

Fig. H.—Locus of Coexistence of Three Phases in the Ethane-Nitrogen System

maximum when the cell was half-full of liquid, and became less intense for those temperatures at which the meniscus disappeared above or below the half-full level. The approach to this region was frequently made from two directions, and for a given temperature in no instance was there a difference greater than 1.0 psia in the pressure at which the liquid phase disappeared.

III. Partial Miscibility in the Liquid Phase

At certain low temperatures, mixtures containing from 5-80% ethane form two immiscible liquid phases in equilibrium with a vapor phase. The locus of conditions under which the three phases coexist (pressure vs. temperature curve) is shown in Fig. H. The vapor pressure curve for nitrogen is given for reference. The maximum point at which three phases coexist is -220°F and 605 psia. The locus terminates in the system quadruple point, -300.5°F and 40 psia, at which two liquids, a vapor, and a solid coexist.

For the 15% ethane mixture two liquid phases coexist in the region between the three-phase locus and the dew point curve at temperatures below -220°F (Fig. A). Various other mixtures will exhibit similar behavior. When curves for all mixtures are available, the effect of temperature at constant pressure on the miscibility of the two liquid phases can be shown by cross plots of the data. The experimental data indicate that at constant pressure the effect of temperature on the solubility of the two liquid phases is slight, especially at low pressures.

IV. Single and Double Retrograde Phenomena

Mixtures containing 1.98-95% ethane exhibited retrograde phenomena. The size of the retrograde regions encountered and the amount of liquid formed varied markedly from mixture to mixture. The following types of retrograde behavior were observed: isothermal condensation, isobaric vaporization between dew points, and isobaric vaporization between bubble points.

The 15% ethane mixture exhibited unique behavior in that (as shown in Fig. A, curve 8) no bubble point was observed on the phase envelope within the pressures attainable with the experimental equipment. With pressure reduction at constant temperature between -235° and -220°F from a point in the single-phase region above the dew point curve, two immiscible liquid phases formed upon isothermal condensation of the saturated vapor phase, a phenomenon termed double retrograde condensation by van der Waal.²³

The phase envelopes of mixtures containing 30.00 and 49.82% ethane could not be completed because of equipment limitations, but it is expected that mixtures in the range of 10-60% ethane will exhibit behavior similar to that of the 15% mixture. The phase boundary (P-T) curves for the 5 and 68% ethane mixtures terminate in the three-phase locus and give limits beyond which the double retrograde phenomenon does not extend. Each of the retrograde processes is considered in detail in Sec. III of Discussion.

V. Gas Phase Pressure-Volume-Temperature Data

Constant density (isometric) pressure-temperature data for five mixtures of ethane and nitrogen were determined over the temperature range from the two-phase boundary curve to $+110^{\circ}\text{F}$, and pressures to 4000 psia; they constitute the primary P-V-T data. The compositions of the five mixtures investigated and the experimental data are recorded in Table II, *Tabulated Data*. Fig. J presents a plot of the isometric data for the 50.26% ethane-49.74% nitrogen mixture. The two-phase dew and bubble point boundary curve for the mixture is shown as a dashed line. The behavior illustrated is typical of that exhibited by the other four mixtures; seven or eight isometrics were determined for each mixture.

The nearly linear variation of pressure with temperature for the isometrics facilitates the use of this type of plot for extrapolation of experimental data to higher temperatures, and interpolation between experimental temperatures. The isometrics are nearly linear in the gas-phase as well as two-phase regions, but the slopes of the lines are different in the two regions. Phase boundary data can be obtained from the intersection of the gas-phase and two-phase lines, as shown in Fig. J (the interpolated points). The phase boundary data thus obtained do not have the accuracy of the primary data obtained with dew and bubble point apparatus, as visual observation of the dew point is not made, and the isometrics are not truly linear. For all five mixtures the isometrics exhibit a slight downward curvature for densities lower than the critical density, and then exhibit a slight upward curvature at densities higher than the critical. This is in accord with the general behavior of pure substances. The isometric type of plot is not used extensively in engineering calculations; isometrics for the other four mixtures are not presented graphically.

For use in engineering calculations, the most general method of presenting the P-V-T behavior of gas mixtures is in the form of compressibility

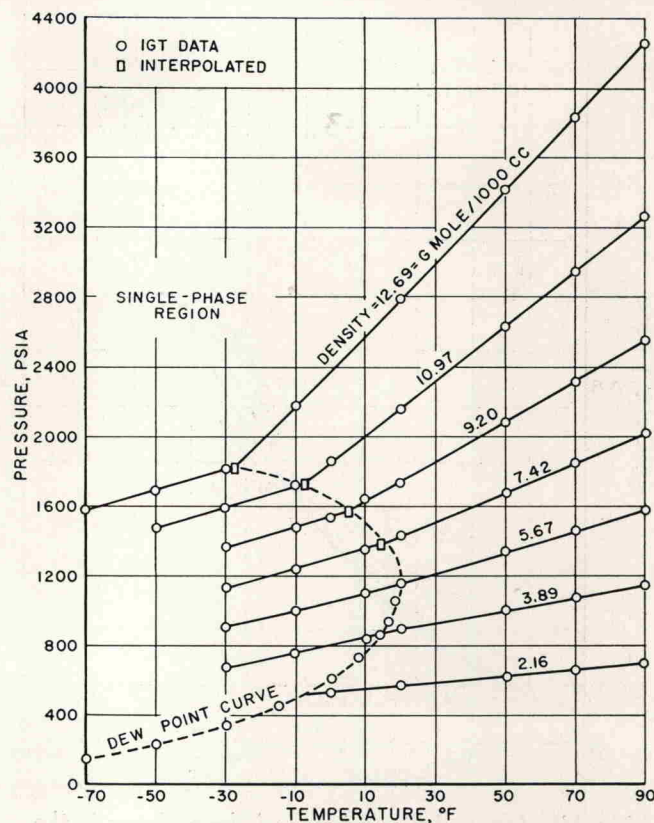


Fig. J.—Experimental Isometric Pressure-Temperature Data for a 50.26% Ethane-49.74% Nitrogen Mixture

factor plots. The compressibility factor, z , in a modification of the ideal gas law to permit calculating the behavior of actual gases, is defined by the equation:

$$z = P/RT\rho = PV/RT$$

P = absolute pressure

R = universal gas law constant, the value of which depends only upon the units used to express the pressure, temperature, and density, and not upon the nature of the gas

T = absolute temperature

ρ = density of the gas in moles per unit volume

V = molal volume = $1/\rho$

The compressibility factor is a measure of the deviation of a gas from the ideal gas behavior and is 1.000 for an ideal gas. Its value is readily calculated by application of the above equation to the experimentally measured pressure, temperature and density. Compressibility factors plotted versus pressure along lines of constant temperature are shown in Fig. K for five mixtures. Comparisons of these data with those obtained by an equation of state are presented in *Discussion*.