

Chapter 10

Vapor/Liquid Equilibrium: Introduction

Preceding chapters have dealt largely with pure substances or with constant-composition mixtures. e.g., air. However, composition changes are the desired outcome, not only of chemical reactions, but of a number of industrially important mass-transfer operations.

The most commonly encountered coexisting phases in industrial practice are vapour and liquid, although liquid/liquid, vapour/solid, and liquid/solid systems are also found.

10.1 THE NATURE OF EQUILIBRIUM

Equilibrium is a static condition in which no changes occur in the macroscopic properties of a system with time. This implies a balance of all potentials that may cause change. In engineering practice, the assumption of equilibrium is justified when it leads to results of satisfactory accuracy. For example, in the reboiler for a distillation column, equilibrium between vapour and liquid phases is commonly assumed. For finite vaporization rates this is an approximation, but it does not introduce significant error into engineering calculations. An isolated system consisting of liquid and vapour phases in intimate contact eventually reaches a final state wherein no tendency exists for change to occur within the system. The temperature, pressure, and phase compositions reach final values which thereafter remain fixed. The system is in equilibrium.

Measures of Composition

The three most common measures of composition are mass fraction, mole fraction, and molar concentration. Mass or mole fraction is defined as the ratio of the mass or number of moles of a particular chemical species in a mixture or solution to the total mass or number of moles of the mixture or solution:

$$x_i \equiv \frac{m_i}{m} = \frac{\dot{m}_i}{\dot{m}} \quad \text{OR} \quad x_i \equiv \frac{n_i}{n} = \frac{\dot{n}_i}{\dot{n}}$$

Molar concentration is defined as the ratio of the mole fraction of a particular chemical species in a mixture or solution to its molar volume:

$$C_i \equiv \frac{x_i}{V}$$

This quantity has units of moles of i per unit volume. For flow processes convenience suggests its expression as a ratio of rates. Multiplying and dividing by molar flow rate \dot{n} gives:

$$C_i = \frac{\dot{n}_i}{q}$$

where \dot{n}_i is molar flow rate of species i , and q is volumetric flow rate.

The molar mass of a mixture or solution is, by definition, the mole-fraction-weighted sum of the molar masses of all species present:

$$M \equiv \sum_i x_i M_i$$

10.3 VLE: QUALITATIVE BEHAVIOR

Vapor/liquid equilibrium (VLE) is the state of coexistence of liquid and vapour phases. In this qualitative discussion, we limit consideration to systems comprised of two chemical species, because systems of greater complexity cannot be adequately represented graphically.

A schematic three-dimensional diagram illustrating these surfaces for VLE is shown in Fig. 10.1.

This figure shows schematically the P-T-composition surfaces which contain the equilibrium states of saturated vapor and saturated liquid for a binary system.

