

## 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  $\Delta S$  at constant pressure, we expect it to be bigger than  $\Delta S$  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  $\lambda$  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

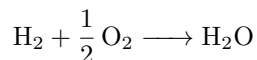
$$G = H - TS$$

- 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  $\delta w$  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  $\Delta G = 237.1 \text{ kJ/mol}$ .

- $\Delta H$  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%!
- $\Delta G$  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

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

- 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  $\alpha$  is the **thermal expansion coefficient** and  $\kappa$  is the **isothermal compressibility**.

- **Thermal expansion coefficient:** The following constant. Denoted by  $\alpha$ . Given by

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

- **Isothermal compressibility:** The following constant. Denoted by  $\kappa$ . Given by

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

## 5.4 Office Hours (PGS)

- So is the content of the midterm Chapters 17-22 plus parts of Chapter 25 (the Maxwell-Boltzmann distribution)?
- Are there going to be any surprises I should look out for (a la surface tension)?
- Will questions be like homework questions, quiz questions?
- Are we going to have to know derivations or just formulas?

## 5.5 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

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

- **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  $T_{\text{trs}}$  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  $T = 0 - 15$  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  $\Theta_D$ .*
- **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  $\text{N}_2$  based on various thermodynamic data.
- **Standard entropy:** An entropy value of a gas as presented in the literature. *Denoted by  $S^\circ$ . 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  $\text{N}_2$ , 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 ( $\text{CO}_2$ ).
- 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,  $\text{Br}_2$  is a liquid at 298 K, but we can still calculate  $S^\circ[\text{Br}_{2(\text{g})}]$  by imagining the following path: Raise  $\text{Br}_{2(\text{l})}$  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 N<sub>2</sub>O.
  - 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  $T_{\text{fus}}$ , 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 H<sub>3</sub>CD 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.

## 5.6 Chapter 22: Helmholtz and Gibbs Energies

- 2/14:
- Since the  $dS \geq 0$  criterion for isolated systems is quite restrictive (only applies to isolated systems), we introduce two new state functions that will help determine the direction of a spontaneous process in a non-isolated system.
  - **Helmholtz energy:** A state function describing the energy of a system at constant volume and temperature. *Denoted by  $A$ . Given by*

$$A = U - TS$$

- Since  $dV = dT = 0$ , we know that

$$\begin{aligned} dU &= \delta q + \delta w \\ &\leq T dS - P dV \\ dU - T dS - S dT &\leq 0 \\ d(U - TS) &\leq 0 \end{aligned}$$

where equality holds for a reversible process and inequality holds for an irreversible process (by the properties of the Clausius inequality).

- Thus, the Helmholtz energy will decrease until all spontaneous processes have occurred. At this point,  $dA = 0$  and  $A$  will be at a minimum.
- $dA \leq 0$  is the analog of  $dS \geq 0$  for a spontaneous process to occur.
- “A process for which  $\Delta A > 0$  cannot take place spontaneously in a system at constant  $T$  and  $V$ . Consequently, something, such as work, must be done on the system to effect the change” (McQuarrie & Simon, 1997, p. 883).
- “The Helmholtz energy represents this compromise between the tendency of a system to decrease its energy and to increase its entropy” (McQuarrie & Simon, 1997, p. 883).
- Note that the sign of  $U$  is more important at low  $T$  and vice versa for high  $T$  by  $U - TS$ .
- McQuarrie and Simon (1997) applies the definition of  $A$  to the mixing of two ideal gases, showing that  $\Delta A < 0$  for it.

- A physical interpretation to  $\Delta A$ .

- When a process is carried out along a reversible path,

$$\Delta A = \Delta U - q_{\text{rev}} = w_{\text{rev}}$$

meaning that  $\Delta A$  is either the maximum work that can be pulled out of the system or the minimum work required to drive the process (depending on its sign).

- **Gibbs energy:** A state function describing the energy of a system at constant pressure and temperature. Denoted by  $G$ . Given by

$$G = H - TS$$

- Since  $dP = dT = 0$ , we know that

$$\begin{aligned} dU &= \delta q + \delta w \\ &\leq T dS - P dV \\ dU + P dV + V dP - T dS - S dT &\leq 0 \\ d(U + PV - TS) &\leq 0 \\ d(H - TS) &\leq 0 \end{aligned}$$

where equality holds for a reversible process and inequality holds for an irreversible process (by the properties of the Clausius inequality).

