CHAPTER 6 LECTURE NOTES

Degrees of Freedom:

The number of degrees of freedom (number of variables we can change without affecting the "nature" of the system) is determined by the equation known as the **phase rule**:

$$f = c - p + 2, \tag{6.2}$$

where f is the no. of degrees of freedom, p is the number of phases present and the "2" represents the two variables temperature and pressure.

Applying this rule to a one-component phase diagram such as that of water, we see that in the interior of the solid, liquid or vapor regions, where only one phase is present, we get two degrees of freedom, since $f = 1 - 1 + 2 = 2$. This means that we can change two variables, in this case temperature and pressure, and still have a system consisting only of one phase.

When we have two phases in equilibrium, the number of degrees of freedom decreases to 1: $f = 1 - 2 + 2 = 1$. This means that if we wish to change the conditions and still retain the equilibrium between the two phases, we can only change one of the variables independently. The other variable is then determined by the equilibrium condition.

When three phases are in equilibrium, as at the triple point, the number of degrees of freedom drops to zero. Therefore, the triple point is a unique point for the system. In some cases, as in the case of sulfur, multiple triple points are present (see Fig. 6.1). Each of these are unique points with zero degree of freedom.

Components:

Determining the number of components in a system is not a trivial task. We may make up a formula for this as follows:

$$c = n - e - o,$$

where c is the number of components, n is the number of chemical species present, e is the number of equilibria between them, and o represents any other relationships that may determine the relative amount of one species with respect to another. See Section 6.1 to see applications of these ideas.

Examples: 6.1, 6.2, Problems: 6.1, 6.3, 6.4–6.6.

6.3. Binary systems involving vapor:

Liquid-vapor systems consisting of two components are commonly represented in pressure-composition diagrams at fixed temperature, or temperature-composition diagrams at fixed pressure.

Two equations govern their behavior. These are derived below. Consider a binary (two-component) system consisting of components 1 and 2. Then

$$y_1 = P_1/P \qquad \text{(Dalton's Law)} \qquad (6.8)$$

$$P = P_1 + P_2 = x_1 P_1{}^* + x_2 P_2{}^* \qquad \text{(Raoult's Law)}$$

The last equation may be re-written for a binary system as

$$\boxed{P = x_1 P_1^* + (1 - x_1) P_2^* = P_2^* + (P_1^* - P_2^*) x_1 .} \qquad (6.9)$$

When pressure is lowered on a solution containing x_1 mole fraction of component 1, the first bubble appears when pressure reaches the value predicted by Eq. (6.9). Therefore, this equation is called the **bubble-point line** equation.

Substituting this expression for the total pressure in Eq. (6.8), we get

$$y_1 = \frac{P_1}{P_2^* + (P_1^* - P_2^*) x_1} = \frac{x_1 P_1^*}{P_2^* + (P_1^* - P_2^*) x_1}$$

which gives the composition of the vapor contained in the bubble.

However, it is more useful to obtain an expression for the variation of total pressure as a function of vapor composition. This is done as follows. From the equation above, we get

$$x_1 = \frac{y_1 P_2^*}{P_1^* + (P_2^* - P_1^*) y_1} \qquad (6.10)$$

Also, $\qquad y_1 P = x_1 P_1^* .$

Using Eq. (6.10) to substitute for x_1 in the following equation, we get

$$\boxed{P = \frac{P_1^* P_2^*}{P_1^* + (P_2^* - P_1^*) y_1} ,} \qquad (6.11)$$

which is the desired equation. This equation is called the **dew-point line** equation because when pressure is increased on a vapor at composition y_1 , the first drop of condensate (dew) is formed when the pressure reaches the value predicted by Eq. (6.11).

The bubble-point line is a linear equation in pressure-composition space but the dew-point line is nonlinear. Fig. 6.2 gives good examples of both equations plotted together on the same graph.

