Calorimetric Determination of the Isothermal Effect of Pressure on the Enthalpy of Methane and Two Methane-Propane Mixtures

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By using an isothermal throttling calorimeter, built for recirculating vapor operation, the effects of pressure on the enthalpy of methane and two methane-propane (93.9 and 86.2% methane) mixtures were measured. Pure methane was run at 150°F. and the two mixtures were studied at 90, 150, and 200°F. The pressures for these experiments were 500, 1,000, 1,500, and 2,000 lb./sq.in.abs.

The resulting data were compared with similar data from other sources for these same systems and conditions. Agreement is good with enthalpy values obtained from both experimental volumetric and Joule-Thomson data.

Prediction methods for the isothermal pressure effect on the enthalpy are compared with these data. These methods demonstrate the reliability of the Redlich-Kwong and Benedict-Webb-Rubin equations and Pitzer's corresponding states correlation for calculating isothermal enthalpy changes for these systems and conditions.

For both pure substances and mixtures, the change of enthalpy with temperature can be accurately calculated at zero pressure, where enthalpies are additive for mixture components. Enthalpies, and other properties of the ideal gas state, have been selected and compiled elsewhere (*1*).

Isothermal changes in enthalpy with pressure for constant composition systems (pure components or mixtures) can be computed by an equation of state or derived from compressibility factor compilations. The development and testing of such predictive methods are important problems in the technical data area.

In a previous experimental investigation of the isothermal effect of pressure on the enthalpy of hydrocarbon mixtures, an isothermal throttling calorimeter was built and operated on the propane-benzene system (*16, 17*). For the investigations described in this paper (*4*), the previously built apparatus was modified and used to study the methane-propane system.

EXPERIMENTAL APPARATUS AND PROCEDURE

The equipment we used is a modification of that constructed by Yarborough (*16*). The details of its design and operation are described elsewhere (*16, 17*). The calorimeter portion of the equipment used in this study is identical to Yarborough's; only the peripheral apparatus has been changed. Thus, only the modifications will be described.

The equipment was originally designed for liquid-phase feed to the equipment, once-through operation, and effluent collection by condensation. For the present study, each of these features proved impractical, and modifications were made to yield the apparatus shown schematically in Figure 1.

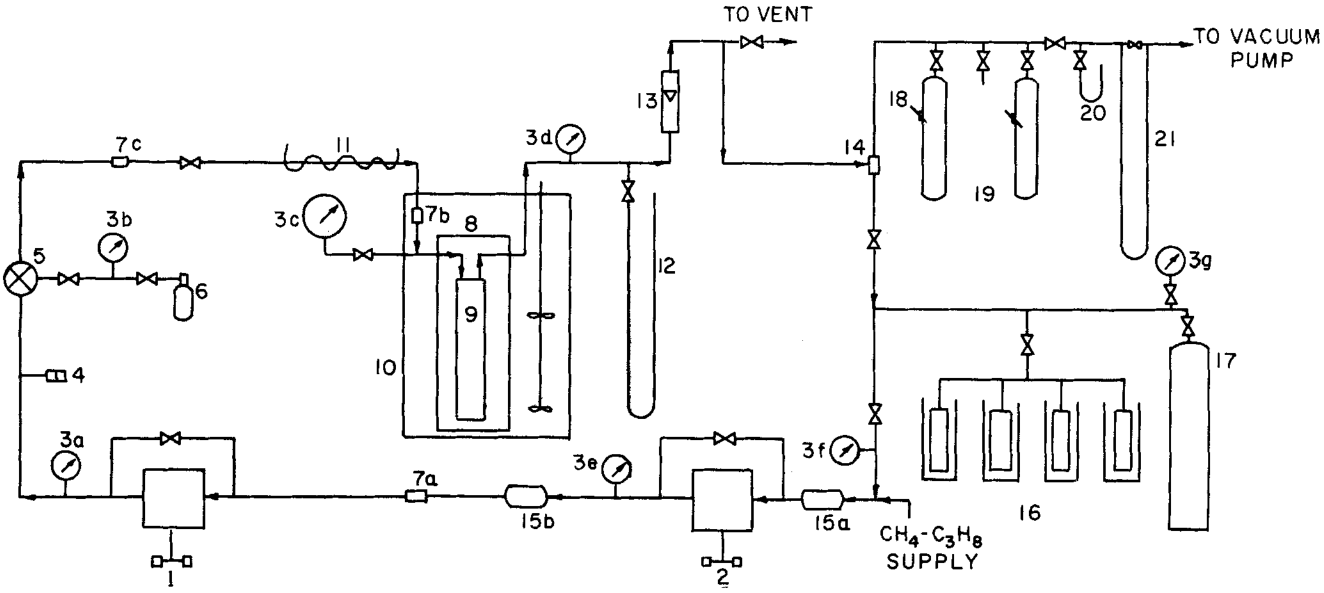
The first modification was to arrange for continuous recycle operation by installation of a closed loop employing two stages of compression, 1 and 2. Long line-out times required to reach steady state operation (with subsequently high gas consumption) led to abandonment of once-through operations and the adoption of the recycle operation.

