Table I. Solubility Products of Thallium(I) Thiocyanate at Various Temperatures

°C	40.0	36.0	30.0	25.0	21.0	15.0	10.0
$K \times 10^4$	6.76	4.84	2.89	1.82	1.32	0.72	0.46

volume of doubly distilled water in a hard glass cell (12 cm long, 3.5 cm in diameter), with continuous agitation by means of a glass-covered magnetic stirrer. To prevent condensation on the walls, the entire inner space of the closed cell was below the water level in the thermostat, whose temperature was controlled to ±0.1°C. Saturation was generally achieved within 24 hr, this being checked by continuing the analyses over longer periods.

Thiocyanate activities were measured by means of a thiocyanate specific-ion electrode (Orion Research Inc., Model 94-58) and a double-junction reference electrode (Model 90-02), connected to an Orion Model 407 specific-ion meter. Before use, the electrodes were first brought to the thermostat temperature while immersed in distilled water and in the outer-chamber filling solution, respectively; they were then quickly blotted dry and inserted in the test solution. A steady meter response was usually obtained within 5 min, and the thiocyanate activity could be measured to within $\pm 1 \times 10^{-4} M$.

The thiocyanate solutions used for calibrating the specific-ion meter were prepared from reagent-grade sodium thiocyanate and standardized by titration against silver nitrate with fluorescein as indicator (*7*). The mean ionic activities of these standard solutions were calculated at each temperature by use of the Güntelberg form (*3*) of the Debye-Hückel equation.

Results and Discussion

The solubility products $[K = (a_{Tl^+})(a_{SCN^-})]$ were calculated by assuming that the activity of the thallium ion (a_{Tl^+}) is equal to that of the thiocyanate (a_{SCN^-}). The results at various temperatures are presented in Table I.

A plot of log K against the reciprocal of the absolute temperature (T) was rectilinear, giving a correlation coefficient of 0.98, and the four points obtained from data of previous workers were scattered on either side (Figure 1). A least-squares analysis of the present results gives the expression:

$$\log_{10} K = (-3460/T) + 7.879$$

from which the heat of solution of TlSCN is 66.25 ± 0.34 kJ mol^{-1}.

Literature Cited

(1) Fedorov, V. A., Isaev, I. D., Robov, A. M., Vertiprakhov, A. V., Mironov, V. E., *Russ. J. Inorg. Chem.*, **17** (4), 495 (1972).

(2) Golub, A. M., Skorobogatko, E. P., *Ukr. Khim. Zh.*, **27**, 16 (1961).

(3) Güntelberg, E., *Z. Phys. Chem.*, **123**, 199 (1926).

(4) Oleszkiewicz, J., Lipiec, T., *Rocz. Chem.*, **40**, 541 (1966).

(5) Sundaram, A. K., Sundaresan, M., Vartak, D. G., *Proc. Indian Acad. Sci.*, **44A**, 139 (1956).

(6) Suzuki, S., *J. Chem. Soc. Jpn., Pure Chem. Sect.*, **73**, 153 (1952).

(7) Vogel, A. I., "A Textbook of Quantitative Inorganic Analysis," 3rd ed., p 263, Longmans, London, England, 1962.

Received for review November 18, 1974. Accepted April 23, 1975.

Enthalpies to 100 bar for Nitrogen–Methane Mixtures in Range 247.5–366.7K

Richard A. Dawe[1] and Peter N. Snowdon

Chemical Engineering Department, Leeds University, Leeds LS2 9JT, U.K.

The enthalpy-pressure behavior up to 100 bar for three nitrogen–methane gaseous mixtures with 90, 50, and 25 mol % methane content is determined from measurements of the Joule-Thomson effect along five isotherms at 247.50, 273.15, 298.15, 333.25, and 366.70K. Data for pure nitrogen at 247.50K are also reported. The Joule-Thomson effect, when expansion takes place to atmospheric pressure, and derived enthalpies are represented as functions of pressure. The precision of the enthalpies is believed to be 5 J mol^{-1}. Values of the heat of mixing for these mixtures over the range of conditions are calculated and compared with the results of other workers.

