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Joule-Thomson Effects in Gas Mixtures: The Nitrogen-Methane-Ethane System

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Pressure-temperature data were obtained along isenthalps for nitrogen, methane, and three ternary nitrogen-methane-ethane mixtures. These data were differentiated to obtain Joule-Thomson coefficients over the temperature range from ambient to 200°K. and at pressures from 165 atm. to about 5 atm. Data for nitrogen was obtained down to 140°K.

The resulting Joule-Thomson coefficients were compared with predictions based on the Beattie-Bridgeman and Benedict-Webb-Rubin equations of state and on the virial equation of state truncated after the third virial coefficient. These comparisons show that the Benedict-Webb-Rubin equation could predict the data with a deviation averaging 1.7%. The Beattie-Bridgeman predictions were highly dependent upon the mixture rules used, with the best set of mixture rules giving an absolute average deviation of 4.8%. Predictions using the virial equation with virial constants obtained from the Lennard-Jones potential energy function using a geometric mean minimum potential energy deviated from the experimental data by 5%. In all of these comparisons, the virial coefficients of ethane appear to be in greatest uncertainty, and the predictions of mixture data high in ethane were least satisfactory. Thus it appears that improved data on the pure components, particularly ethane, are vital to any satisfactory evaluation of mixture properties.

Most methods for treating the thermodynamic properties of gas mixtures make a basic assumption that equations of state for mixtures have the same form as the equations that describe the component species. Constants for mixture relations are obtained by a combination of the constants of the components. Many empirical rules have been proposed as means of making these combinations. This research was concerned with a comparison and evaluation of a number of such mixing rules. First, effort was directed toward developing a body of accurate data for ternary gas mixtures, over a useful range of pressures, temperatures, and compositions. Second, these data were used to test the ability of mixing rules for empirical and virial equations of state to predict properties for multicomponent mixtures. Third, the experimental mixtures were observed under conditions at which one of the component species was condensable in its pure state; these data were used to examine the extrapolation of equation-of-state parameters for the condensable species.

Three mixtures of ethane, methane, and nitrogen were investigated. Experiments consisted of measuring Joule-Thomson effects across an insulated throttling valve. The apparatus is suited to operation at temperatures from —200 to 25°C. and pressures to 165 atm. A three-fold variation in ethane concentration was chosen and experiments spanned a broad region in which this component is condensed when pure. The Beattie-Bridgeman, Benedict-Webb-Rubin, and virial equations were the basis for examination of mixing rules.

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EXPERIMENTAL APPARATUS

The experimental apparatus has been described by Stockett and Wenzel (*13*). It consists of a recycle system in which the system gas is brought to the desired temperature and pressure before admission to a specially designed throttling valve. From the valve the gas returns through a heat exchanger and flow meter to the compressor. Gas flow rates up to 3.5 standard cu. ft./min. at pressures to 3,500 lb./sq. in. abs. are possible. Gas temperatures approaching the valve can be controlled from 100 to −300°F. with a stability of ± 0.01°F.

The throttling valve has been redesigned, and it is shown in Figure 1. Gas entered in ⅛ in. copper tubing, which made several turns around the lower or inlet section of the valve. The inlet line teed into one of two Conax thermocouple glands. It entered the valve proper at the bottom. The inlet gas-stream thermocouple was immersed for a distance of about 16 in.; its junction was ¼ in. upstream of the entrance to the throttling orifice. The latter was a 1/16 in. hole, with conical inlet and outlet channels, in a circular disk of nylon. Nylon was chosen to limit heat transfer both parallel to the direction of flow and normally, especially at the throat, for resistance to distortion and dimensoinal change in the presence of large temperature gradients and rapid temperature changes. Gas flow paths to and from the orifice were enclosed in lucite flow guides backed by multilayer insulation. This design was used to reduce conductive and convective transfer between the gas stream and valve body by insertion of a barrier of low conductivity. Regeneration served the same purpose by limiting thermal driving forces and the polished inner and outer surfaces of the valve helped to limit radiative transfer.

Flow rate was adjusted with a lucite pintle extended downward into the outlet section of the valve and orifice from the top. A perforated lucite baffle was placed above the conical tip of the pintle to break up the emerging gas jet and induce uniform velocity and temperature profiles. Lucite was used to minimize conduction from the surroundings along this path. The pintle passed through the top of the valve by means of a needle valve bonnet assembly. The gas discharge path was similar to the inlet path. The outlet gas stream thermocouple was immersed in the flow channel for a distance of 9 in. before leaving the valve body. The thermocouple junction was located ¼ in. downstream of the lucite disk.

Pressure sensing lines left the top and bottom of the valve and passed through the constant temperature bath before connecting to a pair of precision Bourdon tube guages. Valve surface thermocouples were affixed to inlet and outlet sections of the valve. All thermocouples were coiled extensively before leaving the insulation around the valve. The success of the lucite baffle, thermocouple immersion, flow guides, pressure line location, etc., in limiting subjective errors due to heat leak and kinetic effects was judged favorably on the basis of reference gas measurements.