The second modification of the apparatus was a change in method of flow rate measurement. Existing facilities for condensing the calorimeter effluent proved inadequate for the methane-propane system. Thus, the condensation method of flow rate determination was replaced by the equipment to the right of the solenoid valve, 14. After steady state conditions were reached in recycle operation, flow was diverted to high pressure aluminum bombs immersed in liquid nitrogen, 16, and makeup gas was supplied above the surge tank, 15. By using the valve directly above the high pressure bombs, the calorimeter effluent pressure was adjusted to approximately 1 atm. Valve 14 was then actuated to divert flow into originally evacuated glass collection bombs, 19.

Flow into this collection system was continued for a measured time, until the calorimeter effluent pressure returned to the initial pressure as indicated by manometer, 12. Flow was then returned to the aluminum bombs. From the known pressure, 21, and temperature, 18, of the gas in the calibrated volume of the sample system, the mass of gas was calculated by using the known low pressure volumetric behavior of the gas. The mass and flow time served to establish flow rate.

The calorimeter effluent temperature and pressure during flow measurements differed from the values for which the energy measurements were made. During line-out on recycle operations, the low capacity of the compressor system required that the intake pressure to the first stage compressor be as high as 50 lb./sq. in. (for the 2,000 lb./sq. in. runs). Thus, during line-out, the calorimeter outlet pressure was as high as 50 lb./sq.in. During flow measurement, however, this pressure was reduced to less than 1 atm. If, as was believed, critical flow conditions existed at the capillary outlet at the higher pressure, this outlet pressure difference caused no change in flow rate through the capillary. Also, experimental data indicated that the temperature change accompanying the pressure change was small; and its effect on flow rate was negligible. A pressure regulating valve at the outlet of the calorimeter would have permitted operating at a uniform pressure, but a suitable regulating valve could not be found. Flow measurements would have been simplified and operations made easier with such a regulating valve and/or larger compressors.

A third modification of the equipment involved relocation of thermocouples used to measure the gas inlet and outlet temperatures. These thermocouples were removed from thermal wells and sealed directly in the fluid stream in an effort to reduce the time lag in response to changes in energy input to the calorimeter.



1 - AMINCO AIR-DRIVEN DIAPHRAGM GAS COMPRESSOR
2 - ELECTRICALLY-DRIVEN DIAPHRAGM GAS COMPRESSOR
3 - PRESSURE GAUGE
4 - RUPTURE DISK
5 - MITY-MITE PRESSURE REGULATOR
6 - NITROGEN SUPPLY CYLINDER
7 - MICRON FILTER
8 - STAGNANT AIR BATH
9 - CALORIMETER
10 - CONSTANT TEMPERATURE GLYCOL BATH
11 - PREHEATER
12 - MANOMETER
13 - ROTAMETER
14 - THREE-WAY SOLENOID VALVE
15 - SURGE TANK
16 - COLLECTION BOMBS IMMERSED IN LIQUID NITROGEN
17 - 12-GALLON STORAGE CYLINDER
18 - THERMOMETER
19 - GLASS COLLECTION BOMBS
20 - McLEOD GAUGE
21 - ABSOLUTE MANOMETER

Fig. 1. Schematic flow diagram of isothermal throttling calorimeter.

