CHEM 26200 (Thermodynamics) Notes

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Contents

List of Figures

List of Tables

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

$$PV = nN_A \frac{R}{N_A} T$$
$$PV = N k_B T$$

  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.

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[1]This derivation differs from that on Labalme (2021a, pp. 3–4) and Labalme (2021d, 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

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

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).

$$= 2m \cdot \frac{N}{V} \cdot \frac{1}{2} \langle v_x^2 \rangle$$
$$= \frac{N}{V} m \langle v_x^2 \rangle$$
$$PV = Nm \cdot \langle v_x^2 \rangle$$

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

$$= Nm \cdot \frac{1}{3} \langle v^2 \rangle$$
$$= \frac{2}{3} N \cdot \frac{1}{2} m \langle v^2 \rangle$$
$$= \frac{2}{3} N \cdot \langle E_{KE} \rangle$$
$$\langle E_{KE} \rangle = \frac{3}{2} \frac{PV}{N}$$
$$\langle E_{KE} \rangle = \frac{3}{2} k_B T$$

- 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 $k_B T$.

  - The activation energy of Arrhenius (1889): "To collide is to react" is inaccurate; it must collide with sufficient energy. The molecule must be "activated."

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

- ■ 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:

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

■ $\ln Q$ is the ratio inside vs. outside the membrane.

■ $F = N_A e$ where e is the charge of an electron.

■ Thus,

$$\Delta E = \frac{RT}{nF} = \frac{k_B T}{ne}$$

■ If the potential across the membrane is approximately $k_B T$, then $\ln Q \approx 1$, so $Q \approx e$.

■ Thus, at body temperature ($T = 310\,\text{K}$), $k_B T/e = 26\,\text{mV}$.

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

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

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3 k_B T}{m}}$$

$$v_{\text{rms}} = \sqrt{\frac{3 k_B T}{m}}$$

■ 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 $k_B T$. Additionally, the quantum mechanical kinetic energy of a molecule aligns with this, as $\hbar^2 k^2/2m \approx k_B T$. Furthermore, the particle-wave duality relates the momentum to wavelength by $p = \hbar k = h/\lambda$. Therefore,

$$\lambda \approx \sqrt{\frac{h^2}{2 m k_B T}}$$

■ 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 $300\,\text{K}$ has de Broglie wavelength $\lambda = 1.78\,\text{Å}$.

■ Note that the quantum mechanical kinetic energy of a free particle is derived as follows.

$$\hat{H}\psi = E\psi$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \left(e^{ikx} \right) = E e^{ikx}$$

$$\frac{\hbar^2 k^2}{2m} e^{ikx} = E e^{ikx}$$

$$E = \frac{\hbar^2 k^2}{2m}$$

• **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*

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

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

– Consistency check: Given

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

we do indeed have

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

  – 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 $p_2/p_1 = \mathrm{e}^{-(E_2-E_1)/k_B T}$, 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,
  $$\frac{p(E_2)}{p(E_1)} = \frac{N_2}{N_1}\mathrm{e}^{-(E_2-E_1)/k_B T}$$

- 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.
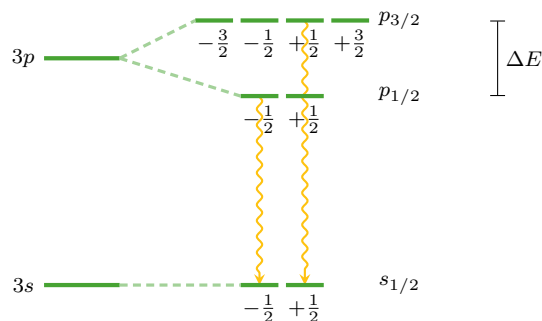
Figure 1.1: Sodium lamp energy levels.

  – 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

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

  where $\lambda_1 = 589.6\,\text{nm}$ and $\lambda_2 = 589.0\,\text{nm}$.
- Thus, $e^{-\Delta E/k_B T} \approx 1$ for $T = 300\,\text{K}$ (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 $B = 6\,\text{T}$ and $T = 310\,\text{K}$ (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*

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

- 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 $300\,\text{K}$,

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

    - As before $J = 1$ corresponds to states $j = -1, 0, 1$.
  - There is a range of angular momenta due to the temperature that for $T = 300\,\text{K}$ peaks around $J = 5$.
  - See Figure 2.1.

- 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

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

  for CO, meaning that at $300\,\text{K}$, CO will be largely in its ground state.

- The partition function tells us everything we would want to know about a system.

$$Q = \sum_i e^{-E_i/k_B T}$$

- – 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 average energy of a system from the partition function.

- – Take the energy E_1 of the ground state to be our zero of energy.
- – Under this assumption, we may rewrite the partition function as follows.

$$Q = \sum_i e^{-(E_i - E_1)/k_B T} = \frac{p_1}{p_1} + \frac{p_2}{p_1} + \frac{p_3}{p_1} + \cdots = 1 + e^{\frac{-(E_2 - E_1)}{k_B T}} + e^{\frac{-(E_3 - E_1)}{k_B T}} + \cdots$$

- – From MathChapter B, the expected energy is equal to

$$\langle E \rangle = E_1 p_1 + E_2 p_2 + E_3 p_3 + \cdots$$

- – Since $E_1 = 0$, the above can be rewritten as

$$\langle E \rangle = p_1 \left[E_2 \frac{p_2}{p_1} + E_3 \frac{p_3}{p_1} + \cdots \right]$$

- – With this result established, we now take a moment to note that

$$\frac{\partial}{\partial T} \left(e^{-E_i/k_B T} \right) = \frac{E_i}{k_B T^2} e^{-E_i/k_B T} = \frac{1}{k_B T^2} \left(E_i \frac{p_i}{p_1} \right)$$

and

$$p_1 = 1 - (p_2 + p_3 + \cdots)$$
$$= 1 - p_1 \left(\frac{p_2}{p_1} + \frac{p_3}{p_1} + \cdots \right)$$
$$= 1 - p_1 (Q - 1)$$
$$p_1 = \frac{1}{Q}$$

- – Therefore,

$$\langle E \rangle = p_1 k_B T^2 \frac{\partial}{\partial T} \left(\frac{p_1}{p_1} + \frac{p_2}{p_1} + \cdots \right)$$
$$= \frac{1}{Q} k_B T^2 \frac{\partial Q}{\partial T}$$
$$\langle E \rangle = k_B T^2 \frac{\partial \ln Q}{\partial T}$$

- – The above is an important result.

• Changing the origin of energy.

- – We know that

$$Q(E_0) = Q(E_0') e^{-(E_0' - E_0)/k_B T}$$
$$\ln Q(E_0) = \ln Q(E_0') - \frac{E_0' - E_0}{k_B T}$$

– Thus,

$$\langle E \rangle_{E_0} = k_B T^2 \frac{\partial}{\partial T} (\ln Q(E_0))$$

$$= k_B T^2 \left(\frac{\partial}{\partial T} (\ln Q(E_0')) - \frac{\partial}{\partial T} \left(\frac{E_0' - E_0}{k_B T} \right) \right)$$

$$= \langle E \rangle_{E_0'} + (E_0' - E_0)$$

$$\langle E \rangle_{E_0} + E_0 = \langle E \rangle_{E_0'} + E_0'$$

– 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, $\langle E \rangle = 3k_B T/2$. 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.

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

  ■ 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,
  $$Q_{KE_{v_x}} = \int_{-\infty}^{\infty} e^{-\frac{1}{2} m v_x^2 / k_B T} \, dv_x = \sqrt{\frac{2\pi k_B T}{m}}$$

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

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

  and
  $$\langle KE \rangle = \langle KE_x \rangle + \langle KE_y \rangle + \langle KE_z \rangle = \frac{3}{2} k_B T$$

  – Therefore, this result holds beyond the specific case of an ideal gas![2]

- Now for the potential energy of a harmonic oscillator.

  – $PE = \frac{1}{2} k x^2$; calculate the partition function for the coordinate x.

  $$Q_x = \int_{-\infty}^{\infty} e^{-\frac{1}{2} k x^2 / k_B T} \, dx = \sqrt{\frac{2\pi k_B T}{k}}$$

_____

[2]This is why this derivation is preferable over the one presented in the book. Note that the "gas" here is assumed to be made of hard spheres.

    – Thus,
$$\langle PE_x \rangle = \frac{k_B T}{2}$$

    – For a 3D harmonic oscillator,
$$\langle PE \rangle = \frac{3}{2} k_B T$$

- 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 $k_B T/2$, the potential in any system will be related (i.e., have a factor of $k_B T$).

- 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,
$$Q_\omega = \int_{-\infty}^{\infty} e^{-\frac{1}{2} I \omega^2 / k_B T} \, d\omega = \sqrt{\frac{2\pi k_B T}{I}}$$
making
$$\langle E_{\text{rot}} \rangle = \frac{k_B T}{2}$$
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
$$\frac{1}{2} m v^2 + \frac{1}{2} k r^2$$

  – Thus,
$$\langle E_{\text{atom}} \rangle = \frac{3}{2} k_B T + \frac{3}{2} k_B T = 3 k_B T$$
$$\langle E_{\text{solid}} \rangle = 3 N k_B T = 3 n N_A k_B T = 3 n R T$$

  – 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 $T \to 0\,\text{K}$, 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 $(n + 1/2)h\nu$.
  – Taking our zero of energy to be $0.5\,E_\mathrm{h}$, the partition function of the vibration of the quantum harmonic oscillator is

$$Q = 1 + \mathrm{e}^{-h\nu/k_B T} + \mathrm{e}^{-2h\nu/k_B T} + \cdots$$
$$Q = (\mathrm{e}^{-h\nu/k_B T})^0 + (\mathrm{e}^{-h\nu/k_B T})^1 + (\mathrm{e}^{-h\nu/k_B T})^2 + \cdots$$
$$Q - Q\mathrm{e}^{-h\nu/k_B T} = 1$$
$$Q = \frac{1}{1 - \mathrm{e}^{-h\nu/k_B T}}$$

  when we take the zero point energy as our zero of energy.

  – It follows that

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

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

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

  – 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*

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

- **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 Q, $Q(N, V, \beta)$, $Q(N, V, T)$. Given by*

$$Q = \sum_j e^{-E_j/k_B T}$$

- 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 $\epsilon_1, \ldots, \epsilon_N$ 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 jth 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 $f(E) = e^{\beta E}$ [3].
  - ■ To check that our definition of f satisfies the above equation, note that

$$e^{\beta(E_n - E_l)} = e^{\beta(E_n - E_m)} e^{\beta(E_m - E_l)}$$

- Deriving an expression for a_m.
  - From the above result, we have that

$$\frac{a_m}{a_n} = e^{\beta(E_n - E_m)}$$
$$a_m e^{\beta E_m} = a_n e^{\beta E_n}$$

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

$$\frac{a_m}{a_n} = e^{\beta(E_n - E_m)}$$
$$a_m = a_n e^{\beta E_n} e^{-\beta E_m}$$
$$a_m = C e^{-\beta E_m}$$

- Determining C.
  - We have that

$$C \sum_j e^{-\beta E_j} = \sum_j a_j = \mathcal{A}$$
$$C = \frac{\mathcal{A}}{\sum_j e^{-\beta E_j}}$$

  - Thus,

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

  - 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

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

- We will later show that $\beta = 1/k_B T$.
  - 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

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

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

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

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

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta}$$

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

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

$$\frac{\partial f}{\partial \beta} = -k_B T^2 \frac{\partial f}{\partial T}$$

so

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

- 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

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

  – Therefore,

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} = \frac{3N}{2}\frac{\mathrm{d}\ln\beta}{\mathrm{d}\beta} = \frac{3N}{2\beta} = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

- 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,

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

■ "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 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,

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

• 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

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

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

– It follows as before that
$$\overline{C}_V = 3R \left(\frac{h\nu}{k_B T}\right)^2 \frac{e^{-h\nu/k_B T}}{(1 - e^{-h\nu/k_B T})^2}$$

• **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

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

  - Therefore,

$$\langle P \rangle = k_B T\frac{\partial \ln Q}{\partial V} = \frac{Nk_B T}{V}$$
$$PV = Nk_B T$$

  - 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

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

- 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

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

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

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

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*

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

- 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 $E_{ijk\ldots} = \varepsilon_i + \varepsilon_j + \varepsilon_k + \cdots$ 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

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

  - 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.

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

- The probability that a molecule is in its jth 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 ith translational, j^{th} rotational, k^{th} vibrational, and l^{th} electronic state is given by

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

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

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

- It follows that

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

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

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

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 natural log), 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 $\lambda_{\mathrm{DB}} = \sqrt{h^2/2mk_BT}$, we may write

  $$q_x = \sum_{n_x} \mathrm{e}^{-h^2/8mk_BTL_x^2} = \sum_{n_x} \mathrm{e}^{-\lambda_{\mathrm{DB}}^2 n_x^2/4L_x^2}$$

- The number of states are occupied/have energy within k_BT of the ground state.

  - $-\lambda_{\mathrm{DB}}^2 n_x^2/4L_x^2$ is on the order of 1, implying that n_x is on the order of $2L/\lambda_{\mathrm{DB}}$.
  - It follows if L is on a macroscopic scale (e.g., $L \approx 1\,\mathrm{m}$) 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, $\mathrm{e}^{-\lambda_{\mathrm{DB}}^2 n_x^2/4L_x^2} \approx 1/\mathrm{e}$.
  - It follows that in a $1\,\mathrm{m}^3$ 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

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

- 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
    $$q_{elec} = g_1 e^{-(-D_e/k_B T)} + g_2 e^{-E_2/k_B T}$$
    - If $dT \ll (E_2 + D_e)$, then $q_{elec} = g_1 e^{D_e/k_B T}$.

- 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

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

- The **rotational temperature** leads to

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

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

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

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

  - Thus,

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

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

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

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

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

  - 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.,

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

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 ith 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 $300\,\text{K}$ 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

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

    - 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* Θ_{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.

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

- In terms of Θ_{vib},

$$q_{\text{vib}}(T) = \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}}$$

$$\langle E_{\text{vib}}\rangle = Nk_B \left(\frac{\Theta_{\text{vib}}}{2} + \frac{\Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1}\right)$$

$$\overline{C}_{\text{V,vib}} = R\left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^2}$$

- 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 (2021c).

- 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* $\mathbf{\Theta}_{rot}$. *Given by*

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

  - 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

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

  - As with the translational partition function, for $\Theta_{rot} \ll T$ (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,

$$q_{rot}(T) = \int_0^{\infty} (2J+1)e^{-\Theta_{rot}J(J+1)/T}\,dJ$$
$$= \int_0^{\infty} e^{-\Theta_{rot}x/T}\,dx$$
$$= \frac{T}{\Theta_{rot}} = \frac{8\pi^2 Ik_B T}{h^2}$$

  - 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

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

  - Each of the two rotational degrees of freedom of a diatomic contributes $R/2$ to $\overline{C}_{V,rot}$.

- Contrary to the other component parts of energy, higher energy rotational states are significantly occupied.
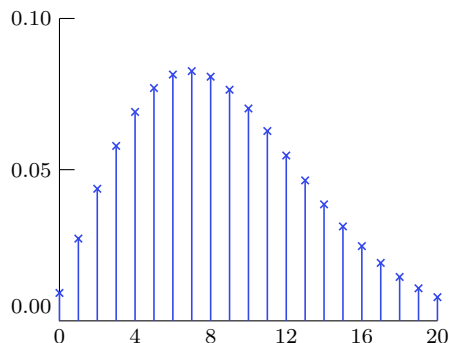
Figure 2.1: The fraction of molecules in the Jth rotational level for CO at $300\,K$.

  - We have that the fraction f_J of molecules in the Jth vibrational state is

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

– 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

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

  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 $-N_A D_e$ 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 jth normal mode.
- It follows that for a polyatomic molecule,

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

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

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

- 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 jth 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 $\Theta_{\text{rot},j} = \hbar^2/2I_j k_B$ 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

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

$$= \frac{1}{\sigma} \int_0^{\infty} (2J+1)^2 e^{-\Theta_{\text{rot}} J(J+1)/T} \, dJ$$

$$= \frac{1}{\sigma} \int_0^\infty 4J^2 e^{-\Theta_{\mathrm{rot}} J^2 / T} \, \mathrm{d}J$$

$$= \frac{4}{\sigma} \int_0^\infty J^2 e^{-aJ^2} \, \mathrm{d}J$$

$$= \frac{4}{\sigma} \cdot \frac{1}{4a} \sqrt{\frac{\pi}{a}}$$

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

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

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

- It follows that

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

- Linear molecule equations.

$$q(V,T) = \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} V \cdot \frac{T}{\sigma \Theta_{\mathrm{rot}}} \cdot \prod_{j=1}^{3n-5} \frac{e^{-\Theta_{\mathrm{vib},j}/2T}}{1 - e^{-\Theta_{\mathrm{vib},j}/T}} \cdot g_{e1} e^{D_e / k_B T}$$

$$\frac{U}{N k_B T} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{3n-5} \left(\frac{\Theta_{\mathrm{vib},j}}{2T} + \frac{\Theta_{\mathrm{vib},j}/T}{e^{\Theta_{\mathrm{vib},j}/T} - 1} \right) - \frac{D_e}{k_B T}$$

$$\frac{C_V}{N k_B} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{3n-5} \left(\frac{\Theta_{\mathrm{vib},j}}{T} \right)^2 \frac{e^{-\Theta_{\mathrm{vib},j}/T}}{(1 - e^{-\Theta_{\mathrm{vib},j}/T})^2}$$

- Nonlinear molecule equations.

$$q(V,T) = \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} V \cdot \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\Theta_{\mathrm{rot},A} \Theta_{\mathrm{rot},B} \Theta_{\mathrm{rot},C}}} \cdot \prod_{j=1}^{3n-6} \frac{e^{-\Theta_{\mathrm{vib},j}/2T}}{1 - e^{-\Theta_{\mathrm{vib},j}/T}} \cdot g_{e1} e^{D_e / k_B T}$$

$$\frac{U}{N k_B T} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3n-6} \left(\frac{\Theta_{\mathrm{vib},j}}{2T} + \frac{\Theta_{\mathrm{vib},j}/T}{e^{\Theta_{\mathrm{vib},j}/T} - 1} \right) - \frac{D_e}{k_B T}$$

$$\frac{C_V}{N k_B} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3n-6} \left(\frac{\Theta_{\mathrm{vib},j}}{T} \right)^2 \frac{e^{-\Theta_{\mathrm{vib},j}/T}}{(1 - e^{-\Theta_{\mathrm{vib},j}/T})^2}$$

Part II

Thermodynamics

Week 3

Kinetic Theory of Gases / The First Law of Thermodynamics

3.1 Maxwell-Boltzmann Distribution

- 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 $p(E) \propto e^{-E/k_B T}$.
  - Thus, to get the probability $p(v)$ of some speed v, we should have $p(v) \propto e^{-mv^2/2k_B T}$ times a constant giving the number of molecules of each speed? This yields

  $$p(v) = A 4\pi v^2 e^{-mv^2/2k_B T}$$

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

  $$1 = \int_0^\infty p(v)\,\mathrm{d}v$$
  $$= A \int_0^\infty 4\pi v^2 e^{-mv^2/2k_B T}\,\mathrm{d}v$$
  $$= A \int_0^\infty 4\pi \left(\frac{2k_B T}{m}\right)^{3/2} u^2 e^{-u^2}\,\mathrm{d}u$$
  $$= A 4\pi \left(\frac{2k_B T}{m}\right)^{3/2} \int_0^\infty u^2 e^{-u^2}\,\mathrm{d}u$$

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

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

– Therefore,

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

– 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 (2021d) 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 $20\,°\mathrm{C}$, $\overline{C}_V = 3R = 25\,\mathrm{J\,mol^{-1}\,K^{-1}}$.
  – 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 (2021d).

- **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 $P_0 T_0$.
    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:
- Thermodynamic derivation of the formula for $\langle P \rangle$ in terms of Q.

    - We have that

$$U = \sum p_j E_j$$
$$\mathrm{d}U = \sum (\mathrm{d}p_j\, E_j + p_j\, \mathrm{d}E_j)$$
$$= \underbrace{\sum \mathrm{d}p_j\, E_j}_{\delta q} + \underbrace{\sum p_j \frac{\partial E_j}{\partial V}\, \mathrm{d}V}_{-P}$$

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

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

- 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
$$
\begin{aligned}
dH &= dU + P\,dV + V\,dP \\
&= \delta q - P\,dV + P\,dV + V\,dP \\
&= \delta q + V\,dP
\end{aligned}
$$

  – At constant pressure ($dP = 0$), we have that $dH = \delta q$.
  – At constant volume, we have that $dH = \delta q$ 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,
$$
\begin{aligned}
dH &= dU + d(PV) \\
&= nC_V\,dT + nR\,dT \\
&= n(C_V + R)\,dT
\end{aligned}
$$

  – Recall this result from Labalme (2021d).

- Considers heat diagrams.

  – Recall the enthalpy of phase changes ΔH_{fus}, ΔH_{vap}, and ΔH_{sub}.
  – It follows that
$$
H(T) - H(T_0) = \int_{T^0}^{T} C_p\,dT + \sum \Delta H_{\text{phase changes}}
$$

- **Hess's Law**: $\Delta H = 0$ around a closed loop.

  - This is because H is a state function.

- **Standard enthalpy of formation**. The enthalpy of formation of a substance, as calculated from its constituent elements in their standard state (i.e., 1 bar, 298.15 K). *Denoted by* $\boldsymbol{\Delta H_f^\circ}$. *Units* **kJ/mol**.

- We have, for example, that the $\Delta H_{\mathrm{vap}}^\circ$ 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, $dU = \delta q_{\mathrm{rev}} - P\,dV$. In this case

$$\delta q_{\mathrm{rev}} = dU + P\,dV = nC_V\,dT + P\,dV \neq d(nC_V T + PV)$$

so δq_{rev} is not a state function.

  - However,

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

is a state function.

3.4   Chapter 27: 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 $\frac{3}{2}k_B T$. From classical mechanics, we also have that $\langle E_{\text{trans}} \rangle = \frac{1}{2}m \langle u^2 \rangle$. *This* is why we may let

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

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

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

    – For example, a homogeneous gas is isotropic, and this is what allows us to state that $\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$.

- McQuarrie and Simon (1997) derives

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

    – u_{rms} is an estimate of the average speed since $\langle u^2 \rangle \neq \langle u \rangle^2$ in general.

- McQuarrie and Simon (1997) states without proof that the speed of sound u_{sound} in a monatomic ideal gas is given by

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

- Assumptions of the kinetic theory of gases.

    – Particles collide elastically with the wall.

        ■ Justified because although each collision will not be elastic (the particles in the wall are moving too), the average collision will be elastic.

    – Particles do not collide with each other.

        ■ Justified because "if the gas is in equilibrium, on the average, any collision that deflects the path of a molecule... will be balanced by a collision that replaces the molecule" (McQuarrie & Simon, 1997, p. 1015).

- Note that we can do the kinetic derivation at many levels of rigor, but more rigorous derivations offer results that differ only by constant factors on the order of unity.

- Deriving a theoretical equation for the distribution of the *components* of molecular velocities.

    – Let $h(u_x, u_y, u_z)\,\mathrm{d}u_x\,\mathrm{d}u_y\,\mathrm{d}u_z$ 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

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

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

$$2u\frac{\partial u}{\partial u_x} = 2u_x$$

$$\frac{\partial u}{\partial u_x} = \frac{u_x}{u}$$

we have that

$$\frac{\partial \ln h}{\partial u_x} = \frac{\mathrm{d} \ln h}{\mathrm{d} u}\frac{\partial u}{\partial u_x} = \frac{u_x}{u}\frac{\mathrm{d} \ln h}{\mathrm{d} u}$$

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

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

$$\frac{\mathrm{d} \ln f(u_j)}{u_j\,\mathrm{d} u_j} = -\gamma$$

$$\frac{1}{f}\frac{\mathrm{d} f}{\mathrm{d} u_j} = -\gamma u_j$$

$$\int \frac{\mathrm{d} f}{f} = \int -\gamma u_j\,\mathrm{d} u_j$$

$$\ln f = -\frac{\gamma}{2}u_j^2 + C$$

$$f(u_j) = A\mathrm{e}^{-\gamma u_j^2}$$

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.

$$1 = \int_{-\infty}^{\infty} f(u_x)\,\mathrm{d} u_x$$

$$= 2A\int_{0}^{\infty} \mathrm{e}^{-\gamma u_x^2}\,\mathrm{d} u_x$$

$$= 2A\sqrt{\frac{\pi}{4\gamma}}$$

$$A = \sqrt{\frac{\gamma}{\pi}}$$

- 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. This fact was also demonstrated in Week 1, Lecture 3.

- **Doppler broadening**: The broadening of spectral lines due to the distribution of molecular velocities.

  - Ideally, spectral lines will be very narrow.
  - However, due to the Doppler effect, if an atom or molecule emits radiation of frequency ν_0 while moving away or toward the observer with speed u_x, then the observed frequency will be

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

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

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

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

- Deriving **Maxwell-Boltzmann distribution**.

---

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

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

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

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

- Thus, the Maxwell-Boltzmann distribution in terms of speed is

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

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

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 $dF/du = 0$.

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

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

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

- 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 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 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., $\Delta U = U_2 - U_1 = \int_1^2 dU$. 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

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

- 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 $1000\,\text{kg}$ weight to compress a gas to half its original volume vs. using a $10\,\text{kg}$ 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.

    - – Path 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

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

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

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

- We can also express the above in terms of pressure

$$\left(\frac{P_2 V_2 / nR}{P_1 V_2 / nR}\right)^{3/2} = \frac{V_1}{V_2}$$

$$P_1 V_1^{5/3} = P_2 V_2^{5/3}$$

- For a diatomic gas, we end up with

$$P_1 V_1^{7/5} = P_2 V_2^{7/5}$$

- Note that for an isothermal expansion, Boyle's law applies: $P_1 V_1 = P_2 V_2$.

- Relating work and heat to molecular properties.

  - By comparing recently derived equations with previously derived equations, we have that

$$U = \sum_j p_j E_j$$

$$dU = \sum_j p_j \, dE_j + \sum_j E_j \, dp_j$$

$$= \sum_j p_j \left(\frac{\partial E_j}{\partial V}\right)_N dV + \sum_j E_j \, dp_j$$

  - 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

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

  - 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

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

  - Thus, at constant pressure,

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

- 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* **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).

- Note that

$$R = 0.083\,14\,\frac{\text{L\,bar}}{\text{mol\,K}}$$

- 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 $\Delta_r H = H_{\mathrm{prod}} - H_{\mathrm{react}}$.

- **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.

- To calculate $\Delta_r H$ for the general chemistry equation

$$a\,\mathrm{A} + b\,\mathrm{B} \longrightarrow y\,\mathrm{Y} + z\,\mathrm{Z}$$

using standard heats of formation, we decompose the reactants into their component elements in their normal states and then reassemble them into the products.

  - Mathematically,

$$\Delta_r H = y\Delta_f H^\circ[Y] + z\Delta_f H^\circ[Z] - a\Delta_f H^\circ[A] - b\Delta_f H^\circ[B]$$

- The enthalpies of reaction at temperatures T_1, T_2 are related by

$$\Delta_r H(T_2) - \Delta_r H(T_1) = \int_{T_1}^{T_2} \Delta C_P(T)\,\mathrm{d}T$$

where

$$\Delta C_P(T) = yC_{P,Y}(T) + zC_{P,Z}(T) - aC_{P,A}(T) - bC_{P,B}(T)$$

Week 4

Entropy and the Second Law of Thermodynamics

4.1 Entropy Equations

- We define a new state function S by $\mathrm{d}S = \delta q_{\mathrm{rev}}/T$ 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: $\Delta S_{\mathrm{total}} = 0$.
    - Ideal gas:

$$\Delta S_{\mathrm{total}} = \Delta S_1 + \Delta S_2$$
$$= \int \frac{\delta q_{\mathrm{rev}_1}}{T} - \int \frac{\delta q_{\mathrm{rev}_1}}{T}$$
$$= \int \frac{\delta q_{\mathrm{rev}_1}}{T} + \int \frac{\delta q_{\mathrm{rev}_2}}{T}$$

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

– We have that

$$\Delta S = \int \frac{\delta q_{\mathrm{rev}}}{T} = \int_{V_0}^{2V_0} \frac{P\,\mathrm{d}V}{T} = \int_{V_0}^{2V_0} \frac{nRT}{V}\frac{1}{T}\,\mathrm{d}V = nR\ln 2$$

• 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.

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

$$\Delta S_1 = \int_T^{T_b} \frac{C_{P_l}}{T}\,\mathrm{d}T \qquad \Delta S_2 = \frac{\Delta H_{\mathrm{vap}}}{T_b} \qquad \Delta S_3 = nR\ln\frac{P_0}{P} \qquad \Delta S_4 = \int_{T_b}^T \frac{C_{P_g}}{T}\,\mathrm{d}T$$

and that

$$\Delta S_0 = \frac{\Delta H_{\mathrm{vap}}}{T}$$

– We know that ΔS around the loop is zero since S is a state function. We neglect the heat capacity effect. Thus,

$$\frac{\Delta H_{\mathrm{vap}}}{T_b} + nR\ln\frac{P_0}{P} - \frac{\Delta H_{\mathrm{vap}}}{T} = 0$$

$$\ln\frac{P_0}{P} = \frac{\Delta H_{\mathrm{vap}}}{nR}\left(\frac{1}{T} - \frac{1}{T_b}\right)$$

$$P = P_0 e^{-\Delta H_{\mathrm{vap}}/nR(1/T - 1/T_b)}$$

– 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

$$\frac{\Delta H_{\mathrm{vap}}}{T_b} \approx 85 \pm 5\,\mathrm{J\,mol^{-1}\,K^{-1}}$$

– Discovered this rule as an undergrad after an afternoon's manipulation of data from a book of tables.

– This rule reflects the fact that

$$\frac{\Delta H_{\mathrm{vap}}}{T_b} = \Delta S_{\mathrm{vap}}$$

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

$$\delta q_{\mathrm{rev}_1} = \delta q_{\mathrm{rev}_2}$$
$$C_{V_1}\,\mathrm{d}T_1 = -C_{V_2}\,\mathrm{d}T_2$$

– Thus,

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

– 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

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

▪ 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 $W(n_1, \ldots, n_r)$.
  - 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,

$$S = A k_B \sum_i (-p_i \ln p_i)$$

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

4.3　Further Entropy Relations and Phenomena

2/4:　　• Verifying that the entropy is at a maximum when all the states have equal probability.

– In the case of just two states,

$$
\begin{aligned}
S &= N k_B (-p_1 \ln p_1 - p_2 \ln p_2) \\
\mathrm{d}S &= N k_B [-\,\mathrm{d}(p_1 \ln p_1) - \mathrm{d}(p_2 \ln p_2)] \\
&= N k_B \Big[-\,\mathrm{d}p_1 \cdot \ln p_1 - p_1 \cdot \frac{\mathrm{d}p_1}{p_1} - \mathrm{d}p_2 \cdot \ln p_2 - p_2 \cdot \frac{\mathrm{d}p_2}{p_2} \Big] \\
&= N k_B (-\,\mathrm{d}p_1)(\ln p_1 - \ln p_2) \\
&= 0
\end{aligned}
$$

if $p_1 = p_2$.

■ Thus, since $\mathrm{d}S/\mathrm{d}p_1 \,|_{p_1=1/2} = 0$, we know that a graph of entropy vs. p_1 has a maximum at $p_1 = 1/2$.

– In the case of many buckets,

$$\mathrm{d}S = -N k_B \sum_i \ln p_i \, \mathrm{d}p_i = 0$$

iff all p_i are the same, because then we could pull out the $\ln p_i$ and take $\sum \mathrm{d}p_i = 0$.

• Fluctuations from the equilibrium state are very unlikely in a macroscopic system. Entropy measures the likelihood.

– At equilibrium, we have a number of configurations W_{eq}. Outside of equilibrium, we have a number of configurations W.

– Thus,

$$\Delta S = S - S_{\mathrm{eq}} = k_B \ln \frac{W}{W_{\mathrm{eq}}}$$

$$\frac{W}{W_{\mathrm{eq}}} = \mathrm{e}^{\Delta S/k_B}$$

– For $\Delta S = R = 8.31 \, \mathrm{J\,mol^{-1}\,K^{-1}}$, we have that $W = W_{\mathrm{eq}} \mathrm{e}^{N_A}$, which will never happen?

• Deriving the Boltzmann factor by identifying the thermodynamic and statistical entropies.

– Consider two states E_1, E_2. Then $\delta q_{\mathrm{rev}} = (E_1 - E_2)$.

– We have

$$\mathrm{d}S = \frac{\delta q_{\mathrm{rev}}}{T} \qquad\qquad \begin{aligned} \mathrm{d}S &= -k_B N \, \mathrm{d}(p_1 \ln p_1 + p_2 \ln p_2) \\ &= -k_B N (\ln p_1 - \ln p_2) \, \mathrm{d}p_1 \end{aligned}$$

– Setting them equal to each other, we get

$$\frac{\mathrm{d}p_1\,(E_1 - E_2)}{T} = -k_B \ln \frac{p_1}{p_2}\,\mathrm{d}p_1$$

$$\frac{E_1 - E_2}{k_B T} = -\ln \frac{p_1}{p_2}$$

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

which is the Boltzmann factor, as desired.

- Expressing the entropy in terms of the partition function.

