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* $\boldsymbol{Q(T)}$. *Given by*

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

• **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

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

- "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 $N/N_\mathrm{A} = n$ and $M/N_\mathrm{A} = m$, we have that

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

• Important values of molecular speed u.

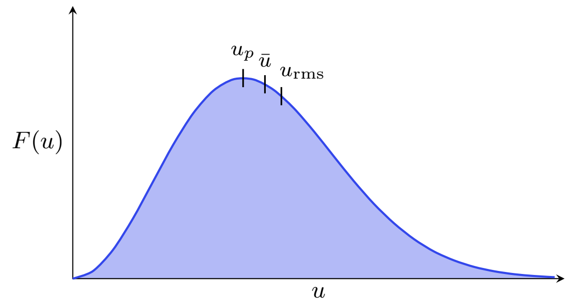


Figure 27.1: Important values of molecular speed.

- **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* $\boldsymbol{f(u)}$. *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* $\boldsymbol{u_p}$. *Given by*

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

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

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

- 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 $u_x, u_x + \mathrm{d}u_x$, $u_y, u_y + \mathrm{d}u_y$, and $u_z, u_z + \mathrm{d}u_z$, where $f(u_i)$ is the probability distribution of components i.
    - Note that $h(u)$ is *not* the speed distribution with velocity components between $u, u + \mathrm{d}u$.
  - Clever step: Note that the logarithmic form of the above equation leads to
  $$\begin{aligned} \ln h(u) &= \ln f(u_x) + \ln f(u_y) + \ln f(u_z) \\ \left(\frac{\partial \ln h}{\partial u_x}\right)_{u_y,u_z} &= \frac{\mathrm{d}\ln h}{\mathrm{d}u}\left(\frac{\partial u}{\partial u_x}\right)_{u_y,u_z} \\ &= \frac{u_x}{u}\frac{\mathrm{d}\ln h}{\mathrm{d}u} \end{aligned}$$
  where we evaluate $\partial u/\partial u_x$ by using the generalized Pythagorean theorem definition of u.

- Additionally, we have that

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

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

$$\frac{\mathrm{d}\ln h(u)}{u\,\mathrm{d}u} = \frac{\mathrm{d}\ln f(u_x)}{u_x\,\mathrm{d}u_x}$$

- It follows since the gas is isotropic that

$$\frac{\mathrm{d}\ln h(u)}{u\,\mathrm{d}u} = \frac{\mathrm{d}\ln f(u_x)}{u_x\,\mathrm{d}u_x} = \frac{\mathrm{d}\ln f(u_y)}{u_y\,\mathrm{d}u_y} = \frac{\mathrm{d}\ln f(u_z)}{u_z\,\mathrm{d}u_z}$$

- 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

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

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,

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

should help rationalize the 2.

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

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

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

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

- Solving for γ.
  - We know from the previous lecture that

$$\begin{aligned}\frac{1}{3}m\left\langle u^2\right\rangle &= RT\\ \left\langle u^2\right\rangle &= \frac{3RT}{M}=\frac{3k_\mathrm{B}T}{m}\\ \left\langle u_x^2\right\rangle &= \frac{RT}{M}\end{aligned}$$

  - 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)

$$\left\langle u_x^2\right\rangle=\int_{-\infty}^{\infty}u_x^2f(u_x)\,\mathrm{d}u_x$$

  - Thus, we have that

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

- It follows that

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

- 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.
$$I(\nu) \propto \mathrm{e}^{-mc^2(\nu-\nu_0)^2/2\nu_0 k_\mathrm{B}T}$$
- Thus, the variance of the spectral line is
$$\sigma^2 = \frac{\nu_0^2 k_\mathrm{B}T}{mc^2} = \frac{\nu_0^2 RT}{Mc^2}$$
- 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
$$\begin{aligned}\langle u_x+\rangle &= \int_0^\infty u_x f(u_x)\,\mathrm{d}u_x\\ &= \sqrt{\frac{m}{2\pi k_\mathrm{B}T}}\int_0^\infty u_x \mathrm{e}^{-mu_x^2/2k_\mathrm{B}T}\\ &= \sqrt{\frac{m}{2\pi k_\mathrm{B}T}}\cdot\frac{2k_\mathrm{B}T}{2m}\\ &= \sqrt{\frac{m}{2\pi k_\mathrm{B}T}}\end{aligned}$$
  - 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
$$F(u)\,\mathrm{d}u \approx f(u_x)\,\mathrm{d}u_x\, f(u_y)\,\mathrm{d}u_y\, f(u_z)\,\mathrm{d}u_z$$
    - 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
$$F(u)\,\mathrm{d}u \approx \left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} \mathrm{e}^{-m(u_x^2+u_y^2+u_z^2)/2k_\mathrm{B}T}\,\mathrm{d}u_x\,\mathrm{d}u_y\,\mathrm{d}u_z$$
    from where we can convert to spherical coordinates using $u^2 = u_x^2 + u_y^2 + u_z^2$ and $4\pi u^2\,\mathrm{d}u = \mathrm{d}u_x\,\mathrm{d}u_y\,\mathrm{d}u_z$ to get our final result.
$$F(u)\,\mathrm{d}u = 4\pi\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} u^2\mathrm{e}^{-mu^2/2k_\mathrm{B}T}\,\mathrm{d}u$$
  - 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 $u_x, u_x + \mathrm{d}u_x$, $u_y, u_y + \mathrm{d}u_y$, and $u_z, u_z + \mathrm{d}u_z$.
- $f(u_x) = \sqrt{M/2\pi RT}\mathrm{e}^{-Mu_x^2/2RT}$ is the distribution of molecular speed componentwise in Cartesian coordinates, and has a Gaussian distribution.
- $F(u) = 4\pi\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} u^2\mathrm{e}^{-mu^2/2k_\mathrm{B}T}$ 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

$$\langle u\rangle = \sqrt{\frac{8RT}{\pi M}} \qquad u_\mathrm{rms} = \sqrt{\frac{3RT}{M}} \qquad u_\mathrm{mp} = \sqrt{\frac{2k_\mathrm{B}T}{m}}$$

27.3 Energy Distribution and Collision Frequency

4/1:

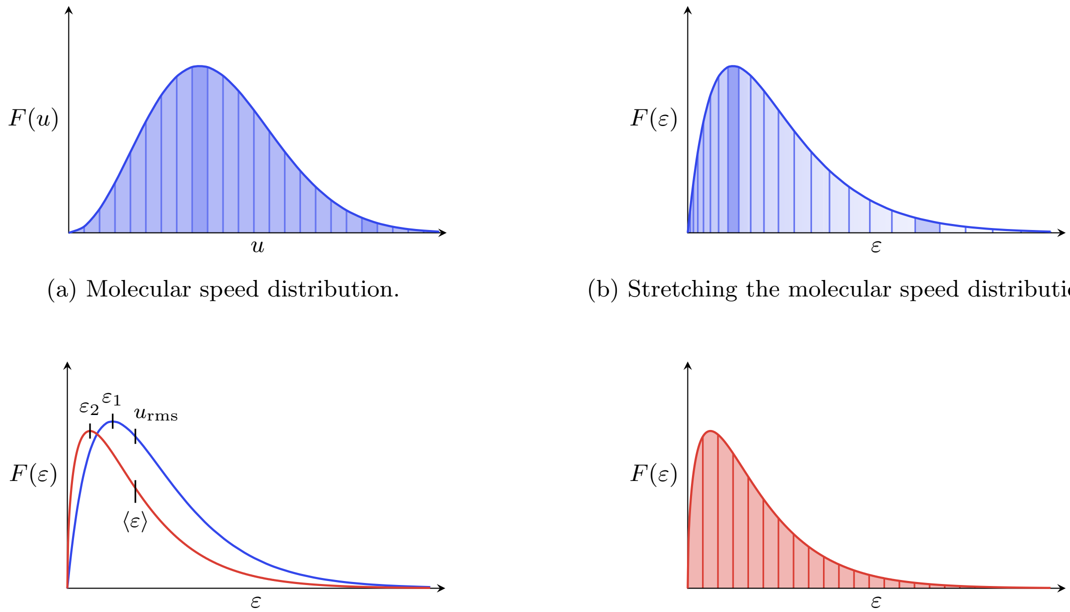
- The final exam is 50 minutes on the last day of class.
- We can also express the M-B distribution in terms of kinetic energy.
  - We know that energy $\varepsilon = \frac{1}{2}mu^2$, so $u = \sqrt{2\varepsilon/m}$ and thus $\mathrm{d}u = \mathrm{d}\varepsilon/\sqrt{2m\varepsilon}$.
  - This allows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

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

  - Thus, we can calculate that

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

    as expected.
- Aside: Understanding the probability distribution $F(u)\,\mathrm{d}u$ and the relation between $F(u)\,\mathrm{d}u$ and $F(\varepsilon)\,\mathrm{d}\varepsilon$.
  - $F(u)$ 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).



(a) Molecular speed distribution.

(b) Stretching the molecular speed distribution.

(c) Comparing the energy and speed distributions.

(d) Molecular energy distribution.

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.

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

  - The most probable energy calculated from the most probable speed via $\frac{1}{2}mu_{\text{mp}}^2$ is $k_{\mathrm{B}}T$, so the actual value is one-half the predicted value (notice how $\varepsilon_2 = \frac{1}{2}\varepsilon_1$).

- Since $\langle\varepsilon\rangle = \left\langle\frac{1}{2}mu^2\right\rangle$, $\langle\varepsilon\rangle$ is related to the root mean square speed.
  - This relates $u_{\text{rms}}^2 = 3k_{\mathrm{B}}T/m$ to $\langle\varepsilon\rangle = 3k_{\mathrm{B}}T/2$ 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.

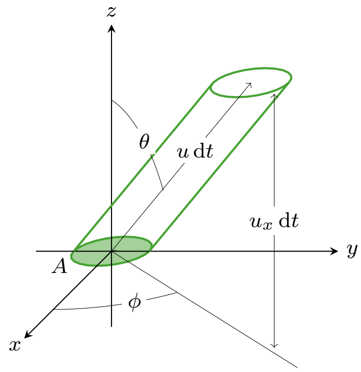


Figure 27.3: Collision frequency cylinder.

  - 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 $\mathrm{d}t$.
  - Its volume is $V = Au\cos\theta\,\mathrm{d}t$.
  - The number of molecules in the cylinder is ρV, where ρ is the number density.
  - The fraction of molecules that have a speed between $u, u+\mathrm{d}u$ is $F(u)\,\mathrm{d}u$.
  - The fraction travelling within a solid angle bounded by $\theta, \theta+\mathrm{d}\theta$ and $\phi, \phi+\mathrm{d}\phi$ is $\sin\theta\,\mathrm{d}\theta\cdot\mathrm{d}\phi\,/4\pi$, where 4π represents a complete solid angle.
  - The number $\mathrm{d}N_{\text{coll}}$ of molecules colliding with the area A from the specified direction in the time interval $\mathrm{d}t$ is

$$\mathrm{d}N_{\text{coll}} = \rho(Au\,\mathrm{d}t)\cos\theta\cdot F(u)\,\mathrm{d}u\cdot\frac{\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi}{4\pi}$$

  - The number of collisions per unit time per unit area with the wall by molecules whose speeds are in the range $u, u+\mathrm{d}u$ and whose direction lies within the solid angle $\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$ is

$$\mathrm{d}z_{\text{coll}} = \frac{1}{A}\frac{\mathrm{d}N_{\text{coll}}}{\mathrm{d}t} = \frac{\rho}{4\pi}uF(u)\,\mathrm{d}u\cdot\cos\theta\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

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

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

- Deriving the pressure through the collision frequency.
  - We have

$$\begin{aligned}
\mathrm{d}P &= (2mu\cos\theta)\,\mathrm{d}z_{\text{coll}}\\
&= (2mu\cos\theta)\frac{\rho}{4\pi}uF(u)\,\mathrm{d}u\cos\theta\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\\
&= \rho\left(\frac{m}{2\pi k_{\text{B}}T}\right)^{3/2}(2mu\cos\theta)u^3\mathrm{e}^{-mu^2/2k_{\text{B}}T}\,\mathrm{d}u\cos\theta\sin\theta\,\mathrm{d}\phi
\end{aligned}$$

  - Thus, since

$$\int_0^{\pi/2}\cos^2\theta\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi = \frac{2\pi}{3} \qquad 4\pi\left(\frac{m}{2\pi k_{\text{B}}T}\right)^{3/2}\int_0^\infty u^4\mathrm{e}^{-mu^2/2k_{\text{B}}T}\,\mathrm{d}u = \langle u^2\rangle$$

    we have that

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

27.4 Office Hours (Tian)

- Can you explain the whole $F(u)\,\mathrm{d}u$ differential notation for probability?
  - $F(u)$ is the probability function. $F(u)$ is the y axis of the individual points. Probability density.
  - $F(u)\,\mathrm{d}u$ 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.
  - $\int_0^\infty F(u)\,\mathrm{d}u = 1$ (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
$$\begin{aligned}\langle\varepsilon\rangle &= \left\langle \frac{1}{2}mu^2 \right\rangle\\ &= \frac{1}{2}m\left\langle u^2\right\rangle\\ &= \frac{1}{2}mu_{\text{rms}}^2\\ &= \frac{m}{2}\cdot\frac{3k_\text{B}T}{m}\\ &= \frac{3k_\text{B}T}{2}\end{aligned}$$
- 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:
$$4\pi = \int_{-\pi/2}^{\pi/2} \sin\theta\,\mathrm{d}\theta \int_0^{2\pi}\mathrm{d}\phi$$
- 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 bassed 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.

