Notes on Phase Relations of Binary Mixtures in the Region of the Critical Point

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Many papers have appeared presenting the phase equilibrium of binary mixtures in the critical region, but rarely do the authors present all five common means of representing such data, namely, (1) pressure vs. temperature at constant composition, (2) pressure vs. liquid and vapor compositions at constant temperature, (3) temperature vs. liquid and vapor compositions at constant pressure, (4) vapor composition vs. liquid composition at constant pressure, and (5) vapor composition vs. liquid composition at constant temperature. It is the purpose of this note to show the general interrelationship among the diagrams, useful for comparison of the work of various experimenters.

A *P-t* diagram for the ethane–heptane system, as reported by Kay (*4*), typical of many binary mixtures, is given in Figure 1, and the other corresponding phase diagrams are shown in Figures 2, 3, 4, and 5. The two phases existing at equilibrium are defined by a horizontal line cutting the isotherm on the *P-x, y* diagram (Figure 2). For any isotherm the curve to the left is the bubble-point curve, to the right, the dew-point curve. Where these curves meet, and the properties of the liquid and vapor become identical, is the critical point *C*, by definition. The critical point *C* is clearly the point of maximum pressure on this isotherm. As shown in the *P-t* diagram (Figure 1) the locus of points of highest pressure for any composition at specified temperatures is the envelope curve, which then must be the locus of the critical point. The critical point accordingly shifts around the nose of the constant composition loop so that it is always at the point of tangency, as shown.

In Figures 1, 2, and 3 the loci of the critical points *C*, the maximum pressure points *E*, and the maximum temperature points *F* are shown.

In Figure 1; in mixtures with composition loops tangent to the envelope between *M*, the maximum pressure possible for the two-phase system, and C_b, the critical of pure heptane, the critical point lies between the point of maximum pressure *E* and the point of maximum temperature (cricondentherm point) *F*, and the mixture exhibits both types of retrograde condensation. Between *M* and C_a, the critical of pure ethane, the critical point lies outside this range, and the mixture exhibits retrograde condensation of the first kind only.

Figure 2 shows the cricondentherm *F* to be the maximum composition point for the isotherm, for clearly at any higher temperature than the isotherm under consideration, two phases do not exist. The locus of maximum pressure points *E* is the envelope curve, as this is the maximum pressure that can exist for any temperature at a specified composition.

The existence of the three separate singular points for the mixture and the region of retrograde condensation requires that the nose of a constant composition *P-t* loop be rounded, and similarly the nose of an isotherm on the *P-x, y* diagram. On an isothermal *y-x* diagram (Figure 4) and an isobaric *y-x* diagram (Figure 5) such behavior is shown by the isotherm or isobar approaching the 45° line with a negative slope, as given by *FC* in Figure 4 and E_1C_1, E_2C_2 in Figure 5.

The *t-x, y* diagram is represented by

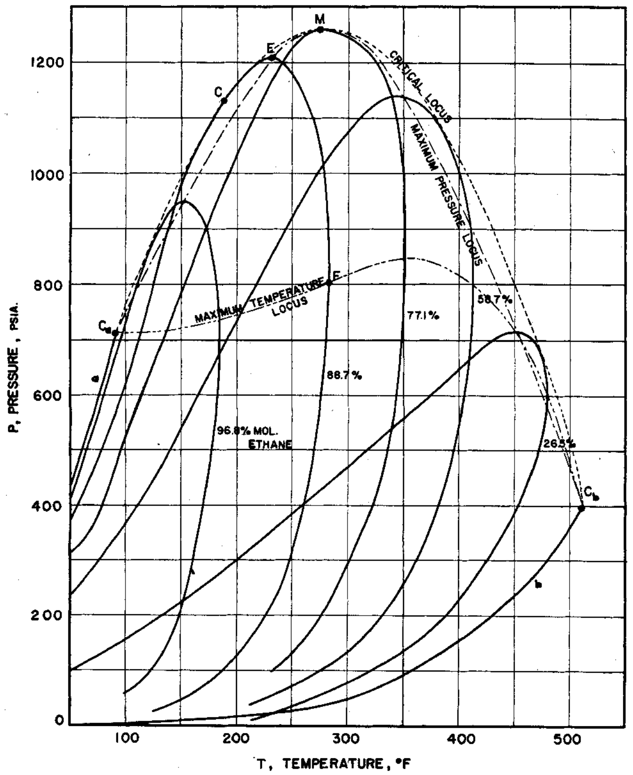


Fig. 1. Pressure-temperature diagram for the ethane-heptane system.

