

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 $H^\circ(T)$ is the standard enthalpy at T and $S^\circ(T)$ is the standard entropy at T . Denoted by $G^\circ(T)$. Given by

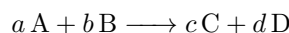
$$G^\circ(T) = H^\circ(T) - TS^\circ(T)$$

- 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 $G(T, P)$ at nonstandard pressure is

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

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

- If



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 $(\partial U / \partial L)_T = T(\partial S / \partial L)_T + f$.

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

- 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.

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

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

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