CHEM 26200 (Thermodynamics) Notes

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Part I

Statistical Mechanics

Week 1

The Boltzmann Factor and Partition Functions

1.1 Overview of Major Results

1/10:

- In this course, we will review thermochemistry from intro chem, but go deeper with statistical mechanics.
- TA: Haozhi.
  - Did his undergrad at Oxford.
  - Has already taught this class in the PME.
- **Boltzmann constant**: The following constant. *Denoted by* $\boldsymbol{k_B}$. *Given by*

$$k_B = 1.381 \times 10^{-23}\ \text{J/K}$$

  - Equal to the quotient of the ideal gas constant and Avogadro's constant.
- **Ideal gas law**: The following relationship between the pressure P, volume V, number of moles n, and temperature T of an ideal gas, and the ideal gas constant R.

$$PV = nRT$$

  - Multiplying by the quotient of Avogadro's constant with itself yields

$$\begin{aligned} PV &= nN_A\frac{R}{N_A}T \\ PV &= Nk_BT \end{aligned}$$

    where N is the number of molecules in the system.
  - The unit for PV is Joules.
  - Thus, the above form states that PV is equal to the number of particles times a tiny unit of energy.
- Relating PV to the kinetic energy of gas molecules/atoms[1].
  - Pressure originates microscopically from the collisions of particles with the walls of their container.
  - As such, we first seek to derive an expression for the number of collisions per second per area.

[1]This derivation differs from that on Labalme (2021a, pp. 3–4) and Labalme (2021c, pp. 18–19), in that its approach is from a flux perspective.

        - Consider the number $N(v_x)$ particles with speed v_x in the x-direction.
        - The quotient $N(v_x)/V$ is the density in the container of particles with speed v_x.
        - Thus, the flux "through"/to/at the wall is this density, times the area of the wall, times the x-velocity of the particles.
    - Assume an elastic collision of each particle with the wall. Thus, when each particle of mass m collides with the wall, it transfers $2mv_x$ of momentum.
    - Therefore, since $F = \mathrm{d}p/\mathrm{d}t$, the overall force exerted on the wall by the gas particles moving with speed v_x is $2mv_x$, $N(v_x)/V \cdot v_x \cdot$ Area times per second.
    - But, of course, we must sum over all possible v_x, so the total force

$$F = \int_{v_x>0} 2mv_x \cdot \frac{N(v_x)}{V} \cdot v_x \cdot \text{Area}\,\mathrm{d}v_x$$

    - It follows that

$$\begin{aligned} P &= \frac{F}{\text{Area}} \\ &= \int_{v_x>0} 2mv_x^2 \cdot \frac{N(v_x)}{V}\,\mathrm{d}v_x \end{aligned}$$

    The factor of 1/2 in the following line comes from the fact that we are only integrating over half of the possible v_x^2s (i.e., the positive ones).

$$\begin{aligned} &= 2m \cdot \frac{N}{V} \cdot \frac{1}{2}\left\langle v_x^2 \right\rangle \\ &= \frac{N}{V} m \left\langle v_x^2 \right\rangle \\ PV &= Nm \cdot \left\langle v_x^2 \right\rangle \end{aligned}$$

    Assuming that the gas is not moving in any one direction means that $\left\langle v_x^2 \right\rangle = \left\langle v_y^2 \right\rangle = \left\langle v_z^2 \right\rangle = \frac{1}{3}\left\langle v^2 \right\rangle$. Therefore,

$$\begin{aligned} &= Nm \cdot \frac{1}{3}\left\langle v^2 \right\rangle \\ &= \frac{2}{3}N \cdot \frac{1}{2}m\left\langle v^2 \right\rangle \\ &= \frac{2}{3}N \cdot \langle E_{KE} \rangle \\ \langle E_{KE} \rangle &= \frac{3}{2}\frac{PV}{N} \\ \langle E_{KE} \rangle &= \frac{3}{2}k_BT \end{aligned}$$

    - Note that this applies to all sorts of regimes — we used no properties of the particles (e.g., atom vs. molecule) to derive this relationship.

- Getting the distribution of the gas energies or speed is the next logical step.
- First, though, we consider alternate occurrences of k_BT.
    - The activation energy of Arrhenius (1889): "To collide is to react" is inaccurate; it must collide with sufficient energy. The molecule must be "activated."

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

        - The first E_a is the molar energy of activation; the second is the molecular energy of activation.

- Yields the probability distribution of a molecule reacting.

– Nernst equation:

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{RT}{nF}\ln Q$$

- $\ln Q$ is the ratio inside vs. outside the membrane.
- $F = N_A e$ where e is the charge of an electron.
- Thus,

$$\Delta E = \frac{RT}{nF} = \frac{k_BT}{ne}$$

- If the potential across the membrane is approximately k_BT, then $\ln Q \approx 1$, so $Q \approx \mathrm{e}$.
- Thus, at body temperature ($T = 310\,\mathrm{K}$), $k_BT/\mathrm{e} = 26\,\mathrm{mV}$.

– The speed of sound: Certainly sound cannot travel faster than the molecules. Therefore, we can derive the following approximation for the speed of sound.

$$\begin{aligned}\frac{1}{2}m\left\langle v^2\right\rangle &= \frac{3}{2}k_BT\\ \sqrt{\langle v^2\rangle} &= \sqrt{\frac{3k_BT}{m}}\\ v_{\text{rms}} &= \sqrt{\frac{3k_BT}{m}}\end{aligned}$$

- This estimate is within $20-30\,\%$ — take m to be the average mass of air.

– de Broglie wavelength: A molecule has a kinetic energy approximately equal to k_BT. Additionally, the quantum mechanical kinetic energy of a molecule aligns with this, as $\hbar^2k^2/2m \approx k_BT$. Furthermore, the particle-wave duality relates the momentum to wavelength by $p = \hbar k = h/\lambda$. Therefore,

$$\lambda \approx \sqrt{\frac{h^2}{2mk_BT}}$$

- Thus, a gas at STP has a very small de Broglie wavelength and behaves classically.
- Only at very low temperatures with very light gasses do quantum considerations come into play.
- A H_2 molecule at $300\,\mathrm{K}$ has de Broglie wavelength $\lambda = 1.78\,\text{Å}$.
- Note that the quantum mechanical kinetic energy of a free particle is derived as follows.

$$\begin{aligned}\hat{H}\psi &= E\psi\\ -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(\mathrm{e}^{ikx}\right) &= E\mathrm{e}^{ikx}\\ \frac{\hbar^2k^2}{2m}\mathrm{e}^{ikx} &= E\mathrm{e}^{ikx}\\ E &= \frac{\hbar^2k^2}{2m}\end{aligned}$$

- **Boltzmann factor**: Gives the relative probability p_2/p_1 of two states E_1, E_2, provided their respective energies E_1, E_2. *Given by*

$$\frac{p_2}{p_1} = \mathrm{e}^{-(E_2-E_1)/k_BT}$$

– Consider states $E_1, E_2, E_3, \ldots$, denoted by their energies.

– Consistency check: Given

$$\frac{p_2}{p_1} = \mathrm{e}^{\frac{-(E_2-E_1)}{k_BT}} \qquad \frac{p_3}{p_2} = \mathrm{e}^{\frac{-(E_3-E_2)}{k_BT}}$$

we do indeed have

$$\frac{p_3}{p_1} = \frac{p_3}{p_2}\cdot\frac{p_2}{p_1} = \mathrm{e}^{\frac{-(E_3-E_2)}{k_BT}+\frac{-(E_2-E_1)}{k_BT}} = \mathrm{e}^{\frac{-(E_3-E_1)}{k_BT}}$$

- We'll take this as God-given for now. Boltzmann derived it with a very good knowledge of the thermodynamics of freshman chemistry.

- We're starting with the above exciting result, and then going back and building up to it over the next three weeks.
- We write the Boltzmann factor for degenerate states as follows.
  - Consider four states at E_2 and one state at E_1.
  - The Boltzmann factor still tells us that $p_2/p_1 = \mathrm{e}^{-(E_2-E_1)/k_BT}$, but we have to make the following adjustment. Indeed, the total probability of being in one of the four states at energy E_2 is $p(E_2) = 4p_2$, while the total probability of being in the one state at energy E_1 is still just $p(E_1) = 1p_1$.
  - In each state E_2,

$$\frac{p(E_2)}{p(E_1)} = \frac{N_2}{N_1}\mathrm{e}^{-(E_2-E_1)/k_BT}$$

- The weekly quiz.
  - The first quiz will be next week.
  - A Canvas quiz – we'll have 24 hours to take it, but only 1 hour to take it.

1.2 Boltzmann Factor Examples / Partition Function

1/12:
- We will apply the Boltzmann factor to electronic, magnetic, translational, rotational, and vibrational molecular states.
- Example: Sodium lamp – two lines at 589.6 nm and 589.0 nm with intensity ratio 1:2.

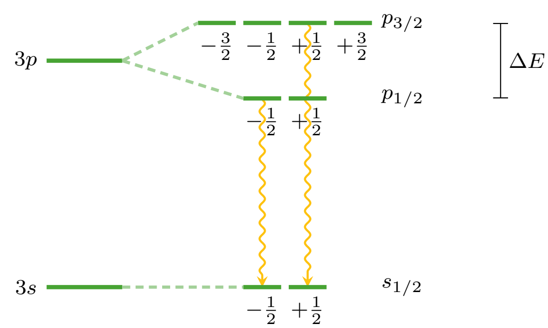


Figure 1.1: Sodium lamp energy levels.

  - Street lamps use this (very efficient).
  - Also used in astronomy.
  - In the sodium atom, there are two energy levels ($3s$ and $3p$).
  - The states have a spin-orbit coupling effect.
    - $3s$ (with $S = 1/2$) splits into two degenerate states $s_{\pm 1/2}$ based on spin.
    - $3p$ (with $L = 1$ and $S = 1/2$) splits into two nondegenerate states ($l = \pm 1$ [called $p_{3/2}$] and $l = 0$ [called $p_{1/2}$]), which further subdivide into four (resp. two) degenerate states ($-3/2, -1/2, 1/2, 3/2$ and $-1/2, 1/2$).

- Let ΔE be the difference in energy between the $p_{3/2}$ and $p_{1/2}$. Then

$$\frac{\Delta E}{k_B} = \frac{1}{k_B}\left(\frac{hc}{\lambda_1} - \frac{hc}{\lambda_2}\right) = 25\,\mathrm{K}$$

  where $\lambda_1 = 589.6\,\mathrm{nm}$ and $\lambda_2 = 589.0\,\mathrm{nm}$.
- Thus, $\mathrm{e}^{-\Delta E/k_BT} \approx 1$ for $T = 300\,\mathrm{K}$ (the temperature in the sodium vapor lamp).
- Therefore,

$$\frac{p(E_2)}{p(E_1)} = \frac{4}{2} \cdot 1$$
$$p(E_2) = 2p(E_1)$$

- Example: MRI.
  - The magnetic field polarizes the spins of the hydrogen protons in our body with $\Delta E = \mu_B B$.
  - If we also take $B = 6\,\mathrm{T}$ and $T = 310\,\mathrm{K}$ (body temperature), then

$$\frac{\mu_B B}{k_B T} = 2 \times 10^{-5}$$

  - Thus, very few protons actually flip, but with modern technology we can still measure this.
- **Proton magnetic moment**: The magnetic moment of a proton. *Denoted by* $\boldsymbol{\mu_B}$. *Given by*

$$\mu_B = 1.4 \times 10^{-26}\,\mathrm{J/T}$$

- Example: Rotational.
  - The rotational energy E_J of a molecule depends on the angular momentum quantum number J and the moment of inertia of the molecule $I = \mu R^2$ via the following relation.

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

  - Microwave spectroscopy can be used to find molecules out in the universe.
  - At 300 K,

$$\frac{p(J=1)}{p(J=0)} = \frac{3}{1}\mathrm{e}^{\frac{-(E_1-E_0)}{k_BT}} = 2.95$$

    - As before $J = 1$ corresponds to states $j = -1, 0, 1$.
  - See Figure 18.5 in the textbook.
  - There is a range of angular momenta due to the temperature that for $T = 300\,\mathrm{K}$ peaks around $J = 5$.
- Example: Vibrational.
  - Here, $\Delta E = E_n - E_{n-1} = h\nu$ for every energy level since $E_n = h\nu(n + 1/2)$.
  - It follows that

$$\frac{h\nu}{k_B} = 2800\,\mathrm{K}$$

    for CO, meaning that at 300 K, CO will be largely in its ground state.
- The partition function tells us everything we would want to know about a system.

$$Q = \sum_i \mathrm{e}^{-E_i/k_BT}$$

- All we need to know is the energy of every state in the system.
- This is impossible for an infinite system, but the Schrödinger equation gives us the energy of a system, so its a great place to start.

- Calculating the total energy from the partition function.
  - To construct it, start with
$$Q = \frac{p_1}{p_1} + \frac{p_2}{p_1} + \frac{p_3}{p_1} + \cdots = 1 + \mathrm{e}^{\frac{-(E_2-E_1)}{k_BT}} + \mathrm{e}^{\frac{-(E_3-E_1)}{k_BT}} + \cdots$$
  - The total energy is equal to
$$\langle E\rangle = E_1p_1 + E_2p_2 + E_3p_3 + \cdots$$
  - Taking $E_1 = 0$ gives
$$\langle E\rangle = p_1\left[E_2\frac{p_2}{p_1} + E_3\frac{p_3}{p_1} + \cdots\right]$$
  - Note that
$$\frac{\partial}{\partial T}\left(\mathrm{e}^{-E_2/k_BT}\right) = \frac{E_2}{k_BT^2}\mathrm{e}^{-E_2/k_BT} = \frac{1}{k_BT^2}\left(E_2\frac{p_2}{p_1}\right)$$
  - Additionally,
$$\begin{aligned}
p_1 &= 1 - (p_2 + p_3 + \cdots)\\
&= 1 - p_1\left(\frac{p_2}{p_1} + \frac{p_3}{p_1} + \cdots\right)\\
&= 1 - p_1(Q-1)\\
p_1 &= \frac{1}{Q}
\end{aligned}$$
  - Therefore,
$$\begin{aligned}
\langle E\rangle &= p_1k_BT^2\frac{\partial}{\partial T}\left(\frac{p_1}{p_1} + \frac{p_2}{p_1} + \cdots\right)\\
&= p_1k_BT^2\frac{\partial Q}{\partial T}\\
&= \frac{1}{Q}k_BT^2\frac{\partial Q}{\partial T}\\
\langle E\rangle &= k_BT^2\frac{\partial}{\partial T}(\ln Q)
\end{aligned}$$
  - The above is an important result.

