

CHEM 26300 (Chemical Kinetics and Dynamics) Notes

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Chapter 27

Kinetic Theory of Gases

27.1 Background and Ideal Gas Distributions

3/28:

- Learning objectives for CHEM 263.
 - The time-dependent phenomena.
 - Reaction rate and rate laws.
 - Reaction mechanisms and reaction dynamics.
 - Surface chemistry and catalysis.
 - Experimental design and instruments.

- Before we move into the content of CHEM 263, a few important notes from CHEM 262.

- **Partition function** (for a system with N states): The following function of temperature. *Denoted by $Q(T)$. Given by*

$$Q(T) = \sum_{n=1}^N e^{-E_n/k_B T}$$

- **Observable:** A quantum mechanical operator.
- Consider a system described by the partition function Q . Let $|i\rangle$ denote the state with energy E_i , and let A be an observable. Then the expected value of the observable A is given by

$$\langle A \rangle = \frac{1}{Q} \sum_{|i\rangle} \langle i|A|i\rangle e^{-E_i/k_B T}$$

- “This fundamental law is the summit of statistical mechanics, and the entire subject is either the slide-down from this summit, as the principle is applied to various cases, or the climb-up to where the fundamental law is derived and the concepts of thermal equilibrium and temperature T clarified” Richard Feynman, Statistical Mechanics.
- Now onto the CHEM 263 content.
- Tian duplicates the derivation of the ideal gas law given on Labalme (2021b, pp. 18–19).
 - Note that if M is the molar mass, m is the mass of a single molecule, N_A is Avogadro’s number, N is the number of particles present, and n is the number of moles present, then since $N/N_A = n$ and $M/N_A = m$, we have that

$$M = \frac{Nm}{n}$$

- Important values of molecular speed u .

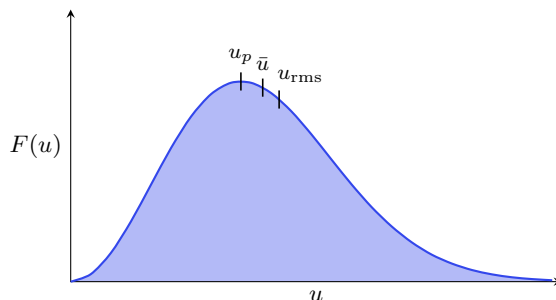


Figure 27.1: Important values of molecular speed.

- **Maxwell Speed Distribution Function:** The following normalized function, which gives the probability that a particle in an ideal gas will have a given speed. Denoted by $f(u)$. Given by

$$f(u) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} u^2 \exp \left(-\frac{Mu^2}{2RT} \right)$$

- **Most probable speed:** The speed that a particle in an ideal gas is most likely to have. Denoted by u_p . Given by

$$u_p = \sqrt{\frac{2RT}{M}}$$

- **Mean speed:** The average speed of all of the particles in an ideal gas. Denoted by \bar{u} . Given by

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}}$$

- **Root mean squared speed:** The square root of the average of the speeds squared. Denoted by u_{rms} . Given by

$$u_{\text{rms}} = \langle u^2 \rangle^{1/2} = \sqrt{\frac{3RT}{M}}$$

- The distributions of the molecular speed and velocity components are different.
 - While speed follows the Maxwell-Boltzmann distribution, velocity follows (on each Cartesian axis) a Gaussian distribution centered at zero.
 - At higher temperatures, both distributions “flatten out,” but maintain their shape.
- Deriving the distribution of the velocity component.
 - The velocity components are independent.
 - Let

$$h(u) = h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

be the distribution of speed with velocity components between $u_x, u_x + du_x$, $u_y, u_y + du_y$, and $u_z, u_z + du_z$, where $f(u_i)$ is the probability distribution of components i .

- Note that $h(u)$ is *not* the speed distribution with velocity components between $u, u + du$.
- Clever step: Note that the logarithmic form of the above equation leads to

$$\begin{aligned} \ln h(u) &= \ln f(u_x) + \ln f(u_y) + \ln f(u_z) \\ \left(\frac{\partial \ln h}{\partial u_x} \right)_{u_y, u_z} &= \frac{d \ln h}{du} \left(\frac{\partial u}{\partial u_x} \right)_{u_y, u_z} \\ &= \frac{u_x}{u} \frac{d \ln h}{du} \end{aligned}$$

where we evaluate $\partial u / \partial u_x$ by using the generalized Pythagorean theorem definition of u .

- Additionally, we have that

$$\left(\frac{\partial \ln h}{\partial u_x} \right)_{u_y, u_z} = \frac{d \ln f(u_x)}{du_x}$$

since the $\ln f(u_i)$ ($i \neq x$) terms are constant with respect to changes in u_x .

- Thus, combining the last two results, we have that

$$\frac{d \ln h(u)}{u du} = \frac{d \ln f(u_x)}{u_x du_x}$$

- It follows since the gas is isotropic that

$$\frac{d \ln h(u)}{u du} = \frac{d \ln f(u_x)}{u_x du_x} = \frac{d \ln f(u_y)}{u_y du_y} = \frac{d \ln f(u_z)}{u_z du_z}$$

- But since the three speed components are independent of each other, the above term is constant.
- It follows if we call the constant -2γ , then

$$\begin{aligned} \frac{d \ln f(u_i)}{u_i du_i} &= -2\gamma \\ f(u_i) &= A e^{-\gamma u_i^2} \end{aligned}$$

for $i = x, y, z$.

- We will pick up with solving for A and γ in the next lecture.

27.2 Velocity vs. Speed

3/30:

- Exam preferences.
 - Asks for midterm preferences. People prefer a take-home exam.
 - Asks for final preferences. Probably a 2-hour test?
- Continuing with the derivation for the distribution of the velocity component.
 - Note that we choose -2γ because we know we're gonna have to integrate and we want the final form to be as simple as possible. For instance,

$$\frac{d \ln f(u_i)}{u_i du_i} = \frac{d \ln f(u_i)}{\frac{1}{2} du_i^2}$$

should help rationalize the 2.

- Solving for A .
 - We apply the normalization requirement.

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} f(u_i) du_i \\ &= A \int_{-\infty}^{\infty} e^{-\gamma u_i^2} du_i \\ &= 2A \int_0^{\infty} e^{-\gamma u_i^2} du_i \\ &= 2A \sqrt{\frac{\pi}{4\gamma}} \\ A &= \sqrt{\frac{\gamma}{\pi}} \end{aligned}$$

- Thus, for $i = x, y, z$, we have

$$f(u_i) = \sqrt{\frac{\gamma}{\pi}} e^{-\gamma u_i^2}$$

- Solving for γ .