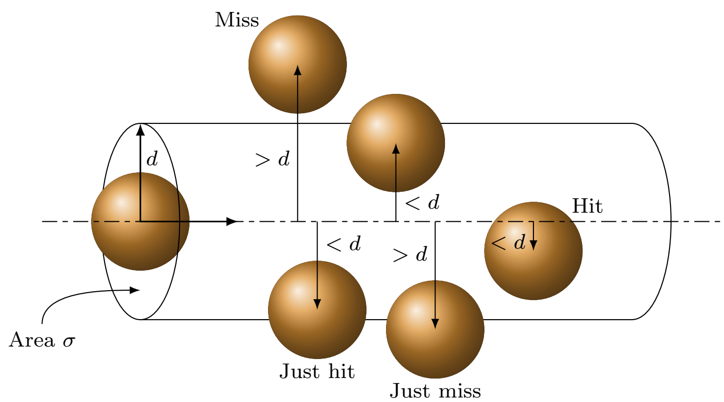


Figure 27.4: Collision cylinder.

  - 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 $\mathrm{d}t$ is

$$\mathrm{d}N_{\text{coll}} = \rho\sigma \langle u \rangle \mathrm{d}t$$

    where $\rho = N/V$.
  - The collision frequency z_A is

$$z_A = \frac{\mathrm{d}N_{\text{coll}}}{\mathrm{d}t} = \rho\sigma \langle u \rangle = \rho\sigma\sqrt{\frac{8k_{\mathrm{B}}T}{\pi m}}$$

  - 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 $\rho = PN_\text{A}/RT$ by its ideal gas value, then we have

$$l = \frac{RT}{\sqrt{2}N_\text{A}\sigma P} = \frac{k_\text{B}T}{\sqrt{2}\sigma\rho}$$

  - Now $k_\text{B}T$ 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 $E = k_\text{B}T$ 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 $\mathrm{d}x$ tells us over how much space we're moving.
    - $\sigma\,\mathrm{d}x$ 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 $x, x + \mathrm{d}x$ is

$$\begin{aligned}
n(x) - n(x+\mathrm{d}x) &= \sigma\rho n(x)\,\mathrm{d}x \\
\frac{n(x+\mathrm{d}x) - n(x)}{\mathrm{d}x} &= -\sigma\rho n(x) \\
\frac{\mathrm{d}n}{\mathrm{d}x} &= -\sigma\rho n
\end{aligned}$$

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

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

    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 $x, x + \mathrm{d}x$ is $n(x) - n(x + \mathrm{d}x)$.
  - The probability that one of the initial n_0 molecules will collide in this interval is

$$p(x)\,\mathrm{d}x = \frac{n(x) - n(x+\mathrm{d}x)}{n_0} = -\frac{1}{n_0}\frac{\mathrm{d}n}{\mathrm{d}x}\,\mathrm{d}x = \frac{1}{l}\mathrm{e}^{-x/l}\,\mathrm{d}x$$

- 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 $P(x)$.
$$P(x) = \int_0^x p(x')\,\mathrm{d}x'$$

- 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
$$\sigma_{AB} = \pi \left(\frac{d_A + d_B}{2}\right)^2 \qquad \langle u_r \rangle = \sqrt{\frac{8k_\mathrm{B}T}{\pi\mu}} \qquad \mu = \frac{m_A m_B}{m_A + m_B}$$
    - 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 $u, u + \mathrm{d}u$ and whose direction lies within the solid angle $\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$ is approximately $u^3 \mathrm{e}^{-mu^2/2k_\mathrm{B}T}$.
  - 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 $u, u + \mathrm{d}u$.
    - We have that $\mathrm{d}Z_{AB} \propto u_r^3 \mathrm{e}^{-\mu u_r^2/2k_\mathrm{B}T}\,\mathrm{d}u_r$. Thus, if A is a proportionality constant, then
$$\mathrm{d}Z_{AB} = A u_r^3 \mathrm{e}^{-\mu u_r^2/2k_\mathrm{B}T}\,\mathrm{d}u_r$$

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

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

- Thus, we know that

$$\mathrm{d}Z_{AB} = \sigma_{AB}\rho_A\rho_B\sqrt{\left(\frac{\mu}{k_\text{B}T}\right)^3\cdot\frac{2}{\pi}}\mathrm{e}^{-\mu u_r^2/2k_\text{B}T}u_r^3\,\mathrm{d}u_r$$

  - 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

$$PV = \frac{1}{3}Nm\left\langle u^2\right\rangle$$

    as a fundamental equation of KMT, as it relates a macroscopic property PV to a microscopic property $m\left\langle u^2\right\rangle$.
  - 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 $\frac{3}{2}k_BT$. From classical mechanics, we also have that $\langle E_\text{trans}\rangle = \frac{1}{2}m\left\langle u^2\right\rangle$. *This* is why we may let

$$\frac{1}{2}m\left\langle u^2\right\rangle = \frac{3}{2}k_BT$$

    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 $\left\langle u_x^2 \right\rangle = \left\langle u_y^2 \right\rangle = \left\langle u_z^2 \right\rangle$.
- McQuarrie and Simon (1997) derives

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

  - u_{rms} is an estimate of the average speed since $\left\langle u^2 \right\rangle \neq \left\langle u \right\rangle^2$ 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 $h(u_x, u_y, u_z)\,\mathrm{d}u_x\,\mathrm{d}u_y\,\mathrm{d}u_z$ be the fraction of molecules with velocity components between u_j and $u_j + \mathrm{d}u_j$ 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

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

  - Since

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

[1] This can be proven.

we have that

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

which generalizes to

$$\frac{\mathrm{d}\ln h(u)}{u\,\mathrm{d}u} = \frac{\mathrm{d}\ln f(u_x)}{u_x\,\mathrm{d}u_x} = \frac{\mathrm{d}\ln f(u_y)}{u_y\,\mathrm{d}u_y} = \frac{\mathrm{d}\ln f(u_z)}{u_z\,\mathrm{d}u_z}$$

- 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

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

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.