- Changing the origin of energy.
  - We know that
$$\begin{aligned}
Q(E_0) &= Q(E_0')\mathrm{e}^{-(E_0'-E_0)/k_BT}\\
\ln Q(E_0) &= \ln Q(E_0') - \frac{E_0'-E_0}{k_BT}
\end{aligned}$$
  - Thus,
$$\begin{aligned}
\langle E\rangle_{E_0} &= k_BT^2\frac{\partial}{\partial T}(\ln Q(E_0))\\
&= k_BT^2\left(\frac{\partial}{\partial T}(\ln Q(E_0')) - \frac{\partial}{\partial T}\left(\frac{E_0'-E_0}{k_BT}\right)\right)\\
&= \langle E\rangle_{E_0'} + (E_0'-E_0)\\
\langle E\rangle_{E_0} + E_0 &= \langle E\rangle_{E_0'} + E_0'
\end{aligned}$$

- So the change of the energy origin does indeed change the total energy by the same amount.

1.3 Calculating Average Energies

1/14: - We derived that for an ideal gas, $\langle E\rangle = 3k_BT/2$. But this may change at higher pressures.
- Calculating the average kinetic energy at higher temperatures.
  - Use the main result from last time, which gives us the energy in terms of the partition function.
  - We have different degrees of freedom since KE and PE are on different coordinates (KE is on speed and PE is on position).
  - When we write the Boltzmann factor, we'll have an exponential with the sum of the kinetic and potential energy.

$$Q = \sum_{ij} \mathrm{e}^{-(E_{KE_i} - E_{PE_j})/k_BT} = \sum_{ij} \mathrm{e}^{-E_{KE_i}/k_BT} \mathrm{e}^{-E_{PE_j})/k_BT} = Q_{KE} Q_{PE}$$

    - The second equality holds because KE depends on the velocity coordinates and PE depends on position coordinates; thus, they are independent.
  - Kinetic energy partition function.

$$E_{KE} = \frac{1}{2} m v_x^2$$

    - Thus,

$$Q_{KE_{v_x}} = \int_{-\infty}^{\infty} \mathrm{e}^{-\frac{1}{2} m v_x^2/k_BT} \,\mathrm{d}v_x = \sqrt{\frac{2\pi k_BT}{m}}$$

    - This function doesn't depend on anything of significant import.
  - It follows that

$$\langle KE_x\rangle = k_BT^2 \frac{\partial}{\partial T}\left(\ln Q_{KE_{v_x}}\right) = k_BT^2 \frac{\partial}{\partial T}\left(\ln\sqrt{\frac{2\pi k_B}{m}} + \frac{1}{2}\ln T\right) = \frac{k_BT}{2}$$

    and

$$\langle KE\rangle = \langle KE_x\rangle + \langle KE_y\rangle + \langle KE_z\rangle = \frac{3}{2} k_BT$$

  - Therefore, this result holds beyond the specific case of an ideal gas!
- Now for the potential energy of a harmonic oscillator.
  - $PE = \frac{1}{2}kx^2$; calculate the partition function for the coordinate x.

$$Q_x = \int_{-\infty}^{\infty} \mathrm{e}^{-\frac{1}{2}kx^2/k_BT} \,\mathrm{d}x = \sqrt{\frac{2\pi k_BT}{k}}$$

  - Thus,

$$\langle PE_x\rangle = \frac{k_BT}{2}$$

  - For a 3D harmonic oscillator,

$$\langle PE\rangle = \frac{3}{2} k_BT$$

- Average potential energy of a gravitational potential.
  - Apply the virial theorem (relates the average kinetic energy of a system in a conservative potential to the potential energy).

  - Since we've shown that for any system, the average kinetic energy in one dimension is $k_BT/2$, the potential in any system will be related (i.e., have a factor of k_BT).
- What it means to cool something down, if KE always follows the same formula.
  - Although the formula does not change, $\langle KE\rangle \propto T$, so decreasing the temperature decreases the kinetic energy.
  - Similarly, as things change phase, more and more potentials take hold (e.g., in the gas phase, there is no potential energy, but there is significant potential energy in the solid and liquid phases).
- Rotational kinetic energy.
  - Consider N_2, with its two rotational degrees of freedom.
  - Classically,
$$E_{\text{rot}} = \frac{1}{2}I\omega^2$$
  - Thus, once again,
$$Q_\omega = \int_{-\infty}^{\infty} \mathrm{e}^{-\frac{1}{2}I\omega^2/k_BT}\,\mathrm{d}\omega = \sqrt{\frac{2\pi k_BT}{I}}$$
    making
$$\langle E_{\text{rot}}\rangle = \frac{k_BT}{2}$$
    for one degree of freedom.
- **Law of Dulong and Petit**: The heat capacity of elemental solids is about $3nR$.
  - Observed in 1819.
  - A major result in an era where atomic structure was just emerging.
  - Imagine an atom bound in a three-dimensional (octahedral) potential. It's energy is thus
$$\frac{1}{2}mv^2 + \frac{1}{2}kr^2$$
  - Thus,
$$\begin{aligned}\langle E_{\text{atom}}\rangle &= \frac{3}{2}k_BT + \frac{3}{2}k_BT = 3k_BT\\ \langle E_{\text{solid}}\rangle &= 3Nk_BT = 3nN_Ak_BT = 3nRT\end{aligned}$$
  - Some heat capacities are lower than $3nR$ (solids of rare gases that are heavier and need more heat to behave ideally), and some are higher (the potential is not a harmonic potential).
- As experiments got better, people realized that heat capacity, as a function of temperature, decreases as $T \to 0\,\mathrm{K}$, and was only asymptotic at $3nR$ at temperatures sufficiently close to room temperature.
  - Quantum mechanics, especially the work of Einstein, solved this mystery.
  - Atomic motion is quantized in units of energy.
    - If the temperature is much higher than the quantized energies, the system behaves classically.
    - If the temperature drops below the quantization energies of the vibration, we will not have equal population of energy levels (most will be in the ground state, making the energy 0; thus, there is no derivative of it and no heat capacity).
- Partition function of a quantum harmonic oscillator and the energy of the oscillator.
  - Recall that the energies are given by $(n+1/2)h\nu$.

- The partition function of the vibration of the quantum harmonic oscillator is

$$\begin{aligned} Q &= 1 + \mathrm{e}^{-h\nu/k_BT} + \mathrm{e}^{-2h\nu/k_BT} + \cdots \\ Q &= (\mathrm{e}^{-h\nu/k_BT})^0 + (\mathrm{e}^{-h\nu/k_BT})^1 + (\mathrm{e}^{-h\nu/k_BT})^2 + \cdots \\ Q - Q\mathrm{e}^{-h\nu/k_BT} &= 1 \\ Q &= \frac{1}{1-\mathrm{e}^{-h\nu/k_BT}} \end{aligned}$$

  when we take the zero point energy as our zero of energy.
- It follows that

$$\begin{aligned} \langle E\rangle &= k_BT^2\frac{\partial}{\partial T}\left[\ln\left(\frac{1}{1-\mathrm{e}^{-h\nu/k_BT}}\right)\right] \\ &= \frac{h\nu}{\mathrm{e}^{h\nu/k_BT}-1} \end{aligned}$$

- As $T\to\infty$, $h\nu/k_BT$ gets very small. But since $\mathrm{e}^x \approx 1+x$ at small x, as $T\to\infty$, we have that

$$\langle E\rangle \approx \frac{h\nu}{(1+h\nu/k_BT)-1} = k_BT$$

- Therefore, as $T\to\infty$, we recover the energy of a classical harmonic oscillator.
- On the other hand, as $T\to 0$, $E\to 0$.

- Note that heat capacity $C = \partial E/\partial T$.

1.4 Chapter 17: The Boltzmann Factor and Partition Functions

From McQuarrie and Simon (1997).

1/23:

- Up to this point, we have established that all physical systems' energy states are quantized. Now, we address questions such as "what fraction of the molecules are to be found in the ground vibrational state, the first excited vibrational state, and so on" (McQuarrie & Simon, 1997, p. 693).
  - We will see how notions such as 'higher temperature systems should have more populated excited states' translate into precise mathematics.
  - Our two most important tools to address such questions are the **Boltzmann factor** and the **partition function**.
- **Boltzmann factor**: The relation between the probability that a system will be in a given state to the energy of that state. *Given by*

$$p_j \propto \mathrm{e}^{-E_j/k_BT}$$

- **Partition function**: A function in terms of which we can express all of the macroscopic properties of a given system, such as energy, heat capacity, and pressure. *Denoted by* $\boldsymbol{Q}$, $\boldsymbol{Q(N,V,\beta)}$, $\boldsymbol{Q(N,V,T)}$. *Given by*

$$Q = \sum_j \mathrm{e}^{-E_j/k_BT}$$

- Determining on what quantities the energies of a macroscopic system (such as some volume of fluid, gas, or solid) depend.
  - Consider an ideal gas confined to a cubic box of side length a (we will not generalize this result explicitly even though it can be).

  - In such a system, the constituent particles do not interact, so the energy of the system will be a simple sum
$$E_j(N,V) = \epsilon_1 + \cdots + \epsilon_N$$
of the energies $\epsilon_1, \dots, \epsilon_N$ of the N particles with no higher-degree interaction terms necessary.
  - Additionally, the confinement means that quantum mechanically, every particle exists in a potential of zero within the cubic box and is subject to infinite potential outside the box.
  - Thus, if we consider only the translational energies of each particle, we may apply the particle in a 3D cubic box model from Chapter 3 of McQuarrie and Simon (1997) to learn that each
$$\epsilon_i = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$$
  - Notice that E_j depends on N and V in this system via the N terms in the summation and the dependence of each ϵ_i on $a = \sqrt[3]{V}$.
  - These are the most important (and general) factors on which E_j depends, and hence we often denote the energy of the j^{th} state of the system by $E_j(N,V)$

- **Heat reservoir**: An essentially infinite heat bath.
- **Ensemble**: A huge collection of systems with identical values of N, V, and T in thermal contact with a heat reservoir at a temperature T.
  - For a given ensemble, we denote the number of systems in state j by a_j and the total number of systems by $\mathcal{A}$.
- Finding the relative number a_m/a_n of systems in the ensemble in states a_n and a_m.
  - a_m/a_n will depend on the energies E_n and E_m via some function f, i.e.,
$$\frac{a_m}{a_n} = f(E_n, E_m)$$
  - Energies are given relative to some zero, but a_m/a_n will not depend on the arbitrary choice of this zero. Thus, the math must make said zero cancel, so we take
$$\frac{a_m}{a_n} = f(E_n - E_m)$$
  - The above equation must hold for any two energy states, so we can also write $a_l/a_m = f(E_m - E_l)$ and $a_l/a_n = f(E_n - E_l)$ for instance. But this implies that
$$\frac{a_l}{a_n} = \frac{a_m}{a_n} \cdot \frac{a_l}{a_m}$$
$$f(E_n - E_l) = f(E_n - E_m)f(E_m - E_l)$$
  - The above equation uniquely describes an exponential function, so we take $f(E) = \mathrm{e}^{\beta E}$[2].
    - To check that our definition of f satisfies the above equation, note that
$$\mathrm{e}^{\beta(E_n - E_l)} = \mathrm{e}^{\beta(E_n - E_m)}\mathrm{e}^{\beta(E_m - E_l)}$$
- Deriving an expression for a_m.

[2]Note that the base need not be e, but we can take it to be e WLOG since $\mathrm{e}^{\beta E} = (\mathrm{e}^{\beta})^E$ and we may take β such that e^{β} equals any positive real number.

- From the above result, we have that

$$\begin{aligned}\frac{a_m}{a_n} &= \mathrm{e}^{\beta(E_n - E_m)} \\ a_m \mathrm{e}^{\beta E_m} &= a_n \mathrm{e}^{\beta E_n}\end{aligned}$$

  i.e., that the value of $a_n \mathrm{e}^{\beta E_n}$ is the same (hence constant) for any n since m is arbitrary. Thus, let $C = a_n \mathrm{e}^{\beta E_n}$.

- It follows that

$$\begin{aligned}\frac{a_m}{a_n} &= \mathrm{e}^{\beta(E_n - E_m)} \\ a_m &= a_n \mathrm{e}^{\beta E_n} \mathrm{e}^{-\beta E_m} \\ a_m &= C \mathrm{e}^{-\beta E_m}\end{aligned}$$

- Determining C.
  - We have that

$$\begin{aligned}C \sum_j \mathrm{e}^{-\beta E_j} = \sum_j a_j &= \mathcal{A} \\ C &= \frac{\mathcal{A}}{\sum_j \mathrm{e}^{-\beta E_j}}\end{aligned}$$

  - Thus,

$$\frac{a_j}{\mathcal{A}} = \frac{1}{\sum_j \mathrm{e}^{-\beta E_j}} \mathrm{e}^{-\beta E_j(N,V)}$$

  - Taking the limit as the number of systems in the ensemble goes to infinity makes $a_j/\mathcal{A} \to p_j$, where p_j is the *probability* that a system will be in state j (see MathChapter B).
  - Recognizing that the denominator above is the partition function (and a function of N, V, and β), we have that

$$p_j(N,V,\beta) = \frac{1}{Q(N,V,\beta)} \mathrm{e}^{\beta E_j(N,V)}$$

- We will later show that $\beta = 1/k_BT$.
  - Note, however, that from a theoretical point of view, β can be just as useful as T.
- Expressions for the average energy $\langle E \rangle$ of a system.
  - From the definition of $\langle E \rangle$ in MathChapter B, we have that

$$\langle E \rangle = \sum_j p_j E_j = \sum_j \frac{E_j \mathrm{e}^{-\beta E_j}}{Q}$$

  - We can also express $\langle E \rangle$ entirely in terms of Q since

$$\begin{aligned}\frac{\partial \ln Q}{\partial \beta} &= -\sum_j \frac{E_j \mathrm{e}^{-\beta E_j}}{Q} = -\langle E \rangle \\ \langle E \rangle &= -\frac{\partial \ln Q}{\partial \beta}\end{aligned}$$

- Substituting $\beta = 1/k_BT$ and applying the chain rule to $\partial \ln Q/\partial T$ yields

$$\begin{aligned}\frac{\partial f}{\partial T} &= \frac{\partial f}{\partial \beta}\cdot\frac{\partial \beta}{\partial T} = \frac{\partial f}{\partial \beta}\cdot\frac{1}{k_B}\frac{\partial}{\partial T}\left(\frac{1}{T}\right) = \frac{\partial f}{\partial \beta}\cdot -\frac{1}{k_BT^2}\\ \frac{\partial f}{\partial \beta} &= -k_BT^2\frac{\partial f}{\partial T}\end{aligned}$$

  so

$$\langle E\rangle = k_BT^2\frac{\partial \ln Q}{\partial T}$$

- Using results from Chapter 14, McQuarrie and Simon (1997) calculates the average energy of a bare proton in a magnetic field, concluding that at $T = 0$ (i.e., zero thermal energy), the proton orients itself in the direction of the magnetic field with certainty while as $T \to \infty$, the thermal energy is such that the proton becomes equally likely to be in either state.
- Calculating the average energy of a monatomic ideal gas.
  - From Chapter 18,

$$Q(N,V,\beta) = \frac{[q(V,\beta)]^N}{N!} \qquad\qquad q(V,\beta) = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2}V$$

