The Direct Determination of the Effect of Pressure on Enthalpy of a Mixture of Methane and Propane

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A new throttling flow calorimeter has been incorporated into the recycle facility of the Thermal Properties Laboratory. Energy is added to the expanding gas while it flows through a stainless steel capillary tubing from an insulated resistance wire located inside the entire length of the capillary. The calorimeter is designed to operate at pressures up to 2,000 lb./sq.in.abs. in the temperature range from —240 to +250° F.

Data on the isothermal effect of pressure on enthalpy for a mixture containing 5 mole % propane in methane are presented and compared with data from the literature.

A knowledge of the thermodynamic properties of both pure components and mixtures over wide ranges of pressure and temperature is desirable for use in engineering design and for comparison with theoretical calculations or correlations of these properties. The effect of temperature on enthalpy using an isobaric flow calorimeter has been determined at the University of Michigan for a number of pure components and mixtures (17, 20, 21, 23). For complete definition of the thermodynamic properties, a knowledge of the effect of pressure upon enthalpy is also required. Values of this effect can be estimated from P-V-T data, but differentiation of the data is required with consequent loss of accuracy of about one order of magnitude. Values can also be calculated from equations of state with constants evaluated from various types of thermodynamic data. Direct determinations of high accuracy are desirable either for immediate use, for obtaining constants in an equation of state, or to serve as a check on other thermodynamic data and/or theories.

Joule-Thomson measurements, which require determination only of the temperature change associated with a pressure drop, were considered because of the experimental simplicity. However, with the notable exception of Roebuck (29, 30), few workers have been able to prevent significant heat leak which invalidates the results. The problem of heat leakage can be minimized by determination of the isothermal throttling effect. The first accurate measurements of this type were made in 1932 by two different investigators. Eucken, Clusius, and Berger (13) employed a throttling valve, and after the gas expanded, it was passed over heating wires to bring the outlet temperature back to that of the inlet. Keyes and Collins (18) used a platinum capillary to cause the pressure drop and the capillary itself served as the resistance heater. In later models (6, 7), a heating element consisting of resistance wire supported upon pyrex tubes was inserted into a short length of tubing. Some workers (1, 32) have used removable orifices to cause the pressure drop, but recently workers have used throttling valves (5, 16) or the capillary tube (14, 33).

This paper reports the development of a calorimeter for accurate measurements of the isothermal effect of pressure on enthalpy, it presents data obtained on a mixture of methane and propane, and compares the experimental results with other data and prediction methods.

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THERMODYNAMIC RELATIONS

For a properly designed flow calorimeter, operated under steady state conditions with negligible potential and kinetic energy effects, the first law of thermodynamics reduces to

$$(\underline{H}_{T_2,P_2} - \underline{H}_{T_1,P_1})_x = \frac{\dot{Q} - \dot{W}}{F} \qquad (1)$$

With proper care, the rate of heat leak, $\dot{Q}$, can be made negligible. In operation the outlet temperature, T_2, is brought to approximately the same value as the inlet temperature, T_1, and a correction is made for this small difference by using values of C_p at the outlet pressure:

$$(\underline{H}_{P_2} - \underline{H}_{P_1})_{T_1,x} = -\frac{\dot{W}}{F} - \int_{T_2}^{T_1} C_p dT_{P_2} \qquad (2)$$

Equation (2) yields integral values of the isothermal enthalpy change associated with the measured values of pressure drop, $P_2 - P_1$. Point values of the isothermal throttling coefficient, ϕ, are estimated from the integral values by application of the following relation:

$$\phi \equiv \left(\frac{\partial H}{\partial P} \right)_T \equiv \frac{\lim}{P_2 \to P_1} \left[\frac{\underline{H}_{P_2} - \underline{H}_{P_1}}{P_2 - P_1} \right]_T \qquad (3)$$

Experimental values of ϕ can be compared with values calculated from experimental data of other types.

