

The 25 and 31.7% nitrogen mixtures were duplicated after a period of four months, and experimental data were reproduced within the experimental accuracy. Phase boundary data on two of the mixtures were obtained with the P-V-T apparatus by determination of the intersection of the isometric lines in the two-phase and single-phase regions. These data agree very well with those obtained with the dew and bubble point apparatus, and show that the experimental data are constant. Cross plots of dew and bubble point data in the form of P-X, T-X and Y-X diagrams are consistent and smooth. K values when plotted against pressure on logarithmic scale are linear.

The duplication of three-phase data and the dew-bubble points of pure components indicated that no marked impurities were present. Starting with any mixture, points on the three-phase locus agreed within 1 psi and 0.1°F.

II. Phase Equilibria

A. Phase Rule

The phase rule is a thermodynamic law, first stated by Gibbs,¹⁴ that relates the number of phases present to the number of components and degrees of freedom (variants) for a heterogeneous system in equilibrium.¹⁹ It is assumed that the only determinative variables are temperature, pressure, and composition of the phases. The rule is applicable to heterogeneous systems in either chemical or physical equilibrium, so long as they are dynamic and reversible, in contrast to the static equilibrium of mechanics.

The phase rule states that for a heterogeneous system having *C* components present in *P* phases in equilibrium, the number of degrees of freedom, *F*, is, $F = C - P + 2$. The number of intensive variables, consisting of temperature, pressure, and compositions of the different phases, which have to be specified to completely define the state of a system, is *F*. For example, a single component system if in a single phase requires both the temperature and pressure to be known to define the system; if two phases are present, and either temperature or pressure is known, the other will be known; if three phases are present, both temperature and pressure will be fixed, as the three phases can exist at only a single set of conditions.

B. Application of the Phase Rule to Binary Systems

For systems consisting of two components the phase rule indicates a maximum of four phases in equilibrium with each other when the degree of

freedom, *F*, is zero. This will be a unique point, known as the quadruple point of the system, and will not depend on any intensive variables. The composition of each of the four phases and the temperature and pressure will be fixed. For the ethane-nitrogen system the four phases in equilibrium at the quadruple point are liquid-1, liquid-2, solid, and vapor, designated *L*₁, *L*₂, *S* and *V*.

Similarly, when three phases are in equilibrium, there is one degree of freedom, and any one of the intensive variables can be specified. If all three phases are true solutions, the following types of equilibria will be possible: *L*₁-*L*₂-*V*, *L*₁-*L*₂-*S*, *L*-*S*-*V*, *L*-*S*₁-*S*₂, *L*-*V*₁-*V*₂, *S*₁-*S*₂-*V*, and *S*-*V*₁-*V*₂. Many occurrences of *L*-*S*-*V* phase equilibrium have been reported in the literature; for example, the methane-water,¹⁶ hydrogen sulfide-water,¹⁰ and methane-carbon dioxide systems.¹² The ethane-nitrogen system exhibits the *L*₁-*L*₂-*V* three-phase phenomena, and it is possible that at lower temperatures than those investigated, *L*₁-*L*₂-*S* equilibrium would be exhibited.

When two phases are present in a binary mixture there are two degrees of freedom, and two of the intensive variables must therefore be specified to define the system. The types of two-phase equilibrium possible are: *S*₁-*S*₂, *S*-*L*, *S*-*V*, *L*₁-*L*₂, *L*-*V*, and *V*₁-*V*₂. The *S*₁-*S*₂ and *S*-*L* equilibria are important in the study of metals. Recent data for the ammonia-helium system reported by Tsiklis²² have indicated the existence of *V*₁-*V*₂ equilibria.

The *L*-*V* equilibrium data are of most importance in the study of hydrocarbon systems. The ethane-nitrogen system exhibited *L*-*V* and *L*₁-*L*₂ equilibria in the two-phase regions.

C. Liquid-Liquid Equilibria

If two partially miscible liquids are mixed, two liquid phases of different composition will result throughout a limited overall composition range, with both phases containing some of each component.²⁰ The addition of component *A* to a two-phase mixture of *A* and *B* at constant temperature and pressure will increase the relative amount of the phase rich in *A*, and decrease that of the phase lean in *A*. When a two-phase two-component system is maintained at a constant pressure, sufficiently high to prevent formation of a gas phase, the system will be univariant and for each temperature there will be definite concentrations of the components in each liquid phase. As the temperature is changed, the composition of the two solutions will change, and two solubility curves will

be obtained, showing the solubility of A in B, and B in A, as a function of temperature. The solubility may decrease or increase with increasing temperature, depending on whether heat is evolved or absorbed when one liquid is dissolved in the other. The temperature at which the two phases become completely miscible is called the *critical solution temperature*, and may exist as either a maximum, a minimum, or both. The ethane-nitrogen system exhibits phenomena indicating the existence of a maximum critical solution temperature.

