

Week 5

Entropy and the Third Law of Thermodynamics

5.1 Entropy and the Third Law

2/7: • An experimental determination of entropy.

- We have that

$$\begin{aligned}dU &= \delta q_{\text{rev}} + \delta w_{\text{rev}} \\ &= T dS - P dV\end{aligned}$$

- 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

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

- 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

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

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 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 K and measure properties such as entropy there, we appeal to the Debye model to determine entropy there and in the vicinity.

- **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 K,

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

– Justifying the Debye model.

- According to the Einstein model, each atom is a harmonic oscillator of frequency $h\nu$. This implies, however, that $C_P(T) \approx 1/(e^{h\nu/k_B T} - 1)$ 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, its 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 K, as described in McQuarrie and Simon (1997).

5.2 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

$$\begin{aligned} T dS - P dV &= \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial V} dV \\ dS &= \frac{1}{T} \frac{\partial U}{\partial T} dT + \frac{1}{T} \left(P + \frac{\partial U}{\partial V} \right) dV \\ &= \frac{C_V dT}{T} + \frac{1}{T} \left(P + \frac{\partial U}{\partial V} \right) dV \end{aligned}$$

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

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

- Since

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

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

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

- **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

$$\begin{aligned} S(0 \text{ K}) &= -k_B \sum_j p_j \ln p_j \\ &= -k_B \sum_{j=1}^n \frac{1}{n} \ln \frac{1}{n} \\ &= k_B \ln n \end{aligned}$$

- Nevertheless, even for a degeneracy of N_A , we will only have $S(0 \text{ K}) \approx 7.56 \times 10^{-22} \text{ J mol}^{-1} \text{ K}^{-1}$, 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).

$$\begin{aligned} S(T) &= S(0) + S(T) - S(0) \\ &= S(0) + \Delta S \\ &= S(0) + \int_0^T \frac{C_P(t)}{t} dt \\ &= \int_0^T \frac{C_P(t)}{t} dt \end{aligned}$$

- 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,

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

- It follows that, as applicable,

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

- Note that with typical values plugged in, $\Delta_{\text{fus}} S \ll \Delta_{\text{vap}} S$.
- **Debye T^3 law:** As $T \rightarrow 0$ (i.e., for about $T = 0 - 15 \text{ K}$), $C_P^s(T) \rightarrow T^3$ for most nonmetallic crystals and $C_P^s(T) \rightarrow aT + bT^3$ ($a, b \in \mathbb{R}_{\geq 0}$) 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 Θ_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 K, but we can still calculate $S^\circ[\text{Br}_{2(g)}]$ by imagining the following path: Raise $\text{Br}_{2(l)}$ to its boiling point; vaporize it; cool it back down to 298 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*

$$\bar{S}_{\text{calc}} - \bar{S}_{\text{exp}}$$

- 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 N₂O.
 - 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 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), $\bar{S}(0\text{ K}) = R \ln 2$ here.
- We can similarly account for the larger still residual entropy in H₃CD by noting that the ground state is four-fold degenerate, and thus $\bar{S}(0\text{ K}) = R \ln 4$ here.
- We can use standard molar entropies to calculate the entropy changes of chemical reactions.