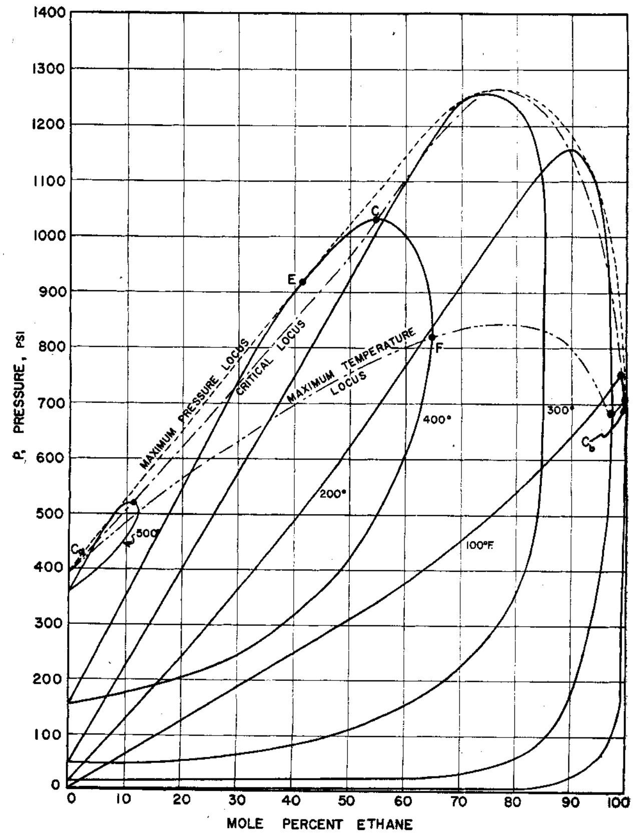


Fig. 2. Pressure-composition diagram for the ethane-heptane system.

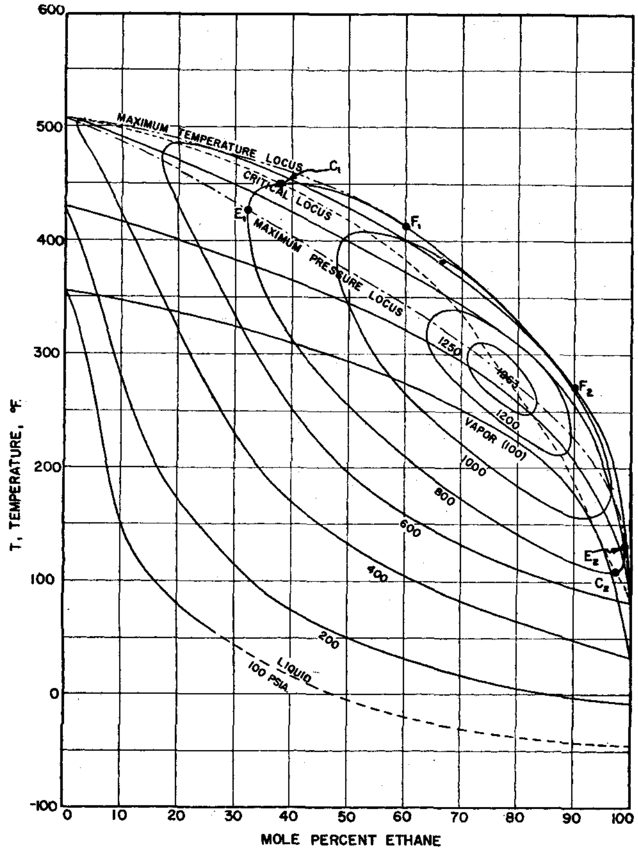


Fig. 3. Temperature-composition diagram for the ethane-heptane system.

