f = evaluated at the average film temperature, $t_f^\circ = (t_s^\circ + t_g^\circ)/2$
g = evaluated at conditions of the gas in the reaction chamber
o = evaluated at the initial conditions
p = solid product
r = solid reactant
s = evaluated at the external surface of the pellet

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Experimental Heats of Mixing for Gaseous Nitrogen and Methane

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The excess enthalpy of binary gas phase mixtures has been measured by direct experiment, using a continuous flow, isothermal calorimeter. Heat of mixing data are presented for the methane-nitrogen system for compositions of 25 to 80 mole % methane in nitrogen, at temperatures of 40°, 0°, −20°, −40°, −60°, and −78°C. and pressures from 250 to 1,500 lb./sq. in. abs. These data are in agreement with the literature to within the experimental uncertainty of this work, 4%.

The experimental results agree well with values predicted using the Benedict-Webb-Rubin and the Redlich-Kwong equations of state. The virial equation of state truncated after the third coefficient fits the low density data only. The liquid theories of Scott predict the enthalpies of the mixtures in a qualitative way.

The heat of mixing or excess enthalpy is defined by the equation

$$H^E = H_m - \sum_i y_i H_i \quad (\text{constant } p \text{ and } T) \qquad (1)$$

It provides one means of obtaining the enthalpy of solutions whose practical importance for the design and analysis of heat exchange equipment is obvious. It is also of scientific importance since it provides a test of mixing rules for an equation of state and a test of theories of molecular interactions. Experimental data on the enthalpy of gas mixtures are quite limited and engineers have been obliged to calculate values needed for design by various approximate methods.

METHODS OF PREDICTING H_m

Before describing the experiments it seems appropriate to consider various ways by which H_m can be calculated. The differential equations relating H_m to the variables of state are well known and rigorous but their integration requires either an equation of state or the equivalent pressure-volume-temperature data. The application of equations of state to a mixture involves empirical mixing rules whose validity is uncertain, and in many cases there are no experimental data against which to test the methods. In the course of this work we have tested three equations of state: a modified Redlich-Kwong (R-K) equation, the Benedict-

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Webb-Rubin (B-W-R), and the virial equation truncated after the third coefficient. The results of these calculations will be compared with the experimental data in a later section.

The isothermal enthalpy difference function $H^\circ - H/Tc$ has been tabulated versus P_r, T_r, and Z_c by Lydersen, Greenkorn, and Hougen (L-G-H) (*20*) and as a function of P_r, T_r, and ω by Curl and Pitzer (*8**). These tabulations enable one to estimate the effect of pressure on the enthalpy of any pure substance whose critical properties are known if the L-G-H tables are used, or P_c, T_c, and the factor ω if the Curl and Pitzer tables are used. To obtain enthalpy over a temperature range one needs C_p or C_V at low pressure. To get the enthalpy of solutions one applies mixture rules, a number of which are available in the literature.

Brewer and Geist (*5*) compared four methods for calculating enthalpies of methane-nitrogen mixtures. One of two better methods was based on the virial equation of state truncated after the third coefficient. The other used the corresponding states tabulations of Curl and Pitzer, extended to mixtures by some empirical mixing rules for P_c, T_c, and ω. Edmister and co-workers (*8a*, *10*, *25*) calculated enthalpies of binary solutions of methane with various light hydrocarbons using the B-W-R and R-K equations of state and a corresponding states method based on pseudoreduced P and T and an average acentric factor. The R-K equation gave as good results as the B-W-R but the corresponding states method was better than either equation of state. Edmister and Canjar (*9*) generalized the partial molal enthalpy difference $\overline{H}_i - H_i^\circ$ in terms of reduced P, T, and a reduced normal boiling point. In principle these generalized values could be used to calculate the enthalpy of almost any mixture, but it remains to be demonstrated how well the method applies to other than aliphatic hydrocarbons.

Beenakker et al. (*2*, *24*) applied the liquid state theories of Prigogine and Scott to dense gas mixtures and obtained qualitative agreement with their experimental data. We have applied the one-, two-, and three-liquid models in the form developed by Scott (*23*) to our own data with the results to be presented below. Knoester and Beenakker (*18*) reported additional calculations of H^E based on the liquid theories of Scott (*23*) and compared them with the experimental data of Knoester, Taconis, and Beenakker (*19*). With the exception of the data for nitrogen-argon, where H^E is relatively small, the two-liquid model gave fairly reliable predictions.

EXPERIMENTAL METHODS FOR H_m

The five methods which have been used for this purpose will be briefly described. We restrict the discussion to the case of homogeneous systems (no phase change). Method 1 is a calorimetric one and consists of adding heat to the system, usually by converting electrical energy, at constant pressure and measuring the temperature rise. An example of this method is furnished by the work of Jones et al. (*15*) on the enthalpy of methane. A second method is to make adiabatic throttling (Joule-Thomson) expansions giving values of $(\Delta T/\Delta p)_H$ from which enthalpies can be derived by well-known methods. Numerous examples are found in the literature of such measurements on pure gases but very few have been made on mixtures. The third involves isothermal expansion with heat being added during or after the expansion to equalize the initial and final temperatures. Examples of this method are to be found in papers by Keyes and Collins (*16*), Gilliland and Lukes (*13*), and Yarborough and Edmister (*25*). Only the last mentioned deals with mixtures. The fourth method consists in measuring the PVT relations of the solution, and calculating $H^\circ - H$ from the exact thermodynamic relation for H as a function of P and T or T and V. This method was used by Bloomer et al. (*3*) to obtain the values for the two mixtures of methane-nitrogen presented in Bulletin 21 of the Institute of Gas Technology. A graphical method was used by Sage and co-workers on various mixtures of light hydrocarbons, and a typical case is that of methane-ethane studied by Sage and Lacey (*22*).