Enthalpy values of a fluid or fluid mixture as a function of temperature and pressure are needed in determining energy and heat transfer effects in much process equipment, as well as for the testing of fluid theories.

Because of the inadequacies of existing predictive methods based on equations of state and mixing rules, it is preferable if enthalpies can be experimentally determined over the range of conditions involved.

There have been very few direct measurements of the high-pressure enthalpies of industrially important mixtures because most of the calorimeters are complicated, slow to reach a thermal steady state, and use large quantities of materials, which can be very costly. Some heat of mixing data have been published, but to be really useful, these require an accurate knowledge of the pure component enthalpies, which are not always available. The method of Joule-Thomson throttling (an isenthalpic process) can be used to determine high-pressure enthalpies.

The Joule-Thomson effect is the overall temperature change in a fluid undergoing an isenthalpic expansion between fixed pressures. It is a measure of the nonideality of the fluid and can be used to obtain its thermodynamic quantities at high pressure. The virtues of determining enthalpies of gases above atmospheric pressure using an adiabatic Joule-Thomson expansion method are that, in theory, only the intensive variables, temperature and pressure, need be measured and that mixture enthalpies can be obtained as readily

---

[1] Present address, Petroleum Engineering Section, Department of Mining, Imperial College, Prince Consort Rd., London SW7 2AZ, England. To whom correspondence should be addressed.

as for pure gases. There is no need for the accurate measurement of flow rate or for energy input as in isothermal Joule-Thomson methods. A fuller discussion of the advantages of the adiabatic technique has appeared elsewhere (*1*, *2*). If the expansion is to atmospheric pressure, the enthalpies can be obtained using only measurements of the temperature and pressure, the compositions, and a knowledge of the atmospheric enthalpies. If the latter have not been measured directly, they can usually be predicted with reasonable accuracy from ideal gas values and the use over the pressure range zero to one atmosphere of, for example, the virial equation of state.

This paper reports the determination of the enthalpy using measurements of the Joule-Thomson effect of three methane–nitrogen gaseous mixtures with 90, 50, and 25 mol % methane content over five isotherms covering the range 247.5–366.7K and 1–100 bar. From these data and the enthalpies of the pure compounds reported previously (*3*, *4*) (except for nitrogen at 247.50K presented here), the heats of mixing for these mixtures over the range of conditions have been calculated.

Experimental

The expansion was carried out in a packed bed contained in a small bore tube, itself enclosed within an evacuated chamber. To cover the range of inlet pressure, 1–100 bar, without exceeding the desired flow rates (1–7 l. min^{-1}), three expansion units had to be used. Each unit was identical except for the size of powder used to pack the tube. The apparatus and experimental procedure have been fully described previously (*1–3*) and have been summarized in this journal recently (*4*).

The gaseous mixtures were contained at high pressure in 10 m^3 cylinders, regulated to the desired inlet pressure, and brought to the required inlet temperature by passing through a conditioning coil immersed in the thermostat housing the expansion units. An isenthalpic expansion to atmospheric pressure took place. The inlet and outlet temperatures were measured by calibrated precision platinum resistance thermometers and the pressures by calibrated Bourdon tube gauges.

The three gaseous mixtures used in this work were supplied by Gas and Equipment Ltd., Edgmond, Salop, U.K., and produced by L'Air Liquide, Paris, France. They were prepared by the L'Air Liquide low-pressure bath technique with a guaranteed preparation accuracy for these particular gas mixtures of ±0.2% absolute. Subsequent check analysis by L'Air Liquide confirmed the preparation accuracy ±1.0% relative, therefore enabling one of the mixtures (mixture 2) to be guaranteed to be accurate to ±0.1% absolute. The mixtures were analyzed in this laboratory by gas chromatography which confirmed the check analyses and preparation guarantee of L'Air Liquide. The pure compounds, mixtures 1 and 5, were also analyzed, and no significant impurities could be found. The mixtures used had the following compositions, measured in % volumes (which at the gas chromatograph pressure can be taken to be the % mole fractions without loss of accuracy).