  – Derives
  $$S = k_B T \frac{\partial \ln Q}{\partial T} + k_B \ln Q$$
  from $S = -Nk_B \sum_i p_i \ln p_i$ as in McQuarrie and Simon (1997).

- Entropy of an ideal monatomic gas.

  – Derives
  $$S = \frac{5}{2} N k_B + N k_B \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{V}{N} g_{e1} \right]$$
  as in McQuarrie and Simon (1997).

  – Note that
  $$\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \approx \left(\frac{1}{\lambda_{dB}} \right)^3$$
  where λ_{dB} is the de Broglie wavelength.

- The Carnot engine. The most efficient thermal engine between two temperature reservoirs.

  – Recall that the area inside the cycle on a P/V diagram is the work produced by the cycle.
  – It is adiabatic expansion, isothermal expansion, adiabatic compression, isothermal compression.
  – Does the same efficiency analysis as in McQuarrie and Simon (1997).
  – PGS says it's ok to treat the processes as reversible because they're isothermal by definition.

4.4 Office Hours (PGS)

- Week 1, Lecture 3: When we calculate the average kinetic energy to be $3k_B T/2$, what constraints do we have on the system. Is it truly any system that can be described by a partition function? And if so, why does this result differ from the one presented in McQuarrie and Simon (1997) for a diatomic ideal gas?

  – There aren't constraints on the system under study.
  – $PV = \frac{2}{3} \langle KE \rangle$ is true without ideality.
  – $\langle E \rangle = 3k_B T/2$ is only true with a monatomic ideal gas.
  – DOFs contribute to $\langle E \rangle$ (at very high temperatures).
    ■ But in the equation from Chapter 17 for a diatomic, some terms disappear as $T \to \infty$.

- Week 1, Lecture 3: What does calculating the expected energy of a harmonic oscillator have to do with anything? Are you just doing it to show that we can for the quantized system? Also, are we integrating because this is a "continuous" partition function, and if it is a continuous partition function, is it so because the harmonic oscillator can, in theory, assume any bond distance even though its *energies* are quantized?

- Week 1, Lecture 3: How is $k_B T$ the average energy of a classical harmonic oscillator? Is it the sum of the kinetic energy and potential energy, both equal to $k_B T/2$? Is this the virial theorem again?

  - Also a high-temperature limit thing.

- What was Week 1 about? It mostly seemed like a lot of examples to sort of motivate the course.

  - Yes, this was basically just to motivate the course.
  - Take away: $k_B T$ determines the range of energies you'll be in for everything.
    - Things much higher in energy won't be **thermally populated**.
    - Things much lower are equally populated.

- Quiz 1, Questions 5-6. Plus will things like surface tension be on the midterm?

  - Surface tension is the same thing as pressure in two dimensions.
  - We can do $\gamma A = nRT$.
  - $A\gamma$ becomes 2 of the kinetic energy $1/2k_B T$.
    - Work this out for myself!

- Week 2, Lecture 2: The vibrational partition function at $T = h\nu/k_B$ equals zero. What is the significance of this? Is it just that, that the average vibrational energy is equal to zero here?

- Do the rotational and vibrational temperatures have a nice physical interpretation?

  - They are the energies of vibrations/rotations on a scale of temperature instead of energy (the two are directly proportional).
  - The theoretical rotational/vibrational temperature/energy.
    - It's the same temperature as the speeds. When molecules collide, they exchange energy.
    - After enough collisions (as a system tends toward thermal equilibrium), the rotational temperature becomes the same as vibrational.

- Week 3, Lecture 1: In your derivation of the Maxwell-Boltzmann distribution, where does the $4\pi v^2$ come from? Is the sphere you referred to in class the same one as in the textbook, this "velocity space?" If so, could you explain a bit more what a velocity space is?

- The internal energy of a system is only a function of temperature because in the expression for $\langle E \rangle$ in terms of Q, T is the only variable that is algebraically in the equation and the partial derivative is held constant with respect to all variables except T.

- I'm very confused on the distinction between a reversible and irreversible process.

  - Reversible means that at every point, you are in thermal equilibrium, so you can specify the state of the system.
    - Remember that T is not always specified for a system (only for systems in thermal equilibrium, i.e., that obey the Maxwell-Boltzmann distribution)! The same goes for P and V.
  - If the process happens very suddenly or you don't know what the temperature/pressure are during the process, that's irreversible. Something burning in a closed container is irreversible, but at the beginning and end you are in thermal equilibrium, so you can imagine a reversible path between the two.
  - Energy is the same regardless of path, entropy is the same regardless of path.
  - Temperature is not uniform throughout the system during an expansion of a gas from a filled container into a vacuumed container (the system is not in thermal equilibrium). The particles in the filled container will still be at the initial temperature, but those that have left are expending their KE to do so and cooling drastically.

- – *Any* line on a PV diagram describes a reversible process. The processes may differ in terms of non-state functions such as heat exchange or work, but the net ΔU, ΔH, and ΔS will be the same.
  - ■ The internal energy will be different *along* different paths, but it will make the same net change.
- – A reversible process need not be isothermal. We can merely consider a piecewise path that contains isothermal components because they are easy to work with mathematically, if the quantity we're interested in calculating is a state function.
- – If we want to calculate the work for a reversible process, we need $w = -\int_1^2 P\,dV$. If we want to calculate ΔU, we need the state variables T_1 and T_2 but that's it (since U is a state function of T).

- Could you also speak to exact vs. inexact differentials and how to tell if something is a state function by its differential?

  - – If you have a state function, this means that you can express it in terms of the state variables, but you need to know them.
  - – Examples of state variables are energy, temperature, volume, and number of moles.
  - – Once you have a relation between those variables, the state function is uniquely defined between those variables. Entropy is absolute (with physical meaning); enthalpy and energy have defined values once we choose a zero. These latter values, however, have no physical meaning; they only allow us to calculate ΔU and ΔH, which do have physical meaning.
  - – We find that $\delta q_{\text{rev}} = C_V\,dT$ and $\delta w = -P\,dV$. When we take $\delta q_{\text{rev}} = dU + P\,dV$, this differential does not describe a state function because it is not the derivative of any function (P is a state variable, but it's also a function of V and T [the latter being the problem since it appears in a term with only dV]). However, if we divide by T for an ideal gas, then we can get the form $M(T)\,dT + N(V)\,dV$, where $M(T) = C_V(T)/T$ and $N(V) = nR/V$.
    - ■ Note that this differential satisfies $dN/dT = dM/dV = 0$ as per Labalme (2021b). In fact, this directly expresses the fact that M is constant with respect to y and N is constant with respect to x.
    - ■ Note that according to this definition, we don't theoretically need M, N to only be functions of one variable.
  - – Maxwell's relation: A function $f(x, y)$ such that $df/dx\,dy = df/dy\,dx$.
    - ■ Allows us to relate variables that we might not generally be able to.

- Week 3, Lecture 3: I know you said when you were working with the differential of entropy that $dH = \delta q$ at constant pressure ($dP = 0$). This makes sense. Did you say that at constant volume, we have that $dH = \delta q$ as well?

- Week 3, Lecture 3: How do we obtain the enthalpies of formation at nonstandard temperatures?

- Do we need to know anything about Doppler broadening? I believe you alluded to it once.

- How are P_{ext} and P related, especially in the context of a PV graph? What exactly is the "P" in $w = -\int_1^2 P\,dV$?

  - – In a reversible process, the pressures are the same. This extends to *any* path along a PV diagram, not just an isothermal one, as per our previous discussion.

- What is with the isothermal approximation thing? Do we just approximate everything as isothermal? When can and can't we do this?

- Page 39 of my notes questions.

- What gives us the right to express work during an adiabatic process as an integral with respect to temperature? Is there an equivalent formulation in terms of an integral with respect to V?

- Quiz 2, Question 4.

- Week 4, Lecture 1: You calculated that $\Delta S = nR \ln 2$ for n moles of a gas expanding to twice it's initial volume. I assume this doesn't relate to the Gibbs Paradox?

  - The Gibbs paradox says that the final and initial states of two gases mixing are the same, and thus there is no change in entropy.
  - However, we are implicitly assuming that the gases are expanding by virtue of the fact that they're initially separated and thus distinguishable.
  - A paradox doesn't mean that something isn't true, it just means that our understanding is incomplete.
  - The $nR \ln 2$ isn't characteristic of the Gibbs paradox; it's characteristic of a doubling in volume, in whatever context.

- Week 4, Lecture 3: How do you get to $W = W_{\text{eq}} e^{-\Delta S/T}$?

  - It is $+\Delta S$; it's just that ΔS is a negative quantity when you're moving away from equilibrium.

- In an irreversible process vs. a reversible process, is there a difference in entropy?

  - See the Clausius inequality. If you want more heat, do reversible. If you want more work, do irreversible.

- The experiment in Homework 2, Question 1.

  - The Clément-Desormes experiment.

- Do we need another variable for HW2, Q2?

  - You do need an initial temperature T_h.
  - PGS will send a note.

4.5 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 $N_1, \ldots, N_r$ where $N_1 + \cdots + N_r = N$.

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

- 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 $\int_1^n \ln x \, dx$. Thus, we take

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

  - A refinement of the approximation is the following.

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

4.6 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 the 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

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

  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 S. Given by*

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

- **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 $\mathrm{d}S = \delta q_{\mathrm{rev}}/T$ 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,

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

– Since V_A, V_B are fixed, $dV = 0$, meaning that $dU = \delta q_{\text{rev}} + 0$. It follows that

$$dS = dS_A + dS_B$$
$$= \frac{dU_A}{T_A} + \frac{dU_B}{T_B}$$
$$= dU_B \left(\frac{1}{T_B} - \frac{1}{T_A} \right)$$

– Since the gases A and B can still mix without absorbing energy, we define dS_{prod} as the entropy produced by the system and redefine $\delta q / T$ as dS_{exch} (the entropy exchanged with the surroundings via a transfer of heat).

– It follows that for an reversible process ($dS_{\text{prod}} = 0$), we have

$$dS = \frac{\delta q_{\text{rev}}}{T}$$

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

$$dS = dS_{\text{prod}} + \frac{\delta q_{\text{irr}}}{T} > \frac{\delta q_{\text{irr}}}{T}$$

- **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, $dS \geq \delta q / T$, 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 $j = 1, 2, \ldots, \Omega(E)$.

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

$$S = k_B \ln W$$

---

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

■ 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 $S = k_B \ln \Omega$.

2/3:
- Since entropy is a state function, we calculate entropy changes via a reversible process.

  – Imagine a gas expanding from V_1 to V_2 in a non-isolated system.

  – Although this is an adiabatic process, since entropy is a state function, we may perform the easier isothermal calculation for the "equivalent" reversible process.

  $$\Delta S_{\text{sys}} = \int_1^2 \frac{\delta q_{\text{rev}}}{T} = -\int_1^2 \frac{\delta w_{\text{rev}}}{T} = \int_{V_1}^{V_2} \frac{P}{T} \, \mathrm{d}V = nR \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = nR \ln \frac{V_2}{V_1}$$

    ■ Note that it is the change to an isothermal integral that allows us to assume $\mathrm{d}U = 0$ (internal energy is a function of only temperature).

  – However, there is still a difference between reversible and irreversible processes.

    ■ In the reversible, isothermal process, $q_{\text{rev}} = -w_{\text{rev}} = -nRT \ln(V_2/V_1)$. Thus,

    $$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = nR \ln \frac{V_2}{V_1} - nR \ln \frac{V_2}{V_1} = 0$$

    as we would expect for an reversible process.

    ■ In the irreversible, adiabatic process, however, $\Delta S_{\text{surr}} = 0^{[2]}$. Thus,

    $$\Delta S_{\text{univ}} = nR \ln \frac{V_2}{V_1} > 0$$

    as we would expect for an irreversible process.

- The isothermal mixing of two ideal gases (say N_2 and Br_2).

  – Because the two gases are ideal, they act independently of each other. Thus,

  $$\Delta S_{N_2} = n_{N_2} R \ln \frac{V_{N_2} + V_{Br_2}}{V_{N_2}} \qquad\qquad \Delta S_{Br_2} = n_{Br_2} R \ln \frac{V_{N_2} + V_{Br_2}}{V_{Br_2}}$$

  – It follows that

  $$\begin{aligned}
  \Delta S &= \Delta S_{N_2} + \Delta S_{Br_2} \\
  &= -n_{N_2} R \ln \frac{V_{N_2}}{V_{N_2} + V_{Br_2}} - n_{Br_2} R \ln \frac{V_{Br_2}}{V_{N_2} + V_{Br_2}} \\
  &= -n_{N_2} R \ln \frac{n_{N_2}}{n_{N_2} + n_{Br_2}} - n_{Br_2} R \ln \frac{n_{Br_2}}{n_{N_2} + n_{Br_2}} \\
  \Delta \overline{S} &= -\frac{n_{N_2}}{n_{N_2} + n_{Br_2}} R \ln \frac{n_{N_2}}{n_{N_2} + n_{Br_2}} - \frac{n_{Br_2}}{n_{N_2} + n_{Br_2}} R \ln \frac{n_{Br_2}}{n_{N_2} + n_{Br_2}} \\
  \frac{\Delta_{\text{mix}} \overline{S}}{R} &= -y_{N_2} \ln y_{N_2} - y_{Br_2} \ln y_{Br_2}
  \end{aligned}$$

  where $V \propto n$ by the ideal gas law, $\Delta \overline{S}$ is the *molar* change in entropy, and y_{N_2} is the mole fraction of N_2 (same for bromine), and $\Delta_{\text{mix}} \overline{S}$ indicates that this is the molar change in entropy for the *mixing* of two gases.

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[2]McQuarrie and Simon (1997) justify $\Delta S_{\text{surr}} = 0$ for an irreversible *isothermal* process by $\Delta U = 0$ and $P_{\text{ext}} = 0$ imply $w_{\text{irr}} = 0$ and therefore $q_{\text{irr}} = 0$.

- For the isothermal mixing of N ideal gases, we have

$$\Delta_{\mathrm{mix}}\overline{S} = -R\sum_{j=1}^{N} y_j \ln y_j$$

- ΔS when two equal sized pieces of the same metal at different temperatures (T_h, T_c) are brought into thermal contact and then isolated from the surroundings.

  - Both pieces of metal will approach the same final temperature T as per

  $$C_V(T_h - T) = C_V(T - T_c)$$
  $$T = \frac{T_h + T_c}{2}$$

  - There is essentially no work done, so $\mathrm{d}U = \delta q_{\mathrm{rev}}$.
  - Thus, taking C_V to be constant from T_c to T_h yields

  $$\Delta S = \int_{T_1}^{T_2} \frac{\delta q_{\mathrm{rev}}}{T} = \int_{T_1}^{T_2} \frac{C_V\,\mathrm{d}T}{T} = C_V \ln \frac{T_2}{T_1}$$

- Therefore, we have

$$\Delta S_h = C_V \ln \frac{T_h + T_c}{2T_h} \qquad\qquad \Delta S_c = C_V \ln \frac{T_h + T_c}{2T_c}$$

- It follows that

$$\Delta S = \Delta S_h + \Delta S_c = C_V \ln \frac{(T_h + T_c)^2}{4T_h T_c}$$

where

$$(T_h - T_c)^2 = T_h^2 - 2T_h T_c + T_c^2 > 0$$
$$T_h^2 + 2T_h T_c + T_c^2 = (T_h + T_c)^2 > 4T_h T_c$$

implies that $\Delta S > 0$, as desired for an irreversible process.

- The Carnot cycle (for a steam engine).

  - Each cycle, the engine (system) "withdraws energy $[q_h]$ as heat from some high-temperature thermal reservoir, uses some of the energy to do work $[w]$, and then discharges the rest of the energy $[q_c]$ as heat to a lower-temperature thermal reservoir" (McQuarrie & Simon, 1997, p. 838).
  - Treating the process as reversible (since both internal energy and entropy as state functions) gives us the following analysis.
  - Since this is a cycle, we have that

  $$\Delta U_{\mathrm{engine}} = w + q_{\mathrm{rev,h}} + q_{\mathrm{rev,c}} = 0 \qquad\qquad \Delta S_{\mathrm{engine}} = \frac{\delta q_{\mathrm{rev,h}}}{T_h} + \frac{\delta q_{\mathrm{rev,c}}}{T_c}$$

  - It follows if we define the maximum efficiency of the engine to be the quotient of work done by the engine $(-w)$ and heat input $(q_{\mathrm{rev,h}})$ that

  $$\mathrm{maximum\ efficiency} = \frac{-w}{q_{\mathrm{rev,h}}}$$
  $$= \frac{q_{\mathrm{rev,h}} + q_{\mathrm{rev,c}}}{q_{\mathrm{rev,h}}}$$
  $$= 1 + \frac{-T_c q_{\mathrm{rev,h}}/T_h}{q_{\mathrm{rev,h}}}$$
  $$= \frac{T_h - T_c}{T_h}$$

- It follows for typical values of $T_h = 573\,\text{K}$ and $T_c = 373\,\text{K}$ that maximum efficiency $\approx 35\%$.
- Moreover, it implies that engines run with higher-temperature heat reservoirs and lower-temperature cold reservoirs are more efficient, regardless of design.
- Note that $T_h = T_c$ implies that maximum efficiency $= 0\%$, i.e., no net work can be obtained from an isothermal cyclic process.

- The above result leads to **Kelvin's statement of the Second Law**.

- **Kelvin's statement of the Second Law**: A closed system operating in an isothermal cyclic manner cannot convert heat into work without some accompanying change in the surroundings.

- Expressing entropy in terms of a partition function.

$$S_{\text{ensemble}} = k_B \ln W$$

$$= k_B \ln \frac{\mathcal{A}!}{\prod_j a_j!}$$

$$= k_B \ln \mathcal{A}! - k_B \sum_j \ln a_j!$$

$$= k_B \mathcal{A} \ln \mathcal{A} - k_B \mathcal{A} - k_B \sum_j a_j \ln a_j + k_B \sum_j a_j \qquad \text{(Stirling's approximation)}$$

$$= k_B \mathcal{A} \ln \mathcal{A} - k_B \sum_j a_j \ln a_j \qquad \qquad (\textstyle\sum_j a_j = \mathcal{A})$$

$$= k_B \mathcal{A} \ln \mathcal{A} - k_B \sum_j p_j \mathcal{A} \ln p_j \mathcal{A} \qquad \qquad (p_j = a_j/\mathcal{A})$$

$$= k_B \mathcal{A} \ln \mathcal{A} - k_B \mathcal{A} \sum_j p_j \ln p_j - k_B \mathcal{A} \ln \mathcal{A} \sum_j p_j$$

$$\frac{S_{\text{ensemble}}}{\mathcal{A}} = -k_B \sum_j p_j \ln p_j \qquad \qquad (\textstyle\sum_j p_j = 1)$$

$$S_{\text{system}} = -k_B \sum_j p_j \ln p_j$$

$$= -k_B \sum_j \frac{e^{-\beta E_j}}{Q}(-\beta E_j - \ln Q)$$

$$= \beta k_B \sum_j \frac{E_j e^{-\beta E_j}}{Q} + k_B \ln Q \sum_j \frac{e^{-\beta E_j}}{Q}$$

$$= \frac{1}{T} \cdot \langle E \rangle + k_B \ln Q$$

$$S_{\text{system}} = k_B T \frac{\partial \ln Q}{\partial T} + k_B \ln Q$$

- For a monatomic ideal gas where all atoms are in their ground electronic state, we have

$$\overline{S} = \frac{5}{2}R + R \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{\overline{V} g_{e1}}{N_A}\right]$$

- The mixing of two ideal gases (say N_2 and Br_2) from a molecular perspective.

- Since the natural log in $\overline{S}$ for a monatomic ideal gas contains the same number of terms involving V as for a diatomic ideal gas, we have that

$$S = N k_B \ln V + \text{terms not involving } V$$

$$= n R \ln V + \text{terms not involving } V$$

for both N_2 and Br_2.

- Thus, the initial state is given by

$$S_1 = S_{1,N_2} + S_{1,Br_2}$$
$$= n_{N_2} R \ln V_{N_2} + n_{Br_2} R \ln V_{Br_2} + \text{terms not involving } V$$

and the final state is given by

$$S_2 = S_{2,N_2} + S_{2,Br_2}$$
$$= n_{N_2} R \ln(V_{N_2} + V_{Br_2}) + n_{Br_2} R \ln(V_{N_2} + V_{Br_2}) + \text{terms not involving } V$$

- Therefore,

$$\Delta_{\text{mix}} S = S_2 - S_1$$
$$= n_{N_2} R \ln \frac{V_{N_2} + V_{Br_2}}{V_{N_2}} + n_{Br_2} R \ln \frac{V_{N_2} + V_{Br_2}}{V_{Br_2}}$$
$$\frac{\Delta_{\text{mix}} \overline{S}}{R} = -y_{N_2} \ln y_{N_2} - y_{Br_2} \ln y_{Br_2}$$

as expected.

- Relating $S = k_B \ln W$ to $dS = \delta q_{\text{rev}} / T$ (and proving that $\beta = 1/k_B T$!).

  - We have that

$$S = -k_B \sum_j p_j \ln p_j$$
$$\frac{dS}{dp_j} = -k_B \sum_j \left(p_j \cdot \frac{1}{p_j} + 1 \cdot \ln p_j \right)$$
$$dS = -k_B \sum_j (dp_j + \ln p_j \, dp_j)$$
$$= -k_B \sum_j (-\beta E_j - \ln Q) \, dp_j$$
$$= \beta k_B \sum_j E_j \, dp_j + \ln Q \sum_j dp_j$$
$$= \beta k_B \, \delta q_{\text{rev}} \qquad\qquad (\sum_j p_j = 1 \Rightarrow \sum dp_j = 0)$$

as desired.

- Additionally, the above result implies that βk_B is an integrating factor of δq_{rev}, i.e.,

$$\beta k_B = \frac{1}{T}$$
$$\beta = \frac{1}{k_B T}$$

Week 5

Entropy and the Third Law of Thermodynamics

5.1 Entropy and the Third Law

- An experimental determination of entropy.

  - We have that

  $$dU = \delta q_{\mathrm{rev}} + \delta w_{\mathrm{rev}}$$
  $$= T \, dS - P \, dV$$

  - At constant V, $dV = 0$, so $dS = dU / T = C_V \, dT / T$.
  - More rigorously, we can do the rest of the derivation as in McQuarrie and Simon (1997) to get

  $$\left(\frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T} \qquad\qquad \left(\frac{\partial S}{\partial V} \right)_T = \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right]$$

  - It follows that $\Delta S = \int_{T_1}^{T_2} C_V / T \, dT$.
    - This is one way to measure the change in entropy.
    - However, it's not very practical since it's very hard to do constant volume chemistry.

- Derives

  $$\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_P}{T} \qquad\qquad \left(\frac{\partial S}{\partial P} \right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial P} \right) - V \right]$$

  as in McQuarrie and Simon (1997).

  - It follows that $\Delta S = \int_{T_1}^{T_2} C_P / T \, dT$, too.
  - However, since this is ΔS at constant pressure, we expect it to be bigger than ΔS at constant volume because work is done.

- **Third Law**: The entropy of pure ordered crystals is zero at $0\,\mathrm{K}$.

  - Solid CO is *not* ordered, as discussed in McQuarrie and Simon (1997).
  - Derive with $S = k_B \ln W$.

- Since we can't actually achieve $0\,\mathrm{K}$ and measure properties such as entropy there, we appeal to the Debye model to determine entropy there and in the viscinity.

- **Debye model**: The statement that $C_P(T) \propto T^3 = AT^3$ for insulating crystals.

  - It follows that for T_0 sufficiently close to $0\,\mathrm{K}$,

  $$\Delta S = \int_0^{T_0} \frac{AT^3}{T}\,\mathrm{d}T = \frac{1}{3}AT_0^3 = \frac{C_P(T_0)}{3}$$

  - Justifying the Debye model.
    - According to the Einstein model, each atom is a harmonic oscillator of frequency $h\nu$. This implies, however, that $C_P(T) \approx 1/(\mathrm{e}^{h\nu/k_B T} - 1)$ drops too fast at low T.
    - Debye says that sound waves are harmonic oscillators with very low frequencies. If you take $h\nu \ll k_B T$, or $hc/\lambda \ll k_B T$, you are concerned with all λ sufficiently large (or wavevectors $k = 2\pi/\lambda$ sufficiently small). The wavevectors are within a sphere in a wavevector space with basis k_x, k_y, k_z. The radius of this sphere is proportional to T. Thus, it's volume, which contains what we're interested in, is $4/3\pi r^3$ and thus the sum of all the wavevectors is proportional to T^3. Thus, the number of states of energy less than $k_B T$ is proportional to T^3 and each has $k_B T$ of energy (thus, if you were trying to find a scaling for the energy, it would be $U(T) \approx T^4$). Note also $h\nu = hc/\lambda = 2\pi\hbar c/\lambda = c\hbar k$.

- Comparing experimental and theoretical values of entropy of gases to the theory value from the partition function.

  - Ideal gas phase S is accurately calculated with $Q = q^N/N!$.
  - Table 21.4 compares the agreement for seven substances and finds it accurate to within 0.1%.
  - The discrepancies come from disorder at $0\,\mathrm{K}$, as described in McQuarrie and Simon (1997).

5.2 Introduction to Free Energies

2/9:
- Discusses the entropy trends from Chapter 21.

  - More atoms ($CO < CO_2$) increases entropy.
  - Heavier atoms increases entropy.
  - Floppier molecules (pentane > cyclopentane) have greater entropy.
  - Gases have greater entropy (this rule is king).

- Example (21-42):

  - When determining which chemical reaction has the greatest increase in entropy, look at the change in number of moles of gas as the first tie-breaker.

- Consider two systems: Water and ice in a container in thermal contact with a surrounding at zero celsius, and water at room temperature and ice at zero celsius in a thermally isolated container.

  - The first process is reversible since we can melt by raising the temperature slightly (allowing heat flow into the system) and vice versa for freezing.
  - The second process is irreversible because it tends toward thermal equilibrium and there is no way to undo the final equilibrium.
  - We can consider reversible paths for both processes though to calculate state functions.
  - Goes over how to calculate the final temperature T in the second process, which is necessary to get the entropy componentwise.

- Free energies decrease in a spontaneous process.

  - We know that $\mathrm{d}S \geq 0$ for an isolated system, and that $\mathrm{d}S \geq \delta q/T$ for any system (equality holds for reversible processes).

- Rearranging, we have that
$$0 \geq \delta q - T \, \mathrm{d}S$$

- It follows since $\mathrm{d}U = \delta q + \delta w$ that
$$\mathrm{d}U - T \, \mathrm{d}S = (\delta q - T \, \mathrm{d}S) + \delta w$$
$$\leq \delta w$$

- But since $A = U - TS$ is clearly a state function (as a combination of state functions and state variables),
$$\mathrm{d}A = \mathrm{d}U - T \, \mathrm{d}S - S \, \mathrm{d}T$$
is an exact differential for a state function. In particular, at constant temperature,
$$\mathrm{d}A = \mathrm{d}U - T \, \mathrm{d}S$$

- Therefore, $\mathrm{d}A \leq \delta w$ at constant temperature.
- Thus, at constant T, V, w, $\mathrm{d}A \leq 0$. In other words, A is monotonically decreasing.

- **Helmholtz free energy**: The state function A defined above.

  - We use this because it's more "natural" to think about finding the lowest free *energy* state than the largest *entropy* state.
  - The Helmholtz free energy is most often used in physics where there isn't often a "pressure bath." Chemists prefer the **Gibbs free energy**, which is constructed exactly the same way.

- **Gibbs free energy**: The state function describing the free energy of a system at constant pressure. *Denoted by* **G**. *Given by*
$$G = H - TS$$

  - It follows from our prior results that at constant temperature,
$$\begin{aligned} \mathrm{d}G &= \mathrm{d}H - T \, \mathrm{d}S \\ &= \mathrm{d}U + \mathrm{d}(PV) - T \, \mathrm{d}S \\ &= \delta q + \delta w + P \, \mathrm{d}V + V \, \mathrm{d}P - T \, \mathrm{d}S \\ &= \delta q - P \, \mathrm{d}V + \delta w_{\text{non-rev } PV} + P \, \mathrm{d}V + V \, \mathrm{d}P - T \, \mathrm{d}S \\ &= \delta q - T \, \mathrm{d}S + \delta w_{\text{non-rev } PV} + V \, \mathrm{d}P \\ &\leq 0 + \delta w_{\text{non-rev } PV} + V \, \mathrm{d}P \end{aligned}$$

  - Thus, at constant T, P and with no other w done on the system, $\mathrm{d}G \leq 0$.
  - In a reversible process (constant T, P), $\mathrm{d}G = \delta w_{\text{non-rev } PV}$.

- Note that δw is the work put into the system, so $\delta w \geq \delta w_{\text{rev}} = \mathrm{d}A$.

- The system produces more work when operated reversibly.

- Gibbs free energy and electrochemical work: The case of hydrogen fuel cells vs. thermal engines.

  - The hydrogen fuel cell is based off of the reaction
$$\mathrm{H}_2 + \frac{1}{2}\,\mathrm{O}_2 \longrightarrow \mathrm{H}_2\mathrm{O}$$
  with $\Delta H = 285.76 \, \mathrm{kJ/mol}$ and $\Delta G = 237.1 \, \mathrm{kJ/mol}$.
  - ΔH can be used to produce heat $q = \Delta H$.
  - If we want to produce work, we have to run a thermal engine that will have efficiency bounded above by the Carnot cycle's $(T_h - T_c)/T_h$.

- ■ With new materials, people have been able to use hotter thermal reservoirs and achieve efficiencies up to 50%!
  - ΔG can be converged to work directly (as current and voltage in the fuel cell). Thus, in theory, runnning a reversible fuel cell produces more work than burning H_2 in a reversible engine.
    - ■ The limitation is overpotential, though, and we would need a better hydrogen burning catalyst.
- Maxwell relations:
$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$
- If we want to show that $(\partial P/\partial T)_V = (\partial S/\partial V)_T$, we take
$$dA = \delta q_{\text{rev}} - T\,dS - S\,dT - P\,dV$$
$$= -S\,dT - P\,dV$$
$$= \left(\frac{\partial A}{\partial T}\right)_V + \left(\frac{\partial A}{\partial V}\right)_T$$

so that
$$\frac{\partial P}{\partial T} = \frac{\partial}{\partial T}\left(-\frac{\partial A}{\partial V}\right) = -\frac{\partial^2 A}{\partial T \partial V} = -\frac{\partial^2 A}{\partial V \partial T} = \frac{\partial}{\partial V}\left(-\frac{\partial A}{\partial T}\right) = \frac{\partial S}{\partial V}$$

  - Facts like these help us show things such as
$$\Delta S = \int_{V_1}^{V_2} \frac{\partial S}{\partial V}\,dV = \int_{V_1}^{V_2} \frac{\partial P}{\partial T}\,dV = \int_{V_1}^{V_2} \frac{nR}{V}\,dV = nR\ln\frac{V_2}{V_1}$$

so we don't need to measure the heat flow to measure entropy when we have a more complex equation of state than $PV = nRT$.

5.3 Differential Relations

2/11:
- A useful equation for the change in energy per unit volume at constant temperature, and equation of state.
  - We have that
$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$
  - It follows that
$$dU = T\,dS - P\,dV$$
$$= T\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV - P\,dV$$
$$= \underbrace{T\left(\frac{\partial S}{\partial T}\right)_V}_{(\partial U/\partial T)_V} dT + \underbrace{\left[\left(\frac{\partial S}{\partial V}\right)_T - P\right]}_{(\partial U/\partial V)_T} dV$$
  - Thus, by Maxwell relations,
$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$
$$= T\left(\frac{\partial P}{\partial T}\right)_V - P$$

 – This equation can be evaluated given the equation of state.
 – For an ideal gas, we get
$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{nR}{V} - P = 0$$
 – For a van der Waals gas (just the excluded volume b part, not the a term), we get
$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\partial}{\partial T}\left(\frac{nRT}{V-nb}\right) - P = \frac{nRT}{V-nb} - P = 0$$
 – Now for small enough volume, we know that a gas will compress into a liquid. In other words, $T(\frac{\partial P}{\partial T})_V \geq P$ always, where equality is only a good approximation at sufficiently large volumes.

- A similar method can be applied to enthalpy changes with pressure.

 – We can derive in an analogous method that
$$\left(\frac{\partial H}{\partial P}\right)_T = V + T\left(\frac{\partial S}{\partial P}\right)_T$$

- You can only apply the chain rule to partial derivatives held constant with respect to the same variable(s).

- **Natural variables** (of a state function): A set of state variables for which the partial derivatives of the state function with respect to said variables are (simple expressions of) state variables or state functions.

 – For example, S, P are the natural variables of U since $\partial U/\partial S = T$ and $\partial U/\partial V = -P$ as shown by
$$dU = T\,dS - P\,dV$$
 – V, T are not natural variables of U, as we showed earlier, since the partial derivatives of U with respect to them are complicated expressions.
 – For the other state functions, we have
$$dH = T\,dS + V\,dP \qquad\qquad dA = -S\,dT - P\,dV$$
$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV \qquad\qquad dG = -S\,dT + V\,dP$$
 – Note that natural variables are not unique, as we also have
$$dS = \frac{1}{T}\,dH - \frac{V}{T}\,dP$$

- An example of using Maxwell relations to getting C_V to C_P (19-27 and 22-11).

