Enthalpy of Gaseous Methane in Range 224.00–366.70K and 1–100 bar

Richard A. Dawe[1] **and Peter N. Snowdon**
Chemical Engineering Department, Leeds University, Leeds LS2 9JT, United Kingdom

The enthalpy-pressure behavior for methane in the vapor phase is determined with a method based on measurements of the Joule-Thomson throttling effect. Data along six isotherms at 224.00, 247.50, 273.15, 298.15, 333.25, and 366.70K are measured. The experimental data and derived enthalpies are reported as polynomial functions of pressure up to a maximum of 100 bar. The enthalpy values are believed to be precise to within ±5 J mol^{-1}. Comparisons are made with the calorimetric data of Jones et al., the derived enthalpies from the equation of state of Vennix et al., and the values calculated by Harrison et al. from the accurate p-V-T work of Douslin et al.

The literature describing experimental measurements of the physical properties of methane is extensive, but there are many discrepancies. The compilation by Tester (*17*) summarizes many of these disagreements and deficiences. Recently, there have been accurate low-temperature p-V-T measurements by Vennix et al. (*19*) and Roe (*16*) and at higher temperatures by Douslin et al. (*6*). Goodwin and Prydz (*8–10, 15*) have measured the vapor pressure and compressed liquid densities. Vennix and Kobayashi (*20*), Goodwin and Prydz (*10*), and Bender (*1*) have presented multiconstant equations of state, covering a wide range of density, by use of p-V-T data of several authors. From these and the complete literature survey to 1968 of heat capacity measurements by Touloukian and Makita (*18*), it is clear that there is only one set of direct, accurate, calorimetric measurements of the enthalpy of methane vapor with which to compare the values derived from these equations of state (*13*). However, these measurements were made on methane only 99.45% pure, which rather limits their usefulness for accurate comparisons.

This paper reports measurements of the Joule-Thomson throttling effect and derived enthalpies for methane gas over six isotherms covering the range 224.00–366.70K and 1–100 bar.

Experimental

The Joule-Thomson effect is the temperature change undergone by a gas or gas mixture during adiabatic throttling. The process is isenthalpic; therefore,

$$H(p, T_1) = H(p_A, T_2) \tag{1}$$

where $H(p, T_1)$ and $H(p_A, T_2)$ are the enthalpies of the gas before and after expansion. In this work the expansion is to atmospheric pressure, p_A, and $H(p_A, T_2)$, the enthalpy at atmospheric pressure, can be calculated with considerable confidence.

A simple apparatus has been developed for the fast accurate measurement under steady flow conditions of the Joule-Thomson throttling effect. Design features incorporated into the unit are low gas consumption and a rapid attainment of equilibrium so that a substantial number of measurements can be obtained from a single supply cylinder. In addition, care has been taken to achieve the smallest possible heat leaks and simple but accurate measurements of the temperatures and pressures. Full details of the apparatus, experimental procedure, and interpretation of results have been described in previous publications (*2–5*).

Basically, the expansions were carried out in a small bore tube packed with solid particles and enclosed within an evacuated chamber. This gave the expansion unit a portable robust structure which can easily be accommodated in a small thermostat bath. The gas was regulated to the desired inlet pressure and then brought to the required inlet temperature by passing through a copper coil immersed in the thermostat containing the expansion apparatus. Three expansion units were used to cover the inlet pressure range 1–100 bar, so that the flow rates at atmospheric conditions were kept within 1–7 l. min^{-1}. The units are identical except for the size of powder used to pack the tube. A degree of overlap of inlet pressure ranges provides a means of measuring the expansion effect in different units at different flow rates, thereby checking the precision of the results. The temperatures of the inlet and outlet gas close to the expansion zone were measured by calibrated platinum resistance thermometers, and the inlet pressure was measured by a calibrated Bourdon test gauge.

Methane gas (99.95% methane, supplied from L'Air Liquide, Paris, France, by Gas and Equipment Ltd., Edgmond, Salop., UK) was used direct from a high-pressure cylinder. No significant impurities were found on analysis by gas chromatography.

Joule-Thomson Throttling Results

Six isotherms, namely 224.00, 247.50, 273.15, 298.15, 333.25, and 366.70K, have been measured. The first two cover the pressure range 1–85 bar and the others to 1–100 bar.

The measured temperature change ΔT $(= T_1 - T_2)$, where T_1 and T_2 are the inlet and outlet temperatures, respectively, is corrected for minor heat leaks caused by radiation, for kinetic energy effects and for small variations in inlet temperature. These corrections have been discussed fully previously (*2–5*). Typical experimental data and the corrections applied are given in Table I. For a constant inlet temperature T_1, the values of ΔT are correlated as a power series in inlet pressure p, by least-squares regression analysis, so that the experimental precision and reproducibility may be examined and interpolation of measurements at convenient pressures performed.

These equations reproduce the results, except for one case, within a mean deviation of 0.03K, which is the expected experimental error. This is also the most economical way of storing the data. Values of ΔT, and hence T_2, may then be obtained at any desired inlet pressure. Details of the regression coefficients for the six isotherms are given in Table II. The precision of the experimental data is believed to be better than 0.05K. Full details of all the experimental results and their analysis have been deposited with the National Engineering Laboratory, East

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[1] To whom correspondence should be addressed.

