

formed begins to vaporize until a temperature P is attained; there the entire quantity of liquid formed between M and N is vaporized. The vaporization from N to P is retrograde, and is further qualified as being isobaric and between dew points. Normal condensation occurs when the mixture is cooled from M to N.

#### D. Double Retrograde Condensation

In experiments on binary mixtures at high pressures it was found that two liquid layers would form, especially when one component was polar. Van der Waal discusses data on ethane-alcohol and carbon dioxide-nitrobenzene mixtures which formed two liquid layers.<sup>23</sup> A saturated vapor of systems of this type might give two liquids, instead of the usual single liquid formation, by retrograde condensation upon isothermal reduction of the pressure at temperatures above the critical. To distinguish the phenomena in which two liquids are condensed or vaporized in a retrograde manner, they were called "double retrograde" condensation or vaporization by van der Waal. The same nomenclature that has been used when a single liquid phase is condensed or vaporized applies when two liquid phases are condensed or vaporized, except for the prefix "double."

The phase boundary curve for a 15% ethane-85% nitrogen mixture in Fig. 4 shows that this mixture exhibits pronounced retrograde behavior and a tendency to form two liquid phases at or below  $-220^{\circ}\text{F}$  below the phase envelope and above the three-phase locus. If the fluid in the single-phase region at Q is expanded isothermally at  $-228^{\circ}\text{F}$ , it will form two liquid phases at a pressure of 1600 psia at R; on further reduction of pressure only the relative amount of the two phases will change until a pressure of 495 psia is reached at S, when a third or gas phase will appear. Below this pressure only a liquid and a vapor phase exist in equilibrium with each other.

It is believed that behavior of mixtures in the range of 10-60% ethane will be similar to that of 15% ethane-85% nitrogen. The 68.3% ethane mixture has a normal bubble point curve, which meets the three-phase locus from below at  $-223^{\circ}\text{F}$ , very near the maximum coexistence temperature for three phases, while the phase boundary curve for the 5% ethane mixture exhibits a very large retrograde region and terminates in the three-phase locus curve from above at  $-230.0^{\circ}\text{F}$ . For this mixture there is no clearly defined transition between dew and bubble points, since the liquid

forms two phases very close to the critical point. Any mixture containing more than 5% and less than 68.3% ethane will have the critical point much higher than  $-220^{\circ}\text{F}$ , and if it behaves normally should have a bubble point at this temperature. Normal bubble point curves will have to terminate in the three-phase locus or run below the locus, so mixtures containing more than 5% and less than 68.3% ethane should not exhibit normal bubble phenomena, but behave similar to the 15% ethane-85% nitrogen mixture.

The data of this investigation are not sufficient to show the phase boundary curve of the liquid-vapor, liquid-liquid and liquid-solid regions that also terminate in the three-phase locus throughout its existence range. The locus has its lower terminus in the quadruple point for the system.

### IV. Utility of the Data

#### A. Liquid-Vapor Phase Equilibrium Data

The liquid-vapor phase equilibrium data can be used directly to predict the pressure-temperature conditions required for the separation of mixtures of ethane and nitrogen into the pure components.

As mentioned previously, ethane-nitrogen mixtures form two immiscible liquid phases at temperatures below  $-220^{\circ}\text{F}$ , pressures above the three-phase locus curve but below the dew point curve, and in the composition range of approximately 5-80% ethane. As the vapor pressure during the existence of the three phases lies between the vapor pressures of the pure components, it is possible to separate the mixture into pure components by distillation.

The degree of separation of ethane from nitrogen obtained solely by partial condensation or evaporation can be readily determined from Fig. C. Consider, for example, a mixture composed of 70% ethane-30% nitrogen, held at a pressure of 300 psia. Referring to Fig. C, the dew point will be found to be  $-9.2^{\circ}\text{F}$ . Cooling below this temperature will, in the absence of supercooling, bring about condensation of liquid to an extent which depends on the temperature. Referring to the figure, it will be seen that when the above mixture is brought to a temperature of  $-100^{\circ}\text{F}$  at 300 psia a partial separation will occur: a liquid composed of 94.3% ethane and 5.7% nitrogen, and a vapor 14.0% ethane and 86.0% nitrogen, will result. Comparison of the lengths of the temperature tie-line to the left and right of the feed composition permits calculation of the extent of lique-

fraction; for the above example:

$$\frac{86.0 - 30.0\%}{86.0 - 5.7\%} \times 100 = 69.7\%$$

These figures indicate the degree of separation and liquefaction obtainable in a perfect separator.