  - We have that

$$\begin{aligned}\ln Q &= N\ln q - \ln N!\\ &= -\frac{3N}{2}\ln\beta + \frac{3N}{2}\ln\left(\frac{2\pi m}{h^2}\right) + N\ln V - \ln N!\\ &= -\frac{3N}{2}\ln\beta + \text{terms not involving } \beta\end{aligned}$$

  - Therefore,

$$\langle E\rangle = -\frac{\partial \ln Q}{\partial \beta} = \frac{3N}{2}\frac{\mathrm{d}\ln\beta}{\mathrm{d}\beta} = \frac{3N}{2\beta} = \frac{3}{2}Nk_BT = \frac{3}{2}nRT$$

- The above result leads us to a fundamental postulate of physical chemistry: "The ensemble average of any quantity, as calculated using the probability distribution [$p_j = \frac{1}{Q}\mathrm{e}^{-\beta E_j}$], is the same as the experimentally observed value of that quantity" (McQuarrie & Simon, 1997, p. 700).
- The experimentally observed energy of a system is denoted by U.
- A molar quantity is denoted by an overbar (e.g., $\overline{U}$ is the experimentally observed energy of one mole of a system).
- Calculating the average energy of a diatomic ideal gas.
  - From Chapter 18,

$$Q(N,V,\beta) = \frac{[q(V,\beta)]^N}{N!} \qquad\qquad q(V,\beta) = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2}V\cdot\frac{8\pi^2 I}{h^2\beta}\cdot\frac{\mathrm{e}^{-\beta h\nu/2}}{1-\mathrm{e}^{-\beta h\nu}}$$

    for the rigid rotator-harmonic oscillator model of an ideal diatomic gas.
    - The first term in the expression for $q(V,\beta)$ is translational (and identical to that of a monatomic ideal gas), the second term is rotational, and the third term is vibrational.
  - Using the same procedure as before, we can calculate that for one mole of a diatomic ideal gas,

$$\overline{U} = \frac{3}{2}RT + RT + \frac{N_Ah\nu}{2} + \frac{N_Ah\nu\mathrm{e}^{-\beta h\nu}}{1-\mathrm{e}^{-\beta h\nu}}$$

    - "The first term represents the average translational energy, the second term represents the average rotational energy, the third term represents the zero-point vibrational energy, and the fourth term represents the average vibrational energy" (McQuarrie & Simon, 1997, p. 701).
    - Note that the fourth term becomes significant only at higher temperatures.

- **Constant-volume heat capacity**: A measure of how the energy of a system changes with temperature at constant amount and volume. *Denoted by* $\boldsymbol{C_V}$. *Given by*

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial U}{\partial T}$$

  - We can express C_V in terms of Q via our above expression for $\langle E \rangle$ as a function of Q.

- For an ideal monatomic gas,

$$\overline{C}_V = \frac{3}{2}R$$

- For an ideal diatomic gas,

$$\overline{C}_V = \frac{5}{2}R + R\left(\frac{h\nu}{k_BT}\right)^2 \frac{\mathrm{e}^{-h\nu/k_BT}}{(1-\mathrm{e}^{-h\nu/k_BT})^2}$$

- Molar heat capacity of a crystal, as per the **Einstein model of atomic crystals**.
  - Because each lattice site is identical, assume further that all atoms vibrate with the same frequency.
  - The associated partition function is thus

$$Q = \mathrm{e}^{-\beta U_0}\left(\frac{\mathrm{e}^{-\beta h\nu/2}}{1-\mathrm{e}^{\beta h\nu}}\right)^{3N}$$

    where ν is characteristic of the particular crystal and U_0 is the **sublimation energy** (at $0\,\mathrm{K}$).
  - It follows as before that

$$\overline{C}_V = 3R\left(\frac{h\nu}{k_BT}\right)^2 \frac{\mathrm{e}^{-h\nu/k_BT}}{(1-\mathrm{e}^{-h\nu/k_BT})^2}$$

- **Einstein model of atomic crystals**: A model of a crystal as N atoms situated at lattice sites, with each atom vibrating as a three-dimensional harmonic oscillator.
- **Sublimation energy** (at T): The energy needed to separate all the atoms from one another at T.
- One important consequence of this result is that by experimentally measuring the heat capacity of a crystal at different temperatures, we can determine its fundamental frequency ν.
- Another is the **law of Dulong and Petit**.
- **Law of Dulong and Petit**: The molar heat capacities of atomic crystals should level off at a value of $3R = 24.9\,\mathrm{J\,mol^{-1}\,K^{-1}}$ at high temperatures.
- Expressions for the average pressure $\langle P \rangle$ of a system.
  - From Chapter 19, the pressure of a macroscopic system in state J is

$$P_j(N,V) = -\frac{\partial E_j}{\partial V}$$

  - From the definition of $\langle P \rangle$ in MathChapter B, we have that

$$\langle P \rangle = \sum_j -\frac{\partial E_j}{\partial V}\frac{\mathrm{e}^{-\beta E_j}}{Q}$$

- We can make the above more compact since

$$\frac{\partial Q}{\partial V} = -\beta \sum_j \frac{\partial E_j}{\partial V} \mathrm{e}^{-\beta E_j} = Q\beta \langle P \rangle$$

  so

$$\langle P \rangle = \frac{1}{\beta} \frac{\partial \ln Q}{\partial V} \qquad\qquad \langle P \rangle = k_B T \frac{\partial \ln Q}{\partial V}$$

- Just like we did with energy, we equate the ensemble average pressure with the observed pressure via $P = \langle P \rangle$.
- Deriving the ideal-gas equation of state.
  - We restrict ourselves at first to the special case of a monatomic ideal gas.
  - As before, we have that

$$\begin{aligned}\ln Q &= \frac{3N}{2} \ln \left(\frac{2\pi m}{h^2 \beta} \right) + N \ln V - \ln N! \\ &= N \ln V + \text{terms not involving } V\end{aligned}$$

  - Therefore,

$$\begin{aligned}\langle P \rangle &= k_B T \frac{\partial \ln Q}{\partial V} = \frac{N k_B T}{V} \\ PV &= N k_B T\end{aligned}$$

  - Since only the terms not involving V change for diatomic and polyatomic gases, the above equation of state holds for all ideal gases.
- The partition function associated with the van der Waals equation is

$$Q(N, V, \beta) = \frac{1}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^{3N/2} (V - Nb)^N \mathrm{e}^{\beta a N^2 / V}$$

  - Indeed, going through the same process as above with this equation yields

$$\left(P + \frac{aN^2}{V^2} \right) (V - Nb) = N k_B T$$

- Since we lack the computational power to calculate the set $\{E_j\}$ of eigenvalues of the N-body Schrödinger equation, we often approximate each E_j as the sum of the energies of the constituent particles of a system.
- Consider a system of independent, *distinguishable* particles.
  - A good example of one is the Einstein model of atomic crystals, since each atom is assumed to vibrate independently of the others and each atom is distinguishable by its position in the crystal lattice.
  - Applying the summation approximation, we get

$$E_l(N, V) = \underbrace{\varepsilon_i^a(V) + \varepsilon_j^b(V) + \varepsilon_k^c(V) + \cdots}_{N \text{ times}}$$

  where each ε_i^a denotes the energy of an individual particle (i being the energy state, and a being the index of the particle [they are distinguishable]).

- Under this approximation, the partition function of the system becomes

$$Q(N,V,T) = \sum_l \mathrm{e}^{-\beta E_l} = \sum_{i,j,k,\dots} \mathrm{e}^{-\beta(\varepsilon_i^a(V)+\varepsilon_j^b(V)+\varepsilon_k^c(V)+\cdots)}$$

- Since we can sum over the indices separately (i.e., one after another), the above summation can mathematically be rewritten

$$\begin{aligned} Q(N,V,T) &= \sum_i \mathrm{e}^{-\beta\varepsilon_i^a} \sum_j \mathrm{e}^{-\beta\varepsilon_j^b} \sum_k \mathrm{e}^{-\beta\varepsilon_k^c} \cdots \\ &= q_a(V,T) q_b(V,T) q_c(V,T) \cdots \end{aligned}$$

  where each $q(V,T)$ is a **molecular partition function**.

- **Molecular partition function**: A partition function pertaining to a particular molecule within a system. *Denoted by* $q(V,T)$. *Given by*

$$q(V,T) = \sum_j \mathrm{e}^{-\varepsilon_j/k_BT}$$

  - Often able to be evaluated since they only depend on the allowed energies of individual atoms or molecules.

- **Boson**: A particle whose wave function must be symmetric under the interchange of two identical particles.
  - Particles of integer spin (such as photons [spin 1] and deuterons [spin 0]) are bosons.
  - Two identical fermions *can* occupy the same single-particle energy state.

- **Fermions**: A particle whose wave function must be antisymmetric under the interchange of two identical particles.
  - Particles of half-integer spin (such as electrons, protons, and neutrons [all with spin 1/2]) are fermions.
  - Two identical fermions *cannot* the same single-particle energy state.

- Consider a system of independent, *indistinguishable* particles.
  - As before, we have that $E_{ijk\dots} = \varepsilon_i + \varepsilon_j + \varepsilon_k + \cdots$ for N terms, but we since we cannot distinguish between particles, we cannot sum over the indices separately.
  - Thus, our partition function is set at

$$Q(N,V,T) = \sum_{i,j,k,\dots} \mathrm{e}^{-\beta(\varepsilon_i+\varepsilon_j+\varepsilon_k+\cdots)}$$

  - If the particles in question are fermions, the indices are not independent of each other.
    - In particular, we cannot have a $\varepsilon_1 + \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \cdots$ term in the summation because no two fermions can occupy the same single-particle energy state.
    - This restriction omits all terms with more than one particle in the same energy state from the summation.
  - If the particles in question are bosons, then we must avoid summing identical terms.
    - In particular, terms such as $\varepsilon_1 + \varepsilon_2 + \varepsilon_2 + \varepsilon_2 + \cdots$ and $\varepsilon_2 + \varepsilon_1 + \varepsilon_2 + \varepsilon_2 + \cdots$ represent the same state, and thus should be included only once in the summation. However, an unrestricted summation would include N such terms.
    - On the other end of the spectrum, there are $N!$ terms that include $\epsilon_1 + \epsilon_2 + \epsilon_3 + \cdots + \epsilon_N$ in some order.

- In either case, the terms causing the problems are those with two or more identical indices.
- If it were not for such terms, we could carry out the summation in an unrestricted manner, obtaining $[q(V,T)]^N$ as with distinguishable particles (forcing each particle to have a different state is mathematically equivalent to making them distinguishable), and then divide by $N!$, obtaining $[q(V,T)]^N/N!$, to account for the over-counting.
- But such terms do exist in the summation. However, there are times when their presence is negligible.
  - If, for example, the number of quantum states available to any particle is significantly greater than the number of particles, it is very unlikely that two particles will ever be in the same state.
  - Indeed, most quantum-mechanical systems have an infinite number of energy states. However, at any given temperature, many of these states will be energetically inaccessible.
  - Thus, we can only invoke the $[q(V,T)]^N/N!$ approximation if the number of quantum states with energies less than k_BT (which is roughly the average energy of a molecule) is much larger than the number of particles.
- In particular, if

$$\frac{N}{V}\left(\frac{h^2}{8mk_BT}\right)^{3/2} \ll 1$$

then we may approximate

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!}$$

  - This criterion favors large particle mass, high temperature, and low density.
  - It is easily satisfied in most conventional cases.
  - Quantum systems that do not satisfy this criterion must be treated by special methods beyond the scope of McQuarrie and Simon (1997).

- **Boltzmann statistics**: Statistics in which the number of available molecular states is much greater than the number of particles.
  - Favored by high temperatures.
- Relating the average energy $\langle E\rangle$ of a system to the average energy $\langle \varepsilon\rangle$ of a constituent molecule.

$$\begin{aligned}\langle E\rangle &= k_BT^2\frac{\partial \ln Q}{\partial T}\\ &= k_BT^2\frac{\partial}{\partial T}\left(\ln\left(\frac{q^N}{N!}\right)\right)\\ &= Nk_BT^2\frac{\partial \ln q}{\partial T}\\ \langle E\rangle &= N\langle \varepsilon\rangle\end{aligned}$$

- The probability that a molecule is in its j^{th} molecular energy state is denoted by π_j.
- Assuming $\varepsilon = \varepsilon_i^{\text{trans}} + \varepsilon_i^{\text{rot}} + \varepsilon_i^{\text{vib}} + \varepsilon_i^{\text{elec}}$ allows us to write $q = q_{\text{trans}}q_{\text{rot}}q_{\text{vib}}q_{\text{elec}}$ since the various energy terms are distinguishable here (hence we can sum over the indices separately).
- The probability that a molecule is in its i^{th} translational, j^{th} rotational, k^{th} vibrational, and l^{th} electronic state is given by

$$\pi_{ijkl} = \frac{e^{-\varepsilon_i^{\text{trans}}/k_BT}e^{-\varepsilon_j^{\text{rot}}/k_BT}e^{-\varepsilon_k^{\text{vib}}/k_BT}e^{-\varepsilon_l^{\text{elec}}/k_BT}}{q_{\text{trans}}q_{\text{rot}}q_{\text{vib}}q_{\text{elec}}}$$

- Since the total probability π_k^{vib} that a molecule is in its k^{th} vibrational state (for example) encompasses all probabilities of it being in any translational, rotational, or vibrational state, we have by summation that

$$\pi_k^{\text{vib}} = \sum_{i,j,l} \pi_{ijkl} = \frac{\sum_i \left(\mathrm{e}^{-\varepsilon_i^{\text{trans}}/k_BT}\right) \sum_j \left(\mathrm{e}^{-\varepsilon_j^{\text{rot}}/k_BT}\right) \sum_l \left(\mathrm{e}^{-\varepsilon_l^{\text{elec}}/k_BT}\right) \mathrm{e}^{-\varepsilon_k^{\text{vib}}/k_BT}}{q_{\text{trans}}q_{\text{rot}}q_{\text{vib}}q_{\text{elec}}} = \frac{\mathrm{e}^{-\varepsilon_k^{\text{vib}}/k_BT}}{q_{\text{vib}}}$$

- It follows that

$$\left\langle \varepsilon^{\text{vib}} \right\rangle = \sum_k \varepsilon_k^{\text{vib}} \frac{\mathrm{e}^{-\varepsilon_k^{\text{vib}}/k_BT}}{q_{\text{vib}}} = -\frac{\partial \ln q_{\text{vib}}}{\partial \beta} = k_BT^2 \frac{\partial \ln q_{\text{vib}}}{\partial T}$$

  - Analogous results hold for $\langle \varepsilon^{\text{trans}} \rangle$, $\langle \varepsilon^{\text{rot}} \rangle$, and $\left\langle \varepsilon^{\text{elec}} \right\rangle$.