- We know from the previous lecture that

$$\begin{aligned}\frac{1}{3}m \langle u^2 \rangle &= RT \\ \langle u^2 \rangle &= \frac{3RT}{M} = \frac{3k_B T}{m} \\ \langle u_x^2 \rangle &= \frac{RT}{M}\end{aligned}$$

- But we also have by definition that (taking u_x in particular because γ is the same in the equations for u_x, u_y, u_z)

$$\langle u_x^2 \rangle = \int_{-\infty}^{\infty} u_x^2 f(u_x) du_x$$

- Thus, we have that

$$\begin{aligned}\frac{RT}{M} &= \int_{-\infty}^{\infty} u_x^2 f(u_x) du_x \\ &= \sqrt{\frac{\gamma}{\pi}} \int_{-\infty}^{\infty} u_x^2 e^{-\gamma u_x^2} du_x \\ &= 2\sqrt{\frac{\gamma}{\pi}} \int_0^{\infty} u_x^2 e^{-\gamma u_x^2} du_x \\ &= 2\sqrt{\frac{\gamma}{\pi}} \cdot \frac{1}{4\gamma} \sqrt{\frac{\pi}{\gamma}} \\ &= \frac{1}{2\gamma} \\ \gamma &= \frac{M}{2RT}\end{aligned}$$

- It follows that

$$f(u_i) = \sqrt{\frac{M}{2\pi RT}} e^{-Mu_i^2/2RT} = \sqrt{\frac{m}{2\pi k_B T}} e^{-mu_i^2/2k_B T}$$

- Now we can compute other speeds, such as the average velocity $\langle u_x \rangle$.
 - Evaluating the odd integrand gives us $\langle u_x \rangle = 0$, as expected.
- As per the Gaussian distribution, if the temperature increases or mass decreases, the distribution of speeds broadens and flattens.
- **Doppler effect:** The change in frequency of a wave in relation to an observer who is moving relative to the wave source. *Also known as Doppler shift.*
 - Example: The change of pitch heard when a vehicle sounding a horn approaches and recedes from an observer. Compared to the emitted frequency, the received frequency is higher during the approach, identical at the instant of passing by, and lower during the recession.
- An application of the velocity distribution: The Doppler effect and spectral line broadening.
 - Radiation emitted from a gas will be spread out due to the motion of the molecules.
 - The frequency ν detected by the observer and the frequency ν_0 emitted by the emitter are related by

$$\nu \approx \nu_0 \left(1 + \frac{u_x}{c} \right)$$

- Algebraic rearrangement gives us

$$u_x = \frac{c(\nu - \nu_0)}{\nu_0}$$

- Doppler-broadened spectral lineshape.

$$I(\nu) \propto e^{-mc^2(\nu - \nu_0)^2 / 2\nu_0 k_B T}$$

- Thus, the variance of the spectral line is

$$\sigma^2 = \frac{\nu_0^2 k_B T}{mc^2} = \frac{\nu_0^2 RT}{Mc^2}$$

- The result is that if gas particles are at rest, the emission line spectrum will have very narrow lines. If the gas particles are moving, the lines are broadened.

■ This is why so much spectroscopy is done at super-low temperatures and with heavier molecules! In particular, because Doppler broadening blurs results.

- We know that the average velocity is zero. But we can also consider the average velocity in the positive direction.

- We calculate

$$\begin{aligned} \langle u_x \rangle &= \int_0^\infty u_x f(u_x) du_x \\ &= \sqrt{\frac{m}{2\pi k_B T}} \int_0^\infty u_x e^{-mu_x^2 / 2k_B T} \\ &= \sqrt{\frac{m}{2\pi k_B T}} \cdot \frac{2k_B T}{2m} \\ &= \sqrt{\frac{m}{2\pi k_B T}} \end{aligned}$$

- This will be one-fourth the average speed from Figure 27.1, though.

- Moving from velocity to speed: Deriving the Maxwell-Boltzmann Speed Distribution.

- Define

$$F(u) du \approx f(u_x) du_x f(u_y) du_y f(u_z) du_z$$

■ This function gives us the velocity of each particle in the velocity space. But the speed of each particle is just it's distance from the origin.

- We have that

$$F(u) du \approx \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-m(u_x^2 + u_y^2 + u_z^2) / 2k_B T} du_x du_y du_z$$

from where we can convert to spherical coordinates using $u^2 = u_x^2 + u_y^2 + u_z^2$ and $4\pi u^2 du = du_x du_y du_z$ to get our final result.

$$F(u) du = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} u^2 e^{-mu^2 / 2k_B T} du$$

- Note that we invoke the equals sign only at the end because speed is inherently spherical in the velocity space; any use of Cartesian infinitesimals must by definition be an approximation at best.

- Some important differences.

- $h(u) = h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$ is the distribution of molecular speeds with velocity components (in Cartesian coordinates) between $u_x, u_x + du_x$, $u_y, u_y + du_y$, and $u_z, u_z + du_z$.
- $f(u_x) = \sqrt{M/2\pi RT} e^{-Mu_x^2/2RT}$ is the distribution of molecular speed componentwise in Cartesian coordinates, and has a Gaussian distribution.
- $F(u) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} u^2 e^{-mu^2/2k_B T}$ is the distribution of molecular speed, and has a Maxwell-Boltzmann distribution as per spherical coordinates.
- Maxwell-Boltzmann speed distribution of noble gases.
 - Heavier Noble gases have more “flattened” M-B distributions.
- Different metrics of M-B speed distribution.
 - We can, from the above formula, calculate the average speed $\langle u \rangle$, the root mean square speed $\langle u^2 \rangle$, and the most probable speed by taking a derivative and setting it equal to zero.
 - We get

$$\langle u \rangle = \sqrt{\frac{8RT}{\pi M}} \quad u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad u_{\text{mp}} = \sqrt{\frac{2k_B T}{m}}$$

27.3 Energy Distribution and Collision Frequency

4/1:

- The final exam is 50 minutes on the last day of class.
- We can also express the M-B distribution in terms of kinetic energy.
 - We know that energy $\varepsilon = \frac{1}{2}mu^2$, so $u = \sqrt{2\varepsilon/m}$ and thus $du = d\varepsilon/\sqrt{2m\varepsilon}$.
 - This allows us to write

$$\begin{aligned} F(\varepsilon) d\varepsilon &= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot \frac{2\varepsilon}{m} \cdot e^{-\varepsilon/k_B T} \frac{d\varepsilon}{\sqrt{2m\varepsilon}} \\ &= \frac{2\pi}{(\pi k_B T)^{3/2}} \varepsilon^{1/2} e^{-\varepsilon/k_B T} d\varepsilon \end{aligned}$$

- Thus, we can calculate that

$$\begin{aligned} \langle \varepsilon \rangle &= \int_0^\infty \varepsilon f(\varepsilon) d\varepsilon \\ &= \frac{3}{2} k_B T \end{aligned}$$

as expected.