Mixture	CH_4	N_2	Guarantee of accuracy
1	99.95	. . .	. . .
2	90.00 ± 0.10	10.00 ± 0.10	By analysis
3	50.00 ± 0.20	50.00 ± 0.20	From preparation
4	25.00 ± 0.20	75.00 ± 0.20	From preparation
5	. . .	99.9	. . .

The gases were used direct from high-pressure cylinders.

Joule-Thomson Throttling Results

The inlet and outlet temperatures, T_1 and T_2, respectively, the inlet pressure, p, atmospheric pressure, p_A, and the flow rate of the outlet gas were measured along five inlet isotherms, usually up to a pressure of 100 bar. Typical results are similar to those already described for nitrogen (*2*, *3*) and for methane (*4*) where sample data are given.

The Joule-Thomson effect $\Delta T (= T_1 - T_2)$, after minor corrections for heat leaks owing to radiation and kinetic energy effects and for the inlet temperature value not being exactly at the prescribed isotherm, was correlated as a polynomial function of inlet pressure by the method of least squares. Ex-

Table I. Regression Coefficients for Joule-Thomson Effect, $\Delta T (= T_1 - T_2)$ for Mixtures When Expanded from T and p to Atmospheric Pressure (1.0132 bar)[a]

T, K	No. of points	Mean dev T, K	$p_{\max}$	a	b	10^4c	10^6d	10^8e
				Mixture 2, $y_{CH_4} = 0.90$				
366.70	12	0.02_5	100	−0.25987	0.25698	0.23422	−0.89658	. . .
333.25	12	0.01_4	100	−0.32567	0.32019	1.93464	−1.82726	. . .
298.15	13	0.01_8	100	−0.41258	0.40710	4.94318	−2.96940	. . .
273.15	13	0.03_0	100	−0.49994	0.49279	3.98669	5.50786	−5.39704
247.50	11	0.02_3	85	−0.60133	0.59205	10.62017	8.04335	−7.52676
				Mixture 3, $y_{CH_4} = 0.50$				
366.70	12	0.02_2	100	−0.19848	0.19825	−2.62260	2.23876	−1.37454
333.25	13	0.01_6	100	−0.24943	0.24488	−0.19700	−1.22033	. . .
298.15	13	0.02_2	100	−0.32064	0.31386	0.56203	−1.74072	. . .
273.15	13	0.02_5	100	−0.38191	0.37612	1.91531	−2.43765	. . .
247.50	12	0.04_2	85	−0.46934	0.46011	−0.58451	11.18038	−11.56511
				Mixture 4, $y_{CH_4} = 0.25$				
366.70	12	0.01_4	100	−0.15869	0.15900	−1.04225	−0.53953	. . .
333.25	13	0.01_5	100	−0.20715	0.20345	−1.39969	−0.51976	. . .
298.15	13	0.01_5	100	−0.26559	0.26041	−0.58908	−1.34679	. . .
273.15	13	0.01_5	100	−0.31810	0.31247	0.17311	−1.98153	. . .
247.50	13	0.01_9	100	−0.39027	0.38410	−0.67148	0.68798	−1.72261
				Mixture 5, $y_{N_2} = 1.00$				
247.50	13	0.01_7	100	−0.31886	0.31381	−0.76290	−1.67242	. . .

[a] $\Delta T/\text{K} = a + b(p/\text{bar}) + c(p/\text{bar})^2 + d(p/\text{bar})^3 + e(p/\text{bar})^4$. $p_{\max}$ is the greatest pressure at inlet temperature T for which the expression is valid.

perimental precision could be examined, and interpolation at convenient pressures performed. The regression coefficients for the three mixtures at five isotherms and for nitrogen at 247.50K (not previously reported) are given in Table I. As can be seen, the mean deviation is always small, usually being less than 0.02K. The overall precision of the data is believed to be better than 0.05K as discussed fully previously (*2–4*). Full details of the method of analysis, including the incorporated corrections, have already been given (*2–4*). The complete experimental data have been fully tabulated and deposited with the National Engineering Laboratory, East Kilbride, Glasgow, Scotland, contract number NEL/123/23.