The isothermal throttling coefficient ϕ is related to the Joule-Thomson coefficient $\mu = (\partial T/\partial P)_{\underline{H}}$ by the mathematical identity:

$$\phi = -\mu C_p \qquad (4)$$

Values of ϕ can be derived from P-V-T data or an equation of state using the relation:

$$\phi = \underline{V} - T \left(\frac{\partial \underline{V}}{\partial T} \right) P \qquad (5)$$

The virial equation of state, which is derived from statistical mechanics, is a power series in density:

$$z = \frac{P\underline{V}}{RT} = 1 + \frac{B}{\underline{V}} + \frac{C}{\underline{V}^2} + \text{----------------} \qquad (6)$$

This equation is sometimes written as a power series in pressure:

$$z = 1 + B'P + C'P^2 + \text{----------------} \qquad (7)$$

The coefficients of the two series are related by:

$$B' = B/RT \tag{8}$$

$$C' = (C - B^2)/(RT)^2 \tag{9}$$

By using Equations (5), (7), (8), and (9), ϕ can be expressed as:

$$\phi = - T^2 \left[\frac{d}{dT} \left(\frac{B}{T} \right) + P \frac{d}{dT} \left(\frac{C}{T} \right) + \cdots \cdots \right] \tag{10}$$

The zero pressure value of ϕ is finite and depends only on B:

$$\phi^0 = B - T \left(\frac{dB}{dT} \right) \tag{11}$$

For mixtures, B has the form:

$$B_m = x_1^2 B_{11} + 2x_1 \, x_2 \, B_{12} + x_2^2 \, B_{22} \tag{12}$$

and

$$\frac{dB_m}{dT} = x_1^2 \frac{dB_{11}}{dT} + 2x_1 x_2 \frac{dB_{12}}{dT} + x_2^2 \frac{dB_{22}}{dT} \tag{13}$$

Experimental values of ϕ can be integrated to obtain enthalpy departures for comparison with correlations using the following equation:

$$(H^o - H^p)_T = \Delta H_T = - \int_0^P \phi \; dP \tag{14}$$

THE ISOTHERMAL THROTTLING CALORIMETER

A detailed drawing of the calorimeter developed in the course of this work is shown in Figure 1. The pressure drop is caused by passing the fluid through a fine capillary. This method has been used previously; however, this calorimeter is unique in that an insulated heating wire passes inside the capillary and electrical energy is added to make the outlet temperature essentially equal to that at the inlet.

The calorimeter is part of a recycle system described earlier (24). In this system, the fluid is brought to the desired conditions of pressure and temperature and enters the upper portion of the calorimeter vacuum jacket. Here the pressure tap and thermowell serve to measure the inlet conditions of the fluid, before it passes to the throttle chamber. Inside the chamber is a removable capillary coil which causes the pressure drop in the fluid. In this work, three different capillary sizes were employed of 16 Birmingham Wire Gauge, 17 Birmingham Wire Gauge, and 19 Birmingham Wire Gauge hypodermic tubing, all about 10 ft. in length. (The nominal I.D. of these capillaries is 0.047, 0.042, and 0.027 in. respectively.) The chamber closure is a temperature compensated coupling using a stainless steel O-ring. Although this closure was initially successful, the seal was found to leak after it had been opened a number of times. It was necessary to use 1 mil Mylar gaskets on both sides of the O-ring for subsequent experiments to obtain a seal.

When ϕ is negative, the fluid temperature tends to decrease as the pressure drops. To offset this cooling effect, electrical energy is added to the flowing fluid by means of an insulated Nichrome resistance wire (36 Brown and Sharp wire gauge, nominal 0.005 in. O.D.) which is inside the capillary. The lead wire for this heater is brought from the vacuum jacket into the pressure capsule through a Conax gland, which uses a Teflon sealant. The other end of the heater wire is soldered to the low pressure end of the capillary to ground it electrically. The fluid jetting from the capillary is passed back and forth through three copper baffles to reduce kinetic energy effects and smooth out temperature fluctuations before passing to the exit thermowell and the exit pressure tap. The line in which the fluid leaves the calorimeter is enclosed by a vacuum tube for a distance of 3 ft. after leaving the calorimeter to minimize heat conduction back from the surroundings.