- Aside: Understanding the probability distribution $F(u) du$ and the relation between $F(u) du$ and $F(\varepsilon) d\varepsilon$.
 - $F(u)$ is a probability distribution. Thus, its graph (see Figure 27.2a) indicates the number density of particles we’d expect to find at a given velocity u by the vertical height of the curve. Importantly, if we imagine filling in the area under the curve with each particle at its u -position and evenly spaced in the F direction, eventually we’d get a continuous color under the curve (as in Figure 27.2a; the darkened regions are illustrated as such for the sole purpose of contrast with Figure 27.2b, as discussed below).
 - We note that $\varepsilon = \frac{1}{2}mu^2$ is a stretching operation. This means that as u increases, ε increases faster. For example, as u increases 1, 2, 3, 4, ε increases proportionally by 1, 4, 9, 16. Thus, we can approximate $F(\varepsilon)$ by stretching the graph of $F(u)$ horizontally by greater and greater amounts (see Figure 27.2b).

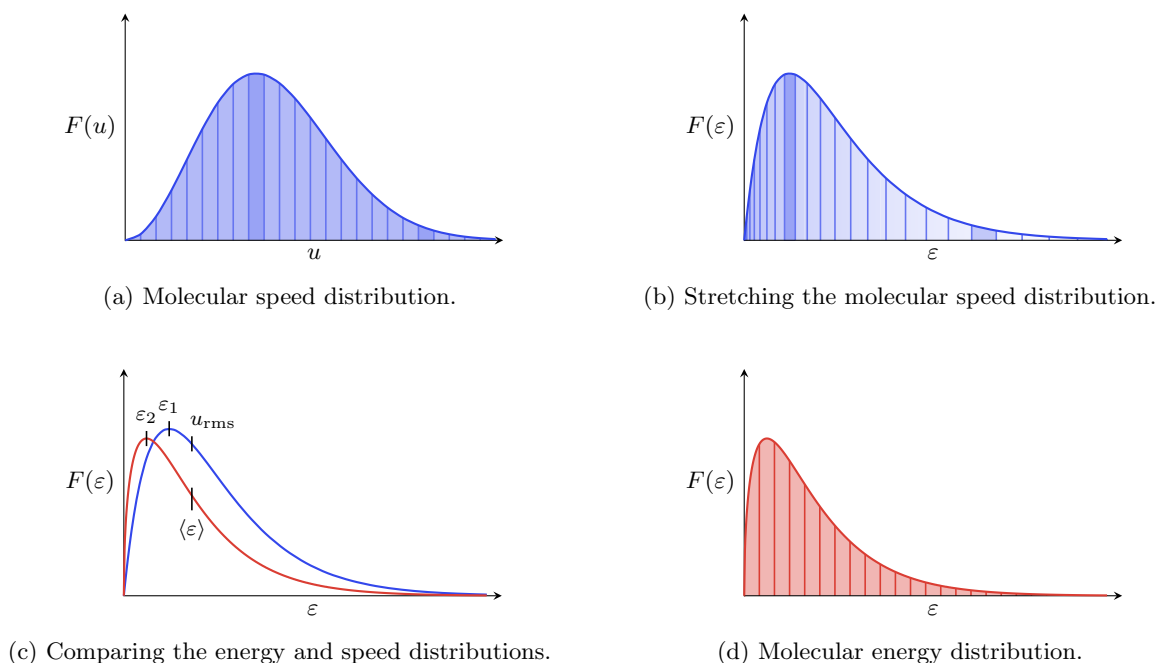


Figure 27.2: Relating molecular speed and molecular energy.

- An important consequence of this is that the particles moving within a certain range of velocities have a larger range of energies (compare the darkly shaded blocks of Figures 27.2a and 27.2b, as well as the general increase in spacing of the vertical lines).
- However, when we approximate by stretching, we ignore some of the other changes in the equation. For instance, when we sketch the actual energy distribution, its most probable energy $\varepsilon_{\text{mp}} = \varepsilon_2$ has a lower value than that predicted by just stretching the graph of the speed distribution (which we denote in Figure 27.2c by $\varepsilon_1 = \frac{1}{2}mu_{\text{mp}}^2$). All in one equation,

$$\varepsilon_{\text{mp}} \neq \frac{1}{2}mu_{\text{mp}}^2$$

- Additionally, note that the actual curve (Figure 27.2d) has even density beneath it.
- Calculating the most probable kinetic energy.

$$\begin{aligned} \frac{dF}{d\varepsilon} &= \frac{2\pi}{(\pi k_B T)^{3/2}} \left[\frac{\varepsilon^{-1/2} e^{-\varepsilon/k_B T}}{2} - \frac{e^{-\varepsilon/k_B T} \cdot \varepsilon^{1/2}}{k_B T} \right] \\ 0 &= \frac{2\pi e^{-\varepsilon/k_B T}}{(\pi k_B T)^{3/2}} \left[\frac{1}{2\sqrt{\varepsilon}} - \frac{\sqrt{\varepsilon}}{k_B T} \right] \\ \varepsilon_{\text{mp}} &= \frac{k_B T}{2} \end{aligned}$$

- The most probable energy calculated from the most probable speed via $\frac{1}{2}mu_{\text{mp}}^2$ is $k_B T$, so the actual value is one-half the predicted value (notice how $\varepsilon_2 = \frac{1}{2}\varepsilon_1$).
- Since $\langle \varepsilon \rangle = \langle \frac{1}{2}mu^2 \rangle$, $\langle \varepsilon \rangle$ is related to the root mean square speed.
 - This relates $u_{\text{rms}}^2 = 3k_B T/m$ to $\langle \varepsilon \rangle = 3k_B T/2$ by a factor of $m/2$.
 - This linear relation appears in Figure 27.2c, where u_{rms} and $\langle \varepsilon \rangle$ occur in the same place and differ only by a vertical stretch factor ($m/2$).

- Calculating the frequency of collisions.

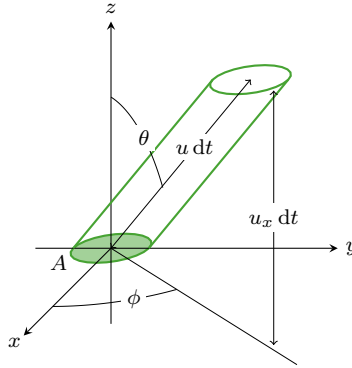


Figure 27.3: Collision frequency cylinder.

- Construct a cylinder to enclose all those molecules that will strike the area A at an angle θ with speed u in the time interval dt .
- Its volume is $V = Au \cos \theta dt$.
- The number of molecules in the cylinder is ρV , where ρ is the number density.
- The fraction of molecules that have a speed between $u, u + du$ is $F(u) du$.
- The fraction travelling within a solid angle bounded by $\theta, \theta + d\theta$ and $\phi, \phi + d\phi$ is $\sin \theta d\theta \cdot d\phi / 4\pi$, where 4π represents a complete solid angle.
- The number dN_{coll} of molecules colliding with the area A from the specified direction in the time interval dt is

$$dN_{\text{coll}} = \rho(Au dt) \cos \theta \cdot F(u) du \cdot \frac{\sin \theta d\theta d\phi}{4\pi}$$

- The number of collisions per unit time per unit area 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

$$dz_{\text{coll}} = \frac{1}{A} \frac{dN_{\text{coll}}}{dt} = \frac{\rho}{4\pi} u F(u) du \cdot \cos \theta \sin \theta d\theta d\phi$$

- If we integrate over all possible speeds and directions, then we obtain

$$\begin{aligned} z_{\text{coll}} &= \frac{\rho}{4\pi} \int_0^\infty u F(u) du \int_0^{\pi/2} \cos \theta \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{\rho \langle u \rangle}{4} \end{aligned}$$

- Deriving the pressure through the collision frequency.