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

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

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

- Therefore,

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

- 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

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

- We can also calculate that $\langle u_x^2 \rangle = RT/M$ and $m\langle u_x \rangle^2/2 = k_BT/2$ 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

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

  i.e., that $I(\nu)$ is of the form of a Gaussian centered at ν_0 with variance $\sigma^2 = \nu_0^2k_BT/mc^2$.
- Deriving **Maxwell-Boltzmann distribution**.
  - Let the probability that a molecule has speed between u and $u + \mathrm{d}u$ be defined by a continuous probability distribution $F(u)\,\mathrm{d}u$. In particular, we have from the above isotropic condition that

$$\begin{aligned}F(u)\,\mathrm{d}u &= f(u_x)\,\mathrm{d}u_x\,f(u_y)\,\mathrm{d}u_y\,f(u_z)\,\mathrm{d}u_z\\ &= \left(\frac{m}{2\pi k_BT}\right)^{3/2}\mathrm{e}^{-m(u_x^2+u_y^2+u_z^2)/2k_BT}\,\mathrm{d}u_x\,\mathrm{d}u_y\,\mathrm{d}u_z\end{aligned}$$

  - 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 $4\pi u^2\,\mathrm{d}u = \mathrm{d}u_x\,\mathrm{d}u_y\,\mathrm{d}u_z$.
  - Thus, the Maxwell-Boltzmann distribution in terms of speed is

$$F(u)\,\mathrm{d}u = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}u^2\mathrm{e}^{-mu^2/2k_BT}\,\mathrm{d}u$$

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

[2]See 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 odd
$=$	$\frac{(n/2)!}{\alpha^{(n+2)/2}}$	n 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* $\boldsymbol{u}_{\text{mp}}$. *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

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

- 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.

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

  - Note that the above equation is of the form $u^3e^{-mu^2/2k_BT}$ whereas M-B distribution is of the form $u^2e^{-mu^2/2k_BT}$.
    - 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.
$$\rho = \frac{N}{V} = \frac{N_\text{A}n}{V} = \frac{N_\text{A}P}{RT}$$
- (Re)deriving $P = \rho m \left\langle u^2 \right\rangle /3$ 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 $u+\mathrm{d}u$ that lie within the solid angle $\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$ is
$$\begin{aligned}\mathrm{d}P &= (2mu\cos\theta)\,\mathrm{d}z_\text{coll}\\ &= \rho\left(\frac{m}{2\pi k_\text{B}T}\right)^{3/2}(2mu\cos\theta)u^3\mathrm{e}^{-mu^2/2k_\text{B}T}\,\mathrm{d}u\cos\theta\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\end{aligned}$$
  - It follows since
$$\int_0^{\pi/2}\cos^2\theta\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi = \frac{2\pi}{3} \qquad 4\pi\left(\frac{m}{2\pi k_\text{B}T}\right)^{3/2}\int_0^\infty u^4\mathrm{e}^{-mu^2/2k_\text{B}T}\,\mathrm{d}u = \left\langle u^2\right\rangle$$
that
$$P = \rho m\cdot\frac{\left\langle u^2\right\rangle}{2\pi}\cdot\frac{2\pi}{3} = \frac{1}{3}\rho m\left\langle u^2\right\rangle$$

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* $\boldsymbol{\sigma}$. *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_2H_4	430	0.580

Table 27.2: Collision diameters and collision cross sections.

- Calculating the number of collisions $\mathrm{d}N_{\mathrm{coll}}$ the moving molecule makes in the time $\mathrm{d}t$.
  - The volume of the collision cylinder is the product of its cross section σ and its length $\langle u\rangle \,\mathrm{d}t$.
  - Whenever the center of another molecule lies within this cylinder, a collision will occur.
  - Thus, since $\sigma \langle u\rangle \,\mathrm{d}t$ represents a small volume within the overall volume the gas occupies, the expected number of collisions $\mathrm{d}N_{\mathrm{coll}}$ would be equal to the number of molecules expected to lie in the volume $\sigma \langle u\rangle \,\mathrm{d}t$.
  - 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

$$\mathrm{d}N_{\mathrm{coll}} = \rho\sigma \langle u\rangle \,\mathrm{d}t$$

  - 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* $\boldsymbol{z_A}$. *Given by*

$$\begin{aligned} z_A = \frac{\mathrm{d}N_{\mathrm{coll}}}{\mathrm{d}t} &= \rho\sigma \langle u_r\rangle = \rho\sigma\sqrt{\frac{8k_{\mathrm{B}}T}{\pi\mu}} \\ &= \sqrt{2}\rho\sigma \langle u\rangle = \sqrt{2}\rho\sigma\sqrt{\frac{8k_{\mathrm{B}}T}{\pi m}} \end{aligned}$$

- **Mean free path**: The average distance that a molecule travels between collisions. *Denoted by* $\boldsymbol{l}$. *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 $\rho = N/V = nN_{\mathrm{A}}/V = PN_{\mathrm{A}}/RT$ yields

$$l = \frac{RT}{\sqrt{2}N_{\mathrm{A}}\sigma P}$$

- 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 $\mathrm{d}x$. It follows that the volume of the "collision cylinder" is $1 \cdot \mathrm{d}x = \mathrm{d}x$.
  - Consequently, the number of molecules having center within the collision cylinder is equal to the number density times the volume, or $\rho\,\mathrm{d}x$.
  - Thus, if each molecule has target area σ, then the total target area presented by these molecules (neglecting overlap) is $\sigma\rho\,\mathrm{d}x$.
  - 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 $\sigma\rho\,\mathrm{d}x$.
    - Note that this squares with the definition of the probability of a collision as $\rho\sigma\langle u\rangle\,\mathrm{d}t$ with $\mathrm{d}x = \langle u\rangle\,\mathrm{d}t$, as we'd expect.
- As we can see, the probability of a collision increases with increasing distance traveled $\mathrm{d}x$.
- 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 $x, x + \mathrm{d}x$ is $n(x)\sigma\rho\,\mathrm{d}x$.
  - Furthermore, said number is naturally equal to $n(x) - n(x + \mathrm{d}x)$.
  - Thus, we have that

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

  where no factor of $\sqrt{2}$ appears because of the assumption that the other molecules do not move.
- Therefore, the probability $p(x)\,\mathrm{d}x$ that one of the initial n_0 molecules will collide in the interval $x, x+\mathrm{d}x$ is

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

  - 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.