Efforts were made to reduce heat transfer to the surroundings. The calorimeter was immersed in a constant temperature bath controlled at the calorimeter inlet temperature. The calorimeter capsule was positioned in a vacuum jacket maintained at 1 to 5 μ through the vacuum line and a radiation shield located inside the vacuum

1. Entrance Thermocouple Well
2. Mechanical Partition
3. Calorimeter Heater Capsule
4. Calorimeter Baffles
5. Exit Thermocouple Well
6. Radiation Shield
7. Conax Heater Lead Gland
8. Capillary
9. Entrance Pressure Tap
10. Exit Pressure Tap
11. Vacuum Line
12. Temperature Compensated Coupling

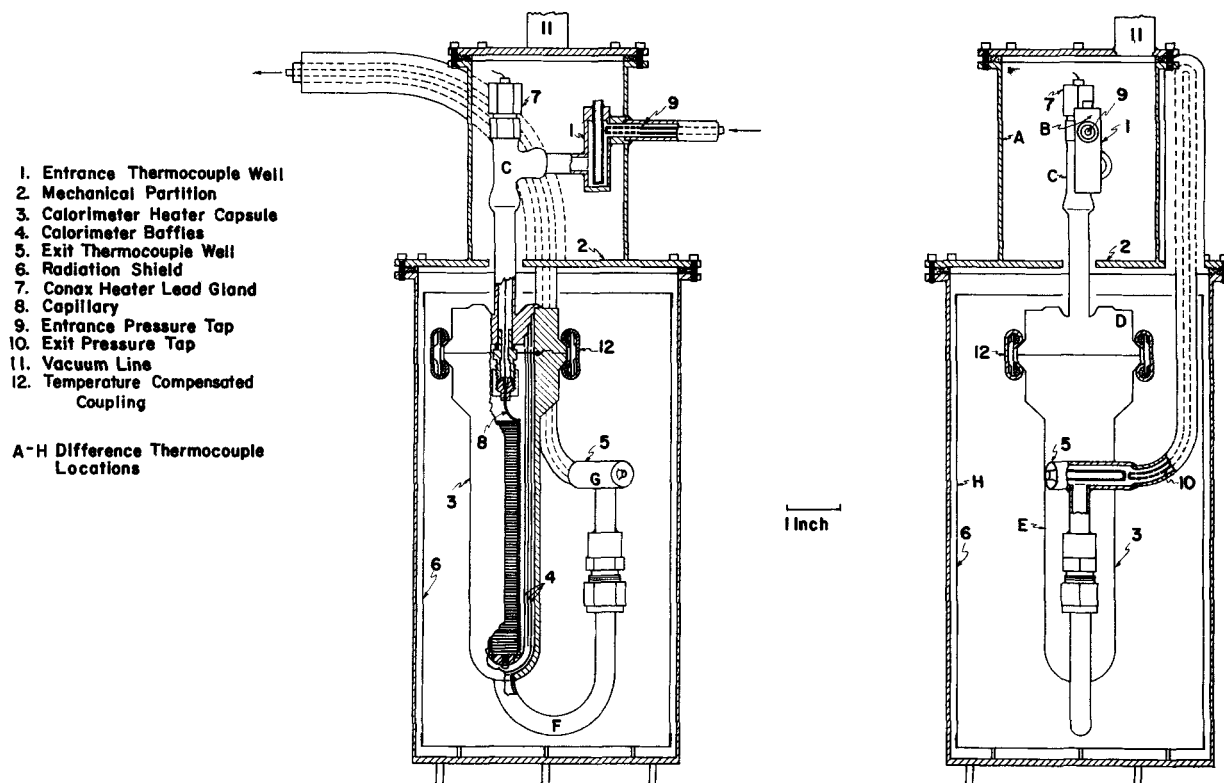A-H Difference Thermocouple Locations

1 Inch

Fig. 1. Isothermal throttling calorimeter.