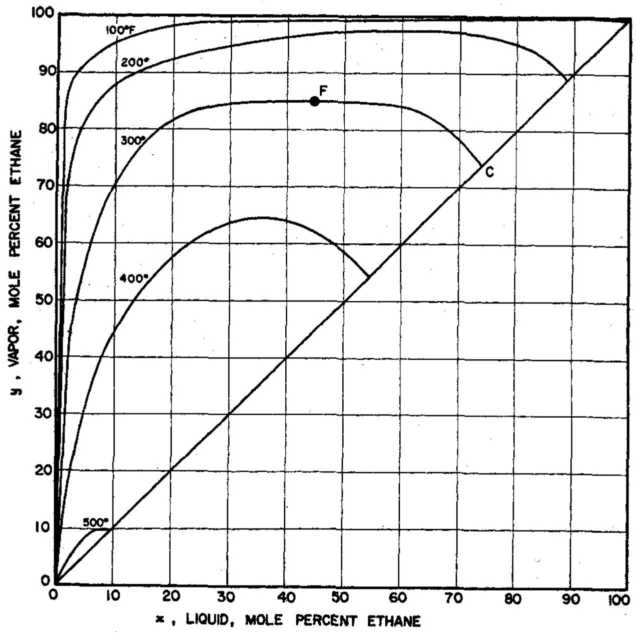
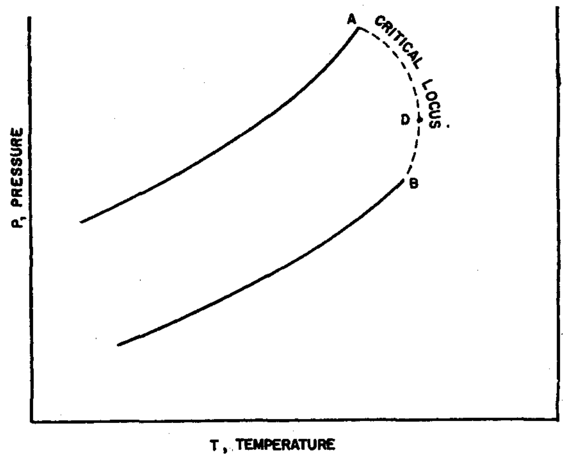
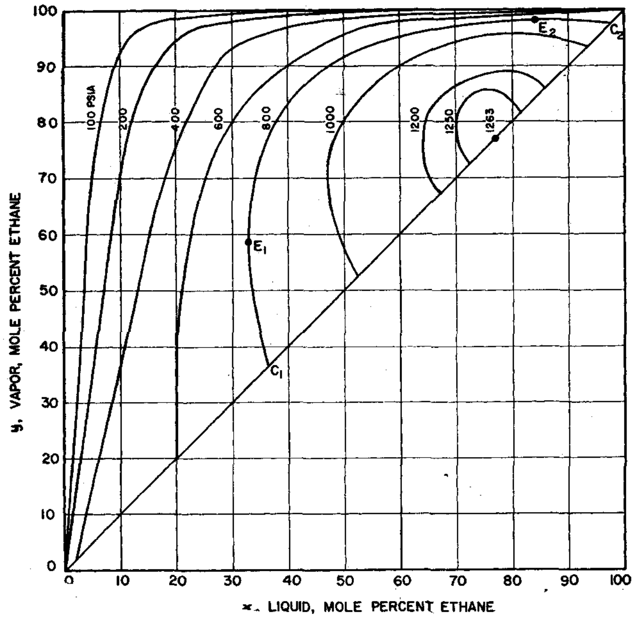


Fig. 4. Isothermal vapor composition-liquid composition diagram for the ethane-heptane system.





→ Fig. 6. Pressure-temperature diagram for a system exhibiting two limiting compositions on a pressure-composition diagram.

← Fig. 5. Isobaric vapor composition-liquid composition diagram for the ethane-heptane system.

Figure 3. The condition of the isobars becoming critical at both ends is given by systems that have a critical pressure for the mixture greater than the critical for either component. For the isotherms to become critical at both ends on a *P-x, y* diagram requires a critical locus as given by the *P-t* diagram (Figure 6), a more unusual case. Such systems for compositions with critical points lying between *B* and *D* then exhibit retrograde condensation of the second kind only. It should be noted, however, that the approximate shape of the *t-x, y* diagram, in general, is not a mirror image of the *P-x, y* diagram, as is sometimes stated.

Some systems such as ethanol water, as reported by Griswold et al. (*3*) and Barr-David (*1*), and 2-propanol water, Barr-David (*1*), have sharp-pointed *P-t* and *P-x, y* curves. Thus the three singular points coincide and the systems do not exhibit retrograde condensation. Also the critical points of mixtures lie between the critical points of the pure components.

Other shapes of the critical locus exist, and the critical behavior of the mixtures may be deduced in a manner similar to that described above. For example, the N_2O–C_2H_6 system, as reported by Kuenen (*5*), has phase properties such that the center portion of an isotherm on a *P-x, y* diagram is the first part to become critical. Another characteristic locus is given by the occurrence of gas-gas equilibrium, as reported by Dodge and Lindroos (*2*) and others. Binary systems in which the critical points for the components are widely separated have interesting *P-x, y* diagrams, in which the isotherms spread out as the temperature is lowered and the critical pressure increases to such a high value that the solidification line may be reached.

LITERATURE CITED

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