- We have

$$\begin{aligned} dP &= (2mu \cos \theta) dz_{\text{coll}} \\ &= (2mu \cos \theta) \frac{\rho}{4\pi} u F(u) du \cos \theta \sin \theta d\theta d\phi \\ &= \rho \left(\frac{m}{2\pi k_B T} \right)^{3/2} (2mu \cos \theta) u^3 e^{-mu^2/2k_B T} du \cos \theta \sin \theta d\phi \end{aligned}$$

- Thus, since

$$\int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi = \frac{2\pi}{3} \quad 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty u^4 e^{-mu^2/2k_B T} du = \langle u^2 \rangle$$

we have that

$$P = \frac{1}{3} \rho m \langle u^2 \rangle = \frac{1}{3V} N m \langle u^2 \rangle$$

27.4 Office Hours (Tian)

- Can you explain the whole $F(u) du$ differential notation for probability?
 - $F(u)$ is the probability function. $F(u)$ is the y axis of the individual points. Probability density.
 - $F(u) du$ is the infinitesimal probability at u , but only within an infinitely small range. It's an abbreviation/approximation for the tiny infinitesimal rectangle under the curve that we picture as we integrate.
 - $\int_0^\infty F(u) du = 1$ (summing all of the tiny probabilities) gets you to 1 for a normalized probability distribution.
- What is up with the relation between u_{rms} and $\langle \varepsilon \rangle$?
 - We have

$$\begin{aligned}
 \langle \varepsilon \rangle &= \left\langle \frac{1}{2} m u^2 \right\rangle \\
 &= \frac{1}{2} m \langle u^2 \rangle \\
 &= \frac{1}{2} m u_{\text{rms}}^2 \\
 &= \frac{m}{2} \cdot \frac{3k_{\text{B}}T}{m} \\
 &= \frac{3k_{\text{B}}T}{2}
 \end{aligned}$$

- Post lecture notes before class? Write down what's on the lecture slides or listen?
 - He has been and will continue to post the slides the night before the lecture.
 - When will HW 1 be posted?
 - No homework this week.
 - The first homework will be posted next Monday.
 - He will post a homework every Monday that will be due the next Monday.
 - When are gases isotropic?
 - A gas is isotropic unless there is a driving force.
 - For example, gas in a closed box is isotropic, but gas in a cylinder with a fan at one end is not isotropic (particles are more likely to move in one direction).
 - What is the total solid angle geometrically?
 - Hard to visualize three dimensionally. You get 4π by doing the integrals for the components:
- $$4\pi = \int_{-\pi/2}^{\pi/2} \sin \theta d\theta \int_0^{2\pi} d\phi$$
- We don't need to memorize most of the derivations, but we do need to know the conclusions and the assumptions we need to get them.
 - We won't be asked to give a derivation unless we're given the full starting point.
 - The final can't have much heavy calculation on it because there's not that much time.
 - The midterm will be a online take-home exam with limited time (probably 2 hours).
 - Not every topic in the remainder of McQuarrie and Simon (1997) will be covered; some sections will be skipped.
 - He will focus a lot on the practical applications. Once the student understands the basic principle, he wants us to be able to apply it to research and life.

27.5 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 27.3.
 - 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 .

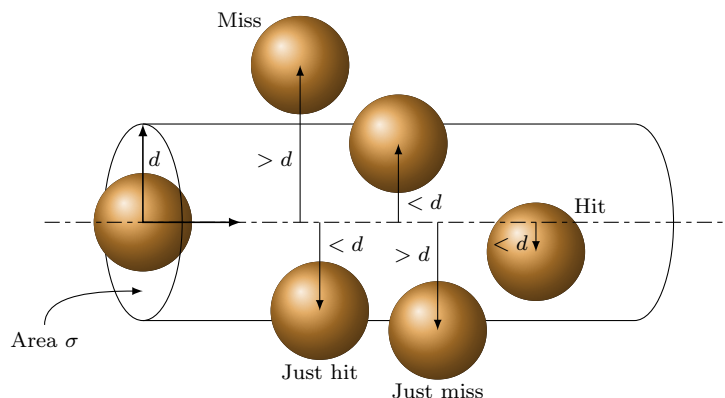


Figure 27.4: Collision cylinder.

- 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 $\rho = P N_A / RT$ 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

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

27.6 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.

27.7 Chapter 27: The Kinetic Theory of Gases

From McQuarrie and Simon (1997).

- 3/28:
- **Kinetic theory of gases:** A simple model of gases in which the molecules (pictured as hard spheres) are assumed to be in constant, incessant motion, colliding with each other and with the walls of the container.
 - McQuarrie and Simon (1997) does the KMT derivation of the ideal gas law from Labalme (2021a). Some important notes follow.
 - McQuarrie and Simon (1997) emphasizes the importance of

$$PV = \frac{1}{3} N m \langle u^2 \rangle$$

as a fundamental equation of KMT, as it relates a macroscopic property PV to a microscopic property $m \langle u^2 \rangle$.

- In Chapter 17-18, we derived quantum mechanically, and then from the partition function, that the average translational energy $\langle E_{\text{trans}} \rangle$ for a single particle of an ideal gas is $\frac{3}{2} k_B T$. From classical mechanics, we also have that $\langle E_{\text{trans}} \rangle = \frac{1}{2} m \langle u^2 \rangle$. *This* is why we may let

$$\frac{1}{2} m \langle u^2 \rangle = \frac{3}{2} k_B T$$

recovering that the average translational kinetic energy of the molecules in a gas is directly proportional to the Kelvin temperature.

- **Isotropic** (entity): An object or substance that has the same properties in any direction.