 – We have that
$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$
 – We also have that
$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$
 – It follows if we let $dV = 0$ in the above expression that
$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}$$

– Therefore,

$$C_P - C_V = T\left[-\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$= -T\frac{(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T}$$

$$= -T\frac{V^2\alpha^2}{-V\kappa}$$

$$= \frac{TV\alpha^2}{\kappa}$$

where α is the **thermal expansion coefficient** and κ is the **isothermal compressibility**.

- **Thermal expansion coefficient**: The following constant. *Denoted by $\boldsymbol{\alpha}$. Given by*

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

- **Isothermal compressibility**: The following constant. *Denoted by $\boldsymbol{\kappa}$. Given by*

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

5.4   Office Hours (PGS)

- So is the content of the midterm Chapters 17-22 plus parts of Chapter 25 (the Maxwell-Boltzmann distribution)?

- Are there going to be any surprizes I should look out for (a la surface tension)?

- Will questions be like homework questions, quiz questions?

- Are we going to have to know derivations or just formulas?

5.5   Chapter 21: Entropy and the Third Law of Thermodynamics

From McQuarrie and Simon (1997).

2/3:
- In this chapter, we will learn how to calculate absolute (as opposed to relative) values of entropy.

- Relating thermodynamic quantities to entropy.

  – It follows from the First Law of Thermodynamics that

$$dU = \underbrace{T\,dS}_{\delta q_{\text{rev}}}\underbrace{-P\,dV}_{\delta w_{\text{rev}}}$$

  – We have that the total differential of $U(V, T)$ is

$$dU = \frac{\partial U}{\partial T}\,dT + \frac{\partial U}{\partial V}\,dV$$

  – Combining the two above equations, we have that

$$T\,dS - P\,dV = \frac{\partial U}{\partial T}\,dT + \frac{\partial U}{\partial V}\,dV$$

$$dS = \frac{1}{T}\frac{\partial U}{\partial T}\,dT + \frac{1}{T}\left(P + \frac{\partial U}{\partial V}\right)dV$$

$$= \frac{C_V\,dT}{T} + \frac{1}{T}\left(P + \frac{\partial U}{\partial V}\right)dV$$

- It follows by comparing the above with the total differential of $S(V, T)$ that

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad\qquad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

- Since

$$\mathrm{d}H = \mathrm{d}U + P\,\mathrm{d}V + V\,\mathrm{d}P = T\,\mathrm{d}S + V\,\mathrm{d}P$$

we can proceed in a similar manner to the above to obtain

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \qquad\qquad \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right) - V\right]$$

- **Third Law of Thermodynamics**: Every substance has a finite positive entropy, but at zero kelvin, the entropy may become zero, and does so in the case of a perfectly crystalline substance.

  - While the first and second laws provide state functions (internal energy and entropy, respectively), the third law provides a numerical scale for entropy.

- The third law, although formulated before quantum mechanics, follows nicely from it: At absolute zero, every system in an ensemble will be in the same energy state, so $W = 1$; it follows that $S = k_B \ln 1 = 0$.

  - If, however, the ground state has a degeneracy of n, then

$$S(0\,\mathrm{K}) = -k_B \sum_j p_j \ln p_j$$

$$= -k_B \sum_{j=1}^{n} \frac{1}{n} \ln \frac{1}{n}$$

$$= k_B \ln n$$

  - Nevertheless, even for a degeneracy of N_A, we will only have $S(0\,\mathrm{K}) \approx 7.56 \times 10^{-22}\,\mathrm{J\,mol^{-1}\,K^{-1}}$, which is far less than any measurable value.

- Because of the third law, we can define entropy absolutely (assuming no phase change between 0 and T).

$$S(T) = S(0) + S(T) - S(0)$$
$$= S(0) + \Delta S$$
$$= S(0) + \int_0^T \frac{C_P(t)}{t}\,\mathrm{d}t$$
$$= \int_0^T \frac{C_P(t)}{t}\,\mathrm{d}t$$

- Accounting for phase changes.

  - A phase change is a great example of a reversible process since we only need the temperature to be slightly above or slightly below the transition temperature T_{trs} to accomplish it.

  - Thus,

$$\Delta_{\mathrm{trs}}S = \frac{q_{\mathrm{rev}}}{T_{\mathrm{trs}}} = \frac{\Delta_{\mathrm{trs}}H}{T_{\mathrm{trs}}}$$

  - It follows that, as applicable,

$$S(T) = \int_0^{T_{\mathrm{fus}}} \frac{C_P^s(t)}{t}\,\mathrm{d}t + \frac{\Delta_{\mathrm{fus}}H}{T_{\mathrm{fus}}} + \int_{T_{\mathrm{fus}}}^{T_{\mathrm{vap}}} \frac{C_P^l(t)}{t}\,\mathrm{d}t + \frac{\Delta_{\mathrm{vap}}H}{T_{\mathrm{vap}}} + \int_{T_{\mathrm{vap}}}^{T} \frac{C_P^g(t)}{t}\,\mathrm{d}t$$

- Note that with typical values plugged in, $\Delta_{\text{fus}}S \ll \Delta_{\text{vap}}S$.

- **Debye T^3 law**: As $T \to 0$ (i.e., for about $T = 0 - 15\,\text{K}$), $C_P^s(T) \to T^3$ for most nonmetallic crystals and $C_P^s(T) \to aT + bT^3$ ($a, b \in \mathbb{R}_{\geq 0}$) for most metallic crystals.

  - It follows by the absolute definition of S that

  $$S(T) = \frac{C_P(T)}{3}$$

  at low temperatures for nonmetallic solids.

- **Debye temperature**: A constant characteristic of the solid. *Denoted by* $\mathbf{\Theta_D}$.

- **Third-law entropy**: An absolute entropy value calculated according to the convention that $S(0\,\text{K}) = 0$. *Also known as* **practical absolute entropy**.

- McQuarrie and Simon (1997) calculates the third-law entropy of N_2 based on various thermodynamic data.

- **Standard entropy**: An entropy value of a gas as presented in the literature. *Denoted by* $\mathbf{S^\circ}$. *Units* $\mathbf{J\,mol^{-1}\,K^{-1}}$.

  - Standard entropies are, by convention, corrected for the nonideality of the gas at one bar (for how to calculate this correction, see Chapter 22).

- McQuarrie and Simon (1997) rederives $S(0\,\text{K}) = k_B \ln n$ from a partition function approach, and then gives a specific example for N_2, noting how well this value correlates with the one from the previous example.

  - "This type of agreement is quite common, and in many cases the statistical thermodynamic value is more accurate than the calorimetric value... The accepted literature values are often a combination of statistical thermodynamic and calorimetric values" (McQuarrie & Simon, 1997, p. 863).
  - Also gives a linear symmetric example (CO_2).

- Entropy trends.

  1. "The standard molar entropies of the gaseous substances are the largest, and the standard molar entropies of the solid substances are the smallest" (McQuarrie & Simon, 1997, p. 865).
  2. "The increase in standard molar entropy of the noble gases is a consequence of their increasing mass as we move down the periodic table" (McQuarrie & Simon, 1997, p. 865).
     - More mass implies more translational energy levels are available implies more disorder.
     - This is a consequence of quantum mechanics — considering the formula for the energy of a particle in a 3D box, note that m is in the denominator. Thus, increasing m means that the levels are more closely spaced, and hence more are readily accessible.
  3. "Generally speaking, the more atoms of a given type in a molecule, the greater is the capacity of the molecule to take up energy and thus the greater is its entropy" (McQuarrie & Simon, 1997, p. 866).
     - More atoms implies more vibrational modes implies more disorder.
  4. "For molecules with approximately the same molecular masses, the more compact the molecule is, the smaller is its entropy" (McQuarrie & Simon, 1997, p. 867).
     - Between isomers, the one with more unrestricted motion will have greater entropy.

- We can calculate the entropy for substances that "don't exist" via alternate paths.

  - For example, Br_2 is a liquid at $298\,\text{K}$, but we can still calculate $S^\circ[Br_{2(g)}]$ by imagining the following path: Raise $Br_{2(l)}$ to its boiling point; vaporize it; cool it back down to $298\,\text{K}$.

– This calculated value is in agreement with the spectroscopic value.

- **Residual entropy**: The difference between the calculated molar entropy of a substance and its experimental molar entropy. *Given by*
$$\overline{S}_{\text{calc}} - \overline{S}_{\text{exp}}$$

  – We define residual entropy this way because wherever there are discrepancies, it so happens that $S_{\text{calc}} > S_{\text{exp}}$.

- Large residual entropies are encountered for the linear molecules CO and N_2O.

  – This is because these molecules have small dipole moments, so upon crystallization, there is not a strong tendency for the molecule to align in the most energetically favorable way.

  – Thus, with molecules already locked in higher energy states at T_{fus}, as we cool to $0\,\text{K}$, we do not have a "perfect" crystal.

  – Since the ground state is two-fold degenerate in both of these cases (we have CO and OC, and NNO and ONN), $\overline{S}(0\,\text{K}) = R\ln 2$ here.

- We can similarly account for the larger still residual entropy in H_3CD by noting that the ground state is four-fold degenerate, and thus $\overline{S}(0\,\text{K}) = R\ln 4$ here.

- We can use standard molar entropies to calculate the entropy changes of chemical reactions.

5.6   Chapter 22: Helmholtz and Gibbs Energies

2/14:
- Since the $dS \geq 0$ criterion for isolated systems is quite restrictive (only applies to isolated systems), we introduce two new state functions that will help determine the direction of a spontaneous process in a non-isolated system.

- **Helmholtz energy**: A state function describing the energy of a system at constant volume and temperature. *Denoted by* **A**. *Given by*
$$A = U - TS$$

  – Since $dV = dT = 0$, we know that

$$\begin{aligned} dU &= \delta q + \delta w \\ &\leq T\,dS - P\,dV \\ dU - T\,dS - S\,dT &\leq 0 \\ d(U - TS) &\leq 0 \end{aligned}$$

  where equality holds for a reversible process and inequality holds for an irreversible process (by the properties of the Clausius inequality).

  – Thus, the Helmholtz energy will decrease until all spontaneous processes have occurred. At this point, $dA = 0$ and A will be at a minimum.

  – $dA \leq 0$ is the analog of $dS \geq 0$ for a spontaneous process to occur.

  – "A process for which $\Delta A > 0$ cannot take place spontaneously in a system at constant T and V. Consequently, something, such as work, must be done on the system to effect the change" (McQuarrie & Simon, 1997, p. 883).

  – "The Helmholtz energy represents this compromise between the tendency of a system to decrease its energy and to increase its entropy" (McQuarrie & Simon, 1997, p. 883).

  – Note that the sign of U is more important at low T and vice versa for high T by $U - TS$.

- McQuarrie and Simon (1997) applies the definition of A to the mixing of two ideal gases, showing that $\Delta A < 0$ for it.

- A physical interpretation to ΔA.

    - When a process is carried out along a reversible path,

    $$\Delta A = \Delta U - q_{\mathrm{rev}} = w_{\mathrm{rev}}$$

    meaning that ΔA is either the maximum work that can be pulled out of the system or the minimum work required to drive the process (depending on its sign).

- **Gibbs energy**: A state function describing the energy of a system at constant pressure and temperature. *Denoted by* **G**. *Given by*

    $$G = H - TS$$

    - Since $\mathrm{d}P = \mathrm{d}T = 0$, we know that

    $$\mathrm{d}U = \delta q + \delta w$$
    $$\leq T\,\mathrm{d}S - P\,\mathrm{d}V$$
    $$\mathrm{d}U + P\,\mathrm{d}V + V\,\mathrm{d}P - T\,\mathrm{d}S - S\,\mathrm{d}T \leq 0$$
    $$\mathrm{d}(U + PV - TS) \leq 0$$
    $$\mathrm{d}(H - TS) \leq 0$$

    where equality holds for a reversible process and inequality holds for an irreversible process (by the properties of the Clausius inequality).

    - The Gibbs energy is analogous in almost every way to the Helmholtz energy.
    - We can also write $G = A + PV$ to relate G, A in the same manner that H, U are related, respectively.

- **Molar Gibbs energy of vaporization**: The following quantity. *Denoted by* $\boldsymbol{\Delta_{\mathbf{vap}}\overline{G}}$. *Given by*

    $$\Delta_{\mathrm{vap}}\overline{G} = \Delta_{\mathrm{vap}}\overline{H} - T\Delta_{\mathrm{vap}}\overline{S}$$

    - Note that $\Delta_{\mathrm{vap}}\overline{G} = 0$ at $1\,\mathrm{atm}$ and $100\,^{\circ}\mathrm{C}$. This means that the phases are in equilibrium under these conditions.
    - A slight increase in temperature, however, makes $\Delta G < 0$ (i.e., makes vaporization spontaneous), while a slight decrease in temperature makes $\Delta G > 0$ (i.e., makes condensation spontaneous).
    - McQuarrie and Simon (1997) covers that in a reversible process, $\Delta G = w_{\mathrm{non\ PV}}$, i.e., the maximum non-pressure/volume work available from a process or minimum non-pressure/volume work required to drive a process.

        ∎ $w_{\mathrm{non\ PV}}$ can be electrical work, for example.

- **Maxwell relation**: An relation obtained by equating the second cross partial derivatives of a function.

- **Thermodynamic equation of state**: An equation that relates a thermodynamic function to functions of P, V, and T.

- McQuarrie and Simon (1997) notes that

    $$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

    meaning that energy does depend on volume somewhat (it's not entirely a function of temperature).

    - We can show that the above derivative reduces to zero for an ideal gas, however.

- McQuarrie and Simon (1997) plays around with partial derivatives for a while.

    - Discusses the α, κ definition of $C_P - C_V$.

- We can also use Maxwell relations and differentials to derive the following results.

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad\qquad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

- Covers natural variables.

Thermodynamic energy	Differential expression	Corresponding Maxwell relations
U	$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V$	$\left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial P}{\partial S}\right)_V$
H	$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P$	$\left(\dfrac{\partial T}{\partial P}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_P$
A	$\mathrm{d}A = -S\,\mathrm{d}T - P\,\mathrm{d}V$	$\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$
G	$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P$	$\left(\dfrac{\partial S}{\partial P}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_P$

Table 5.1: Thermodynamic energies, differentials, and Maxwell relations.

- Calculating corrections to the standard molar entropy of a gas.
  - Basically, we want to find $S^\circ(1\,\text{bar}) - \overline{S}(1\,\text{bar})$. To do so, we consider

  $$S^\circ(1\,\text{bar}) - \overline{S}(1\,\text{bar}) = [S^\circ(1\,\text{bar}) - \overline{S}(P_{\text{id}})] + [\overline{S}(P_{\text{id}}) - \overline{S}(1\,\text{bar})]$$

  where P_{id} is a pressure sufficiently low such that the gas in question behaves ideally.
  - We know from the definition of changes in entropy as an integral and Table 5.1 that

  $$S^\circ(1\,\text{bar}) - \overline{S}(P_{\text{id}}) = \int_{P_{\text{id}}}^{1\,\text{bar}} \left(\frac{\partial S}{\partial P}\right)_T \mathrm{d}P \qquad \overline{S}(P_{\text{id}}) - \overline{S}(1\,\text{bar}) = \int_{1\,\text{bar}}^{P_{\text{id}}} \left(\frac{\partial S}{\partial P}\right)_T \mathrm{d}P$$

  $$= -\int_{P_{\text{id}}}^{1\,\text{bar}} \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}P \qquad\qquad = -\int_{1\,\text{bar}}^{P_{\text{id}}} \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}P$$

  $$= -\int_{P_{\text{id}}}^{1\,\text{bar}} \frac{R}{P}\,\mathrm{d}P \qquad\qquad = \int_{P_{\text{id}}}^{1\,\text{bar}} \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}P$$

    - Note that we calculate the first change using the ideal gas law and the second change using the equation of state describing the real gas.
  - Adding the above two equations yields

  $$S^\circ(1\,\text{bar}) - \overline{S}(1\,\text{bar}) = \int_{P_{\text{id}}}^{1\,\text{bar}} \left[\left(\frac{\partial V}{\partial T}\right)_P - \frac{R}{P}\right] \mathrm{d}P$$

  - We can evaluate this equation using only the second virial coefficient (see Chapter 16).
- McQuarrie and Simon (1997) discusses $G = G^\circ + RT \ln Q$.

- **Gibbs-Helmholtz equation**: An equation for the temperature dependence of G. *Given by*

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2}$$

  - Derivation:

$$G = H - TS$$
$$\frac{G}{T} = \frac{H}{T} - S$$
$$\left(\frac{\partial G/T}{\partial T}\right)_P = \left[\frac{\partial}{\partial T}\left(\frac{1}{T} \cdot H\right)\right]_P - \left(\frac{\partial S}{\partial T}\right)_P$$
$$= \left[\frac{\partial}{\partial T}\left(\frac{1}{T}\right) \cdot H\right]_P + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$$
$$= -\frac{H}{T^2} + \frac{C_P}{T} - \left(\frac{\partial S}{\partial T}\right)_P$$
$$= -\frac{H}{T^2}$$

- McQuarrie and Simon (1997) discusses the graph of $G(T)$.

  - It offers an alternate explanation for continuity, namely that since $\Delta_{\text{trs}}S = \Delta_{\text{trs}}H/T_{\text{trs}}$, then

$$0 = \Delta_{\text{trs}}H - T_{\text{trs}}\Delta_{\text{trs}}S = \Delta_{\text{trs}}G$$

Part III

Applications of Thermodynamics and Statistical Mechanics

Week 6

Deviations from Ideality

6.1 Thermodynamics of the Rubber Band

• Midterm:

- Take for two hours, any two hours tomorrow.
- Upload a single PDF file for your answer.
- Do not discuss the questions with anybody.

• **Standard Gibbs free energy** (at T): The following energy, where $H^\circ(T)$ is the standard enthalpy at T and $S^\circ(T)$ is the standard entropy at T. *Denoted by* $\boldsymbol{G^\circ(T)}$. *Given by*

$$G^\circ(T) = H^\circ(T) - TS^\circ(T)$$

- It follows that since the enthalpy is taken at constant pressure and the entropy $S(T, P)$ at non-standard pressure is given by $S(T, P) = S^\circ(T) + R \ln P/P_0$ that the Gibbs free energy $S(T, P)$ at nonstandard pressure is

$$G(T, P) = H^\circ(T) - TS(T, P)$$
$$= H^\circ(T) - T\left(S^\circ(T) + R \ln \frac{P}{P_0}\right)$$
$$= G^\circ(T) - RT \ln \frac{P}{P_0}$$

• Gibbs free energy and equilibrium at constant T, P.

- If
$$a\,\mathrm{A} + b\,\mathrm{B} \longrightarrow c\,\mathrm{C} + d\,\mathrm{D}$$
is in equilibrium where A, B, C, D are ideal gases, then $\Delta G = 0$.
- This implies that
$$a\Delta G_a + b\Delta G_b = c\Delta G_c + d\Delta G_d$$
which is the **law of mass action**.

• Example of phase equilibrium ($G(T)$ for solid/liquid/gas phases).

- We have from the total differential of G that
$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

- Since $S \geq 0$ always, G is monotonically decreasing.

- During the liquid phase, there is a relatively constant slight negative slope in the $G(T)$ graph.
- During the gas phase, S is much bigger, so there is a larger negative slope in the $G(T)$ graph.
- Additionally, at the heats of vaporization and fusion, the system is in equilibrium (hence the energies are the same), so the graph is continuous.

- Rubber band temperature analysis.

  - A rubber band heats up when stretched:
    - We have that $dU = T\,dS + f\,dL$.
    - We want to show that $(\partial U/\partial L)_T = T(\partial S/\partial L)_T + f$.

$$dU = T\left(\frac{\partial S}{\partial T}\right)_L dT + \left(\frac{\partial S}{\partial L}\right)_T dL + f\,dL$$
$$= T\left(\frac{\partial S}{\partial T}\right)_L dT + \left[\left(\frac{\partial S}{\partial L}\right)_T + f\right] dS$$

    - All that's left is to show that $-(\partial S/\partial L)_T = (\partial f/\partial T)_L$, which we can do using Maxwell relations.

$$dA = -S\,dT + f\,dL$$
$$\left(\frac{\partial U}{\partial L}\right)_T = -T\left(\frac{\partial f}{\partial T}\right)_L + f$$

  - Stating the equation of state for the "ideal" rubber band.

$$f = T\phi(L)$$

    - It follows that $(\partial f/\partial T)_L = f/T$, and $(\partial U/\partial L)_T = -T \cdot f/T + f = 0$.
  - We are now ready to answer the question of does it cool down or heat up when stretched adiabatically.

$$dU = \left(\frac{\partial U}{\partial L}\right)_T dL + \left(\frac{\partial U}{\partial T}\right)_L dT = \delta q + f\,dL$$
$$\left(\frac{\partial U}{\partial T}\right)_L dT = f\,dL$$
$$C_L\,dT = f\,dL$$
$$dT = \frac{f}{C_L}\,dL > 0$$

  so since $dT > 0$, the rubber band heats up as it stretches.
  - For intuitive motivation, PGS discusses Figure 17.1 of Labalme (2021a).

- Building a statistical model of the rubber band.

  - Consider the rubber band to be made up of segments (you can think of each segment as part of a polymer). These segments can be oriented up or down. In a stretched rubber band, the polymers will be straight, i.e., all the segments will point the same way.
  - The difference in energy ΔE between a segment (of length ℓ_0) pointing up or down is $2f$.
  - Thus, the partition function for each segment is

$$q = e^{-f\ell_0/k_B T} + e^{f\ell_0/k_B T}$$

    - Note that this is the same as the partition function for a paramagnet (which can also either be up or down) except that $f\ell_0$ becomes $\mu_B B_z$.

– When we sum the energies, we multiply the component partition functions. Thus,

$$Q = q^N$$

– We know that

$$L = N(p + p_0 + p - (-p_0)) = Np_0(p + (-p)) = N\ell_0 \tanh\left(\frac{f\ell_0}{k_B T}\right)$$

6.2 Van der Waals Phase Transitions

2/16:

- Wrapping up the rubber band analysis.

- Note that we can approximate $\tanh x \approx x$ for small x. Thus,

$$L = N\ell_0 \cdot \frac{f\ell_0}{k_B T}$$

for small f.

- Therefore, statistical mechanics predicts the rubber band "ideal" equation of state, $f = T\phi(L)$, where f is the stretching force. Note that this is not at all like a mechanical spring constant; it is purely an entropy effect.

  – $dS = dS_{\text{orientation}} + dS_{\text{thermal}} = dS_{\text{orientation}} + C/T\, dT$.
  – $dU = C\, dT + T\, dS = 0$, implying that $dT = -T/C\, dS$.

- Adiabatic stretching decreases orientation entropy and increases the temperature.

- The same model predicts the Curie law of paramagnetism, $M = CB/T$.

  – We have

$$M = N\mu \tanh \frac{\mu B}{k_B T}$$

$$M = \frac{N\mu^2}{k_B} \frac{B}{T}$$

  where the second equation only holds for small B.

- Adiabatic demagnetization allows you to go from $4\,\text{K}$ to $1\,\text{K}$ using He_4 to He_3 liquefaction. Adiabatic demagnetization increases spin entropy and reduces the temperature.

  – To achieve $4\,\text{K}$, we let He_4 adiabatically expand, which makes it very cold. However, at temperatures below $4\,\text{K}$, He_4 is a liquid and it can no longer adiabatically expand like a gas.
  – To achieve temperatures lower than $4\,\text{K}$, you stick copper salt in a cryostat, subject it to a magnetic field, and cool it to $4\,\text{K}$ with the above method. The magnet aligns the spins. When you take the salt out of the magnetic field, the spins will randomize entropically, but this takes energy. You use the lattice energy to raise the spin energy.

- The challenge of protein folding and structure determination.

  – We have $\Delta G = \Delta(H - TS)$.
  – Protein folding necessitates $\Delta S < 0$ (you are creating order). Thus, we must have $\Delta H < \Delta(TS) = T\Delta S$, i.e., the protein must adopt a very, very stable conformation.
  – Estimating ΔS:
$$\Delta S = k_B \ln W = k_B \ln 3^{100} = 914\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$$

- Using **Levinthal's paradox**, we can estimate the number of possible configurations of a protein.
  - Each segment (essentially a C–C bond) has about three dihedral angle possibilities for the segments at either end.
  - Thus, for a protein that is 100 segments long, $W \approx 3^{100}$.
  - At $300\,\text{K}$, $T\Delta S = 274\,\text{kJ/mol}$.
    - It doesn't take much of a temperature difference to alter or prevent protein folding.
  - About 15 hydrogen bonds or a single disulfide bond is about $274\,\text{kJ/mol}$ of energy, so we can find ways to stabilize proteins over the entropic barriers.
  - Just recently, a UChicago grad student (who had been working with a UChicago professor who's been studying the protein folding problem for a long time) headed a team at Google that has an AI that looks like it will be able to solve the protein folding problem.

- **Levinthal's paradox**: The observation that finding the native folded state of a protein by a random search among all possible configurations can take an enormously long time. Yet proteins can fold in seconds or less.

- Real gases deviate from ideality due to molecular interactions.

- **Compressibility factor**: *Denoted by z. Given by*

$$z = \frac{P\overline{V}}{RT}$$

- The van der Waals equation of state (where $\overline{V}$ is the molar volume):

$$\left(P + \frac{a}{\overline{V}^2}\right)(\overline{V} - b) = RT$$

  - We can also rewrite this as
  $$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

  - Note that $a, b \geq 0$.
  - The compressibility is
  $$z = \frac{\overline{V}}{\overline{V} - b} - \frac{a}{RT\overline{V}}$$

- The van der Waals equation of state is cubic in $\overline{V}$ and can predict two different molar volumes (gas and liquid) for one pressure.

Figure 6.1: The van der Waals isotherm of CO_2 at $0\,°\text{C}$.

– We have that

$$RT = \left(P + \frac{a}{\overline{V}^2}\right)(\overline{V} - b)$$

$$= P\overline{V} - bP + \frac{a}{\overline{V}} - \frac{ab}{\overline{V}^2}$$

$$\frac{RT\overline{V}^2}{P} = \overline{V}^3 - b\overline{V}^2 + \frac{a}{P}\overline{V} - \frac{ab}{P}$$

$$0 = \overline{V}^3 - \left(b + \frac{RT}{P}\right)\overline{V}^2 + \frac{a}{P}\overline{V} - \frac{ab}{P}$$

– Since it is cubic in $\overline{V}$, this means we can have up to three different molar volumes for one pressure.
– This also reflects the fact that as we compress a gas, it behaves ideally for a while, and then pressure is constant as condensation takes hold, and then we must apply massive amounts of pressure to make the volume any smaller.
– On $\overline{\text{AG}}$, the system is a gas. On $\overline{\text{LD}}$, it is a liquid. On $\overline{\text{AD}}$, pressure is constant as we compress more and more because condensation takes hold, so highly compressed gas molecules become liquid, reducing the pressure.
– Drawing the line $\overline{\text{AD}}$: The points at which gas stops and liquid starts must be at the same pressure.
– We must also have the area above and below the line equal (**Maxwell equal area construction**).
  ■ Phase equilibrium (like we have along $\overline{\text{AD}}$) means that free energy does not change. Mathematically, $\Delta G(\text{A}) = \Delta G(\text{D})$.
  ■ If A and D represent gas and liquids at the same temperature, they are in equilibrium and they must have the same molar Gibbs free energy.
  ■ We have $dG = -S\,dT + V\,dP$.
  ■ Since T is constant (this is an isotherm), $dG = V\,dP$.
  ■ Thus, we can integrate along the curve $\overline{\text{DA}}$ to find an appropriate $\overline{\text{DA}}$ such that the integral is zero.

$$0 = \Delta G(\text{A}) - \Delta G(\text{D})$$

$$= \int_{\text{D}}^{\text{A}} dG$$

$$= \int_{\text{D}}^{\text{A}} V\,dP$$

  ■ See Problem 23-46 for the "Maxwell equal area construction rule."

6.3 More van der Waals Phenomena

2/18: • The cubic vdW equation of state predicts a critical point at T_c at and above which only one P for (V, T) solution is possible.

– The behavior of isotherms around the critical temperature.
  ■ For isotherms below the critical temperature, there will be a range of volumes where the gas and liquid phases are in equilibrium.
  ■ For isotherms above the critical temperature, we only have the gas phase, so there is no region of constant pressure as we compress the system.
  ■ This means that at the critical temperature $T = T_c$, there will only be a single volume V_c and hence pressure P_c at which the gas and liquid phases are in equilibrium. Mathematically, this means that each of the three roots of the cubic van der Waals equation exist at the same point V_c, i.e., that the equation is of the form $(V - \overline{V}_c)^3$.

– Expanding, we have

$$0 = \overline{V}^3 - \left(b + \frac{RT}{P}\right)\overline{V}^2 + \frac{a}{P}\overline{V} - \frac{ab}{P}$$
$$= \overline{V}^3 - 3\overline{V}_c\overline{V}^2 + 3\overline{V}_c^2\overline{V} - \overline{V}_c^3$$

– Thus, at T_c,

$$b + \frac{RT_c}{P_c} = 3\overline{V}_c \qquad\qquad \frac{a}{P_c} = 3V_c^2 \qquad\qquad \frac{ab}{P_c} = \overline{V}_c^3$$

– One immediate consequence is that

$$\overline{V}_c^3 = \frac{a}{P_c}\cdot b$$
$$\overline{V}_c^3 = 3V_c^2 b$$
$$\overline{V}_c = 3b$$

■ Thus, the critical volume is on the order of magnitude of the molecular volume.
■ Note that we can't manipulate the first equation into a different relation between $\overline{V}_c$ and b using the ideal gas law substitution because this is a van der Waals gas.

– It follows that

$$3V_c^2 = \frac{a}{P_c} \qquad\qquad\qquad b + \frac{RT_c}{P_c} = 3\overline{V}_c$$
$$P_c = \frac{a}{3(3b)^2} \qquad\qquad\qquad b + RT_c\cdot\frac{27b^2}{a} = 3(3b)$$
$$P_c = \frac{a}{27b^2} \qquad\qquad\qquad T_c = \frac{8a}{27Rb}$$

– Thus,

$$z_c = \frac{P_cV_c}{RT_c} = \frac{3}{8}$$

■ Indeed, the vdW equation predicts the compressibility at the critical point to be $3/8$. The Redlich-Kwong predicts $1/3$. The Peng-Robinson predicts 0.307. The experimental values are around 0.3. Water and ammonia deviate significantly: 0.23 and 0.24, respectively, due to their strong dipole moments/hydrogen bonding. Table 16.5 gives a lot of related data.

– Also, at T_c, V_c, we have that $(\partial P/\partial V)_T = 0$ and $\kappa \to \infty$ (recall that κ is the isothermal compressibility).
■ It follows from the vdW that $\kappa \propto (\overline{V} - \overline{V}_c)^{-1}$.
■ Experimental value: *Every* gas satisfies $\kappa \propto (\overline{V} - \overline{V}_c)^{-1.24}$.
■ The mystery was solved theoretically in the 1970s with renormalization group theory.

• Law of corresponding states.

– We define the reduced pressure, volume, and temperature by

$$P_R = \frac{P}{P_c} \qquad\qquad V_R = \frac{V}{V_c} \qquad\qquad T_R = \frac{T}{T_c}$$

– Note that

$$\frac{RT}{P_cV_c} = \frac{RT_c}{P_cV_c}\frac{T}{T_c} = \frac{1}{z_c}\frac{T}{T_c} = \frac{8}{3}T_R$$

– Thus,

$$RT = \left(P + \frac{a}{\overline{V}^2} \right) (\overline{V} - b)$$

$$= \left(P + \frac{3\overline{V}_c^2 P_c}{\overline{V}^2} \right) \left(\overline{V} - \frac{\overline{V}_c}{3} \right)$$

$$\frac{RT}{P_c V_c} = \left(\frac{P}{P_c} + \frac{3\overline{V}_c^2}{\overline{V}^2} \right) \left(\frac{\overline{V}}{\overline{V}_c} - \frac{1}{3} \right)$$

$$\frac{8}{3} T_R = \left(P_R + \frac{3}{\overline{V}_R^2} \right) \left(\overline{V}_R - \frac{1}{3} \right)$$

- Virial expansion to experimentally determine the vdW coefficients a, b from the compressibility near ideal conditions.

    – We let

$$z = 1 + \frac{B_{2V}(T)}{\overline{V}} + \frac{B_{3V}(T)}{\overline{V}^2} + \cdots$$

    where $B_{iV}(T)$ is the ith **virial coefficient**.

    – It follows that

$$\frac{P\overline{V}}{RT} = \frac{\overline{V}}{V - b} - \frac{a}{RT\overline{V}}$$

$$= \frac{1}{1 - b/\overline{V}} - \frac{a}{RT\overline{V}}$$

$$= 1 + \left(\frac{b}{\overline{V}} - \frac{a}{RT\overline{V}} \right) + \text{terms in } \frac{1}{\overline{V}^2} + \cdots$$

    where we get from the second to the third line using the expansion

$$\frac{1}{1 - x} = 1 + x + x^2 + \cdots$$

    – Thus,

$$B_{2V}(T) = b - \frac{a}{RT}$$

- Microscopic origin of the vdW coefficients from the interaction potential.

    – Draws the interaction potential for a diatomic molecule.

        ■ The repulsion comes from the Fermi exclusion principle.

    – Discusses dipole-induced dipole moments.

        ■ $-1/2 \propto E^2 \propto 1/r^6$.

    – The origin of vdW (or London dispersion) interaction is quantum mechanical.