The fifth method and the one used in our work consists in a direct measurement of the heat of mixing. The gases are mixed at constant pressure in a calorimeter and the temperatures before and after mixing equalized by adding or subtracting heat, depending on whether the ΔH of mixing is positive or negative. Addition of heat can be conveniently and accurately controlled and measured by the use of electric energy converted to heat in a resistor, but the removal of heat is more difficult. In our work only positive ΔH's were measured.

SCOPE OF THE EXPERIMENTS

The system employed was methane-nitrogen and it was chosen for three main reasons: good enthalpy data are available for the pure components; both molecules are simple and nonpolar; and the system is of industrial importance. The gas phase was studied at six temperatures: 40°, 0°, −20°, −40°, −60° and −78°C. over a pressure range of 18 to 104 atm. and compositions ranging from 0.25 to 0.80 mole fraction of methane.

PREVIOUS WORK IN THE LITERATURE

When this research was started no work had been reported on the measurement of the heat of mixing of gases. During the course of our work the results of Beenakker and his co-workers appeared in the literature. Beenakker and Coremans (*1*) announced that the Kamerlingh Onnes Laboratory was starting work on direct measurement of H^E and presented a few preliminary results. They determined H^E at one composition around 50 mole % for the systems nitrogen-hydrogen, argon-hydrogen, argon-nitrogen, methane-hydrogen, and methane-argon as a function of pressure up to about 120 atm. at a few temperatures below 295°K. The results were presented as graphs of H^E versus p at constant T. At lower gas densities H^E was linear in p in accord with the relation

$$H^E = 2\, y_1 y_2 \left(E - T\,\frac{dE}{dT}\right) p \tag{2}$$

This equation is derived from the simplified virial equation of state

$$\frac{pv}{RT} = 1 + \frac{B_m}{v} \tag{3}$$

combined with

$$B_m = y_1^2 B_{11} + 2y_1 y_2 B_{12} + Y_2^2 B_{22} \tag{4}$$

E is defined by

$$E = B_{12} - \frac{1}{2}\,(B_{11} + B_{22}) \tag{5}$$

This equation, of course, assumes that collisions other than binary ones can be neglected.

To deal with the higher densities Beenakker and co-workers applied the theories of Prigogine (*21*) and Scott (*23*) developed for liquid solutions. They used the so-called "single-liquid" and "two-liquid" models and assumed the Lennard-Jones potential for molecular interactions with simple mixing rules to obtain the force constants for a mixture from those of the pure components. Surprisingly good qualitative agreement was obtained with their experimental values; the two-liquid model was the better prediction method.

Knoester et al. (*19*) measured H^E for hydrogen-nitrogen at five temperatures in the range 147° to 239°K., for hydrogen-argon at four temperatures in the range 169° to 293°K., and for nitrogen-argon in the range 169° to 293°K. In most cases the maximum pressure was 120 to 130 atm., and three mixtures of approximate mole fractions 0.25, 0.50, and 0.75 were investigated.

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*Curl and Pitzer used the function $H^\circ - H/RT_c$.

Van Eijnsbergen and Beenakker (*24*) determined H^E for three or four mixtures of the systems methane-argon, nitrogen-methane, and helium-methane at three temperatures in the range 200° to 293°K. and at pressures up to 120 atm., and at four temperatures from 170° to 293°K. for helium-argon. Their results are given in tabular form and in the form of graphs of H^E versus p at constant T and y.

The parabolic dependence of H^E on compositions as demanded by Equation (2) holds only at low densities. For higher densities they found that the polynominal equation

$$H^E = y_1 y_2 [a + b(y_1 - y_2) + c(y_1 - y_2)^2] \tag{6}$$

where a, b, and c are coefficients independent of y but functions of T and possibly p, gave a good approximation to their results at not too high a pressure.

EXPERIMENTAL METHOD

Figure 1 shows a flow diagram of the apparatus. The individual gases, stored in standard gas cylinders, flow at a steady rate through separate lines up to the calorimeter E where they are mixed. Constant flow is maintained by establishing a constant pressure drop across flow-control valves VA-2 and VB-2 through the setting of the pressure-regulating valves PRA and PRB and the back-pressure valve BPR. The latter establishes the operating pressure in the calorimeter, which is measured on PG-1. Constancy of flow is indicated by the rotameters RMA, RMB, and RMT. Total flow rate of mixed gas, which was varied over a range of 0.4 to 0.8 std. cu. ft./min., was measured by collecting a volume of about 12,000 ml. (0.424 cu. ft.) for a period of 0.5 to 1.0 min. in a water-sealed gasometer under known conditions of pressure, temperature, and humidity. For temperature control the calorimeter is immersed in a thermostat G consisting of a stainless steel Dewar flask. For temperatures above 0°C. the bath fluid was water, and below 0°C. it was a eutectic mixture of carbon tetrachloride and chloroform. The temperature could be controlled to about 0.01°C. at all temperature levels. When operating below ambient temperature, an excess of liquid nitrogen was added and compensated by addition of heat from the element B. The incoming pure gases are brought to bath temperature by heat exchangers C and F before entering the calorimeter.

A cross section of the calorimeter is shown in Figure 2 and the accompanying legend gives some of the details of construction. The gases are believed to be thoroughly mixed by passing through the narrow annuli between cylinders and by the abrupt changes in direction. Heat transfer to the mixed gases other than by the heater is made negligible by the insulating effect of cylinder P, and the polished cylinders M, N, and O act as radiation shields against transfer of heat from the heater to surrounding objects. In other words we believe that the design of the calorimeter ensures that the energy input to the heater all goes to the mixed gas and that any other transfer of heat to the gases is minimized. The temperatures of the gas streams before mixing and of the mixed gas before heating are measured by single-junction thermocouples of 24-gauge copper-constantan. The differential temperature between inlet unmixed gases and thoroughly mixed gases after heating is measured by a 20-junction (10 at each location) thermocouple also of 24-gauge copper-constantan. The electric power input required to keep the temperature of the mixed gas the same as that of the pure gases introduced into the calorimeter was determined by careful measurements of the voltage drop across calibrated resistances (*17*). Gas composition was measured by a chromatograph on a sample of mixed gases withdrawn as shown in Figure 1. The gases used 99.95% pure methane and 99.995% pure nitrogen.