- For example, a homogeneous gas is isotropic, and this is what allows us to state that $\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$.
- McQuarrie and Simon (1997) derives

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$
 - u_{rms} is an estimate of the average speed since $\langle u^2 \rangle \neq \langle u \rangle^2$ in general.
- McQuarrie and Simon (1997) states without proof that the speed of sound u_{sound} in a monatomic ideal gas is given by

$$u_{\text{sound}} = \sqrt{\frac{5RT}{3M}}$$

- Assumptions of the kinetic theory of gases.
 - Particles collide elastically with the wall.
 - Justified because although each collision will not be elastic (the particles in the wall are moving too), the average collision will be elastic.
 - Particles do not collide with each other.
 - Justified because “if the gas is in equilibrium, on the average, any collision that deflects the path of a molecule... will be balanced by a collision that replaces the molecule” (McQuarrie & Simon, 1997, p. 1015).
- Note that we can do the kinetic derivation at many levels of rigor, but more rigorous derivations offer results that differ only by constant factors on the order of unity.
- Deriving a theoretical equation for the distribution of the *components* of molecular velocities.
 - Let $h(u_x, u_y, u_z) du_x du_y du_z$ be the fraction of molecules with velocity components between u_j and $u_j + du_j$ for $j = x, y, z$.
 - Assume that the each component of the velocity of a molecule is independent of the values of the other two components^[1]. It follows statistically that

$$h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

- Note that we use just one function f for the probability distribution in each direction because the gas is isotropic.
 - We can use the isotropic condition to an even greater degree. Indeed, it implies that any information conveyed by u_x is necessarily and sufficiently conveyed by u_y , u_z , and u . Thus, we may take

$$h(u) = h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

- It follows that

$$\frac{\partial \ln h(u)}{\partial u_x} = \frac{\partial}{\partial u_x} (\ln f(u_x) + \text{terms not involving } u_x) = \frac{d \ln f(u_x)}{du_x}$$

- Since

$$\begin{aligned} u^2 &= u_x^2 + u_y^2 + u_z^2 \\ \frac{\partial}{\partial u_x} (u^2) &= \frac{\partial}{\partial u_x} (u_x^2 + u_y^2 + u_z^2) \\ 2u \frac{\partial u}{\partial u_x} &= 2u_x \\ \frac{\partial u}{\partial u_x} &= \frac{u_x}{u} \end{aligned}$$

¹This can be proven.

we have that

$$\begin{aligned}\frac{\partial \ln h}{\partial u_x} &= \frac{d \ln h}{du} \frac{\partial u}{\partial u_x} = \frac{u_x}{u} \frac{d \ln h}{du} \\ \frac{d \ln h(u)}{u du} &= \frac{d \ln f(u_x)}{u_x du_x}\end{aligned}$$

which generalizes to

$$\frac{d \ln h(u)}{u du} = \frac{d \ln f(u_x)}{u_x du_x} = \frac{d \ln f(u_y)}{u_y du_y} = \frac{d \ln f(u_z)}{u_z du_z}$$

- Since u_x, u_y, u_z are independent, we know that the above equation is equal to a constant, which we may call $-\gamma$. It follows that for any $j = x, y, z$, we have that

$$\begin{aligned}\frac{d \ln f(u_j)}{u_j du_j} &= -\gamma \\ \frac{1}{f} \frac{df}{du_j} &= -\gamma u_j \\ \int \frac{df}{f} &= \int -\gamma u_j du_j \\ \ln f &= -\frac{\gamma}{2} u_j^2 + C \\ f(u_j) &= A e^{-\gamma u_j^2}\end{aligned}$$

where we have incorporated the $1/2$ into γ .

- To determine A and γ , we let arbitrarily let $j = x$. Since f is a continuous probability distribution, we may apply the normalization requirement.

$$\begin{aligned}1 &= \int_{-\infty}^{\infty} f(u_x) du_x \\ &= 2A \int_0^{\infty} e^{-\gamma u_x^2} du_x \\ &= 2A \sqrt{\frac{\pi}{4\gamma}} \\ A &= \sqrt{\frac{\gamma}{\pi}}\end{aligned}$$

- Additionally, since we have that $\langle u_x^2 \rangle = \frac{1}{3} \langle u^2 \rangle$ and $\langle u^2 \rangle = 3RT/M$, we know that $\langle u_x^2 \rangle = RT/M$. This combined with the definition of $\langle u_x^2 \rangle$ as a continuous probability distribution yields

$$\begin{aligned}\frac{RT}{M} &= \langle u_x^2 \rangle \\ &= \int_{-\infty}^{\infty} u_x^2 f(u_x) du_x \\ &= 2\sqrt{\frac{\gamma}{\pi}} \int_0^{\infty} u_x^2 e^{-\gamma u_x^2} du_x \\ &= 2\sqrt{\frac{\gamma}{\pi}} \cdot \frac{1}{4\gamma} \sqrt{\frac{\pi}{\gamma}} \\ &= \frac{1}{2\gamma} \\ \gamma &= \frac{M}{2RT}\end{aligned}$$

- Therefore,

$$f(u_x) = \sqrt{\frac{M}{2\pi RT}} e^{-Mu_x^2/2RT}$$

- It is common to rewrite the above in terms of molecular quantities m and k_B .
- It follows that as temperature increases, more molecules are likely to be found with higher component velocity values.
- We can use the above result to show that

$$\langle u_x \rangle = \int_{-\infty}^{\infty} u_x f(u_x) du_x = 0$$

- We can also calculate that $\langle u_x^2 \rangle = RT/M$ and $m \langle u_x^2 \rangle / 2 = k_B T / 2$ from the above result^[2].
 - An important consequence is that the total kinetic energy is divided equally into the x -, y -, and z -components.
- **Doppler broadening:** The broadening of spectral lines due to the distribution of molecular velocities.
 - Ideally, spectral lines will be very narrow.
 - However, due to the Doppler effect, if an atom or molecule emits radiation of frequency ν_0 while moving away or toward the observer with speed u_x , then the observed frequency will be

$$\nu \approx \nu_0 \left(1 + \frac{u_x}{c} \right)$$

- Indeed, “if one observes the radiation emitted from a gas at temperature T , then it is found that the spectral line at ν_0 will be spread out by the Maxwell distribution of u_x of the molecule emitting the radiation” (McQuarrie & Simon, 1997, p. 1021).
- It follows by the definition of $f(u_x)$ and the above that

$$I(\nu) \propto e^{-mc^2(\nu-\nu_0)^2/2\nu_0^2k_B T}$$

i.e., that $I(\nu)$ is of the form of a Gaussian centered at ν_0 with variance $\sigma^2 = \nu_0^2 k_B T / mc^2$.

- **Deriving Maxwell-Boltzmann distribution.**
 - Let the probability that a molecule has speed between u and $u + du$ be defined by a continuous probability distribution $F(u) du$. In particular, we have from the above isotropic condition that

$$\begin{aligned} F(u) du &= f(u_x) du_x f(u_y) du_y f(u_z) du_z \\ &= \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-m(u_x^2 + u_y^2 + u_z^2)/2k_B T} du_x du_y du_z \end{aligned}$$

- Considering F over a **velocity space**, we realize that we may express the probability distribution F as a function of u via $u^2 = u_x^2 + u_y^2 + u_z^2$ and the differential volume element in every direction over the sphere of equal velocities (a sphere by the isotropic condition) by $4\pi u^2 du = du_x du_y du_z$.
- Thus, the Maxwell-Boltzmann distribution in terms of speed is

$$F(u) du = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} u^2 e^{-mu^2/2k_B T} du$$

- **Maxwell-Boltzmann distribution:** The distribution of molecular speeds.