jacket completely surrounds the calorimeter capsule. Single junction copper-constantan difference thermocouples are attached to the skin of the calorimeter at various points (A through H in Figure 1) to indicate the temperature profile along the calorimeter. A check of the difference thermocouples under experimental conditions revealed that the calorimeter was isothermal within the accuracy of the thermocouple readings ($\pm$ 0.1°F.).

The pressure drop across the calorimeter is measured by the differential pressure balance of Roebuck (28), while the inlet pressure is measured by a Mansfield and Green pressure balance. Heise gauges serve as indicators and provide a crosscheck of the measurements. The electrical energy input to the heater is supplied by a Kepco DC power supply and the voltage and current are determined by using standard resistors. The temperature difference between the entrance and exit thermowells is sensed by duplicate six-junction copper-constantan differential thermopiles using a K-3 potentiometer. The temperature of the calorimeter bath, which is assumed to be the temperature of the fluid entering the calorimeter, is measured with a platinum resistance thermometer. This thermometer, as well as the thermopiles, were calibrated by the National Bureau of Standards.

The flow rate of fluid is determined by a Meriam laminar flow element which is located in the low pressure (80 lb./sq.in. gauge) section of the recycle system in a constant temperature bath. The pressure drop–mass flow rate calibration is made by direct weighing of about 180 g. of mixture collected over a measured time interval. A 180 in. mercury manometer is used to measure the inlet pressure to the flow element in order to make small corrections for density and viscosity changes. Three calibrations were made during the course of the methane-propane work. A cubic equation fits all 34 calibration points with an average deviation of 0.17%.

EXPERIMENTAL MATERIALS AND PROCEDURE

The methane used in this research had a purity of 99.7%. The propane had a minimum purity of 99.9%. The composition of the mixture studied is given in Table 1.

Using the recycle system, the mixture was brought to the desired pressure and temperature conditions at the inlet to the calorimeter. A pressure drop across the calorimeter of 100 to 300 lb./sq. in. was obtained by varying the flowrate of the fluid through the calorimeter section. The voltage supplied to the heater wire was adjusted until the temperature difference between the inlet and outlet was less than 0.05°F. When steady state was reached, usually in 30 to 60 min., values of all the pertinent variables were recorded.
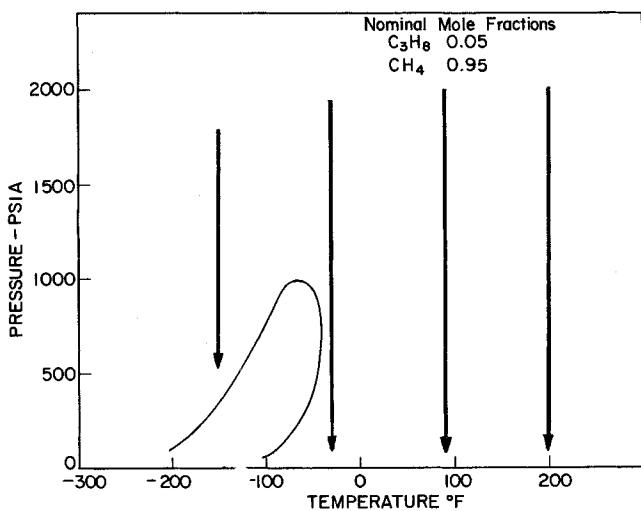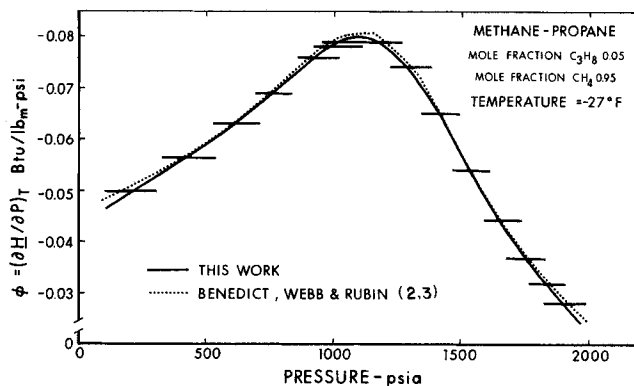
Fig. 2. Range of measurements.