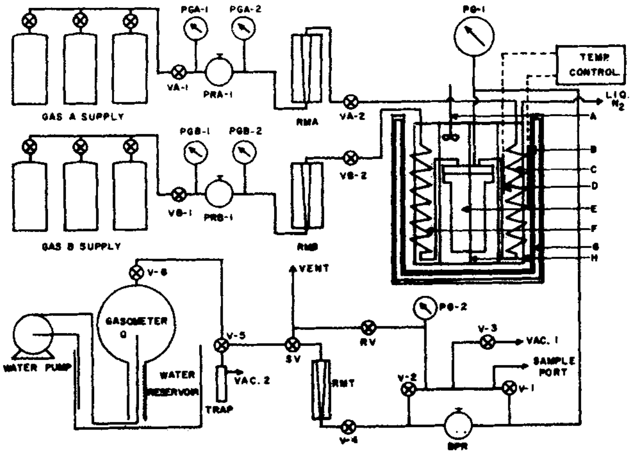

Fig. 1. Flow diagram of the heat of mixing apparatus. *A*, stirrer; *B*, heating element; *C*, *F*, heat exchangers for incoming unmixed gases; *D*, temperature controller; *E*, mixing calorimeter; *G*, constant temperature bath; *Q*, gasometer; *V1-V5*, *VA*, *VB*, *RV*, *SV*, valves; *PG*, pressure gauges; *BPR*, back-pressure regulator; *RM*, rotameters; *PR*, pressure regulators.

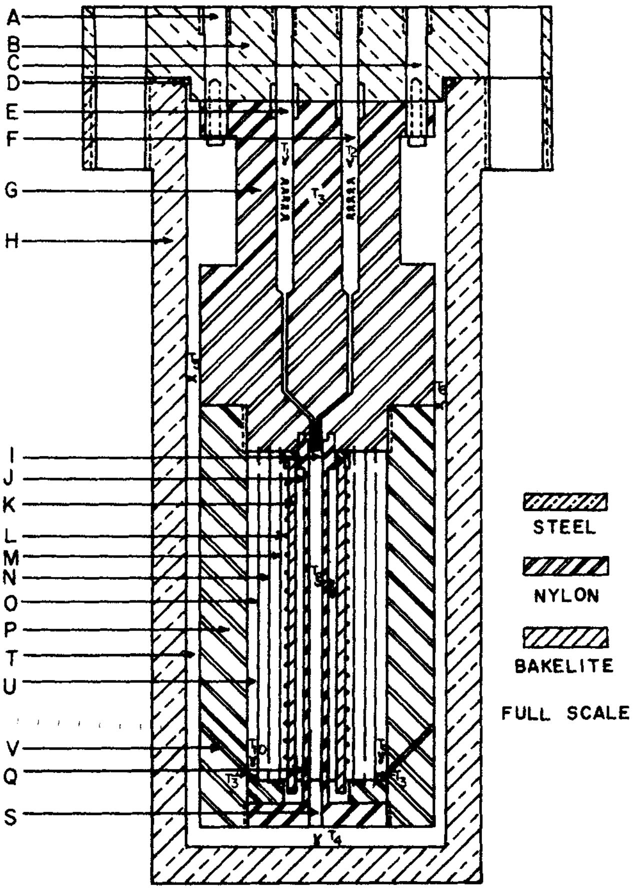

Fig. 2. Heat of mixing calorimeter. *A*, thermocouple and lead wire conduit; *B*, pressure vessel cover, stainless steel; *C*, mixture outlet port; *D*, Teflon-coated, stainless steel O-ring; *E*, *F*, gas entrance port; *G*, nylon insulating head; *H*, pressure vessel, stainless steel; *I*, mixing point; *J*, nylon cylinder; *K*, heater support rods; *L*, resistance wire heater, No. 28 Chromel A; *M*, *N*, *O*, stainless steel cylinders; *P*, nylon cylinder; *Q*, gas outlet ports; *S*, heater lead wire port; *T*, annulus between pressure vessel and nylon core; *U*, annulus containing thermocouples; *V*, gas outlet ports; T_1, T_2, entrance gas absolute thermocouple; T_3, differential thermopile; T_4, T_5, T_6, T_8, temperature profile thermocouples; T_9, T_{10}, mixture absolute thermocouples.

PROCEDURE

After setting the pressure and temperature controllers and adjusting flow rates about 3 hr. were normally required to establish steady operating conditions, and another hour was required to obtain a zero reading on the differential thermopile. In the majority of runs the flow rate was 0.50 std. cu. ft./min. This rate was established as the minimum desirable one by operating at a series of rates and finding the rate at which the value of H^E first became constant. At lower rates the value of H^E were higher, presumably owing to spurious heat transfer. The data taken were temperature and pressure of gases in the calorimeter, voltage and amperage of heater for mixed gases, gas compositions, volume of gas collected in the gasometer, its temperature, the time interval, and barometric pressure. The power input to the heater was corrected for losses. From the flow rate, converted to a molar basis, and the power input, the heat of mixing is obtained by dividing the one by the other.

EXPERIMENTAL RESULTS

The experimental values of the enthalpy of mixing are given by Klein (*17*) at the various temperatures, pressures, and compositions which were actually measured. The temperatures were set at the desired values of 40°, 0°, −20°, −40°, −60°, and −78°C., and these levels could be reproduced to 0.1°C., their estimated accuracy. However, it was not possible to set the values of the pressure and the composition so close to any desired levels, so that the individual effects of these variables are not readily ascertained from the raw data. It is desirable to report the data at even values of p and y, and the method of doing so is described in what follows. The results of the smoothing procedure are given in Table 1, and the values in this table are the basis for subsequent graphical presentations of the data (Figures 3 to 6).

