

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 $h\nu = hc/\lambda = 2\pi\hbar c/\lambda = \hbar ck$.
- 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 Introduction to Free Energies

2/9:

- Discusses the entropy trends from Chapter 21.
 - More atoms ($\text{CO} < \text{CO}_2$) 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 $dS \geq 0$ for an isolated system, and that $dS \geq \delta q/T$ for any system (equality holds for reversible processes).

- Rearranging, we have that

$$0 \geq \delta q - T dS$$

- It follows since $dU = \delta q + \delta w$ that

$$\begin{aligned} dU - T dS &= (\delta q - T dS) + \delta w \\ &\leq \delta w \end{aligned}$$

- But since $A = U - TS$ is clearly a state function (as a combination of state functions and state variables),

$$dA = dU - T dS - S dT$$

is an exact differential for a state function. In particular, at constant temperature,

$$dA = dU - T dS$$

- Therefore, $dA \leq \delta w$ at constant temperature.
- Thus, at constant T, V, w , $dA \leq 0$. 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 G . Given by

$$G = H - TS$$

- It follows from our prior results that at constant temperature,

$$\begin{aligned} dG &= dH - T dS \\ &= dU + d(PV) - T dS \\ &= \delta q + \delta w + P dV + V dP - T dS \\ &= \delta q - P dV + \delta w_{\text{non-rev } PV} + P dV + V dP - T dS \\ &= \delta q - T dS + \delta w_{\text{non-rev } PV} + V dP \\ &\leq 0 + \delta w_{\text{non-rev } PV} + V dP \end{aligned}$$

- Thus, at constant T, P and with no other w done on the system, $dG \leq 0$.
- In a reversible process (constant T, P), $dG = \delta w_{\text{non-rev } PV}$.

- Note that δw is the work put into the system, so $\delta w \geq \delta w_{\text{rev}} = dA$.
- 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



with $\Delta H = 285.76 \text{ kJ/mol}$ and $\Delta G = 237.1 \text{ kJ/mol}$.

- 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 converted to work directly (as current and voltage in the fuel cell). Thus, in theory, running 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

$$\begin{aligned} dA &= \delta q_{\text{rev}} - T dS - S dT - P dV \\ &= -S dT - P dV \\ &= \left(\frac{\partial A}{\partial T} \right)_V + \left(\frac{\partial A}{\partial V} \right)_T \end{aligned}$$

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

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

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 Differential Relations

- 2/11: • A useful equation for the change in energy per unit volume at constant temperature, and equation of state.

- We have that

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

- It follows that

$$\begin{aligned} dU &= T dS - P dV \\ &= T \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV - P dV \\ &= \underbrace{T \left(\frac{\partial S}{\partial T} \right)_V}_{(\partial U / \partial T)_V} dT + \underbrace{\left[\left(\frac{\partial S}{\partial V} \right)_T - P \right]}_{(\partial U / \partial V)_T} dV \end{aligned}$$

- Thus, by Maxwell relations,

$$\begin{aligned} \left(\frac{\partial U}{\partial V} \right)_T &= T \left(\frac{\partial S}{\partial V} \right)_T - P \\ &= T \left(\frac{\partial P}{\partial T} \right)_V - P \end{aligned}$$

- This equation can be evaluated given the equation of state.
- For an ideal gas, we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{nR}{V} - P = 0$$

- For a van der Waals gas (just the excluded volume b part, not the a term), we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{\partial}{\partial T} \left(\frac{nRT}{V - nb} \right) - P = \frac{nRT}{V - nb} - P = 0$$

- Now for small enough volume, we know that a gas will compress into a liquid. In other words, $T(\frac{\partial P}{\partial T})_V \geq P$ always, where equality is only a good approximation at sufficiently large volumes.
- A similar method can be applied to enthalpy changes with pressure.
 - We can derive in an analogous method that

$$\left(\frac{\partial H}{\partial P}\right)_T = V + T \left(\frac{\partial S}{\partial P}\right)_T$$

- You can only apply the chain rule to partial derivatives held constant with respect to the same variable(s).
- **Natural variables** (of a state function): A set of state variables for which the partial derivatives of the state function with respect to said variables are (simple expressions of) state variables or state functions.

- For example, S, P are the natural variables of U since $\partial U / \partial S = T$ and $\partial U / \partial V = -P$ as shown by

$$dU = T dS - P dV$$

- V, T are not natural variables of U , as we showed earlier, since the partial derivatives of U with respect to them are complicated expressions.
- For the other state functions, we have

$$\begin{aligned} dH &= T dS + V dP & dA &= -S dT - P dV \\ dS &= \frac{1}{T} dU + \frac{P}{T} dV & dG &= -S dT + V dP \end{aligned}$$

- Note that natural variables are not unique, as we also have

$$dS = \frac{1}{T} dH - \frac{V}{T} dP$$

- An example of using Maxwell relations to getting C_V to C_P (19-27 and 22-11).

- We have that

$$C_P - C_V = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

- We also have that

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

- It follows if we let $dV = 0$ in the above expression that

$$\left(\frac{\partial P}{\partial T}\right)_V = - \frac{(\partial V / \partial T)_P}{(\partial V / \partial P)_T}$$

– Therefore,

$$\begin{aligned}
 C_P - C_V &= T \left[-\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} \right] \left(\frac{\partial V}{\partial T} \right)_P \\
 &= -T \frac{(\partial V/\partial T)_P^2}{(\partial V/\partial P)_T} \\
 &= -T \frac{V^2 \alpha^2}{-V \kappa} \\
 &= \frac{TV \alpha^2}{\kappa}
 \end{aligned}$$

where α is the **thermal expansion coefficient** and κ is the **isothermal compressibility**.

- **Thermal expansion coefficient:** The following constant. Denoted by α . Given by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

- **Isothermal compressibility:** The following constant. Denoted by κ . Given by

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

5.4 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° . Units $\text{J mol}^{-1} \text{K}^{-1}$.*
 - 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 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.