Mixture enthalpies. From the isenthalpic nature of the experiment,

$$H(p, T_1) = H(p_A, T_2) \qquad (1)$$

the values of the enthalpies at the high pressure p and temperature T_1 may be obtained from values of $\Delta T (= T_1 - T_2)$ of Table I and the enthalpy at atmospheric pressure for temperature T_2. The atmospheric enthalpies for the mixtures have been calculated from the pure components, assuming that the gases mix ideally at this pressure. Over the temperature range used in this work, this assumption will cause negligible error, since the maximum heat of mixing, that at 150K, is less than 2 J mol^{-1} for $y(CH_4)$ = 0.5 [calculated by the virial correlation of Zellner et al. (*10*)]. Thus,

$$H_m(p, T_1) = H_m(p_A, T_2) = y_{N_2}H_{N_2}(p_A, T_2) + y_{CH_4}(p_A, T_2) \qquad (2)$$

Table II. Atmospheric Enthalpies for Mixtures Relative to Ideal Gas at 273.15K in J mol^{-1} [a]

y_{CH_4}	$-a$	b	-10^3c	10^5d	-10^8e
1.00	9585.283	39.37112	33.45620	7.06880	2.35447
0.90	9433.990	38.45287	30.46130	6.40156	2.11902
0.50	8828.806	34.77990	18.48169	3.73260	1.17723
0.25	8450.567	32.48429	10.99444	2.06450	0.58862
0.00	8072.329	30.18868	3.50719	0.39640	...

[a] $\{H(p_A, T) - H(0, 273.15\text{K})\} = a + b(T/\text{K}) + c(T/\text{K})^2 + d(T/\text{K})^3 + e(T/\text{K})^4$. These equations are valid from 150 to 410K.

The enthalpies at atmospheric pressure of pure nitrogen and methane have been obtained as functions of temperature previously (*3, 4*). The values of the coefficients used in this work have been calculated by Equation 2 and are given in Table II. The equations are valid between 150 and 410K, and it is felt that they are as accurate as available data permit.

The enthalpy along the five isotherms at selected values of pressure have been calculated from Equation 1, using the values of ΔT and atmospheric enthalpy calculated from the coefficients in Tables I and II.

Further polynomials were then obtained by regression analysis which describe the enthalpy-pressure behavior. The values of these coefficients [including for completeness the appropriate values for methane given previously (*4*) and values for nitrogen calculated from the data given earlier (*2, 3*) except for the isotherm at 247.5K which was measured in this work since data near this temperature have not been previously reported] are given in Table III. No errors are introduced by using these polynomials since they reproduce the values determined from Equation 1 to within 0.08 J mol^{-1}. Values for the enthalpies for the mixtures and the pure compounds covering the range of pressure up to 100 bar are given in Table IV.

Table III. Regression Coefficients Describing Enthalpy of Mixtures at p and T_1 Relative to Ideal Gas at 273.15K [a]

T, K	p_{max}	a	b	10^3c	10^5d	10^7e
			Mixture 1, y_{CH_4} = 1.00			
366.70	100	3423.804	−10.52133	−2.01508	4.55388	...
333.25	100	2158.201	−12.64612	−5.90804	5.78349	...
298.15	100	882.409	−15.55255	−12.23194	−1.66683	6.46796
273.15	100	0.707	−18.14336	−27.34769	−0.81917	8.34008
247.50	85	−884.937	−21.74605	−35.81628	−39.46192	23.71775
			Mixture 2, y_{CH_4} = 0.90			
366.70	100	3353.848	−9.70891	0.75402	3.15794	...
333.25	100	2117.232	−11.64671	−4.74916	6.30942	...
298.15	100	866.675	−14.31157	−14.27294	9.99757	...
273.15	100	0.531	−16.95881	−11.09673	−17.75144	17.62918
247.50	85	−871.475	−20.04535	−33.05107	−25.70546	24.08761
			Mixture 3, y_{CH_4} = 0.50			
366.70	100	3074.177	−6.73294	9.36515	−7.60153	4.61644
333.25	100	1953.593	−8.12183	1.38338	3.89067	...
298.15	100	804.587	−10.19336	−0.87366	5.44617	...
273.15	100	−0.178	−12.07020	−5.04045	7.56145	...
247.50	85	−816.268	−14.62120	2.73485	−35.21733	36.30962
			Mixture 4, y_{CH_4} = 0.25			
366.70	100	2899.589	−5.02309	3.47917	1.65940	...
333.25	100	1851.743	−6.34114	4.60745	1.56285	...
298.15	100	766.127	−8.02436	2.13588	4.06755	...
273.15	100	−0.070	−9.56911	−0.17436	5.96821	...
247.50	100	−781.380	−11.70750	2.36552	−2.17430	5.22928
			Mixture 5, y_{CH_4} = 0.00			
366.70	100	2724.146	−3.64070	2.66854	1.53491	...
333.25	100	1750.019	−4.77367	4.42076	1.33173	...
298.15	100	728.136	−6.22271	4.80760	2.00630	...
273.15	100	0.658	−7.50303	4.00370	3.10230	...
247.50	100	−746.069	−9.15701	2.15866	4.88838	...