The time required to perform a single run was on the order of 8 to 12 hr. This length of time was required to reach steady state operation. The high total heat capacity of the calorimeter relative to that of the fluid led to a sluggish response of changes in power input.

EXPERIMENTAL RESULTS

Compositions of the two mixtures studied are given in Table 1. Experimental results are given in Table 2 for methane and the two mixtures. The uncorrected Δh values are the raw data, that is, the enthalpy differences between the outlet and inlet conditions of the calorimeter. These Δh values were corrected from the calorimeter outlet pressure (15 to 50 lb./sq. in. abs.) to zero outlet pressure and for small differences between the inlet and outlet temperatures of the calorimeter (~0.2°F.). The pressure corrections were made using a truncated virial equation of state and experimental second virial coefficients for the gases (*5*, *8*). Ideal gas state heat capacities (*1*) and a generalized correlation for the effect of pressure on heat capacity (*9*) were used in making temperature correc-

TABLE 1. COMPOSITIONS OF METHANE-PROPANE MIXTURES

	Mole Percent Compositions	
Component	94%CH_4	86%CH_4
methane	93.90	86.23*
ethane	0.27	0.28
propane	5.09	12.57*
carbon dioxide	0.20	0.41
oxygen	0.01	0.01
nitrogen	0.53	0.49
isobutane	Trace	Trace
	100.00	100.00

* Adjusted from original values of 86.47 ± 0.5 and 12.61 ± 0.4 to give a total of 100.00.

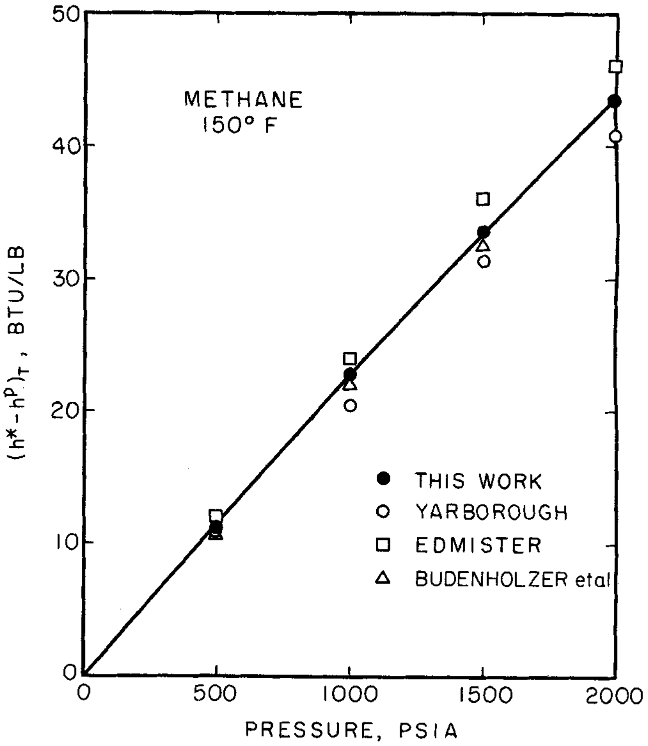


Fig. 2. Enthalpy of methane at 150°F.