The smoothing procedure depends on fitting an equation to the data by the method of least squares. The data will be represented by the equation

$$H^E = \sum_{m=0}^{M-1} a_m \, q_m (p, y) \tag{7}$$

where the a_m are constants and the $q_m(p, y)$ are functions having a form defined by the value of the index m. The q_m can be chosen simply as all possible powers of p and y, but it is preferable to choose the function so that the correlating equation is based on some theoretical form.

TABLE 1. SMOOTHED HEAT OF MIXING DATA FOR THE METHANE-NITROGEN SYSTEM

Pressure, atm.	y_{CH_4}	H^E (joules/g.-mole) 40°C.	0°C.	−20°C.	−40°C.	−60°C.	−78°C.
20	0.4	12.9	16.8	19.7	27.4	38.9	45
20	0.5	13.6	17.8	21.1	28.1	39.1	48
20	0.6	13.1	17.3	20.7	26.5	31.8	47
20	0.7	11.4	15.3	18.5	22.7	19.3	43
40	0.4	27.9	40.4	52.5	70.6	103.0	250
40	0.5	29.6	43.2	56.8	76.0	113.8	349
40	0.6	28.7	42.4	56.3	74.1	110.0	298
40	0.7	24.9	37.7	50.7	65.7	94.1	243
60	0.4	45.0	70.9	98.2	149.7	303.9	1,145
60	0.5	48.2	76.4	107.1	166.7	346.7	1,348
60	0.6	46.8	75.3	106.9	168.0	365.3	1,525
60	0.7	40.7	67.2	96.6	153.8	354.8	1,598
80	0.4	64.3	108.3	159.2	261.5	577.8	910
80	0.5	69.4	117.3	172.0	293.5	660.5	1,040
80	0.6	67.5	116.0	172.3	301.9	705.9	1,090
80	0.7	58.6	103.9	156.2	282.7	695.9	972
100	0.4	85.7	228.8	228.8	379.2	684.5	687
100	0.5	93.0	251.6	251.6	420.1	777.7	733
100	0.6	90.7	252.8	252.8	438.2	817.9	678
100	0.7	78.7	229.6	229.6	419.0	775.3	555

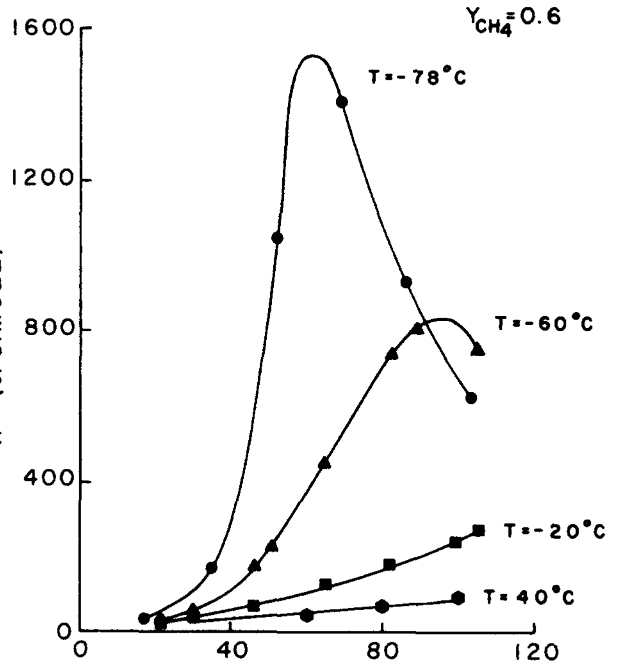

Fig. 3. Isotherms of H^E for the methane-nitrogen system versus pressure.

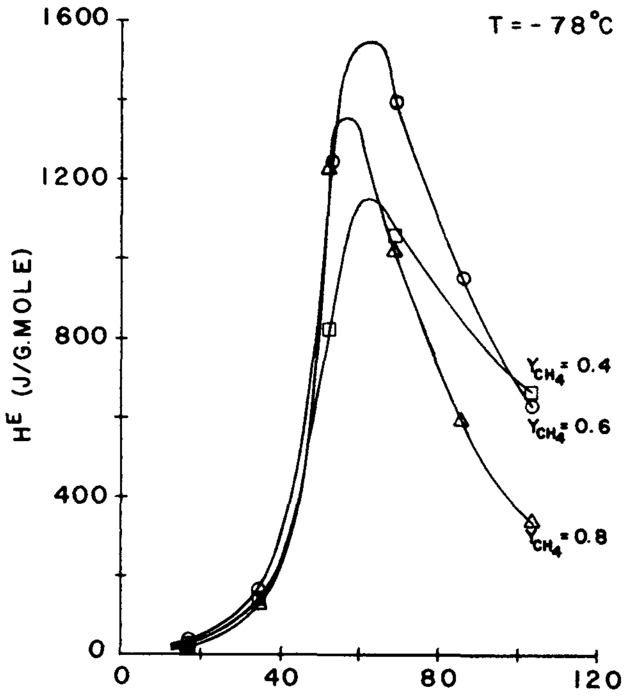

Fig. 4. Heat of mixing of methane-nitrogen versus pressure.

