Joule-Thomson Effects for Mixtures of Helium-Nitrogen-Methane and Hydrogen-Nitrogen-Methane

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Experimental isenthalps and corresponding Joule-Thomson coefficients are reported for nitrogen and equimolar ternary mixtures of helium-nitrogen-methane and hydrogen-nitrogen-methane. The estimated precision of the Joule-Thomson coefficients was within 1.5% of recent literature values.

These Joule-Thomson coefficients are compared with predictions from the virial equation and Beattie-Bridgman, Benedict-Webb-Rubin, and Redlich-Kwong equations of state. The predicted Joule-Thomson coefficients are as accurate as predictions for the pure species. Standard mixing rules and methods of combining equations of state constants are satisfactory at higher temperatures. At low temperatures the predictions from the equations of state are poor.

This paper presents a body of reliable thermodynamic data for two ternary gas mixtures over a practical range of pressures and temperatures. The prediction methods for Joule-Thomson coefficients are then applied using the virial equation and several other empirical equations of state.

Several of the standard mixture rules were used for the constants in these equations in an effort to shed light on the question of how to use equations of state in cases where gas mixtures include simple, but dissimilar gas molecules.

MATERIALS

Two ternary gas mixtures, each containing one of the so-called quantum gases, were chosen for study. It was felt that these would afford a relatively difficult application for equation of state mixing rules, as well as being of some current practical interest.

One mixture (*A*) was an equimolar mixture of helium, nitrogen, and methane, and the other mixture (*B*) was an equimolar mixture of hydrogen, nitrogen, and methane. The two ternary mixtures were obtained as mixtures of chemically pure grade helium, hydrogen, and methane, and a prepurified grade of nitrogen, from Air Products and Chemicals, Inc.

Nominal compositions of the gas mixtures were checked by chemical analysis of samples drawn from the experimental system at the end of each run in the program. The composition of mixture A was obtained by a weighted average of four analyses from two industrial analytical laboratories to give 34.1 ± 0.2 mole % helium, 33 5 ± 0.7 mole % nitrogen, and 32.4 ± 0.5 mole % methane. Mixture *B* was analyzed by the same laboratories from three separate samples to give 32.6 ± 0.3 mole % hydrogen, 33.2 ± 0.7 mole % nitrogen, and 34.2 ± 0.5 mole % methane.

EXPERIMENT

The experimental procedure, as described by Stockett and Wenzel (25) and by Ahlert and Wenzel (2), consisted of measuring integral Joule-Thomson effects by expanding the gas across an insulated throttling valve. Once equilibrium was established in the circulating gas system observations were recorded at 5-min. intervals over a period of 45 min. The criterion for equilibrium was that the variations in temperature of all the thermocouples in the system was within 0.06 to 0.08°K. over a 15-min. period. The usual variation experienced in this investigation over a 15-min. period was about 0.02°K. Each set of observations included the recording of the inlet and outlet gas temperatures, the two corresponding valve surface temperatures, the flow rate, and the inlet and outlet pressures. Temperatures and pressures were read to 0.002°K. and 0.1 lb/sq.in., respectively. The usual procedure in developing the isenthalp was to pass through a series of decreasing outlet pressures while maintaining the inlet pressure and temperature constant. The pressure was reduced in steps of 150 to 200 lb./sq.in.abs.

Errors in this system were carefully analyzed by Ahlert and Wenzel (2), and this analysis was confirmed both analytically and experimentally here. The cumulative effect of all errors is heavily influenced by pressure gauge precision and hence depends on the size of the Joule-Thomson coefficient. For $\mu = 0.1$ the errors, accumulated as temperature uncertainties, would be 0.03°K, whereas for $\mu = 1.0$ the errors are 0.3°K.

DATA TREATMENT

Isenthalps for both mixtures were obtained at five inlet temperatures: 297°, 283°, 255°, 227°, and 199°K. Starting pressure for the isenthalp at each of these temperatures was about 2,400 lb./sq.in.abs. In addition to these five isenthalps, five more isenthalps were obtained for both mixtures at an inlet temperature of 297°K. In these latter isenthalps the inlet pressures were 2,000 1,600, 1,200, 800 and 400 lb./sq.in. abs., respectively. In addition to the ternary mixtures, isenthalps were also obtained for nitrogen.

The raw data represent integral Joule-Thomson effects. To obtain the corresponding Joule-Thomson coefficients, the temperature pairs along the isenthalps were fit to a polynominal expression of the form

$$T = A + BP + CP^2 + DP^3 + \dots$$

by the method of least squares. Various orders of fit were tried. However, based on the variance of each order and also that in order to obtain Joule-Thomson coefficients the data must be differentiated, the order of fit was taken as 3. In order to obtain coefficients of the least squares fit as manageable quantities of a reasonable magnitude, the curve fit was made with reduced pressure being the independent variable and reduced

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TABLE 1. COEFFICIENTS AND VARIANCES FOR MIXTURE *A* POLYNOMIALS

$$T_{pr} = A + BP_{pr} + CP_{pr}^2 + DP_{pr}^3$$

Isenthalp	A	$B \times 10^2$	$C \times 10^3$	$D \times 10^5$	Variance $\times 10^8$
Run 1	2.65445	3.59459	−2.43408	5.31838	10.1761
Run 2	2.67004	3.60227	−2.66737	8.54441	6.6075
Run 3	2.68974	3.36062	−1.76253	−2.89703	0.845
Run 4	2.70987	4.09773	−7.45041	103.2554	17.039
Run 5	2.73650	3.16200	−1.44855	——	1.387
Run 6	2.76580	2.77613	0.27807	——	0.150
Run 7	2.50687	4.275153	−3.36500	11.70276	4.7782
Run 8	2.20385	5.57422	−4.79418	19.0771	82.5447
Run 9	1.90068	6.89435	−6.10405	24.29042	34.052
Run 10	1.56247	9.76301	−10.4982	48.4068	7.7014

For this mixture T_{pc} = 105.95°K., P_{pc} = 26.82 atm.