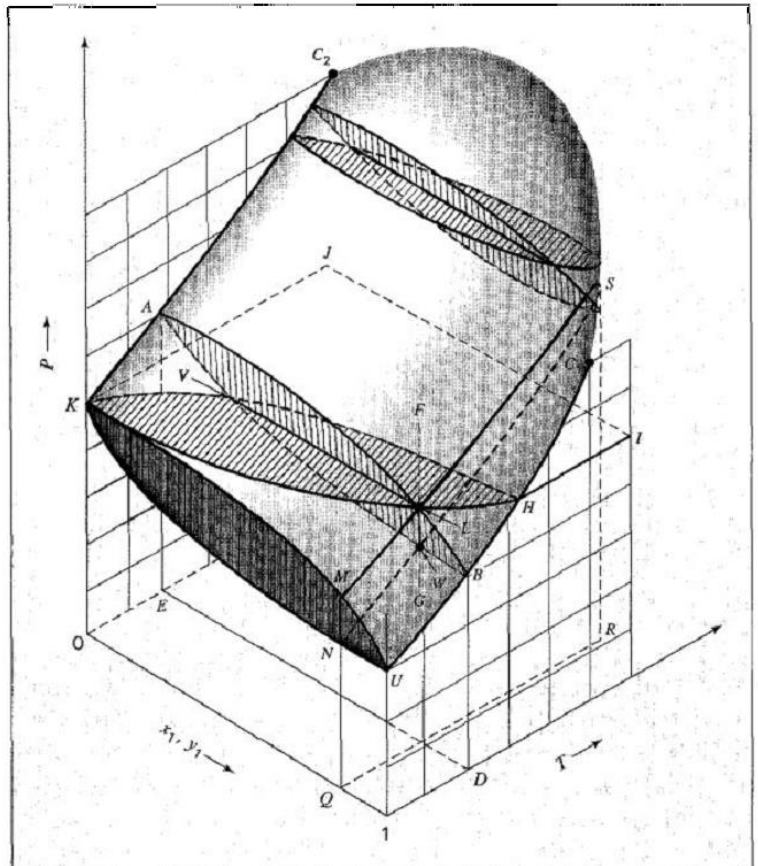


Figure 10.1 $PTxy$ diagram for vapor/liquid equilibrium

Two-Component Mixtures

Phase Diagrams of Two-Component Mixtures

The behaviour of a mixture of two components is not as simple as the behaviour of a pure substance. Instead of a single line representing the vapour-pressure curve, there is a broad region in which two phases coexist. This region is called the saturation envelope, phase envelope, or two-phase region. Figure 2-13 shows the typical shape of the phase diagram for a mixture of two components. The two-phase region of the phase diagram is bounded on one side by a bubble-point line and the other side by a dew-point line. The two lines join at the critical point.

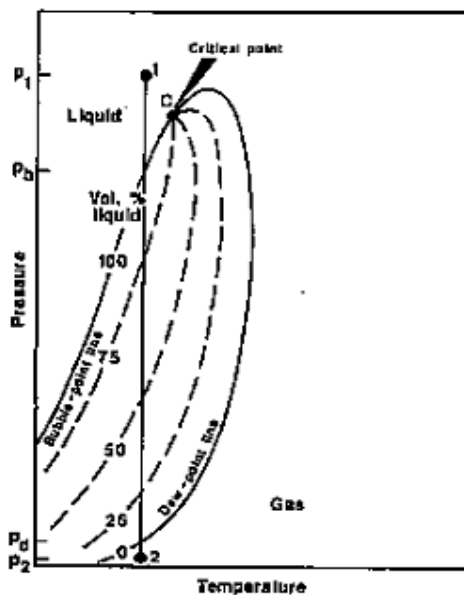


Fig. 2-13. Typical diagram of a two-component mixture with line of isothermal expansion, 12.

The Critical Point

The definition of the critical point as applied to a pure substance does not apply to a two-component mixture. The definition of the critical point is simply the point at which the bubble-point line and the dew-point line join. A more rigorous definition of the critical point is that it is the point at which all properties of the liquid and the gas become identical.

Figure 2-14 shows the vapor-pressure lines of the two components of a mixture superimposed on the phase diagram of the mixture. The saturation envelope for the mixture lies between the vapor pressure lines of the two components. The critical temperature of the mixture lies between the critical temperatures of the two pure components. However, the critical pressure of the mixture is above the critical pressures

of both of the components. The critical pressure of a two-component mixture usually will be higher than the critical pressure of either of the components.

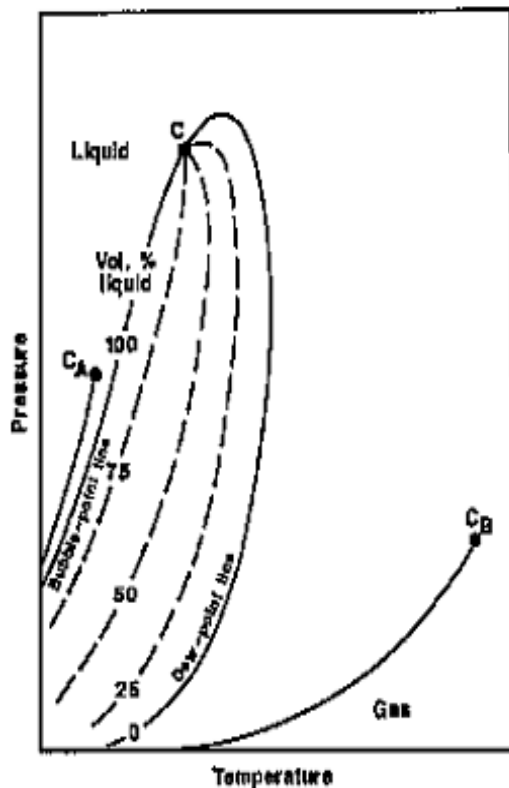


Fig. 2–14. Typical phase diagram of a two-component mixture with vapor-pressure lines of the two pure components.

The P-T diagram of Fig. 10.5 is typical for mixtures of nonpolar substances such as hydrocarbons. A P-T diagram for a very different kind of system, methanol (1)/benzene(2), is shown in Fig. 10.7. The nature of the curves in this figure suggests how difficult it can be to predict phase behaviour for species so dissimilar as methanol and benzene.