Table 2. Experimental Results

Temp. °F.	Pressure lb./sq.in. abs.	Uncorrected $h^o - h^p$ B.t.u./lb.	Temp. Correction B.t.u./lb.	Pressure Correction B.t.u./lb.	$(h^* - h^p)_T$ B.t.u./lb.	$(H^* - H^p)_T$ B.t.u./lb.-mole
methane						
150	500	11.258	0.026	0.112	11.40	182.8
150	1,000	22.267	−0.076	0.533	22.72	364.5
150	1,500	33.075	−0.178	0.809	33.71	540.7
150	2,000	42.857	0.174	0.283	43.31	694.8
5.1 mole % propane in methane						
90	500	13.973	−0.026	0.472	14.42	254.1
90	1,000	29.242	−0.099	0.793	29.94	527.5
90	1,500	45.256	−0.049	1.051	46.26	815.1
90	2,000	58.276	0.169	1.557	60.00	1,057.2
150	500	12.189	−0.062	0.354	12.48	219.9
150	1,000	23.733	−0.054	0.596	24.28	427.7
150	1,500	35.191	−0.017	0.898	36.07	655.6
150	2,000	43.135	0.052	1.151	44.34	781.2
200	500	13.709	−0.216	0.471	13.96	246.0
200	500	12.161	−0.072	0.496	12.59	221.8
200	500	9.021	−0.023	0.528	9.53	167.9
200	500	9.382	−0.066	0.528	9.85	173.5
200	500	9.830	−0.180	0.528	10.18	179.3
200	500	10.135	−0.185	0.528	10.48	184.6
200	1,000	23.945	−0.088	0.491	24.35	429.0
200	1,000	17.921	0.152	0.894	18.97	334.2
200	1,000	18.726	−0.158	0.889	19.46	342.8
200	1,500	28.219	−0.083	0.733	28.87	508.7
200	2,000	34.912	−0.101	0.972	35.78	630.5
200	2,000	34.785	−0.224	0.976	35.51	625.7
12.6 mole % propane in methane						
90	500	15.904	0.112	0.868	16.88	334.9
90	1,000	32.488	−0.002	0.885	35.37	701.6
90	1,500	52.826	−0.020	1.309	54.11	1,073.3
90	2,000	70.154	−0.150	1.538	71.54	1,419.0
150	500	13.611	−0.092	0.619	14.14	280.4
150	1,000	26.682	0.016	0.605	27.30	541.6
150	1,500	51.834	−0.055	0.874	42.65	846.0
150	2,000	53.053	0.124	1.144	54.32	1,077.4
200	500	10.799	0.008	0.561	11.37	225.5
200	2,000	42.749	0.106	0.978	43.83	869.4
200	1,500	34.516	−0.262	0.734	34.99	694.0
200	1,000	22.685	0.024	0.525	23.23	460.9

tions. These corrections normally amount to about 3% of the reported values. The final corrected results are the difference between the ideal and real gas enthalpies.

Early experimental measurements showed deviations from the mean for duplicate runs to be a maximum of 2.3 B.t.u./lb. However, refinements in experimental technique on later runs (the 12.6% propane runs) led to improved results, believed to be precise to within ± 1 B.t.u./lb.

COMPARISONS

Comparisons of the above results with values from other sources are given in Figures 2 through 8. The points labeled Yarborough are from a calculational treatment (*15*) of the volumetric data of Sage and Lacey (*14*). Budenholzer, et al. (*3*) points refer to enthalpies from Joule-Thomson measurements. Edmister points are from a Mollier chart for methane (*6*), based on data from multiple sources. The Manker (*10*) and Mather, et al. (*11*) points are from a companion project to the present study performed at the University of Michigan.

An examination of Figures 2 through 8 reveals that the observed Δ*h* values at 2,000 lb./sq.in.abs. are higher than Yarborough's derived Δ*h* for methane at 150°F. but lower for the 94% methane at 90, 150, and 200°F. For the 86% methane system, the agreement is very good, however. There is no apparent explanation for this inconsistency.

The Δ*h* values of Manker and Mather were read from their published Mollier charts (*11*). Figures 3, 6, and 7 show that values from these Mollier charts diverge appreciably at high pressures from the present data. Minor differences between the mixture compositions used in the present work and those of Manker and Mather cannot account for the divergence noted in the figures. However, an important fact, relative to these comparisons, is that the data taken by Manker and Mather were isobaric data. They employed Budenholzer's Joule-Thomson data to establish the effect of pressure on enthalpy for their Mollier charts. This required extrapolation of Budenholzer's data above 1,500 lb./sq. in. abs. Thus, the above comparisons should not be construed to be a direct comparison of the experimental data of Manker and Mather with the present data.