²See the equipartition of energy theorem from Labalme (2021b).

- **Velocity space:** A rectangular coordinate system in which the distances along the axes are u_x, u_y, u_z .
- The above integral as well as some other variations occur commonly in the study of kinetics.

$\int_0^\infty x^{2n} e^{-\alpha x^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} \alpha^n} \left(\frac{\pi}{\alpha}\right)^{1/2}$	$n \geq 1$
$\int_0^\infty x^{2n+1} e^{-\alpha x^2} dx = \frac{n!}{2\alpha^{n+1}}$	$n \geq 0$
$\int_0^\infty x^{n/2} e^{-\alpha x} dx = \frac{n(n-2)(n-4) \cdots (1)}{(2\alpha)^{(n+1)/2}} \left(\frac{\pi}{\alpha}\right)^{1/2}$	$n \text{ odd}$
$= \frac{(n/2)!}{\alpha^{(n+2)/2}}$	$n \text{ even}$

Table 27.1: Common integrals in the kinetic theory of gases.

- We may use the above result to calculate that

$$\langle u \rangle = \sqrt{\frac{8RT}{\pi m}}$$

which only differs from u_{rms} by a factor of 0.92.

- **Most probable speed:** The most probable speed of a gas molecule in a sample that obeys the Maxwell-Boltzmann distribution. *Denoted by u_{mp} . Given by*

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

– Derived by setting $dF/du = 0$.

- We may also express the Maxwell-Boltzmann distribution in terms of energy via $u = \sqrt{2\varepsilon/m}$ and $du = d\varepsilon / \sqrt{2m\varepsilon}$ to give

$$F(\varepsilon) d\varepsilon = \frac{2\pi}{(\pi k_B T)^{3/2}} \sqrt{\varepsilon} e^{-\varepsilon/k_B T} d\varepsilon$$

- We can also confirm our previously calculated values for $\langle u^2 \rangle$ and $\langle \varepsilon \rangle$.

4/6:

- Deriving an expression for the frequency of collisions that the molecules of a gas make with the walls of its container (refer to Figure 27.3 throughout the following).

- Note that this quantity is central to the theory of rates of surface reactions.
- McQuarrie and Simon (1997) gets to the following equation as in class.

$$dz_{\text{coll}} = \frac{1}{A} \frac{dN_{\text{coll}}}{dt} = \frac{\rho}{4\pi} u F(u) du \cdot \cos \theta \sin \theta d\theta d\phi$$

- Note that the above equation is of the form $u^3 e^{-mu^2/2k_B T}$ whereas M-B distribution is of the form $u^2 e^{-mu^2/2k_B T}$.
 - Thus, the above equation peaks at higher values of u .
 - This reflects the fact that molecules traveling at a higher speed (than average) are more likely to strike the wall in a given window of time.
- McQuarrie and Simon (1997) finishes the derivation to obtain the equation for z_{coll} and notes that Problems 27-49 through 27-52 develop its applications to effusion rate theory.

- Note that we can calculate the number density ρ from pressure and temperature data via the ideal gas law as follows.

$$\rho = \frac{N}{V} = \frac{N_A n}{V} = \frac{N_A P}{RT}$$

- (Re)deriving $P = \rho m \langle u^2 \rangle / 3$ from a collision frequency perspective.
 - If θ is the angular deviation in the particle's path from the normal to the wall, then the component of momentum of a particle of mass m moving with speed u that lies perpendicular to the wall is $mu \cos \theta$.
 - This particles change in momentum upon colliding elastically with the wall is thus $2mu \cos \theta$.
 - Since pressure is the force per unit area and force is the change in momentum per unit time, the pressure is equal to the product of the change in momentum per collision and the frequency (number per unit time) of collisions per unit area. Mathematically, the infinitesimal pressure applied by just the molecules with speeds between u and $u + du$ that lie within the solid angle $\sin \theta d\theta d\phi$ is

$$\begin{aligned} dP &= (2mu \cos \theta) dz_{\text{coll}} \\ &= \rho \left(\frac{m}{2\pi k_B T} \right)^{3/2} (2mu \cos \theta) u^3 e^{-mu^2/2k_B T} du \cos \theta \sin \theta d\theta d\phi \end{aligned}$$

- It follows since

$$\int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi = \frac{2\pi}{3} \quad 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty u^4 e^{-mu^2/2k_B T} du = \langle u^2 \rangle$$

that

$$P = \rho m \cdot \frac{\langle u^2 \rangle}{2\pi} \cdot \frac{2\pi}{3} = \frac{1}{3} \rho m \langle u^2 \rangle$$

4/10:

- McQuarrie and Simon (1997) discusses Kusch and coworker's experimental verification of the M-B distribution, which used a beam of potassium atoms and a rotating velocity selector.
 - Kusch was awarded the Nobel prize in physics in 1955.
- We now discuss the frequency of collisions between the molecules in a gas.
- We first consider the frequency of collisions of a single gas-phase molecule.
- Assumptions.
 - The molecules are hard spheres of diameter d .
 - All molecules other than the one in question are stationary; we will account for their motion at the end of the derivation.
- **Collision cylinder:** A cylinder of diameter $2d$ that the molecule in question sweeps out as it travels along.
 - The molecule in question will collide with any molecule whose center lies within this cylinder.
 - See Figure 27.4.
- **Collision cross section:** The target of effective radius d presented by each hard sphere molecule. Denoted by σ . Given by

$$\sigma = \pi d^2$$

- See Table 27.2 for some example values.

Gas	d (pm)	σ (nm ²)
He	210	0.140
Ar	370	0.430
Xe	490	0.750
H ₂	270	0.230
N ₂	380	0.450
O ₂	360	0.410
Cl ₂	540	0.920
CH ₄	410	0.530
C ₂ H ₄	430	0.580

Table 27.2: Collision diameters and collision cross sections.

- Calculating the number of collisions dN_{coll} the moving molecule makes in the time dt .
 - The volume of the collision cylinder is the product of its cross section σ and its length $\langle u \rangle dt$.
 - Whenever the center of another molecule lies within this cylinder, a collision will occur.
 - Thus, since $\sigma \langle u \rangle dt$ represents a small volume within the overall volume the gas occupies, the expected number of collisions dN_{coll} would be equal to the number of molecules expected to lie in the volume $\sigma \langle u \rangle dt$.
 - If the N molecules can be expected to be evenly distributed throughout the volume V with number density $\rho = N/V$, then we have that

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

- We must now undue the one assumption that cannot stay: That all other molecules are stationary.
 - To do this, we treat the motion of the two bodies by the reduced mass.
- **Collision frequency:** The expected number of collisions per unit time. *Denoted by Z_A . Given by*

$$\begin{aligned} z_A = \frac{dN_{\text{coll}}}{dt} &= \rho \sigma \langle u_r \rangle = \rho \sigma \sqrt{\frac{8k_B T}{\pi \mu}} \\ &= \sqrt{2} \rho \sigma \langle u \rangle = \sqrt{2} \rho \sigma \sqrt{\frac{8k_B T}{\pi m}} \end{aligned}$$

- **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 ratio 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 unlike molecules): The following quantity. *Denoted by Z_{AB} . Given by*

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

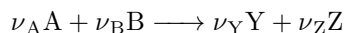
- The discussion of the rate of gas-phase chemical reactions is nearly identical to that given in class.