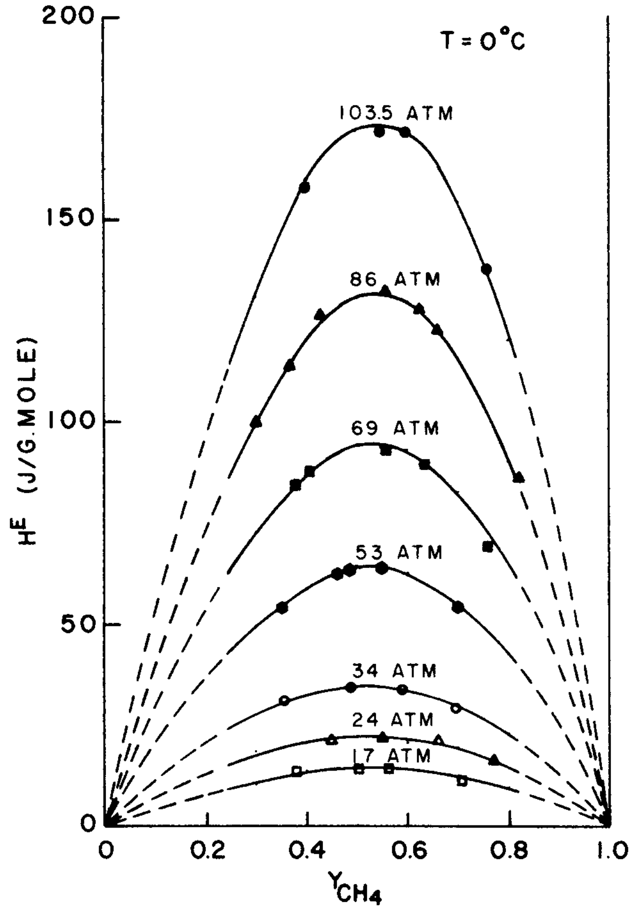

Fig. 5. Isobars of H^E versus Y_{CH_4} for the methane-nitrogen system at 0°C.

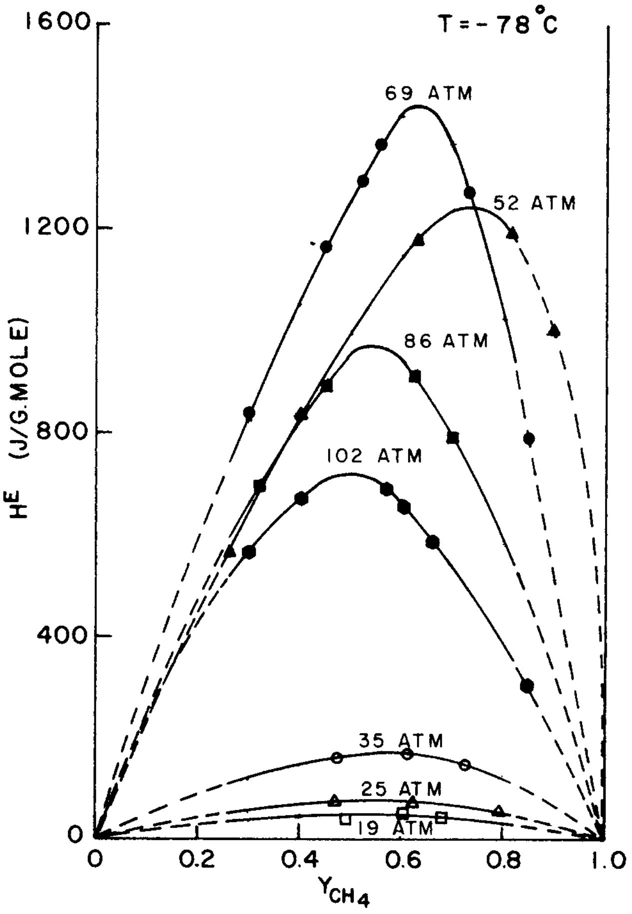

Fig. 6. Isobars of H^E versus Y_{CH_4} for the methane-nitrogen system at −78°C.

We shall use an expansion based on the virial equation of state in the form

$$\frac{pv}{RT} = 1 + B'\,p + C'\,p^2 + D'\,p^3 + \cdots . \tag{8}$$

From this equation, the coefficient $\left(\frac{\partial H}{\partial p}\right)_T$ is evaluated by

$$\left(\frac{\partial H}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p \tag{9}$$

The enthalpy of a real gas referred to zero pressure is given by

$$H = H_0 + \int_0^p \left(\frac{\partial H}{\partial p}\right)_T dp \tag{10}$$

The use of Equations (8) and (9) with Equation (10) leads to

$$H = H_0 - RT^2\left[\frac{dB'}{dT}\,p + \frac{1}{2}\,\frac{dC'}{dT}\,p^2 + \frac{1}{3}\,\frac{dD'}{dT}\,p^3 + \cdots\right] \tag{11}$$

This expression for H (with suitable values of B', C', . . .) applies to the mixture and also to the pure components. It is substituted into the definition

$$H^E = H_m - y_1H_1 - y_2H_2 \tag{12}$$

Equation (11) can be written for the mixture and also for each individual component. When these three equations for H_m, H_1, and H_2 are substituted into Equation (12), since H^E in zero at zero pressure, we obtain

$$\begin{aligned}\frac{-H^E}{RT^2} &= \frac{dB'_m}{dT}\,p + \frac{1}{2}\,\frac{dC'_m}{dT}\,p^2 + \frac{1}{3}\,\frac{dD'_m}{dT}\,p^3 + \cdots\\ &-y_1\left[\frac{dB'_{11}}{dT}\,p + \frac{1}{2}\,\frac{dC'_{111}}{dT}\,p^2 + \frac{1}{3}\,\frac{dD'_{1111}}{dT}\,p^3 + \cdots\right]\\ &-y_2\left[\frac{dB'_{22}}{dT}\,p + \frac{1}{2}\,\frac{dC'_{222}}{dT}\,p^2 + \frac{1}{3}\,\frac{dD'_{2222}}{dT}\,p^3 + \cdots\right]\end{aligned} \tag{13}$$