TABLE 2. COEFFICIENTS AND VARIANCES FOR MIXTURE *B* POLYNOMIALS

$$T_{pr} = A + BP_{pr} + CP_{pr}^2 + DP_{pr}^3$$

Isenthalp	A	$B \times 10^2$	$C \times 10^3$	$D \times 10^5$	Variance $\times 10^8$
Run 1	2.31715	5.40910	−3.84625	9.87242	7.7397
Run 2	2.34080	5.28856	−3.6209	6.83707	4.0977
Run 3	2.36808	5.12264	−3.34668	5.72752	1.6815
Run 4	2.39759	5.56607	−8.21025	117.9083	15.7150
Run 5	2.43164	4.99640	−2.85532	−39.6053	2.097
Run 6	2.47023	4.49120	−0.71475	——	0.116
Run 7	2.17980	6.29976	−5.05748	16.8040	8.2434
Run 8	1.88932	8.16021	−7.00459	24.0100	104.894
Run 9	1.59893	11.0114	−12.18882	58.9731	7.5204
Run 10	1.240523	17.5584	−25.1845	148.9479	55.0025

For this mixture T_{pc} = 118.01°K., P_{pc} = 30.96 atm.

temperature as the dependent variable.

$$T_r = A + BP_r + CP_r^2 + DP_r^3 + \dots.$$

The polynominal expressions for the two mixtures are summarized in Tables 1 and 2. The advantage in using an analytical expression for the insenthalp is that one can easily extrapolate to obtain the zero-pressure Joule-Thomson coefficients which are obtained by means of the differential

$$\mu = \frac{\partial T_r}{\partial P_r} = B + 2\,CP_r + 3\,DP_r^2 + \dots.$$

and one can easily interpolate between data points.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Reference Gas

The main objective of determining the isenthalps of nitrogen was to check the reproducibility of the apparatus by comparing the data with those obtained by Ahlert (*1*). Ahlert's data had been compared to those of Roebuck (*21*), Din (*8*), Strowbridge (*26*), and Mage (*15*), and were shown to be within ±3% of their measured or predicted values of the Joule-Thomson coefficient.

Critical constants of 126°K. and 33.5 atm. were employed to convert experimental data to the reduced form. At high pressures and low temperatures the deviations are the largest. Average deviations for the data of this investigation relative to those of Ahlert for each of the four nitrogen isenthalps are outlined in Table 3. Although the experimental inlet temperatures used were slightly different from those used by Ahlert (a maximum difference of 1.2%), the Joule-Thomson coefficients were within 1.5% of Ahlert's values. Only two points out of a total of 46 points had a deviation of 3% in the Joule-Thomson coefficient. In the overall evaluation of temperature and Joule-Thomson data for nitrogen, data consistently fall within the limits of variation of the best current literature sources (*26, 8, 15, 22*). These results further prove the reproducibility of Joule-Thomson coefficient data from the experimental apparatus.

Ternary Mixtures

The isenthalps for the two mixtures are plotted in Figures 1 through 4. The points plotted in these figures are the actual experimental data and the curve through these points represents the polynomial fit. As described earlier the data were fit to simple polynomial expressions of the form

$$T_{pr} = A + BP_{pr} + CP_{pr}^2 + DP_{pr}^3 + \dots.$$

where T_{pr} and P_{pr} are pseudoreduced temperature and pressure, respectively, based on nominal pseudocritical constants for the mixtures obtained by Kaye's rule. The pseudocritical constants for the two mixtures are included in Tables 1 and 2.

The largest deviations in the isenthalp occurred at the 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.

For all isenthalps observed, the Joule-Thomson coefficient increases quite regularly with decreasing temperature

TABLE 3. AVERAGE DEVIATIONS FOR JOULE-THOMSON COEFFICIENTS OF NITROGEN

Run No.	Isenthalp inlet temperature, °K.	Average deviation percent relative to data of Ahlert
1	296.36	1.50
2	282.22	1.20
3	256.37	0.85
4	197.24	1.62
Overall average deviation, %		1.29

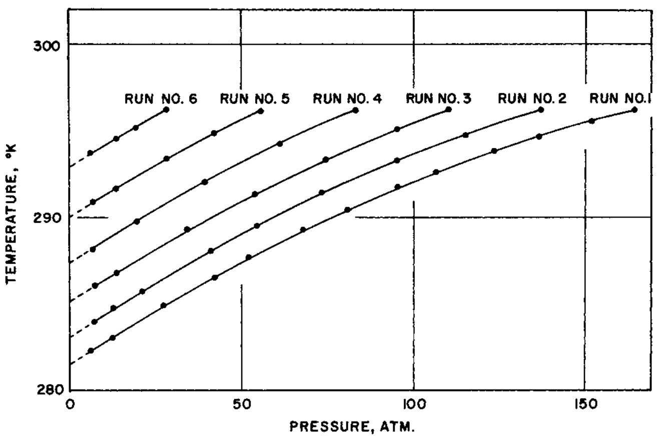

Fig. 1. Experimental isenthalps for mixture *A*.

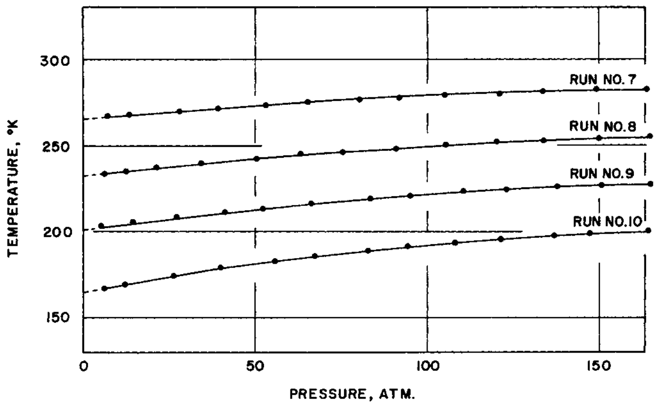

Fig. 2. Experimental isenthalps for mixture *A*.

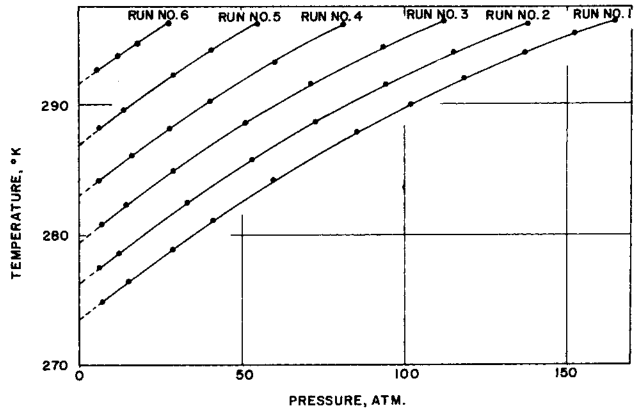

Fig. 3. Experimental isenthalps for mixture *B*.