Chapter 28

Rate Laws

28.1 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

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

- 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.

28.2 Integrated Rate Laws

4/11:

- First order reactions have exponential integrated rate laws.
 - Suppose $A + B \longrightarrow$ products.
 - Suppose the reaction is first order in A .
 - If the concentration of A is $[A]_0$ at $t = 0$ and $[A]$ at time t , then

$$\begin{aligned} v(t) &= -\frac{d[A]}{dt} = k[A] \\ \int_{[A]_0}^{[A]} \frac{d[A]}{[A]} &= -\int_0^t k dt \\ \ln \frac{[A]}{[A]_0} &= -kt \\ [A] &= [A]_0 e^{-kt} \end{aligned}$$

is the integrated rate law.

- Goes over both the concentration plot and the linear logarithmic plot.

- The half-life of a first-order reaction is independent of the initial amount of reactant.

- The half-life is found from the point

$$[A(t_{1/2})] = \frac{[A(0)]}{2} = \frac{[A]_0}{2}$$

- We have

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

$$t_{1/2} = \frac{\ln 2}{k} \approx \frac{0.693}{k}$$

- Notice that the above equation does not depend on [A] or [B]!

- Second order reactions have inverse concentration integrated rate laws.

- Suppose $A + B \longrightarrow$ products, as before, and that the reaction is second order in A.

- Then

$$-\frac{d[A]}{dt} = k[A]^2$$

$$\int_{[A]_0}^{[A]} -\frac{d[A]}{[A]^2} = \int_0^t k \, dt$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

is the integrated rate law.

- The half-life of a second-order reaction is dependent on the initial amount of reaction.

- We have that

$$\frac{1}{[A]_0/2} = \frac{1}{[A]_0} + kt_{1/2}$$

$$\frac{1}{[A]_0} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

- If a reaction is n^{th} -order in a reactant for $n \geq 2$, then the integrated rate law is given by

$$-\frac{d[A]}{dt} = k[A]^n$$

$$\int_{[A]_0}^{[A]} -\frac{d[A]}{[A]^n} = \int_0^t k \, dt$$

$$\frac{1}{n-1} \left(\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right) = kt$$

- The associated half life is

$$\frac{1}{n-1} \left(\frac{1}{([A]_0/2)^{n-1}} - \frac{1}{[A]_0^{n-1}} \right) = kt_{1/2}$$

$$\frac{1}{n-1} \cdot \frac{2^{n-1} - 1}{[A]_0^{n-1}} = kt_{1/2}$$

$$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$$

- Second order reactions that are first order in each reactant.

- We have that

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$$

$$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A][B]_0}{[B][A]_0}$$

- The actual determination is more complicated (there is a textbook problem that walks us through the derivation, though).

- When $[A]_0 = [B]_0$, the integrated rate law simplifies to the second-order integrated rate laws in $[A]$ and $[B]$.

- In this limited case, the half-life is that of the second-order integrated rate law, too, i.e., $t_{1/2} = 1/k[A]_0$.

- The reaction paths and mechanism for parallel reactions.

- Suppose A can become both B and C with respective rate constants k_B and k_C .

- Then

$$\frac{d[A]}{dt} = -k_B[A] - k_C[A] = -(k_B + k_C)[A] \quad \frac{d[B]}{dt} = k_B[A] \quad \frac{d[C]}{dt} = k_C[A]$$

- The integrated rate laws here are

$$[A] = [A]_0 e^{-(k_B + k_C)t} \quad [B] = \frac{k_B}{k_B + k_C} [A]_0 \left(1 - e^{-(k_B + k_C)t}\right) \quad [C] = \frac{k_C}{k_B + k_C} [A]_0 \left(1 - e^{-(k_B + k_C)t}\right)$$

- The ratio of product concentrations is

$$\frac{[B]}{[C]} = \frac{k_B}{k_C}$$

- The yield Φ_i is the probability that a given product i will be formed from the decay of the reactant

$$\Phi_i = \frac{k_i}{\sum_n k_n} \quad \sum_i \Phi_i = 1$$

- Example: If we have parallel reactions satisfying $k_B = 2k_C$, then

$$\Phi_C = \frac{k_C}{k_B + k_C} = \frac{k_C}{2k_C + k_C} = \frac{1}{3}$$

28.3 Office Hours (Tian)

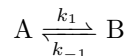
- Why does the reduced mass work in the collision frequency derivation?

- We need to start with a simpler case, or the problem will be really hard; thus, we begin by assuming that the particles all are static.

- We use the reduced mass to consider the relative speed u_r of the particles with respect to the moving particle as our reference frame. So all the others are the relative speeds to our particle. But this necessitates using the relative mass of the particles to our particle (which is the reduced mass).

28.4 Reversible Reactions

4/13: • Let



be a reversible reaction, where k_1 is the rate constant for the forward reaction and k_{-1} is the rate constant for the reverse reaction.

- In this case, we have an equilibrium constant expression

$$K_c = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}}$$

- Additionally, the kinetic conditions for equilibrium are

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0$$

- If the reaction is first order in both $[A]$ and $[B]$, then

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$$

- If $[A] = [A]_0$ at $t = 0$, then $[B] = [A]_0 - [A]$ and

$$-\frac{d[A]}{dt} = (k_1 + k_{-1})[A] - k_{-1}[A]_0$$

- Note that $[B] = [A]_0 - [A]$ iff there is no initial concentration of B, the initial equation was balanced (i.e., each unit of A forms one unit of B), and there is not another component C into which A decomposes.

- Integrating yields

$$[A] = ([A]_0 - [A]_{\text{eq}})e^{-(k_1 + k_{-1})t} + [A]_{\text{eq}}$$

- Note that this equation reduces to the irreversible first order equation as $k_{-1} \rightarrow 0$ and hence $[A]_{\text{eq}} \rightarrow 0$ as well.
 - Similarly, if only the reverse reaction takes place (and we have no initial concentration of B), then $[A] = [A]_{\text{eq}}$ and the above equation reduces to exactly that statement, as desired.

- Since

$$\ln([A] - [A]_{\text{eq}}) = \ln([A]_0 - [A]_{\text{eq}}) - (k_1 + k_{-1})t$$

we have a straight line that allows us to determine the sum $k_1 + k_{-1}$. However, we cannot determine each term individually from the above.