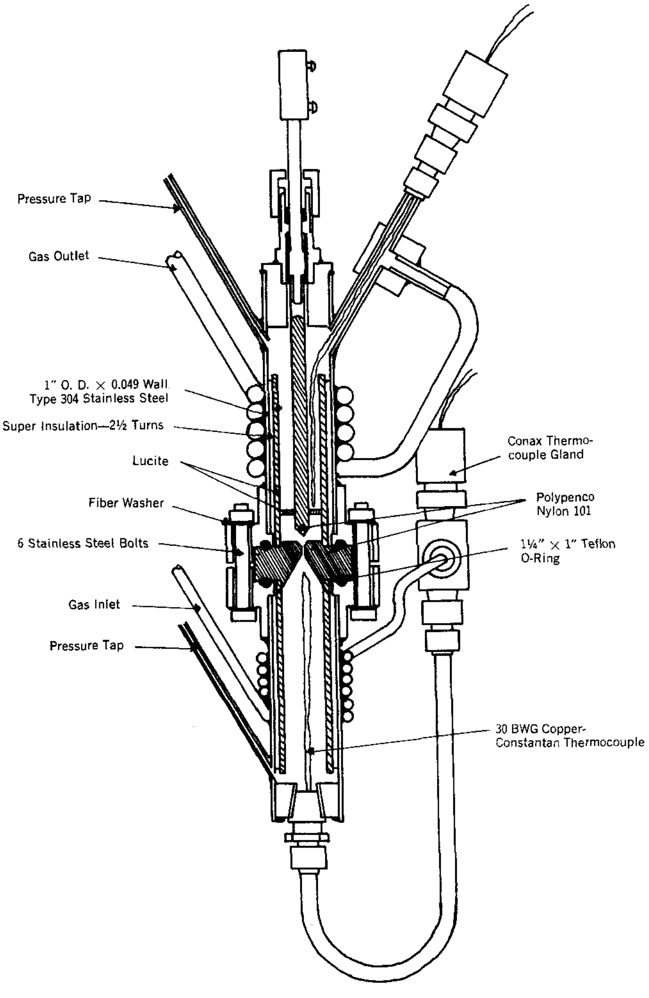

Fig. 1. Detail of Joule-Thomson valve.

ERROR ANALYSIS

Careful consideration of errors in temperature and pressure measurement lead to the conclusion that pressure gauge error, which could be as great as 3 lb./sq.in. is dominant. Translated into terms of temperature variation this error corresponds to temperature deviations of 0.02 and 0.2°K. for Joule-Thomson coefficients of 0.1 and 1.0°K./atm. respectively. Considering temperature measurement errors using calibrated thermocouples, the composite error is estimated at 0.03 to 0.2°K. for the Joule-Thomson coefficient range indicated.

The complex geometry of the Joule-Thomson valve makes it impossible to develop detailed analyses of subjective errors (heat leak and kinetic energy effects). Treatment of these errors is divided into two phases. The first phase was the design and construction of the apparatus, and the ability to detect that steady state conditions had been established. A procedure for measurement of skin temperature and valve inlet and outlet temperatures and pressures was developed to insure a period of invariance prior to the recording of data. The second phase of subjective error treatment was in effect an *a posteriori* proof of apparatus performance. It consisted of a continuing operational calibration with reference gases of known properties. Nitrogen and methane were run repeatedly during the course of this program. Integral Joule-Thomson effects were in excellent agreement with literature values. Reference gas observations led to the conclusion that errors of the subjective type are not significant.

DATA TREATMENT

At each setting of valve inlet temperature and pressure and valve outlet pressure several measurement sets were made. These raw measurements of valve inlet and outlet pressures and temperatures were averaged linearly. Estimates of measurement population standard deviations were employed to evaluate and control the scatter of measurements about the mean. Standard deviations of temperature and pressure measurements never exceeded 0.05°K. and 1.0 lb./sq.in., respectively. In most cases, they were well below these values; average values for the over-all program were equivalent to 0.01°K. and 0.3 lb./sq.in. Corrected inlet pressures and temperatures for a single isenthalp were averaged linearly to arrive at the coordinates of the initial point of the isenthalp. The standard deviations of individual means around the group means for one linlet temperature and pressure were less than 0.01°K. and 0.2 lb./sq.in. respectively.

A set of measurements taken with a common inlet temperature and pressure represent an isenthalp. To allow the measured integral Joule-Thomson effects to be differentiated to give Joule-Thomson coefficients, each isenthalp was fitted to an equation of the form:

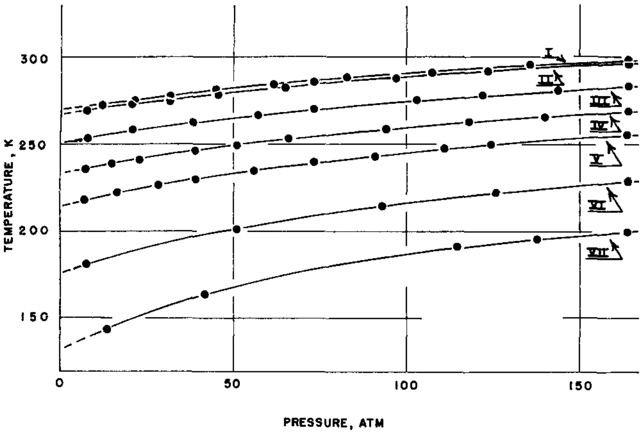

Fig. 2. Experimental isenthalps for nitrogen.

$$T_r = a + bP_r + cP_r^2 + dP_r^3 + \ldots\ldots\ldots\ldots\ldots \quad (1)$$

In general a fourth-order polynomial fit the data within the predicted experimental error. Reduced values of temperature and pressure were used for convenience in machine computation.

After fitting, data were examined to determine whether observations made at the upper and lower extremes of the flow rate range deviated to a larger extent or in a systematic direction relative to the combined data. No evidence for a measurable error, related functionally to flow rate, was encountered.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Reference Gases

Nitrogen and methane were selected as reference gases to have broad ranges of gas phase conditions available for observation and to allow a large variation in Joule-Thomson coefficients. Measurements on these gases were interspersed with measurements on three experimental mixtures to verify continuing satisfactory performance of the apparatus. In all, nine isenthalps were determined, seven for nitrogen and two for methane. Nitrogen and methane isenthalps are plotted in Figures 2 and 3, respectively.

