Week 5

Entropy and the Third Law of Thermodynamics

5.1 Entropy and the Third Law

- An experimental determination of entropy.

  - We have that

  $$\mathrm{d}U = \delta q_{\mathrm{rev}} + \delta w_{\mathrm{rev}}$$
  $$= T\,\mathrm{d}S - P\,\mathrm{d}V$$

  - At constant V, $\mathrm{d}V = 0$, so $\mathrm{d}S = \mathrm{d}U\,/T = C_V\,\mathrm{d}T\,/T$.
  - 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 $\Delta S = \int_{T_1}^{T_2} C_V/T\,\mathrm{d}T$.
    - ■ 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 $\Delta S = \int_{T_1}^{T_2} C_P/T\,\mathrm{d}T$, 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.

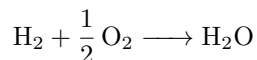- **Gibbs free energy**: The state function describing the free energy of a system at constant pressure. *Denoted by* $\boldsymbol{G}$. *Given by*
$$G = H - TS$$

  - 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
$$\mathrm{H_2} + \frac{1}{2} \, \mathrm{O_2} \longrightarrow \mathrm{H_2O}$$
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

$$\mathrm{d}A = \delta q_{\text{rev}} - T\,\mathrm{d}S - S\,\mathrm{d}T - P\,\mathrm{d}V$$
$$= -S\,\mathrm{d}T - P\,\mathrm{d}V$$
$$= \left(\frac{\partial A}{\partial T}\right)_V + \left(\frac{\partial A}{\partial V}\right)_T$$

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

$$\Delta S = \int_{V_1}^{V_2} \frac{\partial S}{\partial V}\,\mathrm{d}V = \int_{V_1}^{V_2} \frac{\partial P}{\partial T}\,\mathrm{d}V = \int_{V_1}^{V_2} \frac{nR}{V}\,\mathrm{d}V = nR\ln\frac{V_2}{V_1}$$

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 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

$$\mathrm{d}U = \underbrace{T\,\mathrm{d}S}_{\delta q_{\text{rev}}} \underbrace{-P\,\mathrm{d}V}_{\delta w_{\text{rev}}}$$

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

$$\mathrm{d}U = \frac{\partial U}{\partial T}\,\mathrm{d}T + \frac{\partial U}{\partial V}\,\mathrm{d}V$$

– Combining the two above equations, we have that

$$T\,\mathrm{d}S - P\,\mathrm{d}V = \frac{\partial U}{\partial T}\,\mathrm{d}T + \frac{\partial U}{\partial V}\,\mathrm{d}V$$
$$\mathrm{d}S = \frac{1}{T}\frac{\partial U}{\partial T}\,\mathrm{d}T + \frac{1}{T}\left(P + \frac{\partial U}{\partial V}\right)\mathrm{d}V$$
$$= \frac{C_V\,\mathrm{d}T}{T} + \frac{1}{T}\left(P + \frac{\partial U}{\partial V}\right)\mathrm{d}V$$

- 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* $\boldsymbol{\Theta_D}$.

- **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* $\boldsymbol{S^\circ}$. *Units* $\textbf{J mol}^{-1}\,\textbf{K}^{-1}$.

  - 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.