        ■ We use perturbation theory to calculate the interaction between two neighboring quantum dipoles.

$$\Delta E^{(1)} = \langle \psi_A^\circ \psi_B^\circ | H_{int} | \psi_A^\circ \psi_B^\circ \rangle = 0$$

        ■ Thus we need the second order correction:

$$\Delta E^{(2)} = -\sum_{ij} \frac{|\langle \psi_A^\circ \psi_B^\circ | H_{int} | \psi_A^\circ \psi_B^\circ \rangle|}{E_a^A + E_j^B - (E_0^A + E_0^B)} \approx -\frac{c}{r^6}$$

        where $c \geq 0$.

6.4   Office Hours (PGS)

- Integrating along the curve in Figure 6.1?

  - Integrating along the curve with respect to P means (geometrically) that we take the area "under" (to the left of) the curve from A to C, then subtract the area under from C to B, and then add the area under from B to A. This calculation gets us overall the area of the bottom chunk as negative and the area of the top chunk as positive.

6.5   Chapter 16: The Properties of Gases

From McQuarrie and Simon (1997).

2/21:
- Outline:

  - Having studied ad nauseam the properties of individual atoms and molecules, we now turn our attention to systems consisting of large numbers of atoms and molecules.
  - The ideal gas equation is discussed, the van der Waals equation as the most famous extension of it, and then **virial expansions** as an even more systematic and accurate approach.
  - Relating virial coefficients to the intermolecular interaction energy reveals that deviations from ideal gas behavior provide great insight into molecular interactions.

- **Virial expansion**: An expression for the pressure of a gas as a polynomial in the density.

- **Ideal-gas equation of state**: An equation of state relating the pressure, volume, and temperature of a gas that is sufficiently dilute (i.e., with particles sufficiently far apart) for the intermolecular interactions to be negligible. *Given by*

$$PV = nRT \qquad\qquad\qquad P\overline{V} = RT$$

- **Ideal gas**: A gas that obeys the ideal-gas equation of state.

  - All gases, regardless of the shape or size of the molecules or how the molecules interact with each other, obey behave ideally if they are sufficiently dilute.
  - "Experimentally, most gases satisfy [the ideal-gas equation of state] to approximately 1% at one atm and $0\,°C$" (McQuarrie & Simon, 1997, p. 638).

- **Extensive quantity**: A quantity that is directly proportional to the size of the system in question. *Also known as* **extensive variable**.

- **Intensive quantity**: A quantity that does not depend on the size of the system in question. *Also known as* **intensive variable**.

- "If we divide an extensive quantity by the number of particles or the number of moles in a system, we obtain an intensive quantity" (McQuarrie & Simon, 1997, p. 638).

- **Liter**: A unit of volume. *Denoted by* **L**. *Given by*

$$1\,\text{L} = 1\,\text{dm}^3$$

  - The SI unit of volume is m^3, but liters are an acceptable unit of volume in the IUPAC system.

- **Pascal**: The SI unit of pressure. *Denoted by* **Pa**. *Given by*

$$1\,\text{Pa} = 1\,\tfrac{\text{N}}{\text{m}^2} = 1\,\tfrac{\text{kg}}{\text{m}\,\text{s}^2}$$

- "Pressure can be measured experimentally by observing how high a column of liquid (usually mercury) is supported by the gas" (McQuarrie & Simon, 1997, p. 638).

- – If m is the mass of the liquid, g is the **gravitational acceleration constant**, A is the base area of the column, ρ is the density of the liquid, and h is the height of the column, then

$$P = \frac{F}{A} = \frac{mg}{A} = \frac{\rho h A g}{A} = \rho h g$$

- **Gravitational acceleration constant**: The acceleration of an object due to gravity at the surface of the Earth. *Denoted by* **g**. *Given by*

$$g = 9.8067 \,\tfrac{\text{m}}{\text{s}^2}$$

- The pressure exerted by a $76.000\,\text{cm}$ column of mercury ($\rho(\text{Hg}) = 13.596\,\text{g}\,\text{cm}^{-3}$) is

$$
\begin{aligned}
P &= \rho g h \\
&= 1.0133 \times 10^6 \,\tfrac{\text{g}}{\text{cm}\,\text{s}^2} \\
&= 1.0133 \times 10^5 \,\tfrac{\text{kg}}{\text{m}\,\text{s}^2} \\
&= 1.0133 \times 10^5 \,\text{Pa} \\
&= 101.33 \,\text{kPa}
\end{aligned}
$$

- **Atmosphere**: The pressure that supports a $76.0\,\text{cm}$ column of mercury. *Denoted by* **atm**. *Given by*

$$1\,\text{atm} = 101.325\,\text{kPa}$$

- **Bar**: The SI standard of pressure. *Denoted by* **bar**. *Given by*

$$1\,\text{bar} = 10^5\,\text{Pa}$$

- **Torr**: The pressure that supports a $1.00\,\text{mm}$ column of mercury. *Denoted by* **torr**. *Given by*

$$1\,\text{torr} = \frac{1}{760}\,\text{atm}$$

- "Because we are experiencing a transition period between the widespread use of atm and torr on the one hand and the future use of bar and kPa on the other hand, students of physical chemistry must be proficient in both sets of pressure units" (McQuarrie & Simon, 1997, p. 639).

- Temperatures as low as $1 \times 10^{-7}\,\text{K}$ and as high as $1 \times 10^8\,\text{K}$ have been achieved in the laboratory.

- **Triple point**: The point (P, V, T) at which all three of a given substance's phases are in equilibrium.

- **Kelvin**: The SI unit of temperature, defined as $1/273.16$ of the temperature of the triple point of water. *Denoted by* **K**.

- "We will use the lower case t for $^\circ$C and the upper case T for K" (McQuarrie & Simon, 1997, p. 640).

- **Room temperature**: The temperature $25\,^\circ\text{C} = 298.15\,\text{K}$.

- If we plot $P\overline{V}$ vs. P for several gases at $T = 273.15\,\text{K}$, all the data can be extrapolated to a common value of $P\overline{V} = 22.414\,\text{L}\,\text{atm}$ as $P \to 0$. Thus,

$$
\begin{aligned}
R = \frac{P\overline{V}}{T} = \frac{22.414\,\text{L}\,\text{atm}}{273.15\,\text{K}} &= 0.082\,058 \,\tfrac{\text{L}\,\text{atm}}{\text{mol}\,\text{K}} \\
&= 8.3145 \,\tfrac{\text{J}}{\text{mol}\,\text{K}} \\
&= 0.083\,145 \,\tfrac{\text{L}\,\text{bar}}{\text{mol}\,\text{K}}
\end{aligned}
$$

- **Compressibility factor**: The following quantity. *Denoted by* **Z**. *Given by*

$$Z = \frac{P\overline{V}}{RT}$$

(a) Changing the gas type.

(b) Changing the gas temperature.

Figure 6.2: Plots of the compressibility factor vs. pressure.

- We use the compressibility factor, which is constant at 1 for an ideal gas, to visualize deviations from ideality for different gases (Figure 6.2a) at different temperatures (Figure 6.2b).
- At lower temperatures, intermolecular attraction takes hold, reducing the true volume and making $Z < 1$.
- At higher temperatures, molecules are moving fast enough to make negligible their attractions. Here, only repulsions due to their nonzero volume take hold at higher pressures.

- "The closer the gas is to the point at which it begins to liquify, the larger the deviations from ideal behavior will be" (McQuarrie & Simon, 1997, p. 642).

- **Van der Waals equation**: The most well known of the gaseous equations of state which account for intermolecular interactions. *Given by*

$$\left(P + \frac{a}{\overline{V}^2}\right)(\overline{V} - b) = RT$$

  - Note that as $\overline{V} \to \infty$, the van der Waals equation becomes the ideal-gas equation of state.
  - The van der Waals equation is also commonly written in the following form.

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

- **Van der Waals constants**: The constants a, b in the van der Waals equation, whose value depend upon the particular gas.

  - We will see later that "the value of a reflects how strongly the molecules of a gas attract each other and the value of b reflects the size of the molecules" (McQuarrie & Simon, 1997, p. 643).
  - Table 16.3 lists van der Waals constants for various substances.

- The van der Waals equation approximates the behavior depicted in Figure 6.2 since

$$Z = \frac{P\overline{V}}{RT} = \frac{\overline{V}}{\overline{V} - b} - \frac{a}{RT\overline{V}}$$

  - At high pressures ($\overline{V} \to 0$), the first term above dominates because $\overline{V} - b$ gets really small.
  - At low pressures, the second term dominates.
  - Notice that this also relates to the previously mentioned roles of a, b (e.g., at high pressures, the size of the molecules [and b] becomes significant).

- To solve the van der Waals equation for a molar volume given the other state variables, we must find the roots of a cubic equation via Newtons' method.

$$\overline{V}^3 - \left(b + \frac{RT}{P}\right)\overline{V}^2 + \frac{a}{P}\overline{V} - \frac{ab}{P} = 0$$

- **Redlich-Kwong equation**: A relatively simple equation of state that is much more accurate than the van der Waals equation. *Given by*

$$P = \frac{RT}{\overline{V} - B} - \frac{A}{\overline{V}(\overline{V} + B)\sqrt{T}}$$

  - Table 16.4 lists Redlich-Kwong parameters for various substances.
  - As a cubic equation (Problem 16-26):

$$\overline{V}^3 - \frac{RT}{P}\overline{V}^2 - \left(B^2 + \frac{BRT}{P} - \frac{A}{P\sqrt{T}}\right)\overline{V} - \frac{AB}{P\sqrt{T}} = 0$$

- **Peng-Robinson equation**: Another relatively simple equation of state that is much more accurate than the van der Waals equation. *Given by*

$$P = \frac{RT}{\overline{V} - \beta} - \frac{\alpha}{\overline{V}(\overline{V} + \beta) + \beta(\overline{V} - \beta)}$$

  - α is a somewhat complicated function of temperature, so α, β values are not listed.
  - Problem 16-28 gives the Peng-Robinson equation as a cubic.

- As a general rule, the van der Waals equation fails beyond $200\,\mathrm{bar}$ while the Redlich-Kwong and Peng-Robinson equations remain nearly quantitative all the way into regions where the gas liquifies.

  - Additionally, the Peng-Robinson equation is better in the liquid-vapor phase transition region, and the Redlich-Kwong equation is better at higher pressures (these equations were actually constructed for these purposes).

- There exist many more sophisticated equations of state, some containing 10+ parameters, that can quantitatively reproduce experimental data over a wide range of state variables.

- A note on the drawing of Figure 6.2.

  - The curves in the figure were plotted with the Redlich-Kwong equation of state (since it is the one that most accurately depicts reality at high pressures).
  - To plot said curves, we need $Z(P)$. Much like with the van der Waals equation, we can write that

$$Z = \frac{P\overline{V}}{RT} = \frac{\overline{V}}{\overline{V} - B} - \frac{A\overline{V}}{RT\overline{V}(\overline{V} + B)\sqrt{T}}$$

  - However, the above equation expresses Z as a function of $\overline{V}$, not P. Fortunately, we can solve the Redlich-Kwong equation for P using Cardano's formula.
  - Comparing the cubic form of the Redlich-Kwong equation to the general cubic $ax^3 + bx^2 + cx + d = 0$ yields

$$a = 1 \qquad b = -\frac{RT}{P} \qquad c = \frac{A}{P\sqrt{T}} - \frac{BRT}{P} - B^2 \qquad d = -\frac{AB}{P\sqrt{T}}$$

  - We now depress $ax^3 + bx^2 + cx + d = 0$ into $t^3 + pt + q = 0$ via the substitutions

$$t = x + \frac{b}{3a} \qquad p = \frac{3ac - b^2}{3a^2} \qquad q = \frac{2b^3 - 9abc + 27a^2d}{27a^3}$$

- Since $4p^3 + 27q^2 > 0$ for all $P \in (0, 1000]$ (as we can verify graphically), the depressed cubic $t^3 + pt + q = 0$ has the real root

$$t = \sqrt[3]{-\frac{q}{2} + \sqrt{\frac{q^2}{4} + \frac{p^3}{27}}} + \sqrt[3]{-\frac{q}{2} - \sqrt{\frac{q^2}{4} + \frac{p^3}{27}}}$$

- It follows by returning the substitution for x that the original cubic has the real root

$$x = -\frac{b}{3a} + \sqrt[3]{-\frac{q}{2} + \sqrt{\frac{q^2}{4} + \frac{p^3}{27}}} + \sqrt[3]{-\frac{q}{2} - \sqrt{\frac{q^2}{4} + \frac{p^3}{27}}}$$

i.e., that the above equation provides values $\overline{V}$ that make the Redlich-Kwong equation true for arbitrary P. In other words, the above equation equals $\overline{V}(P)$.

- It is a simple matter then to consider $Z(\overline{V}(P))$.

2/24:
- Equations of state that can be written as cubic equations in $\overline{V}$ describe both the gaseous and the liquid regions of a substance.

- *PV*-diagram terminology. *Figure 16.7.*

- **Isotherm**: An experimentally determined plot of P as a function of $\overline{V}$ at constant T.

- **Coexistence curve**: The curve on a PV diagram such that any point within the curve corresponds to liquid and gas coexisting in equilibrium with each other and any point on or outside the curve corresponds to only one phase.

- **Critical temperature**: The temperature above which a gas cannot be liquefied, regardless of the pressure. *Denoted by* $\boldsymbol{T_c}$.

- **Critical point**: The point along the curve $P(\overline{V}, T_c)$ at which $\partial P / \partial \overline{V} = 0$.

  - The global maximum of the coexistence curve.

- **Critical pressure**: The pressure at the critical point. *Denoted by* $\boldsymbol{P_c}$.

- **Critical volume**: The volume at the critical point. *Denoted by* $\overline{\boldsymbol{V}}_{\boldsymbol{c}}$.

- **Critical density**: The density of the system at the critical point.

- McQuarrie and Simon (1997) describes how pressure remains constant during a phase transition at a subcritical temperature.

- At the critical point, the meniscus between liquid and vapor disappears and both take on the same critical density.

- The spurious loops obtained from the van der Waals and Redlich-Kwong equation for $T < T_c$ (see Figure 6.1) result from the approximate nature of these equations of state.

  - However, the segment AB is a metastable region corresponding to the superheated vapor, the segment CD corresponds to the supercooled liquid, and the segment BC signifies an unstable region not observed for equilibrium systems.

- The **Maxwell equal-area construction** will be justified in Chapter 23.

- The three roots of the equations of state along isotherms for $T < T_c$.

  - A is the molar volume of the vapor in equilibrium.
  - D is the molar volume of the liquid in equilibrium.
  - The third root in the middle has no physical meaning.

- – We can thus use our cubic equations of state to calculate the molar volume of the liquid and gas phases of a given substance.

  - ∎ Note that since it was designed to behave the best in the liquid region, the Peng-Robinson equation gives the best result here.

- Since the critical point is an inflection point along the isotherm corresponding to the critical temperature, we have that

$$\left(\frac{\partial P}{\partial \overline{V}}\right)_T = 0 \qquad\qquad\qquad \left(\frac{\partial^2 P}{\partial \overline{V}^2}\right)_T = 0$$

at it.

  - – We can use these conditions to derive the critical constants in terms of a and b.

- An easier way to derive said expressions, though, is to note that the cubic van der Waals equation has three real roots for $T < T_c$ and one real root (plus two complex roots) for $T > T_c$, so at $T = T_c$, all three of its roots merge into one, i.e., the equation is of the form $(\overline{V} - \overline{V}_c)^3 = 0$.

  - – It follows by expanding the trinomial and comparing coefficients with the van der Waals equation written as a cubic that

$$3\overline{V}_c = b + \frac{RT_c}{P_c} \qquad\qquad 3V_c^2 = \frac{a}{P_c} \qquad\qquad \overline{V}_c^3 = \frac{ab}{P_c}$$

  - – It follows that

$$\overline{V}_c = 3b \qquad\qquad P_c = \frac{a}{27b^2} \qquad\qquad T_c = \frac{8a}{27bR}$$

  - – For the Redlich-Kwong equation,

$$\overline{V}_c = 3.8473B \qquad\qquad P_c = 0.029894\frac{A^{2/3}R^{1/3}}{B^{5/3}} \qquad\qquad T_c = 0.34504\left(\frac{A}{BR}\right)^{2/3}$$

- From the above equations, we can show that

$$\frac{P_c\overline{V}_c}{RT_c} = 0.375 \qquad\qquad\qquad \frac{P_c\overline{V}_c}{RT_c} = 0.333$$

where the left estimate is provided by the van der Waals equation and the right by the Redlich-Kwong equation.

  - – The significance is that both equations of state predict that the compressibility factor at the critical point is the same for all substances (there is no a, b or A, B dependence in the terms on the right of the equalities). However, there is a slight disparity in the predicted value of Z.

  - – While neither prediction is particularly quantitative (that of the Peng-Robinson is a bit more so), all three equations of state predict a constant Z. This prediction is borne out reasonably well by experimental data.

- **Law of corresponding states**: The properties of all gases are the same if we compare them under the same conditions relative to their critical point.

  - – In particular, this means that gas properties are identical when their **reduced quantities** are equal.

- Note that in practice, the van der Waals and Redlich-Kwong constants are obtained from data at the critical point, not the other way around.

2/25:

- Also note that there is some ambiguity in how we do so, since there are three pieces of data $(P_c, \overline{V}_c, T_c)$ describing a gas at the critical point but only two constants a, b or A, B.

- **Reduced quantity**: The quotient of a state variable of a gas and the value of that state variable for the gas at the critical point. *Denoted by $\boldsymbol{X_R}$ (if X is a state variable).*

  - For example, the reduced pressure of a gas is $P_R = P/P_c$ where P is its current pressure and P_c is its critical pressure.

- By recombining some of our previous equations, we can rewrite the van der Waals equation in the form

$$\left(P_R + \frac{3}{\overline{V}_R^2}\right)\left(\overline{V}_R - \frac{1}{3}\right) = \frac{8}{3}T_R$$

  - Since the above equation doesn't contain any gas characteristics (e.g., $a, b, A, B, \alpha, \beta$), it is a universal equation for all gases.
  - For example, it implies that any gas at the same reduced temperature and volume will have the same reduced pressure.
  - This prediction is borne out by experimental data and forms the foundation of the law of corresponding states.

- **Corresponding states** (of gases A and B): A state (P_A, V_A, T_A) of gas A and (P_B, V_B, T_B) of gas B such that

$$P_{R_A} = \frac{P_A}{P_{c_A}} = \frac{P_B}{P_{c_B}} = P_{R_B} \qquad V_{R_A} = \frac{V_A}{V_{c_A}} = \frac{V_B}{V_{c_B}} = V_{R_B} \qquad T_{R_A} = \frac{T_A}{T_{c_A}} = \frac{T_B}{T_{c_B}} = T_{R_B}$$

- The compressibility factor also obeys the law of corresponding states.

  - For the van der Waals equation,

$$\begin{aligned}
Z &= \frac{P\overline{V}}{RT} \\
&= \frac{\overline{V}}{\overline{V} - b} - \frac{a}{RT\overline{V}} \\
&= \frac{\overline{V}}{\overline{V} - \overline{V}_c/3} - \frac{3P_c\overline{V}_c^2}{RT\overline{V}} \\
&= \frac{\overline{V}/\overline{V}_c}{\overline{V}/\overline{V}_c - 1/3} - \frac{3 \cdot 3RT_c/8 \cdot \overline{V}_c}{RT\overline{V}} \\
&= \frac{\overline{V}_R}{\overline{V}_R - 1/3} - \frac{9}{8T_R\overline{V}_R}
\end{aligned}$$

  - For the Redlich-Kwong equation,

$$Z = \frac{\overline{V}_R}{\overline{V}_R - 0.25992} - \frac{1.2824}{T_R^{3/2}(\overline{V}_R + 0.25992)}$$

- Physical interpretation of the law of corresponding states: All temperature, pressure, volume, etc. scales on gases are arbitrary, even kelvin. The only values that matter as far as a gas is concerned are its reduced quantities.

- **Virial equation of state**: The most fundamental equation of state, i.e., the one with the most sound theoretical foundation. *Given by*

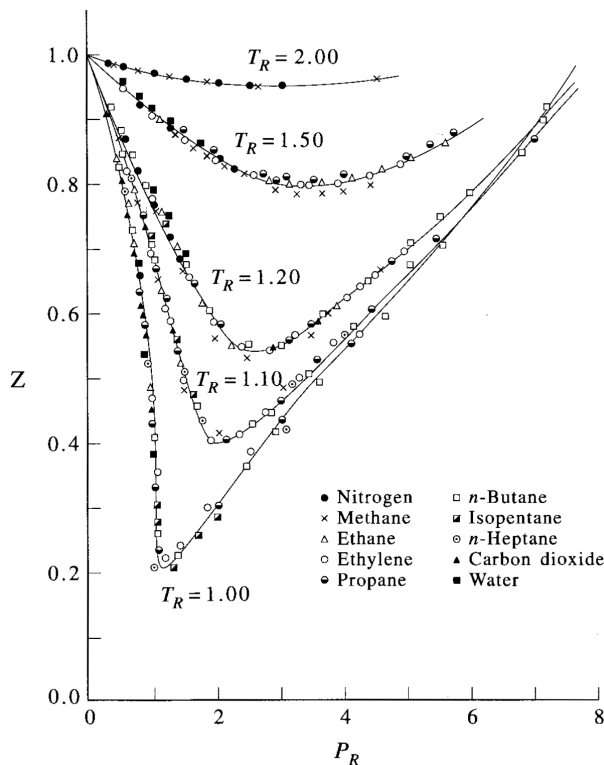$$Z = \frac{P\overline{V}}{RT} = 1 + \frac{B_{2V}(T)}{\overline{V}} + \frac{B_{3V}(T)}{\overline{V}^2} + \cdots$$

Figure 6.3: Experimental evidence for the law of corresponding states.

- **Virial coefficients**: The coefficients in the above polynomial in $\overline{V}$.

- i^{th} **virial coefficient**: The virial coefficient $B_{iV}(T)$.

- **Virial expansion**: The expression of another property, such as energy or entropy, as a polynomial in $1/\overline{V}$.

- A useful virial expansion is the expression of $Z(P)$ given by

$$Z = \frac{P\overline{V}}{RT} = 1 + B_{2P}(T)P + B_{3P}(T)P^2 + \cdots$$

  where

$$B_{iV}(T) = RTB_{iP}(T)$$

- Note that in the above virial expansions, $\overline{V} \to \infty$ and $P \to 0$ as $Z \to 1$, as we would expect.

- The terms in the virial expansion converge rapidly.

- "The second virial coefficient is the most important virial coefficient because it reflects the first deviation from ideality as the pressure of the gas is increased (or the volume is decreased)" (McQuarrie & Simon, 1997, p. 659).

  - It can be measured from the slope of a plot of Z vs. P (at low pressures).

  - $B_{2V}(T)$ is negative at low temperatures and increases with temperature, going through a shallow positive maximum and then decreasing asymptotically toward zero.

- **Boyle temperature**: The temperature at which $B_{2V}(T) = 0$, i.e., at which the repulsive and attractive parts of the intermolecular attractions cancel each other and the gas appears to behave ideally.

- The virial equation of state allows us to derive an exact relation between the virial coefficients and the intermolecular interactions.

  - The interaction of two molecules depends on their distance apart and orientation in space. However, due to rapid molecular motion, we'll pretend that their orientation averages out (a good approximation for molecules of low polarity) and that only the intermolecular distance r is important.

  - Let $u(r)$ denote the potential energy of two molecules separated by a distance r. Then we can show that

    $$B_{2V}(T) = -2\pi N_A \int_0^\infty [e^{-u(r)/k_B T} - 1] r^2 \, dr$$

  - Note that as we'd expect, $B_{2V}(T) = 0$ if $u(r) = 0$, i.e., there are no deviations from ideality if there are no intermolecular interactions.

  - In principle, $u(r)$ can be calculated from quantum mechanics, but this is complicated. Thus, we the approximation from perturbation theory that

    $$u(r) \to -\frac{c_6}{r^6}$$

    for large values of r where c_6 is a constant depending on the molecules in question.

    - The negative sign represents attraction.
    - At low temperatures, it is this attraction that leads to condensation.

  - Although there is no known exact expression for $u(r)$ at small distances, it must reflect intermolecular repulsions, so we usually choose

    $$u(r) \to \frac{c_n}{r^n}$$

    for small r where $n \in \mathbb{N}$ (but n is often taken to be 12) and c_n, again, depends on the molecules in question.

  - An intermolecular potential that accounts for both forces is the sum of the two, often written with the substitutions $c_{12} = 4\varepsilon\sigma^{12}$ and $c_6 = 4\varepsilon\sigma^6$.

    $$u(r) = \frac{c_{12}}{r^{12}} - \frac{c_6}{r^6} = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

- **Lennard-Jones potential**: The above expression for $u(r)$ in terms of ε and σ.

- **Lennard-Jones parameters**: The values ε and σ.

  - Let's calculate the value at which the Lennard-Jones potential achieves its minimum.

    $$\begin{aligned}
    0 &= \frac{du}{dr} \\
    &= 4\epsilon \left[-\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} \right] \\
    \frac{12\sigma^{12}}{r^{13}} &= \frac{6\sigma^6}{r^7} \\
    2\sigma^6 &= r^6 \\
    r_{\min} &= 2^{1/6}\sigma
    \end{aligned}$$

  - It follows that

    $$u(r_{\min}) = 4\epsilon \left[\left(\frac{\sigma}{2^{1/6}\sigma}\right)^{12} - \left(\frac{\sigma}{2^{1/6}\sigma}\right)^6 \right] = 4\epsilon \left(\frac{1}{4} - \frac{1}{2}\right) = -\epsilon$$

    i.e., that ϵ is the depth of the potential well relative to infinite separation.

■ Thus, ϵ is a measure of how strongly the molecules attract each other.

– Additionally, we have that

$$u(\sigma) = 4\varepsilon \left[\left(\frac{\sigma}{\sigma} \right)^{12} - \left(\frac{\sigma}{\sigma} \right)^{6} \right] = 0$$

■ Thus, when $r = \sigma$, the intermolecular attraction and repulsion cancel, i.e., the molecules are finally close enough that their repulsion is becoming significant (in layman's terms, they're touching).

■ This means that σ is a measure of the size of the constituent molecules.

• Substituting the Lennard-Jones potential into our expression for $B_{2V}(T)$ in terms of $u(r)$ yields

$$B_{2V}(T) = -2\pi N_A \int_0^\infty \left[\exp\left\{ -\frac{4\varepsilon}{k_B T} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \right\} - 1 \right] r^2 \, \mathrm{d}r$$

• Substituting a reduced temperature $T^* = k_B T/\varepsilon$, $x = r/\sigma$, and a reduced second virial coefficient $B_{2V}^*(T^*) = B_{2V}(T^*)/(2\pi\sigma^3 N_A/3)$ yields

$$B_{2V}^*(T^*) = -3 \int_0^\infty \left[\exp\left\{ -\frac{4}{T^*} (x^{-12} - x^{-6}) \right\} - 1 \right] x^2 \, \mathrm{d}x$$

where the integral must be evaluated numerically for each T^*. Extensive tabulations of these values are available, though.

– Note that this equation is another example of the law of corresponding states. Plotting $B_{2V}^*(T^*)$ vs. T^* for almost any gas will generate much the same curve.

• Another interpretation of $B_{2V}(T)$.

– Consider the virial expansion in terms of pressure under conditions such that terms P^2 and higher are negligible. Then

$$\frac{P\overline{V}}{RT} = 1 + B_{2P}(T)P$$

$$= 1 + \frac{B_{2V(T)}}{RT} P$$

$$\overline{V} = \frac{RT}{P} + B_{2V}(T)$$

$$B_{2V}(T) = \overline{V} - \overline{V}_{\text{ideal}}$$

• Note that in much the same way we actually use critical point information to calculate van der Waals and Redlich-Kwong constants, we actually use $B_{2V}(T)$ data to calculate Lennard-Jones parameters.

• "Because the second virial coefficient reflects the initial deviations from ideal behavior, which are caused by intermolecular interactions, experimental P-V-T data turn out to be a rich source of information concerning intermolecular interactions" (McQuarrie & Simon, 1997, p. 665).

– Once the Lennard-Jones parameters of a substance are known, they can be used to calculate properties such as viscosity, thermal conductivity, heats of vaporization, and various crystal properties.

• We now consider in more depth the form of the r^{-6} attraction term.

• Consider two molecules with dipoles μ_1, μ_2.

– If we assume that these molecules rotate randomly in the gas phase, their average dipole-dipole interactions would be zero.

– However, because different conformations (e.g. head-to-head vs. head-to-tail) have different energies, the various states do not occur with equal probabilities. This gives us the following expression for the average interaction between two molecular dipoles.

$$u_{d.d}(r) = -\frac{2\mu_1^2\mu_2^2}{(4\pi\varepsilon_0)^2(3k_BT)}\frac{1}{r^6}$$

- Consider two molecules, one with a permanent dipole and the other without a permanent dipole.

   – Dipole moments can be induced in molecules without a permanent one since all atoms and molecules are **polarizable**.

   – Thus,

$$u_{\text{induced}}(r) = -\frac{\mu_1^2\alpha_2}{(4\pi\varepsilon_0)^2 r^6} - \frac{\mu_2^2\alpha_1}{(4\pi\varepsilon_0)^2 r^6}$$

   – The first term above represents a permanent dipole moment in molecule 1 and an induced dipole moment in molecule 2, and the second represents the opposite situation.

- **Polarizability**: The proportionality constant between the induced dipole moment μ_{induced} and the external electric field strength E. *Denoted by* $\boldsymbol{\alpha}$.

   – "The easier it is for the electric field to deform the atomic or molecular charge distribution, the greater is the polarizability" (McQuarrie & Simon, 1997, pp. 667–68).

- **Polarizability volume**: The quantity $\alpha/4\pi\varepsilon_0$, which has units of volume.

   – The polarizability of an atom or molecule is proportional to its size, hence another reason for introducing the polarizability volume.

- Consider two molecules, neither of which has a permanent dipole.

   – Because of the **London dispersion attraction**, their energy of interaction is

$$u_{\text{disp}}(r) = -\frac{3}{2}\left(\frac{I_1 I_2}{I_1 + I_2}\right)\frac{\alpha_1\alpha_2}{(4\pi\varepsilon_0)^2}\frac{1}{r^6}$$

   where I_j is the ionization energy of atom or molecule j.

   – Since u_{disp} is proportional to the product of the polarizability volumes, the importance of u_{disp} increases with the sizes of the atoms or molecules.

- **London dispersion attraction**: A strictly quantum-mechanical effect that draws all molecules together, even nonpolar ones.

   – Named for the German scientist Fritz London who first calculated it in 1930.

   – Note that the classical picture taught in intro chem of electrons and protons shifting isn't strictly accurate — it's more about the distortion/perturbation of wave functions as particles draw near.

- It follows that the total contribution to the r^{-6} term of the Lennard-Jones potential is given by the sum of the previous three results, i.e.,

$$c_6 = \frac{2\mu^4}{3(4\pi\varepsilon_0)^2 k_B T} + \frac{2\alpha\mu^2}{(4\pi\varepsilon_0)^2} + \frac{3}{4}\frac{I\alpha^2}{(4\pi\varepsilon_0)^2}$$

for identical atoms and molecules.

Week 7

Phase Equilibria and Solutions

7.1 Virial Coefficients and Fugacity

• Relation between the interaction potential and the first virial coefficient (Equation 16.25).

  – Statistical mechanics is important because it gives us the relation

  $$B_{2V}(T) = -2\pi N_A \int_0^\infty \left(e^{-u(r)/k_B T} - 1 \right) r^2 \, dr$$

  ■ We can derive this with our knowledge of statistical mechanics, but PGS will not go through this.

  – Now recall the Lennard-Jones potential

  $$u(r) = 4\epsilon \left[\left(\frac{\sigma}{\pi} \right)^{12} - \left(\frac{\sigma}{\pi} \right)^6 \right]$$

  ■ Note that the minimum is at $(2^{1/6}\sigma, -\epsilon)$.
  ■ The limiting case of the Lennard-Jones potential is hard sphere repulsion (the repulsion as you approach a hard sphere, which is zero up until you're at the surface and then infinite repulsion). Thus, with no intermolecular attraction, $a = 0$, so in this case,

  $$B_{2V}(T) = -2\pi N_A \int_0^\sigma (-1) r^2 \, dr$$
  $$= \frac{2\pi N_A \sigma^3}{3}$$
  $$= b - \frac{0}{RT}$$

  – Now consider a potential that is van der Waals (c/r^6) up until a point and then hard sphere. In this case,

  $$B_{2V}(T) = \frac{2\pi N_A \sigma^3}{3} - 2\pi N_A \int_\sigma^\infty \left(e^{-c/r^6 k_B T} - 1 \right) r^2 \, dr$$
  $$= \frac{2\pi N_A \sigma^3}{3} - 2\pi N_A \int_\sigma^\infty \left(-\frac{c}{r^6 k_B T} \right) r^2 \, dr$$
  $$= b + \frac{2\pi N_A c}{k_B T} \cdot -\frac{1}{3\sigma^3}$$

  where we have used $e^x = 1 + x + \cdots$ to get from the first line to the second.

■ Therefore,

$$a = \frac{2\pi N_A^2}{3} \frac{c}{\sigma^2}$$

- Derivation of the relation between $B_{2V}(T)$ and the interaction potential $u(r)$.