CALCULATIONAL METHODS

In Table 3 comparisons of three enthalpy calculational methods with smoothed experimental values are presented for the systems and conditions covered in this investigation. The three methods used in calculating the isothermal effect of pressure were: Method A, Redlich-Kwong (*R-K*) equation of state (*13*); Method B, Benedict-Webb-Rubin (*BWR*) equation of state (*2*); and Method C, Pitzer et al. generalized correlation of thermodynamic properties (*12*). The use of these equations of state for enthalpy calculations is discussed elsewhere (*2*, *7*). Critical constants used in the *R-K* equation were taken from (*6*) and *BWR* constants from (*2*).

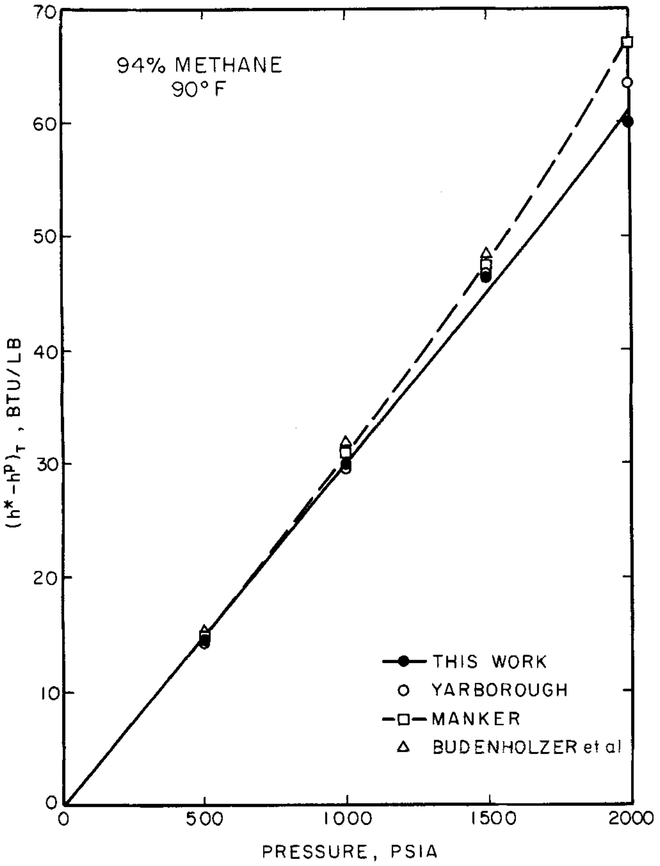


Fig. 3. Enthalpy of methane-propane mixture at 90°F.

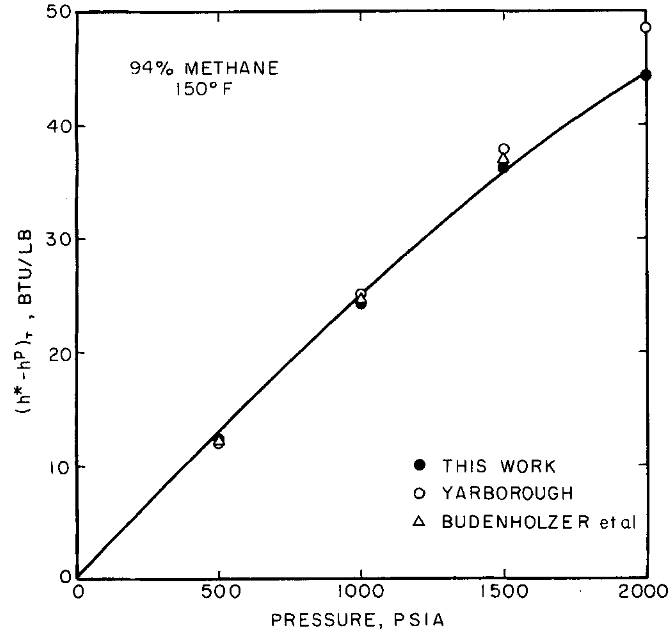


Fig. 4. Enthalpy of methane-propane mixture at 150°F.