[a] $\{H(p, T_1) - H(0, 273.15\text{K})\}/\text{J mol}^{-1} = a + b(p/\text{bar}) + c(p/\text{bar})^2 + d(p/\text{bar})^3 + e(p/\text{bar})^4$. p_{max} is the greatest pressure for which each expression is valid.

Table IV. Selected Values of Enthalpies of Mixtures at p and T, Relative to Ideal Gas at 273.15K, in J mol^{-1}

T, K	p, bar	$y_{\mathrm{CH_4}} = 1.00$	$y_{\mathrm{CH_4}} = 0.90$	$y_{\mathrm{CH_4}} = 0.50$	$y_{\mathrm{CH_4}} = 0.25$	$y_{\mathrm{CH_4}} = 0.00$
366.70	1	3413	3344	3067	2895	2721
	50	2898	2874	2754	2659	2551
	80	2592	2598	2575	2529	2458
	100	2397	2422	2466	2449	2402
333.25	1	2145	2106	1945	1845	1745
	50	1518	1531	1556	1548	1524
	80	1138	1187	1333	1382	1403
	100	892	968	1194	1279	1330
298.15	1	867	852	794	758	721
	50	76	128	300	375	431
	80	−422	−318	11	158	271
	100	−747	−607	−169	25	173
273.15	1	−17	−16	−12	−9	−7
	50	−971	−886	−607	−472	−361
	80	−1596	−1446	−959	−736	−558
	100	−2012	−1808	−1182	−899	−679
247.50	1	−907	−891	−831	−793	−755
	50	−2096	−1973	−1562	−1360	−1192
	80	−2959	−2720	−2000	−1693	−1440
	100	...	...	...	−1898	−1591

Table V. Values of Heats of Mixing $H^E(p, T)$ at Pressure p and Temperature T for Three Mixtures, in J mol^{-1}

T, K	p, bar	Mixture 2, $y_{\mathrm{CH_4}} =$ 0.90	Mixture 3, $y_{\mathrm{CH_4}} =$ 0.50	Mixture 4, $y_{\mathrm{CH_4}} =$ 0.25
366.70	20	3	10	8
	40	8	23	17
	60	13	37	27
	80	19	50	37
	100	25	65	48
333.25	20	4	12	8
	40	9	27	20
	60	15	43	32
	80	23	62	45
	100	32	83	59
298.15	20	5	15	11
	40	12	34	25
	60	22	59	42
	80	34	87	61
	100	48	118	83
273.15	20	6	17	13
	40	17	43	31
	60	30	77	54
	80	46	118	81
	100	71	163	113
247.50	20	9	23	16
	40	22	59	41
	60	46	112	78
	80	87	199	127

The uncertainties in these enthalpies are due to experimental errors represented in the polynomials in Table I and to inaccuracies in the mixture compositions and in the atmospheric enthalpies of Table II. The experimental Joule-Thomson effect data, i.e., ΔT, are believed to be precise to 0.05K, which is equivalent to approximately 2 J mol^{-1} in the enthalpy. The uncertainties in the mixture preparation should cause a maximum error of less than 3 J mol^{-1} under the experimental conditions used in this work. Thus, the results are believed to be precise to 5 J mol^{-1}. However, the uncertainties in the absolute values of the atmospheric enthalpies cannot be estimated until further experimental measurements of the atmospheric heat capacities have been made. Should they be inaccurate, the enthalpy values calculated from the Joule-Thomson data of Table I can readily be revised.