  - Consider a system of independent, indistinguishable particles.
  - The total Hamiltonian for the system has a kinetic energy part and an interaction part.

  $$\hat{H}(p_i, r_i) = \sum_i \frac{\hat{p}_i^2}{2m} + \sum_{i<j} \hat{u}(r_i, r_j)$$

  - The kinetic part (which ignores intermolecular interactions) will lead to the ideal gas partition function. The nonideal part of the partition function will come from the interaction potentials. Mathematically,

  $$\begin{aligned} Q &= \frac{1}{N!} \int e^{-\beta E(p_i, r_i)} \, d^3 p_i \, d^3 r_i \\ &= \frac{1}{N!} \int \exp\left\{ -\beta \left[\sum_i \frac{p_i^2}{2m} + \sum_{i<j} u(r_i, r_j) \right] \right\} d^3 p_i \, d^3 r_i \\ &= \frac{1}{N!} \left(\int \exp\left[-\beta \sum_i \frac{p_i^2}{2m} \right] d^3 p_i \right) \left(\int \exp\left[-\beta \sum_{i<j} u(r_i, r_j) \right] d^3 r_i \right) \\ &= \underbrace{\frac{V^N}{N!} \left(\int \exp\left[-\beta \sum_i \frac{p_i^2}{2m} \right] d^3 p_i \right)}_{Q_{\text{ideal}}} \cdot \underbrace{\frac{1}{V^N} \left(\int \exp\left[-\beta \sum_{i<j} u(r_i, r_j) \right] d^3 r_i \right)}_{Q_u} \end{aligned}$$

  - Define

  $$f_{ij} = e^{-u(r_i, r_j)/k_B T} - 1$$

  - Now note that the interaction between molecules is pretty small, and in fact $f_{ij} \to 0$ as $|r_i - r_j| \to \infty$.
  - Thus,

  $$\begin{aligned} Q_u &= \frac{1}{V^N} \int \exp\left[-\beta \sum_{i<j} u(r_i, r_j) \right] d^3 r_i \\ &= \frac{1}{V^N} \int \prod_{i<j} (f_{ij} + 1) \, d^3 r_i \end{aligned}$$

  - We can do a **cluster expansion** on this small f_{ij}:

  $$\prod_{i<j} (f_{ij} + 1) = 1 + \sum_{i<j} f_{ij} + \sum_{i<j} \sum_{k<\ell} f_{ij} f_{k\ell}$$

  - In particular, $\sum_{i<j}$ is the sum of pairwise interactions while $f_{ij} \cdot f_{k\ell}$ are binary interactions, $f_{ij} f_{k\ell} f_{mn}$ are tertiary interactions, and so on and so forth.

– But at low density, the dominant term is the pairwise interaction so we have

$$Q_u = \frac{1}{V^N} \int \left(1 + \sum_{i<j} f_{ij}\right) d^3 r_i$$

$$= \frac{1}{V^N} \left(V^N + \frac{N(N-1)}{2} V^{N-2} \int f_{12} \, d^3 r_1 \, d^3 r_2\right)$$

$$= 1 + \frac{N(N-1)}{2V} \int (e^{-\beta u(r)} - 1) \, d^3 r$$

– It follows that

$$Q = Q_{\text{id}} \left[1 + \frac{N(N-1)}{2V} \int \left(e^{-\beta u(r)} - 1\right) d^3 r\right]$$

– But now we need to extract an equation of state from the partition function. To do so, we use

$$P = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$$

$$= k_B T \left(\frac{\partial \ln Q_{\text{id}}}{\partial V}\right)_{N,T} + k_B T \left(\frac{\partial \ln Q_u}{\partial V}\right)_{N,T}$$

– We know that the first term above is equal to $N k_B T/V$, but it takes a bit more work for the second one.

– We have that

$$\ln Q_u = \ln \left(1 + \underbrace{\frac{N(N-1)}{2V}}_{\substack{\text{Approximately} \\ \text{the intermolecular} \\ \text{distance } 1/\rho^3}} \underbrace{\int \left(e^{-\beta u(r)} - 1\right) d^3 r}_{\substack{\text{Approximately} \\ \text{the molecular} \\ \text{volume } a^3}}\right)$$

$$= \frac{N(N-1)}{2V} \int \left(e^{-\beta u(r)} - 1\right) d^3 r$$

since the second term is a small number and the natural log of a small number plus 1 is approximately that small number.

– Thus,

$$\left(\frac{\partial \ln Q_u}{\partial V}\right)_{N,T} = -\frac{N(N-1)}{2V^2} \int \left(e^{-\beta u(r)} - 1\right) d^3 r$$

so

$$P = \frac{N k_B T}{V} - \frac{N k_B T}{V} \frac{N-1}{2V} \int \left(e^{-\beta u(r)} - 1\right) d^3 r$$

$$= \frac{RT}{\overline{V}} - \frac{RT}{\overline{V}} \frac{N-1}{2V} \int \left(e^{-\beta u(r)} - 1\right) d^3 r$$

– Consequently,

$$Z = \frac{P\overline{V}}{RT} = 1 - \frac{N_A}{\overline{V}} \cdot \frac{1}{2} \int \left(e^{-\beta u(r)} - 1\right) d^3 r$$

– Therefore, by comparison with the virial expansion,

$$B_{2V}(T) = -\frac{N_A}{2} \int \left(e^{-\beta u(r)} - 1\right) d^3 r$$

$$= -\frac{N_A}{2} \int_0^\infty \left(e^{-\beta u(r)} - 1\right) 4\pi r^2 \, dr$$

$$= -2\pi N_A \int_0^\infty \left(e^{-u(r)/k_B T} - 1\right) r^2 \, dr$$

- Free energy as a function of (T, P) for a real gas. Definition of fugacity and fugacity coefficients.

    - We want to find $\Delta G(T, P)$.
    - We have that $\mathrm{d}\overline{G} = -\overline{S}\,\mathrm{d}T + \overline{V}\,\mathrm{d}P$. It follows that

    $$\left(\frac{\partial \overline{G}}{\partial P}\right)_T = \overline{V}$$

    - Thus,

    $$\overline{G}(T, P) = \overline{G}(T, P_0) + \int_{P_0}^{P} \overline{V}\,\mathrm{d}P$$

    - In the ideal case,

    $$\overline{G}_{\text{ideal}}(T, P) = \overline{G}_{\text{ideal}}(T, P_0) + \int_{P_0}^{P} \frac{RT}{P}\,\mathrm{d}P$$
    $$= \overline{G}_{\text{ideal}}(T, P_0) + RT \ln \frac{P}{P_0}$$

    - In the nonideal case, we define a fugacity f by

    $$\overline{G}_{\text{ideal}}(T, P) = \overline{G}_{\text{ideal}}(T, P_0) + RT \ln \frac{f}{P_0}$$

        - ■ The second term in the above equation refers to the Gibbs free energy of an ideal gas at $P_0 = 1\,\text{bar}$ or $P_0 = 1\,\text{atm}$. Note that even at $P_0 = 1\,\text{atm}$, however, there is too much pressure for truly ideal behavior, so $f \neq P_0$.
    - Imagine that $\Delta \overline{G}_1$ takes us from a real gas at (T, P) to an ideal gas at (T, P). Then

    $$\Delta \overline{G}_1 = \overline{G}_{\text{ideal}}(T, P) - \overline{G}_{\text{real}}(T, P)$$
    $$= \left[\overline{G}_{\text{ideal}}(T, P_0) + RT \ln \frac{P}{P_0}\right] - \left[\overline{G}_{\text{ideal}}(T, P_0) + RT \ln \frac{f}{P_0}\right]$$
    $$= -RT \ln \frac{f}{P}$$

    - Now let $\Delta \overline{G}_2$ take us from a real gas at (T, P) to a real gas at T and $P \to 0$, which will be the same as an ideal gas at T and $P \to 0$. Then let $\Delta \overline{G}_3$ take us from this ideal gas at T and $P \to 0$ to an ideal gas at (T, P). It follows that

    $$\Delta \overline{G}_2 = -\int_{P \to 0}^{P} \overline{V}\,\mathrm{d}P' \qquad\qquad \Delta \overline{G}_2 = \int_{P \to 0}^{P} \frac{RT}{P'}\,\mathrm{d}P'$$

    - Thus, since $\Delta \overline{G}_1 = \Delta \overline{G}_2 + \Delta \overline{G}_3$ (G is a state function),

    $$-RT \ln \frac{f}{P} = \int_{P \to 0}^{P} \left(-\overline{V} + \frac{RT}{P'}\right)\,\mathrm{d}P'$$

    - We then define γ to be the **fugacity coefficient** by $\gamma = f/P$. It follows that

    $$\ln \gamma = \int_{0}^{P} \frac{Z - 1}{P'}\,\mathrm{d}P'$$

- Fugacity coefficient expressed in terms of the compressibility deviation from unity.

    - At low temperature, $Z < 1$, so $\gamma < 1$ and hence $f < p$.
    - At high pressure, $Z > 1$ (excluded volume), so $\gamma > 1$ and hence $f > P$.

- Introduces phase diagrams and their notable properties.

7.2 Phase Equilibria

2/23:
- Goes over midterm answer key (and posted it to Canvas).

  - 1d.
    - We needed to say that $\max S = nk_B \ln 2$.
    - We also needed to indicate that the slope is vertical at 0 and 1.
  - Question 3.
    - Often looking for a derivation from some fundamental law of thermodynamics.
    - For example, for 3a, since this is an isolated system, we know that $\mathrm{d}U = 0$. Moreover, since $\mathrm{d}U = C_1 \, \mathrm{d}T_1 + C_2 \, \mathrm{d}T_2$, we have that $C_1 \, \mathrm{d}T_1 = -C_2 \, \mathrm{d}T_2$.
  - 3b.
    - The appropriate derivation was

$$\mathrm{d}S = \mathrm{d}S_1 + \mathrm{d}S_2$$
$$= \frac{C_1 \, \mathrm{d}T_1}{T_1} + \frac{C_2 \, \mathrm{d}T_2}{T_2}$$
$$= C_1 \, \mathrm{d}T_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

      from which it follows since $T_2 > T_1$ (and hence $1/T_1 - 1/T_2 > 0$), since $\mathrm{d}S > 0$, and since $C_1 > 0$ that $\mathrm{d}T_1 > 0$.
  - I need a lot of help on Question 4.

- In the video of a liquid becoming a supercritical fluid, the path along the phase diagram is along the liquid-gas coexistence curve to the critical point and beyond.

- The heat of vaporization actually isn't constant; it varies with temperature.

  - At the critical temperature, it becomes zero and the line has vertical slope.

- The densities of gas and liquid also converge as $T \to T_c$.

- The slope of coexistence curves on PT phase diagrams; the Clapeyron equation.

  - Since the molar free energies $\overline{G}_\alpha, \overline{G}_\beta$ of the two phases α, β are equal when said phases are in equilibrium,

$$\mathrm{d}\overline{G}_\alpha = \mathrm{d}\overline{G}_\beta$$
$$\left(\frac{\partial \overline{G}_\alpha}{\partial T} \right)_P \mathrm{d}T + \left(\frac{\partial \overline{G}_\alpha}{\partial P} \right)_T \mathrm{d}P = \left(\frac{\partial \overline{G}_\beta}{\partial T} \right)_P \mathrm{d}T + \left(\frac{\partial \overline{G}_\beta}{\partial P} \right)_T \mathrm{d}P$$
$$-\overline{S}_\alpha \, \mathrm{d}T + \overline{V}_\alpha \, \mathrm{d}P = -\overline{S}_\beta \, \mathrm{d}T + \overline{V}_\beta \, \mathrm{d}P$$
$$(\overline{S}_\beta - \overline{S}_\alpha) \, \mathrm{d}T = (\overline{V}_\beta - \overline{V}_\alpha) \, \mathrm{d}P$$
$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\overline{S}_\beta - \overline{S}_\alpha}{\overline{V}_\beta - \overline{V}_\alpha} = \frac{\Delta \overline{S}_{\text{trans}}}{\Delta \overline{V}_{\text{trans}}}$$

  - Clearly, the last line above gives the slope of the coexistence curves on a phase diagram.
  - Since $T \Delta \overline{S}_{\text{trans}} = \Delta \overline{H}_{\text{trans}}$ ($\Delta G = 0$), we also have

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta \overline{H}_{\text{trans}}}{T \Delta \overline{V}_{\text{trans}}}$$

    - Since both $\Delta \overline{H}_{\text{trans}}, \Delta \overline{V}_{\text{trans}} \to 0$ as $T \to T_c$, $\mathrm{d}P/\mathrm{d}T$ depends on the rates at which the two quantities approach zero.

- Deriving an expression for the vapor pressure (in equilibrium with liquid).

    - We know that $\Delta \overline{V}_{\text{vap}} = \overline{V}_g - \overline{V}_l$ where $\overline{V}_g \gg \overline{V}_l$. Therefore, we may approximate $\Delta \overline{V}_{\text{vap}} \approx \overline{V}_g$.
    - Additionally, we have that $\overline{V}_g = RT/P$.
    - It follows that

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta \overline{H}_{\text{vap}}}{T\overline{V}_g}$$

$$= \frac{P\Delta \overline{H}_{\text{vap}}}{RT^2}$$

$$\frac{\mathrm{d}P}{P} = \frac{\Delta \overline{H}_{\text{vap}}}{R} \frac{\mathrm{d}T}{T^2}$$

$$\ln \frac{P}{P_0} = \frac{\Delta \overline{H}_{\text{vap}}}{R} \left(-\frac{1}{T} + \frac{1}{T_0} \right)$$

    - It follows that if $P_0 = 1\,\text{atm}$ and $T_0 = T_b$ (the standard boiling temperature), then the vapor pressure P at temperature T is

$$P = P_0 \exp \left[\frac{\Delta \overline{H}_{\text{vap}}}{R} \left(\frac{1}{T_b} - \frac{1}{T} \right) \right]$$

        - Note that we take $\Delta \overline{H}_{\text{vap}}$ to be the molar heat of vaporization at temperature T, i.e., we assume it's constant from there up until T_b which it technically isn't as we mentioned earlier.
    - Note that you can also use this equation and (P, T) data to calculate ΔH_{vap}.

- Relative slopes of S-G and L-G coexistence lines at the triple point.

    - When drawing a phase diagram, you should exaggerate the discontinuity in the slopes of the S-G and L-G coexistence curves at the triple point.
    - In particular, $\mathrm{d}P_{\text{SG}}/\mathrm{d}T > \mathrm{d}P_{\text{LG}}/\mathrm{d}T$ since $\Delta \overline{H}_{\text{SG}} = \Delta \overline{H}_{\text{SL}} + \Delta \overline{H}_{\text{LG}} > \Delta \overline{H}_{\text{LG}}$ and $\Delta \overline{V}_{\text{SG}} \approx \Delta \overline{V}_{\text{LG}}$.
    - Quantitatively, the ratio of the slopes is

$$\frac{\mathrm{d}P_{\text{SG}}/\mathrm{d}T}{\mathrm{d}P_{\text{LG}}/\mathrm{d}T} = \frac{\Delta \overline{H}_{\text{SG}}}{\Delta \overline{H}_{\text{LG}}} = 1 + \frac{\Delta \overline{H}_{\text{SL}}}{\Delta \overline{H}_{\text{LG}}}$$

7.3 Chemical Potential and Raoult's Law

2/25:
- Today we begin the topic of solutions.

    - We'll introduce ideal solutions and then discuss nonideal solutions.
    - Today: Ideal solutions, i.e., solutions in which we negate the interactions between the solutes. The statistical entropy gives rise to boiling point elevation, freezing point depression, Raoult's law, and osmotic pressure.

- Chemical potential.

    - To discuss equilibrium, we start by discussing the energy of a solution $G(T, P, n_1, n_2)$ where n_1 is the number of moles of solute and n_2 is the number of moles of solvent.
    - The total differential is

$$\mathrm{d}G = \left(\frac{\mathrm{d}G}{\mathrm{d}T} \right)_{P,n_1,n_2} \mathrm{d}T + \left(\frac{\mathrm{d}G}{\mathrm{d}P} \right)_{T,n_1,n_2} \mathrm{d}P + \left(\frac{\mathrm{d}G}{\mathrm{d}n_1} \right)_{T,P,n_2} \mathrm{d}n_1 + \left(\frac{\mathrm{d}G}{\mathrm{d}n_2} \right)_{T,P,n_1} \mathrm{d}n_2$$

- **Chemical potential**: The following partial derivative. *Denoted by μ_1. Given by*

$$\mu_i = \left(\frac{\mathrm{d}G}{\mathrm{d}n_i}\right)_{T,P,n_j}$$

for all $j \neq i$.

  - For a pure substance, chemical potential is the molar free energy for a given ratio of concentration.
  - μ_i is a function of $T, P, n_j \neq n_i$.

- Equilibrium in terms of relation between chemical potentials.

  - Consider a system in equilibrium between the liquid and gas phases where both phases have two components n_1^l, n_2^l and n_1^g, n_2^g.
  - We know that the free energy G is the sum of the free energies of the two systems G^l, G^g.
  - Since we are in equilibrium, $\mathrm{d}G = \mathrm{d}G^l + \mathrm{d}G^g = 0$.
  - At constant T, P, it follows that

$$\mu_1^l \, \mathrm{d}n_1^l + \mu_2^l \, \mathrm{d}n_2^l + \mu_1^g \, \mathrm{d}n_1^g + \mu_2^g \, \mathrm{d}n_2^g = 0$$

  - Furthermore, matter is conserved, i.e., $\mathrm{d}n_i^l = -\mathrm{d}n_i^g$.
  - Thus, we may write

$$(\mu_1^l - \mu_1^g) \, \mathrm{d}n_1^l + (\mu_2^l - \mu_2^g) \, \mathrm{d}n_2^l = 0$$

  - It follows that $\mu_1^l - \mu_1^g = 0$ and $\mu_2^l - \mu_2^g = 0$, i.e., that the chemical potentials of species in each phase are equal at equilibrium.

- **Raoult's law**: The partial pressure P_i of each component in a solution is equal to its pure vapor pressure P_i^* times its mole fraction x_i in solution. *Given by*

$$P_i = x_i P_i^*$$

for all i.

  - It's only the mole fraction of the solute that matters, not whether it's as big as a protein or as small as an ion.
  - This is only in **ideal solutions**, however.

- **Ideal solution**: A solution that has a small amount of solutes.

  - In the same way that any gas is ideal at low pressure, any solution is ideal with few enough solutes.

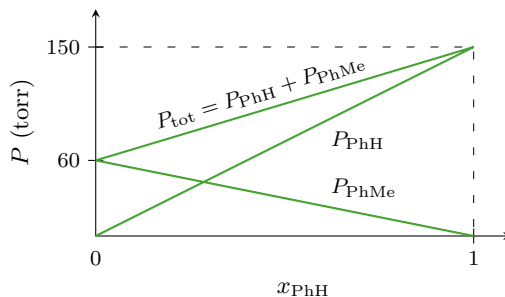- Example of vapor pressure in equilibrium with an ideal solution of benzene and toluene.

Figure 7.1: Raoult's law example.

- We'll see deviations from Figure 7.1 later, such as Henry's law.

- Chemical potential of a component in an ideal solution.

  - If the vapor is ideal, then

  $$\overline{G}^g(T, P) = \overline{G}^{\circ g}(T) + RT \ln \frac{P}{P_0}$$

  - For a pure substance, we have

  $$G^{\circ g}(T) + RT \ln \frac{P}{P_0} = G^{\circ l}(T)$$
  $$P = P_0 e^{-\Delta G / RT}$$

  where $\Delta G = G^{\circ g} - G^{\circ l}$.

  - When we have a solution,

  $$\overline{G}^l(T, x_1) = \overline{G}^g(T) + RT \ln \frac{x_1 P_1^*}{P_0}$$
  $$\overline{G}^{\circ l}(T) + ? = \overline{G}^g(T) + RT \ln \frac{x_1 P_1^*}{P_0}$$
  $$? = RT \ln \frac{x_1 P_1^*}{P_0} - RT \ln \frac{P_0}{P_1^*}$$
  $$= RT \ln x_1$$

  so

  $$\overline{G}^{\circ l}(T, x_1) = \overline{G}^{\circ l}(T) + RT \ln x_1$$

  - This result implies that the free energy of the pure substance with mole fraction x_1 in solution is equal to the free energy of the solution plus $RT \ln x_1$.

- The chemical potential for an ideal solution is a pure entropy effect.

  - For the mixing of two solutions, we have as with gases that

  $$\Delta S = k_B \ln W$$
  $$= k_B \ln \frac{(N_1 + N_2)!}{N_1! N_2!}$$
  $$= k_B [(N_1 + N_2) \ln(N_1 + N_2) - (N_1 + N_2) - (N_1 \ln N_1 - N_1) - (N_2 \ln N_2 - N_2)]$$
  $$= k_B \left(N_1 \ln \frac{N_1 + N_2}{N_1} + N_2 \ln \frac{N_1 + N_2}{N_2} \right)$$
  $$= -k_B N_A (n_1 \ln x_1 + n_x \ln x_2)$$
  $$= -R(n_1 \ln x_1 + n_x \ln x_2)$$

  - It follows that without enthalpic mixing (i.e., with $\Delta H = 0$), we have

  $$\Delta G = \Delta H - T \Delta S$$
  $$= RT(n_1 \ln x_1 + n_x \ln x_2)$$

  - Thus, since $\Delta \overline{G}_1 = RT \ln x_1$, $RT \ln x_1$ is purely from entropy!

  - Note that also as before, the slope of ΔS vs x_1 is infinite at 0 and 1.

    ■ This reflects the fact that mixing is a more purely entropic effect in the limit of very little solute (i.e., in the limit of an ideal solution).

7.4   Office Hours (PGS)

2/25:   • Plotting the coexistence curve and determining the Maxwell equal area contraction line mathematically.

- You can do these things with Mathematica and numerical approximations.
- PGS does not know of an easy way to do this by hand. It looks like I would have to go all the way through the cubic formula and integrals.

• I'm getting confused on treating the van der Waals equation as a cubic in $\overline{V}$, because it's graph doesn't ever cross the x-axis, and, in fact, the equation is asymptotic to both the x- and y-axes. So what are its roots, and exactly what properties of it as a cubic are preserved?

- It is cubic because it is cubic in $\overline{V}$ (and solving for $\overline{V}$ given P, T requires solving a cubic), not because it looks like the plot of a cubic function.

• Why do intermolecular interactions behave the same way as intramolecular bonding interactions? B/c we used the Lennard-Jones potential for bond distance initially, and now we've applied it to two molecules interacting through their polarity?

- The Lennard-Jones potential only applies to spherically symmetric distributions (e.g., not H_2O at short distances).
- Not molecules of strong dipole or charge transfer either.
- Thus perfect for **rare** (or inert) gases.
- r^{-6} works well for any solids that are not charged.

• What is the σ in the hard sphere potential? Isn't it the radius of the hard sphere? Because McQuarrie and Simon (1997) says it's the diameter multiple times.

- If the molecule centered at the origin is a hard sphere of radius $\sigma/2$ and the molecule approaching the hard sphere centered at the origin is also a hard sphere of radius $\sigma/2$, then they won't interact until their centers are a distance σ apart.

• Why can we use the ideal gas law to relate B_{iV} and B_{iP}?

• PSet 3, Question 2.

- Use the two state model from class. Use a partition function with two states for N particles.
- Curie's law probably isn't gonna be valid in this regime.
- You need the heat capacity at 4 kelvin via the Debye model. You'll need the Debye temperature from the internet.

7.5   Chapter 16: The Properties of Gases

From McQuarrie and Simon (1997).

• Since the results of the Lennard-Jones potential can't be evaluated analytically, we often use other approximations that can be.

• **Hard-sphere potential**: The potential of a hard sphere of radius σ. *Given by*

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases}$$

- This is the simplest representative potential.
- Despite its simplicity, it does account for the finite size of molecules, which turns out to be the dominant feature in determining the structure of liquids and solids.

- It does not account for intermolecular attractions, but since such attractions lessen as temperature increases, it is a good model for that condition.

- Under the hard-sphere potential,

$$B_{2V}(T) = -2\pi N_A \int_0^\infty \left(e^{-u(r)/k_B T} - 1\right) r^2 \, dr$$

$$= -2\pi N_A \left[\int_0^\sigma (0-1)r^2 \, dr + \int_\sigma^\infty (1-1)r^2 \, dr\right]$$

$$= \frac{2\pi\sigma^3 N_A}{3}$$

  - Thus, $B_{2V}(T)$ is equal to $1/2$ the volume of N_A hard spheres of radius σ.
  - Although this formula for the second virial coefficient is not temperature dependent, it is indeed a good approximation at high temperatures, just the same way the potential is.

- **Square-well potential**: The potential of a hard-sphere of radius σ that is attractive at a consistent level from its surface up until a finite distance away. *Given by*

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$$

  - ε is the depth of the well and $(\lambda - 1)\sigma$ is its width.

- Under the square-well potential,

$$B_{2V}(T) = -2\pi N_A \left[\int_0^\sigma (0-1)r^2 \, dr + \int_\sigma^{\lambda\sigma} (e^{\varepsilon/k_B T} - 1)r^2 \, dr + \int_{\lambda\sigma}^\infty (1-1)r^2 \, dr\right]$$

$$= -2\pi N_A \left[-\frac{\sigma^3}{3} + \frac{\sigma^3}{3}(\lambda^3 - 1)(e^{\varepsilon/k_B T} - 1) + 0\right]$$

$$= \frac{2\pi\sigma^3 N_A}{3}[1 - (\lambda^3 - 1)(e^{\varepsilon/k_B T} - 1)]$$

- The agreement of the square-well potential with experimental data is very good, but it does have 3 adjustable parameters.

- Relating the second virial coefficient to the van der Waals constants.

  - With the help of the expansion $1/(1-x) = 1 + x + x^2 + \cdots$, we have that

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

$$= \frac{RT}{\overline{V}} \frac{1}{1 - b/\overline{V}} - \frac{a}{\overline{V}^2}$$

$$= \frac{RT}{\overline{V}} \left[1 + \frac{b}{\overline{V}} + \frac{b^2}{\overline{V}^2} + \cdots\right] - \frac{a}{\overline{V}^2}$$

$$= \frac{RT}{\overline{V}} + (RTB - a)\frac{1}{\overline{V}^2} + \frac{RTb^2}{\overline{V}^3} + \cdots$$

  - It follows that

$$Z = \frac{P\overline{V}}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\overline{V}} + \frac{b^2}{\overline{V}^2} + \cdots$$

– Thus,

$$B_{2V}(T) = b - \frac{a}{RT}$$

for the van der Waals equation.

- Relating the van der Waals constants to the Lennard-Jones parameters.

  – Consider the following intermolecular potential, which is a hybrid of the hard-sphere and Lennard-Jones potentials.

  $$u(r) = \begin{cases} \infty & r < \sigma \\ -\frac{c_6}{r^6} & r > \sigma \end{cases}$$

  – We can now calculate $B_{2v}(T)$ in terms of $u(r)$ with the help of the approximation $e^x = 1 + x$ (applicable since the argument of the exponent function will be very small).

  $$\begin{aligned} B_{2V}(T) &= -2\pi N_A \left[\int_0^\sigma (0-1)r^2\, dr + \int_\sigma^\infty (e^{c_6/k_B T r^6} - 1)r^2\, dr \right] \\ &= \frac{2\pi\sigma^3 N_A}{3} - \frac{2\pi N_A c_6}{k_B T} \int_\sigma^\infty \frac{1}{r^6} \cdot r^2\, dr \\ &= \frac{2\pi\sigma^3 N_A}{3} - \frac{2\pi N_A c_6}{k_B T} \left[-\frac{1}{3r^3} \right]_\sigma^\infty \\ &= \frac{2\pi\sigma^3 N_A}{3} - \frac{2\pi N_A c_6}{3k_B T \sigma^3} \end{aligned}$$

  – It follows by comparison with the result from the previous section that

  $$a = \frac{2\pi N_A^2 c_6}{3\sigma^3} \qquad\qquad b = \frac{2\pi\sigma^3 N_A}{3}$$

  – Physical interpretations: $a \propto c_6$ and b is one-half the volume of the molecules.

- In a similar fashion, we can relate $B_{2V}(T)$ to the Redlich-Kwong constants and Peng-Robinson functions.

  $$B_{2V}(T) = B - \frac{A}{RT^{3/2}} \qquad\qquad B_{2V}(T) = \beta - \frac{\alpha}{RT}$$

7.6   Chapter 22: Helmholtz and Gibbs Energies

From McQuarrie and Simon (1997).

- Generalizing the equation $\overline{G} = G^\circ + RT \ln Q$ to the case of a real gas.

  – We begin by substituting the virial expansion in terms of pressure into the equation $(\partial \overline{G}/\partial P)_T = \overline{V}$.

  $$\begin{aligned} \left(\frac{\partial \overline{G}}{\partial P} \right)_T &= \overline{V} \\ &= \frac{RT}{P} \left[1 + B_{2P}(T)P + B_{3P}(T)P^2 + \cdots \right] \\ \int_{P^{id}}^P d\overline{G} &= RT \int_{P^{id}}^P \frac{dP'}{P'} + RT B_{2P}(T) \int_{P^{id}}^P dP' + RT B_{3P}(T) \int_{P^{id}}^P P'\, dP' \\ \overline{G}(T,P) &= \overline{G}(T,P^{id}) + RT \ln \frac{P}{P^{id}} + RT B_{2P}(T)P + RT B_{3P}(T) \frac{P^2}{2} + \cdots \end{aligned}$$

  – Note that we neglect P_{id} in every term except the first because it is so close to zero.

– Substituting $\overline{G}(T, P^{\text{id}}) = G^\circ(T) + RT \ln P^{\text{id}}/P^\circ$ and combining the first two terms yields

$$\overline{G}(T, P) = G^\circ(T) + RT \ln \frac{P}{P^\circ} + RTB_{2P}(T)P + RTB_{3P}(T)\frac{P^2}{2} + \cdots$$

- The above equation is exact, but complicated and different for each gas (depending on the virial coefficients).

- It will be more convenient to, especially for calculations involving chemical equilibria, to define the **fugacity**.

- **Fugacity**: A state function of P and T describing the nonideality of the energy of a system. *Denoted by $\boldsymbol{f}$. Given by*

$$\overline{G}(T, P) = G^\circ(T) + RT \ln \frac{f(P, T)}{f^\circ}$$

- Fugacity must have the property that $f(P, T) \to P$ as $P \to 0$, so that the above equation can reduce to $\overline{G} = G^\circ + RT \ln P/P^\circ$.

- By setting the above equal to the virial expansion, we learn that

$$\frac{f(P, T)}{f^\circ} = \frac{P}{P^\circ} \exp\left[B_{2P}(T)P + B_{3P}(T)P^2 + \cdots\right]$$

- "The standard state of the real gas...is taken to be the corresponding ideal gas at one bar" (McQuarrie & Simon, 1997, p. 906).

    – Mathematically, $f^\circ = P^\circ$.

    – Note that we can also derive this from the virial expansion expression for $f(P, T)/f^\circ$ since all of the virial coefficients are equal to zero in the standard state.

- McQuarrie and Simon (1997) goes through the derivation of

$$\ln \frac{f}{P} = \int_0^P \left(\frac{\overline{V}}{RT} - \frac{1}{P'}\right) \mathrm{d}P'$$

exactly as in class.

    – The above equation allows us to calculate the ratio of the fugacity to the pressure of a gas at any pressure and temperature, given either P-V-T data or an equation of state.

- **Fugacity coefficient**: The following ratio. *Denoted by $\boldsymbol{\gamma}$. Given by*

$$\gamma = \frac{f}{P}$$

- Also note the equation

$$\ln \gamma = \int_0^P \frac{Z - 1}{P'} \mathrm{d}P'$$

and that we can use this equation with the reduced pressure.

7.7   Chapter 23: Phase Equilibria

From McQuarrie and Simon (1997).

2/27:
- **Gibbs phase rule**: The number of components C and the number of phases P in a system are related to the number of degrees of freedom F by the equation

$$F = C - 2 - P$$

- Describes phase diagrams.

- **Vapor pressure**: The pressure at which solid and gas or liquid and gas are in equilibrium.

- **Solid-gas coexistence curve**: The curve separating the solid and gas regions of a phase diagram.
    - At points along this curve, the system will be in equilibrium between solid and gas.
    - As such, this curve specifies the vapor pressure as a function of temperature.

- **Triple point**: The point of intersection of the three lines in a phase diagram, at which the solid, liquid, and gaseous phases of the substance coexist at equilibrium.

- "Within a single-phase region, both the pressure and the temperature must be specified, and we say that there are two degrees of freedom within a single-phase region of a pure substance" (McQuarrie & Simon, 1997, p. 927).

- "Along any of the coexistence curves, either the pressure or the temperature alone is sufficient to specify a point on the curve, so we say that there is one degree of freedom" (McQuarrie & Simon, 1997, p. 927).

- "The triple point is a fixed point, so there are no degrees of freedom there" (McQuarrie & Simon, 1997, p. 927).

- Thus, the number of degrees of freedom f is related to the number of phases in equilibrium by the equation

$$f = 3 - p$$

- **Normal melting point**: The temperature at which a substance melts under $1\,\text{atm}$ of pressure.

- **Standard melting point**: The temperature at which a substance melts under $1\,\text{bar}$ of pressure.

- **Boiling point**: The temperature at which the vapor pressure equals the atmospheric pressure.

- **Normal boiling point**: The boiling point at $1\,\text{atm}$.

- **Standard boiling point**: The boiling point at $1\,\text{bar}$.

- **Sublime**: To pass directly from the solid to the gas phase.

- H_2O, antimony, and bismuth all expand upon freezing.