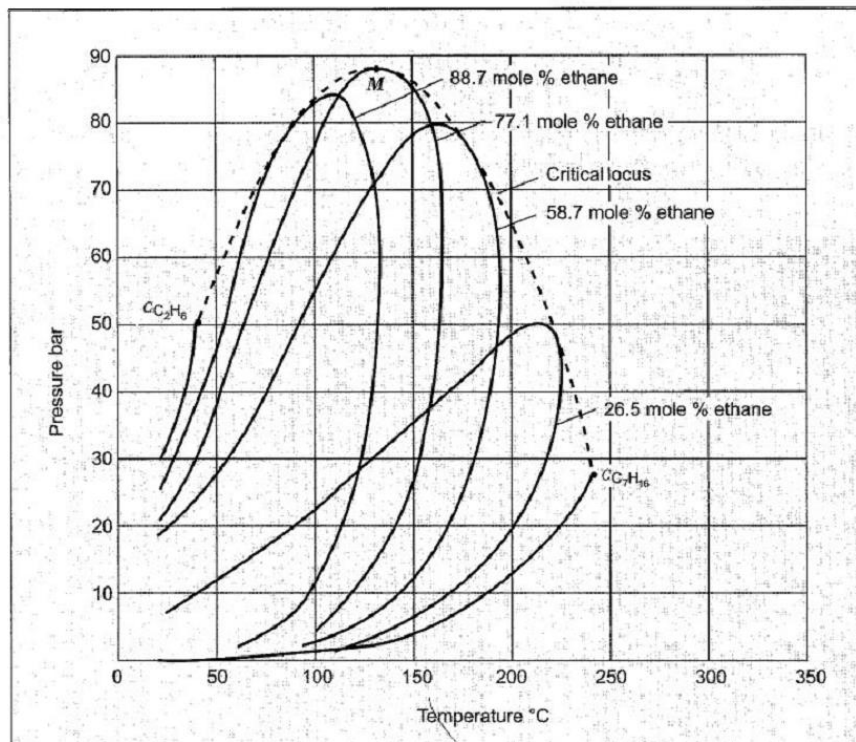


Figure 10.5 *PT* diagram for ethane/n-heptane. (Redrawn from F. H. Barr-Davie *AIChE J.*, vol. 2, pp. 426–427, 1956 with permission.)

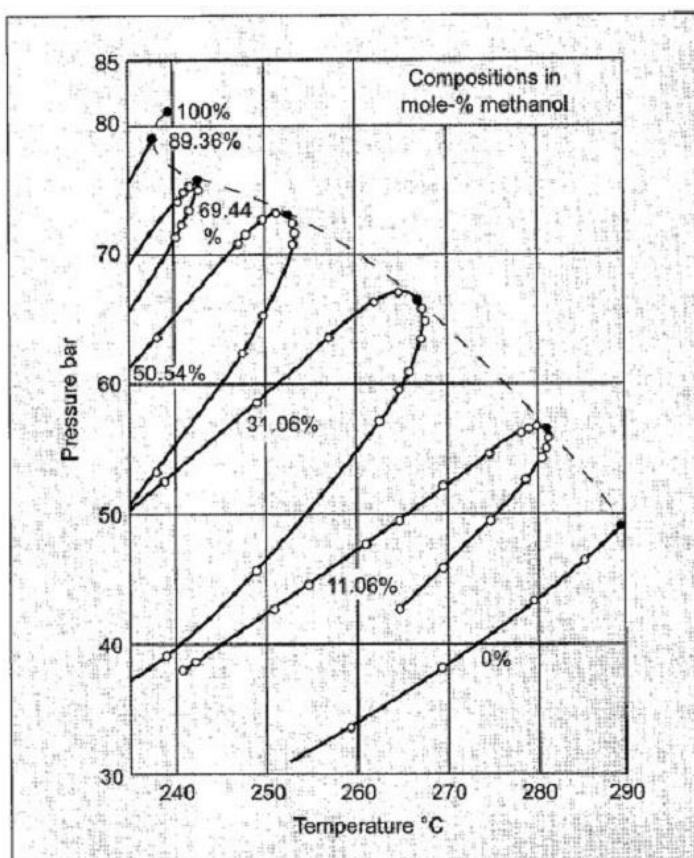


Figure 10.7 *PT* diagram for methanol/benzene. (Redrawn from *Chem. Eng. Sci.*, vol. 19, J. M. Skaates and W. B. Kay, "The phase relations of binary systems that form azeotropes," pp. 431–444, copyright 1964, with permission from Elsevier Science Ltd., Pergamon Imprint, The Boulevard, Langford Lane, Kidlington OX5 1GB, UK)