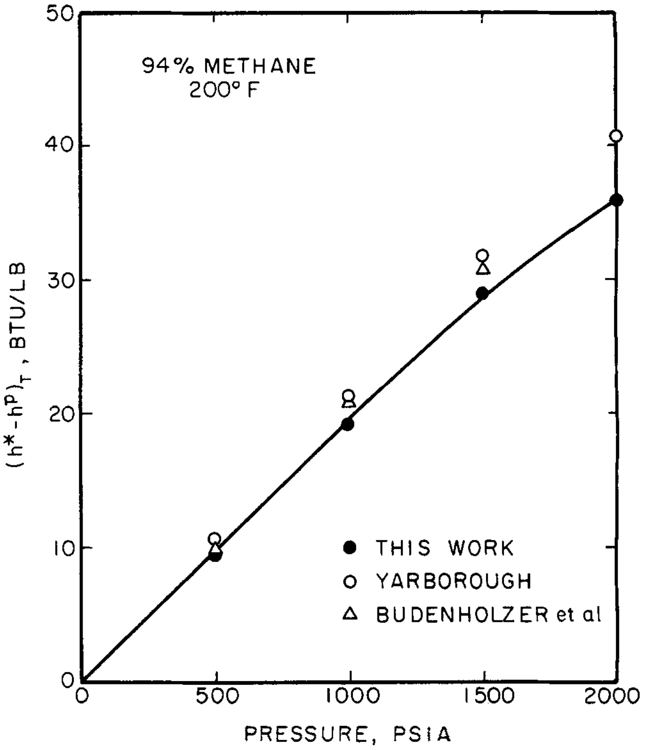


Fig. 5. Enthalpy of methane-propane mixture at 200°F.

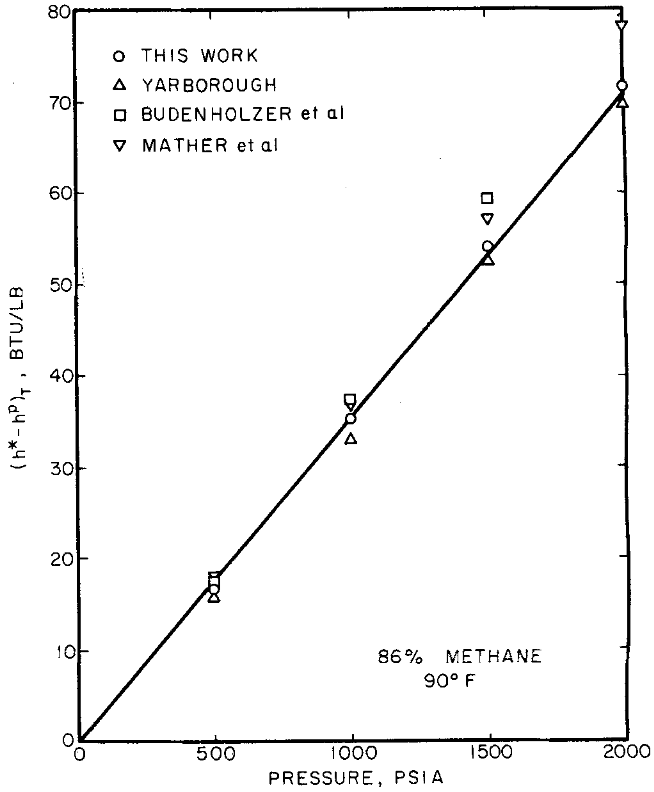


Fig. 6. Enthalpy of methane-propane mixture at 90°F.

Pseudocritical temperatures and pressures and molar average acentric factors were used in applying the Pitzer, et al. generalized correlations and calculating the Δh values given under Method C.

As can be seen by the comparisons in Table 3, the two equation methods and the Pitzer, et al. correlation agree with the smoothed experimental values to within ± 2 B.t.u./lb.