Chapter 28

Rate Laws

28.1 Definitions and Methods of Determination

4/8:

- Consider a general chemical equation

$$\nu_{\mathrm{A}}\mathrm{A} + \nu_{\mathrm{B}}\mathrm{B} \longrightarrow \nu_{\mathrm{Y}}\mathrm{Y} + \nu_{\mathrm{Z}}\mathrm{Z}$$

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

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

- The rate of change (moles/second) is

$$\frac{\mathrm{d}n_A}{\mathrm{d}t} = -\nu_A \frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad\qquad \frac{\mathrm{d}n_Y}{\mathrm{d}t} = \nu_Y \frac{\mathrm{d}\xi}{\mathrm{d}t}$$

- Deriving the rate of reaction for a gas-based chemical reaction.
  - Time-dependent concentration changes

$$\frac{1}{V}\frac{\mathrm{d}n_A}{\mathrm{d}t} = \frac{\mathrm{d}[A]}{\mathrm{d}t} = -\frac{\nu_A}{V}\frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad\qquad \frac{1}{V}\frac{\mathrm{d}n_Y}{\mathrm{d}t} = \frac{\mathrm{d}[Y]}{\mathrm{d}t} = -\frac{\nu_Y}{V}\frac{\mathrm{d}\xi}{\mathrm{d}t}$$

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

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

  - 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 $2\,\mathrm{NO}_{(\mathrm{g})} + \mathrm{O}_{2(\mathrm{g})} \longrightarrow 2\,\mathrm{NO}_{2(\mathrm{g})}$, we have

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

  - It follows that $v(t) = k[\mathrm{NO}]^2[\mathrm{O}_2]$.
  - 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 $\mathrm{H}_2 + \mathrm{Br}_2 \longrightarrow 2\,\mathrm{HBr}$ has rate law

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

- 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

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

    - 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.

28.2 Integrated Rate Laws

4/11:
- First order reactions have exponential integrated rate laws.
  - Suppose $\mathrm{A} + \mathrm{B} \longrightarrow$ products.
  - Suppose the reaction is first order in A.
  - If the concentration of A is $[\mathrm{A}]_0$ at $t = 0$ and $[\mathrm{A}]$ at time t, then

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

    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
$$[\mathrm{A}(t_{1/2})] = \frac{[\mathrm{A}(0)]}{2} = \frac{[\mathrm{A}]_0}{2}$$
  - We have
$$\begin{aligned}\ln\frac{1}{2} &= -kt_{1/2}\\ t_{1/2} &= \frac{\ln 2}{k} \approx \frac{0.693}{k}\end{aligned}$$
  - Notice that the above equation does not depend on [A] or [B]!
- Second order reactions have inverse concentration integrated rate laws.
  - Suppose $\mathrm{A} + \mathrm{B} \longrightarrow$ products, as before, and that the reaction is second order in A.
  - Then
$$\begin{aligned}-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} &= k[\mathrm{A}]^2\\ \int_{[\mathrm{A}]_0}^{[\mathrm{A}]} -\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^2} &= \int_0^t k\,\mathrm{d}t\\ \frac{1}{[\mathrm{A}]} &= \frac{1}{[\mathrm{A}]_0} + kt\end{aligned}$$
    is the integrated rate law.
- The half-life of a second-order reaction is dependent on the initial amount of reaction.
  - We have that
$$\begin{aligned}\frac{1}{[\mathrm{A}]_0/2} &= \frac{1}{[\mathrm{A}]_0} + kt_{1/2}\\ \frac{1}{[\mathrm{A}]_0} &= kt_{1/2}\\ t_{1/2} &= \frac{1}{k[\mathrm{A}]_0}\end{aligned}$$
- If a reaction is n^{th}-order in a reactant for $n \geq 2$, then the integrated rate law is given by
$$\begin{aligned}-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} &= k[\mathrm{A}]^n\\ \int_{[\mathrm{A}]_0}^{[\mathrm{A}]} -\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^n} &= \int_0^t k\,\mathrm{d}t\\ \frac{1}{n-1}\left(\frac{1}{[\mathrm{A}]^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right) &= kt\end{aligned}$$
  - The associated half life is
$$\begin{aligned}\frac{1}{n-1}\left(\frac{1}{([\mathrm{A}]_0/2)^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right) &= kt_{1/2}\\ \frac{1}{n-1}\cdot\frac{2^{n-1}-1}{[\mathrm{A}]_0^{n-1}} &= kt_{1/2}\\ t_{1/2} &= \frac{2^{n-1}-1}{k(n-1)[\mathrm{A}]_0^{n-1}}\end{aligned}$$

- Second order reactions that are first order in each reactant.
  - We have that
    $$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}]$$
    $$kt = \frac{1}{[\mathrm{A}]_0 - [\mathrm{B}]_0} \ln \frac{[\mathrm{A}][\mathrm{B}]_0}{[\mathrm{B}][\mathrm{A}]_0}$$
  - The actual determination is more complicated (there is a textbook problem that walks us through the derivation, though).
  - When $[\mathrm{A}]_0 = [\mathrm{B}]_0$, 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., $t_{1/2} = 1/k[\mathrm{A}]_0$.
- 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
    $$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_B[\mathrm{A}] - k_C[\mathrm{A}] = -(k_B + k_C)[\mathrm{A}] \qquad \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_B[\mathrm{A}] \qquad \frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k_C[\mathrm{A}]$$
  - The integrated rate laws here are
    $$[\mathrm{A}] = [\mathrm{A}]_0 \mathrm{e}^{-(k_B+k_C)t} \quad [\mathrm{B}] = \frac{k_B}{k_B + k_C}[\mathrm{A}]_0 \left(1 - \mathrm{e}^{-(k_B+k_C)t}\right) \quad [\mathrm{C}] = \frac{k_C}{k_B + k_C}[\mathrm{A}]_0 \left(1 - \mathrm{e}^{-(k_B+k_C)t}\right)$$
  - The ratio of product concentrations is
    $$\frac{[\mathrm{B}]}{[\mathrm{C}]} = \frac{k_B}{k_C}$$
  - The yield Φ_i is the probability that a given product i will be formed from the decay of the reactant
    $$\Phi_i = \frac{k_i}{\sum_n k_n} \qquad \sum_i \Phi_i = 1$$
- 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

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

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

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

- Additionally, the kinetic conditions for equilibrium are

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

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

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

- If $[\mathrm{A}] = [\mathrm{A}]_0$ at $t = 0$, then $[\mathrm{B}] = [\mathrm{A}]_0 - [\mathrm{A}]$ and

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

  - Note that $[\mathrm{B}] = [\mathrm{A}]_0 - [\mathrm{A}]$ 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

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

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

- Since

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

  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, $\mathrm{d}[\mathrm{A}]/\mathrm{d}t = 0$, so the differential rate law reduces to

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

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

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

• **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.

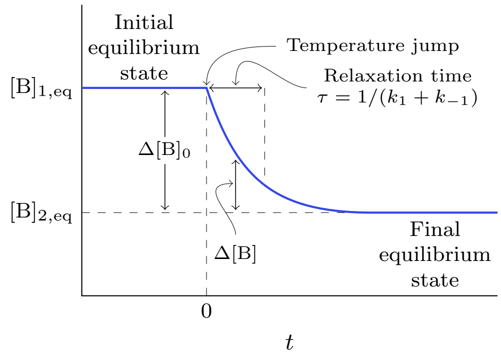


Figure 28.1: Relaxation methods to determine rate constants.

