

5.3: Calculations- Numerical and Derivations

We now have 12 variables (U, P, V, T, ∂q , ∂w , H, C_V , C_P , S, A, and G) that can change via four distinct mechanisms (isothermal or adiabatic \times reversible or irreversible). This lends itself to 48 types of thermodynamic calculations, although this is actually an over estimation because changes in state variables (U, H, A, G, S) are the same regardless of the condition due to exactness. We will now review methods to calculate ΔA and ΔG for gas expansion / contraction problems, although some problems don't have simple solutions. This chapter is also the last holdout for these types of pressure-volume questions, because in Chapter 6 and beyond we will apply thermodynamic calculations to chemical transformations.

5.3.1 Thermodynamic Calculations. We start with calculate changes in Gibbs and Helmholtz energies for gas pressure-volume transitions under isothermal and adiabatic conditions. The fact that G and A are state variables means that there are some generalities that make these problems easier. For example, the changes in Gibbs and Helmholtz energies for either reversible or irreversible isothermal transitions are both equal to the reversible work: $\partial A = \partial G = \partial w_{rev}$. Since we have discussed calculations of reversible work extensively in previous chapters, there isn't much else to say here!

The next two conditions are the reversible and irreversible adiabatic cases. Concerning the adiabatic reversible, the change in Gibbs energy is:

$$\partial G = \partial H - \partial(TS) = \partial H - S\partial T - T\partial S$$

and since the system entropy is constant ($\partial S = 0 \text{ J/K}$) and $\partial H = C_P \partial T$ under adiabatic reversible conditions:

$$\partial G = \partial H - S\partial T = C_P \partial T - S\partial T$$

Here we see that the change in Gibbs energy can be calculated once the change in temperature has been determined. Using the same procedure we can show:

$$\partial A = C_V \partial T - S\partial T$$

which also demonstrates the ability to calculate the change in Helmholtz energy with temperature. This requires that the absolute value of the entropy of the system (S) must be known, and it can be using the 3rd Law of Thermodynamics as discussed in the next chapter. However, this is a bit complex so we won't consider this further.

Calculations of A and G for adiabatic irreversible transitions are problematic; consider for example: $\partial A = \partial H - \partial(TS)$. Here, both S and T are simultaneously changing because entropy is a function of temperature. We encountered a similar problem with enthalpy: $\partial H = \partial U + \partial(PV)$, where the complicating $\partial(PV)$ term was resolved using the perfect gas law as: $\partial(PV) = nR\partial T$. However, we don't have a perfect gas law for entropy and temperature, and as such calculating the changes in Helmholtz and Gibbs energies for adiabatic irreversible transitions is not straightforward. We also question the value of knowing the changes of Gibbs and Helmholtz energies for adiabatic transitions because they do not represent total entropy and are not directly applicable towards determining the spontaneity of a process.

5.3.2 Pressure and Volume. Knowledge of Helmholtz and Gibbs energies allow us to examine more complex thermodynamic proofs. We have already established that $\left(\frac{\partial G}{\partial V}\right)_T = -P$, which means that the Gibbs energy of a substance goes down with increasing volume ($-P$ can only be negative). What is more important is how Gibbs energy changes with pressure, its natural variable, at constant temperature. Beginning with $\partial G = V\partial P - S\partial T = V\partial P$, since $\partial T = 0 \text{ K}$, then $\left(\frac{\partial G}{\partial P}\right)_T = V$ which means that Gibbs energy always goes up with increasing pressure as volume is always positive. This probably doesn't sound interesting now, but it will be very important to understand phase diagrams later in Chapter 8. Examining how Helmholtz and Gibbs Energies change with temperature is a bit more complex as discussed below.

5.3.3 Temperature and the Gibbs-Helmholtz Equation. As stated at the beginning of this chapter, the Earth is best described as a constant temperature and pressure system. Under these conditions a negative change in Gibbs energy means that the total entropy of a process is increasing, which determines spontaneity. Thus, knowing how Gibbs energy changes with temperature is very important.