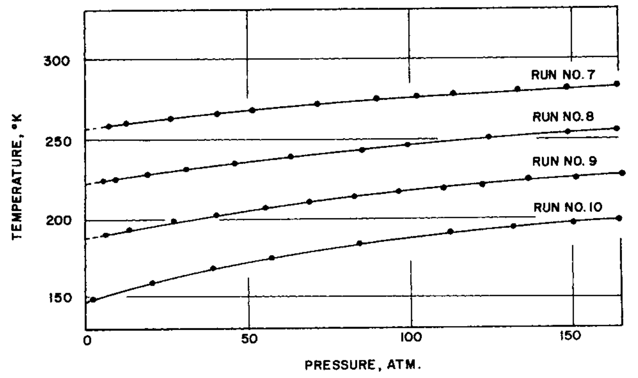

Fig. 4. Experimental isenthalps for mixture *B*.

and pressure along the isenthalp. As a consequence, the estimated experimental error increases in the same manner along the isenthalp and reaches its maximum at the extrapolated value of the zero-pressure Joule-Thomson coefficient.

Of the 120 observations taken for mixture *A*, one point deviates by 0.29°K. from the fitting polynomial and two points deviate by 0.12°K. However, all differences between observed and calculated outlet temperatures for mixture *A* are below the maximum predicted experimental error of 0.3°K. The average difference for all the data of mixture *A* is 0.03°K. Of the 86 points measured on mixture *B*, six points deviate by about 0.14°K. and one point differs by 0.28°K. from the fitting polynomial. Here again all differences between observed and calculated outlet temperatures for mixture *B* are below the maximum predicted error of 0.3°K. The average difference between the observed and calculated outlet temperatures for all the data of mixture *B* is 0.04°K.

PREDICTION METHODS

Virial Equation of State

For this work the virial equation of state and expressions for heat capacity and the Joule-Thomson coefficient in terms of the virial coefficients and their temperature derivatives are those described by Ahlert and Wenzel (*2*). The Lennard-Jones 6-12 potential was used as the intermolecular potential function. The Lennard-Jones parameters selected for this work are shown in Table 4. Complete tables of reduced second and third virial coefficients and their derivatives are published elsewhere (*11*).

Virial coefficients greater than the third were assumed to be zero. Second virial coefficients were combined in quadratic form and the third virial coefficients were combined in cubic form according to the following equations:

$$B_{\text{mix}} = \sum_{i}^{n} \sum_{j}^{n} x_i \, x_j \, B_{ij}$$

and

$$C_{\text{mix}} = \sum_{i}^{n} \sum_{j}^{n} \sum_{k}^{n} x_i \, x_j \, x_k \, C_{ijk}$$

where $B_{ij} = B_{ji}$ and $C_{iij} = C_{iji} = C_{jii}$.

The first approach to mixing adopted the assumptions of inelastic, spherical particles and predominance of London dispersion forces. The appropriate mixing rules for Lennard-Jones parameters were

$$\epsilon_{ij} = (\epsilon_{ii} \cdot \epsilon_{jj})^{1/2}$$

and

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$$

These rules were extended to the ternary interactions as follows:

$$\epsilon_{ijk} = (\epsilon_{ii} \cdot \epsilon_{jj} \cdot \epsilon_{kk})^{1/3}$$

and

$$\sigma_{ijk} = (\sigma_{ii} + \sigma_{jj} + \sigma_{kk})/3$$

TABLE 4. SELECTED LENNARD-JONES PARAMETERS

Species	ϵ/k, °K.	σ, °A.	Reference
Helium	6.03	2.63	*19*
Hydrogen	29.20	2.87	*20*
Nitrogen	95.05	3.698	*17*
Methane	148.20	3.817	*18*

Note: κ is the Boltzmann constant.

The second approach to mixing was that proposed by Halsey and Fender (*10*). Mixing for the zero potential separation σ was unchanged. However, the minimum potential energy of simple unlike particle interactions was given by

$$\epsilon_{ij} = \frac{2\epsilon_{ii} \cdot \epsilon_{jj}}{(\epsilon_{ii} + \epsilon_{jj})}$$

Halsey and Fender did not recommend an analogous rule for the ternary interactions. They concluded that basic uncertainties in the treatment of ternary interaction integrals were so large as to preclude any added sophistication in the mixing rules. Keeping this in mind and for lack of suitable mixing rule for the ternary interaction, we propose a mixing rule for the ternary interaction given by

$$\epsilon_{ijk} = \frac{3\epsilon_{ii} \cdot \epsilon_{jj} \cdot \epsilon_{kk}}{(\epsilon_{ii} \cdot \epsilon_{jj}) + (\epsilon_{jj} \cdot \epsilon_{kk}) + (\epsilon_{ii} \cdot \epsilon_{kk})}$$

The third approach to mixing was to try the Lorentz combinations for the minimum potential energy ϵ, and a linear combination for the zero potential separation σ.

Thus for a binary interaction

$$\epsilon_{ij} = \frac{(\epsilon_{ii}^{1/3} + \epsilon_{jj}^{1/3})^3}{8}$$

and

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$$

The fourth approach to mixing was a modification of the first approach as proposed by Leland, Kobayashi, and Mueller (*12*).

$$\epsilon_{ij} = \xi\ (\epsilon_{ii} \cdot \epsilon_{jj})^{1/2}$$

where the empirical correlation factor ξ is defined as the absolute value of the difference in the effective molecular volume of a binary pair, a number proportional to ϕV_c, divided by the total atomic number of the two molecules. It thus represents a volume difference per electron in the oscillating pair, and accounts for the effect of electronic configuration differences in the atoms. According to these authors, for a binary interaction

$$|\Delta\phi V_c| = |\phi_1\, V_{c1} - \phi_2\, V_{c2}|$$

Extending this to a ternary interaction we get

$$|\Delta\phi\ V_c|_{\text{ternary}} = |\phi_1\, V_{c1} - \phi_2\, V_{c2}| + |\phi_2\, V_{c2} - \phi_3\, V_{c3}| + |\phi_3\, V_{c3} - \phi_1\, V_{c1}|$$

where the ϕ's are the quantum effects on the force constants of the various gases and were determined from a graph of ϕ versus $1/V_c^{1/3}\sqrt{MT_c}$, also presented by Leland et al.

Explicit Equations of State

In addition to the virial equation several explicit equations of state were used to predict Joule-Thomson coefficients under the experimental conditions. Those chosen were the Beattie-Bridgeman, Benedict-Webb-Rubin, and Redlich-Kwong equations. Selection was prefaced on a desire to evaluate the performance of equations of state that are in common use and have been successful with other systems. Based on initial results of these equations, simple modifications were made in an attempt to improve predictions.

All state expressions were placed in a form explicit in pressure and substituted into the thermodynamic functions for heat capacity and the Joule-Thomson coefficient. Calculations of the Joule-Thomson coefficients were carried out by computer. The crux of the program prepared for these calculations was the estimation of volume by Newton's method of iteration. The ideal gas volume served as a useful first approximation; volumes suited to the explicit equations were approximated to better than one part in ten thousand in less than six trials.