The effect of pressure on the critical solution temperature depends, according to the principle of Le Chatelier and the equation of Clapeyron, on the volume change which occurs when one of the pure components is added to a nearly saturated solution. The critical solution temperature of the ethane-nitrogen system as a function of pressure is shown in Fig. H, page 11.

D. Liquid-Liquid-Vapor Equilibria

A two-component system existing in three phases has one degree of freedom. When one variable, such as temperature, is specified, the system becomes invariant and it can be deduced that at constant temperature the vapor pressure is constant so long as two liquid phases are present. If vapor pressure is plotted versus overall composition at constant temperature, as illustrated for the ethane-nitrogen system in Fig. 1, the curve will exhibit a horizontal portion for the region over which a vapor and two liquid phases exist. This horizontal portion may be either above or between the vapor pressures of the pure components at that temperature; it is not possible for the vapor pressure of a system of two liquid phases to be lower than that of the least volatile component. As shown in Fig. 2, in the ethane-nitrogen system the vapor pressure of the liquid-liquid occurrence lies between the vapor pressures of the pure components.

Similarly, when temperatures are plotted versus overall composition at constant pressure, the curve will exhibit a horizontal portion for the region over which a vapor and two liquid phases coexist. This horizontal portion may be either below or between the boiling temperatures of the two pure components; the three-phase coexistence temperature of a system cannot be higher than the boiling point of the least volatile component. The phase behavior of the ethane-nitrogen system at 400 psia as a function of temperature is shown in Fig. 3.

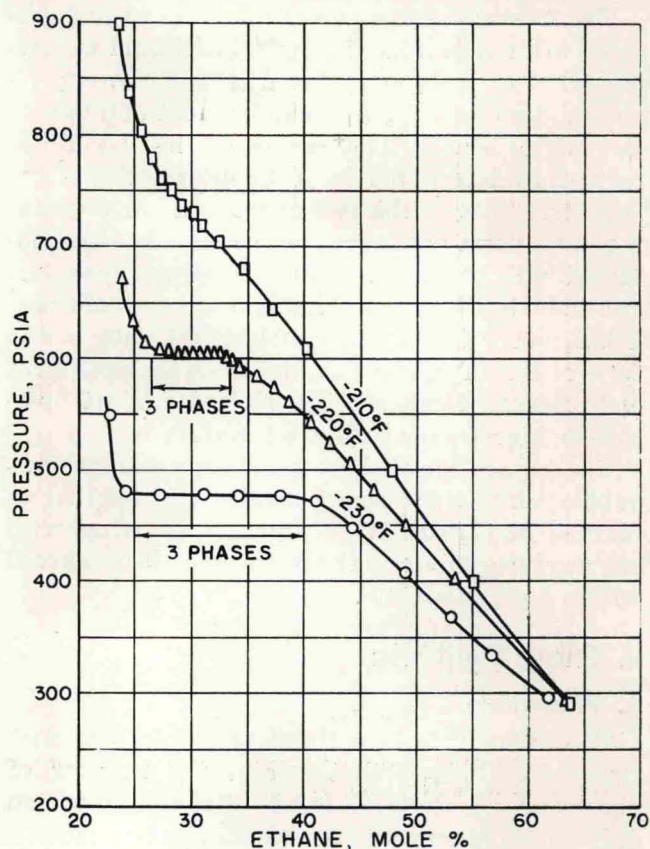


Fig. 1.—Isothermal Vapor Pressure-Composition Curves for the Ethane-Nitrogen Three-Phase Region

1. Pressure-Composition Diagram. An isothermal pressure-composition diagram for the ethane-nitrogen binary system at -240°F is presented in Fig. 2. The horizontal straight line ABC represents the three-phase pressure for this temperature. There is a break in the slope of the dew point curve at this three-phase pressure. The lines AD and BE represent the relations of bubble point pressure to composition for the two liquids. From the slope of the lines AF and BG it is seen that the liquids of this system become more miscible with an increase in pressure.

It is of interest to follow the path of an isothermal condensation on this diagram. If a gaseous mixture corresponding to X₁ is compressed isothermally, the system remains entirely gaseous until the dew point is reached at H. At this point condensation commences and continues with further increase in pressure until the three-phase line is reached, beyond which all of the gas will be condensed and the system composed entirely of the two liquid phases represented by points A and B. If the pressure is still further increased, the system would move along the line JK and the only