Further separation could be obtained by use of a fractionator in which contact between a rising vapor stream and a descending liquid stream would be effected on a series of bubble cap plates or their equivalent. The data of Fig. C can be used to estimate the number of equilibrium vaporizations required for a desired separation of ethane from a given mixture of nitrogen and ethane.

The separation of a feed mixture into nearly pure ethane and up to 99.8% nitrogen can be carried out in an ordinary distillation column so long as operation is maintained above the three-phase line. To obtain a pure nitrogen product, the 99.8% nitrogen stream from this column could be chilled to below  $-248^{\circ}\text{F}$  and fed to a second column. In this unit separation into pure nitrogen and a liquid of the composition indicated at E could be attained. The liquid of composition E could then be returned to the first column and retreated.

This process is more easily described by use of a Y-X diagram. Other procedures may be required for rigorous calculation, but for the sake of simplicity Fig. 5 was prepared; it is a Y-X diagram to which the McCabe-Thiele graphical method of computation has been applied. No attempt will be made to present the method in detail, and the reader is referred to standard reference works on fractional distillation.

Fig. 5 employs an equilibrium curve for a pressure of 300 psia, together with the lines used for computing the number of equilibrium vaporizations required to separate a mixture of 70% ethane and 30% nitrogen into two streams, 98% ethane-2% nitrogen and 2% ethane-98% nitrogen. Perfect separation is theoretically impossible. The numbered points on the equilibrium line show the composition of the equilibrium liquid and vapor at each theoretical vaporization; 1 is the top contact. A on the operating line shows the relation of the composition of the liquid 1 to the composition of

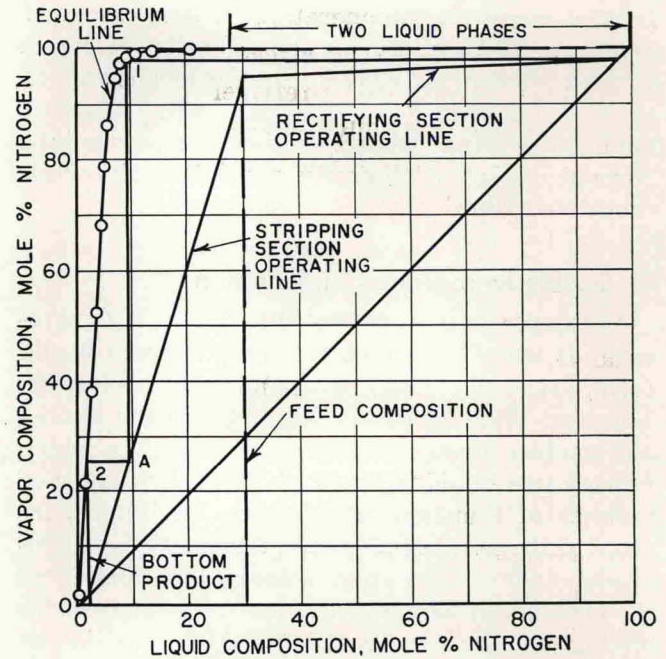


Fig. 5.—Equilibrium Composition Diagram at 300 Psia Showing the Determination of the Number of Theoretical Contact Stages Required to Effect a Selected Degree of Separation of Ethane and Nitrogen from a Specific Mixture

the vapor rising from vaporization at 2. There are separate operating lines for the rectifying section above the introduction of the feed, and for the stripping section. The operating lines represent material balance lines; their location depends on the heat content or enthalpy of the feed (that is, whether it is at its bubble point or only partially liquefied), and also on the reflux ratio. Reflux is obtained by condensing part of the vapor from the top of the column and returning it to the top of the column, so there will be liquid to interact with the rising vapor.

In the illustration given in Fig. 5, two theoretical equilibrium vaporization stages are required to effect the desired separation under the conditions selected. The effect of an increase in pressure will be to reduce the curvature of the equilibrium line, which will increase the number of vaporizations required for the separation. Thus, the higher the operating pressure, the greater the number of vaporizations, and, the greater the required height of the fractionator.