- **Orthobaric densities**: The densities of two phases that are in equilibrium with each other (i.e., of a substance along a coexistence curve).

- The orthobaric densities of the liquid and gas phases approach each other as $T \to T_c$.

- $\Delta \overline{H}_{\text{vap}}$ decreases as $T \to T_c$.
    - This is because $\Delta \overline{S}_{\text{vap}} \to 0$ as $T \to T_c$ (the phases become less distinct), so naturally $\Delta \overline{H}_{\text{vap}} = T \Delta \overline{S}_{\text{vap}} \to 0$ as $T \to T_c$.

- **Critical opalescence**: The fluctuations between the liquid and vapor state of a fluid very near its critical point which scatter light very strongly, causing the substance in question to appear milky.

- Because of the critical point, it is possible to transform a gas into a liquid (or vice versa) without ever passing through a two-phase state. To do so, just follow a path out and around the critical point along the phase diagram.

- The solid-liquid coexistence curve does not end as abruptly as the liquid-gas coexistence curve since the differences between solid and liquid are ones of intrinsically different structure as opposed to degree of motion. Thus, the solid-liquid coexistence curve of a substance either continues on indefinitely or dead ends into another solid state (some substances have multiple, such as water, which can be solid even above its normal boiling point at very high pressures).

- Connecting the Gibbs energy of a substance to its phase diagram.
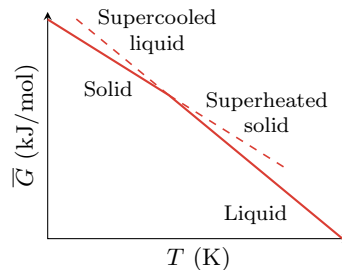
Figure 7.2: The energetic stabilization of phase transitions.

- Recall that the plot of $\overline{G}(T)$ for a substance is a continuous curve with two discontinuities in the slope (one for each phase transition).

- Consider the point at one such discontinuity (say between the solid and liquid phases). If we were to extrapolate the liquid line to lower temperatures, we would be describing a **supercooled liquid** and vice versa with a **superheated solid**.

- However, a substance does not ordinarily exist as a liquid below its melting point because its Gibbs energy is reduced by transitioning to a solid. Similarly, a substance does not ordinarily exist as a solid above its melting point because its Gibbs energy is reduced by transitioning to a liquid.

- The influence of $G = H - TS$: At low temperatures, TS is small, so we favor a small H (and solids have the lowest enthalpy of the three phases). Likewise, at higher temperatures, a larger H can be evened out by the large TS.

- Note that we can do the same kind of analysis for $\overline{G}(P)$. However, in this case, we have the chance that with some substances (such as water), we will go from gas to solid to liquid as pressure increases.

- **Supercooled liquid**: A liquid with temperature below its freezing point that is not nevertheless not a solid.

- **Superheated solid**: A solid with temperature above its melting point.

- **Metastable state**: A state of a substance that has greater molar Gibbs energy than the usual state encountered under some conditions.

- Consider a system consisting of the gas and liquid phases of a pure substance in equilibrium with each other.

- If G^l is the Gibbs energy of the liquid phase and G^g is the Gibbs energy of the gaseous phase, then the total Gibbs energy G of this system is $G = G^l + G^g$.

- Now if dn moles are transferred from the liquid phase to the vapor phase at constant T, P, the corresponding change in Gibbs energy is

$$dG = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} dn^g + \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T} dn^l$$

- Since $dn^l = -dn^g$, it follows that

$$dG = \left[\left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} - \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T}\right] dn^g$$

- Rewriting in terms of **chemical potentials**, we have

$$dG = (\mu^g - \mu^l)\, dn^g$$

- **Chemical potential**: The change in Gibbs energy of a substance in a phase α with respect to the change in the number of moles of the substance present. *Denoted by* $\boldsymbol{\mu^\alpha}$. *Given by*

$$\mu^\alpha = \left(\frac{\partial G^\alpha}{\partial n^\alpha}\right)_{P,T}$$

  - "Just as electric current flows from a higher electric potential to a lower electric potential, matter 'flows' from a higher chemical potential to a lower chemical potential" (McQuarrie & Simon, 1997, p. 937).
  - An equivalent definition is that since $G \propto n$ for any system, μ is the proportionality constant. Here's how we know the definitions are equivalent:

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{P,T} = \left(\frac{\partial n\mu(T, P)}{\partial n}\right)_{P,T} = \mu(T, P)$$

    ■ In other words, μ is an intensive quantity representing the same thing as Gibbs energy.

- If two phases are in equilibrium between liquid and gas, then since $dG = 0$ and $dn^g \neq 0$, $\mu^g = \mu^l$.

- "If the two phases are not in equilibrium with each other, a spontaneous transfer of matter from one phase to the other will occur in the direction such that $dG < 0$" (McQuarrie & Simon, 1997, p. 937).

  - For example, if $\mu^g > \mu^l$, we must have $dn^g < 0$ for dG to be negative, meaning that matter will transfer from the vapor phase to the liquid phase.

- McQuarrie and Simon (1997) derives the equation for dP/dT exactly as in class.

- **Clapeyron equation**: The relation between the slope of the two-phase boundary line in a phase diagram and the values of $\Delta_{\text{trs}}\overline{H}$ and $\Delta_{\text{trs}}\overline{V}$ for a transition between those two phases. *Given by*

$$\frac{dP}{dT} = \frac{\Delta_{\text{trs}}\overline{H}}{T\Delta_{\text{trs}}\overline{V}}$$

- Note that $\Delta_{\text{fus}}\overline{H}$ and $\Delta_{\text{fus}}\overline{V}$ do vary with pressure, but not always significantly.

- **Clausius-Clapeyron equation**: The relation between the vapor pressure of a liquid and its temperature. *Given by*

$$\frac{d\ln P}{dT} = \frac{\Delta_{\text{vap}}\overline{H}}{RT^2}$$

  - Two assumptions were made in the derivation of the Clausius-Clapeyron equation form the Clapeyron equation: $\overline{V}^g \gg \overline{V}^l$ and the vapor pressure is so low that the gas can be treated as ideal (so we can replace $\overline{V}^g$ with RT/P).

- – Thus, the Clausius-Clapeyron equation is easier to use, but the Clapeyron equation is more general.

- – Furthermore, if $\Delta_{\mathrm{vap}}\overline{H}$ does not vary with temperature over the integration limits of T, then

$$\ln\frac{P_2}{P_1} = -\frac{\Delta_{\mathrm{vap}}\overline{H}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- Taking the indefinite integral of the Clausius-Clapeyron equation shows that $\ln P$ and $1/T$ have a linear relation with slope $-\Delta_{\mathrm{vap}}\overline{H}/R$.

  - – This relation can be used to experimentally measure $\Delta_{\mathrm{vap}}\overline{H}$.

  - – By representing $\Delta_{\mathrm{vap}}\overline{H}$ as a Taylor polynomial in T, we can also find more exact values for it based on (P, T) data.

- McQuarrie and Simon (1997) shows that the slope of the solid-gas coexistence curve is greater than the slope of the liquid-gas coexistence curve the same way PGS did in class.

- Deriving an expression for the chemical potential μ in terms of the partition function Q.

  - – We know that

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} \qquad\qquad S = k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k_B \ln Q$$

  - – It follows that

$$A = U - TS$$
$$= -k_B T \ln Q$$

  - – Additionally, the total differential of $A(T, V, n)$ is

$$dA = \left(\frac{\partial A}{\partial T}\right)_{n,V} dT + \left(\frac{\partial A}{\partial V}\right)_{n,T} dV + \left(\frac{\partial A}{\partial n}\right)_{T,V} dn$$
$$= -S\,dT - P\,dV + \left(\frac{\partial A}{\partial n}\right)_{T,V} dn$$

  and the total differential of $G(T, P, n)$ is

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial n}\right)_{T,P} dn$$
$$= -S\,dT + V\,dP + \mu\,dn$$

  - – But since

$$dG = dA + d(PV) = -S\,dT + V\,dP + \left(\frac{\partial A}{\partial n}\right)_{T,V} dn$$

  we have by direct comparison that

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

  - – It follows by substituting our previous expression for $A(Q)$ that

$$\mu = -k_B T \left(\frac{\partial \ln Q}{\partial n}\right)_{V,T} = -RT \left(\frac{\partial \ln Q}{\partial N}\right)_{V,T}$$

- For an ideal gas where $Q = q^N/N!$, we have by Stirling's approximation that

$$
\begin{aligned}
\mu &= -RT\frac{\partial}{\partial N}\left(\ln\frac{q^N}{N!}\right) \\
&= -RT\frac{\partial}{\partial N}(N\ln q - N\ln N + N) \\
&= -RT(\ln q - \ln N - 1 + 1) \\
&= -RT\ln\frac{q(V,T)}{N}
\end{aligned}
$$

- Note that this expression for μ in terms of the partition function easily yields one for G in terms of the partition function via $G = n\mu$.

- McQuarrie and Simon (1997) discusses alternate forms of μ and μ°.

7.8 Chapter 24: Solutions I — Liquid-Liquid Solutions

From McQuarrie and Simon (1997).

2/28:
- In this chapter, we consider in particular solutions of two volatile liquids.

- Having discussed the thermodynamics of one-component systems, we now move into the thermodynamics of two-component systems, though many of our results generalize to multicomponent solutions.

- McQuarrie and Simon (1997) analyzes $G(T, P, n_1, n_2)$ as in class.

- **Partial molar entropy**. The following quantity. *Denoted by $\overline{S}_j$. Given by*

$$
\overline{S}_j = \left(\frac{\partial S}{\partial n_j}\right)_{T,P,n_i}
$$

for all $i \neq j$.

- **Partial molar volume**. The following quantity. *Denoted by $\overline{V}_j$. Given by*

$$
\overline{V}_j = \left(\frac{\partial V}{\partial n_j}\right)_{T,P,n_i}
$$

for all $i \neq j$.

- In general, extensive thermodynamic properties Y have associated partial molar quantities $\overline{Y}_j$ defined analogously to the above.

- **Binary solution**: A solution composed of two different liquids.

3/1:
- Deriving a formula for G in terms of n_1, n_2 at constant T, P.

  - At constant T, P, we have that
  $$
  dG = \mu_1\,dn_1 + \mu_2\,dn_2
  $$

  - Now imagine that we increase the amount of each component linearly from 0 to n_i.

  - Then the amount of each component present at a given time can be represented as $n(\lambda) = n_i\lambda$ where λ varies from 0 to 1.

  - It follows that $dn_i = n_i\,d\lambda$ and, since G is extensive, $dG = G\,d\lambda$.

- Therefore, it follows from the above equation that

$$\int_0^1 G\,\mathrm{d}\lambda = \int_0^1 n_1\mu_1\,\mathrm{d}\lambda + \int_0^1 n_2\mu_2\,\mathrm{d}\lambda$$

$$G\int_0^1 \mathrm{d}\lambda = n_1\mu_1\int_0^1 \mathrm{d}\lambda + n_2\mu_2\int_0^1 \mathrm{d}\lambda$$

$$G(T, P, n_1, n_2) = \mu_1 n_1 + \mu_2 n_2$$

- Similarly,

$$Y = \sum_{i=1}^m \overline{Y}_i n_i$$

for any quantity Y (like entropy or volume) in an m-component system.

- Note that this implies that the final volume of a solution is not necessarily a straight sum of the component volumes, but rather depends on the partial molar volumes.

- Extending $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P$ into multicomponent systems.

    - If we consider the Gibbs energy as $G(T, P, n_1, \ldots, n_m)$, then since $G = H - TS$, we have that

$$\left(\frac{\partial G}{\partial n_j}\right)_{T,P,n_i} = \left(\frac{\partial H}{\partial n_j}\right)_{T,P,n_i} - T\left(\frac{\partial S}{\partial n_j}\right)_{T,P,n_i}$$

    - It follows that

$$\mu_j = \overline{G}_j = \overline{H}_j - T\overline{S}_j$$

    - Using the Maxwell relations

$$\overline{S}_j = -\left(\frac{\partial \mu_j}{\partial T}\right)_{P,n_i} \qquad\qquad \overline{V}_j = \left(\frac{\partial \mu_j}{\partial P}\right)_{T,n_i}$$

    and the total differential of μ_j, we can determine that

$$\mathrm{d}\mu_j = -\overline{S}_j\,\mathrm{d}T + \overline{V}_j\,\mathrm{d}P$$

- Similarly, the Gibbs-Helmholtz equation for multicomponent systems is

$$\left(\frac{\partial \mu_j/T}{\partial T}\right)_P = -\frac{\overline{H}_j}{T^2}$$

- **Gibbs-Duhem equation**: The relation between the chemical potential of one component in a binary solution as a function of composition to the other. *Given by*

$$n_1\,\mathrm{d}\mu_1 + n_2\,\mathrm{d}\mu_2 = 0$$

or

$$x_1\,\mathrm{d}\mu_1 + x_2\,\mathrm{d}\mu_2 = 0$$

    - Derivation: The total differential of $\mathrm{d}G = n_1\mu_1 + n_2\mu_2$ is

$$\mathrm{d}G = \mu_1\,\mathrm{d}n_1 + \mu_2\,\mathrm{d}n_2 + n_1\,\mathrm{d}\mu_1 + n_2\,\mathrm{d}\mu_2$$

    from which we can subtract $\mathrm{d}G = \mu_1\,\mathrm{d}n_1 + \mu_2\,\mathrm{d}n_2$ to get the former form and divide that by $n_1 + n_2$ to get the latter form.

- Note that we can also derive Gibbs-Duhem type equations for other intensive properties (such as the partial molar volume).

- Y^*: A property of a pure substance.

    - For example, μ_1 denotes the chemical potential of substance 1 (which may be affected by $n_2, \ldots, n_m$) whereas μ_1^* denotes μ_1 at $x_1 = 1$.

- If one component of a binary solution obeys **Raoult's law** over the complete concentration range, the other component does, too.

    - Suppose the chemical potential of one component in a binary solution is given by

    $$\mu_2 = \mu_2^* + RT \ln x_2$$

    - Then

    $$d\mu_1 = -\frac{x_2}{x_1} \, d\mu_2$$
    $$= -\frac{x_2}{x_1} \cdot RT \frac{dx_2}{x_2}$$
    $$= -RT \frac{dx_2}{x_1}$$
    $$= RT \frac{dx_1}{x_1}$$
    $$\int_1^{x_1} d\mu_1 = RT \int_1^{x_1} \frac{dx_1'}{x_1'}$$
    $$\mu_1 = \mu_1^* + RT \ln x_1$$

- McQuarrie and Simon (1997) derives, exactly as in class, $\mu_j^\alpha = \mu_j^\beta$ for any component j and two phases α, β in equilibrium.

- An important consequence of this is that "the chemical potential of each component in liquid solution can be measured by the chemical potential of that component in the vapor phase" (McQuarrie & Simon, 1997, p. 970).

    - If the pressure P_j of the vapor phase is sufficiently low[1], we may treat it as ideal and employ

    $$\mu_j^{\text{sln}} = \mu_j^{\text{vap}} = \mu_j^\circ(T) + RT \ln P_j$$

    - It follows if j is pure ($x_j = 1$) that

    $$\mu_j^*(l) = \mu_j^\circ(T) + RT \ln P_j^*$$

    - By subtracting the above two equations, we can derive an expression for the the chemical potential of component j in solution in terms of its chemical potential as a pure substance, its vapor pressure, and its vapor pressure as a pure substance.

    $$\mu_j^{\text{sln}} = \mu_j^*(l) + RT \ln \frac{P_j}{P_j^*}$$

- **Raoult's law**: The partial vapor pressure of each component of a solution is directly proportional to its mole fraction in solution. *Given by*

    $$P_j = x_j P_j^*$$

    - Note that x_j reflects the fraction of the solution *surface* that is occupied by molecules of type j (since it is these molecules that can escape into the vapor phase).

---

[1]Technically, we should use fugacities throughout, but vapor pressures under standard conditions typically are small enough so that the difference between the pressure and the fugacity is negligible.

- **Ideal solution**: A solution that obeys Raoult's law over the entire composition range.

- At a molecular level, ideal binary solutions look like two types of molecules distributed randomly throughout solution.

  - This occurs when the molecules are of similar size and shape, and the intermolecular forces are all similar.

- Between our expression for μ_j^{sln} in terms of the characteristics of the pure substance and Raoult's law, we have that

$$\mu_j^{\text{sln}} = \mu_j^*(l) + RT \ln x_j$$

- Deriving an expression for the total vapor pressure of an ideal binary solution.

$$\begin{aligned} P_{\text{tot}} &= P_1 + P_2 \\ &= x_1 P_1^* + x_2 P_2^* \\ &= (1 - x_2) P_1^* + x_2 P_2^* \\ &= P_1^* + x_2 (P_2^* - P_1^*) \end{aligned}$$

  - The above formula is a straight line that evaluates to P_1^* at $x_2 = 0$ and P_2^* at $x_2 = 1$, as we would expect (see Figure 7.1).

- Deriving an expression for the total vapor pressure of a binary solution in terms of the mole fraction y_2 of component 2 in the vapor phase.

  - By Dalton's law of partial pressures, which asserts that the partial pressure P_2 of the vapor of component 2 is equal to its mole fraction y_2 in the vapor phase, we have that

$$y_2 = \frac{P_2}{P_{\text{tot}}} = \frac{x_2 P_2^*}{P_{\text{tot}}} = \frac{x_2 P_2^*}{P_1^* + x_2 (P_2^* - P_1^*)}$$

  - Solving for x_2 yields

$$x_2 = \frac{P_1^* y_2}{P_2^* - y_2 (P_2^* - P_1^*)}$$

  - Therefore,

$$\begin{aligned} P_{\text{tot}} &= P_1^* + x_2 (P_2^* - P_1^*) \\ &= P_1^* + \frac{P_1^* y_2}{P_2^* - y_2 (P_2^* - P_1^*)} (P_2^* - P_1^*) \end{aligned}$$

- **Pressure-composition diagram**: A diagram that plots the total vapor pressure as a function of the composition of both the liquid phase and the vapor phase.
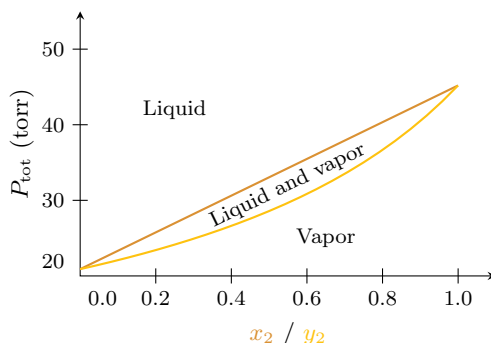

Figure 7.3: Pressure-composition diagram for a 1-propanol/2-propanol solution.

- In Figure 7.3, the brown line plots the total vapor pressure as a function of the composition of the liquid phase, and the yellow line plots the total vapor pressure as a function of the composition of the vapor phase (as per the equations derived above).

- A vertical line in Figure 7.3 corresponds to a single solution as pressure varies. If the vertical line is not at zero or 1, we see that high pressures yield exclusively the liquid phase, low pressures yield exclusively the vapor phase, and there is a region of pressures where both liquid and vapor coexist.

- **Tie line**: A horizontal line in a pressure-composition diagram that, for a given pressure, connects the concentration that will give entirely liquid to the composition that will give entirely vapor.

- Determining the relative amounts of liquid and vapor.

  - The mole fractions of component 2 in the liquid and vapor phases are, respectively,

$$x_2 = \frac{n_2^l}{n_1^l + n_2^l} = \frac{n_2^l}{n^l} \qquad\qquad y_2 = \frac{n_2^g}{n_1^g + n_2^g} = \frac{n_2^g}{n^g}$$

  - The overall mole fraction of component 2 is

$$x_a = \frac{n_2^l + n_2^g}{n^l + n^g}$$

  - It follows that

$$x_a(n^l + n^g) = x_2 n^l + y_2 n^g \frac{n^l}{n^g} \qquad\qquad = \frac{y_2 - x_a}{x_a - x_2}$$

- **Lever rule**: The balance of the number of moles in each phase and the excess fractions of liquid and vapor. *Given by* the above.

  - "Note that $n^l = 0$ when $x_a = y_2$ (vapor curve) and that $[n^g = 0]$ when $x_a = x_2$ (liquid curve)" (McQuarrie & Simon, 1997, p. 973).

- **Temperature-composition diagram**: A diagram that plots the composition of the solution and vapor phases at various temperatures.

  - Pressure is held constant in such a diagram, so choose 760 torr.
  - It follows that the mole percent of component 1 at this pressure is

$$760\,\text{torr} = P_2^* - x_1(P_2^* - P_1^*)$$
$$x_1 = \frac{P_2^* - 760\,\text{torr}}{P_2^* - P_1^*}$$

  - We can then find P_1^*, P_2^* at a given temperature either from a table the Clausius-Clapeyron equation (though the latter will be an approximation).
  - Lastly, we can find y_1 as before.

- Fractional distillation in a temperature-composition diagram.

  - During fractional distillation, a substance is repeatedly heated up, some vapor removed, and then heated up higher as now possible.
  - In Figure 7.4, we can see how at any given ratio, we can only heat up the liquid so much before we begin vaporizing both liquids, but by removing some vapor (increasing the concentration of the less volatile substance), we can now heat it up more.
  - The diagram also provides a pictoral representation of the law of diminishing returns (as we can never get all the way over to the top-right corner).
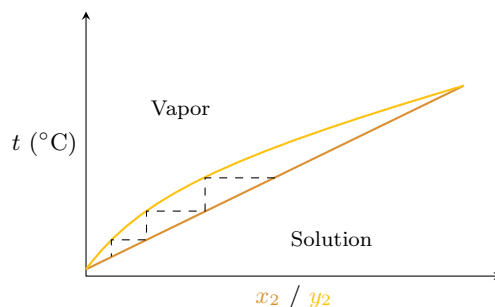
Figure 7.4: Temperature-composition diagram for a 1-propanol/2-propanol solution.

- Calculating the energy of mixing $\Delta_{\mathrm{mix}}G^{\mathrm{id}}$ of two ideal solutions of pure components.

$$\Delta_{\mathrm{mix}}G^{\mathrm{id}} = G^{\mathrm{sln}}(T, P, n_1, n_2) - G_1^*(T, P, n_1) - G_2^*(T, P, n_2)$$
$$= n_1\mu_1^{\mathrm{sln}} + n_2\mu_2^{\mathrm{sln}} - n_1\mu_1^* - n_2\mu_2^*$$
$$= n_1(\mu_1^* + RT\ln x_1) + n_2(\mu_2^* + RT\ln x_2) - n_1\mu_1^* - n_2\mu_2^*$$
$$= RT(n_1\ln x_1 + n_2\ln x_2)$$

  - Since $x_1, x_2 < 1$, we know $\Delta_{\mathrm{mix}}G^{\mathrm{id}} < 1$, i.e., ideal solutions always form spontaneously from their separate components.

- The entropy of mixing of two ideal solutions of pure components.

$$\Delta_{\mathrm{mix}}S^{\mathrm{id}} = -\left(\frac{\partial\Delta_{\mathrm{mix}}G^{\mathrm{id}}}{\partial T}\right)_{P,n_1,n_2} = -R(n_1\ln x_1 + n_2\ln x_2)$$

  - This result is identical to that for the mixing of two ideal gases.
  - However, there are marked differences between solutions and gases, namely in the extent of inter-molecular interactions. The similarity is accounted for by the fact that "in an ideal solution, the interactions in the mixture and those in the pure liquids are essentially identical" (McQuarrie & Simon, 1997, p. 977).

- We can also calculate that

$$\Delta_{\mathrm{mix}}V^{\mathrm{id}} = \left(\frac{\partial}{\partial\Delta_{\mathrm{mix}}G^{\mathrm{id}}}\right)_{T,n_1,n_2} = 0 \qquad \Delta_{\mathrm{mix}}H^{\mathrm{id}} = \Delta_{\mathrm{mix}}G^{\mathrm{id}} + T\Delta_{\mathrm{mix}}S^{\mathrm{id}} = 0$$

  - These results follow from the similarities in particles shape and size, and interaction energy, respectively, assumed for an ideal solution.

Week 8

Solutions

8.1 Vapor Pressure Lowering and Consequences

- Colligative properties.

    - Vapor pressure lowering.
    - Boiling point elevation for non-volatile solutes.
    - Freezing point depression for solutes (excluding solids).
    - Osmotic pressure.

- **Vapor pressure lowering**: The process of adding less volatile solutes to lower the overall vapor pressure via Raoult's law.

- **Boiling point elevation**: The increase in the normal boiling point of a mixture due to vapor pressure lowering.
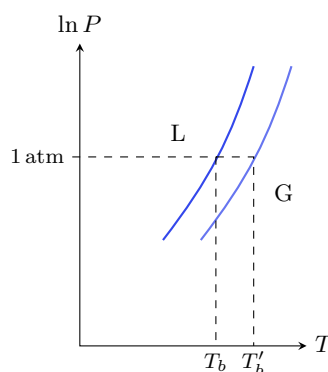
Figure 8.1: Boiling point elevation.

    - In Figure 8.1, the dark blue line is the original liquid-gas coexistence curve and the light blue line is the liquid-gas coexistence curve with vapor pressure lowering — notice how at any given temperature, the corresponding pressure represented by the light blue line is lower than that given by the dark blue line.
    - However, we still need to achieve a vapor pressure of $1\,\mathrm{atm}$ for the liquid to boil.
    - We can get to such a pressure with a higher temperature, i.e., by heating the liquid to T_b' instead of just T_b.

- Calculating the change in the boiling point ΔT_b.

– We can calculate the boiling point elevation from the Clausius-Clapeyron equation.

$$\frac{\Delta P}{\Delta T_b} = \frac{\Delta \overline{H}}{T_b \Delta \overline{V}}$$

$$\Delta T_b = P^*(1-x)\frac{T_b \Delta \overline{V}}{\Delta \overline{H}}$$

$$= P^*(1-x)\frac{T_b \overline{V}_g}{\Delta \overline{H}}$$

$$= P^*(1-x)\frac{T_b R T_b}{P^* \Delta \overline{H}}$$

$$= \frac{RT_b^2}{\Delta H}(1-x)$$

where x is the mole fraction of solutes.

– We can also derive the above result from the chemical potential, where we get to the first to the second equation below because (standard) chemical potentials are equal at equilibrium.

$$\mu_l^\circ(T) + RT \ln x_1 = \mu_g^\circ(T) + RT \ln \frac{P}{P_0}$$

$$RT \ln x_1 = RT \ln \frac{P}{P_0} + [\mu_g^\circ(T) - \mu_l^\circ(T)]$$

$$= RT \ln \frac{P}{P_0} + [\Delta \overline{H}_{\text{vap}} - T\Delta \overline{S}_{\text{vap}}]$$

$$= RT \ln \frac{P}{P_0} + [\Delta \overline{H}_{\text{vap}} - T_b \Delta \overline{S}_{\text{vap}} + (T_b - T)\Delta \overline{S}_{\text{vap}}]$$

$$= RT \ln \frac{P}{P_0} + \Delta T_b \cdot \frac{\Delta \overline{H}_{\text{vap}}}{T_b}$$

$$\Delta T_b = -\frac{RT_b^2}{\Delta \overline{H}_{\text{vap}}} \ln x_1$$

$$= -\frac{RT_b^2}{\Delta \overline{H}_{\text{vap}}} \ln(1-x_2)$$

$$\approx \frac{RT_b^2}{\Delta \overline{H}_{\text{vap}}} x_2$$

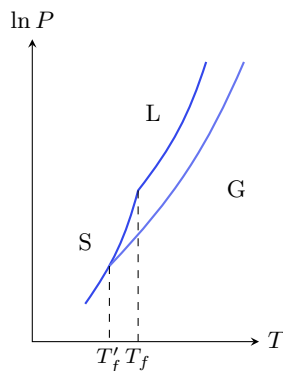• **Freezing point depression**: The decrease in the normal melting point of a mixture due to vapor pressure lowering.

Figure 8.2: Freezing point depression.

– We know that $\mu_g^\circ(T_f) = \mu_l^\circ(T_f)$. Thus,

$$\mu_g^\circ(T) = \mu_l^\circ(T) + RT \ln x_i$$
$$RT \ln x_i = \mu_g^\circ(T) - \mu_l^\circ(T)$$
$$= \Delta \overline{H}_{\text{fus}}(T) - T\Delta \overline{S}_{\text{fus}}$$
$$= (T_f - T)\Delta \overline{S}_{\text{fus}}$$
$$= (T_f - T)\frac{\Delta \overline{H}_{\text{fus}}}{T_f}$$
$$= -\Delta T_f \cdot \frac{\Delta \overline{H}_{\text{fus}}}{T_f}$$
$$\Delta T_f = -\frac{RT_f^2}{\Delta \overline{H}_{\text{fus}}} \ln x_1$$
$$\approx \frac{RT_f^2}{\Delta \overline{H}_{\text{fus}}} x_2$$

– The final result should be

$$\Delta T_f = -\frac{RT_f^2}{\Delta \overline{H}_{\text{fus}}} x_2$$

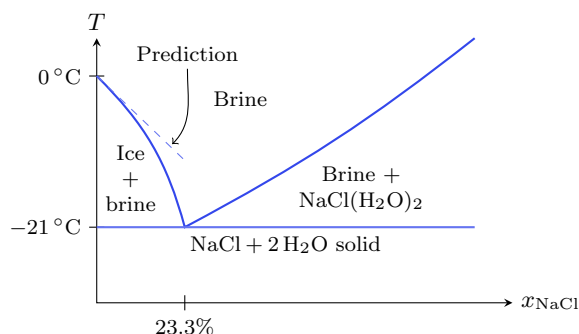- The freezing point of water as more and more salt is added.

Figure 8.3: Freezing point vs. solute concentration.

- Osmotic pressure.

  – Imagine a U-tube with a filter at the bottom that is porous to the solvent but nonporous to the solute.

  – We know from Gen Chem that there will be excess pressure on the side with the impurities.

  – Let $\pi = \rho g h$ be the extra pressure where h is the height difference between the two sides and ρ is the density of the solvent.

$$\mu_l^\circ = \mu_l = \mu_l^\circ + RT \ln x_1 + \pi \overline{V}$$
$$0 = RT \ln x_1 + \pi \overline{V}$$
$$\pi = \frac{RT}{\overline{V}} x_2$$

- Ocean salinity is about $1\,\text{M}$, so $\pi = 24\,\text{atm}$. That means that in the tube, the right hand side will rise about as much as the Sears tower. Thus, the minimum amount of pressure/work you need is the height of the Sears tower minus $24\,\text{atm}$. Still, this is far more efficient than distillation.

8.2   Nonideal Solutions

3/2:
- When solutions are not ideal, we see deviations from Raoult's Law (Figure 7.1).

  - However, all solutions follow Raoult's Law when they are nearly pure.
  - When the actual partial pressure is higher, that means the substance would rather be in the vapor phase. When the actual partial pressure is lower, that means there is a favorable interaction between particles (they'd rather be in the dissolved state).

- **Henry's Law**: Gives the tangent to the vapor pressure vs. mole percent graph at $x_1 = 0$. *Given by*

$$P_1 = k_H x_1$$

  as $x_1 \to 0$.

- We know that $A(g) \to A(\text{solv})$.

  - At equilibrium $\Delta \overline{G} = 0 = \Delta \overline{G}_{\text{solv}} + RT \ln x/P$.
  - Thus,

$$P = x e^{\Delta \overline{G}_{\text{solv}}/RT}$$

  - x is the mixing entropy, P is the gas phase entropy.

- Microscopic enthalpy and entropy of solvation contribute to Henry's law, in addition to mixing entropy.

  - Larger k_H means less soluble.

- Temperature dependence.

$$k_{H,cp} = k_{H,cp}^{\Theta} \exp\left[-C \cdot \left(\frac{1}{T} - \frac{1}{T^{\Theta}} \right) \right]$$

  - Θ indicates reference temperature.
  - It follows that as T increases, k_H increases.
    - For example, O_2 is less soluble in water at higher temperatures.
    - This is consistent with solvation being an exothermic process.

- The activity and activity coefficient of a solute. Using Raoult's law as the reference for fully miscible substances.

  - We have for an ideal solution that $\mu_i = \mu_i^* + RT \ln x_i$ and for an ideal gas that $\mu_i = \mu_i^* + RT \ln \frac{P_i}{P_i^*}$.
  - These two equations together imply Raoult's law.
  - Now we want to keep the nice form of the above equations even with nonideality, so we do something similar to defining fugacity by defining the **activity**.
  - $a_i \to x_i$ as $x_i \to 1$.
  - As $x_i \to 0$, we have that

$$\mu_i^* + RT \ln a_i = \mu_i^* + RT \ln \frac{P_i}{P_i^*}$$

$$= \mu_i^* + RT \ln \frac{k_H}{P_i^*} x_i$$

  i.e., $a_i \to k_H x_i / P_i^*$.
  - As a substance becomes less active, it becomes more reactive.

- **Activity**: A measure of the nonideality of solutions. *Denoted by $\boldsymbol{a_i}$. Given by*

$$\mu_i = \mu_i^* + RT \ln a_i$$

- **Activity coefficient**: The following ratio. *Denoted by* $\boldsymbol{\gamma}$. *Given by*

$$\gamma = \frac{a_i}{x_i}$$

- Example: Carbon disulfide/dimethoxymethane.