Prepurified nitrogen was obtained from two suppliers. Both sources guarantee a minimum purity of 99.996% and a typical oxygen concentration of about 8 p.p.m. Critical constants of 126.06°K. and 33.49 atm. were employed to convert experimental data and comparative temperatures to the reduced form. Comparative thermodynamic data were taken from Strobridge (*15*), Din (*5*) and Mage, et. al. (*9*).

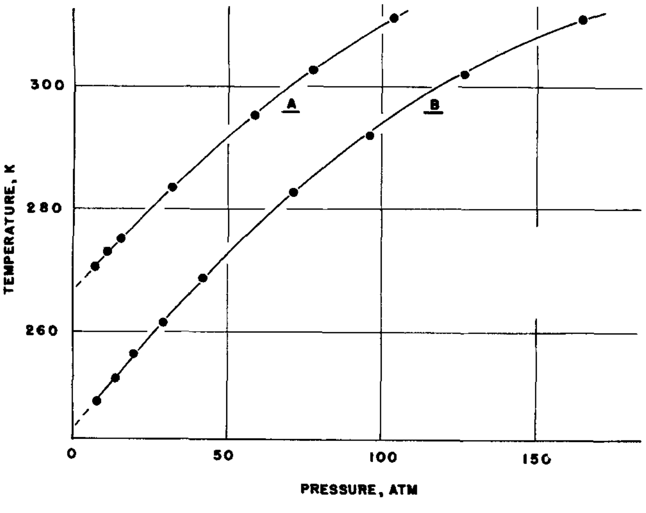

Fig. 3. Experimental isenthalps for methane.

Present data fall within the limits of comparative values in all but two cases; only one of these exceptions is significant. The spread of literature values is greater than differences between experimental data and either compressibility source chosen at random. Joule-Thomson coefficients are compared as well as temperatures. The maximum deviation at any point is 16.2%. However, a number of the largest deviations occur at end points of the isenthalps; the method of fitting with simple polynomials can be expected to yield spurious slopes at the limits of the data. The Joule-Thomson coefficients derived from the data of this work are extremes of the four values (three literature and one experimental) in only five cases; in none of these instances can the difference be described as significant. There are no significant trends to the sign or magnitude of deviations. The average absolute deviation for the data of this program relative to the three sets of comparative data is 3.0%.

Chemically pure methane was used as purchased. Minimum purity was 99.5%; impurities consisted of nitrogen and other hydrocarbons. A critical temperature of 190.66°K. and a critical pressure of 45.80 atm., were chosen. Comparative thermodynamic data of Din (*5*) and Matthews and Hurd (*10*) were employed for critical evaluation.

All experimental temperature values are either equal to or intermediate to the comparative data. The comparison of Joule-Thomson coefficients is less consistent. Maximum deviations of the Joule-Thomson coefficients for methane are larger than for nitrogen, although they appear at the end points in all cases and probably arise as a consequence of the curve fitting procedure. The data of the 310.94°K. (B) isenthalp lie intermediate between the comparative vaules; Joule-Thomson coefficients for the 310.94°K. (A) isenthalp are larger than literature values.

Average absolute deviation of the Joule-Thomson coefficient data from this program relative to the literature sources is 4.6%. The average deviation of the literature values from each other is 6.7%, based on the mean of the two values. Thus, the overall average deviation for the experimental data, relative to the comparative data, is appreciably less than the average deviation between the comparative sources.

Ternary Mixtures

Three mixtures of ethane, methane, and nitrogen were selected for experimental observations. Ethane concentrations varied from 10 to 33.3%. Ethane content was limited to insure an adequate gas phase regime below 100°F.; the latter was the highest temperature desired at the Joule-Thomson valve. Nominal methane concentration varied from 20 to 45%; nominal nitrogen concentration

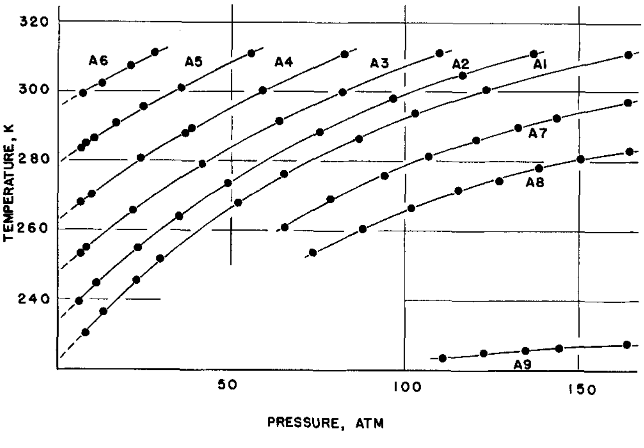

Fig. 4. Experimental isenthalps for mixture A (33.2% C_2H_6, 32.5% CH_4, 34.3% N_2)

varied from 33.3 to 55%. Compositions of the gas mixtures were checked by chemical analyses of samples drawn from the experimental system at random times during the program.

Analyses were performed at Lehigh University and two industrial laboratories. The former were carried out with the aid of a mass spectrometer, while the latter laboratories employed gas chromatographic techniques. Results of mass spectrometer analyses had an accuracy of 5 to 10% based on individual component concentrations. Gas chromatograph analyses had estimated accuracies of 1 to 2%, on the same basis. Normalized compositions obtained from these analyses were, for mixture A, 33.2 mole % ethane, 32.5 mole % methane, and 34.3 mole % nitrogen; for mixture B, 9.6 mole % ethane, 46.0 mole % methane, and 44.4 mole % nitrogen; for mixture C, 26.5 mole % ethane, 22.5 mole % methane, and 51.0 mole % nitrogen.