- The Gibbs energy is analogous in almost every way to the Helmholtz energy.
- We can also write  $G = A + PV$  to relate  $G, A$  in the same manner that  $H, U$  are related, respectively.
- **Molar Gibbs energy of vaporization:** The following quantity. Denoted by  $\Delta_{\text{vap}} \bar{G}$ . Given by

$$\Delta_{\text{vap}} \bar{G} = \Delta_{\text{vap}} \bar{H} - T \Delta_{\text{vap}} \bar{S}$$

- Note that  $\Delta_{\text{vap}} \bar{G} = 0$  at 1 atm and 100 °C. This means that the phases are in equilibrium under these conditions.
- A slight increase in temperature, however, makes  $\Delta G < 0$  (i.e., makes vaporization spontaneous), while a slight decrease in temperature makes  $\Delta G > 0$  (i.e., makes condensation spontaneous).
- McQuarrie and Simon (1997) covers that in a reversible process,  $\Delta G = w_{\text{non PV}}$ , i.e., the maximum non-pressure/volume work available from a process or minimum non-pressure/volume work required to drive a process.
  - $w_{\text{non PV}}$  can be electrical work, for example.
- **Maxwell relation:** An relation obtained by equating the second cross partial derivatives of a function.
- **Thermodynamic equation of state:** An equation that relates a thermodynamic function to functions of  $P$ ,  $V$ , and  $T$ .
- McQuarrie and Simon (1997) notes that

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

meaning that energy does depend on volume somewhat (it's not entirely a function of temperature).

- We can show that the above derivative reduces to zero for an ideal gas, however.
- McQuarrie and Simon (1997) plays around with partial derivatives for a while.
  - Discusses the  $\alpha, \kappa$  definition of  $C_P - C_V$ .

- We can also use Maxwell relations and differentials to derive the following results.

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

- Covers natural variables.

Thermodynamic energy	Differential expression	Corresponding Maxwell relations
$U$	$dU = T dS - P dV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
$H$	$dH = T dS + V dP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
$A$	$dA = -S dT - P dV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
$G$	$dG = -S dT + V dP$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Table 5.1: Thermodynamic energies, differentials, and Maxwell relations.

- Calculating corrections to the standard molar entropy of a gas.

- Basically, we want to find  $S^\circ(1 \text{ bar}) - \bar{S}(1 \text{ bar})$ . To do so, we consider

$$S^\circ(1 \text{ bar}) - \bar{S}(1 \text{ bar}) = [S^\circ(1 \text{ bar}) - \bar{S}(P_{\text{id}})] + [\bar{S}(P_{\text{id}}) - \bar{S}(1 \text{ bar})]$$

where  $P_{\text{id}}$  is a pressure sufficiently low such that the gas in question behaves ideally.

- We know from the definition of changes in entropy as an integral and Table 5.1 that

$$\begin{aligned}S^\circ(1 \text{ bar}) - \bar{S}(P_{\text{id}}) &= \int_{P_{\text{id}}}^{1 \text{ bar}} \left(\frac{\partial S}{\partial P}\right)_T dP & \bar{S}(P_{\text{id}}) - \bar{S}(1 \text{ bar}) &= \int_{1 \text{ bar}}^{P_{\text{id}}} \left(\frac{\partial S}{\partial P}\right)_T dP \\ &= - \int_{P_{\text{id}}}^{1 \text{ bar}} \left(\frac{\partial V}{\partial T}\right)_P dP & &= - \int_{1 \text{ bar}}^{P_{\text{id}}} \left(\frac{\partial V}{\partial T}\right)_P dP \\ &= - \int_{P_{\text{id}}}^{1 \text{ bar}} \frac{R}{P} dP & &= \int_{P_{\text{id}}}^{1 \text{ bar}} \left(\frac{\partial V}{\partial T}\right)_P dP\end{aligned}$$

- Note that we calculate the first change using the ideal gas law and the second change using the equation of state describing the real gas.

- Adding the above two equations yields

$$S^\circ(1 \text{ bar}) - \bar{S}(1 \text{ bar}) = \int_{P_{\text{id}}}^{1 \text{ bar}} \left[ \left(\frac{\partial V}{\partial T}\right)_P - \frac{R}{P} \right] dP$$

- We can evaluate this equation using only the second virial coefficient (see Chapter 16).

- McQuarrie and Simon (1997) discusses  $G = G^\circ + RT \ln Q$ .

- **Gibbs-Helmholtz equation:** An equation for the temperature dependence of  $G$ . *Given by*

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2}$$

– Derivation:

$$\begin{aligned} G &= H - TS \\ \frac{G}{T} &= \frac{H}{T} - S \\ \left(\frac{\partial G/T}{\partial T}\right)_P &= \left[\frac{\partial}{\partial T}\left(\frac{1}{T} \cdot H\right)\right]_P - \left(\frac{\partial S}{\partial T}\right)_P \\ &= \left[\frac{\partial}{\partial T}\left(\frac{1}{T}\right) \cdot H\right]_P + \frac{1}{T} \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P \\ &= -\frac{H}{T^2} + \frac{C_P}{T} - \left(\frac{\partial S}{\partial T}\right)_P \\ &= -\frac{H}{T^2} \end{aligned}$$

- McQuarrie and Simon (1997) discusses the graph of  $G(T)$ .

– It offers an alternate explanation for continuity, namely that since  $\Delta_{\text{trs}}S = \Delta_{\text{trs}}H/T_{\text{trs}}$ , then

$$0 = \Delta_{\text{trs}}H - T_{\text{trs}}\Delta_{\text{trs}}S = \Delta_{\text{trs}}G$$