- Although we have written partition functions as sums over energy *states* up to this point, we can also sum over energy *levels* by including the degeneracy g_J of the level.

  - For example, since the energy and degeneracy of a rigid rotator are, respectively,

$$\varepsilon_j = \frac{\hbar^2}{2I} J(J+1) \qquad\qquad g_J = 2J+1$$

    we can write

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1)\mathrm{e}^{-\hbar^2 J(J+1)/2Ik_BT}$$

Week 2

Partition Functions and Ideal Gases

2.1 System Partition Functions

1/19:
- Decomposing the partition function of a molecule into the product of separate sums as partitioned by degrees of freedom (e.g., translation, rotation, vibration, and electronic).
- The partition functions of **independent**, distinguishable/indistinguishable molecules.
  - We should not double count the same states.
  - The $N!$ in $Q = q^N/N!$ is not important when calculating energy (because of the properties of the ln function), but it is very important when calculating quantities such as entropy.
- **Independent** (particles): A set of particles that do not interact with one another.
- Discusses bosons and fermions.
  - We can have a two fermions in the state $|1,1\rangle$ because it is a symmetric state.
- Recall the Fermi level, the boundary between the filled and unfilled electronic states in a solid.
  - If T is small, this level is a hard boundary.
  - If T is large, electrons can easily be excited and the Fermi level is a soft boundary.
- Does the 3D particle in a box derivation for the translation molecular partition function.
  - Note that since the de Broglie wavelength $\lambda_{\text{DB}} = \sqrt{h^2/2mk_BT}$, we may write
$$q_x = \sum_{n_x} \mathrm{e}^{-h^2/8mk_BTL_x^2} = \sum_{n_x} \mathrm{e}^{-\lambda_{\text{DB}}^2 n_x^2/4L_x^2}$$
- The number of states are occupied/have energy within k_BT of the ground state.
  - $-\lambda_{\text{DB}}^2 n_x^2/4L_x^2$ is on the order of 1, implying that n_x is on the order of $2L/\lambda_{\text{DB}}$.
  - It follows if L is on a macroscopic scale (e.g., $L \approx 1\,\text{m}$) and λ_{DB} is on a sub-angstrom scale that n_x is on the order of 10^{10}. When n_x is at such a scale, $\mathrm{e}^{-\lambda_{\text{DB}}^2 n_x^2/4L_x^2} \approx 1/\mathrm{e}$.
  - It follows that in a $1\,\text{m}^3$ box, we will have about 10^{30} states, so we really are in a regime where the number of states is larger than the number of molecules.
- More precisely, we want
$$N \ll n_x n_y n_z = \left(\frac{8mk_BT}{h^2}\right)^{3/2} L_x L_y L_z$$
where the middle term approximates the number of states so that
$$\frac{N}{V} \ll \left(\frac{8mk_BT}{h^2}\right)^{3/2}$$

- Approximating the translational energy with an integral.
  - Concludes with the translational partition function.
  - Since we can approach this problem from a classical perspective (as we did last Friday) or quantum mechanically (as we did today) to achieve the same result, this system again demonstrates the relation between quantum and classical mechanics.

2.2 Molecular Partition Functions

1/21:

- We approximate the total molecular energy as

$$q = q_{\text{elec}} q_{\text{trans}} q_{\text{vib}} q_{\text{rot}}$$

- The heat capacity in the very high temperature limit where translations, rotations, and vibrations are classical.
  - Translational: $\frac{3}{2}k_B$.
  - Vibrational: Each degree of freedom ($3N-5$ for a linear molecule and $3N-6$ for a nonlinear molecule) contributes k_B.
  - Rotational: Each degree of freedom (2 for a linear molecule and 3 for a nonlinear molecule) contributes $\frac{1}{2}k_B$.
- We can use the above to calculate the heat capacity of various molecules at very high temperatures (note, however, that at such temperatures, molecules would likely dissociate; we're simply theoretically considering the classical limit here).
  - Ne: $\frac{3}{2}k_B$.
  - H_2O: $\frac{3}{2}k_B + 3 \cdot k_B + 3 \cdot \frac{1}{2}k_B = 6k_B$.
  - O_2: $\frac{3}{2} + 1 \cdot k_B + 2 \cdot \frac{1}{2}k_B = \frac{7}{2}k_B$.
  - CO_2: $\frac{3}{2}k_B + 4 \cdot k_B + 2 \cdot \frac{1}{2}k_B = \frac{13}{2}k_B$.
  - $CHCl_3$: $\frac{3}{2}k_B + 9 \cdot k_B + 3 \cdot \frac{1}{2}k_B = 12k_B$.
- Electronic partition function.
  - Consider the bottom D_e of the potential well of a diatomic.
  - D_0 is the ionization energy from the bottom state ($D_e \neq D_0$, but relations can be obtained via spectroscopy).
  - It follows that

$$q_{\text{elec}} = g_1 \mathrm{e}^{-(-D_e/k_BT)} + g_2 \mathrm{e}^{-E_2/k_BT}$$

  - If $\mathrm{d}T \ll (E_2 + D_e)$, then $q_{\text{elec}} = g_1 \mathrm{e}^{D_e/k_BT}$.
- Vibrational partition function.
  - As before with the law of Dulong and Petit.
  - It's a special point where $T = h\nu/k_B$.
- Rotational partition function.
  - Almost always classical.
  - The rotational energy of a polyatomic molecule will almost always be $\frac{3}{2}k_B$.
  - Let's look at a heteronuclear diatomic, such as CO. Derives

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)\mathrm{e}^{-\hbar^2 J(J+1)/2Ik_BT}$$

  - The **rotational temperature** leads to

$$q_{\text{rot}} = \sum_{J=0}^{\infty}(2J+1)\mathrm{e}^{\Theta_{\text{rot}}/T} = \frac{T}{\Theta_{\text{rot}}}$$

  - Thus, at the temperature at which we exist, rotation is equivalent classically to quantum mechanically.

- **Rotational temperature**: The following quantity. *Denoted by* $\mathbf{\Theta_{rot}}$. *Given by*

$$\Theta_{\text{rot}} = \hbar^2/2Ik_B$$

- PGS will not specify whether we need a quantum vs. classical model.
- Homonuclear diatomic (e.g., H_2).
  - The vibrational differences in energy become visible with spectroscopy.
- $q_{\text{rot}} = T/2\Theta_{\text{rot}}$.
- Partition functions:
  - If the molecule is linear, it's of the form T/Θ_{rot}.
  - If the molecule is nonlinear, it's of the form $T/2\Theta_{\text{rot}}$.
  - Spherical top (e.g., CH_4):

$$\frac{\sqrt{\pi}}{\sigma}\left(\frac{T}{\Theta_{\text{rot}}}\right)^{3/2}$$

  - Symmetric top (e.g., NH_3):

$$\frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_{\text{rot},a}^2\Theta_{\text{rot},b}}}$$

    - a and b are the two different symmetry axes.
  - Asymmetric top (e.g., H_2O):

$$\frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_{\text{rot},a}\Theta_{\text{rot},b}\Theta_{\text{rot},c}}}$$

- Application to total energy and heat capacity of a molecule.
  - We have that

$$q = \left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\cdot V\cdot\sqrt{\frac{T^2}{\sigma\Theta_{\text{rot},a}\Theta_{\text{rot},b}\Theta_{\text{rot},c}}}\cdot\sum_{1}^{3N-6}\frac{\mathrm{e}^{-\Theta_{\text{vib}}/2T}}{1-\mathrm{e}^{\Theta_{\text{vib}}/T}}\cdot g_1\mathrm{e}^{D_e/k_BT}$$

  - Thus,

$$\langle E\rangle = k_BT^2\frac{\partial\ln q}{\partial T} = k_BT^2\frac{\partial}{\partial T}\left(\frac{3}{2}\ln T + \text{constant} + \frac{3}{2}\ln T + \text{vibration} - D_e\right)$$

  - The energy of the vibration is $E = k_B\Theta_{\text{vib}}/(\mathrm{e}^{\Theta_{\text{vib}}/k_BT}-1) + k_B\Theta_{\text{vib}}/2$. It follows that

$$C = \frac{\partial E}{\partial T} = k_B\frac{\Theta_{\text{vib}}^2}{T^2}\frac{\mathrm{e}^{-\Theta_{\text{vib}}/T}}{(1-\mathrm{e}^{-\Theta_{\text{vib}}/T})}$$

2.3 Chapter 18: Partition Functions and Ideal Gases

From McQuarrie and Simon (1997).

1/23: - Herein, we will calculate the partition functions and heat capacities of ideal gases.
    - We heavily rely on the expression of the partition function for a system of independent, indistinguishable particles, which ideal gases are likely to satisfy because of their low density.
- Deriving the translational molecular partition function of an atom in a monatomic ideal gas.
    - As mentioned in Chapter 17, if we let the container be cubic, then

$$\varepsilon(n_x,n_y,n_z)=\frac{h^2}{8ma^2}(n_x^2+n_y^2+n_z^2)$$

    - It follows that

$$\begin{aligned}
q_{\text{trans}} &= \sum_{n_x,n_y,n_z=1}^{\infty}\mathrm{e}^{-\beta\varepsilon(n_x,n_y,n_z)}\\
&= \sum_{n_x=1}^{\infty}\exp\left(-\frac{\beta h^2n_x^2}{8ma^2}\right)\sum_{n_y=1}^{\infty}\exp\left(-\frac{\beta h^2n_y^2}{8ma^2}\right)\sum_{n_z=1}^{\infty}\exp\left(-\frac{\beta h^2n_z^2}{8ma^2}\right)\\
&= \left[\sum_{n=1}^{\infty}\exp\left(-\frac{\beta h^2n^2}{8ma^2}\right)\right]^3
\end{aligned}$$

    - The above sum cannot be evaluated in closed form. However, since later terms in the summation get very small, it is an excellent approximation to replace the summation with an integral, i.e.,

$$\begin{aligned}
q_{\text{trans}} &= \left(\int_0^{\infty}\mathrm{e}^{-\beta h^2n^2/8ma^2}\,\mathrm{d}n\right)^3\\
&= \left(\sqrt{\frac{\pi}{4\beta h^2/8ma^2}}\right)^3\\
&= \left(\sqrt{\frac{2\pi m}{\beta h^2}}\right)^3a^3\\
&= \left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}V
\end{aligned}$$

1/24: - Deriving the electronic molecular partition function of an atom in a monatomic ideal gas.
    - We express the partition function here in terms of levels, i.e., by

$$q_{\text{elec}}=\sum_i g_{ei}\mathrm{e}^{-\beta\varepsilon_{ei}}$$

      where g_{ei} is the degeneracy and ε_{ei} is the energy of the i^{th} electronic level.
    - Taking $\varepsilon_{e1}=0$ to be the zero of energy yields

$$q_{\text{elec}}=g_{e1}+g_{e2}\mathrm{e}^{-\beta\varepsilon_{e2}}+\cdots$$

        - Note that since ε's are usually on the order of tens of thousands of wavenumbers, $\mathrm{e}^{-\beta\varepsilon_{e2}}$ is around 10^{-5} for most atoms at ordinary temperatures, so only the first term in the summation is significantly different from zero.
        - For some gases such as halogens, other terms may be important, but even there the sum converges very rapidly.

- Using spectroscopic data, we can show that the fraction of atoms of most gases in the first excited state is very small.
  - For example, the fraction of helium atoms at 300 K in the first excited state is 10^{-334}.
  - For fluorine, however, the fraction is on the order of 10^{-2}, which is significant. In this case, we need to approximate q_{elec} with more than one or two terms.

- McQuarrie and Simon (1997) recalculates the average energy, heat capacity, and pressure of a monatomic ideal gas using the above results.
- Diatomics.
  - The translational partition function is

$$q_{\text{trans}}(V,T) = \left[\frac{2\pi(m_1+m_2)k_BT}{h^2}\right]^{3/2} V$$

  - We take the zero of rotational energy to be the $J=0$ state.
  - We take the zero of vibrational energy to be the bottom of the internuclear potential well of the lowest electronic state (so that the energy of the ground vibrational state is $h\nu/2$).
  - We take the zero of electronic energy to be the energy of the separated atoms at rest in their ground electronic state (so that the energy of the ground electronic state is $-D_e$[1]).
- **Vibrational temperature**: The following quantity. *Denoted by* $\mathbf{\Theta}_{\text{vib}}$. *Given by*

$$\Theta_{\text{vib}} = \frac{h\nu}{k_B}$$

- Deriving the vibrational molecular partition function of a molecule in a diatomic ideal gas.

$$\begin{aligned}
q_{\text{vib}}(T) &= \sum_{v=0}^{\infty} \mathrm{e}^{-\beta(v+1/2)h\nu} \\
&= \mathrm{e}^{-\beta h\nu/2} \sum_{v=0}^{\infty} \mathrm{e}^{-\beta h\nu v} \\
&= \mathrm{e}^{-\beta h\nu/2} \frac{1}{1-\mathrm{e}^{-\beta h\nu}} \\
&= \frac{\mathrm{e}^{-\beta h\nu/2}}{1-\mathrm{e}^{-\beta h\nu}}
\end{aligned}$$

- In terms of Θ_{vib},

$$\begin{aligned}
q_{\text{vib}}(T) &= \frac{\mathrm{e}^{-\Theta_{\text{vib}}/2T}}{1-\mathrm{e}^{-\Theta_{\text{vib}}/T}} \\
\langle E_{\text{vib}}\rangle &= Nk_B\left(\frac{\Theta_{\text{vib}}}{2} + \frac{\Theta_{\text{vib}}}{\mathrm{e}^{\Theta_{\text{vib}}/T}-1}\right) \\
\overline{C}_{\text{V,vib}} &= R\left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{\mathrm{e}^{-\Theta_{\text{vib}}/T}}{(1-\mathrm{e}^{-\Theta_{\text{vib}}/T})^2}
\end{aligned}$$

- Note that the high temperature limit of $\overline{C}_{\text{V,vib}}$ is R, and $\overline{C}_{\text{V,vib}}$ attains $R/2$ at $T = 0.34\,\Theta_{\text{vib}}$.
- Calculating the fraction of molecules in the ground vibrational state reveals that generally, most molecules are in the ground vibrational state.

[1] See Figure 9.7 of Labalme (2021b).