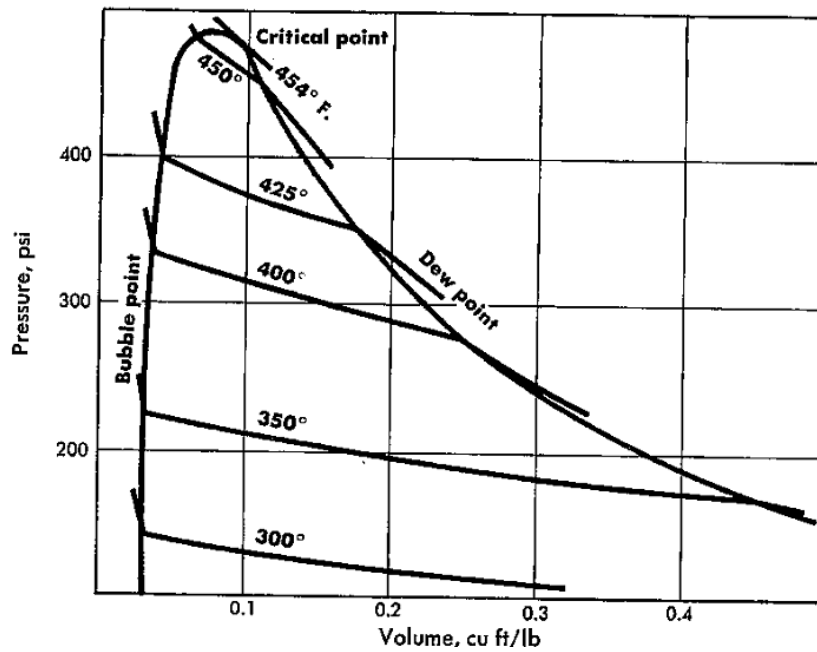


Fig. 2-20. Pressure-volume diagram of a mixture of 47.6 weight percent n-pentane and 52.4 weight percent n-heptane. (From *Volumetric and Phase Behavior of Hydrocarbons*, Bruce H. Sage and William N. Lacey. Copyright 1949, Gulf Publishing Co., Houston. Used with permission.)

Figure 2-20 gives the pressure-volume diagram for a mixture of n-pentane and n-heptane, showing several isotherms and the saturation envelope. Notice that at lower temperatures the changes in slope of the isotherms at the dew points are almost nonexistent. Also notice that the critical point is not at the top of the saturation envelope as it was for pure substances.

Pressure-Composition Diagrams for Two-Component Mixtures

Figure 2-21 gives a typical *pressure-composition diagram* for a two-component mixture at a single temperature. Combinations of composition and pressure which plot above the envelope indicate conditions at which the mixture is completely liquid. Combinations of composition and pressure which plot below the envelope indicate conditions at which the mixture is gas. Any combinations of pressure and composition which plot within the envelope indicate that the mixture exists in two phases, gas and liquid. Bubble point and dew point have the same definitions as previously discussed.

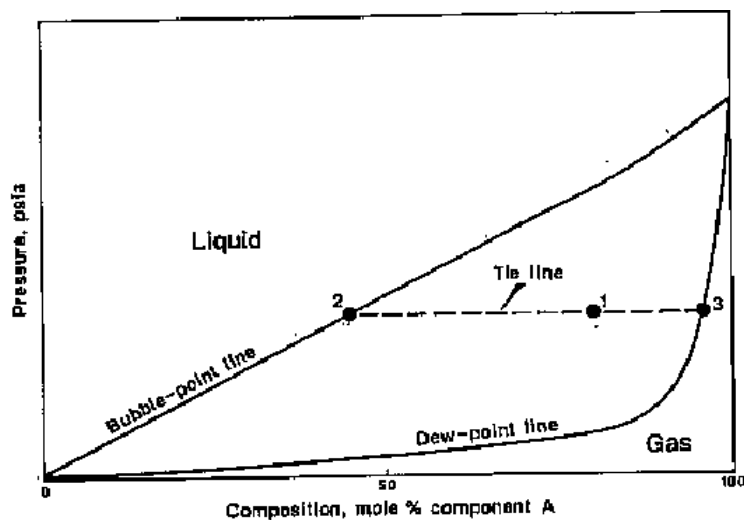


Fig. 2-21. Typical pressure-composition diagram of a two-component mixture with one tie line, 123.

