Lecture 3

Single equilibrium stages and flash calculations

The simplest separation process is one in which two phases in contact are brought to physical equilibrium, followed by phase separation. If the separation factor between two species in the two phases is very large, a single contacting stage may be sufficient to achieve a desired separation between them; if not, multiple stages are required. For example, if a vapor phase is in equilibrium with a liquid phase, the separation factor is the relative volatility, α, of a volatile component called the light key, LK, with respect to a less-volatile component called the heavy key, HK, where $\alpha_{LK,HK} = K_{LK}/K_{HK}$. If the separation factor is 10,000, an almost perfect separation is achieved in a single stage. If the separation factor is only 1.10, an almost perfect separation requires hundreds of stages. In this lecture, only a single equilibrium stage is considered, but a wide spectrum of separation operations is described. In all cases, the calculations are made by combining material balances with phase equilibria relations. When a phase change such as vaporization occurs, or when heat of mixing effects are large, an energy balance must be added.

The description of a single-stage system at physical equilibrium involves intensive variables, which are independent of the size of the system, and extensive variables, which do depend on system size. Intensive variables are temperature, pressure, and phase compositions (mole fractions, mass fractions, concentrations, etc.). Extensive variables include mass or moles and energy for a batch system, and mass or molar flow rates and energy transfer rates for a flow system.

Regardless of whether only intensive variables or both intensive and extensive variables are considered, only a few of the variables are independent; when these are specified, all other variables become fixed. The number of independent variables is referred to as the variance or the number of degrees of freedom, *F*, for the system. The phase rule of J. Willard Gibbs, which applies only to the intensive variables at equilibrium, is used to determine *F*.

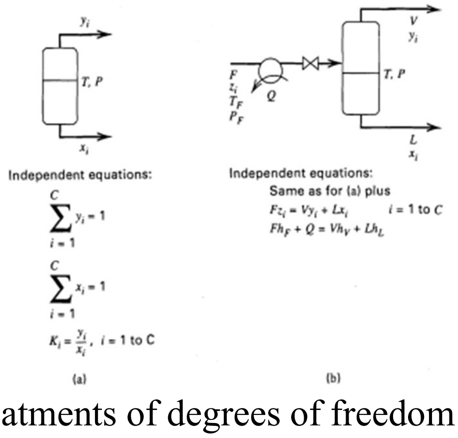

Figure 1 - Different treatments of degrees of freedom for vapor-liquid phase equilibria: (a) Gibbs phase rule (considers equilibrium intensive variables only); (b) general analysis (considers all intensive and extensive variables).

Suppose we have a mixture of 30 mol% H at 150°F. From Figure 2, at point A we have a subcooled liquid with $x_H = 0.3(x_0 = 0.7)$. When this mixture is heated at a constant pressure of 1 atm, the liquid state is maintained until a temperature of 210°F is reached, which corresponds to point B on the saturated-liquid curve. Point B is the bubble point because the first bubble of vapor appears. This bubble is a saturated vapor in equilibrium with the liquid at the same temperature. Thus, its composition is determined by following a tie line, BC from $x_H = 0.3$ to $y_H = 0.7$ ($y_0 = 0.3$).

The tie line is horizontal because the temperalures of the two equilibrium phases are the same. As the temperature of the two-phase mixture is increased to point E, on horizontal tie line DEF at 225°F, the mole fraction of H in the liquid phase decreases to $x_H = 0.17$ (because it is more volatile than 0 and preferentially vaporizes) and correspondingly the mole fraction of H in the vapor phase increases to $y_H = 0.55$.

Throughout the two-phase region, the vapor is at its dew point, while the liquid is at its bubble point. The overall composition of the two phases remains at a mole fraction of 0.30 for hexane. At point E, the relative molar amounts of the two equilibrium phases is determined by the inverse lever-arm rule based on the lengths of the line segments DE and EF. When the temperature is increased to 245°F, point G, the dew point for $y_H = 0.3$ is reached, where only one droplet of equilibrium liquid remains with a composition from the tie line FG at point F of $x_H = 0.06$. A further increase in temperature-say, to point H at 275°F gives a superheated vapor with $y = 0.30$. The steps are reversible starting from point H and moving down to point A.

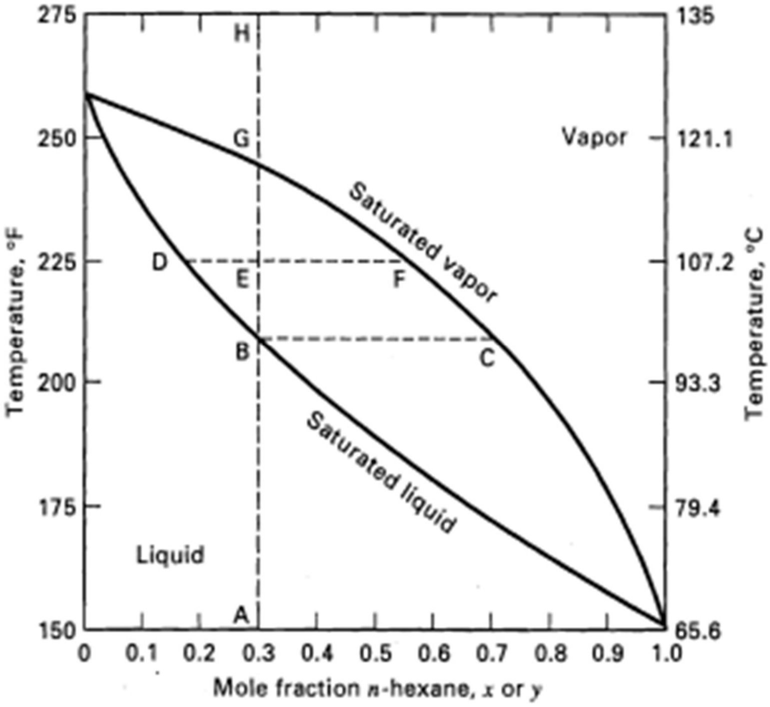

Figure 4.3 Use of the T-y-x phase equilibrium diagram for the normal hexane-normal octane system at 1 atm