  - Exceptions include Br_2, the smaller force constant and larger mass of which lead to a smaller value of Θ_{vib}.
- **Rotational temperature**: The following quantity. *Denoted by* $\mathbf{\Theta}_{\text{rot}}$. *Given by*

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B} = \frac{hB}{k_B}$$

  - B is the rotational constant (see Chapter 5) in the above equation.
- Deriving the rotational molecular partition function of a *heteronuclear* molecule in a diatomic ideal gas.
  - We have

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1)\mathrm{e}^{-\Theta_{\text{rot}}J(J+1)/T}$$

  - As with the translational partition function, for $\Theta_{\text{rot}} \ll T$ (which is true for normal temperatures), we may approximate the above sum via an integral. This approximation is known as the high-temperature limit, and under it,

$$\begin{aligned}
q_{\text{rot}}(T) &= \int_0^\infty (2J+1)\mathrm{e}^{-\Theta_{\text{rot}}J(J+1)/T}\,\mathrm{d}J \\
&= \int_0^\infty \mathrm{e}^{-\Theta_{\text{rot}}x/T}\,\mathrm{d}x \\
&= \frac{T}{\Theta_{\text{rot}}} = \frac{8\pi^2 Ik_BT}{h^2}
\end{aligned}$$

  - For low temperatures or molecules with large values of Θ_{rot} we evaluate some number of terms of the sum directly, but we will not consider these cases further.
- It follows from the above that

$$\langle E_{\text{rot}}\rangle = Nk_BT \qquad\qquad \overline{C}_{V,\text{rot}} = R$$

  - Each of the two rotational degrees of freedom of a diatomic contributes $R/2$ to $\overline{C}_{V,\text{rot}}$.
- Contrary to the other component parts of energy, higher energy rotational states are significantly occupied.

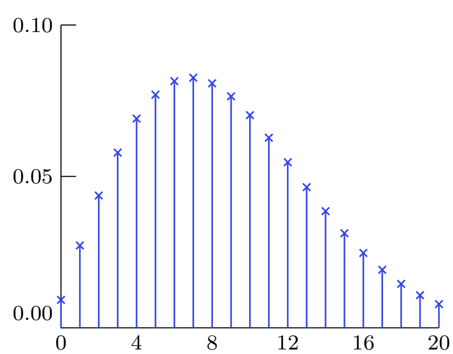


Figure 2.1: The fraction of molecules in the J^{th} rotational level for CO at 300 K.

  - We have that the fraction f_J of molecules in the J^{th} vibrational state is

$$f_J = \frac{(2J+1)\mathrm{e}^{-\Theta_{\text{rot}}J(J+1)/T}}{q_{\text{rot}}} = (2J+1)(\tfrac{\Theta_{\text{rot}}}{T})\mathrm{e}^{-\Theta_{\text{rot}}J(J+1)/T}$$

- We can estimate the most probable value of J by solving $\partial f_J/\partial J = 0$, which gives $J = 7$ in agreement with Figure 2.1.

1/25:

- We now address the rotational molecular partition function for a *homonuclear* diatomic ideal gas molecule.
  - Because of the additional perpendicular C_2 axes of symmetry in a homonuclear diatomic compared to a heteronuclear diatomic, the diatomic's constituent atoms are 'more' indistinguishable, i.e., only nuclear spin can distinguish them.
  - "In particular, if the two nuclei have integral spins (bosons), the molecular wave function must be symmetric with respect to an interchange of the two nuclei; if the nuclei have half odd integer spin (fermions), the molecular wave function must be antisymmetric" (McQuarrie & Simon, 1997, p. 747).
  - This symmetry affects the population of the rotational energy levels in a way that *can* be derived, but we will just state the important result, which is that for a homonuclear diatomic molecule,

$$q_{\text{rot}}(T) = \frac{T}{2\Theta_{\text{rot}}}$$

- To unify the two rotational molecular partition functions, we let

$$q_{\text{rot}}(T) = \frac{T}{\sigma\Theta_{\text{rot}}}$$

in general, where σ is the **symmetry number**.

- **Symmetry number**: The number of different ways a given molecule can be rotated into a configuration indistinguishable from the original. *Denoted by* $\boldsymbol{\sigma}$. *Given by*

$$\sigma = \begin{cases} 1 & \text{heteronuclear} \\ 2 & \text{homonuclear} \end{cases}$$

- Taking the energy of an ideal diatomic gas molecule to be a simple sum of its translational, rotational, vibrational, and electronic energies yields the molecular partition function

$$q(V,T) = \left(\frac{2\pi M k_BT}{h^2}\right)^{3/2} V \cdot \frac{T}{\sigma\Theta_{\text{rot}}} \cdot \frac{\mathrm{e}^{-\Theta_{\text{vib}}/2T}}{1-\mathrm{e}^{-\Theta_{\text{vib}}/T}} \cdot g_{e1}\mathrm{e}^{D_e/k_BT}$$

where we require $\Theta_{\text{rot}} \ll T$, that the only populated electronic state is the ground state, that the zero of electronic energy is the separated atoms at rest in their ground electronic states, and that the zero of vibrational energy is the bottom of the internuclear potential well of the lowest electronic state.

- McQuarrie and Simon (1997) derives the molar energy and heat capacity of a diatomic ideal gas one more time using the above equation.
  - The only difference is that the newly added electronic factor in the partition function adds a term of $-N_AD_e$ to the Chapter 17 formula for $\overline{U}$.
  - Also note that we can greatly improve the agreement of the harmonic oscillator-rigid rotator model with even small first-order corrections, such as including centrifugal distortion and anharmonicity.
- The translational and electronic molecular partition functions of an ideal polyatomic molecule are the same as those of an ideal monatomic or diatomic molecule.
- On the vibrational molecular partition function of an ideal polyatomic molecule.
  - Recall from Chapter 13 that the vibrational motion of a polyatomic molecule can be expressed in terms of normal coordinates.

- Thus, the vibrational energy of a polyatomic molecule in state $v_j = 0, 1, 2, \ldots$ is

$$\varepsilon_{\text{vib}} = \sum_{j=1}^{N_{\text{vib}}} \left(v_j + \tfrac{1}{2}\right) h\nu_j$$

where ν_j is the frequency of the j^{th} normal mode.

- It follows that for a polyatomic molecule,

$$q_{\text{vib}} = \prod_{j=1}^{N_{\text{vib}}} \frac{\mathrm{e}^{-\Theta_{\text{vib},j}/2T}}{1 - \mathrm{e}^{-\Theta_{\text{vib},j}/T}}$$

$$E_{\text{vib}} = Nk_B \sum_{j=1}^{N_{\text{vib}}} \left(\frac{\Theta_{\text{vib},j}}{2} + \frac{\Theta_{\text{vib},j}\mathrm{e}^{-\Theta_{\text{vib},j}/T}}{1 - \mathrm{e}^{-\Theta_{\text{vib},j}/T}} \right)$$

$$C_{V,\text{vib}} = Nk_B \sum_{j=1}^{N_{\text{vib}}} \left[\left(\frac{\Theta_{\text{vib},j}}{T} \right)^2 \frac{\mathrm{e}^{-\Theta_{\text{vib},j}/T}}{(1 - \mathrm{e}^{-\Theta_{\text{vib},j}/T})^2} \right]$$

- Rotational molecular partition functions for linear molecules.
  - We can still apply the rigid-rotator approximation, but with

$$I = \sum_{j=1}^{n} m_j d_j^2$$

where d_j is the distance of the j^{th} nucleus from the center of mass of the molecule.

  - Doing so yields

$$q_{\text{rot}}(T) = \frac{T}{\sigma\Theta_{\text{rot}}}$$

where $\sigma = 1$ for unsymmetrical molecules such as N_2O and COS and $\sigma = 2$ for symmetrical molecules such as CO_2 and C_2H_2.

- Note that the symmetry number of NH_3 is three.
- Rotational molecular partition functions for nonlinear molecules.
  - Recall the discussion surrounding the principal moments of inertia in Chapter 13.
  - We define three characteristic rotational temperatures, namely $\Theta_{\text{rot},j} = \hbar^2/2I_jk_B$ for $j = A, B, C$.
  - Spherical top.
    - In this case, $\Theta_{\text{rot},A} = \Theta_{\text{rot},B} = \Theta_{\text{rot},C} = \Theta_{\text{rot}}$.
    - The quantum-mechanical spherical top can be solved exactly to give

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \qquad\qquad g_J = (2J+1)^2$$

    - Now $\Theta_{\text{rot}} \ll T$ for almost all spherical top molecules at ordinary temperatures, and this has two important consequence. First, we can approximate the partition function with an integral. Second, we can neglect 1 in comparison with J since the important values of J are large. Thus, we have that

$$\begin{aligned} q_{\text{rot}}(T) &= \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1)^2 \mathrm{e}^{-\hbar^2 J(J+1)/2Ik_BT} \\ &= \frac{1}{\sigma} \int_0^{\infty} (2J+1)^2 \mathrm{e}^{-\Theta_{\text{rot}} J(J+1)/T} \,\mathrm{d}J \end{aligned}$$

$$
\begin{aligned}
&= \frac{1}{\sigma}\int_0^\infty 4J^2\mathrm{e}^{-\Theta_{\text{rot}}J^2/T}\,\mathrm{d}J \\
&= \frac{4}{\sigma}\int_0^\infty J^2\mathrm{e}^{-aJ^2}\,\mathrm{d}J \\
&= \frac{4}{\sigma}\cdot\frac{1}{4a}\sqrt{\frac{\pi}{a}} \\
q_{\text{rot}}(T) &= \frac{\sqrt{\pi}}{\sigma}\left(\frac{T}{\Theta_{\text{rot}}}\right)^{3/2}
\end{aligned}
$$

- Similarly, we have respectively for a symmetric top and an asymmetric top that

$$
q_{\text{rot}}(T) = \frac{\sqrt{\pi}}{\sigma}\left(\frac{T}{\Theta_{\text{rot},A}}\right)\sqrt{\frac{T}{\Theta_{\text{rot},C}}} \qquad q_{\text{rot}}(T) = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T}{\Theta_{\text{rot},A}\Theta_{\text{rot},B}\Theta_{\text{rot},C}}}
$$

- It follows that

$$
\overline{U}_{\text{rot}} = \frac{3RT}{2} \qquad \overline{C}_{V,\text{rot}} = \frac{3R}{2}
$$

- Linear molecule equations.

$$
\begin{aligned}
q(V,T) &= \left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2} V\cdot\frac{T}{\sigma\Theta_{\text{rot}}}\cdot\prod_{j=1}^{3n-5}\frac{\mathrm{e}^{-\Theta_{\text{vib},j}/2T}}{1-\mathrm{e}^{-\Theta_{\text{vib},j}/T}}\cdot g_{e1}\mathrm{e}^{D_e/k_BT} \\
\frac{U}{Nk_BT} &= \frac{3}{2}+\frac{2}{2}+\sum_{j=1}^{3n-5}\left(\frac{\Theta_{\text{vib},j}}{2T}+\frac{\Theta_{\text{vib},j}/T}{\mathrm{e}^{\Theta_{\text{vib},j}/T}-1}\right)-\frac{D_e}{k_BT} \\
\frac{C_V}{Nk_B} &= \frac{3}{2}+\frac{2}{2}+\sum_{j=1}^{3n-5}\left(\frac{\Theta_{\text{vib},j}}{T}\right)^2\frac{\mathrm{e}^{-\Theta_{\text{vib},j}/T}}{(1-\mathrm{e}^{-\Theta_{\text{vib},j}/T})^2}
\end{aligned}
$$

- Nonlinear molecule equations.

$$
\begin{aligned}
q(V,T) &= \left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2} V\cdot\frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_{\text{rot},A}\Theta_{\text{rot},B}\Theta_{\text{rot},C}}}\cdot\prod_{j=1}^{3n-6}\frac{\mathrm{e}^{-\Theta_{\text{vib},j}/2T}}{1-\mathrm{e}^{-\Theta_{\text{vib},j}/T}}\cdot g_{e1}\mathrm{e}^{D_e/k_BT} \\
\frac{U}{Nk_BT} &= \frac{3}{2}+\frac{3}{2}+\sum_{j=1}^{3n-6}\left(\frac{\Theta_{\text{vib},j}}{2T}+\frac{\Theta_{\text{vib},j}/T}{\mathrm{e}^{\Theta_{\text{vib},j}/T}-1}\right)-\frac{D_e}{k_BT} \\
\frac{C_V}{Nk_B} &= \frac{3}{2}+\frac{3}{2}+\sum_{j=1}^{3n-6}\left(\frac{\Theta_{\text{vib},j}}{T}\right)^2\frac{\mathrm{e}^{-\Theta_{\text{vib},j}/T}}{(1-\mathrm{e}^{-\Theta_{\text{vib},j}/T})^2}
\end{aligned}
$$

Part II

Thermodynamics

Week 3

Kinetic Theory of Gases / The First Law of Thermodynamics

3.1 Maxwell-Boltzmann Distribution

1/24:
- Applying the molecular partition function to the heat capacity of a water molecule.
  - A water molecule has three vibrational modes, which we will denote by ν_1, ν_2, ν_3 (corresponding to symmetric stretch, antisymmetric stretch, and bend).
  - Main takeaway: Heat capacity can change with temperature.
  - After a while (at several thousand kelvin), it will level off (see Figure 18.7).
- Considers CO_2's vibrational modes, too.
  - The infrared absorption of the bending mode is what's associated with the Greenhouse Effect.
  - The symmetric stretch is IR inactive due to its lack of change of dipole moment.
  - Raman active: Change in the polarizability of the molecule.
- The Maxwell-Boltzmann distribution.
  - Maxwell derived it long before Boltzmann, but Boltzmann's thermodynamic derivation is much easier.
  - We know from the Boltzmann factor that $p(E) \propto \mathrm{e}^{-E/k_BT}$.
  - Thus, to get the probability $p(v)$ of some speed v, we should have $p(v) \propto \mathrm{e}^{-mv^2/2k_BT}$ times a constant giving the number of molecules of each speed? This yields

    $$p(v) = A4\pi v^2 \mathrm{e}^{-mv^2/2k_BT}$$

    where A is a normalization constant.
  - The Maxwell-Boltzmann distribution is such that

    $$\begin{aligned}
    1 &= \int_0^\infty p(v)\,\mathrm{d}v \\
    &= A\int_0^\infty 4\pi v^2 \mathrm{e}^{-mv^2/2k_BT}\,\mathrm{d}v \\
    &= A\int_0^\infty 4\pi \left(\frac{2k_BT}{m}\right)^{3/2} u^2\mathrm{e}^{-u^2}\,\mathrm{d}u \\
    &= A4\pi \left(\frac{2k_BT}{m}\right)^{3/2} \int_0^\infty u^2\mathrm{e}^{-u^2}\,\mathrm{d}u
    \end{aligned}$$

$$= A4\pi \left(\frac{2k_BT}{m}\right)^{3/2} \frac{\sqrt{\pi}}{4}$$

$$A = \left(\frac{m}{2\pi k_BT}\right)^{3/2}$$

- Therefore,

$$p(v) = 4\pi \left(\frac{m}{2\pi k_BT}\right)^{3/2} v^2 \mathrm{e}^{-mv^2/2k_BT}$$

- Any distribution that doesn't look like this isn't in thermal equilibrium.

- A system with all particles having $v = 0$ is at thermal equilibrium with $T = 0\,\mathrm{K}$.
- A system with all particles having constant velocity in the same direction is at thermal equilibrium with $T = 0\,\mathrm{K}$.
  - Think relativity; if you're moving with them, it looks like they're not moving and thus this case is the same as the last one because you're movement doesn't affect the thermodynamics of that system.
- A system with all particles having constant velocity in different directions is not at thermal equilibrium since it does not fit the bell curve but is rather a spike.