TABLE 5. ZERO-PRESSURE HEAT CAPACITIES FOR PURE COMPONENTS

Helium

$$c_p^0 = \frac{5}{2}R$$

Hydrogen [from data of Wooley et al. (*27*)]

$$c_p^0 = 4.52372 + 1.193167 \times 10^{-2}T - 1.651211 \times 10^{-5}T^2 + 6.284882 \times 10^{-9}T^3$$

Nitrogen [from data of Goff and Gratch (*9*)]

$$c_p^0 = 6.94685 + 9.96152 \times 10^{-5}T - 6.93758 \times 10^{-7}T^2 + 1.57338 \times 10^{-9}T^3$$

Methane [from Din (*8*)]

$$c_p^0 = 6.24682 + 3.71123 \times 10^{-2}T - 3.02857 \times 10^{-4}T^2 + 1.11335 \times 10^{-6}T^3 - 0.17400 \times 10^{-8}T^4 + 0.101334 \times 10^{-11}T^5$$

c_p^0 = cal./(g.-mole.)(°K.)
T = °K.
R = 1.987 cal./(g.-mole.)(°K.(

Heat capacities at zero pressure were required for prediction of Joule-Thomson coefficients. These are reported in Table 5. The zero-pressure heat capacities of the two mixtures were computed by linear averaging according to the relation

$$c^0_{P\text{mix}} = x_1\, c^0_{P1} + x_2\, c^0_{P2} - x_3\, c^0_{P3}$$

Since the zero-pressure heat capacity of a gas is a function of the internal structure (rotation, vibration, etc.) and translational energy, this procedure is subject only to the assumption that the individual gas species retain Boltzmann velocity distributions.

Joule-Thomson coefficients were calculated directly by substitution of volume, temperature, and zero-pressure heat capacity into the expressions derived for each equation of state. Machine calculations were performed at various temperatures from 297° to 146°K. for the two gas mixtures at all pressures of interest. Calculations were based on the actual composition corresponding to the experimental run.

The five constants for the Beattie-Bridgeman equation were combined according to the procedure suggested by Beattie and Stockmayer (*3*). The Benedict-Webb-Rubin equation was written in the modified form as suggested by Lin and Naphtali (*13*):

$$P = RT/V + B_0RT/V^2 - A_0/V^2 - C_0/T\beta V^2 + bRT/V^3 - a/V^3 + a\alpha/V^6 + \{c/V^3\, T^2 + c\gamma/V^5\, T^2\} \exp\,(-\gamma/V^2).$$

Instead of as originally suggested by Benedict-Webb-Rubin (*4 to 6*), the A_0, B_0, and γ were combined according to a quadratic relation. A_0 and γ mix geometrically to form interaction terms; B_0 mixes by the Lorentz rule. Benedict-Webb-Rubin suggested that C_0 should be mixed geometrically, however, since C_0 for helium is negative it was decided to obtain C_0 for the helium-bearing mixture by the Lorentz mixing rule. C_0 for the other mixture was obtained by the geometrical mixing rule. The constants a, b, c, and α combine in cubic fashion

$$K_{\text{mix}} = \Sigma_i\, \Sigma_j\, \Sigma_k\, x_i\, x_j\, x_k\, K_{ijk}$$

and all form interaction terms geometrically by

$$K_{ijk} = (K_i \cdot K_j \cdot K_k)^{1/3}$$

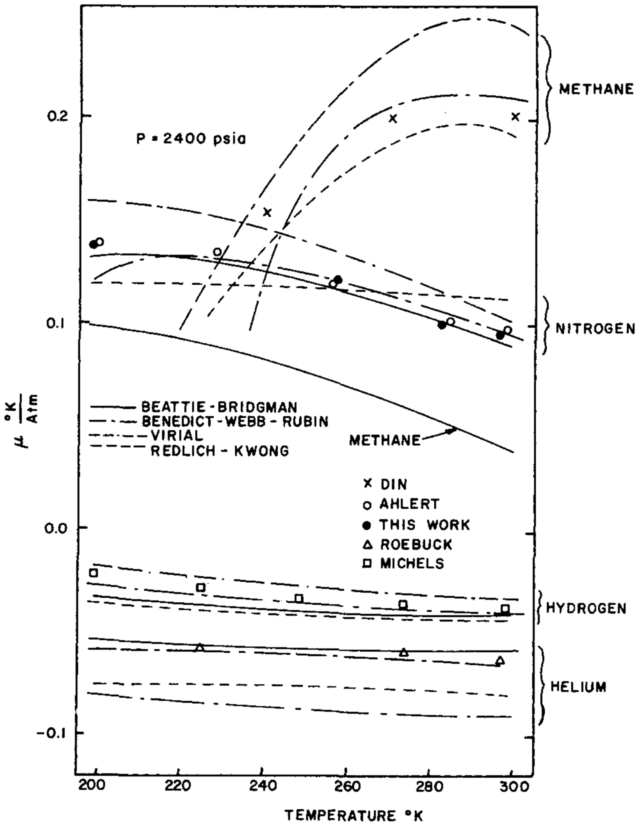

Fig. 5. Comparison of experimental Joule-Thomson coefficients for pure components with predictions from equations of state; 2,400 lb./sq. in. abs.

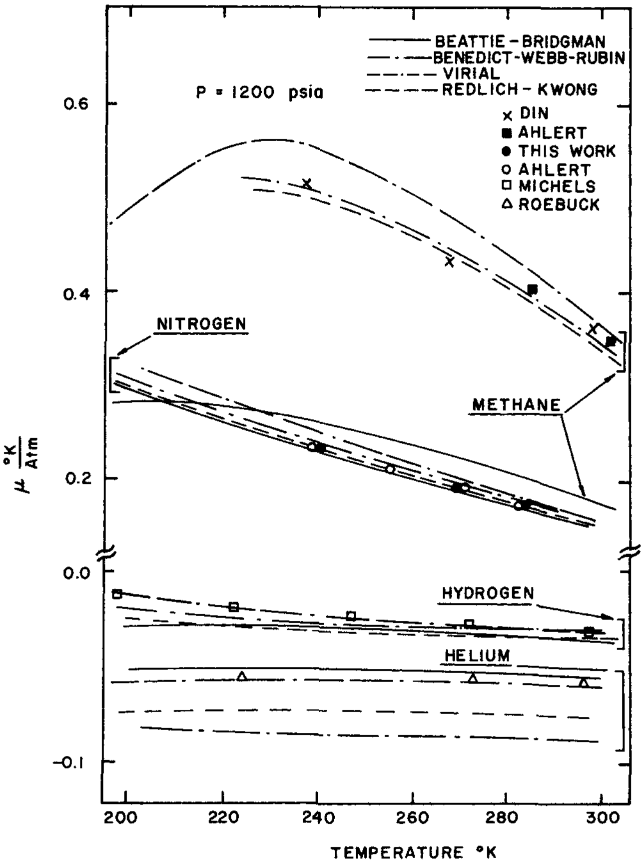

Fig. 6. Comparison of experimental Joule-Thomson coefficients for pure components with predictions from equations of state; 1,200 lb./sq. in. abs.

