4. Phase behaviour of multicomponent systems

4.1 PTx diagrams for binary systems

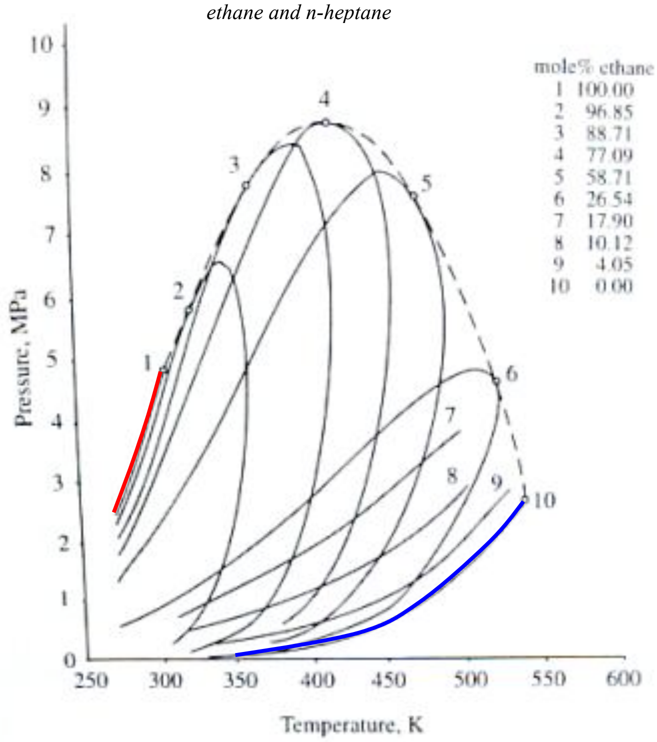
4.1.1 PT Diagrams

For pure substances, the vapor pressure curve in the PT diagram represents both the bubble-point and dew-point curve: they overlap. When an extra component is added, the PT diagram may change and interesting things may happen.

In Slide 13 of Lecture 4, the PT diagram is sketched for an approximate 70/30 mixture (in volume) of ethane and n-heptane. The critical point is also indicated. Left of the critical point is the bubble-point curve. Right of the critical point is the dew-point curve. At a point on the bubble-point curve, we have 100% liquid by volume, at the dew-point curve 0%. Within the region enclosed by the bubble- and dew-points curves exists a region where two phases are present at different pressures/temperatures. In the case of pure substances, the pressure and the temperature stayed the same until a complete change from liquid to vapor, or vice-versa, was made.

The shape of the PT diagram depends strongly on the composition of the mixture. This is illustrated in figure 4-1 that shows the PT diagrams for various mixtures of ethane and n-heptane. The diagram also contains the vapor-pressure curve for pure ethane (line 1) and the vapor-pressure curve for pure n-heptane (line 10). Point 1 is the critical point for pure ethane and point 10 the critical point for pure n-heptane. The dashed curve is the locus of critical points for all possible compositions of the ethane-n-heptane mixture. When the composition of the mixture is evenly distributed by weight (which is the case here for composition 4) the corresponding critical pressure is highest. The critical pressure for the mixture is higher than for either component. The critical temperature lies between the critical temperatures of the lightest and heaviest constituents in the mixture.

Fig 4-1 PT diagrams for various mixtures of ethane and n-heptane



For binary systems composed of two constituents that differ quite a bit in molecular weight, the critical locus encompasses a very wide range of temperatures and pressures. For methane/n-decane mixtures, for example, the maximum pressure on the locus is more than twice that of the above methane/n-heptane mixture. For components very similar in molecular structure (for example propane and n-pentane or n-butane and n-heptane) the loci of the critical points form nearly flat curves connecting the vapor pressure curves of the two components. Figure 4-1 is representative of mixtures of non-polar compounds, such as hydrocarbons. Mixtures of polar, non-similar compounds have different behaviors. Fortunately, we are generally concerned with hydrocarbon materials.

Does it makes sense that, say, PT diagram 6 in figure 4-1 is shifted right and down with regard to PT diagram 2?

Position yourself at some point inside the region enclosed by the bubble-point and dew-point curve of one of the PT diagrams. In this point, what information do you have about the mixture? For example, do you know anything about the composition of the liquid and vapor phases in this point?

4.1.2 Px and Tx Diagrams

In addition to PT diagrams for binary mixtures, information can also be displayed in pressure-composition and temperature-composition mixtures.

In pressure-composition diagrams, the bubble- and dew-point curves are presented for constant temperatures. The bubble-point curve represents the locus of the composition of liquid when two phases are present, while the dew-point curve represents the locus of the composition of gas when two phases are present. Any pressure-composition combination that falls within the bubble- and dew-point curves will exist in liquid-vapor equilibrium, and is also known as the saturation envelope. The composition of the equilibrium gas and liquid phases is determined through a horizontal tie line, connecting the bubble- and dew-point curves. The composition of the liquid is given by the bubble point curve, and the composition of the vapor is given by the bubble-point curve. Similar to the Pv diagrams in Lecture 3, the ratio of gas to liquid can also be determined.

The temperature-composition diagram is similar in appearance and function to the pressure-composition diagrams, although the bubble- and dew-point curves are inverse of each other (as compared to the Px diagrams). In this case, the curves represent constant temperatures.

4.2 Retrograde condensation and vaporization

Two intriguing phenomena may occur in multi-component mixtures: retrograde condensation and retrograde vaporization. To study retrograde condensation let's draw one PT diagram for a certain binary mixture (as seen in Slide 26 of Lecture 4).

The maximum pressure on the PT diagram is called the cricondenbar. The maximum temperature is called the cricondentherm.

Besides the 100% liquid curve (bubble-point) and 0% liquid curve (dew-point) we draw isovol curves for 75%, 50% and 25% liquid in volume. The liquid and gas regions are indicated in the figure, as is the critical point C.

Suppose that we are in point 1 and gradually lower the pressure at constant temperature. We pass the dew-point curve and liquid starts to form at point 2. As the pressure is lowered further, the %vol liquid increases and then decreases as we move toward point 3, on the dew-point curve after which we only have gas.

Can you draw a line in the diagram along which retrograde vaporization takes place?

Can you think of implications of retrograde processes in the petroleum industry?