^2 \\ A &= \sigma_{AB} \rho_A \rho_B \sqrt{\left(\frac{\mu}{k_B T} \right)^3 \cdot \frac{2}{\pi}} \end{aligned}$$

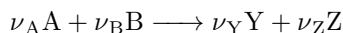
■ Thus, we know that

$$dZ_{AB} = \sigma_{AB} \rho_A \rho_B \sqrt{\left(\frac{\mu}{k_B T} \right)^3 \cdot \frac{2}{\pi}} e^{-\mu u_r^2/2k_B T} u_r^3 du_r$$

- Integrating the above from the certain critical value to infinity yields the desired rate.
- Key information from this chapter.
 - Pressure from a molecular approach.
 - The distribution for speed components and the speed are different.
 - The speeds u_{mp} , $\langle u \rangle$, and u_{rms} .
 - The frequency of collisions per molecule and the total frequency of collisions per volume.
 - Rate of gas phase reactions.

2.3 Rate Law Definitions and Methods of Determination

- 4/8: • Consider a general chemical equation



- The extent of the reaction via the progress variable ξ is

$$n_A(t) = n_A(0) - \nu_A \xi(t) \qquad n_Y(t) = n_Y(0) + \nu_Y \xi(t)$$

- The rate of change (moles/second) is

$$\frac{dn_A}{dt} = -\nu_A \frac{d\xi}{dt} \qquad \frac{dn_Y}{dt} = \nu_Y \frac{d\xi}{dt}$$

- Deriving the rate of reaction for a gas-based chemical reaction.

- Time-dependent concentration changes

$$\frac{1}{V} \frac{dn_A}{dt} = \frac{d[A]}{dt} = -\frac{\nu_A}{V} \frac{d\xi}{dt} \qquad \frac{1}{V} \frac{dn_Y}{dt} = \frac{d[Y]}{dt} = -\frac{\nu_Y}{V} \frac{d\xi}{dt}$$

- The rate (or speed) of reaction, also known as the differential rate law, is

$$v(t) = -\frac{1}{\nu_A} \frac{d[A]}{dt} = -\frac{1}{\nu_B} \frac{d[B]}{dt} = \frac{1}{\nu_Y} \frac{d[Y]}{dt} = \frac{1}{\nu_Z} \frac{d[Z]}{dt} = \frac{1}{V} \frac{d\xi}{dt}$$

- All terms are positive.
- Rate laws with a constant k are of the form

$$v(t) = k[A]^{m_A}[B]^{m_B}$$

- The exponents are known as **orders**.
- The overall order reaction is $\sum m_i$.
- The orders and overall order of the reaction depends on the fundamental reaction steps and the reaction mechanism.
- For example, for the reaction $2\text{NO}_{(g)} + \text{O}_{2(g)} \longrightarrow 2\text{NO}_{2(g)}$, we have

$$v(t) = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{d[\text{O}_2]}{dt} = -\frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$

- It follows that $v(t) = k[\text{NO}]^2[\text{O}_2]$.
- This is a rare elementary reaction that proceeds with the kinetics illustrated by the equation.
- Rate laws must be determined by experiment.
 - Multi-step reactions may have more complex rate law expressions.
 - Oftentimes, $1/2$ exponents indicate more complicated mechanisms.
 - For example, even an equation as simple looking as $\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$ has rate law

$$v(t) = \frac{k'[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k''[\text{HBr}][\text{Br}_2]^{-1}}$$

- Determining rate laws.

- Method of isolation.

- Put in a large initial excess of A so that it's concentration doesn't change that much; essentially incorporates $[A]^{m_A}$ into k for determination of the order of B .
- We can then do the same thing the other way around.

- Method of initial rates.

- We approximate

$$v = -\frac{d[A]}{\nu_A dt} \approx -\frac{\Delta[A]}{\nu_A \Delta t} = k[A]^{m_A}[B]^{m_B}$$

- Consider two different initial values of $[B]$, which we'll call $[B_1], [B_2]$. Then

$$v_1 = -\frac{1}{\nu_A} \left(\frac{\Delta[A]}{\Delta t} \right)_1 = k[A]_0^{m_A}[B]_1^{m_B} \qquad v_2 = -\frac{1}{\nu_A} \left(\frac{\Delta[A]}{\Delta t} \right)_2 = k[A]_0^{m_A}[B]_2^{m_B}$$

- Take the logarithm and solve for m_B .

$$m_B = \frac{\ln(v_1/v_2)}{\ln([B]_1/[B]_2)}$$

- Does an example problem.

2.4 Chapter 27: The Kinetic Theory of Gases

From McQuarrie and Simon (1997).

