4.1: Binary Systems

Thus far, we have focused our attention on single-component systems (also called unary, one-component, or pure-component systems). However, real-life systems are never single-component; they are multicomponent systems. The simplest of this category is the binary system. The good news, however, is that the behavior of multicomponent systems are quite similar to that of binary systems. Therefore, we will focus on binary systems, since they are easier to illustrate.

Let us place two gases (A and B) in an isothermal cell. As we did before, we will keep temperature constant during this experiment (shown in Fig. 4.1)

If we move the piston down, we would compress the gases, causing a decrease in volume. In such a scenario, an increase in pressure would occur. The process starts at point A, as shown in Figure 4.2, an all-vapor condition.
Nothing here is new regarding the compression of the vapor itself. As pressure increases, volume decreases accordingly. After some compression, the first droplet of liquid will appear. That is, we have found the dew point of the mixture (point B). We then proceed with compression. As we further compress the system, more liquid will appear and the volume will continue to decrease.

It would appear that we are seeing here the same features as those of the single-component system that we studied in the previous modules. But wait a minute, is that so?

Actually, there is a difference. During the phase transition, pressure does not remain constant in this experiment. In fact, as compression progresses and more liquid is formed, pressure keeps rising — although not as sharply as in the single-phase vapor region. When the entire system has become liquid, with only an infinitesimal bubble of vapor left, we are at point C — the bubble point of the mixture. Please note that, for binary mixtures (as is the case for multicomponent mixtures,) the dew point and bubble point do not occur at the same pressure for isothermal compression. If you recall, for the single-component system, the dew point and the bubble point coincide. This is not true for binary and multicomponent systems. Compare Figure 4.2 with Figure 3.4 (repeated below from Module 3) to see this point.
WHY?? Why is pressure increasing during the phase transition? At this point we start to realize the ways in which composition plays a fundamental role in the behavior of mixtures.

In a single-component system, both liquid and vapor in the two-phase region have the same composition (there is only one chemical substance within the system). Now, when a mixture exists in a two-phase condition, different molecules of different species are present and they can be either in a liquid or vapor state (two-phase condition). Some of them would “prefer” to be in the gas phase while the others would “prefer” to be in the liquid phase. This “preference” is controlled by the volatility of the given component. When we reach point B (Figure 4.2) and the first droplet of liquid appears, the heaviest molecules are the ones that preferentially go to that first tiny droplet of liquid phase. For ‘heavy’ molecules, given the choice, it is more desirable to be in the condensed state.

As we keep on forming more liquid (by compression), mainly light molecules remain in the vapor phase. However, at the end point of the transition (point C in Figure 4.2) we have forced all of them to go to the liquid state — they no longer have a choice. This enforcement requires greater pressure. If you compare a sample of liquid at dew point conditions (point B in Figure 4.2) to one taken in the middle of the transition, it is clear that the former would be richer in heavy components than the latter. The properties of the heaviest component would be most influential at the dew point (when the liquid first appears); while the properties of the lighter component would be most influential at the bubble point (when the last bubble is about to disappear.)

In the two-phase region, pressure increases as the system passes from the dew point to the bubble point. The composition of liquid and vapor is changing; but — watch out! — the overall composition is always the same! At the dew point, the composition of the vapor is equal to the overall composition of the system; however, the infinitesimal amount of liquid that is condensed is richer in the less volatile component. At the bubble point, the composition of the liquid is equal to that of the system, but the infinitesimal amount of vapor remaining at the bubble point is richer in the more volatile component than the system as a whole.

In general, when two different species are mixed, some of the behaviors of the individual species and their properties will change. Their usual behavior (as pure components) will be altered as a consequence of the new field of molecular interactions that has been created. While kept in a pure condition, molecules only interact with like molecules. On the other hand, in a mixture new interactions between dissimilar molecules occur.

Our next step, in order to continue this discussion in a coherent manner, is to draw the complete P-V diagram for this binary mixture by delineating the two-phase region. In the same way as we did previously, we delineate the two-phase region by drawing a complete family of isotherms in the P-V diagram. Figure 4.3 illustrates this.
Again, the line connecting all of the bubble and dew points will generate the bubble and dew point curve, both of which meet at the critical point. Notice that the critical point does not represent a maximum in the P-V diagram of a mixture. Also note that bubble point pressures and dew point pressures are no longer the same.

Again, the isotherms through the two-phase region are not horizontal but have a definite slope. This must have an implication. In fact, it does. What if we now want to plot the P-T diagram for this mixture? Will we have only a single line, where bubble and dew point curves lie on top of each other, as we had for a single-component system? Of course not. Instead of both curves being together, the bubble point curve will shift to the upper left (higher pressures) and dew point curve will shift to the lower right (lower pressures) — both of them meeting at the critical point. Figure 4.4 shows us a typical phase envelope for a mixture.

Notice the enormous difference between the P-T curve of a multi-component system (binary system in this case, Fig. 4.4) and the P-T curve of a pure (single) component (Fig. 3.1 of Module 3, repeated below). The only system for which the bubble point curve will coincide with the dew point curve is a single component system, where we have a single line for the P-T diagram (for example, the boiling point curve represented in Fig. 3.1). In Fig 3.1, the critical point represents the maximum set of (P,T) values that you could find in the P-T graph.
This is not all. There are some other implications. Can we say now that the critical point is the maximum value of pressure and temperature where liquid and gas can coexist? Look at Figure 4.4 again. Obviously not. The critical point is no longer at the apex or peak of the two-phase region; hence, vapor and liquid can coexist in equilibrium at $T > T_c$ and $P > P_c$. In fact, we can identify two new maxima: condition $P_{cc}$ is the maximum pressure and condition $T_{cc}$ is the maximum temperature at which L+V will be found in equilibrium. We assign special names to these points. There are the cricondenbar and cricondentherm, respectively.

Clearly, the only definition that now can still hold for the critical point — both for mixtures and pure components — is the one shown below.

**Critical Point ($P_c, T_c$):** The temperature and pressure for which liquid and vapor are indistinguishable.

Again, this definition is applicable both for mixtures and pure-component systems; it does not make any reference to maximum values in the curve. These maximum values, as we said, have special names in the case of mixtures. Thus, for mixtures, we have to additionally define:

**Cricondentherm ($T_{cc}$):**

1. The highest temperature in the two-phase envelope.
2. For $T > T_{cc}$, liquid and vapor cannot co-exist at equilibrium, no matter what the pressure is.

**Cricondenbar ($P_{cc}$):**

1. The highest pressure in the two-phase envelope.
2. For $P > P_{cc}$, liquid and vapor cannot co-exist at equilibrium, no matter what the temperature is.

In the case of the unary system, besides dew and bubble point curves lying on top of each other, it is clear that cricondentherm, cricondenbar, and critical conditions are also represented by a single point (that is, the critical point itself.) This is clear from all three previous definitions. Thus, as we saw before, the definition for critical point in unary systems encompasses all three of the definitions given above.

For **pure substances only:**
Cricondentherm = Cricondenbar = Critical Point.

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