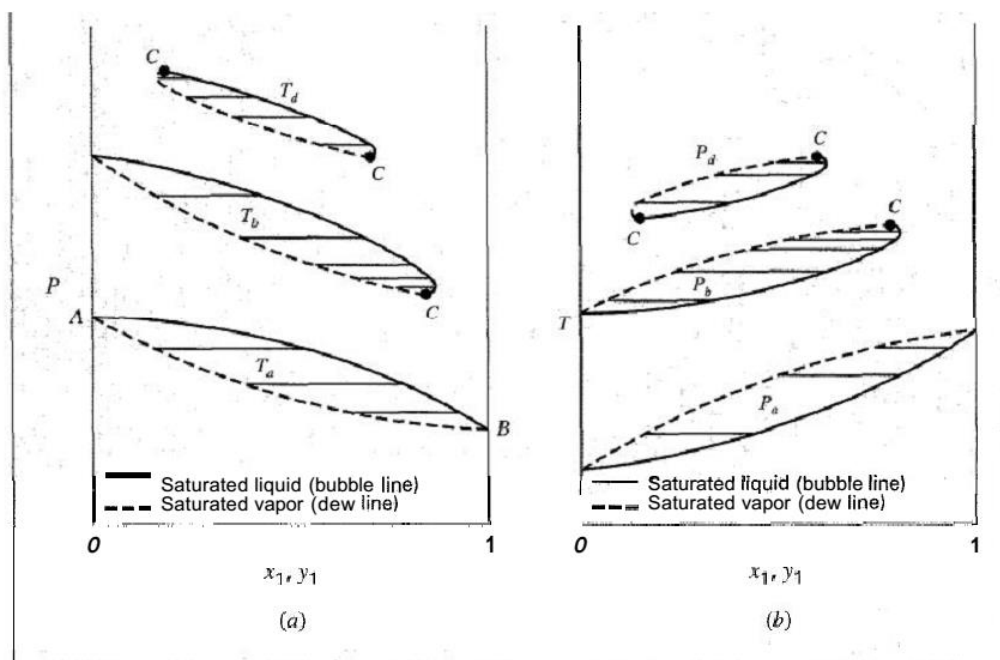


Figure 10.2 (a) Pxy diagram for three temperatures. (b) Txy diagram for three pressures

Fig. 10.2 shows P - x_1 - y_1 plots for three different temperatures and T - x_1 - y_1 for three different pressures.

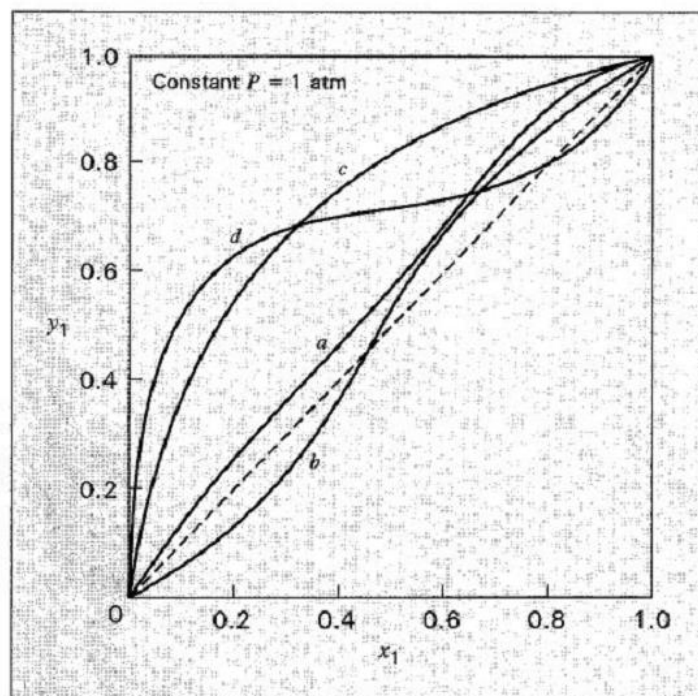


Figure 10.10 yx diagrams at 1 atm: (a) tetrahydrofuran(1)/carbon tetrachloride(2); (b) chloroform(1)/tetrahydrofuran(2); (c) furan(1)/carbon tetrachloride(2) (d) ethanol(1)/toluene(2)