- 4/10: • **Mean free path:** The average distance that a molecule travels between collisions. Denoted by l .
Given by

$$l = \frac{1}{\sqrt{2}\rho\sigma}$$

- Naturally, the average distance that a molecule travels between collisions is equal to how far it travels per unit time (the average speed) divided by the number of collisions per unit time (the collision frequency). Thus, $l = \langle u \rangle / z_A$, which is how the above is derived.
- Substituting $\rho = N/V = nN_A/V = PN_A/RT$ yields

$$l = \frac{RT}{\sqrt{2}N_A\sigma P}$$

- Example: At room temperature and one bar, the mean free path of nitrogen is about 200 times the effective diameter of a nitrogen molecule.
- An alternate physical interpretation of the probability of a collision.
 - Consider a “collision cylinder” with collision cross section of unit area. Let the thickness of this “cylinder” be dx . It follows that the volume of the “collision cylinder” is $1 \cdot dx = dx$.
 - Consequently, the number of molecules having center within the collision cylinder is equal to the number density times the volume, or ρdx .
 - Thus, if each molecule has target area σ , then the total target area presented by these molecules (neglecting overlap) is $\sigma\rho dx$.
 - Therefore, since the probability of a collision can be thought of as the ration of the total target area to the total area (which we have defined to be unity), the probability of a collision is $\sigma\rho dx$.
 - Note that this squares with the definition of the probability of a collision as $\rho\sigma \langle u \rangle dt$ with $dx = \langle u \rangle dt$, as we’d expect.
- As we can see, the probability of a collision increases with increasing distance traveled dx .
- If n_0 molecules are emitted from the origin traveling in the x -direction with equal velocity in a volume of unmoving molecules, let $n(x)$ be the number of molecules that travel a distance x without collision.
 - It follows that the number of molecules that undergo a collision between $x, x + dx$ is $n(x)\sigma\rho dx$.
 - Furthermore, said number is naturally equal to $n(x) - n(x + dx)$.
 - Thus, we have that

$$\begin{aligned} n(x) - n(x + dx) &= \sigma\rho n(x) dx \\ \frac{n(x + dx) - n(x)}{dx} &= -\sigma\rho n(x) \\ \frac{dn}{dx} &= -\sigma\rho n \\ \int_{n_0}^n \frac{dn}{n} &= -\sigma\rho \int_0^x dx \\ \ln(n/n_0) &= -\sigma\rho x \\ n(x) &= n_0 e^{-\sigma\rho x} \end{aligned}$$

where no factor of $\sqrt{2}$ appears because of the assumption that the other molecules do not move.

- Therefore, the probability $p(x) dx$ that one of the initial n_0 molecules will collide in the interval $x, x+dx$ is

$$\begin{aligned} p(x) dx &= \frac{n(x) - n(x+dx)}{n_0} \\ &= -\frac{1}{n_0} \frac{dn}{dx} dx \\ &= \frac{1}{l} e^{-x/l} dx \end{aligned}$$

– The above equation is normalized and has $\langle x \rangle = l$, as expected.

- The distance after which half of the molecules will have been scattered from a beam of initially n_0 molecules is $l \cdot \ln 2$, i.e., about 70% of the mean free path.
- **Total collision frequency per unit volume** (for like molecules): The following quantity. *Denoted by Z_{AA} . Given by*

$$Z_{AA} = \frac{1}{2} \rho z_A = \frac{1}{2} \sigma \langle u_r \rangle \rho^2 = \frac{\sigma \langle u \rangle \rho^2}{\sqrt{2}}$$

– Derived by multiplying the collision frequency for *one* molecule z_A by the number of molecules per unit volume ρ , and dividing by 2 in order to avoid counting a collision between a pair of similar molecules as two distinct collisions.

- **Total collision frequency per unit volume** (for dislike molecules): The following quantity. *Denoted by Z_{AB} . Given by*

$$Z_{AB} = \sigma_{AB} \langle u_r \rangle \rho_A \rho_B$$

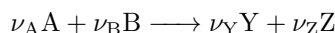
- The discussion of the rate of gas-phase chemical reactions is nearly identical to that given in class.

2.5 Chapter 28: Chemical Kinetics I — Rate Laws

From McQuarrie and Simon (1997).

4/15:

- Whereas McQuarrie and Simon (1997) developed Quantum Mechanics from a set of simple postulates and Thermodynamics from the three laws, “the field of chemical kinetics has not yet matured to a point where a set of unifying principles has been identified” (McQuarrie & Simon, 1997, p. 1047).
 - There are many current theoretical models of kinetics, each of which has its merits and drawbacks.
 - Thus, right now, it is necessary to familiarize ourselves with numerous disparate ideas, as is common in developing fields of inquiry.
- **Rate law:** A differential equation describing the time-dependence of the reactant and product concentrations during a chemical reaction.
- Consider the general chemical reaction described by