Heats of mixing. The heat of mixing or excess enthalpy, $H^E(p, T)$ is defined by

$$H^E(p, T) = \{H_m(p, T) - \sum_i y_i H_i(p, T)\}_{p,T} \tag{3}$$

where $H_m(p, T)$ is the enthalpy of the mixture, H_i the enthalpy of the pure component i, and y_i the mole fraction of component i in the mixture. Because $H_i(p, T)$ for both methane and nitrogen have already been determined in this laboratory, values of $H^E(p, T)$ can be calculated with good accuracy from the experimental values of $H_m(p, T)$ reported here. For methane–nitrogen mixtures, Equation 3 becomes

$$H^E(p, T_1) = H_m(p, T_1) - y_{\mathrm{N_2}}H_{\mathrm{N_2}}(p, T_1) - y_{\mathrm{CH_4}}H_{\mathrm{CH_4}}(p, T_1) \tag{4}$$

Values of $H^E(p, T_1)$ are given in Table V at selected values of pressure.

To obtain an estimation of accuracy for these excess enthalpies, it is necessary to examine the experimental equations further. An inspection of Equation 4 shows that $H^E(p, T_1)$ is equivalent to measurements of isenthalpic expansion to atmospheric pressure for the mixture, pure nitrogen and methane all from the same initial conditions; so that by introducing the isenthalpic condition (Equation 1) for the three gases into Equation 4, it becomes

$$H^E(p, T_1) = H_m(p_A, T_{2_m}) - y_{\mathrm{N_2}}H_{\mathrm{N_2}}(p_A, T_{2_{\mathrm{N_2}}}) - y_{\mathrm{CH_4}}(p, T_{2_{\mathrm{CH_4}}}) \tag{5}$$

and substituting Equation 2 for $H_m(p_A, T_{2_m})$, on rearranging Equation 5, it becomes

$$H^E(p, T_1) = y_{\mathrm{N_2}}\{H_{\mathrm{N_2}}(p_A, T_{2_m}) - H_{\mathrm{N_2}}(p_A, T_{2_{\mathrm{N_2}}})\} + y_{\mathrm{CH_4}}\{H_{\mathrm{CH_4}}(p_A, T_{2_m}) - H_{\mathrm{CH_4}}(p_A, T_{2_{\mathrm{CH_4}}})\} \tag{6}$$

From Equation 6, it can be seen that the uncertainties in $H^E(p, T_1)$ determined by this method of Joule-Thomson expansion depend on errors in the mixture composition, temperature and pressure, and the values of the atmospheric enthalpies. As all the results have been taken on the same appara-