Fig. 3. Typical values of the isothermal throttling calorimeter.

TABLE 1. COMPOSITION OF THE METHANE-PROPANE MIXTURE

Component	Mole Fraction
methane	0.9473 (by difference)
propane	0.051 $\pm$ 0.001
carbon dioxide	0.0003
ethane $\}$ nitrogen $\}$	0.0013
oxygen	0.0001
	1.0000

EXPERIMENTAL RESULTS

Isotherms at 200, 92, -27, and -147°F. were obtained over a range of pressures for a mixture of methane and propane. These isotherms are shown as vertical lines in Figure 2. The data for all four isotherms are presented in the thesis of Mather (26). Results for -27°F. are shown in Figure 3. Here the bars represent the mean value of ϕ over the measured pressure drop as given by Equation (2). An equal area curve passing through the bars yields point values of ϕ as shown by the solid line. Values of ϕ determined in this manner for all four isotherms together with interpolated values are presented in Table 2.

TABLE 2. ISOTHERMAL THROTTLING COEFFICIENTS
FOR THE NOMINAL 5% MIXTURE
ϕ (B.t.u./lb.-lb./sq.in.)
Temperature (°F.)

Pressure lb./sq.in.abs.	-147.4	-27.0	91.6	200.0
0		-0.044	-0.0294	-0.0215
100		-0.047	-0.0297	-0.0214
200		-0.050	-0.0301	-0.0214
300		-0.053	-0.0304	-0.0213
400		-0.056	-0.0308	-0.0212
500	-0.0023	-0.060	-0.0311	-0.0211
600	-0.0018	-0.063	-0.0313	-0.0210
700	-0.0014	-0.067	-0.0315	-0.0209
800	-0.0009	-0.070	-0.0316	-0.0207
900	-0.0005	-0.075	-0.0317	-0.0206
1,000	-0.0002	-0.078	-0.0317	-0.0204
1,100	$+0.0002$	-0.080	-0.0316	-0.0201
1,200	$+0.0004$	-0.078	-0.0315	-0.0199
1,300	$+0.0006$	-0.074	-0.0312	-0.0196
1,400	$+0.0008$	-0.066	-0.0307	-0.0193
1,500	$+0.0011$	-0.057	-0.0302	-0.0190
1,600	$+0.0013$	-0.049	-0.0296	-0.0187
1,700	$+0.0015$	-0.041	-0.0288	-0.0183
1,800	$+0.0017$	-0.034	-0.0279	-0.0178
1,900	$+0.0019$	-0.028	-0.0268	-0.0172
2,000	$+0.0022$	-0.022	-0.0255	-0.0166