All mixtures were examined over a range of valve inlet pressures and temperatures to upper limits of 2,400 lb./sq.in. gauge and 100°F., respectively. Initially, isenthalps were optained at the maximum inlet temperature and inlet pressures of 400 to 2,400 lb./sq. in. gauge, at 400 lb./sq.in. intervals. No pressure fluctuations, indicative of phase change in the Joule-Thomson valve were encountered in any of these cases. Subsequently, isenthalps were observed at the maximum valve inlet pressure and decreasing inlet temperatures, at 25°F. intervals. Condensation of mixture A, B, and C was encountered on isenthalps with 75, 25, and 50°F. inlet temperatures, respectively. Truncated isenthalps were taken at these and lower inlet temperatures, although it was not possible to obtain data for isenthalps at every 25°F. interval. A short isenthalp was taken at the minimum inlet temperature of —50°F. for all mixtures. Calibration factors were applied to thermocouple outputs and data from the pressure gauges. Corrected measurements are plotted in Figures 4 through 6.

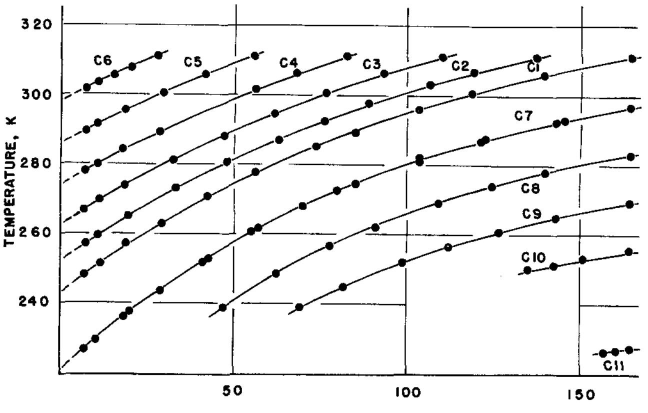

Fig. 6. Experimental isenthalps for mixture C (26.5% C_2H_6, 22.5% CH_4, 51.0% N_2)

Data were fitted to simple polynominal expressions using reduced conditions. Critical constants for nitrogen and methane were quoted above. For ethane, critical temperature is 305.5°K. and critical pressure is 48.2 atm. Isenthalps of mixtures A, B, and C were fitted to Equation (1). Maximum standard deviations for the polynomial relations for the three mixtures were 11 × 10^{-4} (A 1), 3.6 × 10^{-4} (B 8) and 3.1 × 10^{-4} (C 7), respectively. The deviation of the A 1 isenthalp corresponds to 0.22°K., while both of the latter deviations equal about 0.66°K. Constants for these polynomials are reported in Tables 1, 2, and 3.

TABLE 1. POLYNOMIALS FOR ISENTHALPS OF MIXTURE A

Isenthalp	a	$b \times 10$	$c \times 10^2$	$d \times 10^3$	$e \times 10^4$	Variance × 10^8
A1	1.07181	2.38149	—5.76505	9.09602	—7.03691	110.0
A2	1.12705	2.13500	—4.90204	8.25322	—7.71391	64.0
A3	1.19527	1.84611	—3.37585	3.04088	—	86.0
A4	1.26991	1.62492	—2.88851	3.08855	—	16.0
A5	1.34909	1.39269	—1.85572	—	—	30.0
A6	1.42513	1.24432	—1.90115	—	—	0.28
A7	0.97675	2.48319	—4.79106	3.66494	—	5.2
A8	0.93008	2.33807	—4.32184	3.07124	—	3.8
A9	0.97771	0.53496	—0.58175	—	—	0.45

For this mixture: T_c = 207.37°K., P_c = 42.48 atm.

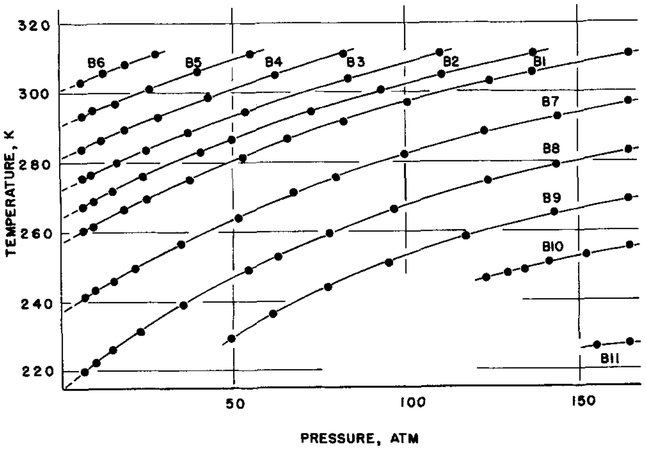

Fig. 5. Experimental isenthalps for mixture B (9.6% C_2H_6, 46.0% CH_4, 44.4% N_2)

For all isenthalps, the Joule-Thomson coefficient increases with decreasing temperature and pressure along the isenthalp. Estimated experimental error increases in the same fashion along the isenthalp and reaches its maximum value at the extrapolated value of temperature for zero pressure. This results from the fact that pressure measurement errors, which predominate, are converted into temperature errors by mutliplying by the Joule-Thomson coefficient. It is of interest to examine the deviations of experimental data points from the fitting polynomial expressions and compare them to estimates of expermiental error. A total of 21 data points out of a grand total of 243 measurements deviate from the chosen polynomial expressions by more than the estimated error at the point. Of these 21 points, 11 deviate from the polynomial by 0.05°K. or less but occur under conditions where the minimum experimental error (0.03°K.) is applied. About half of the 243 data points treated deviate