- Since

$$n_A(t) = n_A(0) - \nu_A \xi(t) \quad n_B(t) = n_B(0) - \nu_B \xi(t) \quad n_Y(t) = n_Y(0) + \nu_Y \xi(t) \quad n_Z(t) = n_Z(0) + \nu_Z \xi(t)$$

we can describe the time-dependent change in the number of moles of each substance by taking a derivative with respect to t , as follows.

$$\frac{dn_A}{dt} = -\nu_A \frac{d\xi}{dt} \quad \frac{dn_B}{dt} = -\nu_B \frac{d\xi}{dt} \quad \frac{dn_Y}{dt} = \nu_Y \frac{d\xi}{dt} \quad \frac{dn_Z}{dt} = \nu_Z \frac{d\xi}{dt}$$

- Since most experimental techniques measure concentration, it is convenient to divide the above equations by the total volume V on both sides to yield the following.

$$\frac{d[A]}{dt} = -\frac{\nu_A}{V} \frac{d\xi}{dt} \quad \frac{d[B]}{dt} = -\frac{\nu_B}{V} \frac{d\xi}{dt} \quad \frac{d[Y]}{dt} = \frac{\nu_Y}{V} \frac{d\xi}{dt} \quad \frac{d[Z]}{dt} = \frac{\nu_Z}{V} \frac{d\xi}{dt}$$

- While each individual quantity above has its purpose, it is useful to define an overall **rate of reaction**.
- **Rate of reaction:** The following quantity. *Denoted by $v(t)$. Given by*

$$v(t) = \frac{1}{V} \frac{d\xi}{dt} \\ = -\frac{1}{\nu_A} \frac{d[A]}{dt} = -\frac{1}{\nu_B} \frac{d[B]}{dt} = \frac{1}{\nu_Y} \frac{d[Y]}{dt} = \frac{1}{\nu_Z} \frac{d[Z]}{dt}$$

- Note that the rate of reaction is always positive (as long as the reaction proceeds only in the forward direction).

- **Rate law:** The relationship between $v(t)$ and the concentrations of the various reactants. *General form*

$$v(t) = k[A]^{m_A}[B]^{m_B} \dots$$

- Some reactions (such as the $\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$ example from class) do not have conventional rate laws.
- **Rate constant:** The proportionality constant between the rate of reaction and the function of the concentrations of the chemical species involved in a rate law. *Denoted by k .*
 - The units of the rate constant depend on the form of the rate law.
- **Order** (of a reactant A): The power to which the concentration of a reactant is raised in a rate law. *Denoted by m_A .*
- **Overall order** (of a chemical reaction that obeys a general-form rate law): The sum of the orders of the reactants.
- We now discuss common methods for the experimental determination of a rate law.
- **Method of isolation:** The following procedure, which as described will determine m_B for a chemical reaction of the form introduced at the beginning of this section but can easily be adapted to determine m_A or be generalized to higher-order situations.

1. Introduce a large excess concentration of A into the initial reaction mixture. This excess will guarantee that $[A]$ remains essentially constant over the course of the reaction.
2. Combine $[A]^{m_A}$ and k into a new “rate constant” k' , reducing the rate law to the form

$$v = k'[B]^{m_B}$$

3. Determine m_B by measuring v as a function of $[B]$.
- Sometimes it is not possible to have one reactant or the other in excess.
 - As such, we need an alternate way to measure the rate.
 - We cannot directly measure $d[A]/dt$, but we can measure $\Delta[A]/\Delta t$ for small Δt and approximate these measurements as $d[A]/dt$.
 - This forms the basis for the **method of initial rates**.
 - **Method of initial rates:** The following procedure, which as described will determine m_B for a chemical reaction of the form introduced at the beginning of this section but can easily be adapted to determine m_A or be generalized to higher-order situations.

1. Take two different measurements of the initial rate (from $t = 0$ to $t = t$). Let the initial concentration of A, $[A]_0$, be the same for each. However, for one, use $[B]_1$ for initial concentration of B, and for the other, use $[B]_2$.
2. Arranging everything into equations, we thus have

$$v_1 = -\frac{1}{\nu_A} \left(\frac{\Delta[A]}{\Delta t} \right)_1 = k[A]_0^{m_A} [B]_1^{m_B} \quad v_2 = -\frac{1}{\nu_A} \left(\frac{\Delta[A]}{\Delta t} \right)_2 = k[A]_0^{m_A} [B]_2^{m_B}$$

where we have used the subscripts 1 and 2 to denote the results of the different experiments and their corresponding initial concentrations of B.

3. We may now solve for m_B by dividing the two equations, taking logarithms, and rearranging to the following.

$$m_B = \frac{\ln(v_1/v_2)}{\ln([B]_1/[B]_2)}$$

- Both the method of isolation and the method of initial rates rely on the assumption that the reactants can be mixed, and then we can measure the rates.
 - However, for some very quick reactions, the time required to mix the reactants is long compared with the reaction itself.
 - For these cases, we need **relaxation methods**.