- One way that we can is by noting that at equilibrium, $d[A]/dt = 0$, so the differential rate law reduces to

$$k_1[A]_{\text{eq}} = k_{-1}[B]_{\text{eq}}$$

- Another way we can resolve each term individually is by noting that

$$\frac{k_1}{k_{-1}} = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = K_c$$

- **Stopped flow method:** Fast mixing of reactants.

- The limit is about 1 microsecond time resolution (mixing rate).
 - Lots of issues?

- **Pump-probe method:** An optical/IR method that ranges from femtoseconds to nanoseconds.

- Nobel Prize (1999) to Zewail “for his studies of the transition states of chemical reactions using femtosecond spectroscopy.”
- **Perturbation-Relaxation method:** You perturb a thermodynamic variable (e.g., T , P , pH, etc.) and then follow the kinetics of relaxation of the system to equilibrium.

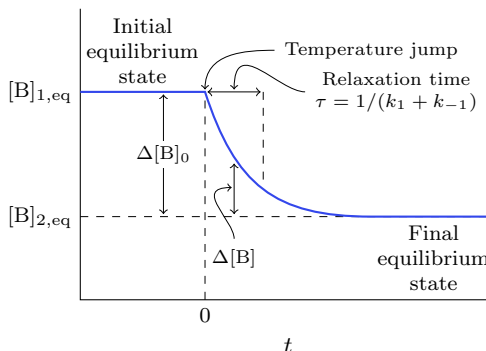


Figure 28.1: Relaxation methods to determine rate constants.

- Nobel Prize (1967) to Porter, Norrish, and Eigen “for their studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short pulses of energy.”
- Example: Consider water autoionization. Here, we’d perturb pH and T .
- Our initial point is the first equilibrium condition; our final point is the second equilibrium condition (i.e., that with the perturbed variables).
- We should have

$$[A] = [A]_{2,eq} + \Delta[A] \qquad [B] = [B]_{2,eq} + \Delta[B]$$

so that

$$\frac{d\Delta[B]}{dt} = k_1[A]_{2,eq} + k_1\Delta[A] - k_{-1}[B]_{2,eq} - k_{-1}\Delta[B]$$

- The sum of the concentrations is constant, so $\Delta([A] + [B]) = \Delta[A] + \Delta[B] = 0$.
- Additionally, detailed balance is satisfied.

$$k_1[A]_{2,eq} = k_{-1}[B]_{2,eq}$$

- As a result,

$$\frac{d\Delta[B]}{dt} = -(k_1 + k_{-1})\Delta[B]$$

- Integrating yields

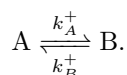
$$\Delta[B]_0 = [B]_{1,eq} - [B]_{2,eq} = \Delta[B]_0 e^{-t/\tau}$$

where τ is the **relaxation time**.

- It follows that

$$\Delta[B] = \Delta[B]_0 e^{-(k_1 + k_{-1})t}$$

- Some textbooks use different notation; we should know this, too.
 - They denote by ξ or ξ_0 the difference between $[A]$ (the initial equilibrium’s concentration) and $[A]_{eq}$ (the final equilibrium’s concentration).
 - They also use k_A, k_B for the initial equilibrium $A \xrightleftharpoons[k_B]{k_A} B$ and k_A^+, k_B^+ for the final equilibrium



- **Relaxation time:** The following quantity. Denoted by τ . Given by

$$\tau = \frac{1}{k_1 + k_{-1}}$$

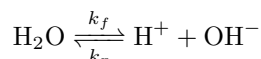
- We'll start with water dissociation next lecture.

28.5 Water Dissociation, Temperature Dependence, and TST

4/15:

- **T-jump:** A temperature perturbation.
- Relaxation methods and water dissociation.

- Consider the equilibrium



- The differential rate laws are

$$\frac{d[\text{H}_2\text{O}]}{dt} = -k_f[\text{H}_2\text{O}] + k_r[\text{H}^+][\text{OH}^-] \quad \frac{d[\text{H}^+]}{dt} = k_f[\text{H}_2\text{O}] - k_r[\text{H}^+][\text{OH}^-]$$

- After the T-jump, the system relaxes to a new equilibrium

$$K_c = \frac{k_f^+}{k_r^+} = \frac{[\text{H}^+]_{eq}[\text{OH}^-]_{eq}}{[\text{H}_2\text{O}]_{eq}}$$

- It follows that

$$\begin{aligned} \frac{d\xi}{dt} &= -k_f^+[\text{H}_2\text{O}] + k_r^+[\text{H}^+][\text{OH}^-] \\ &= -k_f^+\xi - k_r^+\xi([\text{H}^+]_{eq} + [\text{OH}^-]_{eq}) + O(\xi^2) \end{aligned}$$

- Note that we get from the first line to the second by substituting $[\text{H}^+] = [\text{H}^+]_{eq} - \xi$ and $[\text{OH}^-] = [\text{OH}^-]_{eq} - \xi$ and expanding.

- The associated relaxation time is

$$\frac{1}{\tau} = k_f^+ + k_r^+([\text{H}^+]_{eq} + [\text{OH}^-]_{eq})$$

- Note that this implies that this relaxation time can be measured experimentally.

- Rates of reaction depend on temperature.
- The empirical temperature dependence of the rate constant k is given by

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

- If the activation energy is independent of temperature, then

$$\begin{aligned} \ln k &= \ln A - \frac{E_a}{RT} \\ k &= Ae^{-E_a/RT} \end{aligned}$$

i.e., we get the Arrhenius equation.

- If we obtain two rate constants at two temperatures, we can get

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

- Note that plots of k vs. $1/T$ can be nonlinear if the prefactor or “encounter frequency” is temperature-dependent, i.e., if we have

$$k = aT^m e^{-E'/RT}$$

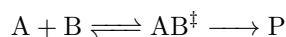
where a , E' , and m are temperature-independent constants.

- Using Transition State Theory (TST) to estimate rate constants.

- Let the following be a chemical reaction and its rate law.



- Suppose that the reaction proceeds by way of a special intermediate species, the activated complex.



- We know that

$$K_c^\ddagger = \frac{[AB^\ddagger]/c^\circ}{[A]/c^\circ[B]/c^\circ} = \frac{[AB^\ddagger]c^\circ}{[A][B]}$$

where c° is the standard-state concentration.

- Write the equilibrium constant expression in terms of the partition functions q_A , q_B , and q^\ddagger for A, B, and AB^\ddagger .

$$K_c^\ddagger = \frac{(q^\ddagger/V)c^\circ}{(q_A/V)(q_B/V)}$$

- If ν_c is the frequency of crossing the barrier top, then

$$\frac{d[P]}{dt} = \nu_c [AB^\ddagger]$$

- Thus, we can relate

$$k = \frac{\nu_c K_c^\circ}{c^\circ}$$

- 2 hour midterm at the end of this month (April) taken at home.

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