TABLE 2. POLYNOMIALS FOR ISENTHALPS OF MIXTURE B

Isen-thalp	a	$b \times 10$	$c \times 10^2$	$d \times 10^3$	Vari-ance $\times 10^8$
B1	1.48555	1.26734	—1.56694	0.82083	3.4
B2	1.52698	1.20330	—1.46892	0.79015	1.6
B3	1.57404	1.12867	—1.32586	0.70501	4.8
B4	1.62583	1.04465	—1.01986	—	3.8
B5	1.68104	0.96760	—0.89902	—	1.1
B6	1.73736	0.92449	—1.03937	—	0.20
B7	1.36781	1.48395	—2.00098	1.13601	1.0
B8	1.24378	1.77848	—2.69335	1.70869	13.0
B9	1.12116	2.06898	—3.34859	2.19420	7.9
B10	1.10730	1.42293	—1.27038	—	0.66
B11	1.18704	0.31565	—	—	0

For this mixture: T_c = 173.07°K., P_c = 40.50 atm.

TABLE 3. POLYNOMIALS FOR ISENTHALPS OF MIXTURE C

Isen-thalp	a	$b \times 10$	$c \times 10^2$	$d \times 10^3$	Vari-ance $\times 10^3$
C1	1.32436	1.60396	—2.33022	1.44245	9.2
C2	1.37251	1.48701	—2.04958	1.20248	3.4
C3	1.42875	1.36335	—1.74335	0.87803	2.1
C4	1.49132	1.22421	—1.26645	—	1.8
C5	1.55700	1.11755	—1.11375	—	1.8
C6	1.62447	1.00898	—0.91955	—	1.3
C7	1.20110	1.95062	—3.20751	2.21262	9.6
C8	1.08318	2.26919	—3.98505	2.82724	5.3
C9	1.01971	2.14088	—3.47069	2.16261	0.40
C10	1.05850	1.27505	—1.15112	—	0.046
C11	1.15608	0.19803	—	—	0.0040

For this mixture: T_c = 183.82°K., P_c = 39.62 atm.

TABLE 4. EXPRESSIONS FOR HEAT CAPACITY AND THE JOULE-THOMSON COEFFICIENT FROM EQUATIONS OF STATE

Beattie-Bridgeman Equation:

$$c_P = c_P^{o} - R + \frac{6cR}{VT^3} + \frac{3B_ocR}{V^2T^3} - \frac{2B_obcR}{V^3T^3}$$

$$+ \frac{\left\{ \frac{R}{V} + \frac{B_oR}{V^2} - \frac{B_obR}{V^3} + \frac{2cR}{V^2T^3} + \frac{2B_ocR}{V^3T^3} - \frac{2B_obcR}{V^4T^3} \right\}^2}{\frac{R}{V^2} + \frac{2B_oR}{V^3} - \frac{3B_obR}{V^4} - \frac{2cR}{V^3T^3} - \frac{3B_ocR}{V^4T^3} + \frac{4B_obcR}{V^5T^3} - \frac{2A_o}{V^3T} + \frac{3A_oa}{V^4T}}$$

$$\mu c_P = \frac{B_oRT - \frac{2B_obRT}{V} - \frac{4cR}{T^2} - \frac{5B_ocR}{VT^2} + \frac{6B_obcR}{V^2T^2} - 2A_o + \frac{3A_oa}{V}}{-RT - \frac{2B_oRT}{V} + \frac{3B_obRT}{V^2} + \frac{2cR}{VT^2} + \frac{3B_ocR}{V^2T^2} - \frac{4B_obcR}{V^3T^2} + \frac{2A_o}{V} - \frac{3A_oa}{V^2}}$$

Benedict-Webb-Rubin Equation:

$$c_P = c_P^{o} - R + \frac{6C_o}{VT^3} - \frac{6c}{\gamma T^3} + \left\{ \frac{6c}{\gamma T^3} + \frac{3c}{V^2T^3} \right\} \exp\left(-\frac{\gamma}{V^2} \right)$$

$$+ \frac{\left[\frac{R}{V} + \frac{B_oR}{V^2} + \frac{bR}{V^3} + \frac{2C_o}{V^2T^3} - \left\{ \frac{2c}{V^3T^3} + \frac{2c\gamma}{V^5T^3} \right\} \exp\left(-\frac{\gamma}{V^2} \right) \right]^2}{\frac{R}{V^2} + \frac{2B_oR}{V^3} - \frac{2A_o}{TV^3} - \frac{2C_o}{V^3T^3} + \frac{3bR}{V^4} - \frac{3a}{TV^4} + \frac{6a\alpha}{TV^7} + \left\{ \frac{3c}{V^4T^3} + \frac{3c\gamma}{V^6T^3} - \frac{2c\gamma^2}{V^8T^3} \right\} \exp\left(-\frac{\gamma}{V^2} \right)}$$

$$\mu c_P = \frac{B_oRT - 2A_o - \frac{4C_o}{T^2} + \frac{2bRT}{V} - \frac{3a}{V} + \frac{6a\alpha}{V^4} + \left\{ \frac{5c}{VT^2} + \frac{5c\gamma}{V^3T^2} - \frac{2c\gamma^2}{V^5T^2} \right\} \exp\left(-\frac{\gamma}{V^2} \right)}{-RT - \frac{2B_oRT}{V} + \frac{2A_o}{V} + \frac{2C_o}{VT^2} - \frac{3bRT}{V^2} + \frac{3a}{V^2} - \frac{6a\alpha}{V^5} - \left\{ \frac{3c}{V^2T^2} + \frac{3c\gamma}{V^4T^2} - \frac{2c\gamma^2}{V^6T^2} \right\} \exp\left(-\frac{\gamma}{V^2} \right)}$$