ANALYSIS OF RESULTS

In contrast to the valve method of determining ϕ, the capillary has the disadvantage that it is not possible to
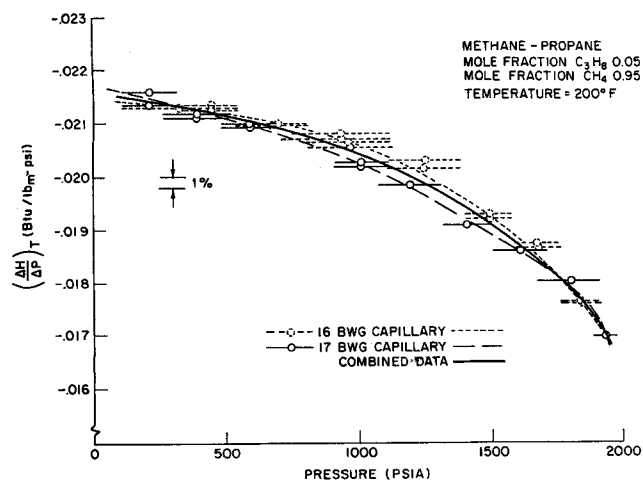
Fig. 4. Experimental values determined in different capillaries.

agreement between calculated and experimental values is very good. Another comparison of values of ϕ, calculated from this equation of state with the experimental results, is shown in Figure 3. The calculated values predict the maximum in ϕ and agree well with the experimental results. Earlier comparisons (25) with data on pure nitrogen did not show such good agreement with the B-W-R equation of state. This is consistent with the fact that the data for pure nitrogen are in disagreement with values calculated from Joule-Thomson data of Roebuck and Osterberg (30), which were used in determining the coefficients of the B-W-R equation of state for nitrogen (31).

Enthalpy departures were calculated from the experimental data using Equation (14) for comparison with results obtained from other data and generalized enthalpy correlations. These experimental values are listed in the first column of Table 3. The direct determinations of ΔH_T for a mixture of methane and propane made by Dillard (10) using the calorimeter described by Yarborough and Edmister (33) are listed in the second column. The fourth column contains the P-V-T data of Reamer, Sage, and Lacey (27), which were used by Edmister and Yarborough (12) to calculate values of ΔH_T by using the integrated form of Equation (5). Subsequent columns contain values estimated from the correlations of Lydersen, Greenkorn, and Hougen (19), Curl and Pitzer (8), and the recent revision of the Lydersen-Greenkorn-Hougen method by Yen (34). Finally, values of ΔH_T were calculated from the B-W-R equation of state and the results are presented in column three. The B-W-R equation of state is consistently better than the generalized correla-

vary flow rate and pressure drop independently. In order to check on possible flow rate dependence, another capillary must be used. The agreement attained is shown in Figure 4 where duplicate runs were made at 200°F. with coils of 17 Birmingham Wire Gauge and 16 Birmingham Wire Gauge tubing. (The mass flow rates differed by about a factor of two.) The agreement is good at higher and lower pressures with a difference of about 2% at midrange. The accuracy of the data taken with the 17 Birmingham Wire Gauge coil is limited by the error in measuring the smaller flow rate, while the accuracy of

TABLE 3. COMPARISON OF EXPERIMENTAL ENTHALPY DEPARTURES WITH VALUES FROM OTHER SOURCES

| Temp. (°F.) | Pressure lb./sq.in.abs. | This work | (10) | $(H^o - H^P)_T$ (B.t.u./lb.m) | | (19) | (34) | (8) |
				(2,3)	(12)			
—27	500	25.9	—	26.2	—	21.4	25.7	24.1
	1,000	60.3	—	61.1	—	55.2	58.4	56.9
	1,500	96.9	—	98.0	—	83.7	89.3	90.7
	2,000	116.0	—	117.5	—	100.9	108.6	111.2
91.6	500	15.1	14.9	15.0	14.0	11.2	15.2	14.6
	1,000	30.9	30.2	30.8	29.8	26.8	29.4	29.7
	1,500	46.5	45.6	46.5	46.2	39.8	45.1	46.4
	2,000	60.6	60.2	60.8	62.9	51.1	58.8	60.5
200	500	10.7	10.0	10.4	10.6	7.2	10.4	11.1
	1,000	21.1	19.8	20.7	21.3	17.1	20.8	21.5
	1,500	31.0	29.1	30.6	31.4	25.5	31.3	31.3
	2,000	40.0	35.8	39.7	40.6	32.5	39.6	39.6

data taken with the 16 Birmingham Wire Gauge coil is limited by the error in measuring the smaller pressure drop. For this reason, a band representing all the data in Figure 4 is plotted in Figure 5 for comparison with other data.