The β in the modified Benedict-Webb-Rubin equation was obtained using the arithmetic mean, geometric mean, and the Lorentz rule in an attempt to find out which mixing rule gives a better prediction. The results using the Lorentz and geometric rule were so close that it was decided to use only the geometrical mixing rule for the graphical illustrations in Figures 9 and 10.

The two constants of the Redlich-Kwong equation, a and b, were formed by quadratic mixing and the interaction terms were obtained by mixing a according to the Lorentz rule and b linearly.

Numerical values for Beattie-Bridgeman constants were taken from Rossini (*23*) and Hirschfelder et al. (*11*). Benedict-Webb-Rubin constants for methane and for nitrogen were taken from Benedict et al. (*4*) and from Hirschfelder et al. (*11*), respectively.

Only one set of constants for helium for the Benedict-Webb-Rubin equation appears in the literature. This set, by Lounasmaa (*14*), was used in the calculations. From this the modified Benedict-Webb-Rubin equation was solved explicitly for pressure for various values of β. The prediction of pressure, as compared to the data of Mann (*16*), seemed to be relatively independent of the value of β, although a value of $\beta = 2.4$ seemed to be optimal. Thus it was decided to try various mixing rules using $\beta = 2.4$ for helium. The geometric and the arithmetic mean mixing rules were also employed in calculations using the original Benedict-Webb-Rubin equation ($\beta = 2$).

Constants for hydrogen for the Benedict-Webb-Rubin

TABLE 6. CONSTANTS FOR THE EQUATIONS OF STATE OF MIXTURES

Equation of state	Constant	Method of combination	Rule of mixing	Numerical values Mixture *A*	Mixture *B*
Beattie-Bridgeman	A_0	Quadratic	Geometric	0.08617140	1.0939018
	B_0	Quadratic	Lorentz	0.03799561	0.041727196
	a	Quadratic	Linear	0.03518259	0.01338298
	b	Quadratic	Linear	−0.00745673	−0.02193200
	c	Quadratic	Geometric	34918.442	39148.335
Benedict-Webb-Rubin	A_0	Quadratic	Geometric	0.76759238	0.90246531
	B_0	Quadratic	Lorentz	0.03685027	0.03553521
	C_0	Quadratic	Lorentz—mixture *A*	3356.0207	
			Geometric—mixture *B*		6629.8607
	a	Cubic	Geometric	0.00519140	0.00456880
	b	Cubic	Geometric	0.00070226	0.00157864
	c	Cubic	Geometric	356.00998	525.25781
	α	Cubic	Geometric	0.00003235	0.00001873
	γ	Quadratic	Geometric	0.00404863	0.00658296
Redlich-Kwong	a	Quadratic	Lorentz	10.482424	13.109004
	b	Quadratic	Linear	0.02428624	0.025120898

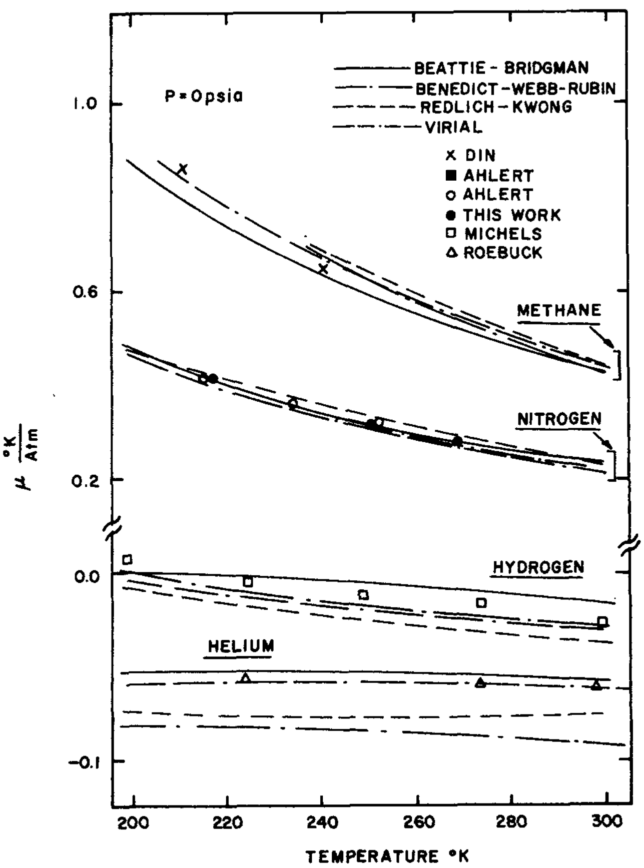

Fig. 7. Comparisons of experimental Joule-Thomson coefficients for pure components with predictions from equations of state; 0 lb./sq. in. abs.

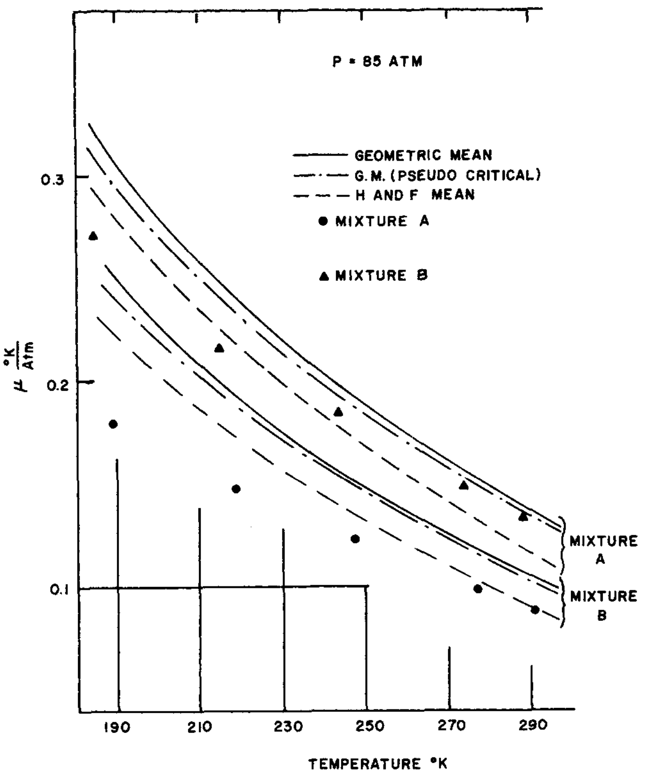

Fig. 8. Comparison of measured Joule-Thomson coefficients for mixtures *A* and *B* with predictions from the virial equation; 85 atm.

equation are reported only by Lin and Naphtali (*13*). They obtained these constants by fitting P-V-T data to their modified form of the equation. The value of β suggested by them for hydrogen is 1.803368. This value of β for hydrogen was mixed geometrically and linearly with $\beta = 2$ for nitrogen and for methane to determine whether any improvement in the predictions of the Joule-Thomson coefficients was possible.