Virial Equation (density expansion):

$$c_p = c_P^{o} - R - RT \left\{ \frac{1}{V} \left[2B'(T) + TB''(T) \right] + \frac{1}{2V^2} \left[2C'(T) + TC''(T) \right] + \ldots \right\}$$

$$+ \frac{R \left\{ 1 + \frac{1}{V} \left[B(T) + TB'(T) \right] + \frac{1}{V^2} \left[C(T) + TC'(T) \right] + \ldots \right\}^2}{\left\{ 1 + \frac{2B(T)}{V} + \frac{3C(T)}{V^2} + \ldots \right\}}$$

$$\mu c_p = -\frac{\left\{ \left[B(T) - TB'(T) \right] + \frac{1}{V} \left[2C(T) - TC'(T) \right] + \ldots \right\}}{\left\{ 1 + \frac{2B(T)}{V} + \frac{3C(T)}{V^2} + \ldots \right\}}$$

by 0.01°K. or less from the fitting expression. Thus, these polynomial expressions are an excellent representation of experimental observations.

PREDICTION METHODS

Empirical Equations of State

The experimental isenthalps were differentiated to obtain Joule-Thomson coefficients over the entire range of pressure and temperautre for each ternary mixture. These were compared with Joule-Thomson coefficients calculated from the Beattie-Bridgeman and the Benedict-Webb-Rubin equations of state and from the virial equation.

Each of the equations of state was placed in a form explicit in pressure and substituted into the thermodynamic functions for heat capacity and the Joule-Thomson coefficient. Results of these steps are outlined in Table 4. Heat capacities at zero pressure were required for prediction of Joule-Thomson coefficients. Din's (*5*) reported polynomials in temperature for the zero pressure heat capacities of methane and ethane were used. For nitrogen the data of Goff and Gratch (*6*) were fitted to temperature polynomials; the cubic expression was used:

$$C_p{}^o = 6.94685 + 9.96152\;10^{-5}T - 6.93758\;10^{-7}T^2 + 1.57338\;10^{-9}T^3 \qquad (2)$$

where T is in °K. The zero pressure heat capacities of mixtures were computed by linear averaging. Calculations were performed at 15°K. intervals, from 210 to 330°K., for the three gas mixtures at all pressures of interest.

In order to use these expressions for predicting Joule-Thomson coefficients of mixtures, the constants for pure components must be combined to give constants characteristic of the mixtures. Because of the controversy over procedures of combination for the constants of the Beattie-Bridgeman equation, two procedures were investigated. The first, referred to as *BB I*, embodied the proposals of Beattie (*1*). All five constants combine with the equation:

$$K_{\text{mix}} = \sum_i \sum_j x_i\, x_j\, K_{ij} \qquad (3)$$

Beattie-Bridgeman constants B_o, a, b, and c are mixed linearly and A_o is mixed geometrically, to obtain the interaction terms. The second procedure, denoted *BB II*, was suggested initially by Beattie and Stockmayer (*2*). Combination of A_o, a, and b is unchanged. Constants c and B_o still combine quadratically, but interaction terms are generated geometrically and with the Lorentz rule, respectively, in this procedure.

The eight constants of the Benedict-Webb-Rubin equation separate into two groups. One group, consisting of A_o, B_o, C_o, and γ, combines according to the quadratic relation of Equation (3). A_o, C_o, and γ mix geometrically to form interaction terms; B_o mixes by the Lorentz rule. The other group, consisting of a, b, c, and α combines in cubic fashion; that is, by the equation:

$$K_{\text{mix}} = \sum_i \sum_j \sum_k x_i\, x_j\, x_k\, K_{ijk} \qquad (4)$$

Interaction terms form geometrically. Numerical values for Beattie-Bridgeman constants were taken from Beattie (*11*). Benedict-Webb-Rubin constants for methane and ethane were taken from (*3*). Constants for nitrogen were found elsewhere (*8*). Differences between experimental and predicted Joule-Thomson coefficients were calculated at the temperatures of the experimental data.

Individual average absolute deviations for each combination of pressure and composition are presented in Table 5 for the Beattie-Bridgeman II equation and the Benedict-Webb-Rubin equation. Also shown are overall average absolute deviations for each composition with each equation of state and grand overall average absolute deviations for all predictions with each equation of state. Results for the Beattie-Bridgeman I equation are not shown. The mixture rules of Beattie (*1*) lead to large deviations at pressures greater than 400 lb./sq.in.abs., so that the grand over-all average deviation is 10.4%. This is over twice the deviation found with the Beattie-Bridgeman II equation and almost as great as deviations found with the van der Waats equation. Thus, choice of mixture rule is crucial in obtaining acceptable accuracy with the five-constant equation of state.