Values of ϕ calculated from Equation (4) using the Joule-Thomson data of Budenholzer, et al. (4), and the heat capacity data of Mather (26), are shown in Figure 5. These results are in good agreement with the experimental band except at the lowest pressures where the Joule-Thomson data of Sage and co-workers are believed to be inaccurate (22).

Also shown in Figure 5 are values of ϕ calculated by using the Benedict-Webb-Rubin (2) equation of state and mixing rules recommended by the same authors (3). Constants for methane and propane based on a combination of P-V-T data, critical properties, and vapor pressure data as reported in the original article (2) were used. The
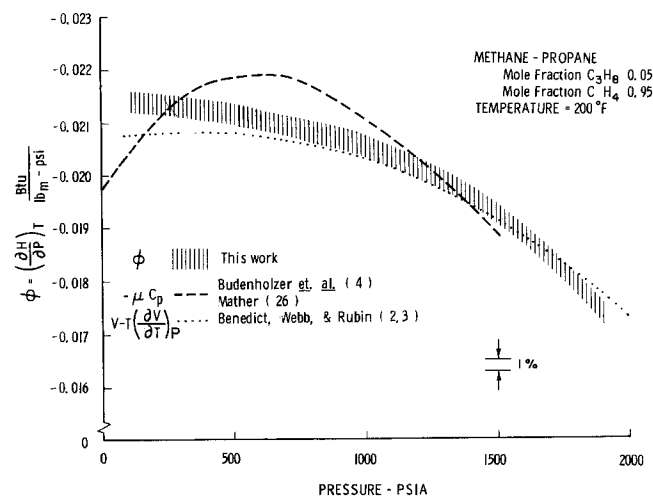

Fig. 5. Comparison of calculated and experimental values of ϕ.

tions and the values derived directly from P-V-T data. The data of Dillard are not precise; however, the average of his experimental values agrees with the present experiments except at the highest temperature.

Experimental values of the second virial coefficient, B, for methane, propane, and methane-propane mixtures were used to calculate the zero-pressure value of ϕ using Equation (11). The data for the second virial coefficient of methane (11, 15), propane (9, 15), and mixtures of methane and propane (15) were graphically differentiated to obtain dB/dT. The results are given in Table 4, together with values of ϕ^o calculated from Equation (11) and values obtained from the experimental data by linear extrapolation to zero pressure. The agreement between the calculated and experimental results is fair.

Superscripts

o = ideal gas state
P = value of a variable under pressure

Subscripts

m = mixture property
P = constant pressure
T = constant temperature
1 = initial state
2 = final state
$11, 22$ = pure components 1 and 2
12 = mixture 1 and 2

TABLE 4. CALCULATION OF ZERO-PRESSURE ISOTHERMAL THROTTLING COEFFICIENTS FROM VIRIAL COEFFICIENT DATA

T (°F.)		B (cc./mole)	dB/dT (cc./mole — °K.)	ϕ^o (Eq. (8)) (B.t.u./lb.$_m$-lb./sq.in.)	ϕ^o (Experimental) (B.t.u./lb.$_m$-lb./sq.in.)
200	CH_4	−20.4	0.30		
	C_3H_8	−247	1.22	−2.45 × 10^{-2}	−2.15 × 10^{-2}
	CH_4-C_3H_8	−85.4	0.49		
91.6	CH_4	−39.7	0.35		
	C_3H_8	−375	2.97	−2.90 × 10^{-2}	−2.94 × 10^{-2}
	CH_4-C_3H_8	−125.8	0.84		

CONCLUSIONS

A new apparatus is described for the measurement of the isothermal throttling coefficient. Data taken over a wide range of pressure and temperature are presented for a mixture of methane and propane. The results are compared with existing data and correlations. The Benedict-Webb-Rubin equation of state predicts values which are in better agreement with the experimental data than any other method considered.