The Redlich-Kwong constants for the pure components were calculated from critical properties from the relations

$$a = 0.4278\ R^2\ T_c^{2.5}/P_c$$

$$b = 0.0867\ R\ T_c/P_c$$

Methods of combination, mixing rules, and numerical values of the equation of state constants for experimental mixtures are presented in Table 6. Units employed in this table are degrees Kelvin, liters, atmospheres, and gram-moles.

PREDICTION RESULTS—PURE COMPONENTS

Measured Joule-Thomson coefficients for each of the pure components, as well as the predictions of the various equations of state, are given in Figures 5 through 7. Experimental values of the Joule-Thomson coefficients of nitrogen from this work and from that of Ahlert (*1*), Roebuck's data for helium (*21*) and Din's (*8*) and Ahlert's (*1*) data for methane are shown on these graphs, to allow the predicted Joule-Thomson coefficients to be compared with the experimental Joule-Thomson coefficients for the pure species. The deviations of the predicted Joule-Thomson coefficients from the experimental ones are summarized in Table 7.

Figures 5, 6, and 7, and their summary in Table 7, show that these several equations of state predict the Joule-Thomson coefficients for nitrogen, methane, and helium with average deviations in the range of 2 to 6%. There is little advantage to be gained from the added complexities of the Beattie-Bridgeman and Benedict-Webb-Rubin equations. With all the equations the Joule-Thomson coefficients for hydrogen are predicted poorly, but the large average deviations reflect the fact that the Joule-Thomson coefficients for hydrogen under the experimental conditions are

TABLE 7. COMPARISON OF PREDICTED JOULE-THOMSON COEFFICIENTS FROM THE VIRIAL AND EMPIRICAL EQUATIONS OF STATE WITH EXPERIMENTAL VALUES

Standard deviation, percent of experimental value

	Virial equation				Beattie-Bridgeman				Benedict-Webb-Rubin				Redlich-Kwong			
Gas	He	H_2	N_2	CH_4	He	H_2	N_2	CH_4	He	H_2	N_2	CH_4	He	H_2	N_2	CH_4
Pressure, lb./sq.in.abs.																
2,400	1.99	3.68	3.77	10.5	2.57	17.3	2.4	16.8	1.9	6.3	8.5	0.67	2.6	15.1	12.9	3.3
1,200	1.99	5.60	1.84	2.15	2.57	55.6	1.1	1.58	1.9	14.0	0.8	2.94	2.6	39.2	1.4	1.9
0	1.99	210.94	1.27	2.37	2.57	74.4	1.6	2.7	1.9	18.7	1.9	3.42	2.6	220.6	3.8	2.2
Overall average deviation	1.99	73.41	2.29	5.07	2.57	49.1	1.7	7.03	1.9	13.0	3.7	2.34	2.6	91.63	6.33	2.5

nearly zero. With hydrogen the Benedict-Webb-Rubin equation is significantly better than the others tested.

TABLE 8. COMPARISON OF JOULE-THOMSON COEFFICIENTS PREDICTED FROM THE VIRIAL EQUATION WITH EXPERIMENTAL VALUES
Standard deviation, percent of experimental value

Mixing rule	Geometric mean		H and F mean		G.M. (pseudocritical)		Lorentz	
Mixture	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Pressure								
165	8.38	6.05	9.87	8.70	7.03	4.33	6.94	4.96
135	10.70	10.95	11.69	12.59	9.46	8.69	9.00	10.10
105	10.44	9.73	10.87	10.53	9.96	7.96	9.40	9.34
85	9.48	7.75	9.69	8.23	7.77	5.17	8.73	7.55
55	7.69	5.17	7.82	5.49	4.59	3.11	7.15	5.09
25	6.12	2.69	6.41	3.24	3.16	1.77	5.52	2.51
0	4.54	1.26	5.07	1.67	2.74	1.29	3.92	1.33
Overall average deviation	8.19	6.23	8.77	7.21	6.39	4.62	7.24	5.84

PREDICTION RESULTS—TERNARY GAS MIXTURES

Virial Equation

The experimental Joule-Thomson coefficients (22) for the two ternary gas mixtures were compared with the predicted values based on the virial equation. The four approaches to mixing described earlier were used. The standard deviations for each of the four approaches to mixing are summarized in Table 8. Here the Leland et al. (12) correction to the minimum potential energy has been labeled as G.M. (pseudocritical). The overall average standard deviation for each mixing rule is also included in this table.

The overall average deviations for mixtures *A* and *B* predictions are, for all of the four mixture rules, consistent with the accuracy of prediction of pure species Joule-Thomson effects. The prediction methods are all more satisfactory at higher temperatures, and the data for mixture *A* are more satisfactorily represented than those for mixture *B*. That is, the hydrogen-containing system is easier to predict than is the helium-containing system. The Leland correction makes a slight improvement in the prediction capability where compared with the other mixing rules. This is especially noticeable at low pressure.

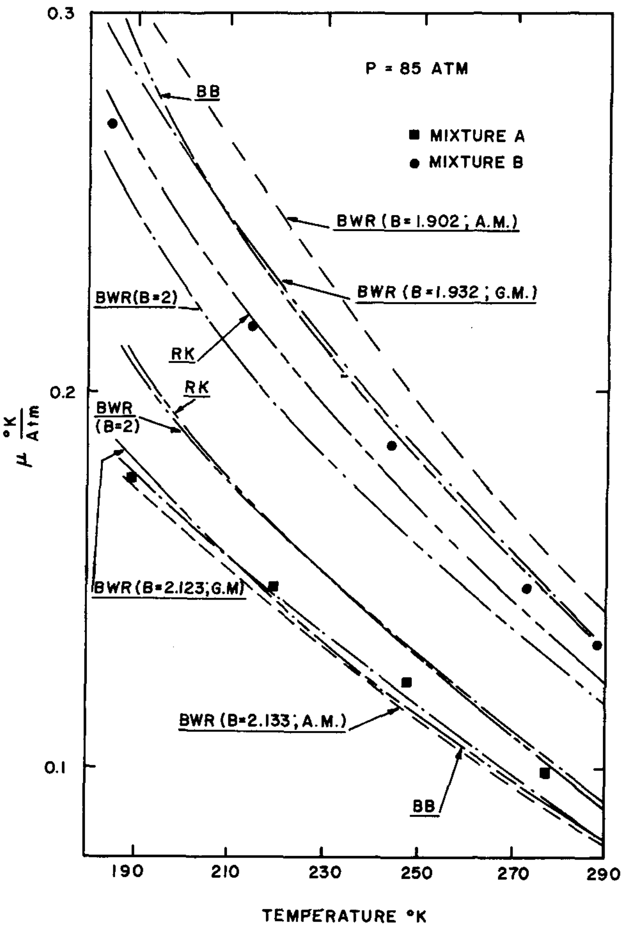

Fig. 9. Comparison of measured Joule-Thomson coefficients for mixtures *A* and *B* with predictions from three explicit equations of state; 85 atm.