TABLE 5. COMPARISON OF PREDICTED JOULE-THOMSON COEFFICIENTS

	Avg. Abs. Deviation, Percent of Experimental Value					
Equation of State:	Beattie-Bridgeman II			Benedict-Webb-Rubin		
Mixture:	A	B	C	A	B	C
Pressure, lb./sq.in.abs.						
0	13.4	4.6	4.7	3.5	1.6	4.3
400	4.9	1.3	1.3	1.9	0.3	0.9
800	0.8	0.8	1.6	0.4	0.2	1.1
1,200	3.9	2.0	5.4	1.1	0.3	1.9
1,600	4.6	2.7	5.8	2.6	0.2	1.0
2,000	8.4	5.1	7.4	2.4	0.8	1.7
2,400	12.5	9.8	9.0	5.6	2.3	3.9
over-all avg. abs. deviation:	6.7	3.5	4.8	2.3	0.8	2.1
grand over-all avg. abs. deviation:		4.8			1.7	

For all of the equations examined, deviations at zero pressure were greater than for higher pressure data. This results from the fact that these values represent an extrapolation of the experimental data, which seldom extended below 4 atm.

The grand overall average deviation for predictions with the Benedict-Webb-Rubin equation is 1.7%. The largest deviation of any of the 128 points compared was observed to be 8.3%. Deviations of 42 points were completely negligible, that is counted as zero. The gain in accuracy resulting from an increase in the number of arbitrary constants is appreciable. The degree of accuracy demonstrated for predictions with this equation is adequate for solution of most problems that arise in practice.

The over-all average deviations for mixture B were smaller than deviations for mixtures A and C based on the same equation of state. Differences between the average deviations for pairs of mixture data were taken at successive pressure levels and assumed to be normally distributed, as a first approximation. Student *t* statistics demonstrated, in all cases, that at the 90% confidence level deviations of mixture B were significantly less than those for mixtures A or C. Thus, there is a high degree of statistical significance to the differences between deviations for mixture B and those for either mixture A or mixture C. Differences between deviations for mixtures A and C were tested and were not significant in any instance.

Experimental mixtures had ethane contents that varied in the order A > C > B. The fact that deviations for mixture B were significantly smaller than those for mixtures A or C suggests that the accuracy of prediction with the empirical equations of state decreases with increasing concentration of the condensible species. Application of equation of state constants over a region in which the pure species is a liquid, although a gas when present in the mixture, might not be justified. The absence of significant differences between deviations of mixtures A and C weakens this hypothesis. Mixture B is also the closest to binary in nature of the three mixtures. This close approach to binary composition, that is less than 10% *of the third* component, may be a factor in enhanced accuracy of prediction.

Virial Equation

Expressions for heat capacity and the Joule-Thomson coefficient, in terms of the virial coefficients and their derivatives, are given in Table 6. Virial coefficients greater than the third were assumed to be zero. Hirschfelder, et al. (*8*) show how second and third virial coefficients can be obtained from Lennard-Jones intermolecular force parameters and tabulate the results of such calculations. Their values of ϵ and σ for nitrogen were used. Constants for ethane were taken from David, Hamann, and Prince (*4*). Strakey (*14*) examined the parameters for methane. A slight change in the values recommended by Hirschfelder, et al. improved the fit appreciably. The values selected for the present program are summarized in Table 6.

TABLE 6. SELECTED LENNARD-JONES PARAMETERS

Species	ϵ/k, °K.	σ, Å	Reference
methane	144.00	3.817	*14*
ethane	217.50	4.613	*4*
nitrogen	95.05	3.698	*8*

Note: k is the Boltzmann constant.

TABLE 7. COMPARISON OF PREDICTED JOULE-THOMSON COEFFICIENTS USING THE VIRIAL EQUATION
Avg. Abs. Deviation, Percent of Experimental Value

Mixing Rule:				Geometric Mean			H and F Mean		
Gas or Mixture:	Methane	Ethane	Nitrogen	A	B	C	A	B	C
Pressure, lb./sq.in.abs.									
0	4.1	9.7	1.5	13.7	5.4	5.1	17.3	7.3	9.8
400	2.5	7.8	0.5	4.8	3.3	3.1	9.6	6.9	9.0
800	1.7	—	0.4	1.5	3.3	2.9	4.7	7.7	9.2
1,200	2.0	—	0.9	4.2	4.2	3.7	2.9	8.6	9.8
1,600	3.1	—	3.9	11.9	5.9	4.7	5.9	10.2	11.6
2,000	5.7	—	6.9	14.3	5.6	4.7	6.6	10.1	9.8
2,400	7.7	—	10.5	17.3	6.9	7.9	21.0	9.9	14.2
Over-all avg. abs. deviation:	3.7	8.8	3.8	9.5	4.8	4.5	9.5	8.5	10.4
Grand over-all avg. abs. deviation:					5.3			9.4	

Second virial coefficients were combined in the quadratic form of Equation (3). Third virial coefficients were combined in cubic form, Equation (4). The first approach to mixing adopted the assumptions of inelastic, *spherical* particles and predominance of London dispersion forces. Appropriate mixing rules for Lennard-Jones parameters required linear averaging for σ and geometric mixing for ϵ. These rules were extended to produce a pseudo-pair potential for the pair-by-pair sum of potentials in the irreducible cluster integral for ternary interactions. Values of C_{ijk} were calculated from Lennard-Jones parameters for the mixture obtained by again using linear averaging for σ and geometric mixing for ϵ. The second approach to mixing was that proposed by Halsey and Fender (*7*). Mixing for the zero potential separation, σ was unchanged. However, the minimum energy of simple unlike particle interactions was given by

$$\epsilon_{ij} = \frac{2\epsilon_i\epsilon_j}{\epsilon_i + \epsilon_j} \tag{5}$$

Halsey and Fender did not recommend an analogous rule for the pseudo-pair potential. They concluded that basic uncertainties in treatment of ternary interaction integrals preclude added sophistication in mixing rules. The first approach is the geometric mean case and the second is the H and F mean case.