Some might ask why we concern ourselves with changes in Gibbs energy with temperature, when ΔG is related to spontaneity (increasing ΔS_{tot}) at constant temperature. It's because a chemical process can be conducted at constant temperature, but we never

said at what temperature. For example, if a reaction is not spontaneous at 25 °C, it might be if we changed the temperature (and then held the temperature constant). The way to know this is to determine $\left(\frac{\partial G}{\partial T}\right)_P$ starting with:

$$\partial G = V\partial P - S\partial T = -S\partial T$$

where we invoked constant pressure ($\partial P = 0$ Pa), and after dividing both sides by ∂T we see: $\left(\frac{\partial G}{\partial T}\right)_P = -S$. Since entropy is always positive according to the 3rd Law as described in Chapter 6, Gibbs energy goes down with increasing temperature in proportion to the entropy. This information gives us much insight- if the products of a reaction have greater entropy than the reactants, then increasing the temperature will likely result in a more negative ΔG which is good.

But now, there is a big problem in that there is no such thing as an entropy “thermometer”, and even worse entropy is a function of temperature. Thus, we need to try to replace entropy with something else to make the determination of $\left(\frac{\partial G}{\partial T}\right)_P = -S$ easier.

Starting with $G = H - TS$, we can see that $S = \frac{H-G}{T}$, which then gives us:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S = \frac{G-H}{T} \quad (5.3.1)$$

Here, we are mathematically “stuck” because we have ∂G on the left side of the equation and G on the right, and we have to have them both on the left side to do anything with Equation 5.8. Unfortunately there is no easy way to algebraically factor G out of $\frac{G-H}{T}$ on the right-hand side.

It turns out that we can simply change the question; rather than try to determine how G changes with T , instead we ask how G/T changes with T . This will work because temperature is always positive, and thus it won’t affect whether ∂G is positive (less spontaneous) or negative (more spontaneous) with increasing temperature. Let us start with:

$$\left(\frac{\partial \frac{G}{T}}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} = \frac{1}{T} \left(\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T}\right) \quad (5.3.2)$$

which comes from the product rule: $\frac{\partial(f \cdot g)}{\partial x} = f \frac{\partial g}{\partial x} + g \frac{\partial f}{\partial x}$, where $f=1/T$, $g=G$, and $x=T$. Going back to equation 5.8: $\left(\frac{\partial G}{\partial T}\right)_P = \frac{G-H}{T}$ to which we make some rearrangements: $\left(\frac{\partial G}{\partial T}\right)_P = \frac{G}{T} - \frac{H}{T}$ we find that:

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

The above is inserted into Equation 5.9:

$$\left(\frac{\partial \frac{G}{T}}{\partial T}\right)_P = \frac{1}{T} \left(\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T}\right) = \frac{1}{T} \left(-\frac{H}{T}\right) = -\frac{H}{T^2}$$

This is the Gibbs-Helmholtz equation, which will be very important in our further developments on phase transitions and colligative properties discussed in later chapters. For now, let’s use it to answer the original question as to whether we should heat up a chemical reaction that isn’t “going” (non-spontaneous) as it has a positive ΔG . For a reaction, we take the Gibbs-Helmholtz

equation $\left(\frac{\partial \frac{G}{T}}{\partial T}\right)_P = -\frac{H}{T^2}$ and we re-write it in terms of changes of those thermodynamic functions:

$$\left(\frac{\partial \frac{\Delta G}{T}}{\partial T}\right)_P = -\frac{\Delta H}{T^2} \quad (5.3.3)$$

Next, an endothermic reaction has a positive ΔH , because enthalpy is heat at constant pressure and endothermic reactions soak in heat. Thus, $-\frac{\Delta H}{T^2}$ is negative and that makes $\left(\frac{\partial \frac{\Delta G}{T}}{\partial T}\right)_P$ negative too. Consequently, if we increase T , then $\frac{\Delta G}{T}$ (and thus ΔG)

becomes more negative, which is good for making a reaction spontaneous. We can also explain this using Le Chatelier's principle. An endothermic reaction has heat as a reactant:

heat + reactants \rightarrow products

and thus adding more heat by increasing the temperature should lead to more products. See, you knew this all the time! Last, if a reaction is exothermic, then you will want to cool the system because doing so lowers ΔG and increases the reaction's spontaneity.

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