Week 5

Entropy and the Third Law of Thermodynamics

5.1 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

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

  - 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

  $$dH = dU + P\,dV + V\,dP = T\,dS + V\,dP$$

  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, $\Delta_{\mathrm{fus}}S \ll \Delta_{\mathrm{vap}}S$.

- **Debye T^3 law**: As $T \to 0$ (i.e., for about $T = 0 - 15\,\mathrm{K}$), $C_P^s(T) \to T^3$ 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 $S°$.*

  - 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 $S°[Br_{2(g)}]$ 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.