Calculations with these mixing rules were compared to the experimental Joule-Thomson coefficients employed in evaluation of empirical equations of state. Average deviations were calculated for each mixture at each pressure of interest. Overall average deviations were also calculated for each mixture. Joule-Thomson coefficients were computed for the pure component species, at the same pressures and 15°K. intervals, and were compared to experimental data of Sage, Webster, and Lacey (*12*) and Stockett (*13*) for ethane, and Din (*5*) and this work for methane and nitrogen. Stockett's data and reference gas data were fit to polynomials. Averaged absolute deviations, as percentages of experimental values, for both mixtures and pure species are summarized in Table 7.

Overall average absolute deviations of Joule-Thomson coefficients predicted on the basis of the geometric mean minimum potential energy are 9.5, 4.8, and 4.5%, respectively, for mixtures A, B, and C. Values for mixture B and C are significantly less than the overall average deviation for mixture A; the former do not differ significantly from each other. With the H and F mean, the corresponding overall average absolute deviations are 9.5, 8.5, and 10.4%. Differences are not significant; with this approach, all mixtures are treated poorly. Grand overall average absolute deviations of the two approaches are 5.3 and 9.4%, respectively. The mixing rule proposed by Halsey and Fender offers no advantage over the geometric mean. It results in poorer predictions for mixtures B and C, an equally large overall average deviation for mixture A and about twice the grand overall average deviation.

The virial equation yields predictions of acceptable accuracy for the Joule-Thomson coefficients of methane and nitrogen. Overall average deviations can be viewed as equal. The evaluation of predictions for ethane is clouded by substantial disagreement between sources of experimental data. Average percent deviations at lower pressures are large. Although not equivalent, comparisons of experimental data are poorer than for the other pure species. The two parameter Lennard-Jones potential cannot be expected to describe ethane with a high degree of accuracy because of the nonspherical structure and gross bulk of the fundamental particles. However, application of a potential of the Kihara type, to acount for complex fluid character, cannot be justified because the variation between experimental data sets is greater than the deviation between virial predictions and either data set. Addition of one or more adjustable constants to the potential function is not warranted without greater consistency in the experimental data from which the constants are derived. Examination of deviations for mixture A, as a function of pressure, leads to the conclusion that extension of ethane properties to the high pressure region, in which pure ethane would be condensed, does not add to the inaccuracies that arise in the region of its gas phase.

Overall average deviations for mixture B and C predictions, with the geometric mean, are consistent with the accuracy of predictions for pure species. The overall average percent deviation of mixture A is significantly larger and reflects the high concentration of ethane and poorer accuracy of predictions for this species. The quality of predictions for mixture B is surprising. Despite the improvements reported by Halsey and Fender, the H and F mean has a significantly degrading effect on the predictions for mixtures B and C. The absence of an effect in the case of mixture A suggests that predictions are not as sensitive to the choice of mixing rules in the presence of a high concentration of a species, such as ethane, that is treated badly in the pure state. The geometric mean is superior to the H and F mean. It produces predictions consistent with the treatment accorded component species. Mixing of ϵ by a simple geometric method is recommended; application of the generalized virial equation to mixtures is limited by deficiencies in the treatment of component species.

CONCLUSIONS

This work has produced an accurate body of data for ternary gas mixtures. Pressure and temperature ranges investigated were 0 to 2,400 lb./sq.in. gauge and − 50 to 100°F., respectively. A formal replication experiment demonstrated that estimates of measurement errors are a satisfactory representation of experimental errors. The maximum uncertainty in any temperature reported in this paper is 0.20°K.; the average uncertainty is about 0.05°K. Reference measurements were carried out on methane and nitrogen. Good agreement of measurements with literature values indicates the experimental apparatus is free of significant errors.

Isenthalpic data were fit to polynomials with pseudoreduced pressure as the independent variable. Polynomial order was selected on the basis of the fitting variance; deviations of experimental data from these polynomials are less than the estimates of measurement errors. Polynomials were differentiated to generate expressions for Joule-Thomson coefficients.

Joule-Thomson coefficients were predicted with Beattie-Bridgeman and Benedict-Webb-Rubin equations. Two sets of mixing rules proposed by Beattie for the Beattie-Bridgeman equation were compared. The set incorporating only linear mixing is appreciably less accurate than the set employing both Lorentz and geometric rules. Mixing rules suggested by Benedict, Webb, and Rubin for their equation are satisfactory. These empirical equations of state and associated mixing rules yield good predictions for Joule-Thomson coefficients. There is an affect of ethane concentration; predictions for mixtures with high ethane concentrations are significantly poorer. Arbitrary constants for ethane are not adequate due to the limited scope of data employed to calculate these constants.

Joule-Thomson coefficients were also predicted with the virial equation using constants calculated from the Lennard-Jones potential. Linear mixing for the zero potential separation and both the geometric mean and a mixing rule proposed by Halsey and Fender for the minimum potential energy were applied. The geometric mean gives superior results. Predictions for mixtures, with the geometric rule for minimum energy and the linear rule for zero potential separation, are as accurate as predictions for pure species. Accuracy, in the case of mixtures, decreases with increasing ethane concentration. Predictions for pure ethane are poor; this difficulty is attributed to failure of the Lennard-Jones potential for complex fluids. However, there are significant discrepancies associated with literature data, suggesting that Lennard-Jones parameters for ethane are not optimum.

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NOTATION

a, b, c, d = coefficient of Polynomial equations developed to fit data
K = general term for virial coefficient or equation of state constant
P_r = reduced pressure
R = gas constant, 82.507 cc. atm./g. mole °K.
T_r = reduced temperature
X = mole fraction
ϵ = minimum potential energy

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