3.2 The First Law of Thermodynamics

1/26: - See Labalme (2021c) for background on/content of today's lecture.
- Joule best quantified how we think about work and energy.
- **System**: Part of the world being investigated. It can contain energy, a number of particles, etc.
- The Newtonian way to change the energy into a system is to do work (mechanical, electrical, etc.) on the system. In chemistry, δw is positive if work is done on the system.
  - We have that

$$\delta w = -P\,\mathrm{d}V$$

- A system at thermal equilibrium has a given temperature characteristic of the system. Some property of the system indicates how hot or cold it is (e.g., volume of mercury, etc.)
- Measure heat transfer using a calorimeter and a thermomenter.
  - Convention: Heat put into a system δq is positive and this heat is transferred if the temperature is lower than another system or surroundings.
  - The heat capacity of a system times the change in temperature is equal to the heat put into the system. It is always positive as heat put into the system raises the temperature.
- Example molar heat capacities.
  - For water vapor at low pressure and $20\,^\circ\mathrm{C}$, $\overline{C}_V = 3R = 25\,\mathrm{J\,mol^{-1}\,K^{-1}}$.
  - For liquid water, it's higher (hydrogen bonding).
  - For ice, it's lower.
- **First law of thermodynamics**: The internal energy of a system changes with heat put into the system and work done on the system.

$$\mathrm{d}U = \delta q + \delta w$$

  - Note that in engineering, $\mathrm{d}U = \delta q - \delta w$.

- **State variable**: A property that describes the system.
  - For example, a system of gas molecules has a state defined by the state variables T, P, V, and n.
- **State function**: A property that depends only upon the state of the system.
  - For example, some equations of state for an ideal gas are $PV = nRT$ or $PV = 2U/3$.
  - The internal energy is a state function.
  - Heat and work are not state functions because they do not depend uniquely on the values at equilibrium.
    - They also depend on the way you do something.
- **Reversible process**: A process that can be represented as a path along state variables, e.g., a line on a PV diagram. This implies that it is also a path where all state variables are known, and is therefore a path where the system is always in quasi-equilibrium.
  - Isothermal, isochoric, isobaric, and adiabatic changes are reversible.
  - All of these processes are analyzed exactly as in Labalme (2021c).
- **Irreversible process**: A process that cannot be drawn on a PV diagram.
- Experiment to measure γ (the ratio of specific heats):
  1. Let sit at P_0T_0.
  2. Pump in a little gas (add Δn) and let sit, measure $P_0 + \Delta P_1, T_0$.
  3. Open the valve to air quickly to P_0. Adiabatic expansion (cools down).
  4. Let sit to measure the new pressure $P + \Delta P_2$ when T is back at T_0.
  5. γ is determined from $\Delta P_1, \Delta P_2$ (this will be a homework problem).
  - In the second step, we add some molecules into the container. We can show that $\Delta P_1/P_0 = \Delta N_1/n_0$.
  - In the third step, we let out the air, and we can show that $\Delta n_2/n_0 = \gamma\Delta P_1/P_0$.
  - In step 4, we have in the container $(n_0 + \Delta n_1 - \Delta n_2)RT_0 = (P_0 + \Delta P_2)V_0$.
  - This implies that $\Delta P_2/\Delta P_1 = 1 - 1/\gamma$.

3.3 Enthalpy

1/28:

- Thermonamic derivation of the formula for $\langle P\rangle$ in terms of Q.
  - We have that
$$\begin{aligned}U &= \sum p_j E_j \\ \mathrm{d}U &= \sum(\mathrm{d}p_j\, E_j + p_j\,\mathrm{d}E_j) \\ &= \underbrace{\sum \mathrm{d}p_j\, E_j}_{\delta q} + \underbrace{\sum p_j \frac{\partial E_j}{\partial V}}_{-P} \mathrm{d}V\end{aligned}$$
    where the last part follows by analogy with $\mathrm{d}U = \delta q - P\,\mathrm{d}V$.
  - It follows that
$$P = -\sum p_j \frac{\partial E_j}{\partial V} = -\left\langle \frac{\partial E}{\partial V}\right\rangle$$

- Thus, we have that

$$\begin{aligned}
P &= -\sum \frac{\mathrm{e}^{-E_j/k_BT}}{Q}\frac{\partial E_j}{\partial V} \\
&= \frac{1}{Q}\sum k_BT \cdot -\frac{1}{k_BT}\mathrm{e}^{-E_j/k_BT}\frac{\partial E_j}{\partial V} \\
&= k_BT\frac{1}{Q}\sum \frac{\partial}{\partial E_j}\left(\mathrm{e}^{-E_j/k_BT}\right)\frac{\partial E_j}{\partial V} \\
&= k_BT\frac{1}{Q}\sum \frac{\partial}{\partial V}\left(\mathrm{e}^{-E_j/k_BT}\right) \\
&= k_BT\frac{1}{Q}\frac{\partial Q}{\partial V} \\
P &= k_BT\frac{\partial \ln Q}{\partial V}
\end{aligned}$$

- Applies the formula to an ideal gas of independent, indistinguishable particles to derive the ideal gas law.
- **Enthalpy**: A state function representign the heat put into the system at constant pressure. *Denoted by* $\boldsymbol{H}$. *Given by*

$$H = U + PV$$

- We have that

$$\begin{aligned}
\mathrm{d}H &= \mathrm{d}U + P\,\mathrm{d}V + V\,\mathrm{d}P \\
&= \delta q - P\,\mathrm{d}V + P\,\mathrm{d}V + V\,\mathrm{d}P \\
&= \delta q + V\,\mathrm{d}P
\end{aligned}$$

  - At constant pressure ($\mathrm{d}P = 0$), we have that $\mathrm{d}H = \delta q$.
  - At constant volume, we have that $\mathrm{d}H = \delta q$ as well?
- **Constant-volume heat capacity**. The following expression. *Denoted by* $\boldsymbol{C_V}$. *Given by*

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}$$

- **Constant-pressure heat capacity**. The following expression. *Denoted by* $\boldsymbol{C_P}$. *Given by*

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{P,N}$$

- For an ideal gas,

$$\begin{aligned}
\mathrm{d}H &= \mathrm{d}U + \mathrm{d}(PV) \\
&= nC_V\,\mathrm{d}T + nR\,\mathrm{d}T \\
&= n(C_V + R)\,\mathrm{d}T
\end{aligned}$$

  - Recall this result from Labalme (2021c).
- Considers heat diagrams.
  - Recall the enthalpy of phase changes ΔH_{fus}, ΔH_{vap}, and ΔH_{sub}.
  - It follows that

$$H(T) - H(T_0) = \int_{T^0}^{T} C_p\,\mathrm{d}T + \sum \Delta H_{\text{phase changes}}$$

- **Hess's Law**: $\Delta H = 0$ around a closed loop.
  - This is because H is a state function.
- **Standard enthalpy of formation**. *Denoted by* $\boldsymbol{\Delta H_f^\circ}$. *Units* **kJ/mol**.
  - Calculated from the constituent elements in their standard state, 1 bar, 298.15 K.
- We have, for example, that the $\Delta H^\circ_{\text{vap}}$ of a substance is the difference of its ΔH_f° in its gaseous state and its ΔH_f° in its liquid state.
- With the standard enthalpy of formation and the heat capacity $C_P(T)$, one gets the enthalpy of formation at nonstandard temperatures.
- To get the enthalpy of formation at non-standard pressures of chemical interest, most of the effect is from the gas components because solids and liquid enthalpy vary little with pressure.
- The direction of change is sometimes in the direction of *positive* enthalpy change.
  - This change is driven by the fact that in these cases, the direction of change is toward the most probable state.
- In a reversible process, $\mathrm{d}U = \delta q_{\text{rev}} - P\,\mathrm{d}V$. In this case

$$\delta q_{\text{rev}} = \mathrm{d}U + P\,\mathrm{d}V = nC_V\,\mathrm{d}T + P\,\mathrm{d}V \neq \mathrm{d}nC_VT + PV$$

  so δq_{rev} is not a state function.
  - However,

$$\begin{aligned}\frac{\delta q_{\text{rev}}}{T} &= nC_V\frac{\mathrm{d}T}{T} + \frac{P\,\mathrm{d}V}{T}\\ &= nC_V\frac{\mathrm{d}T}{T} + nR\frac{\mathrm{d}V}{V}\\ &= \mathrm{d}(nC_V\ln T + nR\ln V)\end{aligned}$$

    is a state function.

3.4 Chapter 25: The Kinetic Theory of Gases

From McQuarrie and Simon (1997).

1/30:
- **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 $\langle E_{\text{trans}}\rangle = \frac{1}{2}m\langle u^2\rangle$. *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 $\langle u_x^2\rangle = \langle u_y^2\rangle = \langle u_z^2\rangle$.
- 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 $h(u_x,u_y,u_z)\,\mathrm{d}u_x\,\mathrm{d}u_y\,\mathrm{d}u_z$ 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

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

[1] This can be proven.

- 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

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

  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 $\langle u_x^2 \rangle = \frac{1}{3} \langle u^2 \rangle$ 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

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

- 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 $m \langle u_x \rangle^2 /2 = k_B T/2$ from the above result[2].
  - An important consequence is that the total kinetic energy is divided equally into the x-, y-, and z-components.
- McQuarrie and Simon (1997) discusses how the Doppler effect applied to moving molecules emitting radiation makes spectral peaks wider than we'd normally predict in a phenomenon known as **Doppler broadening**.
- 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

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

  - 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

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

[2]See the equipartition of energy theorem from Labalme (2021c).

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

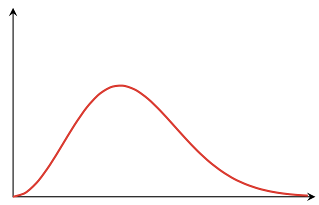


Figure 3.1: The Maxwell-Boltzmann distribution.

- **Velocity space**: A rectangular coordinate system in which the distances along the axes are u_x, u_y, u_z.
- 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 $\mathrm{d}F/\mathrm{d}u = 0$.
- We may also express the Maxwell-Boltzmann distribution in terms of energy via $u = \sqrt{2\varepsilon/m}$ and $\mathrm{d}u = \mathrm{d}\varepsilon\,/\sqrt{2m\varepsilon}$ to give

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

- We can also confirm our previously calculated values for $\langle u^2 \rangle$ and $\langle \varepsilon \rangle$.
- McQuarrie and Simon (1997) does a higher-level derivation of the ideal gas law that is rather analogous to the one done in class (i.e., via its flux perspective).
- McQuarrie and Simon (1997) discusses a simple and Nobel-prize winning experiment that verified the Maxwell-Boltzmann distribution.

3.5 Chapter 19: The First Law of Thermodynamics

From McQuarrie and Simon (1997).

1/31: - **Thermodynamics**: The study of various properties and, particularly, the relations between the various properties of systems in equilibrium.
  - Primarily an experimental science that is still of great practical value to the fields of today.
  - "All the results of thermodynamics are based on three fundamental laws. These laws summarize an enormous body of experimental data, and there are absolutely no known exceptions" (McQuarrie & Simon, 1997, p. 765).
- **Classical thermodynamics**: The development of thermodynamics before the atomic theory of matter.

  - Since thermodynamics was not developed in concert with the atomic theory, we can rest assured that its results will not need to be modified. However, it provides limited insight into what is going on at the molecular level.

- **Statistical thermodynamics**: The molecular interpretation of thermodynamics developed since the atomic theory of matter became generally accepted.
  - Chapters 17-18 are an elementary treatment of statistical thermodynamics.
  - Since atomic structure is still being determined, these results are not on as solid of a footing as classical thermodynamics.
- **First Law of Thermodynamics**: The law of conservation of energy applied to a macroscopic system.
- **System**: The part of the world we are investigating.
- **Surroundings**: Everything else.
- **Heat**: The manner of energy transfer that results from a temperature difference between the system and its surroundings. *Denoted by* $\boldsymbol{q}$.
  - Sign convention: Heat input into a system is positive; heat evolved by a system is negative.
- **Work**: The transfer of energy between the system of interest and its surroundings as a result of the existence of unbalanced forces between the two. *Denoted by* $\boldsymbol{w}$.
  - Sign convention: Work done *on* the system (i.e., that increases the energy of the system) is positive; work done *by* the system (i.e., that increases the energy of the surroundings) is negative.
- Work can be related to raising a mass.
  - If a pressurized gas is capped by a piston with a mass m on top and then it pushes the piston upwards a distance h, it does $w = -mgh$ of work.
  - Knowing that the external pressure $P_{\text{ext}} = F/A = mg/A$ and $Ah = \Delta V$, we recover

$$w = -P_{\text{ext}}\Delta V$$

  - If P_{ext} is not constant,

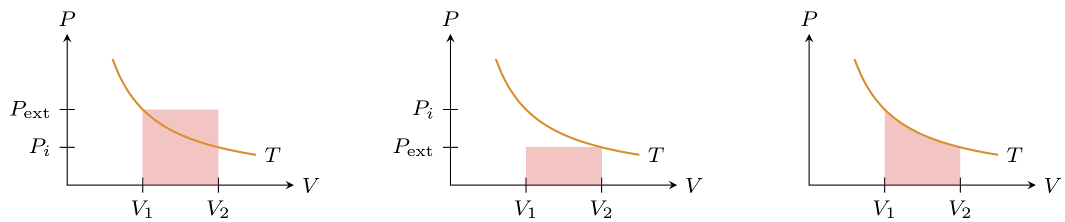
$$w = -\int_{V_i}^{V_f} P_{\text{ext}}\,\mathrm{d}V$$

- **Definite state**: A state of a system in which all of the variables needed to describe the system completely are defined.
  - For example, the state of one mole of an ideal gas can be described completely via P, V, and T. In fact, we need only specify two of these since $PV = RT$ for one mole of gas (in particular, specifying any two specifies the third).
- **State function**: A property that depends only upon the state of the system, not upon how the system was brought to that state.
  - State functions can be integrated in a normal way, i.e., $\Delta U = U_2 - U_1 = \int_1^2 \mathrm{d}U$. In particular, we need not worry about the *path* from state 1 to state 2, only that we got from U_1 to U_2.
  - Energy is a state function, but work and heat are not state functions.
- **Reversible process**: An expansion or compression in which P_{ext} and P differ only infinitesimally.
  - Technically, a reversible process would take infinite time, but it serves as a useful idealized limit regardless.

- To calculate w_{rev} (reversible work) for the compression of an ideal gas isothermally, we may replace P_{ext} by the pressure of the gas P to obtain

$$w_{\text{rev}} = -\int_{V_1}^{V_2} P \, \mathrm{d}V = -\int_{V_1}^{V_2} \frac{nRT}{V} \, \mathrm{d}V = -nRT \ln \frac{V_2}{V_1}$$

- Isothermal compression/expansion of a gas.



