Week 6

Chemical Equilibrium

6.1 Thermodynamics of the Rubber Band

2/14:
- 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 $H°(T)$ is the standard enthalpy at T and $S°(T)$ is the standard entropy at T. *Denoted by* $\boldsymbol{G°(T)}$. *Given by*
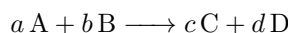
$$G°(T) = H°(T) - TS°(T)$$

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

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

- 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 (2021).

• 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.
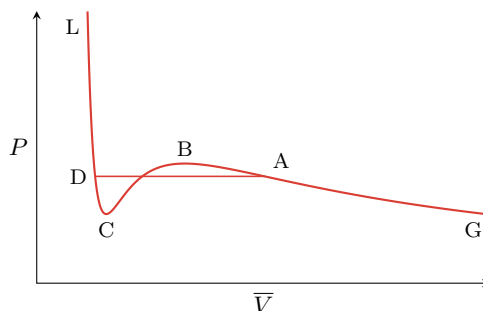

Figure 6.1: The van der Waals isotherm of CO_2 at $0\,°C$.

- 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 $\overline{AG}$, the system is a gas. On $\overline{LD}$, it is a liquid. On $\overline{AD}$, 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 $\overline{AD}$: 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 contraction**).
  - ■ Phase equilibrium (like we have along $\overline{AD}$) means that free energy does not change. Mathematically, $\Delta G(\mathrm{A}) = \Delta G(\mathrm{D})$.
  - ■ 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 $\overline{DA}$ to find an appropriate $\overline{DA}$ such that the integral is zero.

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

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

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

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