

Also, with column operating pressure and composition of the overhead stream fixed, the maximum temperature of the refrigerant used in the reflux condenser is easily determined. This temperature must be at least as low as the dew point of the overhead product at the column pressure.

The liquid-vapor equilibrium data presented in this Bulletin and shown in Fig. 1 also serve to fix the temperature and pressure levels in heat exchangers and condensers. These conditions may be easily evaluated from the plot.

B. Gas Phase Pressure-Volume-Temperature Data

The experimental P-V-T data on the ethane-nitrogen mixtures can be used to calculate the thermodynamic properties of the ethane-nitrogen system. This is most conveniently and accurately accomplished by means of an equation of state. A modification of the Benedict-Webb-Rubin equation developed at the Institute can be used with a high degree of accuracy for these calculations.

In addition, P-V-T data for the mixtures may be used to calculate the fugacity and activity coefficients of ethane and nitrogen in liquid-phase mixtures of the two. Since the fugacity of a component of a liquid solution is equal to the fugacity of the components in the gas phase in equilibrium with the liquid phase, it is only necessary to determine the fugacity of the component in the gas phase. This can be done by using the gas phase P-V-T data and the equation of state.

This latter use of the P-V-T data is of little importance for the binary ethane-nitrogen system, but is of great importance in predicting the phase behavior of ternary and multicomponent mixtures containing ethane and nitrogen.

Equation of State. A means of predicting the compressibility and the thermodynamic properties of a gas mixture is the "equation of state" method, in which the constants in the equation of state for the mixture are evaluated from constants of the pure components of the mixture. This is the method presented by Beattie *et al.*^{2, 3} and Benedict *et al.*^{4, 5} and is generally more accurate than the pseudocritical method. It is, however, very time-

consuming. The modified Benedict-Webb-Rubin equation of state is:

$$P = RT\rho + \left(B_o RT - A_o - \frac{C_o}{T^2} - \frac{D_o}{T^4}\right)\rho^2 + (bRT - a)\rho^3 + \left(\frac{c}{T^2} + \frac{\delta}{T^4}\right)\rho^3(1 + \gamma\rho^2)e^{-\gamma\rho^2} + a\alpha\rho^6 \quad [\text{Equation 1}]$$

P = absolute pressure
R = universal gas constant
T = absolute temperature
 ρ = density

$A_o, B_o, C_o, D_o, a, b, c, \delta, \alpha,$ and γ are empirical constants, the values of which depend on the composition of the gas mixtures. Benedict *et al.* recommended the following combining rules for determining the value of the constants for mixtures from the constants of the pure gases making up the mixture:

$$B_{om} = \sum_i x_i B_{oi} \quad (\text{Linear combination})$$

$$\text{or } B_{om} = 1/4 \left(\sum_i x_i B_{oi}\right) + 3/4 \left(\sum_i x_i B_{oi}^{1/3}\right) \times \left(\sum_i x_i B_{oi}^{2/3}\right) \quad (\text{Lorentz combination})$$

$$A_{om} = \left(\sum_i x_i A_{oi}^{1/2}\right)^2$$

$$C_{om} = \left(\sum_i x_i C_{oi}^{1/2}\right)^2$$

$$a_m = \left(\sum_i x_i a_i^{1/3}\right)^3$$

$$b_m = \left(\sum_i x_i b_i^{1/3}\right)^3$$

$$c_m = \left(\sum_i x_i c_i^{1/3}\right)^3$$

$$\alpha_m = \left(\sum_i x_i \alpha_i^{1/3}\right)^3$$

$$\gamma_m = \left(\sum_i x_i \gamma_i^{1/2}\right)^2$$

where x_i equals mole fraction of the i^{th} component in the mixture. By analogy to these rules, the D_o and δ terms in the modified equation should be combined by linear square root and linear cube root, respectively. This would result in the following rules for the D_o and δ constants:

$$D_{om} = \left(\sum_i x_i D_{oi}^{1/2}\right)^2$$

and

$$\delta_m = \left(\sum_i x_i \delta_i^{1/3}\right)^3$$

Table 1

MODIFIED BENEDICT-WEBB-RUBIN EQUATION OF STATE CONSTANTS FOR C₂H₆ AND N₂

	C ₂ H ₆	N ₂
Mol. wt	30.047	28.014
B ₀	0.0627724	0.0484824
A ₀	4.15556	1.27389
C ₀	179,592.0	4273.00
D ₀	—	7.61781 × 10 ⁶
b	0.0111220	0.00232373
a	0.345160	0.017844
c	32,767.0	475.000
δ	—	832,000
α	0.000243389	0.00015300
γ	0.0118000	0.006500

P = atmospheres

ρ = gram moles/liter

T = °Kelvin (°C + 273.16)

R = universal gas constant = 0.08206

Since the D₀ and δ terms are zero for ethane, these rules reduce to:

$$D_{om} = D_{oN_2} X_{N_2}^2$$

and

$$\delta_m = \delta_{N_2} X_{N_2}^3$$

where X_{N₂} is the mole fraction of nitrogen present in the mixture.

Values of the constants for ethane taken from the paper of Benedict, Webb and Rubin,⁴ and for nitrogen from the work of Bloomer and Rao,⁷ are tabulated in Table 1. Since the values of B₀ for ethane and nitrogen are not too greatly different, the values of B_{om} obtained by the considerably more complicated Lorentz combination will be only slightly different from those obtained by the linear combination method. The Lorentz combination gives smaller values, which is in the right direction to improve the agreement between the calculated and observed values; however, the correction is only a small fraction of that required.

Pressures calculated by use of the modified Benedict-Webb-Rubin equation of state and the above combining rules, with the linear combination rule for B₀, are compared with experimentally measured pressure in Table 2. The agreement between the observed values and those calculated by this method is only fair.

To improve the agreement between the calculated and the observed pressure values, an empirical correction factor for the equation of state was determined and applied successfully to methane-nitrogen⁸ and methane-ethane systems:⁹

$$P_{corrected} = P_{calc \text{ by Eq 1}} - (2x_1 x_2) (0.0625 \rho^2) \quad [\text{Equation 2}]$$

A similar correction factor was recently applied by Benedict and Stutler for the methane-nitrogen system.

The correction given by Equation 2 may also be obtained as an empirical correction to the combination rule for the A₀ term in the equation of state:

$$A_{om} = \left(\sum_i x_i A_{oi}^{1/2} \right)^2 + 0.125 x_1 x_2 \quad [\text{Equation 3}]$$

For the ethane-nitrogen system the values of pressure calculated by the equation of state were lower than the observed values, so the sign of the correction term had to be reversed. With this correction the average error of the calculated pressures is reduced to a value only slightly greater than the average error obtained in fitting the equation to pure components.

To determine the nature of the deviation (P_{observed} - P_{calculated}), plots of deviation versus temperature at constant density and composition, and deviation versus density at constant temperature and composition, were prepared. No simple relationship of the deviation with temperature, density or composition was found. Unlike the methane-ethane and methane-nitrogen systems, the deviation is not independent of temperature and composition but is a function of 1/T and X_{N₂}. Also the deviation is not proportional to ρ², as is assumed in the empirical correction term, but to some power less than 2, of the order of 1.5. However, taking the empirical correction term to be proportional to ρ² seems to take into account the influence of temperature, composition and density, as can be seen from the reduction in the average deviation in Table 2.