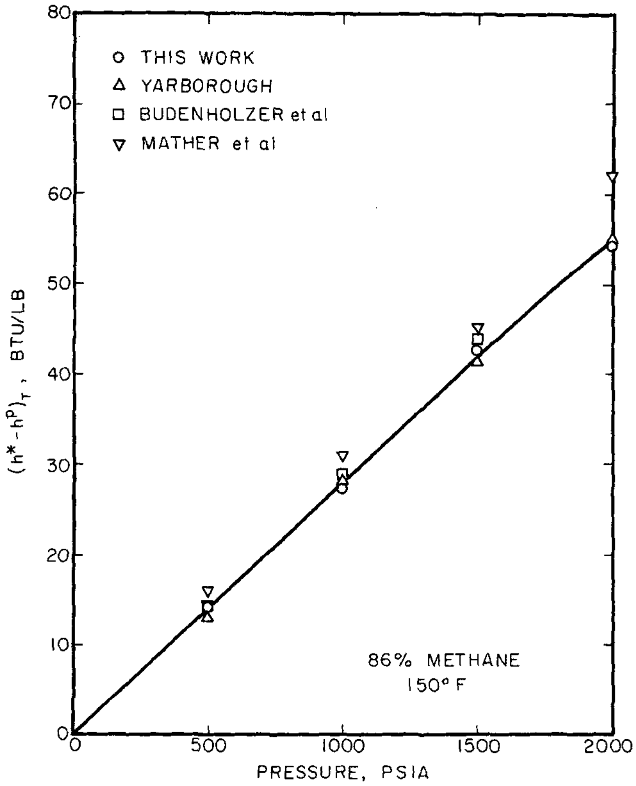


Fig. 7. Enthalpy of methane-propane mixture at 150°F.

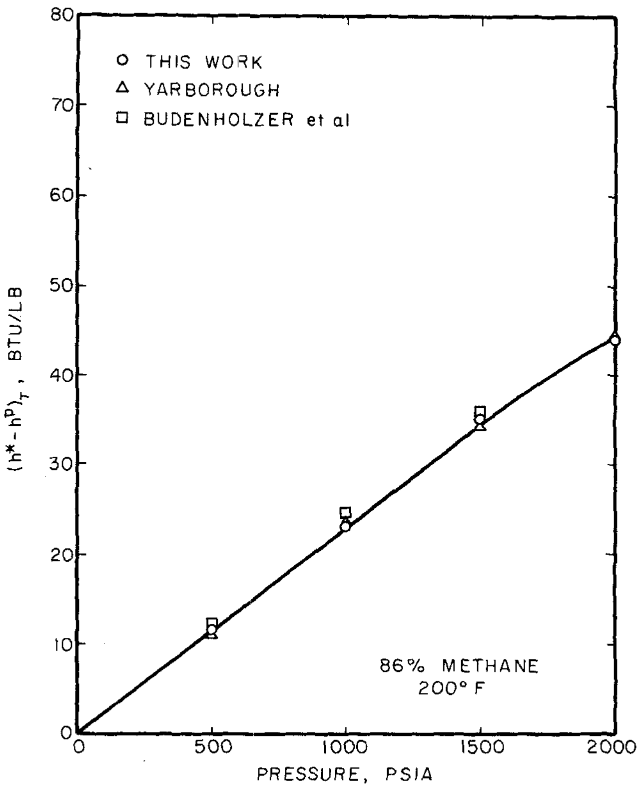


Fig. 8. Enthalpy of methane-propane mixture at 200°F.