ACKNOWLEDGMENT

NOTATION

B, C = virial coefficients in volume expansion
B', C' = virial coefficients in pressure expansion
C_p = heat capacity at constant pressure
F = mass flow rate
H = specific enthalpy
P = pressure
$\dot{Q}$ = rate of heat transfer
R = gas constant
T = temperature
V = specific volume
$\dot{W}$ = rate of electrical energy transfer
x = composition
z = compressibility factor, PV/RT
μ = Joule-Thomson coefficient
ϕ = isothermal throttling coefficient

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Oxidation of Hydrogen in a Helium Stream by Copper Oxide: Analysis of Combined Film and Pore Diffusion with Rapid Irreversible Reaction in a Fixed-Bed Process

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Differential equations were derived to describe the system characterized by a rapid, irreversible reaction of a fluid species in a flowing fluid with a fixed bed of solids in which the reaction rate was controlled by mass transfer of the reacting fluid from the bulk fluid to the reaction site in the solid. Two kinds of mass transfer resistances were assumed, external or film diffusion resistance, and internal pore diffusion resistance. The set of differential equations were solved by a finite-difference method for both the generalized case and for the specific case of reaction of hydrogen in a stream of helium with fixed beds of copper oxide pellets.

The hydrogen-copper oxide reaction is one step in a proposed method for removal of hydrogen as a contaminant in the helium coolant of nuclear reactors. This reaction was experimentally investigated in tests with both differential and deep beds of copper oxide in the temperature range of 400 to 600°C., at pressures of 10.2 to 30.0 atm., with gas mass flow rates of 0.0050 to 0.050 g./sq.cm.-sec, and with inlet hydrogen concentrations of 0.0008 to 1.21 vol. %. These tests showed that the system could be described by the two rate-limiting steps: film and pore diffusion of hydrogen. Differential-bed tests were used to establish hydrogen transport properties within the porous copper oxide pellets, and tests with deep beds were used to establish external mass transport properties.

Generalized breakthrough curves were determined by a computer solution of the mathematical model. These curves can be the basis for design of fixed-bed copper oxide oxidizers for gas-cooled, nuclear reactor purification systems and for design of any fixed-bed system which follows the assumed reaction mechanism.

Hydrogen is one of the major nonradioactive contaminants expected in the helium coolant of gas-cooled nuclear reactors. The hydrogen content of the coolant must be kept at a reasonably low level to maintain a coolant of acceptable properties. A proposed method for removing hydrogen from the helium is a two step process in which the hydrogen is first oxidized to water which is then removed by sorption (1). One oxidizing system that can be used is a fixed bed of copper oxide pellets, which can be alternately depleted of its oxygen content by reaction with hydrogen (copper oxide + hydrogen = copper + water) and then regenerated by air or oxygen (copper + 1/2O$_2$ = copper oxide). In accordance with anticipated requirements for gas-cooled nuclear reactors, the ranges of operating conditions of interest are pressure, 10 to 30 atm.; temperature, 400 to 600°C., contamination level, 0.001 to 1.0 vol.%; gas mass flow rate, 0.005 to 0.050 g./sq.cm.-sec.

Knowledge of the effects of various system parameters on the rate of the reaction is needed so that fixed bed, copper oxide oxidizers for helium purification systems can be designed. The approach taken in this study was to first establish the reaction mechanism for the hydrogen-copper oxide system and then by a mathematical model of the system to predict behavior of the copper oxide bed for the range of anticipated operating conditions. The mathematical solution was extended to the general case, which is useful for any fixed-bed system with porous solids in which a rapid, irreversible reaction occurs and in which the rate of reaction is controlled by the mass transfer of the reacting fluid species from the flowing fluid to the solid reaction site.