

8.1: The Gibbs Phase Rule

In the following sections we will develop various thermodynamic relationships to mathematically “create” a phase diagram, although we have to have some data such as the location of the triple point. We can also show that there cannot be such a thing as a quadruple point, unless the phase diagram has more than one component (i.e. its for a mixture). This can be demonstrated by calculating the number of degrees of freedom of the phase diagram; note this is not the same “degrees of freedom” of a gas molecule that was discussed in Chapter 2. Here we will define what a degree of freedom is by example; if we have a P vs. T diagram, we automatically have two degrees of freedom, which are pressure and temperature. With these two degrees of freedom we may be able to change pressure and temperature independently of each other and remain in a particular state. In plain English, we can heat or cool water a few degrees and still have liquid water, even if we are at a higher or lower pressure altitude (i.e. Death Valley vs. Mexico City).

Of course, if we keep heating the water eventually it will start to boil; at this point we say that the liquid water and steam co-exist. If we increase the temperature further then all the liquid boils off. In contrast, if we wish to maintain the liquid-gas equilibrium at the higher temperature, we can do so by simultaneously increasing the pressure as dictated by the line between the two phases seen in Figures 8.1 and 8.2. This means that pressure is no longer a degree of freedom because it must change in a way that is uniquely determined by the temperature according to the phase diagram. Of course, we can also state that if we change the pressure then we don’t have control over the temperature. It doesn’t really matter because, in either case, we only have one degree of freedom if we are trying to maintain equilibrium between two phases.

Let’s put this discussion into mathematical terms. We start by stating that the number of degrees of freedom in a phase diagram, “ f ”, is at least equal to 2 to represent temperature and pressure: $f = 2$. There could be more than one component “ c ” present. For example, perhaps we are attempting to describe the phase diagram of an ethanol + water mixture. In this case, we are free to decide on how much of each component to add to the diagram, giving us “ c ” more degrees of freedom. Thus, $f = 2 + c$. If there are “ p ” number of phases present, then we have even more degrees of freedom. For example, let’s say that we wish to drop in an ice cube (solid) into our ethanol + water liquid mixture, in which we can decide how much ice to add which is a degree of freedom. Consequently, we have $c \cdot p$ degrees of freedom in addition to temperature and pressure, and thus the total is $f = 2 + c \cdot p$.

However, we have run into a small problem. If we have a one phase system ($p = 1$) composed of two liquid components ($c = 2$), then is it really true that we have 2 additional degrees of freedom aside pressure and temperature? Oddly no, because the system can be characterized by just one variable, which is the percent composition of just one component. For example, in our ethanol + water solution the composition can be known just by the water mole fraction (χ_{water}) because the ethanol composition is automatically: $\chi_{EtOH} = 1 - \chi_{water}$. Thus, there is just one degree of freedom. Let’s use some mathematical representations to understand this in a better and more general way. If we have c components, then it must be true that the sum of their mole fractions is 1:

$$\chi_1 + \chi_2 + \chi_3 + \dots \chi_c = 1$$

This equation represents a loss of a degree of freedom, because you have no choice that the sum of mole fractions is 1. There has to be an equation like this for each phase:

$$\chi_1^\alpha + \chi_2^\alpha + \chi_3^\alpha + \dots \chi_c^\alpha = 1$$

$$\chi_1^\beta + \chi_2^\beta + \chi_3^\beta + \dots \chi_c^\beta = 1$$

...

$$\chi_1^p + \chi_2^p + \chi_3^p + \dots \chi_c^p = 1$$

where α , β refer to “ p ” different phases, like solid, liquid, or vapor. This is necessary because, as we showed in the previous chapter, the compositions of each phase do not have to be equal to each other. Given the above it is clear that there are “ p ” number of equal signs due to this mole fraction restriction, so we must subtract “ p ” from the degrees of freedom:

$$f = 2 + cp - p$$

At this point a rule for the “degrees of freedom” game has been revealed: add the degrees of freedom to “ f ” but subtract the number of equal signs from constraining equations. In terms of constraints, there is an additional one aside the need for mole fractions to

sum properly. This is the fact that, at equilibrium, the chemical potentials of the different components in the different phases must be equal as we showed in C. For example, for water in equilibrium with ice it must be true that:

$$\mu^{\alpha} = \mu^{\beta}$$

(α =liquid, β =ice). This equation represents a constraint that results in further reductions to the degrees of freedom. And while it appears we have $(p - 1)$ such number of equal signs, however there may be other components in difference phases. As shown below, there are c equations that have $(p - 1)$ equal signs:

$$\begin{aligned}\mu_1^{\alpha} = \mu_1^{\beta} = \dots \mu_1^p \mu_2^{\alpha} = \mu_2^{\beta} = \dots \mu_2^p \\ \dots \mu_c^{\alpha} = \mu_c^{\beta} = \dots \mu_c^p\end{aligned}$$

Consequently the number of constraining equations is $c \cdot (p - 1)$. Thus we now have:

$$f = 2 + cp - p - c \cdot (p - 1)$$

A little algebra shows that:

$$f = 2 + c - p \tag{8.1.1}$$

which is known as the **Gibbs phase rule**.

Let's work a few examples. If we are characterizing a single phase of one component in a phase diagram, then the number of degrees of freedom is: $f = 2 + c - p = 2 + 1 - 1 = 2$, which are pressure and temperature. In a phase diagram such as shown in Figure 8.1, only an open (or "flat") region can represent 2 degrees of freedom. In contrast, for two equilibrium phases of a single component the number of degrees of freedom are: $f = 2 + c - p = 2 + 1 - 2 = 1$. In a phase diagram of Figure 8.1, a single degree of freedom must be represented by a solid line because lines have a single independent variable and a corresponding dependent variable. These are why the co-existence of solids and liquids, solids and gases, and liquids and gases are represented by lines in the P vs. T phase diagrams in Figures 8.1 and 8.2. Coexistence of three phases can only be represented by a point, because a point has no degrees of freedom ($f = 0$); this is the triple point. There is no such thing as a quadruple point in a single component phase diagram, because there cannot be negative degrees of freedom.

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