Table 3. Comparison of Calculational Methods

Mole % Methane	Temp. °F.	Pressure lb./sq.in. abs.	Smoothed Exp. Value	$\Delta h = (h^* - h^p)_T$, B.t.u./lb. Method A*	Method B†	Method C‡
100	150	500	11.4	10.63	11.10	11.8
100	150	1,000	22.7	20.97	22.17	22.4
100	150	1,500	33.8	30.67	32.87	35.0
100	150	2,000	42.2	39.38	42.78	43.6
94	90	500	15.0	15.34	14.90	14.4
94	90	1,000	30.3	31.10	30.52	30.9
94	90	1,500	45.9	46.34	46.07	47.3
94	90	2,000	60.5	59.72	60.22	59.6
94	150	500	12.5	12.48	12.01	12.3
94	150	1,000	24.5	24.79	24.14	25.1
94	150	1,500	36.1	36.46	35.92	37.0
94	150	2,000	44.3	46.89	46.79	47.3
94	200	500	10.0	10.67	10.24	10.7
94	200	1,000	19.8	20.98	20.36	21.4
94	200	1,500	29.1	30.63	30.06	31.2
94	200	2,000	35.8	39.28	39.02	39.9
86	90	500	17.3	17.2	17.5	15.8
86	90	1,000	35.6	35.7	36.6	33.6
86	90	1,500	53.5	54.0	55.9	52.6
86	90	2,000	71.4	69.5	72.5	69.2
86	150	500	14.1	14.0	13.9	13.0
86	150	1,000	28.1	28.1	28.3	27.3
86	150	1,500	42.2	41.7	42.4	40.9
86	150	2,000	55.0	53.8	55.2	53.0
86	200	500	11.5	11.9	11.8	11.3
86	200	1,000	23.1	23.7	23.6	22.5
86	200	1,500	34.7	34.8	35.0	33.5
86	200	2,000	44.8	44.8	45.5	43.4

* Calculated via Redlich-Kwong equation of state.
† Calculated via Benedict-Webb-Rubin equation of state.
‡ Calculated via Pitzer's generalized corresponding states correlation.

CONCLUSIONS

The isothermal effect of pressure on the enthalpy of methane, a 5.1 mole % propane in methane mixture, and a 12.6 mole % propane in methane mixture was determined by means of isothermal flow calorimetry. The study covered the range 90 to 200°F. and 500 to 2,000 lb./sq. in. abs. The results are believed to be precise to within ± 2 B.t.u./lb.

Comparison of results with values from other experimental data showed good general agreement. Both the volumetric data of Sage and Lacey, and the Joule-Thomson data of Budenholzer, et al. yield enthalpies in substantial agreement with the present work. The Mollier charts from work at the University of Michigan are in poorer agreement with the data of this work, particularly at high pressures.

Comparisons of the experimental data with calculated enthalpies by using the Redlich-Kwong and Benedict-Webb-Rubin equations of state and Pitzer's corresponding states correlation showed close agreement. The equations of state and Pitzer's correlation predicted enthalpy values usually within 2 B.t.u./lb. of the experimental results, demonstrating the applicability of these predictive techniques in the range of conditions covered by this study.

ACKNOWLEDGMENT

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NOTATION

H = enthalpy, B.t.u./lb. mol.
h = enthalpy, B.t.u./lb.

Superscripts and Subscripts

o = calorimeter outlet pressure
p = calorimeter inlet pressure
T = run temperature
$*$ = ideal gas state

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Condensation from Superheated Gas-Vapor Mixtures

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Superheated mixtures of vapor and noncondensable gas were cooled and condensed in downflow inside a single tube vertical condenser, 0.995 in. I.D. and 3.5 ft. long. The systems studied were air-water, carbon dioxide-water and helium-water. A bulk stream mixing probe was developed which enabled the measurement of point values of the stream temperature and partial pressure at various positions within the condenser. The Reynolds number range of the investigation was 5,700 to 34,000.

A theoretical solution of the problem, using Bras' design method, was solved rigorously on a digital computer. Results indicated excellent agreement between the theoretical and experimental cooling paths and the required transfer area. The inclusion of the Ackerman correction factor (for the sensible heat carried by the diffusing vapor) into the calculation gave significantly better agreement for all cases tested.

When a superheated vapor-gas mixture is contacted with a surface below its dew point, condensation will take place. Owing to the presence of the non-condensable component, the mechanism of the phenomena becomes one of simultaneous heat and mass transfer. Due to this parallel transfer, the changes in the mixture temperature

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