$x_{\mathrm{CS_2}}$	$P_{\mathrm{CS_2}}$ (torr)	$P_{\mathrm{CH_2(OMe)_2}}$ (torr)
0	0	587
0.1	109	529
1	514	0

Table 8.1: Pressure data for $\mathrm{CS_2}$ and $\mathrm{CH_2(OMe)_2}$.

- At $x_{\mathrm{CS_2}} = 0.1$, we have that $a_{\mathrm{CS_2}} = 109/514$.
- As $x \to 0$, $k_{H,\mathrm{CS_2}} = 1130 \,\mathrm{torr}$ so $a_{\mathrm{CS_2}} = \frac{1130}{514} x_{\mathrm{CS_2}}$.
- See McQuarrie and Simon (1997) for using Henry's law as the reference state.

- Nonideality above the Raoult's law diagonal: More "active" than the ideal mixture.

- Nonideality below the Raoult's law diagonal: Less active than at low concentration.

8.3 Quantifying Deviations from Raoult's Law

3/4:
- **Gibbs-Duhem relation**: A relation tying together the partial pressure of one substance to another, regardless of ideality/nonideality.

  - We begin with

$$\mathrm{d}G = \sum \mu_i \, \mathrm{d}n_i + \sum n_i \, \mathrm{d}\mu_i$$

  at constant temperature and pressure.
  - We also know from an earlier class that

$$G = \sum \mu_i n_i$$

  - Differentiating the above, we get

$$\mathrm{d}G = \sum \mu_i \, \mathrm{d}n_i + \sum n_i \, \mathrm{d}\mu_i$$

  - It follows by setting the above two equations equal to each other that

$$\sum n_i \, \mathrm{d}\mu_i = 0$$

- We can apply the Gibbs-Duhem relation to our expression for the chemical potential in terms of the activity coefficient.

  - From last time,

$$\mu_i = \mu_i^* + RT \ln(\gamma_i x_i)$$
$$\mathrm{d}\mu_i = RT \, \mathrm{d}(\ln \gamma_i + \ln x_i)$$

- It follows that

$$0 = n_1 \, d\mu_1 + n_2 \, d\mu_2$$

$$= \frac{1}{n_1 + n_2}(n_1 \, d\mu_1 + n_2 \, d\mu_2)$$

$$= \frac{n_1}{n_1 + n_2} RT \, d(\ln \gamma_1 + \ln x_1) + \frac{n_2}{n_1 + n_2} RT \, d(\ln \gamma_2 + \ln x_2)$$

$$= RT(x_1 \, d\ln x_1 + x_2 \, d\ln x_2 + x_1 \, d\ln \gamma_1 + x_2 \, d\ln \gamma_2)$$

$$= dx_1 + dx_2 + x_1 \, d\ln \gamma_1 + x_2 \, d\ln \gamma_2$$

$$= dx_1 - dx_1 + x_1 \, d\ln \gamma_1 + x_2 \, d\ln \gamma_2$$

$$= x_1 \, d\ln \gamma_1 + x_2 \, d\ln \gamma_2$$

- Takeaway: If we know the activity coefficient for one component across the whole range, we can find the activity coefficient for the other component.
- In other words, knowing the chemical potential for one component gives us the chemical potential for the other.

- Relating P_1, P_2 with the Gibbs-Duhem relation.

- We assume that we are in phase equilibrium. Thus, the chemical potential of the gas phase equals the chemical potential of the solution. In an equation,

$$\mu_1^* + RT \ln \frac{P_1}{P_1^*} = \mu_1 + RT \ln a_1$$

- Thus, applying the Gibbs-Duhem relation,

$$0 = x_1 \, d\ln P_1 + x_2 \, d\ln P_2$$

$$= x_1 \left(\frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} dx_1 + x_2 \left(\frac{\partial \ln P_2}{\partial x_2} \right)_{T,P} dx_2$$

$$= x_1 \left(\frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} - x_2 \left(\frac{\partial \ln P_2}{\partial x_2} \right)_{T,P}$$

- Takeaway: The slopes of the curves on a pressure-concentration diagram are related, regardless of ideality/nonideality.

- **Margules equation**: An expansion to capture the experimental $P(x)$ deviation from Raoult's law.

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3 + \cdots}$$

- An analytical form that gives us a good representation of experimentally-measured vapor pressures.
- Important features: Follows Henry's law at low concentrations of solute and Raoult's Law at high concentrations of solute.

- Margules equation covers Raoult's law and Henry's law.

- We have by the product rule of derivatives that

$$\frac{dP_1}{dx_1} = P_1^* \left[e^{\alpha x_2^2 + \beta x_2^3 + \cdots} + x_1(-2\alpha x_2 - 3\beta x_2^2 - \cdots)e^{\alpha x_2^2 + \beta x_2^3 + \cdots} \right]$$

- As $x_1 \to 1$, $dP_1/dx_1 \to P_1^*$. This can be seen because the above expression can be rewritten

$$\frac{dP_1}{dx_1} = P_1^* e^{\alpha x_2^2 + \beta x_2^3 + \cdots} \left[1 - 2\alpha x_1 x_2 - 3\beta x_1 x_2^2 - \cdots \right]$$

- ■ Implication: We recover Raoult's law as $x_1 \to 1$.
- ■ Additionally, this explains why there is no linear terms in the exponent: If there were, one of the terms in the sum on the right-hand side above wouldn't go to zero as $x_1 \to 1$, meaning that dP_1/dx_1 would not go to P_1^*.
  - Recovering Henry's law as $x_1 \to 0$: As $x_1 \to 0$, $P_1 \to k_H x_1 = P_1^* e^{\alpha+\beta+\cdots} \cdot x_1$.

- Margules equation parameters fitted for P_1 provide a related equation for P_2 based on Gibbs-Duhem (Problem 24-33).
  - To two terms, the Margules equation tells us that

  $$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$$

  - As we showed earlier, the Gibbs-Duhem equation implies that

  $$x_1 \frac{\partial \ln P_1}{\partial x_1} = x_2 \frac{\partial \ln P_2}{\partial x_2}$$

  - Thus, since $x_2 = 1 - x_1$,

  $$\begin{aligned}
  x_1 \frac{\partial \ln P_1}{\partial x_1} &= x_1 \frac{\partial}{\partial x_1} \left(\ln x_1 + \alpha x_2^2 + \beta x_2^3 + \text{terms not involving } x_1 \right) \\
  &= x_1 \left[\frac{1}{x_1} + (-2\alpha x_2) + (-3\beta x_2^2) \right] \\
  &= 1 + x_2(-2\alpha x_1 - 3\beta x_1 x_2) \\
  &= 1 + x_2(-2\alpha x_1 - 3\beta x_1(1 - x_1)) \\
  &= 1 + x_2(-2\alpha x_1 - 3\beta(x_1 - x_1^2)) \\
  &= 1 + x_2[-(2\alpha + 3\beta)x_1 + 3\beta x_1^2]
  \end{aligned}$$

  - Now let

  $$P_2 = x_2 P_2^* e^{ax_1^2 + bx_1^3}$$

  - It follows as before that

  $$x_2 \frac{\partial \ln P_2}{\partial x_2} = 1 + x_2(-2ax_1 - 3bx_1^2)$$

  - Direct comparison reveals that

  $$-2a = -(2\alpha + 3\beta) \qquad\qquad -3b = 3\beta$$
  $$a = \alpha + \frac{3}{2}\beta \qquad\qquad b = -\beta$$

  so

  $$P_2 = x_2 P_2^* e^{(\alpha + \frac{3}{2}\beta)x_1^2 - \beta x_1^3}$$

- **Regular solution**: A solution for which only $\alpha \neq 0$ and every other Margules parameter is zero.
  - In this case,

  $$P_1 = x_1 P_1^* e^{\alpha x_2^2} \qquad\qquad P_2 = x_2 P_2^* e^{\alpha x_1^2}$$

  - This means that the Raoult's activity of the two solutions is entirely symmetric over the range of compositions.
  - This does not necessarily imply that the vapor pressures vary in the same way.

- Mixing Gibbs free energy for a regular solution (24-5).

– We have

$$\frac{\Delta G_{\text{mix}}}{RT} = \underbrace{n_1 \mu_1^{\text{sol}} + n_2 \mu_2^{\text{sol}}}_{\text{mixture}} - \underbrace{(n_1 \mu_1^* + n_2 \mu_2^*)}_{\text{pure}}$$

$$= n_1 \ln \frac{P_1}{P_1^*} + n_2 \ln \frac{P_2}{P_2^*}$$

$$= n_1 \ln x_1 + n_2 \alpha x_2^2 + n_2 \ln x_2 + n_2 \alpha x_1^2$$

$$\frac{\Delta G_{\text{mix}}}{RT(n_1 + n_2)} = x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2^2 + \alpha x_2 x_1^2$$

$$= x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2 (x_1 + x_2)$$

$$\frac{\Delta G_{\text{mix}}}{RT(n_1 + n_2)} = x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2$$

– The left two terms above represent the entropy of mixing (which does not depend on interaction).

– The right term above is the enthalpy/entropy of mixing which depends *only* on interaction.

– Thus, α is the microscopic entropy of mixing for a regular solution.

- The upper critical solution temperature (UCST) (critical temperature above which the components of the mixture are miscible in all proportions).

  – We have
  $$\Delta \overline{G} = RT(x_1 \ln x_1 + x_2 \ln x_2) + \underbrace{RT\alpha}_{\Omega} x_1 x_2$$

  – Graphing the above equation will help us determine what extent of mixing will be most energetically favorable.

    ▪ In particular, if we graph the left two terms, that tells us the entropy of mixing, which will be greatest at $x_1 = x_2$.
    ▪ Graphing the right term on the other hand yields a parabola.
    ▪ As such, since $x_1 \ln x_1 + x_2 \ln x_2$ has vertical slope at $x_1 = 0, 1$ and the other term simply has some positive slope, entropy of mixing will always win at low concentrations of solutes, i.e., when you have a small enough concentration of solute in solvent, you will always observe mixing.
    ▪ However, the overall graph may have minima on the two sides, indicating that forming a fully mixed solution is not energetically favorable, but it is most favorable to separate into substance 1 with a bit of substance 2 and vice versa (think oil and water).
    ▪ At high temperatures, however, this effect goes away and mixing always becomes the most favorable state.

  – The temperature at which the overall graph only has one minimum for the first time is the UCST.

8.4 Office Hours (PGS)

- Can you go over the spontaneous expansion of an ideal gas from one isolated container to two? Is this an adiabatic process or an isothermal process? How can the gas cool down during the expansion if it ends up at the same final temperature?

  – An isoenthalpic expansion? Only as long as we can neglect the back pressure of the far wall. In this moment,

  $$0 = \Delta H$$
  $$= \Delta U + \Delta KE + \Delta(PV)$$

- The gas shooting out is expanding and picking up a lot of kinetic energy, but we need to conserve enthalpy all together, so that kinetic energy comes from vibrational and spin states.

- After everything comes to equilibrium, though, the temperature is the same.

- It's irreversible, so that means that during the process, you do not have well-defined state variables.

- Note that no work is done even for the intermixing of two gases.

  ■ Any work done by one gas is canceled by the work on the other gas and no work comes out of the system; it's a pure entropy effect.

  ■ But work is being done by both gases; just equal and opposite?

- How does the Henry's law we learned relate to the one from Gen Chem (the amount of gas dissolved in solution is proportional to its partial pressure)?

  - The Henry's law of intro chem says that concentration vs. pressure will always be a straight line.

  - We know now that we see deviations at higher concentrations, and that Henry's law is just a good approximation at relatively low pressures.

- Demixing of solutions at lower temperatures?

  - The line connecting all of the two minima with peak at the UCMT is the **spinodal line**.

8.5 Chapter 24: Solutions I — Liquid-Liquid Solutions

From McQuarrie and Simon (1997).

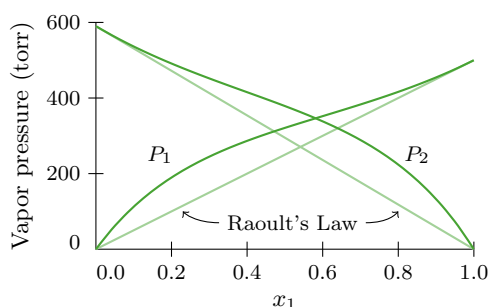- There exist positive and negative deviations from Raoult's Law (see Figure 8.4).

Figure 8.4: Positive deviations from Raoult's law ($CS_2/CH_2(OMe)_2$ at $25\,°C$).

- If 1 and 2 denote two substances that are being mixed, positive deviations occur when 1-2 interactions are more repulsive than either 1-1 or 2-2 interactions, and vice versa for negative deviations.

- If one component of a binary solution exhibits positive deviations from Raoult's law, so must the other component.

  - Follows from "Relating P_1, P_2 with the Gibbs-Duhem relation" as in class.

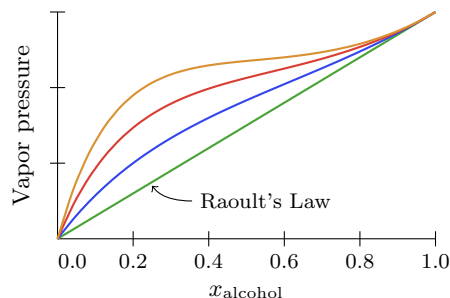- Molecular structure predicts deviations from Raoult's law.

Figure 8.5: Vapor pressure of alcohol/water solutions.

   – The blue line represents MeOH, the red line represents EtOH, and the orange line represents
     PrOH.
   – Notice how as molecular structure gets further from that of H_2O (the solvent), deviations become
     more exaggerated.

- McQuarrie and Simon (1997) discusses the limiting behavior of P_1 in Figure 8.4, noting the Raoult's
  law limit as $x_1 \to 1$ and introducing **Henry's law**.

- **Henry's law**: The partial pressure of a component in solution approaches the linear function $k_{H,i} x_i$
  as $x_i \to 0$.

- **Henry's law constant**: The constant $k_{H,i}$ in the above definition.

- For an ideal solution, $k_{H,i} = P_i^*$, but this is not true in general (as illustrated by Figure 8.4).

- Example: Finding P_1^* and k_H from an equation for P_1.

   – Let $P_1 = 180 x_1 e^{x_2^2 + \frac{1}{2} x_2^3}$.
   – As $x_1 \to 1$, $x_2 \to 0$, so $P_1 \to 180 x_1$. Since this form should be the Raoult's law limit, we can read
     off $P_1^* = 180\,\text{torr}$.
   – As $x_1 \to 0$, $x_2 \to 1$, so $P_1 \to 180 x_1 e^{1 + \frac{1}{2}} = 180 e^{3/2} x_1$. Since this form should be the Henry's law
     limit, we can read off $k_{H,1} = 180 e^{3/2} = 807\,\text{torr}$.

- McQuarrie and Simon (1997) derives

$$x_1 \left(\frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} = x_2 \left(\frac{\partial \ln P_2}{\partial x_2} \right)_{T,P}$$

as in class.

- In a binary solution, if component 1 obeys Raoult's law as $x_1 \to 1$, then component 2 obeys Henry's
  law as $x_2 \to 0$.

   – Suppose component 1 satisfies $P_1 \to x_1 P_1^*$ as $x_1 \to 1$. Then

$$
\begin{aligned}
x_2 \left(\frac{\partial \ln P_2}{\partial x_2} \right)_{T,P} &= x_1 \left(\frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} \\
&= x_1 \frac{\partial}{\partial x_1} (\ln x_1 + \ln P_1^*) \\
&= 1 \\
\ln P_2 &= \int \frac{1}{x_2}\, dx_2 \\
&= \ln x_2 + C \\
P_2 &= k_H x_2
\end{aligned}
$$

as desired.

- The vapor pressure curve of WLOG component 1 of a binary solution can often be represented empirically by

$$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$$

  - α, β reflect the extent of the nonideality of the solution in some manner because $P_1 = x_1 P_1^*$ (ideal) for $\alpha = \beta = 0$.
  - Furthermore, generalizing from the previous example, $k_{H,1} = P_1^* e^{\alpha+\beta}$ and $k_{H,2} = P_2^* e^{\alpha+\beta/2}$ (the latter equation will be derived presently).

- Deriving $P_2 = x_2 P_2^* e^{(\alpha+3\beta/2)x_1^2 - \beta x_1^3}$ from $P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$ in an alternate manner to what was presented in class.

  - We are given that $P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3}$ and that $x_2 = 1 - x_1$.
  - It follows that the chemical potential of component 1 is

$$\begin{aligned}
\mu_1 &= \mu_1^\circ + RT \ln P_1 \\
&= \mu_1^\circ + RT \left[\ln P_1^* + \ln x_1 + \alpha(1-x_1)^2 + \beta(1-x_1)^3 \right]
\end{aligned}$$

  - It follows that the total differential of $\mu_1(x_1)$ is

$$d\mu_1 = RT \left[\frac{1}{x_1} - 2\alpha(1-x_1) - 3\beta(1-x_1)^2 \right] dx_1$$

  - Thus, by the Gibbs-Duhem equation,

$$\begin{aligned}
x_1 \, d\mu_1 + x_2 \, d\mu_2 &= 0 \\
d\mu_2 &= -\frac{x_1}{x_2} \cdot RT \left[\frac{1}{x_1} - 2\alpha(1-x_1) - 3\beta(1-x_1)^2 \right] dx_1 \\
&= RT \left[-\frac{1}{x_2} + 2\alpha x_1 + 3\beta x_1(1-x_1) \right] dx_1
\end{aligned}$$

  - Substitute $x_2 = 1 - x_1$ and integrate.

$$\begin{aligned}
d\mu_2 &= RT \left[\frac{1}{x_2} - 2\alpha(1-x_2) - 3\beta x_2(1-x_2) \right] dx_2 \\
\int_1^{x_2} d\mu_2 &= RT \int_1^{x_2} \left[\frac{1}{x_2'} - 2\alpha(1-x_2') - 3\beta x_2'(1-x_2') \right] dx_2' \\
\mu_2(x_2) - \mu_2(1) &= RT \left[\ln x_2 + \alpha(1-x_2)^2 - \frac{3\beta}{2}(x_2^2 - 1) + \beta(x_2^3 - 1) \right] \\
\mu_2 - \mu_2^* &= RT \left[\ln x_2 + \alpha x_1^2 + \frac{3\beta}{2} x_1^2 - \beta x_1^3 \right]
\end{aligned}$$

  - Therefore, since

$$\mu_2 = \mu_2^\circ + RT \ln P_2 \qquad\qquad \mu_2^* = \mu_2^\circ + RT \ln P_2^*$$

    we have that

$$\begin{aligned}
\ln P_2 &= \ln P_2^* + \ln x_2 + \alpha x_1^2 + \frac{3\beta}{2} x_1^2 - \beta x_1^3 \\
P_2 &= x_2 P_2^* e^{(\alpha+3\beta/2)x_1^2 - \beta x_1^3}
\end{aligned}$$

3/5:
- **Azeotrope**: A mixture for which there is no change in composition upon boiling.

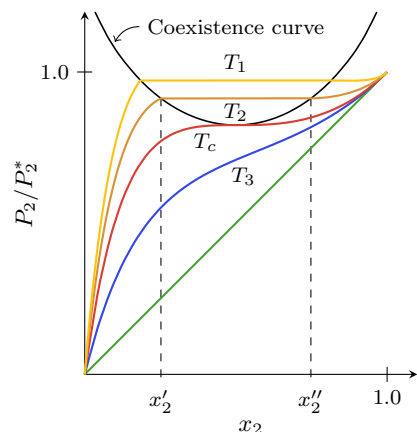- Vapor pressure behavior at various temperatures.

Figure 8.6: The critical behavior of a binary solution.

- – In Figure 8.6, $T_3 > T_c > T_2 > T_1$. Additionally, P_2^* denotes the vapor pressure of the pure substance *at each temperature*, and thus serves to "normalize" all of the curves.

- – At or above the **consulate temperature** T_c, component 1 and component 2 will mix to form a homogenous solution regardless of their relative concentrations.

- – On the other hand, consider the solution formed at $T_2 < T_c$.

  - ■ If $x_2 < x_2'$ or $x_2 > x_2''$, a homogenous solution is formed.
  - ■ However, if x_2 is within this range, the mixture separates into a solution with component 2 concentration x_2' and a solution with component 2 concentration x_2'', with the relative proportions dictated by what will give the constant vapor pressure indicated by Figure 8.6.

- – "Points inside the **coexistence curve** represent two solution phases, whereas points below the coexistence curve represent one solution phase" (McQuarrie & Simon, 1997, p. 985).

- **Consulate temperature**: The temperature below which two liquids are not miscible in all proportions. *Also known as* **critical temperature**. *Denoted by* $\boldsymbol{T_c}$.

- A lever rule that gives the relative amounts of the two phases indicated by Figure 8.6.

  - – Consider a solution of overall composition $x_2 \in (x_2', x_2'')$. Let n_1', n_2' and n_1'', n_2'' be the number of moles of the two components in the phases of composition x_2' and x_2'', respectively.

  - – By definition, we have the relations

$$x_2' = \frac{n_2'}{n_1' + n_2'} \qquad\qquad x_2'' = \frac{n_2''}{n_1'' + n_2''} \qquad\qquad x_2 = \frac{n_2' + n_2''}{n_1' + n_1'' + n_2' + n_2''}$$

  - – It follows that

$$x_2(n_1' + n_1'' + n_2' + n_2'') = x_2'(n_1' + n_2') + x_2''(n_1'' + n_2'')$$
$$\frac{n'}{n''} = \frac{n_1' + n_2'}{n_1'' + n_2''} = \frac{x_2'' - x_2}{x_2 - x_2'}$$

- **Activity** (of component j): A state function describing the nonideality of the chemical potential of component j of a solution. *Denoted by* $\boldsymbol{a_j}$. *Given by*

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln a_j$$

  - – It follows from Raoult's law that $a_j \to x_j$ as $x_j \to 1$.

– We can also represent the activity of component 1 in a binary solution empirically by

$$a_1 = x_1 e^{\alpha x_2^2 + \beta x_2^3 + \cdots}$$

- **Activity coefficient** (of component j): A measure of the deviation of a solution from ideality. *Denoted by γ_j. Given by*

$$\gamma_j = \frac{a_j}{x_j}$$

– It should make intuitive sense that $\gamma_j \to 1$ as $x_j \to 1$.

- Since activity and chemical potential are directly related, activity is really just another way of expressing chemical potential.

– It follows that since the chemical potentials of the components of a binary solution are related by the Gibbs-Duhem equation, the activities of said components are related by

$$\begin{aligned}
0 &= x_1 \, d(\mu_j^* + RT \ln a_1) + x_2 \, d(\mu_j^* + RT \ln a_2) \\
&= RT x_1 \, d \ln a_1 + RT x_2 \, d \ln a_2 \\
&= x_1 \, d \ln a_1 + x_2 \, d \ln a_2
\end{aligned}$$

– Consequently, if $a_1 = x_1$ over the entire composition range, we can use this relation to show that $a_2 = x_2$.

– Similarly, if $a_1 = x_1 e^{\alpha x_2^2}$ over the entire composition range, we can use this relation to show that $a_2 = x_2 e^{\alpha x_1^2}$.

- An activity defined by $a_j = P_j / P_j^*$ is said to be based upon a solvent, or Raoult's law, standard state.

– This is most convenient for substances that are miscible in all proportions, i.e., when there is no clear "solute" and "solvent."

- If one component is only sparingly soluble in the other, however, picking a standard state based on Henry's law is more convenient.

– In this case, $P_j \to x_j k_{H,j}$ as $x_j \to 0$ (we consider x_j close to zero because component j is sparingly soluble, so its concentration is naturally low).

– We thus have that

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln \frac{k_{H,j}}{P_j^*} + RT \ln x_j$$

and must define

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln \frac{k_{H,j}}{P_j^*} + RT \ln a_j$$

– It follows that for these two equations to be the same as $x_j \to 0$, we must take $a_j = P_j / k_{H,j}$.

– Additionally, the standard state must be such that

$$\mu_j = \mu_j^* + RT \ln \frac{k_{H,j}}{P_j^*}$$

or $P_j^* = k_{H,j}$.

– If such a standard state is not achievable in practice, it is called a **hypothetical standard state**.

- Deriving an expression for the Gibbs energy of mixing of binary solutions in terms of the activity coefficients.

– We have that

$$\Delta_{\text{mix}} G = n_1 \mu_1^{\text{sln}} + n_2 \mu_2^{\text{sln}} - n_1 \mu_1^* - n_2 \mu_2^*$$

- Since $\mu_j^{\text{sln}} = \mu_j^* + RT \ln a_j$ for any solution and $\gamma_j = a_j/x_j$, it follows that

$$\frac{\Delta_{\text{mix}}G}{RT} = n_1 \ln x_1 + n_2 \ln x_2 + n_1 \ln \gamma_1 + n_2 \ln \gamma_2$$

$$\frac{\Delta_{\text{mix}}\overline{G}}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

  - Note that the left two terms above represent the Gibbs energy of mixing of an ideal solution.

- We can use the above result to derive a formula for $\Delta_{\text{mix}}\overline{G}$ for a binary solution described by

$$P_1 = x_1 P_1^* e^{\alpha x_2^2} \qquad\qquad P_2 = x_2 P_2^* e^{\alpha x_1^2}$$

  as in class. The final result is

$$\frac{\Delta_{\text{mix}}\overline{G}}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2$$

- Statistical mechanics suggests that α has the form w/RT, where w is a constant. Thus, we can write the above equation as

$$\frac{\Delta_{\text{mix}}\overline{G}}{w} = \frac{RT}{w}(x_1 \ln x_1 + x_2 \ln x_2) + x_1 x_2$$

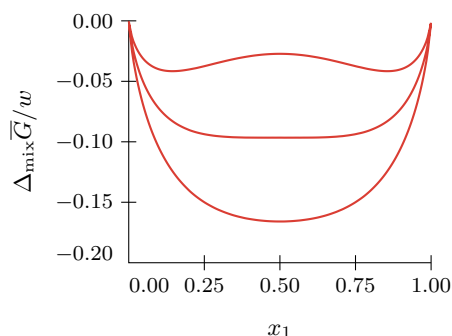- Visualizing the Gibbs energy of mixing.

Figure 8.7: $\Delta_{\text{mix}}\overline{G}$ at various temperatures.

  - The curves with a maximum at $x_1 = 0.5$ have an interesting relation to the extraneous curves in the cubic van der Waals and Redlich-Kwong equations for $T < T_c$. In particular, the region between their two minima corresponds to unmixing of the solutions and should be flatter, as per Figure 8.6.
  - Note that the three curves plotted are for, from the top down, $RT/w = 0.4$, $RT/w = 0.5$, and $RT/w = 0.6$.

- By finding the points where $\partial(\Delta_{\text{mix}}\overline{G}/w)/\partial x_1 = 0$, we can plot the coexistence curve from Figure 8.6.

  - Note that for $RT/w \geq 0.5$, $\partial(\Delta_{\text{mix}}\overline{G}/w)/\partial x_1 = 0$ only has one solution ($x_1 = 0.5$), whereas for $RT/w < 0.5$, $\partial(\Delta_{\text{mix}}\overline{G}/w)/\partial x_1 = 0$ has three solutions ($x_1 = 0.5$ and two others, corresponding to the other minima as in the plot of $RT/w = 0.4$ in Figure 8.7).

- **Regular solution**: A solution that can be described by the equation $\Delta_{\text{mix}}\overline{G}/RT = x_1 \ln x_1 + x_2 \ln x_2 + \alpha x_1 x_2$.

- **Excess Gibbs energy of mixing**: The extra Gibbs energy of mixing present in a solution beyond what would be present in an ideal solution. *Denoted by* $\boldsymbol{G^E}$. *Given by*

$$G^E = \Delta_{\text{mix}}G - \Delta_{\text{mix}}G^{\text{id}}$$

- It follows from the above that

$$\frac{G^E}{RT} = n_1 \ln \gamma_1 + n_2 \ln \gamma_2$$

- **Molar excess Gibbs energy of mixing**: The excess Gibbs energy of mixing for one mole of a solution. *Denoted by* $\overline{G}^E$. *Given by*

$$\frac{\overline{G}^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

- If the solution in question is described by

$$P_1 = x_1 P_1^* e^{\alpha x_2^2} \qquad\qquad P_2 = x_2 P_2^* e^{\alpha x_1^2}$$

then we have that

$$\frac{\overline{G}^E}{RT} = \alpha x_1 x_2$$

8.6 Chapter 25: Solutions II — Solid-Liquid Solutions

From McQuarrie and Simon (1997).

3/6:
- **Solute**: The sparingly soluble component in a binary solution.

    - Related quantities are denoted by a subscript 2.

- **Solvent**: The component in excess in a binary solution.

    - Related quantities are denoted by a subscript 1.

- a_1 (the activity of the solvent) is defined with respect to a Raoult's law standard state. a_2 (the activity of the solute) is defined with respect to a Henry's law standard state.

    - Note that we still define a_2 with respect to its vapor pressure (even though that quantity may be exceedingly small) because it is still meaningful.

- **Molality**: The number of moles of solute per $1000\,\text{g}$ of solvent. *Denoted by* m. *Units* $\mathbf{mol\,kg^{-1}}$. *Given by*

$$m = \frac{n_2}{1000\,\text{g solvent}}$$

- Relating the mole fraction of solute x_2 and the molality m.

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{m}{\frac{1000\,\text{g kg}^{-1}}{M_1} + m}$$

    - M_1 is the molar mass of the solvent.
    - $1000\,\text{g kg}^{-1}/M_1$ is the number of moles of solvent n_1 in $1000\,\text{g}$ of solvent.
    - We convert from the middle equation to the right equation by dividing both the top and bottom of the fraction by $1000\,\text{g}$.

- For H_2O,

$$\frac{1000\,\text{g kg}^{-1}}{M_1} = 55.506\,\text{mol/kg}$$

- We define solute activity in terms of molality by requiring that $a_2 \to m$ as $m \to 0$.

- Under this definition, we can reexpress Henry's law in terms of molality with a related set of Henry's law constants. These give us equations like $P_2 = k_{H,m}$.

- **Molarity**: The number of moles of solute per $1000\,\text{mL}$ of solution. *Denoted by c. Units* $\mathbf{mol\,L^{-1}}$. *Given by*
$$c = \frac{n_2}{1000\,\text{mL solution}}$$

- We can also analogously define solute activity in terms of molarity, requiring $a_2 \to c$ as $c \to 0$.

- Relating the solute mole fraction and molarity via the density.

  - Consider $1\,\text{L}$ of a solution.
  - We can find the mass of this quantity of solution via the density ρ. In particular,
  $$\text{mass of the solution per liter} = (1000\,\text{mL\,L}^{-1})\rho$$

  - We can extract from this, the molarity, and the molar mass of the solute M_2 the mass of solvent per liter.
  $$\text{mass of the solvent per liter} = \text{mass of the solution per liter} - \text{mass of the solute per liter}$$
  $$= (1000\,\text{mL\,L}^{-1})\rho - cM_2$$

  - Therefore, the number of moles of solvent per liter of solution is
  $$\frac{n_1}{1\,\text{L}} = \frac{(1000\,\text{mL\,L}^{-1})\rho - cM_2}{M_1}$$

  so

  $$
  \begin{aligned}
  x_2 &= \frac{n_2}{n_1 + n_2} \\
  &= \frac{n_2}{n_1 + n_2} \cdot \frac{1/1\,\text{L}}{1/1\,\text{L}} \\
  &= \frac{c}{\frac{(1000\,\text{mL\,L}^{-1})\rho - cM_2}{M_1} + c} \\
  &= \frac{cM_1}{(1000\,\text{mL\,L}^{-1})\rho + c(M_1 - M_2)}
  \end{aligned}
  $$

- For a nonvolatile solute, an equation of the form $a_2 = P_2/k_H$ is not practical to use since P_2 is so small. Thus, we invoke the Gibbs-Duhem equation.

  - Consider a solution of water with a small amount of a nonvolatile solute.
  - Since $m \ll 55.506\,\text{mol\,kg}^{-1}$, we have that
  $$x_2 \approx \frac{m}{55.506\,\text{mol\,kg}^{-1}}$$

  - Therefore, since $a_1 \to x_1$ as $x_1 \to 1$ (as we have at low concentrations), we have that
  $$\ln a_1 = \ln x_1 = \ln(1 - x_2) \approx -x_2 \approx -\frac{m}{55.506\,\text{mol\,kg}^{-1}}$$

  - We can now use the form of the Gibbs-Duhem equation relating activities to find a_2.
  - In particular, for $1\,\text{kg}$ of solvent, $n_1 = 55.506\,\text{mol}$ and $n_2 = m$, so we have
  $$(55.506\,\text{mol\,kg}^{-1})\,\text{d}\ln a_1 + m\,\text{d}\ln a_2 = 0$$

  - With the definition of the **osmotic coefficient**, we have that $(55.506\,\text{mol\,kg}^{-1})\,\text{d}\ln a_1 = -\,\text{d}(m\phi)$. Thus,
  $$m\,\text{d}\ln(\gamma_{2m}m) = \text{d}(m\phi)$$
  where γ_{2m} is the molal activity coefficient.