  - 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; out final point is the second equilibrium condition (i.e., that with the perturbed variables).
  - We should have

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

    so that

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

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

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

  - As a result,

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

  - Integrating yields

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

    where τ is the **relaxation time**.
  - It follows that

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

  - 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 $[\mathrm{A}]_{eq}$ (the final equilibrium's concentration).
    - They also use k_A, k_B for the initial equilibrium $\mathrm{A} \underset{k_B}{\overset{k_A}{\rightleftharpoons}} \mathrm{B}$ and k_A^+, k_B^+ for the final equilibrium $\mathrm{A} \underset{k_B^+}{\overset{k_A^+}{\rightleftharpoons}} \mathrm{B}$.

- **Relaxation time**: The following quantity. *Denoted by* $\boldsymbol{\tau}$. *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

$$\mathrm{H_2O} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{H^+} + \mathrm{OH^-}$$

  - The differential rate laws are

$$\frac{\mathrm{d}[\mathrm{H_2O}]}{\mathrm{d}t} = -k_f[\mathrm{H_2O}] + k_r[\mathrm{H^+}][\mathrm{OH^-}] \qquad \frac{\mathrm{d}[\mathrm{H^+}]}{\mathrm{d}t} = k_f[\mathrm{H_2O}] - k_r[\mathrm{H^+}][\mathrm{OH^-}]$$

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

$$K_c = \frac{k_f^+}{k_r^+} = \frac{[\mathrm{H^+}]_{eq}[\mathrm{OH^-}]_{eq}}{[\mathrm{H_2O}]_{eq}}$$

  - It follows that

$$\begin{aligned}\frac{\mathrm{d}\xi}{\mathrm{d}t} &= -k_f^+[\mathrm{H_2O}] + k_r^+[\mathrm{H^+}][\mathrm{OH^-}] \\ &= -k_f^+\xi - k_r^+\xi([\mathrm{H^+}]_{eq} + [\mathrm{OH^-}]_{eq}) + \mathrm{O}(\xi^2)\end{aligned}$$

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

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

    - 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

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

  - If the activation energy is independent of temperature, then

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

    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

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

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.

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{P} \qquad\qquad \frac{\mathrm{d[P]}}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}]$$

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

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB}^\ddagger \longrightarrow \mathrm{P}$$

  - We know that

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

  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 $\mathrm{AB}^\ddagger$.

$$K_c^\ddagger = \frac{(q^\ddagger/V)c^\circ}{(q_\mathrm{A}/V)(q_\mathrm{B}/V)}$$

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

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

  - 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.

28.6 Office Hours (Tian)

- Stopped flow method?
  - Two syringes have substances that get mixed and then become a homogeneous mixture where they start to do all of the interesting chemistry. Before the substances enter the chamber, though, they pass by a detector that monitors the concentration of the initial species. Concentration is measured after good mixing.
  - It is called *stopped* flow because we want to fix the initial concentration of A and B. Inject them, let them mix, stop the flow, measure the concentration, and then let the chemistry proceed.
  - Only used if mixing is much faster than reaction.
  - This is the experimental set-up for the method of initial rates or the method of exhaustion.
  - Caveats/issues: Approximating Δt as $\mathrm{d}t$.
- TST diagram lines?
  - The quantized states lines refer to the energy levels of the reactants and products summarized by the partition function.

  - The reactants reach the activated complex just at some higher quantized energy state!

- Physical interpretation of τ beyond the time it takes the initial reactants to reach 1/e of their initial concentration.
  - You wanna see how fast the transition/relaxation would be, and τ is just a measure of how fast the transition goes.
  - Also relates to k_1 and k_{-1}.
  - Think in terms of adaptability (biological systems). Relation to how fast you can adapt to things like new temperature changes. We want to adapt to environmental changes as fast as possible.
  - A measure of adaptability, response time, and smart materials that labs are developing to respond to changes very quickly. Also instrumentation response time (which you want to be very fast).
  - Sometimes, you don't want to adapt to changes too quickly (such as cold-blooded animals).
- Importance of Chapter 24 (or 26, depending on edition)?
  - Good to know general stuff/big picture ideas as a prerequisite.
  - Don't worry about specific things tho.
- Pump-probe method?
  - No further discussion of it in this chapter; Tian might talk about it more in later chapters, tho.
  - Mostly for intra-molecular reactions, like accessing excited states and seeing how they decay.
  - Optical pumping (form IChem I, PSet 8) is one way to do a pump-probe experiment.
- Parallel reactions?
  - Behave much the same kinetically as others; only difference is there is a yield.

28.7 Chapter 28: Chemical Kinetics I — Rate Laws

- 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

$$\nu_{\mathrm{A}}\mathrm{A} + \nu_{\mathrm{B}}\mathrm{B} \longrightarrow \nu_{\mathrm{Y}}\mathrm{Y} + \nu_{\mathrm{Z}}\mathrm{Z}$$

- Since

$$n_{\mathrm{A}}(t) = n_{\mathrm{A}}(0) - \nu_{\mathrm{A}}\xi(t) \quad n_{\mathrm{B}}(t) = n_{\mathrm{B}}(0) - \nu_{\mathrm{B}}\xi(t) \quad n_{\mathrm{Y}}(t) = n_{\mathrm{Y}}(0) + \nu_{\mathrm{Y}}\xi(t) \quad n_{\mathrm{Z}}(t) = n_{\mathrm{Z}}(0) + \nu_{\mathrm{Z}}\xi(t)$$

  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.

$$\frac{\mathrm{d}n_{\mathrm{A}}}{\mathrm{d}t} = -\nu_{\mathrm{A}}\frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad \frac{\mathrm{d}n_{\mathrm{B}}}{\mathrm{d}t} = -\nu_{\mathrm{B}}\frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad \frac{\mathrm{d}n_{\mathrm{Y}}}{\mathrm{d}t} = \nu_{\mathrm{Y}}\frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad \frac{\mathrm{d}n_{\mathrm{Z}}}{\mathrm{d}t} = \nu_{\mathrm{Z}}\frac{\mathrm{d}\xi}{\mathrm{d}t}$$

- 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.

