Fig. F.—VAPORIZATION EQUILIBRIUM RATIOS FOR NITROGEN IN THE ETHANE-NITROGEN SYSTEM

II. Critical Data for the Ethane-Nitrogen System

The critical and maximum temperatures and pressures for mixtures of ethane and nitrogen are tabulated in Table E. In Fig. G is shown the relationship between the critical temperature and the composition expressed as mole percent nitrogen. The molecular weights of the components are nearly the same, so the critical temperature-mole or weight percent curves are nearly the same. The observed relationship is not linear, as for binary hydrocarbon systems, but gives temperatures greater than those predicted by linear combination of the critical temperatures.

Various empirical methods have been proposed for prediction of critical constants of mixtures. These correlations usually apply only to systems on which they are based, and are not very useful for predicting other systems. The rule proposed by Bloomer[6] expressed by the equation:

$$T_c \text{ of mixture} = \frac{\dfrac{W_1}{M_1}V_{c1}}{\dfrac{W_1}{M_1}V_{c1} + \dfrac{W_2}{M_2}V_{c2}}(T_{c1} - T_{c2}) + T_{c2}$$

T_c = critical temperature V_c = molal volume at the critical point
W = weight fraction   Subscript (1) refers to component (1)
M = molecular weight   Subscript (2) refers to component (2).

gave good agreement with the methane-nitrogen critical data. It deviated to some extent from the ethane-nitrogen data, but as shown in Fig. G the agreement is better than a linear combination of the component criticals. Through a certain range of compositions, partial liquid miscibility of the liquid phases and double retrograde behavior occur. As a result, it is not possible to predict critical temperatures for mixtures in this range.

The behavior of the mixtures containing 15, 25 and 31.7% nitrogen was anomalous in the critical region. When the data on these mixtures were plotted on an expanded scale, the P-T loops, instead of being tangent to the critical locus curve at the critical point, coincided with the curve over a considerable temperature range. Over the temperature range of coincidence the phenomenon observed in the cell changed from that of a dew point to that in which a substantial quantity of liquid
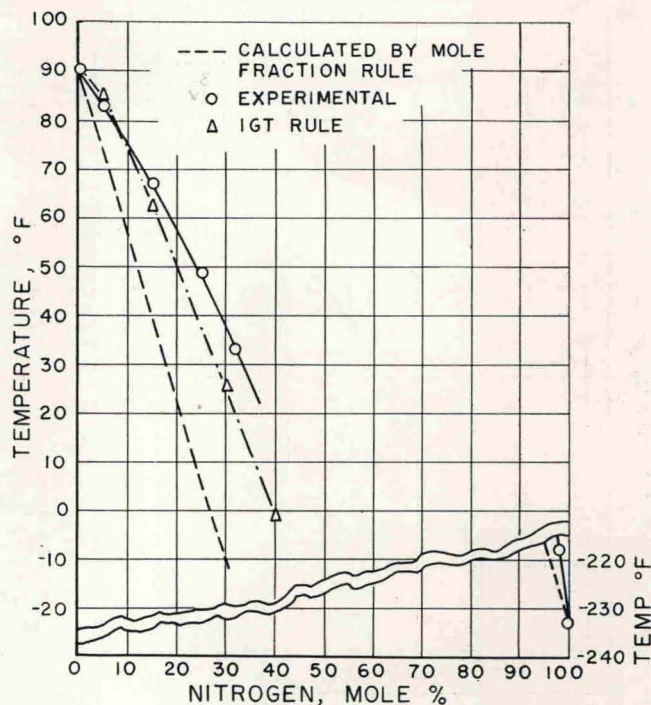

Fig. G.—Locus of Critical Temperatures for Ethane-Nitrogen Mixtures

appeared instantaneously upon cooling. The quantity of liquid which appeared increased through this range until a true bubble point was observed. The temperature range for this phenomenon was approximately 20°F for the 31.7% nitrogen mixture. Similar but less pronounced phenomena were observed for the methane-ethane system.[9]

The exact critical temperatures for these mixtures are in doubt because of this phenomenon. The reported value is the temperature at which the meniscus disappeared with the cell half-full of liquid. The reddish-brown opalescence normally observed at the critical point was apparently at a

Table E.—EXPERIMENTAL CRITICAL CONSTANTS OF THE MIXTURES INVESTIGATED

Composition		Critical Point		Maximum Temp Point		Maximum Press. Point	
Mole % C_2H_6	Mole % N_2	Temp °F	Press. psia	Temp °F	Press. psia	Temp °F	Press. psia
95.02	4.98	82.95	788.4	83.55	775	79.8	808.5
84.99	15.01	67.00	970.0	71.10	895	54.8	1033.5
75.07	24.93	49.10	1166.5	—	—	17.5	1290.0
68.31	31.69	33.47	1320.8	49.05	1035	— 12.0	1472.0
49.82	50.18	—	—	19.55	1175	—	—
30.00	70.00	—	—	—23.05	1175	—	—
14.94	85.06	Does not exist		—71.70	965	—125	1738.0
5.10	94.90	—	—	—127.10	675	—158.5	1211.5
1.98	98.02	—223.0	575.0	—169.45	615	—189.0	837.0