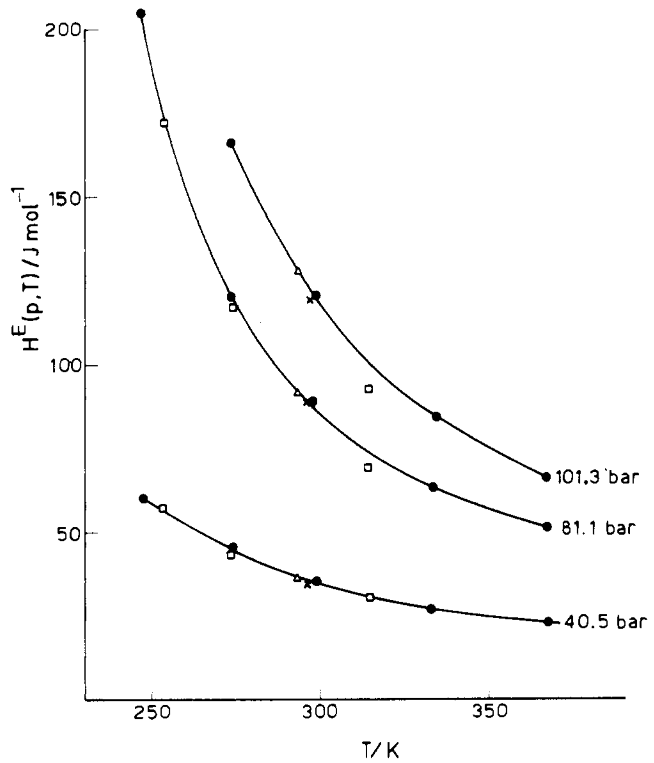

Figure 1. Comparison of heat of mixing data, $H^E(p, T)$ of this work and results in literature for mixture with $y(N_2) = y(CH_4) = 0.5$

● This work
× Lewis (*8*)
△ Van Eijnsbergen and Beenakker (*9*)
□ Klein et al. (*6*)
Values of Lewis and van Eijnsbergen and Beenakker have been interpolated for sake of this comparison

tus, any systematic errors in temperature and pressure should partially cancel. If there are no errors in the values of the atmospheric enthalpies, then the absolute errors caused by experimental errors in temperature or pressure to $H^E(p, T_1)$ of this work should not exceed 4 J mol^{-1}. Any errors in the atmospheric enthalpies could increase this value. [An earlier paper (*4*) gives fuller details about the effects of uncertainties in the atmospheric enthalpies on the high-pressure enthalpies.]

Direct experimental determination of $H^E(p, T)$ for gaseous mixtures by calorimetric methods have been made by a number of workers [Lewis (*8*), Klein et al. (*6*), van Eijnsbergen and Beenakker (*9*), Hejmadi et al. (*5*), and Lee and Mather (*7*)]. The first three groups of workers have made measurements on methane-nitrogen mixtures. Although the range of overlap of temperatures and mixture compositions are limited, a comparison of the various sets of data at three pressures is given in Figure 1. When necessary, the data have been interpolated, but as can be seen for the region of this work, 1-100 bar and 247.5-366.7K, the agreement is excellent, being within the claimed experimental error.

Acknowledgment

The authors thank G. G. Haselden for his interest.

Nomenclature

$H_i(p, T)$ = enthalpy at pressure p and temperature T for species i relative to the ideal gas state at 273.15K
H^E = heat of mixing
p = pressure
p_A = atmospheric pressure
T = temperature
y = mole fraction
$\Delta T = (T_1 - T_2)$, the Joule-Thomson effect

Subscripts

i = for any component of the mixture
m = for the mixture solution
1 = inlet temperature
2 = outlet temperatures on expansion to atmospheric pressure

Literature Cited

(1) Dawe, R. A., Snowdon, P. N., Proceedings of the Sixth ASME Symposium on Thermophysical Properties, P. E. Liley, Ed., p 213, New York, N.Y., 1973.
(2) Dawe, R. A., Snowdon, P. N., *J. Chem. Thermodyn.*, **6**, 65 (1974).
(3) Dawe, R. A., Snowdon, P. N., *ibid.*, p 293; **7**, 607 (1975).
(4) Dawe, R. A., Snowdon, P. N., *J. Chem. Eng. Data*, **19**, 220 (1974).
(5) Hejmadi, A. V., Katz, D. L., Powers, J. E., *J. Chem. Thermodyn.*, **3**, 483 (1971).
(6) Klein, R. R., Bennett, C. O., Dodge, B. F., *AIChE J.*, **17**, 958 (1971).
(7) Lee, J. I., Mather, A. E., *Can. J. Chem. Eng.*, **50**, 95 (1972).
(8) Lewis, K. L., PhD thesis, University of Bristol, Bristol, U.K., 1972.
(9) Van Eijnsbergen, B., Beenakker, J. J. M., *Physica*, **39**, 499 (1968).
(10) Zellner, M. G., Claitor, L. C., Prausnitz, J. M., *Ind. Eng. Chem., Fundam.*, **9**, 549 (1970).

Received for review May 17, 1974. Accepted April 7, 1975. Work carried out at the University of Leeds under an Extra-Departmental contract with the National Engineering Laboratory, Department of Industry. Paper published by permission of the Director of the National Engineering Laboratory.