(a) Isothermal compression. (b) Isothermal expansion. (c) Reversible process.

Figure 3.2: Isothermal manipulation of an ideal gas.

  - Imagine a gas at pressure P, volume V, and temperature T in a container with a moveable piston at the top.
  - Isothermal compression (Figure 3.2a).
    - Let the external pressure be held constant at P_{ext}. If the volume of the gas is initially at V_2 and temperature T, its pressure will be P_i. Thus, to equilibriate with the external pressure, it will compress to volume V_1 and final pressure $P_f = P_{\text{ext}}$ along the isotherm. As the force doing this work is the constant external pressure, the work done will be encapsulated by the red box in Figure 3.2a. Note that the gas necessarily releases an amount of heat equivalent to the work in the red box during the course of the compression to maintain isothermal conditions.
  - Isothermal expansion (Figure 3.2a).
    - Let the external pressure be held constant at P_{ext}. If the volume of the gas is initially at V_1 and temperature T, its pressure will be P_i. Thus, to equilibriate with the external pressure, it will expand to volume V_1 and final pressure $P_f = P_{\text{ext}}$ along the isotherm. As the force doing this work is the constant external pressure, the work done will be encapsulated by the red box in Figure 3.2a. Note that the gas necessarily absorbs an amount of heat equivalent to the work in the red box during the course of the compression to maintain isothermal conditions.
  - Reversible compression/expansion (Figure 3.2c).
    - In a very slow manner, incrementally increase (resp. decrease) P_{ext} so as to allow the gas to reversibly compress (resp. expand).
    - Compressing a gas reversibly and isothermally does the minimum amount of work on the gas. Expanding a gas reversibly and isothermally requires the gas to do the maximum amount of work.
  - This work done on the gas raises the internal energy of the system, right? So shouldn't that raise the temperature, making the process not isothermal?
  - Where does the extra energy above and below the isotherm in the irreversible processes go? Is it converted to heat?
  - Does this mean that if you used a 1000 kg weight to compress a gas to half its original volume vs. using a 10 kg weight to compress a gas to half its original volume, the gas would get 100 times hotter in the former case?

- **Path function**: A function whose value depends on the path from state 1 to state 2, not just the initial and final states.
  - State functions cannot be integrated in the normal way. Mathematically, they have **inexact differentials**, i.e., we write $\int_1^2 \delta w = w$. This is because it makes no sense to write w_1, w_2, $w_2 - w_1$, or Δw, for example.
  - Work and heat are path functions.
- The First Law of Thermodynamics says that $\mathrm{d}U = \delta q + \delta w$ (in differential form) and $\Delta U = q + w$ (in integrated form).
  - An important consequence is that even though δq and δw are separately path functions/inexact differentials, their sum is a state function/exact differential.
- **Adiabatic process**: A process in which no heat is transferred between the system and its surroundings.
- Work during an adiabatic process.
  - For an adiabatic process, $\delta q = 0$.
  - Thus, $w = \Delta U$.
  - But since ΔU is entirely dependent on temperature, we have that

$$w = \Delta U = \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T = \int_{T_1}^{T_2} C_V(T)\,\mathrm{d}T$$

  - Why isn't this an integral of P with respect to V?
- Temperature during an adiabatic process.
  - We have that

$$\begin{aligned}
\mathrm{d}U &= \mathrm{d}w \\
C_V(T)\,\mathrm{d}T &= -P\,\mathrm{d}V \\
n\overline{C}_V(T)\,\mathrm{d}T &= -\frac{nRT}{V}\,\mathrm{d}V \\
\int_{T_1}^{T_2} \frac{\overline{C}_V(T)}{T}\,\mathrm{d}T &= -R\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V}
\end{aligned}$$

  - In the specific case of a monatomic ideal gas, $C_V(T) = 3/2$. Thus, continuing, we have

$$\begin{aligned}
\frac{3}{2}\ln\frac{T_2}{T_1} &= \ln\frac{V_1}{V_2} \\
\left(\frac{T_2}{T_1}\right)^{3/2} &= \frac{V_1}{V_2}
\end{aligned}$$

  - We can also express the above in terms of pressure

$$\begin{aligned}
\left(\frac{P_2V_2/nR}{P_1V_2/nR}\right)^{3/2} &= \frac{V_1}{V_2} \\
P_1V_1^{5/3} &= P_2V_2^{5/3}
\end{aligned}$$

  - For a diatomic gas, we end up with

$$P_1V_1^{7/5} = P_2V_2^{7/5}$$

- Note that for an isothermal expansion, Boyle's law applies: $P_1V_1 = P_2V_2$.

- Relating work and heat to molecular properties.
  - By comparing recently derived equations with previously derived equations, we have that

$$\begin{aligned} U &= \sum_j p_j E_j \\ \mathrm{d}U &= \sum_j p_j \,\mathrm{d}E_j + \sum_j E_j \,\mathrm{d}p_j \\ &= \sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)_N \mathrm{d}V + \sum_j E_j \,\mathrm{d}p_j \end{aligned}$$

  - The above equation suggests that we can interpret the first term as the average change in energy of a system caused by a small change in its volume, i.e., the average work.
  - It follows by the First Law of Thermodynamics that we can interpret the second term as the average heat.
  - This expresses the important but subtle notion that work results from "an infinitesimal change in the allowed energies of a system, without changing the probability distribution of its states" while heat results from "a change in the probability distribution of the states of a system, without changing the allowed energies" (McQuarrie & Simon, 1997, p. 780).
  - In particular, if we take the process under study to be reversible, we have

$$\mathrm{d}U = \underbrace{\sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)_N \mathrm{d}V}_{\delta w_{\text{rev}}} + \underbrace{\sum_j E_j \,\mathrm{d}p_j}_{\delta q_{\text{rev}}} = \underbrace{\sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)_N}_{-P} \mathrm{d}V + \sum_j E_j \,\mathrm{d}p_j$$

  - The second equality above expresses the fact that

$$P = -\left\langle \frac{\partial E}{\partial V} \right\rangle$$

    which we previously used in Chapter 17.

- For a constant-volume process, $w = 0$, so we know that the heat evolved in the process $q_V = \Delta U$.

- Defining a state function analogous to U for constant-pressure processes.
  - We have from the First Law that

$$\Delta U = q + w = q - \int_{V_1}^{V_2} P \,\mathrm{d}V$$

  - Thus, at constant pressure,

$$q_P = \Delta U + P_{\text{ext}} \int_{V_1}^{V_2} \mathrm{d}V = \Delta U + P\Delta V$$

  - The above equation suggests how to define our new state function.

- **Enthalpy**: The state function describing the heat put into a system at constant pressure. *Denoted by* $\boldsymbol{H}$. *Given by*

$$H = U + PV$$

  - ΔH can be determined experimentally as the heat associated with a constant-pressure process.

- Examples.
  - For the melting of ice, ΔV is small, so $\Delta U \approx \Delta H$.
  - For the vaporization of water, ΔV is large, so $\Delta U < \Delta H$.
    - We interpret the excess by the fact that most of the energy goes into raising the internal energy of the water (i.e., breaking the hydrogen bonding), but some of it must go into increasing the volume of the system against the atmospheric pressure.
- For reactions or processes that involve ideal gases,

$$\Delta H = \Delta U + RT\Delta n_{\text{gas}}$$

  where Δn_{gas} is the difference in the number of moles of gaseous products vs. reactants.
- **Extensive quantity**: A quantity that depends on the amount of substance.
  - Heat capacity is an extensive quantity.
- Heat capacity is a path function, as it depends on whether we heat the substance at constant volume or constant pressure.
- We have

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad\qquad C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

  - We expect $C_P > C_V$ since we also have to work against atmospheric pressure.
  - In fact, for a monatomic ideal gas,

$$\begin{aligned}
H &= U + PV \\
&= U + nRT \\
\frac{\mathrm{d}H}{\mathrm{d}T} &= \frac{\mathrm{d}U}{\mathrm{d}T} + nR \\
C_P - C_V &= nR \\
C_P &= \frac{3}{2}R + nR \\
&= \frac{5}{2}R
\end{aligned}$$

  - It follows that the difference between C_P and C_V is significant for gases, but not for solids and liquids.
  - Note that we can also prove a general expression for $C_P - C_V$ (see Chapter 22).
- Relative enthalpies can be determined from heat capacity data and heats of transition.
  - Integrate $C_P(T)$ from T_1 to T_2, adding in $\Delta_{\text{fus}}H$ and $\Delta_{\text{vap}}H$ as necessary.
- **Thermochemistry**: The branch of thermodynamics which concerns the measurement of the evolution or absorption of energy as heat associated with chemical reactions.
- McQuarrie and Simon (1997) reviews exothermic/endothermic reactions, and $\Delta H = H_{\text{prod}} - H_{\text{react}}$.
- **Hess's Law**: The additivity property of $\Delta_r H$ values.
- **Standard reaction enthalpy**: The enthalpy change associated with one mole of a specified reagent when all reactants and products are in their standard states. *Denoted by* $\boldsymbol{\Delta_r H^\circ}$.
  - An intensive quantity.

- **Standard molar enthalpy of formation**: The standard reaction enthalpy for the formation of one mole of a molecule from its constituent elements. *Denoted by* $\boldsymbol{\Delta_f H^\circ}$.
  - We can obtain such values even if a compound cannot be formed directly from its elements via several related reactions and Hess's Law.

Week 4

Entropy and the Second Law of Thermodynamics

4.1 Entropy Equations

1/31: • We define a new state function S by $\mathrm{d}S = \delta q_{\text{rev}} / T$ and call it **entropy**.
  - See notes from last time for why this is a state function.
- Verify that the same definition of entropy is a state function for any system.
  - Consider an ideal gas system in thermal equilibrium with an arbitrary system and drive the ideal gas system along a loop.
  - Around the cycle: $\Delta S_{\text{total}} = 0$.
  - Ideal gas:

$$\begin{aligned}
\Delta S_{\text{total}} &= \Delta S_1 + \Delta S_2 \\
&= \int \frac{\delta q_{\text{rev}_1}}{T} - \int \frac{\delta q_{\text{rev}_1}}{T} \\
&= \int \frac{\delta q_{\text{rev}_1}}{T} + \int \frac{\delta q_{\text{rev}_2}}{T}
\end{aligned}$$

- We must devise a reversible process to calculate the entropy changes for an irreversible process leading to the same final state.

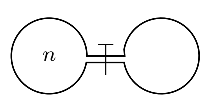


Figure 4.1: Two linked containers.

  - Imagine two linked containers, one filled with n moles of gas and the other vacuumed.
  - Opening the two containers to each other results in an adiabatic expansion. All vibrational/rotational energy of the molecules is consumed and used for translation.
  - Measuring the temperature with spectroscopy (the Maxwell-Boltzmann distribution of each spectral line, plus only the ground rovibrational states are occupied now) shows a drastic drop in temperature.
  - We have $\delta q = 0$ and $\delta w = 0$ so that $\mathrm{d}U = 0$ and $\Delta T = 0$ overall?
  - An isothermal expansion is a reversible process leading to the same final state.

  - $\mathrm{d}U = 0$ implies $\delta q_{\text{rev}} = -\delta w = P\,\mathrm{d}V$.
  - We have that
$$\Delta S = \int \frac{\delta q_{\text{rev}}}{T} = \int_{V_0}^{2V_0} \frac{P\,\mathrm{d}V}{T} = \int_{V_0}^{2V_0} \frac{nRT}{V}\frac{1}{T}\,\mathrm{d}V = nR\ln 2$$

- Using entropy as a state function to predict the vapor pressure in equilibrium with its liquid, from the enthalpy at boiling and the boiling temperature.

$$\begin{tikzcd}
\mathrm{H_2O_{(l)}}\ T, P_0 \arrow[r, "\Delta S_0"] \arrow[dd, "\Delta S_1"'] & \mathrm{H_2O_{(g)}}\ T, P \\
 & \mathrm{H_2O_{(g)}}\ T_b, P \arrow[u, "\Delta S_4"'] \\
\mathrm{H_2O_{(l)}}\ T_b, P_0 \arrow[r, "\Delta S_2"'] & \mathrm{H_2O_{(g)}}\ T_b, P_0 \arrow[u, "\Delta S_3"']
\end{tikzcd}$$

Figure 4.2: Vapor pressure thermodynamic loop.

  - Consider the above thermodynamic loop, where T is the temperature of the water and P is the pressure above the water.
  - We have that
$$\Delta S_1 = \int_T^{T_b} \frac{C_{P_l}}{T}\,\mathrm{d}T \qquad \Delta S_2 = \frac{\Delta H_{\text{vap}}}{T_b} \qquad \Delta S_3 = nR\ln\frac{P_0}{P} \qquad \Delta S_4 = \int_{T_b}^{T} \frac{C_{P_g}}{T}\,\mathrm{d}T$$
and that
$$\Delta S_0 = \frac{\Delta H_{\text{vap}}}{T}$$
  - We know that ΔS around the loop is zero since S is a state function. We neglect the heat capacity effect. Thus,
$$\begin{aligned}
\frac{\Delta H_{\text{vap}}}{T_b} + nR\ln\frac{P_0}{P} - \frac{\Delta H_{\text{vap}}}{T} &= 0\\
\ln\frac{P_0}{P} &= \frac{\Delta H_{\text{vap}}}{nR}\left(\frac{1}{T} - \frac{1}{T_b}\right)\\
P &= P_0\mathrm{e}^{-\Delta H_{\text{vap}}/nR(1/T - 1/T_b)}
\end{aligned}$$
  - The above equation gives the vapor pressure at T in terms of the vapor pressure P_0 at T_b.

- **Trouton's rule**: The statement that
$$\frac{\Delta H_{\text{vap}}}{T_b} \approx 85 \pm 5\,\mathrm{J\,mol^{-1}\,K^{-1}}$$
  - Discovered this rule as an undergrad after an afternoon's manipulation of data from a book of tables.
  - This rule reflects the fact that
$$\frac{\Delta H_{\text{vap}}}{T_b} = \Delta S_{\text{vap}}$$
and implies that ΔS_{vap} is approximately a constant.

- Example of entropy change: The direction of heat flow between two systems (1 and 2) only in thermal contact.

- We have

$$\begin{aligned}\delta q_{\text{rev}_1} &= \delta q_{\text{rev}_2}\\ C_{V_1}\,\mathrm{d}T_1 &= -C_{V_2}\,\mathrm{d}T_2\end{aligned}$$

- Thus,

$$\begin{aligned}\mathrm{d}S &= \mathrm{d}S_1 + \mathrm{d}S_2\\ &= \frac{\delta q_{\text{rev}_1}}{T_1} + \frac{\delta q_{\text{rev}_2}}{T_2}\\ &= \frac{C_V\,\mathrm{d}T_1}{T_1} - \frac{C_V\,\mathrm{d}T_1}{T_2}\\ &= C_V\,\mathrm{d}T_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\end{aligned}$$

- The conclusion is that if $\mathrm{d}T_1 > 0$, then $\mathrm{d}S > 0$. This is the spontaneous direction, the direction that nature chooses, the one in which entropy increases.
- The maximum of S is the equilibrium temperature between the two systems.