For the true virial coefficients of the mixture the equations

$$B_m = \sum_i \sum_j y_i y_j B_{ij} \tag{14}$$

$$C_m = \sum_i \sum_j \sum_k y_i y_j y_k C_{ijk} \tag{15}$$

$$D_m = \sum_i \sum_j \sum_k \sum_l y_i y_j y_k y_l D_{ijkl} \tag{16}$$

are known to apply. The relations between the density virial coefficients in Equations (14) to (16) and the pressure coefficients of Equation (8) are (*11*)

$$B' = \frac{B}{RT} \tag{17}$$

$$C' = \frac{C - B^2}{(RT)^2} \tag{18}$$

$$D' = \frac{D - 3BC + 2B^3}{(RT)^3} \tag{19}$$

$$E' = \frac{E - 2C^2 - 4BD + 10B^2C - 5B^4}{(RT)^4} \tag{20}$$

When Equations (14) through (20) are substituted into Equation (13), extensive algebraic manipulation gives a form similar to Equation (7):

$$z = \frac{H^E}{py(1-y)} = \sum_{m=0}^{M-1} a_m\, q_m\,(p, y) \tag{21}$$

where

$$\begin{array}{llll} q_0 = 1 & q_4 = p^2 & q_8 = p^2y^4 & q_{12} = p^3y^3 \\ q_1 = p & q_5 = p^2y & q_9 = p^3 & q_{13} = p^3y^4 \\ q_2 = py & q_6 = p^2y^2 & q_{10} = p^3y & q_{14} = p^3y^5 \\ q_3 = py^2 & q_7 = p^2y^3 & q_{11} = p^3y^2 & q_{15} = p^3y^6 \end{array} \tag{22}$$

for $M = 16$, corresponding to the use of the virial equation through E. The constants a_m are complicated functions of the temperature derivatives of the virial coefficients, including the cross coefficients. These relations (17) are of no practical use in the correlating procedure. Equations (21) and (22) can be written compactly as

$$z = \sum_{i=1}^{V-1} \sum_{j=1}^{2i-1} b_{ij}\, p^{i-1}\, y^{j-1} \tag{23}$$

In this equation V corresponds to the number of the highest virial coefficient used in the expansion. For example for $V = 5$ there are 16 b_{ij} to find.

From the above equations it is evident that the variable z is a kind of reduced H^E. For a series with $V = 2$, the value of z is unity, so that

$$H^E = a_0\, p\, y\,(1 - y) \tag{24}$$

This equation is equivalent to Equation (2).

The standard least squares method has been used to find the set of b_{ij} which gives the minimum value of the sum $(z_{\text{obs}} - z_{\text{calc}})^2$ over the data points available at each temperature. This procedure is not so rigorous as minimizing $(H^E_{\text{obs}} - H^E_{\text{calc}})^2$; these deviations are more likely to follow a normal distribution than those based on z. Since use of $V = 6$ would correspond to 25 terms in the expansion, and there were only about 40 experimental points at a given temperature,fitting was done only for V of 5 or less. The computer program for the work was written in double precision.

Carrying the expansion to higher terms will reduce the sum of squares, but a better measure of the goodness of fit is the quantity

$$\sigma = \left[\sum_{n=1}^{N} \frac{(z_{\text{obs}} - z_{\text{calc}})^2_n}{N - M - 1} \right]^{1/2} \tag{25}$$

as used, for example, by Forsythe (*12*). The effect of increasing V (and M) on the correlating procedure is illustrated in Table 2 for the data at −40°C. Parameters for the other temperatures are given by Klein (*17*). The value of σ of 0.08714 corresponds to an error of no more than 4.0%. An inspection of the values of $z_{\text{obs}} - z_{\text{calc.}}$ (*17*) confirms that the fitting procedure reproduces the data to within the estimated experimental error. The same may be said for the data at all other temperatures except −78°C. At this lowest temperature the curvature of the lines in Figures 3, 4, and 6 is so sharp that graphical smoothing must be used.

TABLE 2. CORRELATION OF HEAT OF MIXING OF NITROGEN AND METHANE

		−40°C. Values of b_{ij} ($N = 39$)		
	$V = 2$ $M = 1$	$V = 3$ $M = 4$	$V = 4$ $M = 9$	$V = 5$ $M = 16$
b_{11}	2.7585	0.4715	0.4897	1.595
b_{21}		0.02257	0.02694	−0.01204
b_{22}		0.02299	0.03052	−0.05623
b_{23}		0.007576	−0.02019	0.01454
b_{31}			0.0007795	−0.0004014
b_{32}			−0.006887	0.005213
b_{33}			0.02017	−0.002010
b_{34}			−0.02474	−0.005282
b_{35}			0.01118	0.004880
b_{41}				−0.00000627
b_{42}				0.00006215
b_{43}				−0.0003020
b_{44}				−0.0004294
b_{45}				−0.0005141
b_{46}				−0.0003138
b_{47}				0.0001695
σ	1.1549	0.1627	0.1474	0.08714

Some of the results are presented in graphical form to show significant trends. In Figure 3 H^E in joules per gram-mole is plotted versus pressure along four isotherms for a mixture of 0.60 mole fraction methane. Note that at the highest temperature, when the density is relatively low, H^E is linear with p in accord with Equation (2). More and more curvature appears as the temperature is lowered. Finally H^E goes through a sharp maximum at temperatures approaching the critical temperature of methane. Figure 4 shows the maxima in the H^E versus p curves at −78°C. for three different mixtures. It is of interest to note that the maximum increases as y_{CH_4} increases from 0.4 to 0.6 and then decreases as y_{CH_4} is increased to 0.8.

The effect of composition along isobars at two different temperatures is shown in Figures 5 and 6. At 0°C. the curves are in accord with Equation (2) for the case of binary collisions only and the maximum is at about a 50-50 mixture for all pressures. At −78°C. the maximum occurs at the 50% mixture at the lowest pressure, shifts toward a higher methane content as p increases, and then shifts back toward lower methane content as the pressure increases further. These trends are doubtless due to the relative magnitude of the three intermolecular forces involved but are difficult to visualize qualitatively. However, they can be predicted fairly well by an equation of state, as will be shown presently.