Explicit Equations of State

Differences between experimental and predicted Joule-Thomson coefficients for mixtures *A* and *B* were calculated at the temperatures of the experimental data. The average standard deviations are shown in Table 9 and the graphical illustrations in Figures 9 and 10. For mixture *A* the overall average standard deviations for the Beattie-Bridgeman, the Benedict-Webb-Rubin ($\beta = 2$), and the two modified forms of the Benedict-Webb-Rubin equation are 5.13, 6.39, 4.00, and 3.84%, respectively. The Redlich-Kwong equation has an overall average standard deviation which is about 42% larger than those of the other two equations. This is probably due to its predictions at zero atmosphere which yield a standard deviation of 14.57% compared to deviations of 6.9, 4.24, 4.08, and 4.43 for the Benedict-Webb-Rubin, Benedict-Webb-Rubin (G.M.), Benedict-Webb-Rubin (A.M.), and Beattie-Bridgeman equations, respectively. In the pressure range from 0 to 85 atm., the

TABLE 9. COMPARISON OF PREDICTED JOULE-THOMSON COEFFICIENTS FROM EMPIRICAL EQUATIONS OF STATE WITH EXPERIMENTAL VALUES
Standard deviation, percent of experimental value

Equation of state	Beattie-Bridgeman		Benedict-Webb-Rubin ($\beta = 2$)		Benedict-Webb-Rubin ($\beta =$ G.M.)		Benedict-Webb-Rubin ($\beta =$ A.M.)		Redlich-Kwong	
Mixture	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Pressure, atm.										
165	5.07	7.81	6.94	6.99	4.82	7.86	4.68	7.76	3.76	2.48
135	5.67	11.57	7.22	7.59	4.66	8.97	4.49	9.21	5.66	5.23
105	5.47	9.71	6.49	5.00	4.05	6.33	3.88	6.72	6.48	5.36
85	5.21	7.59	5.90	3.69	3.57	5.09	3.42	5.66	6.54	4.63
55	5.00	3.76	5.38	3.27	3.11	5.01	2.97	5.91	6.38	3.87
25	5.05	2.45	5.90	4.05	3.52	6.64	3.37	8.04	6.41	3.12
0	4.43	2.20	6.90	7.10	4.24	10.89	4.08	12.96	14.57	9.68
Overall average deviation	5.13	6.44	6.39	5.38	4.00	7.26	3.84	8.04	7.11	4.91

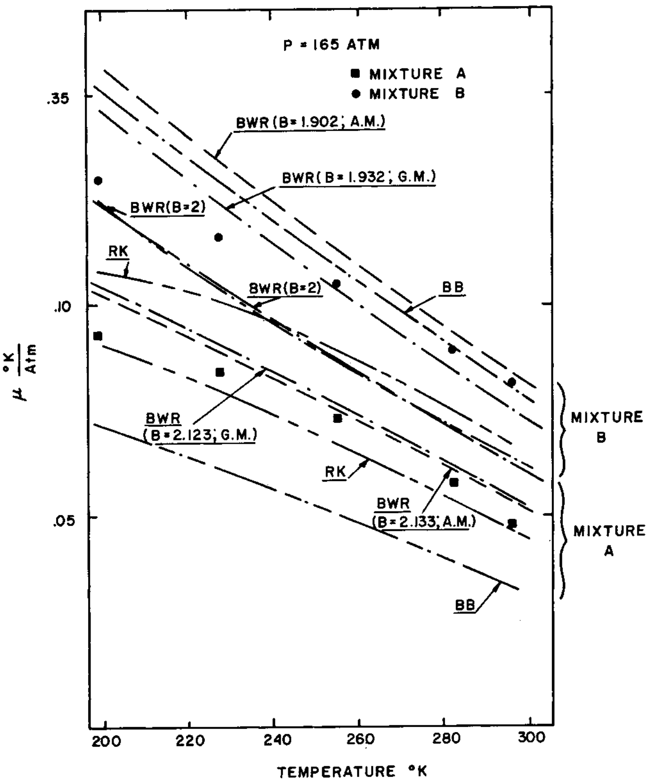

Fig. 10. Comparisons of measured Joule-Thomson coefficients for mixtures *A* and *B* with predictions from three explicit equations of state; 165 atm.

Beattie-Bridgeman equation provides a better correlation of the experimental data. At pressures above 105 atm., the two modifications of the Benedict-Webb-Rubin equation, that is, use of the geometric mean and arithmetic mean, show significant improvement over the other equations. Individual deviations for the two lowest temperature runs are considerably larger than those for the higher temperature runs, thus resulting in a higher overall average deviation. Deviations for the runs at the lower temperatures may be due to quantum effects. For the runs at 296°, 283°, and 255°K. the Beattie-Bridgeman is the best equation at pressures below 85 atm. Above this pressure the Redlich-Kwong and the two modifications of the Benedict-Webb-Rubin equation provide better predictions of the Joule-Thomson coefficient.

The standard deviation for mixture *A* over the entire pressure range is lowest for the Benedict-Webb-Rubin equation (A.M.) at 3.84% and highest for the Redlich-Kwong equation at 7.11%. For mixture *B*, for the first three higher temperature runs, the Beattie-Bridgeman equation is definitely superior to the other equations, although the overall average standard deviations of the Benedict-Webb-Rubin (original) and Redlich-Kwong equations are lower than that for the Beattie-Bridgeman equation. The Benedict-Webb-Rubin (G.M.) equation also predicts the Joule-Thomson coefficients of these runs very well; however, it is slightly inferior to the Beattie-Bridgeman equation. Below pressures of 55 atm. the Redlich-Kwong and Beattie-Bridgeman equations provide excellent correlation over the entire temperature range. From 55 to 165 atm. the Beattie-Bridgeman equation is a better equation for runs at 296°, 283°, and 255°K., while the Redlich-Kwong equation provides a better correlation for the two lowest temperature runs.