– Therefore,

$$m \, \mathrm{d}\phi + \phi \, \mathrm{d}m = m(\mathrm{d}\ln\gamma_{2m} + \mathrm{d}\ln m)$$

$$\mathrm{d}\ln\gamma_{2m} = \mathrm{d}\phi + \frac{\phi - 1}{m} \, \mathrm{d}m$$

$$\int_0^m \mathrm{d}\ln\gamma_{2m} = \int_0^m \mathrm{d}\phi + \int_0^m \frac{\phi - 1}{m'} \, \mathrm{d}m'$$

$$\ln\gamma_{2m} - \ln(1) = \phi - 1 + \int_0^m \frac{\phi - 1}{m'} \, \mathrm{d}m'$$

$$\ln\gamma_{2m} = \phi - 1 + \int_0^m \frac{\phi - 1}{m'} \, \mathrm{d}m'$$

- **Osmotic coefficient**: A quantity that accounts for the discrepancy between experimental solvent activities and ones predicted by the above equation. *Denoted by ϕ. Given by*

$$\ln a_1 = -\frac{m\phi}{55.506 \, \mathrm{mol\,kg^{-1}}}$$

  – Since $\phi = 1$ for an ideal dilute solution, the deviation of ϕ from unity is yet another measure of the nonideality of a solution.

  – ϕ increases as m increases (this should also make intuitive sense).

- **Colligative property**: A property of a solution that depends (in dilute solutions) upon only the number, not the type, of solute particles.

- Deriving an equation for the activity of the solvent in a solution at the freezing point.

  – At the freezing point, $\mu_1^s = \mu_1^{\mathrm{sln}}$. In particular,

$$\mu_1^s = \mu_1^l + RT \ln a_1$$

$$\ln a_1 = \frac{\mu_1^s - \mu_1^l}{RT}$$

  – Differentiating the above with respect to T at constant pressure and concentration, and substituting with the Gibbs-Helmholtz equation, give us

$$\left(\frac{\partial \ln a_1}{\partial T}\right)_{P,x_1} = \frac{1}{R}\left[\frac{\partial}{\partial T}\left(\frac{\mu_1^s}{T}\right) - \frac{\partial}{\partial T}\left(\frac{\mu_1^l}{T}\right)\right]_{P,x_1}$$

$$= \frac{1}{R}\left[-\frac{\overline{H}_1^s}{T^2} + \frac{\overline{H}_1^l}{T^2}\right]$$

$$= \frac{\Delta_{\mathrm{fus}}\overline{H}}{RT^2}$$

  – Integrating the above from pure solvent $a_1 = 1$, $T = T_{\mathrm{fus}}^*$ to a solution with arbitrary values of a_1, T_{fus} allows us to calculate the activity a_1 of said solution.

- **Freezing-point depression constant**: The proportionality constant between the change in freezing point ΔT_{fus} from the pure solvent to the given solution and the molality m of the given solution. *Denoted by K_f. Given by*

$$\Delta T_{\mathrm{fus}} = K_f m$$

- Deriving K_f from our freezing point activity equation.

  – Consider a dilute solution. Assume $\Delta_{\mathrm{fus}}\overline{H}$ is independent of temperature over the temperature range $(T_{\mathrm{fus}}, T_{\mathrm{fus}}^*)$.

- It follows that

$$\ln a_1 = \int_{T_{\text{fus}}^*}^{T_{\text{fus}}} \frac{\Delta_{\text{fus}}\overline{H}}{RT^2} \, dT$$

$$\ln x_1 \approx \frac{\Delta_{\text{fus}}\overline{H}}{R} \int_{T_{\text{fus}}^*}^{T_{\text{fus}}} \frac{dT}{T^2}$$

$$\ln(1 - x_2) \approx \frac{\Delta_{\text{fus}}\overline{H}}{R} \left(\frac{1}{T_{\text{fus}}^*} - \frac{1}{T_{\text{fus}}} \right)$$

$$-x_2 \approx \frac{\Delta_{\text{fus}}\overline{H}}{R} \left(\frac{T_{\text{fus}} - T_{\text{fus}}^*}{T_{\text{fus}}T_{\text{fus}}^*} \right)$$

- Now for two more approximations. First, since ΔT_{fus} is small, we can set $T_{\text{fus}} \approx T_{\text{fus}}^*$ in the denominator of the above equation. Second, since m is small, we may let

$$x_2 = \frac{m}{\frac{1000\,\text{g kg}^{-1}}{M_1} + m} \approx \frac{M_1 m}{1000\,\text{g kg}^{-1}}$$

- Therefore, making the substitutions and rearranging the above gives us

$$-\frac{M_1 m}{1000\,\text{g kg}^{-1}} = \frac{\Delta_{\text{fus}}\overline{H}}{R} \left(\frac{-\Delta T_{\text{fus}}}{(T_{\text{fus}}^*)^2} \right)$$

$$\Delta T_{\text{fus}} = T_{\text{fus}}^* - T_{\text{fus}} = \underbrace{\frac{M_1}{1000\,\text{g kg}^{-1}} \frac{R(T_{\text{fus}}^*)^2}{\Delta_{\text{fus}}\overline{H}}}_{K_f} \cdot m$$

- **Boiling-point elevation constant**: The proportionality constant between the change in boiling point ΔT_{vap} from the pure solvent to the given solution and the molality m of the given solution. *Denoted by $\boldsymbol{K_b}$. Given by*

$$\Delta T_{\text{vap}} = K_b m$$

- We can derive an analogous equation to the freezing-point depression result in an analogous way, yielding

$$\Delta T_{\text{vap}} = T_{\text{vap}} - T_{\text{vap}}^* = \underbrace{\frac{M_1}{1000\,\text{g kg}^{-1}} \frac{R(T_{\text{vap}}^*)^2}{\Delta_{\text{vap}}\overline{H}}}_{K_b} \cdot m$$

- **Semipermeable membrane**: A membrane containing pores that allow one substance to pass through but not another.

- **Osmotic pressure**: The hydrostatic pressure head that is built up as solvent molecules pass through a semipermeable membrane from pure solvent to solute-containing solution.

  - Such a process happens to equalize the chemical potentials on the two sides of the semipermeable membrane.

- Deriving an expression for the osmotic pressure.

  - If P is the pressure exerted on the system and Π is the excess hydrostatic pressure on the solute-containing side, the system seeks Π such that

$$\mu_1^*(T, P) = \mu_1^{\text{sln}}(T, P + \Pi, a_1) = \mu_1^*(T, P + \Pi) + RT \ln a_1$$

- It follows by the Maxwell relation for chemical potential that

$$0 = \mu_1^*(T, P + \Pi) - \mu_1^*(T, P) + RT \ln a_1$$

$$= \int_P^{P+\Pi} \left(\frac{\partial \mu_1^*}{\partial P'}\right)_T dP' + RT \ln a_1$$

$$= \int_P^{P+\Pi} \overline{V}^* dP' + RT \ln a_1$$

- Assuming that $\overline{V}_1^*$ is invariant under changing pressure, the above equation implies that

$$0 = \Pi \overline{V}_1^* + RT \ln a_1$$

$$\Pi \overline{V}_1^* = RT x_2$$

- Since $n_2 \ll n_1$, we may approximate $x_2 = n_2/(n_1 + n_2) \approx n_2/n_1$ to get

$$\Pi = \frac{n_2 RT}{n_1 \overline{V}_1^*}$$

$$= \frac{n_2 RT}{V}$$

$$\Pi = cRT$$

where V is the total volume of solvent.

- **Van't Hoff equation** (for osmotic pressure): The above equation.

- **Reverse osmosis**: The process of applying pressure to seawater in excess of the osmotic pressure to force it through a rigid semipermeable membrane, resulting in fresh water.

  - The most common such membrane is cellulose acetate.

Week 9

Solid-Liquid Solutions and Electrochemistry

9.1 Solute Activity

- At low concentration, solute activity is unity, with the chosen measure of concentration.

- Activity of ions in electrolytes initially decreases rapidly with concentration below $1\,M$. The effect is much stronger than for neutral solutes.

- The Debye-Hückel model reasonably explains why ion activity drops so quickly.

- Practical solution concentration measures are the **molarity** and **molality**, in addition to the mole fraction x.

- **Molality**: The number of moles of solute per kilogram solvent. *Denoted by* **m**. *Given by*

$$m = \frac{n_2}{1\,\text{kg solvent}}$$

- **Concentration**: The number of moles of solute per liter solution. *Also known as* **molarity**. *Denoted by* **c**. *Given by*

$$c = \frac{n_2}{1\,\text{L solution}}$$

- As the solvent gets purer, its vapor pressure approaches the Raoult's law limit.

    - $a_1 = P_1/P_1^* \to x_1$ as $x_1 \to 1$.

- As the solute's concentration diminishes, the solute activity approaches the Henry's law limit.

    - $a_2 = P_2/k_H \to x_2$ as $x_2 \to 0$.

- Using the vapor pressure of the solvent to determine the activity of the non-volatile solute.

    - Use the Gibbs-Duhem relation,

$$0 = n_1 \,\mathrm{d}\ln a_1 + n_2 \,\mathrm{d}\ln a_2$$
$$= (55.506\,\text{mol kg}^{-1})\,\mathrm{d}\ln a_1 + m\,\mathrm{d}\ln a_2$$
$$\ln a_2 = \int_0^m -\frac{55.506}{m'}\,\mathrm{d}(\ln a_1)\,\mathrm{d}m'$$

    - But $\mathrm{d}(\ln a_1)$ may not be very precise; thus, we define the **osmotic coefficient**.

– With this quantity, we have

$$\mathrm{d} \ln a_1 = - \mathrm{d}(m\phi) \cdot \frac{1}{55.506}$$

– Thus, we have that

$$0 = - \mathrm{d}(m\phi) + m \, \mathrm{d} \ln a_2$$
$$\phi \, \mathrm{d}m + m \, \mathrm{d}\phi = m \, \mathrm{d} \ln \gamma_2 + \mathrm{d}m$$
$$\frac{\mathrm{d}m}{m} \phi + \mathrm{d}\phi = \mathrm{d} \ln \gamma_2 + \frac{\mathrm{d}m}{m}$$
$$\mathrm{d} \ln \gamma_2 = \mathrm{d}\phi + \left(\frac{\phi - 1}{m} \right) \mathrm{d}m$$
$$\ln \gamma_2 = (\phi - 1) + \int_0^m \frac{\phi - 1}{m'} \, \mathrm{d}m'$$

• **Osmotic coefficient**: The following quantity. *Denoted by ϕ. Given by*

$$\phi = - \frac{\ln a_1}{x_2} = - \ln a_1 \cdot \frac{55.506 \, \mathrm{mol \, kg}^{-1}}{m}$$

– It is called the osmotic coefficient since $\Pi \overline{V} = -RT \ln a_1$ implies that as $x_2 \to 0$, $\ln a_1 \to -x_2$, so $\phi \to 1$.

– Even in the case of an ideal solution, $\phi \neq 1$ exactly, though, since we must mathematically *approximate* $\ln a_1 \approx -x_2$.

• Ionic solutions deviate strongly from ideal solution, even at small molality.

• Mean ionic activity, molality, and activity coefficient.

– The salt $C_{\nu_+} A_{\nu_-}$ dissociates into ν_+ C^{z+} ions and ν_- A^{z-} ions where

$$\nu_+ z_+ + \nu_- z_- = 0$$

for charge neutrality.

– Let $\nu = \nu_+ + \nu_-$.

– The chemical potential of the salt is

$$\mu_{\mathrm{salt}} = \nu_+ \mu_+ + \nu_- \mu_-$$
$$= \nu_+ \mu_+^\circ + \nu_- \mu_-^\circ + RT(\nu_+ \ln a_+ + \nu_- \ln a_-) + RT \ln \left(\underbrace{a_+^{\nu_+} a_-^{\nu_-}}_{a_2} \right)$$

– Hence,

$$a_2 = a_+^{\nu_+} a_-^{\nu_-}$$
$$= (\gamma_+^{\nu_+} \gamma_-^{\nu_-})(m_+^{\nu_+} m_-^{\nu_-})$$
$$= a_\pm^\nu$$
$$= \gamma_\pm^\nu m_\pm^\nu$$

where $a_\pm$ is the **mean activity**, $\gamma_\pm$ is the **mean activity coefficient**, and $m_\pm$ is the **mean molality**.

– It follows that

$$\mu_2 = \mu_2^\circ + RT \ln a_\pm^\nu$$
$$= \mu_2^\circ + \nu RT \ln a_\pm$$

- Consider a solution of $CaCl_2$ with molality m.

  - It has

  $$m_+ = m \qquad\qquad m_- = 2m$$

  - Thus,

  $$m_\pm = \sqrt{m_+^1 m_-^2}$$
  $$= \sqrt{4m^3}$$
  $$= 4^{1/3} m$$

  - We can do something similar for $\gamma_\pm$ and $a_\pm$.

- Determining the activity of electrolytes.

  - The derivation is pretty similar to before (for nonvolatile solvents), except that now $\ln a_1 = -\nu m \phi / 55.506$.
  - It follows that

  $$0 = n_1 \, d\ln a_1 + n_2 \, d\ln a_2$$
  $$= -\nu \, d(m\phi) + m\nu \, d\ln a_\pm$$

  so ν cancels.
  - This yields the same overall equation as before:

  $$\ln \gamma_\pm = (\phi - 1) + \int_0^m \frac{\phi - 1}{m'} \, dm'$$

- We can do the above, but ion activity can also be measured by electrochemistry.

9.2 Debye-Hückel Model

- For ionic solutions, ϕ is fitted to a function of the form $\phi = \sum a_i m^{i/2}$.

- For neutral solutes, ϕ is fitted to a function of the form $\phi = \sum a_i m^i$.

- Debye-Hückel model for small concentrations: $\ln \gamma_\pm \propto m^{1/2}$.

- We define $pH = -\log a_1$, not $pH = -\log[H_3O^+]$.

  - Thus, $pH = -\log \gamma_\pm - \log[H_3O^+]$.
  - This also gives a method of determining $\gamma_\pm$.

- Activity coefficients and interaction between solutes.

  - If there are *unfavorable* interactions between solutes (as in sucrose), $\gamma > 1$.
  - If there are *favorable* interactions between solutes (as in NaCl), $\gamma < 1$.
  - In terms of energy:

  $$\mu = \overline{\mu} + P\overline{V} - T\overline{S}$$
  $$= \mu^*(x) + RT \ln x$$
  $$= \mu_{\text{ideal}}^* + (\mu^*(x) - \mu_{\text{ideal}}) + RT \ln x$$
  $$= \mu_{\text{ideal}}^* + RT \ln a$$
  $$= \mu_{\text{ideal}}^* + RT \ln \gamma + RT \ln x$$

- It follows that

$$RT \ln \gamma = \mu^*(x) - \mu_{\text{ideal}}$$

$$\gamma = \exp\left(\frac{\mu^*(x) - \mu_{\text{ideal}}}{RT}\right)$$

using only $\bar{\mu} \to \gamma = \exp\left(\frac{\mu^*(x) - \mu_{\text{ideal}}}{RT}\right)$.

■ This mathematically shows that if we stabilize the ion energetically, then $\gamma < 1$.

- Interactions between ions. The Debye length arises due to the screening of the charges. Calculated from the Boltzmann factor.

  - Imagine a charge of magnitude q at the center of our coordinate system.
  - We have a charge density $\rho(\pi)$ at a distance r from the nucleus.
  - We have

$$\rho(r) = \sum_i q_i \left(\frac{N_i}{V}\right) \cdot e^{-q_i \phi(r)/k_B T}$$

  where the latter term is the Boltzmann factor and $\phi(r)$ is the electrostatic potential.

  - We also have the Poisson equation,

$$\nabla \phi(r) = -\frac{\rho(r)}{\varepsilon \varepsilon_0}$$

  - Since everything is depending on each other, it seems we are in a pickle.
  - But if

$$\frac{q_i \phi(r)}{k_B T} < 1$$

  then

$$e^{q_i \phi(r)/k_B T} = 1 - \frac{q_i \phi(r)}{k_B T}$$

  - Therefore,

$$\rho(r) = \sum_i q_i \left(\frac{N_i}{V}\right) \cdot \left(1 - \frac{q_i \phi(r)}{k_B T}\right) = \sum q_i \left(\frac{N_i}{V}\right) - \phi(r) \sum \frac{q_i^2 \left(\frac{N_i}{V}\right)}{k_B T}$$

  where the left term in the right expression above evaluates to zero.

  - We can only have an excess of 1000 ions of one type of charge per liter of solution.
  - It follows that

$$\nabla \phi(r) = \left(\frac{\sum q_i^2 \left(\frac{N_i}{V}\right)}{\varepsilon \varepsilon_0 k_B T}\right) \cdot \phi(r)$$

$$\frac{\partial^2 \phi}{\partial r^2} + \cdots = \kappa^2 \cdot \phi$$

- **Debye length**: κ^{-1}.

- In the one-dimensional case,

$$\frac{\partial^2 \phi}{\partial x^2} = \kappa^2 \phi$$

$$\phi(x) = Ae^{\kappa x} + Be^{-\kappa x}$$

  - In other words, all interactions take place within the Debye length.

- – The distance over which ion concentration differs from perfectly mixed ion potential around a charge.
  - – In electrochemistry, this is where everything happens.
- Ions **screen** other ions.
- We have

$$\kappa^2 = \frac{\sum q_i^2 \left(\frac{N_i}{V}\right)}{\varepsilon \varepsilon_0 k_B T}$$

- **Ionic strength**: The following quantity. *Denoted by I_c. Given by*

$$I_c = \frac{1}{2} \sum z_i^2 c_i$$

- Thus, we have

$$\kappa^{-1} = \frac{1}{\sqrt{I_c}} \cdot \sqrt{\frac{10^{-3}}{e^2 N_A} \cdot \frac{\varepsilon \varepsilon_0 k_B T}{2}}$$

- Calculating the Debye length of NaCl.

  - – For water, $\varepsilon \approx 80$.
  - – For $1\,\text{M}$ NaCl,

$$I_c = \frac{1}{2}(1 \cdot 1 + 1 \cdot 1) = 1\,\text{M}$$

  - – Thus, $\kappa^{-1} = 3\,\text{Å}$.
- Calculating the Debye length of $CaCl_2$.

  - – $I_c = 3\,\text{M}$.
- Interactions lead to the Debye-Hückel model for the mean ionic activity.

  - – We have

$$\mu = -\frac{\kappa q^2}{8\pi \varepsilon \varepsilon_0}$$

    which implies that

$$\ln \gamma = -\frac{\kappa q^2}{8\pi \varepsilon \varepsilon_0 k_B T}$$

  - – Hence, by Problem 25.58,

$$\ln \gamma_{\pm} = \frac{|z_+ z_-| e^2 \kappa}{8\pi \varepsilon \varepsilon_0 k_B T}$$

    where $e^2 \kappa / 8\pi \varepsilon \varepsilon_0$ comes from the Coulombic attraction.
  - – Thus, by the Debye-Hückel model,

$$\ln \gamma_{\pm} = -1.333|z_+ z_-|\sqrt{I_c}$$

- One empirical extension of the Debye-Hückel model is

$$\ln \gamma_{\pm} = \frac{-1.173|z_+ z_-|\sqrt{I_c}}{1 + \sqrt{I_c}} + c_m$$

9.3 Electrochemistry

3/11:
- Example from last time: Calculate the mean ionic activity of $ZnCl_2$ at 0.02 molal.

  – The mean molality is $m_\pm = \sqrt{(0.02)^1(0.04)^2} = 3.17 \times 10^{-2}$.

  – The ionic strength is

 $$I = \frac{1}{2}[(0.02)(+2)^2 + (0.04)(-1)^2]$$
  $$= 0.06$$

  – Calculate the Debye-Hückel mean ionic activity coefficient:

  $$\ln \gamma_\pm = -1.173|z_+ z_-|\sqrt{I_c}$$
  $$= -1.173(2 \cdot 1)\sqrt{0.06}$$
  $$= -0.574$$

  – Thus, by plotting $\ln \gamma_\pm$ vs. c for small concentrations, we can find that $\sqrt{c} \approx 0.14$.

- Electrochemistry: Exchanging chemical free energy with electrical energy.

  – Zinc and copper electrodes in a solution of $CuSO_4$.

    ■ The zinc silvery metal turns red (it's getting coated in copper) and the copper electrode doesn't change.

  – Now picture zinc in a solution of $ZnSO_4$ and copper in a solution of $CuSO_4$, the two containers being connected by a salt bridge and an ammeter.

    ■ The zinc electrode corrodes (gets smaller and smaller).

    ■ The copper electrode grows (copper gets deposited).

    ■ What we have is $Zn \longrightarrow Zn^{2+} + 2e^-$ and $Cu^{2+} + 2e^- \longrightarrow Cu$, so electrons flow through the wire from the zinc anode to the copper cathode.

    ■ The overall redox reaction is

    $$Zn_{(s)} + Cu^{2+} \longrightarrow Zn^{2+} + Cu_{(s)}$$
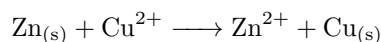
    ■ The relevant molar Gibbs energies of formation $(\Delta \overline{G}_f^\circ)$ are zero for the metals, $-147\,\mathrm{kJ\,mol^{-1}}$ for $Zn^{2+}_{(aq)}$, and $65\,\mathrm{kJ\,mol^{-1}}$ for $Cu^{2+}_{(aq)}$.

    ■ Thus, this reaction is spontaneous with $\Delta \overline{G}^\circ = -147 - 65 = -212\,\mathrm{kJ\,mol^{-1}}$.

  – We know that $\Delta \overline{G}^\circ = w_{\text{non }PV} = \Delta \overline{Q} \cdot E$ at constant T, P, where E is the electrochemical potential.

  – We also know that $\Delta \overline{Q} = -2eN_A = -2F$ (negative since we're losing electrons) where

  $$F = 96\,485\,\mathrm{C}$$

  is the **Faraday constant**.

  – Thus,

  $$E = \frac{\Delta \overline{G}^\circ}{2F} = \frac{-212}{-2F} = \frac{-212000}{-2 \cdot 96485} = 1.1\,\mathrm{V}$$

- Using the Gibbs free energy with the electrostatic potential energy.

  – Hydrogen electrode: You have a reference, and then you bubble H_2 through the solution with $P_{H_2} = 1\,\mathrm{atm}$, using a solution of pH = 1.

    ■ Recall that this does not imply that $[H_3O^+] = 1\,\mathrm{M}$; it means that $\log a_{H_3O^+} = 1$.

- ■ Know that $2\,H^+ + 2\,e^- \longrightarrow H_2$.

- Nernst equation.

$$E = E_0 - \frac{RT}{nF} \ln \frac{a_{\text{reductant}}}{a_{\text{oxidant}}}$$

- In the case of the standard hydrogen electrode,

$$\begin{aligned}
E_{H_2} &= E_0 - \frac{RT}{2F} \ln \frac{P_{H_2}}{a_H^2} \\
&= E_0 - \frac{0.0592}{2} \log \frac{P_{H_2}}{a_H^2} \\
&= E_0 - \frac{0.0592}{2} \log P_{H_2} + 0.0592\,\text{pH}
\end{aligned}$$

- Membrane potential.

  - In a cell, ion pumps establish an electric potential across a membrane of up to 20 times.
  - Assuming that the chemical potentials inside and outside the membrane are equal, we have

  $$\mu_{\text{in}} = \mu_+^* + RT \ln c_{\text{in}} + q\phi \qquad\qquad \mu_{\text{out}} = \mu_+^* + RT \ln c_{\text{out}} + q \cdot 0$$

  where ϕ is the electrical potential difference between the inside and outside of the cell.

  - Setting the two equations equal to each other and noting that $q = eN_A = F$ yields

  $$\begin{aligned}
  RT \ln c_{\text{in}} + R\phi &= RT \ln c_{\text{out}} \\
  \phi &= \frac{RT}{F} \ln \frac{c_{\text{out}}}{c_{\text{in}}} \\
  &= -75\,\text{mV}
  \end{aligned}$$

  for $T = 300\,\text{K}$ and the concentration on the inside being 20 times that on the outside.

- Corrosion and concentration gradients.

  - Metal corrosion occurs when $[M^+]$ is smallest. Here, $M^+ + e^- \longrightarrow M$.
    - ■ Electrons flow from negative to positive.
  - Corrosion occurs where O_2 concentration is the lowest.
    - ■ $O_2 + 4\,e^- + 4\,H^+ \longrightarrow 2\,H_2O$.
    - ■ Low $[O_2]$ implies that
    $$E = E_0 - \frac{RT}{4F} - \ln \frac{1}{[H^+]^4 P_{O_2}}$$
    so E becomes more negative.
    - ■ It is the low potential at places that lack oxygen that causes corrosion.

- Few lines summary of CHEM 26200.

  1. We first thought of $\langle E \rangle = \sum p_i E_i$, i.e., the energy as dependent on the states of a system.
  2. We then defined the entropy $S = -k_B \sum p_i \ln p_i$ that maximizes when everything is most equally distributed. Tells us where nature goes, i.e., toward the most probable outcome.
  3. We can combine energy with the tendency of nature to go to the highest entropy to define the **Lagrange multipliers** $F = U - TS$ and $G = H - TS$; minima of F, G are where the system goes spontaneously.
  4. The partition function $q = \sum e^{-E_i/k_B T}$ allows us to calculate every property of the system it describes. We can also extend this from molecules to systems of distinguishable and indistinguishable particles.
  5. The probabilities of each state depend on their energy via $p_i = e^{E_i/k_B T}/q$.

9.4 Office Hours (PGS)

3/11: • Quiz 1 Question 6.

  – $3000/\sqrt{2} = 2120$.

  – $\omega = \sqrt{k/m}$.

  – Mass doubles, force constant stays the same.

  – One-half of 2120 is 1060, and it's the difference between this (the zero point energy) and 1500, which is half the CD vibration (since D doubles in mass).

9.5 Chapter 25: Solutions II — Solid-Liquid Solutions

From McQuarrie and Simon (1997).

3/8: • Oppositely charged ions in solution interact with each other via a Coulombic potential, which varies proportionally to $1/r$.

  – Note the difference between the strength of this potential and the LDF potential of $1/r^6$ attracting ordinary neutral molecules.

  – It follows that solutions of electrolytes deviate from ideality much more quickly (i.e., at much lower concentrations).

• When ions with higher charges (e.g., $CaCl_2$ vs. $NaCl$) are produced, the deviation from ideality is exacerbated.

• *a-b* **electrolyte**: An electrolyte for which $\nu_+ = a$ and $\nu_- = b$.

  – For example, $CaCl_2$ is a 1-2 electrolyte and $Gd_2(SO_4)_3$ is a 2-3 electrolyte.

• The chemical potential of a salt depends on the potentials of its constituent ions as per

$$\mu_2 = \nu_+\mu_+ + \nu_-\mu_-$$

where $\mu_j = \mu_j^\circ + RT\ln a_j$ for $j = 2, +, -$.

• It follows from the above and the fact that $\mu_2^\circ = \nu_+\mu_+^\circ + \nu_-\mu_-^\circ$, too, that

$$\mu_2^\circ + RT\ln a_2 = \nu_+(\mu_+^\circ + RT\ln a_+) + \nu_-(\mu_-^\circ + RT\ln a_-)$$
$$RT\ln a_2 = \nu_+ RT\ln a_+ + \nu_- RT\ln a_-$$
$$\ln a_2 = \nu_+\ln a_+ + \nu_-\ln a_-$$
$$a_2 = a_+^{\nu_+} a_-^{\nu_-}$$

• We define $\nu = \nu_+ + \nu_-$.

• **Mean ionic activity**: The following quantity. *Denoted by* $a_\pm$. *Given by*

$$a_\pm^\nu = a_+^{\nu_+} a_-^{\nu_-}$$

• We take the activity a_2 of an electrolyte to be its mean ionic activity to the νth power, i.e., $a_2 = a_\pm^\nu$.

• We cannot determine the activities of single ions.

• We define the molalities of individual ions by

$$m_+ = \nu_+ m \qquad\qquad m_- = \nu_- m$$

- We define single-ion activity coefficients by

$$\gamma_+ = \frac{a_+}{m_+} \qquad\qquad \gamma_- = \frac{a_-}{m_-}$$

- **Mean ionic molarity**: The following quantity. *Denoted by $m_\pm$. Given by*

$$m_\pm^\nu = m_+^{\nu_+} m_-^{\nu_-}$$

- **Mean ionic activity coefficient**: The following quantity. *Denoted by $\gamma_\pm$. Given by*

$$\gamma_\pm^\nu = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$$

- It follows that

$$a_2 = a_\pm^\nu = (m_+^{\nu_+} m_-^{\nu_-})(\gamma_+^{\nu_+} \gamma_-^{\nu_-}) = m_\pm^\nu \gamma_\pm^\nu$$

- McQuarrie and Simon (1997) derives

$$\ln \gamma_\pm = (\phi - 1) + \int_0^m \frac{\phi - 1}{m'}\, \mathrm{d}m'$$

- For colligative properties, since x_2 is scaled up by a factor of ν, we get

$$\Delta T_{\mathrm{fus}} = \nu K_f m \qquad\qquad \Delta T_{\mathrm{vap}} = \nu K_b m \qquad\qquad \Pi = \nu c R T$$

for solutions of electrolytes.

- Debye and Hückel showed theoretically in 1925 that at low concentrations, the natural logarithms of the jth ion's activity coefficient and the mean ionic activity coefficient are given by

$$\ln \gamma_j = -\frac{\kappa q_j^2}{8\pi\varepsilon_0\varepsilon_r k_B T} \qquad\qquad \ln \gamma_\pm = -|q_+ q_-|\frac{\kappa}{8\pi\varepsilon_0\varepsilon_r k_B T}$$

where $q_+ = z_+ e$ and $q_- = z_- e$, ε_r is the (unitless) relative permittivity of the solvent, and κ is given by

$$\kappa^2 = \sum_{j=1}^s \frac{q_j^2}{\varepsilon_0\varepsilon_r k_B T}\left(\frac{N_j}{V}\right)$$

s being the number of ionic species and N_j/V being the number density of species j.

  - Converting N_j/V to molarity allows us to rewrite the above as

$$\kappa^2 = N_A(1000\,\mathrm{L\,m^{-3})}\sum_{j=1}^s \frac{q_j^2 c_j}{\varepsilon_0\varepsilon_r k_B T}$$

  - This result is derived in Problems 25-50 through 25-58.

- **Debye-Hückel limiting law**: The above expression for $\ln \gamma_\pm$.

- **Ionic strength**: The following quantity. *Denoted by I_c. Given by*

$$I_c = \frac{1}{2}\sum_{j=1}^s z_j^2 c_j$$

  - c_j is the molarity of the jth ionic species.

- Having defined the ionic strength, we can write express κ in a third form as

$$\kappa^2 = \frac{2e^2 N_A (1000\,\text{L}\,\text{m}^{-3})}{\varepsilon_0 \varepsilon_r k_B T}(I_c/\text{mol}\,\text{L}^{-1})$$

- In the Debye-Hückel limiting law, $\ln \gamma_\pm \propto \kappa \propto \sqrt{I_c} \propto \sqrt{c}$.

  - This is why we curve fit ϕ vs. m data to a polynomial in $m^{1/2}$.

- As $m \to 0$, all curves $\ln \gamma_\pm$ vs. m converge to the same straight line (hence this being a *limiting* law).

- Physically interpreting κ.

  - The net charge in a spherical shell of radius r and thickness $\mathrm{d}r$ surrounding an ion of charge q_i is given by
  $$p_i(r)\,\mathrm{d}r = -q_i \kappa^2 r e^{-\kappa r}\,\mathrm{d}r$$

  - Integrating this equation over all space yields $-q_i$.

  - Thus, "the total charge surrounding an ion of charge q_i is equal and of the opposite sign to q_i. In other words, it expresses the electroneutrality of the solution" (McQuarrie & Simon, 1997, pp. 1033–34).

  - The above equation describes the **ionic atmosphere** about the central ion.

  - Additionally, its maximum occurs at κ^{-1}, so we say that κ is a measure of the thickness of the ionic atmosphere.

- For a 1-1 electrolyte in aqueous solution at $25\,°\text{C}$,

$$\kappa = \frac{304\,\text{pm}}{\sqrt{c/\text{mol}\,\text{L}^{-1}}}$$

- Assumptions of the Debye-Hückel theory:

  - Ions are point particles.

  - They interact with a purely Coulombic potential.

  - The solvent is a continuous medium with a uniform relative permittivity ε_r.

- Clearly, these will start to break down as their concentration increases.

- The Debye-Hückel model has been of important utility mainly in that all models that attempt to treat higher concentrations must reduce to it at lower temperatures.

- Real progress toward a more general theory wasn't made until the 1970s, though.

- **Primitive model**: Ions are considered hard spheres with charges at their centers and the solvent is considered a continuous medium with a uniform relative permittivity.

  - Although, well, primitive, long-range Coulombic interactions and short-range repulsions, which this model encapsulates well, turn out to be major considerations, so the model is pretty good.

- The mean spherical approximation (MSA) provides analytical solutions.

  - A central result is that
  $$\ln \gamma_\pm = \ln \gamma_\pm^{\text{el}} + \ln \gamma^{\text{HS}}$$

  where $\ln \gamma_\pm^{\text{el}}$ is an electrostatic (Coulombic) contribution to $\ln \gamma_\pm$ and $\ln \gamma^{\text{HS}}$ is a hard-sphere contribution.

- For a 1-1 electrolyte,

$$\ln \gamma_{\pm}^{\text{el}} = \frac{x\sqrt{1+2x} - x - x^2}{4\pi \rho d^3}$$

where ρ is the number density of charged particles, d is the sum of the radius of a cation and anion, and $x = \kappa d$. Also,

$$\ln \gamma^{\text{HS}} = \frac{4y - \frac{9}{4}y^2 + \frac{3}{8}y^3}{\left(1 - \frac{y}{2}\right)^3}$$

where $y = \pi \rho d^3 / 6$.

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