ERROR ANALYSIS

The measurements of voltage and amperage to the heater, volume of gas collected, time, and the determination of the null point on the thermopile are the only errors entering directly into the determination of heat of mixing. A spurious transfer of heat is also a possible source of error which is almost impossible to estimate; one attempts to design the calorimeter to minimize it and hopes for the best. Temperature, pressure, and composition are involved only in the fixing of the state at which H^E is obtained. The extent to which these latter affect the heat of mixing depends on their magnitude and we have attempted to estimate a maximum and minimum error. A summary of the error analysis is given in Table 3.

The establishing of the zero ΔT on the differential thermocouple is believed to be so sensitive that any error from this source is negligible. A general check on the measurements was made by mixing methane and nitrogen with themselves at various flow rates. When this was done

Table 3. Sources of Uncertainty in the Heat Mixing Results

Item	Maximum % error	Minimum % error
Power supply	0.015	0.015
Volt box	0.02	0.02
Voltage reading error	0.075	0.075
Shunt box	0.02	0.02
Shunt box reading error		
Composition	2.5	0.0
Temperature	0.6	0.6
Pressure	2.5	0.5
Flow rate	1.0	0.75
Total	6.805	2.03

no detectable temperature differences could be observed on any of the thermocouples. Pressure drop due to flow through the calorimeter was also shown to be negligible.

COMPARISON OF THE EXPERIMENTAL RESULTS WITH THE LITERATURE AND WITH CALCULATIONS BY EQUATIONS OF STATE

The only experimental results in the literature on this system are those of Van Eijnsbergen and Beenakker (*24*) and they are compared with our own in Figure 7 for y_{CH_4} = 0.56 for two pressures at a series of temperature. As can be seen the agreement is very satisfactory.

The B-W-R equation of state as modified by Bloomer and Rao (*4*) by the addition of two more constants D_0 and δ was used, along with the empirical mixing rules suggested by them, to calculate H-$H°$ of the pure components and of mixtures, from which H^E is obtained from Equation (1).

The Redlich-Kwong equation of state, generally considered to be the best of the two-parameter equations, was used with the constants of Chueh and Prausnitz (*7*), determined from saturated vapor volumes and with the special mixing rules developed by them.

The virial equation of state through the third coefficient was used as described by Hirschfelder, Curtiss, and Bird (*14*). The Lennard-Jones potential was used to obtain the values of the second virial coefficients; the force constants and mixing rules given in reference *14* were used. The third virial coefficients were obtained by the corresponding states method (*14*).

Calculations with all three equations were made at $-20°$, $-60°$, and $-78°$C. over the full range of pressure at y_{CH_4} =

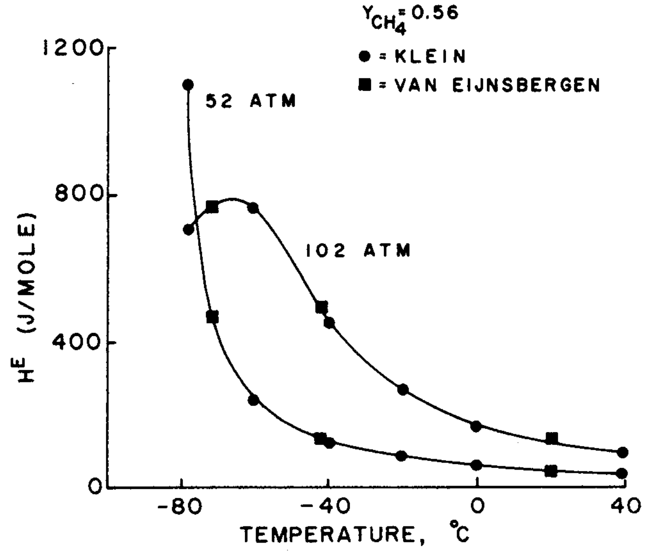

Fig. 7. Comparison of the heat of mixing data of Klein and of Van Eijnsbergen (*24*).

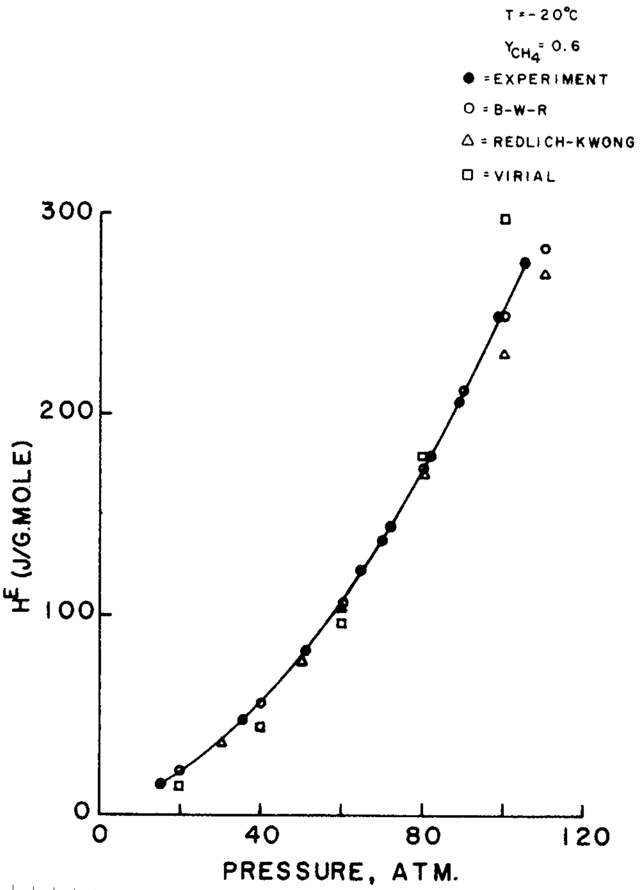

Fig. 8. Comparison of isothermal data with equations of state.

