

Fig. 2.—Isothermal Pressure-Composition Diagram for the Ethane-Nitrogen System at -240°F

change in phase would be that resulting from the effect of pressure upon the miscibility of the two liquids.

During the course of such an isothermal condensation, the relative quantities of any two phases present can be determined by comparison of the lengths of such lines as MN and NP. However, at the three-phase pressure, the relative quantities of the three phases cannot be determined from this diagram. On the liquid-vapor side of this pressure, the quantities of liquid and gas phases are given by the relative lengths of the lines JC and JA, respectively. On the liquid-liquid side of this pressure, the quantities of the two liquid phases are given by the relative lengths of the lines JA and JB.

A somewhat different type of condensation is encountered at compositions between X_B and X_C , such as X_2 in Fig. 2. In this case the system remains entirely gaseous until the dew point is reached at Q, where a liquid phase corresponding to T begins to separate. This process continues until the three-phase pressure is reached at R, where liquids of compositions corresponding to B and A, and a gas corresponding to C, coexist. With a minute increase in pressure, liquid A disappears and the system is made up entirely of gas of a composition corresponding to C and the liquid

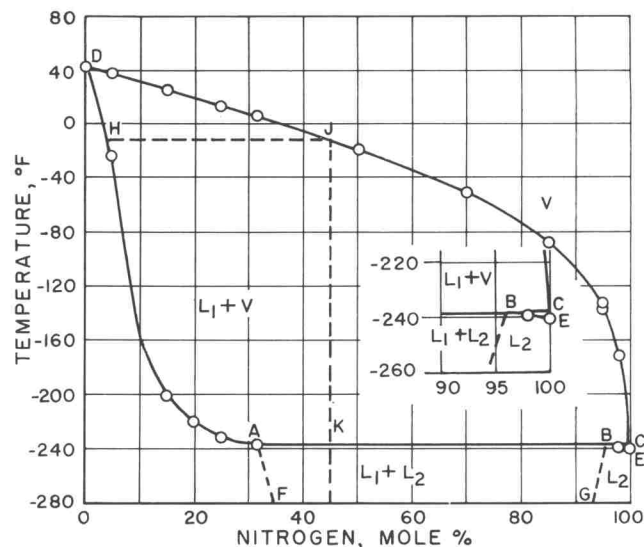


Fig. 3.—Isobaric Temperature-Composition Diagram for the Ethane-Nitrogen System at 400 Psia

at B. With further increase in pressure, the quantity of the gas phase decreases, and the system becomes entirely liquid at S. At compositions from X_D to X_A normal condensation is observed, since only a liquid and a gas phase are involved.

2. Temperature-Composition Diagram. An isobaric temperature-composition diagram of partial-miscibility regions of the binary ethane-nitrogen system is shown in Fig. 3. The horizontal line ABC in Fig. 3 represents the three-phase temperature for this pressure. Lines AD and BE are bubble point lines, while DCE is a dew point curve. As shown by lines AF and BG, the mutual solubility of the liquids increases as temperature decreases.

In a distillation, the total composition of the mixture as it first boils must lie on one of three curves, DA, BE or AB: if along DA or BE the mixture is homogeneous; if along AB, it is heterogeneous. If the composition of the mixture lies on the curve DA, say at H, it will have a vapor J much richer in nitrogen. As distillation is continued, the boiling point of the remaining liquid will rise toward that of pure ethane. If the mean composition of distillate is taken to be K, somewhere between B and A the distillate will separate into two layers on condensation. If the condensed phase is now distilled, it will boil at constant temperature as long as two layers are present, giving a distillate of constant composition C while the relative quantity of the layer of composition A increases. If the distillate of composition C is subjected to fractional distillation, pure nitrogen will be obtained.