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\frac{\nu_\mathrm{A}}{V}\frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = -\frac{\nu_\mathrm{B}}{V}\frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad \frac{\mathrm{d}[\mathrm{Y}]}{\mathrm{d}t} = \frac{\nu_\mathrm{Y}}{V}\frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad \frac{\mathrm{d}[\mathrm{Z}]}{\mathrm{d}t} = \frac{\nu_\mathrm{Z}}{V}\frac{\mathrm{d}\xi}{\mathrm{d}t}$$

- 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* $\boldsymbol{v(t)}$. *Given by*

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

  - 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*

$$v(t) = k[\mathrm{A}]^{m_\mathrm{A}}[\mathrm{B}]^{m_\mathrm{B}}\cdots$$

  - Some reactions (such as the $H_2 + Br_2 \longrightarrow 2\,HBR$ 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* $\boldsymbol{k}$.
  - 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* $\boldsymbol{m_\mathrm{A}}$.
- **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 $[\mathrm{A}]^{m_\mathrm{A}}$ and k into a new "rate constant" k', reducing the rate law to the form

$$v = k'[\mathrm{B}]^{m_\mathrm{B}}$$

  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 $\mathrm{d}[\mathrm{A}]/\mathrm{d}t$, but we can measure $\Delta[\mathrm{A}]/\Delta t$ for small Δt and approximate these measurements as $\mathrm{d}[\mathrm{A}]/\mathrm{d}t$.
  - 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, $[\mathrm{A}]_0$, be the same for each. However, for one, use $[\mathrm{B}]_1$ for initial concentration of B, and for the other, use $[\mathrm{B}]_2$.
2. Arranging everything into equations, we thus have
$$v_1 = -\frac{1}{\nu_\mathrm{A}}\left(\frac{\Delta[\mathrm{A}]}{\Delta t}\right)_1 = k[\mathrm{A}]_0^{m_\mathrm{A}}[\mathrm{B}]_1^{m_\mathrm{B}} \qquad v_2 = -\frac{1}{\nu_\mathrm{A}}\left(\frac{\Delta[\mathrm{A}]}{\Delta t}\right)_2 = k[\mathrm{A}]_0^{m_\mathrm{A}}[\mathrm{B}]_2^{m_\mathrm{B}}$$
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.
$$m_\mathrm{B} = \frac{\ln(v_1/v_2)}{\ln([\mathrm{B}]_1/[\mathrm{B}]_2)}$$

- 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**.

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- McQuarrie and Simon (1997) derives the first-order integrated rate law.
- To determine the rate constant of a first-order reaction from concentration vs. time data, plot the log of the concentration vs. time and perform a linear regression.
- **Half-life**: The length of time required for half of the reactant to disappear. *Denoted by* $\boldsymbol{t_{1/2}}$.
- McQuarrie and Simon (1997) derives the half-life of a first-order reaction.
- "A particular rate law does not provide any information on the magnitude of the rate constant" (McQuarrie & Simon, 1997, p. 1057).
- McQuarrie and Simon (1997) derives the second-order integrated rate law.
- Similarly to first-order reactions, a plot of $1/[\mathrm{A}]$ vs. time will yield a straight line with slope k and intercept $1/[\mathrm{A}]_0$.
- To determine if a reaction is first- or second-order, we can make plots of $\ln[\mathrm{A}]$ and $1/[\mathrm{A}]$ vs. t and see which one is a straight line.
- McQuarrie and Simon (1997) derives the half-life of a second-order reaction.
- McQuarrie and Simon (1997) gives the integrated rate law for a reaction that is first-order in each reactant, and second-order overall.
- **Reversible** (reaction): A reaction that occurs in both directions.
- Consider the reversible reaction
$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$
- The kinetic condition for the above reversible reaction to be at equilibrium is
$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = 0$$
- **Dynamic equilibrium**: An equilibrium in which individual molecules of reactants and products continue interconverting but in such a way that there is no *net* change in either concentration.

- The rate law for the above reversible reaction is

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

  - The first term accounts for the rate at which A reacts to form B.
  - The second term accounts for the rate at which B reacts to form A.
  - "The difference in sign of these two terms reflects that the forward reaction depletes the concentration of A and the back reaction increases the concentration of A with time" (McQuarrie & Simon, 1997, p. 1063).
- McQuarrie and Simon (1997) derives the integrated rate law corresponding to the above differential rate law and the case that $[\mathrm{B}] = 0$.
- **Relaxation method**: A method of determining the rate law for a chemical reaction with half-life shorter than the mixing time, involving perturbing a chemical system at one equilibrium to a state that will require a new equilibrium by suddenly changing a condition.
  - Examples of conditions that can be changed are temperature, pressure, pH, and pOH.
- **Temperature-jump relaxation technique**: A relaxation method in which the temperature of the equilibrium reaction mixture is suddenly changed at constant pressure.
  - The change in temperature causes the chemical system to relax to a new equilibrium state that corresponds to the new temperature.
  - The rate constants for the forward and reverse reactions are related to the time required for the system to relax to its new equilibrium state.
- "Experimentally, the temperature of a solution can be increased by about 5 K in one microsecond by discharging a high-voltage capacitor through the reaction solution" (McQuarrie & Simon, 1997, p. 1067).
  - Since equilibrium constants depend exponentially on the inverse of the temperature ($\ln K_P = -\Delta_r G^\circ/RT$), such a perturbation can cause a large change in equilibrium conditions.
- As per the Van't Hoff equation, the equilibrium concentration of B increases following the temperature jump if $\Delta_r H^\circ$ is positive and decreases if $\Delta_r H^\circ$ is negative.
  - If $\Delta_r H^\circ = 0$, then a temperature-jump relaxation experiment will not yield any useful data.
- Temperature-jump relaxation technique rate law derivation.
  - Suppose the initial temperature is T_1 and we increase the temperature to T_2. Suppose furthermore that $\Delta_r H^\circ < 0$ so that the concentration of B decreases following the perturbation.
  - Let $[\mathrm{A}]_{1,\mathrm{eq}}, [\mathrm{B}]_{1,\mathrm{eq}}$ be the equilibrium concentrations of A and B, respectively, at T_1. Let $[\mathrm{A}]_{2,\mathrm{eq}}, [\mathrm{B}]_{2,\mathrm{eq}}$ be the equilibrium concentrations of A and B, respectively, at T_2. Let k_1, k_{-1} be the rate constants of the forward and reverse reactions, respectively, at T_2. Let $[\mathrm{A}], [\mathrm{B}]$ be the concentrations of A and B, respectively, at some time T after the temperature jump. Let $\Delta[\mathrm{A}], \Delta[\mathrm{B}]$ be the differences in the concentrations of A and B, respectively, from equilibrium at time t.
  - As before, we begin from the fact that

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

    - Notice how the sign convention follows from our hypothesis that $\Delta_r H^\circ < 0$.