- Entropy change of the isothermal mixing of two ideal gases at the same temperature.
  - Consider the same two-container setup from Figure 4.1.
  - We have that

$$\begin{aligned}\Delta S &= Rn_1\ln\frac{V_1+V_2}{V_1} + Rn_2\ln\frac{V_1+V_2}{V_2}\\ &= R(n_1+n_2)\left(\frac{n_1}{n_1+n_2}\ln\frac{V_1+V_2}{V_1} + \frac{n_2}{n_1+n_2}\ln\frac{V_1+V_2}{V_2}\right)\\ &= R(n_1+n_2)(-y_1\ln y_1 - y_2\ln y_2)\\ &= R(n_1+n_2)[-y_1\ln y_1 - (1-y_1)\ln(1-y_1)]\end{aligned}$$

    - Note that $y_1 = n_1/(n_1+n_2) = V_1/(V_1+V_2)$ is the mole fraction, and similarly for y_2.
  - The conclusion is that $\Delta S > 0$.
  - The maximum of ΔS is at $y_1 = y_2 = 1/2$.
- **Gibb's paradox**: Suppose you have the same gas on both sides of the containers. Then $\Delta S = nR\ln 2$ for an indistinguishable gas.
  - This is wrong.
  - Resolved by knowing that the gases *must* be distinguishable.

4.2 Statistical Entropy in Various Systems

2/2:

- For an isolated system, energy is conserved but the entropy keeps on increasing until the system reaches thermal equilibrium.
- Thermal equilibrium is reached when entropy is maximum for a constant energy.
- The sign of the entropy change in a spontaneous process for an isolated system is positive.
- Entropy is the only macroscopic physical quantity that requires a particular direction for time, sometimes called an **arrow of time**.
- **Second law of thermodynamics**: The entropy of an isolated system can only increase.

- **Clasuius inequality**: The following inequality, where equality holds iff the process is reversible.
$$\Delta S \geq \int \frac{\delta q}{T}$$
  - Considers the isolated system to justify.
- Statistical entropy: $S = k_B \ln W$ where W is the number of microstates of the system (i.e., the number of possible ways the system can be arranged).
  - Shows additivity of the log.
  - When doubling the volume available to a gas, $\Delta S = N k_B \ln 2$. $W_{\text{after}} = 2^N W_{\text{before}}$.
  - The statistical definition of entropy avoids the Gibbs paradox since at a molecular level, we can differentiate between particles.
- Goes over calculating $W(n_1, n_2)$.
- The ways we can distinguish the number of molecules in the container becomes smaller and smaller as we increase the number of particles.
- Consider two identical containers at fixed temperature with N non-interacting indistinguishable molecules $n_1 + n_2 = N$.
  - $W(n_1) = W(n_1, n_2)$ is the number of ways to arrange the molecules between containers 1 and 2.
  - We have
$$\begin{aligned}
\ln W(n_1, n_2) &= \ln N! - \ln n_1! - \ln(N - n_1)! \\
&= N \ln N - N - [n_1 \ln n_1 - n_1 + (N - n_1)\ln(N - n_1) - (N - n_1)] \\
&= N \ln N - n_1 \ln n_1 - (N - n_1)\ln(N - n_1) \\
&= (n_1 + n_2)\ln N - n_1 \ln n_1 - n_2 \ln n_2 \\
&= -n_1 \ln \frac{n_1}{N} - n_2 \ln \frac{n_2}{N} \\
&= N\left(-\frac{n_1}{N}\ln\frac{n_1}{N} - \frac{n_2}{N}\ln\frac{n_2}{N}\right)
\end{aligned}$$
  - Therefore,
$$S = N k_B(-p_1 \ln p_1 - p_2 \ln p_2)$$
- Entropy for a set of systems expressed in terms of the probability for these systems to be in a certain state.
  - Covers $W(n_1, \dots, n_r)$.
  - We have
$$\begin{aligned}
\ln W &= \ln A! - \sum_i \ln a_i! \\
&= A \ln A - A - \sum_i (a_i \ln a_i - a_I) \\
&= A \ln A - \sum_i a_i \ln a_i \\
&= \left(\sum_i a_i\right) \ln A - \sum_i a_i \ln a_i \\
&= \sum_i \left(-a_i \ln \frac{a_i}{A}\right) \\
&= A \sum_i \left(-\frac{a_i}{A} \ln \frac{a_i}{A}\right) \\
&= A \sum_i (-p_i \ln p_i)
\end{aligned}$$

- Therefore,

$$S = Ak_B \sum_i (-p_i \ln p_i)$$

- We will use this result to derive the Boltzmann Factor.

4.3 MathChapter J: The Binomial Distribution and Stirling's Approximation

From McQuarrie and Simon (1997).

- Counting the number of ways to arrange N distinguishable objects into two groups of size N_1, N_2 where $N_1 + N_2 = N$.
  - There are $N!$ ways to arrange N distinguishable objects, $N!/(N-N_1)!$ ways to arrange the objects in group 1, and $N_2!$ ways to arrange the objects in group 2. Thus, there are

    $$\frac{N!}{(N-N_1)!} \cdot N_2!$$

    permutations of the N objects in two groups.
    - For example, $N = 4$, $N_1 = 3$, and $N_2 = 1$, we are currently counting both $abc : d$ and $bac : d$ as different ways of arranging the four objects into two groups, when clearly such ordering does not matter.
  - Dividing the above by the number of ways to arrange N_1 objects in the first group ($N_1!$) and the number of ways to arrange N_2 objects in the second group ($N_2!$) gives the desired result.

    $$W(N_1, N_2) = \frac{N!}{N_1!N_2!}$$

    - Now we have a result that, as per the previous example, allows us to count only $abc : d$, $bcd : a$, $cda : b$, and $dab : c$.
- McQuarrie and Simon (1997) reviews the binomial expansion in light of the above result's status as a binomial coefficient.
- Counting the number of ways to arrange N distinguishable objects into r groups of size $N_1, \dots, N_r$ where $N_1 + \cdots + N_r = N$.

  $$W(N_1, \dots, N_r) = \frac{N!}{N_1! \cdots N_r!}$$

- Note that this quantity is called a **multinomial coefficient** because it occurs in the multinomial expansion $(x_1 + \cdots + x_r)^N$.
- **Asymptotic approximation**: An approximation to a function that gets better as the argument of the function increases.
- **Stirling's approximation**: An asymptotic approximation to $\ln N!$. *Given by*

  $$\ln N! = N \ln N - N$$

  - Proof: We have that

    $$\ln N! = \sum_{n=1}^{N} \ln n$$

  - For N large, this sum behaves more and more like the integral $\int_1^n \ln x \,\mathrm{d}x$. Thus, we take

    $$\ln N! = \sum_{n=1}^{N} \ln n \approx \int_1^n \ln x \,\mathrm{d}x = N \ln N - N$$

- A refinement of the approximation is the following.

$$\ln N! = N\ln N - N + \frac{1}{2}\ln(2\pi N)$$

4.4 Chapter 20: Entropy and the Second Law of Thermodynamics

From McQuarrie and Simon (1997).

2/1:
- The change of energy alone is not sufficient to determine the direction of a spontaneous process.
  - Although mechanical and chemical systems tend to evolve in such a way as to minimize their energy, we can find examples of spontaneous chemical processes that are not exothermic.
  - Examples include the mixing of two gases and the highly endothermic (and spontaneous) reaction of $Ba(OH)_2$ and NH_4NO_3.
  - Such processes obey the First Law of Thermodynamics, but their spontaneous direction cannot be explained by it.
- Each of these "special cases" involves an increase in the disorder of the system.
  - For example, in the mixing of gases, we can show quantum mechanically that increasing the volume of teh container increases the number of accessible translational states.
- Competition between the drive to lower energy and the drive to increase disorder.
  - Simple mechanical systems can't become that much more disordered; thus, energy considerations dominate.
  - The mixing of gases doesn't change the energy that much; thus, disorder considerations dominate.
- Defining a quantitative state function describing disorder.
  - Note that

$$\begin{aligned}\delta q_{\text{rev}} &= \mathrm{d}U - \delta w_{\text{rev}}\\ &= C_V(T)\,\mathrm{d}T + P\,\mathrm{d}V\\ &= C_V(T)\,\mathrm{d}T + \frac{nRT}{V}\,\mathrm{d}V\end{aligned}$$

    is an inexact differential since the second term cannot be written as a derivative of some function of T and V (because T depends on V). In particular, the integral depends on what path through T and V we take.
  - However, if we divide both sides of the above by T, we get an exact differential, i.e., a state function.
  - Note that we can show that this result holds for all systems, not just an ideal gas.
- **Entropy**: The state function describing the disorder of a system. *Denoted by* $\boldsymbol{S}$. *Given by*

$$\mathrm{d}S = \frac{\delta q_{\text{rev}}}{T}$$

- **Integrating factor**: A term that converts an inexact differential to an exact (integrable) differential.
  - $1/T$ is an integrating factor of δq_{rev}.
- Since entropy is a state function, $\Delta S = 0$ for a cyclic process, i.e.,

$$\oint \mathrm{d}S = 0$$

- McQuarrie and Simon (1997) calculates ΔS for a process that proceeds from state 1 to state 2 isothermally, and adiabatically/isochorically, to show that the quantity is the same in both cases.
- Justifying $\mathrm{d}S = \delta q_{\text{rev}}/T$ qualitatively:
  - Increase in heat means increase in disorder (check).
  - Same increase in heat at a lower temperature increases disorder more since there is more order at lower temperatures (check).
- **Isolated** (system): A system that is separated from its surroundings by rigid walls that do not allow matter or energy to pass through them.
- Unlike energy, entropy is not necessarily conserved; it can increase within an isolated system if a spontaneous process takes place therein.
- The entropy of a system is at its maximum when the system is equilibrium; at this point, $\mathrm{d}S = 0$.
- Consider an isolated system consisting of two compartments. One compartment holds large, one-component system A, and other holds B. They are separated by a heat-conducting wall.
  - Because of isolation,

$$U_A + U_B = \text{constant} \qquad \begin{aligned} V_A &= \text{constant} \\ V_B &= \text{constant} \end{aligned} \qquad S = S_A + S_B$$

  - Since V_A, V_B are fixed, $\mathrm{d}V = 0$, meaning that $\mathrm{d}U = \delta q_{\text{rev}} + 0$. It follows that

$$\begin{aligned} \mathrm{d}S &= \mathrm{d}S_A + \mathrm{d}S_B \\ &= \frac{\mathrm{d}U_A}{T_A} + \frac{\mathrm{d}U_B}{T_B} \\ &= \mathrm{d}U_B\left(\frac{1}{T_B} - \frac{1}{T_A}\right) \end{aligned}$$

  - Since the gases A and B can still mix without absorbing energy, we define $\mathrm{d}S_{\text{prod}}$ as the entropy produced by the system and redefine $\delta q/T$ as $\mathrm{d}S_{\text{exch}}$ (the entropy exchanged with the surroundings via a transfer of heat).
  - It follows that for an reversible process ($\mathrm{d}S_{\text{prod}} = 0$), we have

$$\mathrm{d}S = \frac{\delta q_{\text{rev}}}{T}$$

    while for an irreversible process ($\mathrm{d}S_{\text{prod}} > 0$), we have

$$\mathrm{d}S = \mathrm{d}S_{\text{prod}} + \frac{\delta q_{\text{irr}}}{T} > \frac{\delta q_{\text{irr}}}{T}$$

- **Inequality of Clausius**: The following inequality. *Given by*

$$\Delta S \geq \int \frac{\delta q}{T}$$

- **Second Law of Thermodynamics**: There is a thermodynamic state function of a system called the entropy S such that for any change in the thermodynamic state of the system, $\mathrm{d}S \geq \delta q/T$, where equality holds iff the change is carried out reversibly.
- "Because the universe itself may be considered to be an isolated system and all naturally occurring processes are irreversible, one statement of the Second Law of Thermodynamics says that the entropy of the universe is constantly increasing. In fact, Clausius summarized the first two laws of thermodynamics by, 'The energy of the Universe is constant; the entropy is tending to a maximum'" (McQuarrie & Simon, 1997, p. 829).

- Relating entropy, a thermodynamic quantity, to a statistical quantity.
  - Consider an ensemble of $\mathcal{A}$ isolated systems, each with number of particles N, volume V, and energy $E(N, V)$.
  - Let $\Omega(E)$ be the degeneracy of E, i.e., the number of quantum states with energy E[1]. Label the $\Omega(E)$ quantum states by $j = 1, 2, \dots, \Omega(E)$.
  - Let a_j be the number of systems in state j.
  - It follows that the number of ways of having a_1 systems in state 1, a_2 systems in state 2, etc. is given by

    $$W(a_1, \dots, a_{\Omega(E)}) = \frac{\mathcal{A}!}{a_1! \cdots a_{\Omega(E)}!} = \frac{\mathcal{A}!}{\prod_j (a_j!)}$$

    with $\sum_j a_j = \mathcal{A}$.
  - If every system is in one totally ordered state (i.e., $a_j = \mathcal{A}$ for some j), $W = 1$. On the other end of the spectrum, W can be massive for disorder.
  - As W is a measure of entropy, we are now free to relate S and W, in particular via

    $$S = k_B \ln W$$

    - We choose a log because we want to be able to split S into $S_A + S_B$ and have the math reflect that. In particular, for two systems A, B, $W_{AB} = W_A W_B$, which nicely works out such that

      $$S_{AB} = k_B \ln W_{AB} = k_B \ln W_A + k_B \ln W_B = S_A + S_B$$

  - McQuarrie and Simon (1997) goes over an alternate "derivation" of the above in terms of the degeneracy to get $S = k_B \ln \Omega$.

[1] Note that for systems relatively far from the ground state, $\Omega(E) \approx \mathrm{e}^N$.

References

Arrhenius, S. A. (1889). Über die dissociationswärme und den einfluß der temperatur auf den dissociationsgrad der elektrolyte. *Zeitschrift für Physikalische Chemie*, *4*, 96–116. https://doi.org/10.1515/zpch-1889-0408

Labalme, S. (2021a). *AP Chemistry notes*. Retrieved January 11, 2022, from https://github.com/shadypuck/APChemNotes/blob/master/main.pdf

Labalme, S. (2021b). *CHEM 26100 (Quantum Mechanics) notes*. Retrieved January 24, 2022, from https://github.com/shadypuck/CHEM26100Notes/blob/master/Notes/notes.pdf

Labalme, S. (2021c). *PHYS 13300 (Waves, Optics, and Heat) notes*. Retrieved January 11, 2022, from https://github.com/shadypuck/PHYS13300Notes/blob/master/Notes/notes.pdf

McQuarrie, D. A., & Simon, J. D. (1997). *Physical chemistry: A molecular approach*. University Science Books.