It thus appears that as the inlet temperature decreases none of the three equations of state and their modifications provide a correlation for the experimental Joule-Thomson coefficients of mixture *A*. At higher temperatures the Beattie-Bridgeman equation does provide excellent correlation of the experimental Joule-Thomson coefficients over the entire pressure range, while the Redlich-Kwong equation provides superior correlation for runs at 227° and 199°K. over the entire pressure range.

The overall average deviations of the two mixtures are consistent with the accuracy of predictions for the pure species. At lower temperatures where quantum effects may become significant, none of the equations of state that have been tried in this investigation provide a satisfactory correlation of experimental Joule-Thomson coefficients. It is worth mentioning that in spite of the fact that the Redlich-Kwong equation has only two constants, the overall average standard deviations for mixture *B* for the high temperature runs are lower than the corresponding deviations for the Beattie-Bridgeman equation. For mixture *A* at all pressures except 0 atm. it predicts the Joule-Thomson coefficients to the same degree of accuracy as predicted by the other equations of state that have a higher number of arbitrary constants.

According to Ahlert (*1*), the two-constant Van der Waals equation was the worst as far as predictions of Joule-Thomson coefficients are concerned. Based on the predictions of Joule-Thomson coefficients by the Redlich-Kwong equation for this investigation, and on Ahlert's discussion, the Redlich-Kwong equation does show merit.

No significant improvement was obtained by modifying the Benedict-Webb-Rubin equation for mixture A, that is, by altering the value of β. Since the constants for the pure components helium, nitrogen, and methane were originally obtained by fitting P-V-T data to the Benedict-Webb-Rubin equation with $\beta = 2$, it appears that these constants, along with a $\beta = 2.4$ for helium, do not influence the Joule-Thomson coefficients.

CONCLUSIONS

An accurate body of data for two ternary gas mixtures has been assembled. Pressures and temperatures investigated included the range from 0 to 165 atm. and from 199° to 297°K. The maximum uncertainty in any temperature measurement reported is 0.3°K.; the average uncertainty is about 0.04°K.

Reproducibility of the data was tested by making measurements of the Joule-Thomson coefficients of pure nitrogen. Good agreement of these measurements with literature values indicates that the experimental apparatus is free of significant sensible errors. The average value of the Joule-Thomson coefficient was within 1.5% of recent literature values.

Joule-Thomson coefficients calculated from experimental data were compared with Joule-Thomson coefficients predicted from various equations of state. Those chosen were the Beattie-Bridgeman, Benedict-Webb-Rubin, and Redlich-Kwong equations. Modifications of the Benedict-Webb-Rubin equation were also tried by altering the exponent of T in the C_0/T^2 term. No significant improvement was attained, although the Benedict-Webb-Rubin (G.M.) and the Benedict-Webb-Rubin (A.M.) seemed to be better than the original equation. The Benedict-Webb-Rubin equation and its modifications, as well as the Beattie-Bridgeman equation, describe mixture *A* to the same degree of accuracy. The overall average deviation of the above equations is approximately in the same order of magnitude. The overall deviation of the Redlich-Kwong equation for mixture *A* is about 42% higher than the deviations of the other equations. The data for the mixture containing hydrogen seemed to be more readily predicted than data for the mixture containing helium.

At low temperatures none of the equations of state predict Joule-Thomson coefficients for mixture *A* adequately, although the Redlich-Kwong equation does provide a reasonable correlation for mixture *B*. At higher temperatures for mixture *B*, the Beattie-Bridgeman equation provides excellent correlation of the Joule-Thomson data over the entire pressure range. For mixture *A* the Beattie-Bridgeman equation provides a fair correlation below 55 atm. Above this pressure the Redlich-Kwong and the Benedict-Webb-Rubin (G.M.) equations are reasonably good for predicting Joule-Thomson coefficients.

Joule-Thomson coefficients were also predicted with the virial equation of state. Four approaches to mixing the pure component constants, namely, the geometric mean, Halsey and Fender mean, geometric mean (pseudocritical), and the Lorentz rule, were tried. The Halsey and Fender mean predicts the data for mixture *A* reasonably well over the entire pressure range at high temperatures, whereas the geometric mean (pseudocritical) provides a reasonable prediction for mixture *B*. At low temperatures and high pressures the deviations are significant. Below 55 atm. even the lowest temperature runs, at 227° and 199°K., are well predicted by the Halsey and Fender mean for mixture *A* and the G.M. (pseudocritical) for mixture *B*. The predictions for the two mixtures are as accurate as the prediction for the pure species.

In summary, predicted Joule-Thomson coefficients for ternary mixtures studied are as accurate as predictions for the pure species. Standard mixing rules and methods of combining equation of state constants are satisfactory at higher temperatures. In general, at higher temperatures the known equations of state provide a reasonable correlation. The deviations between predictions and experimental Joule-Thomson coefficients arise from the fact that the pure species is not predicted with high accuracy.

At low temperatures the predictions from the equations of state are poor due to the inappropriateness of the equations of state, to inadequate mixing rules, or possibly to quantum effects. Deviations are greater for mixture *A* than for mixture *B*.

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NOTATION

A_0, B_0 = Beattie-Bridgeman, Benedict-Webb-Rubin constants
a, b, c = Beattie-Bridgeman, Benedict-Webb-Rubin, and Redlich-Kwong constants
$B(T), C(T)$ = second and third virial coefficients
$B'(T), B''(T), C'(T), B''(T)$ = first and second derivatives of the second and third virial coefficients with respect to temperature
B^*, C^* = reduced second and third virial coefficients
B'^*, B''^*, C'^*, C''^* = reduced first and second derivative of the second and third virial coefficients
C_0 = Benedict-Webb-Rubin constant
c_p = heat capacity at constant pressure per mole
K = equation of state or interaction constant
$\tilde{N}$ = Avogadros number
P = pressure
R = gas constant, 1.987 cal./(g.-mole) (°K.)
T = temperature
V = molar volume
x = mole fraction

Greek Letters

α, γ = Benedict-Webb-Rubin constants
β = exponent in the Benedict-Webb-Rubin equation
Δ = finite difference
ϵ = potential energy of interaction
μ = Joule-Thomson coefficient
σ = intermolecular separation at zero potential energy
ξ = Leland correction factor to the minimum potential energy of interaction
ϕ = Leland's quantum corrector factor to critical volume

Subscripts

c = critical property of pure species
mix = mixture

Superscripts

0 = zero pressure state
$*$ = reduced state

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