Fig. 6.2

Tie-lines:

Horizontal lines (lines drawn at constant pressre in a *P*-*x* diagram or at constant temperature in a *T*-*x* diagram) that connect the compositions of liquid and vapor in equilibrium with each other are called tie-lines.

The lever rule:

The relative amounts of vapor and liquid present at a given *total* composition x_T is given by the lever rule (note error in text!):

$$\frac{n_l}{n_V} = \frac{x_T - y_2}{x_2 - x_T} = \frac{\overline{pv}}{lp}.$$

Example 6.3, Problems 6.9–6.11, 6.13–6.18

Pressure-composition diagram to Temperature-composition diagram:

Figure 6.5, 6.6

Notes:

Higher vapor pressure ⇒ lower boiling point.

Neither the liquid curve or the vapor curve generally appear as straight lines in temperature-composition space.

Temperature-Composition or “Distillation” diagrams:

Fig 6.7

- Temperature-composition diagrams are drawn at fixed pressure, usually 1 atm or 1.013 bar.
- Consider liquid at composition *p*. If we raise the temperature, the liquid will start boiling when it reaches the bubble-point line at that composition, denoted by the point *l*.
- The vapor formed at this temperature has the composition given by the tie-line to the dew-point line, denoted by the point *v*.
- The vapor is richer in the more volatile component. Therefore, the liquid left behind is richer in the less volatile component.
- If this is a sealed system and the vapor is not allowed to escape, the tempearture will remain steady at the boiling point and the liquid and vapor will come to equilibrium.
- On the other hand, if the boiling is allowed to continue and the vapor is continuously removed, the temperature will rise. When it reaches θ_1, the liquid composition is given by the point *R* and the vapor in equilibrium with it will have the composition denoted by the point D.
- If we continue this process of removing the vapor, the liquid will eventually consist of pure component 1, all of component 2 having been removed as vapor.
- If the vapor removed at each stage is allowed to condense to liquid and is boiled again, eventually, the condensate will reach the composition of pure component 2 ($D \rightarrow l' \rightarrow \mathrm{v}' \rightarrow l'' \rightarrow \mathrm{v}'' \rightarrow$.....)
- This is the principle behind the separation technique known as distillation.

Azeotropes:

Positive Deviation from Raoult's Law → Minimum boiling point mixtures.

Fig. 5.8

Fig. 6.9

Negative Deviation from Raoult's Law → Maximum boiling point mixtures:

Fig. 5.9

Fig. 6.10

Azeotropes satisfy two conditions:

1. They boil at temperatures less than either of the pure components (positive deviation) or at temperatures greater than either of the pure components (negative deviation).
2. At the maximum or minimum boiling point (eutectic), the liquid and vapor have the same composition.

Distillation of immiscible liquids:

In a system consisting of two liquids that are almost completely immiscible, the two components separate into mutually exclusive layers. In other words, within each layer, the mole fraction of that component is almost 1. Then, we may write

$$P = P_A^* + P_B^*. \tag{6.20}$$

If n_A and n_B are the compositions of each component in the vapor, we get

$$\frac{n_A}{n_B} = \frac{P_A^*}{P_B^*} \tag{6.21}$$

In other words, the vapor contains more of the more volatile component, as we would normally expect.

Since the molar masses are constants, this immediately gives rise to a useful relationship between the masses of the two substances in the vapor:

$$\frac{w_A}{w_B} = \frac{P_A^* M_A}{P_B^* M_B}.$$

Example 6.4, Problems 6.12–6.14.

Steam distillation is a very useful technique based on these principles for the extraction of organic compounds that are immiscible with water. Since the total vapor pressure of the system is the sum of the two vapor pressures, the liquid mixture boils at temperatures far lower than the boiling points of either liquid. Therefore, it is possible to extract organic compounds that may decompose or undergo reactions if heated to their boiling points.

Reading Assignment: Distillation of partially miscible liquids (p. 246).

Other topics covered:

Partially miscible liquids

Solid-liquid systems

Three-component systems.