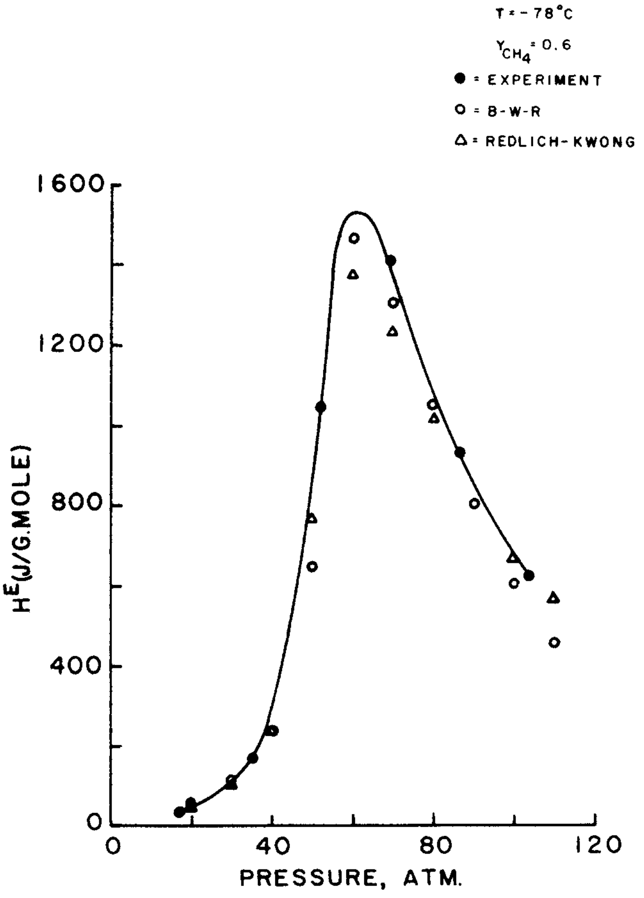

Fig. 9. Comparison of isothermal data with equations of state.

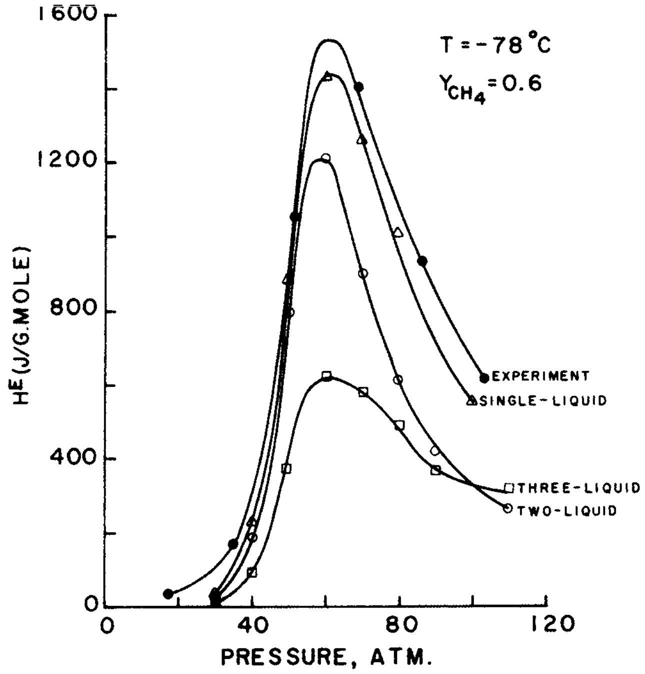

Fig. 10. Comparison of isothermal data with liquid theories.

0.4 and 0.60 for $-20°$ and $-78°$ and only at 0.60 for $-60°$. The results are compared with the experimental values on plots of H^E versus p. Two of these plots are shown here as Figures 8 and 9. At $-78°$C. no points are shown for the virial equation, since it deviated widely from the experimental data above 30 atm. The general conclusion from these calculations is that the B-W-R and R-K equations give very reliable predictions under all our experimental conditions and there is little to choose between them. The truncated virial equation is reliable only at the higher temperatures and at pressures up to about 60 atm.

The method outlined by Brewer and Geist (*5*) was also tested against our data for H^E. The predicted values did not agree with the experimental results, although the percent deviation of the prediction of H_m appears to be acceptable. Since the heat of mixing is a small difference relative to the enthalpy of the mixture, its prediction is a severe test. For our system the equations of state are much better predictors than the law of corresponding states. The tables of Lyderson, Greenkorn, and Hougen (*20*) were also used, but the values predicted deviated widely not only from the experimental data for H^E but from the values predicted by the method based on the acentric factor (*5*).

We also tested the liquid theories based on the treatment of Scott. All three of the liquid models were tested at $-60°$ and $-78°$C. over the full pressure range at $y_{CH_4} = 0.60$. In all cases the agreement was only qualitative but trends were correctly predicted as shown in Figure 10. The single-liquid theory was found to be a much better predictor than the other two, as found by Van Eijnsbergen and Beenakker (*24*).

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NOTATION

$a, b, c,$ = constants
B = second virial coefficient
C = third virial coefficient
Cp = specific heat at constant p
Cv = specific heat at constant V
H = enthalpy
$H°$ = enthalpy at $p = 0$
H^E = excess enthalpy
$\bar{H}_i$ = partial enthalpy of component of a solution
p = pressure
R = universal gas constant
T = absolute temperature
v = molar volume
y = mole fraction in gas phase
z = reduced H^E as defined by Equation (21)
Z = compressibility factor
ω = acentric factor

Subscripts

1, 2 = components of a mixture
c = critical state
m = mixture (solution)
i = any component of a mixture
r = reduced property

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