- It follows by substituting

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

into the above that

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}([\mathrm{B}]_{2,\mathrm{eq}} + \Delta[\mathrm{B}]) &= k_1([\mathrm{A}]_{2,\mathrm{eq}} + \Delta[\mathrm{A}]) - k_{-1}([\mathrm{B}]_{2,\mathrm{eq}} + \Delta[\mathrm{B}])\\ \frac{\mathrm{d}\Delta[\mathrm{B}]}{\mathrm{d}t} &= k_1[\mathrm{A}]_{2,\mathrm{eq}} + k_1\Delta[\mathrm{A}] - k_{-1}[\mathrm{B}]_{2,\mathrm{eq}} - k_{-1}\Delta[\mathrm{B}]\end{aligned}$$

- The fact that $k_1[\mathrm{A}]_{2,\mathrm{eq}} = k_{-1}[\mathrm{B}]_{2,\mathrm{eq}}$ gives us

$$\frac{\mathrm{d}\Delta[\mathrm{B}]}{\mathrm{d}t} = k_1\Delta[\mathrm{A}] - k_{-1}\Delta[\mathrm{B}]$$

- The fact that $\Delta[\mathrm{A}] + \Delta[\mathrm{B}] = 0$ gives us

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

- If $\Delta[\mathrm{B}]_0 = [\mathrm{B}]_{1,\mathrm{eq}} - [\mathrm{B}]_{2,\mathrm{eq}}$, then it follows by integration that

$$\begin{aligned}\int_{\Delta[\mathrm{B}]_0}^{\Delta[\mathrm{B}]} \frac{\mathrm{d}\Delta[\mathrm{B}]}{\Delta[\mathrm{B}]} &= \int_0^t -(k_1 + k_{-1})\,\mathrm{d}t\\ \Delta[\mathrm{B}] &= \Delta[\mathrm{B}]_0\mathrm{e}^{-(k_1+k_{-1})t}\end{aligned}$$

- **Relaxation time**: The reciprocal of the sum of the forward and reverse rate constants. *Denoted by* $\boldsymbol{\tau}$. *Units* **s**. *Given by*

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

  - A measure of how long it takes for $\Delta[\mathrm{B}]$ to decay to $1/\mathrm{e}$ of its initial value.

- Temperature-jump relaxation technique rate law derivation for

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{P}$$

  - We have that

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_1[\mathrm{A}][\mathrm{B}] - k_{-1}[\mathrm{P}]$$

  - If we define $\Delta[\mathrm{P}]$ and the related relevant terms as in the above derivation, then we get

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}([\mathrm{P}]_{2,\mathrm{eq}} + \Delta[\mathrm{P}]) &= k_1([\mathrm{A}]_{2,\mathrm{eq}} + \Delta[\mathrm{A}])([\mathrm{B}]_{2,\mathrm{eq}} + \Delta[\mathrm{B}]) - k_{-1}([\mathrm{P}]_{2,\mathrm{eq}} + \Delta[\mathrm{P}])\\ \frac{\mathrm{d}\Delta[\mathrm{P}]}{\mathrm{d}t} &= k_1([\mathrm{A}]_{2,\mathrm{eq}}[\mathrm{B}]_{2,\mathrm{eq}} + [\mathrm{A}]_{2,\mathrm{eq}}\Delta[\mathrm{B}] + \Delta[\mathrm{A}][\mathrm{B}]_{2,\mathrm{eq}} + \Delta[\mathrm{A}]\Delta[\mathrm{B}]) - k_{-1}([\mathrm{P}]_{2,\mathrm{eq}} + \Delta[\mathrm{P}])\\ &= k_1([\mathrm{A}]_{2,\mathrm{eq}}\Delta[\mathrm{B}] + \Delta[\mathrm{A}][\mathrm{B}]_{2,\mathrm{eq}} + \Delta[\mathrm{A}]\Delta[\mathrm{B}]) - k_{-1}\Delta[\mathrm{P}]\\ &= k_1(-[\mathrm{A}]_{2,\mathrm{eq}}\Delta[\mathrm{P}] - \Delta[\mathrm{P}][\mathrm{B}]_{2,\mathrm{eq}} + \Delta[\mathrm{P}]^2) - k_{-1}\Delta[\mathrm{P}]\\ &= -[k_1([\mathrm{A}]_{2,\mathrm{eq}} + [\mathrm{B}]_{2,\mathrm{eq}}) + k_{-1}]\Delta[\mathrm{P}] + \mathrm{O}(\Delta[\mathrm{P}]^2)\\ \Delta[\mathrm{P}] &\approx \Delta[\mathrm{P}]_0\mathrm{e}^{-t/\tau}\end{aligned}$$

  where

$$\tau = \frac{1}{k_1([\mathrm{A}]_{2,\mathrm{eq}} + [\mathrm{B}]_{2,\mathrm{eq}}) + k_{-1}}$$

- Water dissociation, as per

$$\mathrm{H^+(aq) + OH^-(aq)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{H_2O\,(l)}$$

  - Time-dependent conductivity measurements following a temperature jump in water paired with the known equilibrium constant and the above derivation revealed a relaxation time that corresponds to one of the fastest second-order rate constants ever measured.
- Common temperature dependencies of chemical reactions.
  - As the temperature increases, the rate of reaction increases exponentially.
  - The temperature dependence is exponential until a threshold temperature, and then increases extremely rapidly (i.e., the substance becomes explosive).
  - The temperature dependence increases up until a threshold temperature, and then falls off rapidly (i.e., an enzyme-controlled reaction where the enzyme denatures at a certain temperature).
- In the first case (the most common), the temperature dependence of the rate constant is described approximately by the empirical equation

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

- Integrating yields the **Arrhenius equation**.
- **Arrhenius equation**: The following equation. *Given by*

$$k = A\mathrm{e}^{-E_a/RT}$$

- **Pre-exponential factor**: The constant A in the Arrhenius equation. *Denoted by* $\boldsymbol{A}$.
- **Activation energy**: The constant E_a in the Arrhenius equation. *Denoted by* $\boldsymbol{E_a}$.
- The magnitude of the temperature effect on reaction rates is much too large to be explained in terms of only a change in the translational energy of the reactions. Thus, a chemical reaction require more than just a collision between reactants.
- **Reaction coordinate**: The unit along which a chemical reaction proceeds from reactant to product.
  - "Generally multidimensional, representing the bond lengths and bond angles associated with the chemical process" in question (McQuarrie & Simon, 1997, p. 1073).
  - A simple example, though, is that the I−I bond length serves as the reaction coordinate for the thermal dissociation of I_2.
- The Arrhenius equation is imperfect, and many reactions obey equations of the form

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

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

$$E_a = E' + mRT \qquad\qquad A = aT^m\mathrm{e}^m$$

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