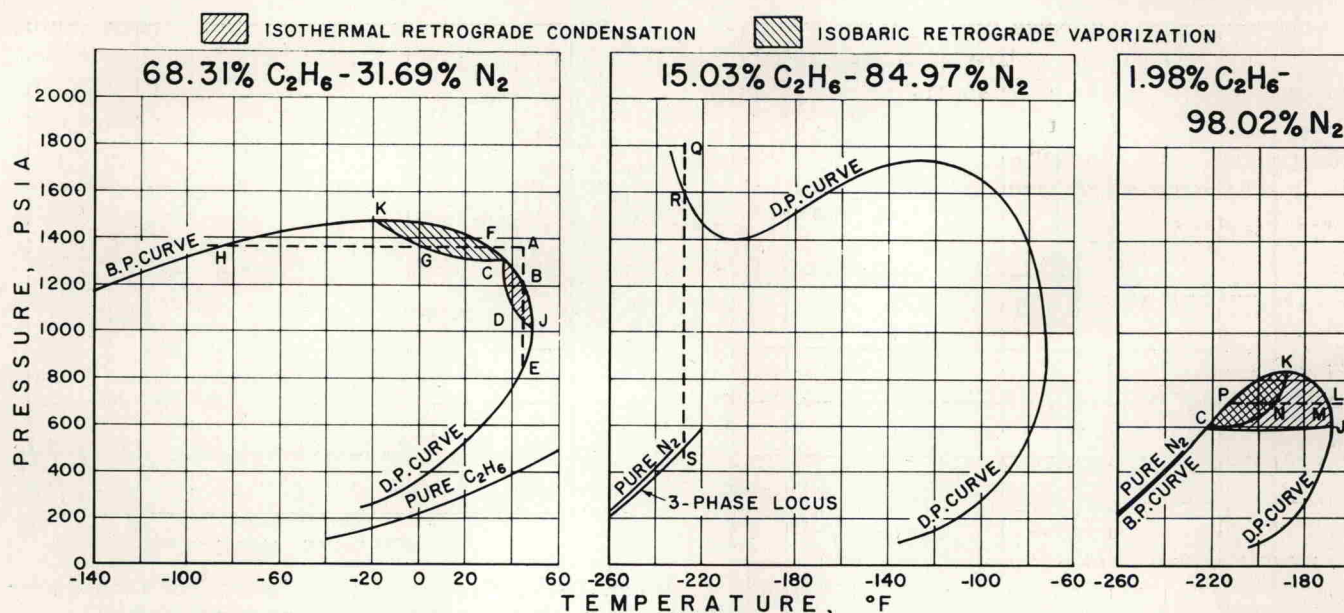


Fig. 4.—TYPES OF RETROGRADE PHENOMENA EXHIBITED BY THE ETHANE-NITROGEN SYSTEM

III. Retrograde Behavior in the Ethane-Nitrogen System

A. Isothermal Retrograde Condensation

This phenomenon may be illustrated by the behavior of the mixture in the 68.31% ethane-31.69% nitrogen diagram of Fig. 4. The mixture in the single phase at A may be expanded to B, the upper dew point, at which pressure the first liquid will appear. Further pressure reduction causes continuous condensation until some point D is reached, where the liquid formed begins to vaporize, until at pressure E the entire quantity of liquid formed between B and D has been vaporized and the mixture is at its lower dew point. The condensation from B to D is retrograde, and may be further qualified as being isothermal and between dew points. From D to E normal vaporization occurs with expansion.

B. Isobaric Retrograde Vaporization Between Bubble Points

Referring again to the 68.31% ethane-31.69% nitrogen diagram in Fig. 4, the fluid at A may be cooled to F, at which temperature a bubble of vapor will appear and grow with further temperature reduction until some point G is reached. From G to H a temperature decrease causes normal condensation. The vaporization from F to G is retrograde, and may be further qualified as being isobaric and between bubble points.

Moving in the opposite direction will cause opposite phenomena; for example, from D to B is retrograde vaporization, and G to F is retrograde condensation. The isothermal retrograde phenomenon may occur only above the critical temperature, C, and below the maximum temperature of two phases, J; the isobaric retrograde phenomenon may occur only above critical pressure, C, but below the maximum pressures of two phases, K. The retrograde phenomenon can occur only in the region corresponding to the cross-hatching.

The position of the critical point is shown between the maximum temperature, J, and the maximum pressure, K; however, this does not have to be. The point C can lie to the right, below maximum temperature J, or to the left, below maximum pressure K. The position of C below maximum temperature J has not been observed in the systems studied thus far, while location of C below maximum pressure K was observed in the 1.98% ethane-98.02% nitrogen system (curve 10, Fig. A, reproduced in Fig. 4).

C. Isobaric Retrograde Vaporization Between Dew Points

This phenomenon is illustrated by the behavior of the 1.98% ethane-98.02% nitrogen mixture in Fig. 4. The mixture in single phase at L may be cooled to M, where liquid will appear; on further cooling more condensation will take place until point N is reached, at which temperature the liquid