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Enthalpy

High-pressure enthalpies along the isotherm, T_1, may be obtained from Equation 1 with the values of ΔT given by the regression coefficients in Table II and values of atmospheric enthalpies at temperature T_2.

Atmospheric enthalpy. Experimental values of the atmospheric heat capacity of methane are scattered, especially below 300K (*17, 18*). Therefore, the enthalpies at atmospheric pressure have been calculated, relative to the ideal gas state at 273.15K, by integration of the ideal gas heat capacity between 273.15K and T_2, followed by a correction at T_2 for the nonideal behavior between the ideal gas state and atmospheric pressure, as shown in Equation 2:

$$\{H(p_A, T_2) - H(0, 273.15\text{K})\} = \int_{273.15K}^{T_2} C_p{}^\circ \, dT + \int_0^{p_A} \{(V - T_2(\partial V/\partial T)_p\} \, dp \quad (2)$$

These enthalpy values were then fitted to a polynomial to obtain a continuous function in temperature.

The ideal gas heat capacity values were calculated from the spectroscopic constants given by McDowell and Kruse (*14*), or in JANAF 1971 (*12*), at 1K intervals over the range 150–430K and then fitted to a cubic polynomial, Equation 3:

$$C_p{}^\circ/R = 4.56383 - 7.11804 \times 10^{-3}(T/\text{K}) + 2.42089 \times 10^{-5}(T/\text{K})^2 - 1.13273 \times 10^{-8}(T/\text{K})^3 \quad (3)$$

where R is the gas constant. The values from Equation 3 are in excellent agreement with JANAF 1971 and in reasonable agreement with those of Goodwin (*8*).

The corrections for nonidealities were made with the virial equation of state with the values of the second and third virial coefficients and their derivatives being estimated by the correlation of Zellner et al. (*22*). The use of a correlation has the advantage that values of B, (dB/dT), C, and (dC/dT) are available at any temperature, whereas tabulated data are not. The values of the coefficients obtained are, in any case, in good agreement with values given in recent compilations (*1, 7*).

The atmospheric enthalpies were calculated at 1K intervals, and a smooth polynomial in T was fitted through them. The result was Equation 4:

$$\{H(p_A, T_2) - H(0, 273.15\text{K})\}/\text{J mol}^{-1} = -9585.28 + 39.37112(T/\text{K}) - 3.34562 \times 10^{-2}(T/\text{K})^2 + 7.06880 \times 10^{-5}(T/\text{K})^3 - 2.35446 \times 10^{-8}(T/\text{K})^4 \quad (4)$$

The enthalpy at atmospheric pressure can then be readily obtained at any required temperature.

Table III gives selected values for the ideal and atmospheric heat capacity, the second and third virial coefficients, and the atmospheric enthalpy obtained by calculation and used in this work. The values must be treated with a little caution in the absence of further experimental measurements, but they are thought to be as accurate as available data permit.

Enthalpies above atmospheric pressure. The values of the enthalpy at 1 bar intervals along the six isotherms

Table I. Typical Experimental Values and Corrections Applied for Methane[a]

Unit	p, bar	T_1, K	T_2, K	f, l. min^{-1}	T_{in}, K	T_{rad}, K	T_{ke}, K	ΔT, K	dT, K
1 Low	9.65	298.32	294.54	2.8	0.01	0.00	0.00	3.79	0.00_1
	19.34	298.29	290.15	6.5	0.01	0.00	−0.03	8.12	0.00_4
2 Medium	22.10	298.29	289.00	1.2	0.01	0.07	0.00	9.37	-0.00_3
	31.16	298.28	284.78	2.1	0.01	0.06	0.00	13.57	-0.04_5
	42.66	298.23	279.44	3.0	0.01	0.06	−0.01	18.85	0.01_2
3 High	42.38	298.21	279.54	1.3	−0.01	0.04	0.00	18.70	0.03_4
	53.20	298.20	274.37	2.1	−0.01	0.03	0.00	23.85	-0.01_0
	62.72	298.16	269.84	2.8	0.00	0.03	0.00	28.35	0.01_1
	73.41	298.15	264.69	3.2	0.00	0.03	−0.01	33.48	-0.01_7
	83.75	298.13	259.74	3.7	−0.01	0.03	−0.01	38.40	-0.00_6
	93.26	298.08	255.20	4.0	−0.03	0.03	−0.01	42.87	0.00_4
	101.54	298.08	251.36	4.5	−0.03	0.03	−0.01	46.71	0.00_4
	1.013	298.15	298.15	...	...	...	...	...	0.00_0

[a] For the isotherm 298.15K, of the inlet pressure p, inlet and outlet temperatures, T_1 and T_2, respectively, flow rate f measured at atmospheric pressure and 293K, and the corrected value of the Joule-Thomson effect, ΔT $(=T_1 - T_2)$. The corrections applied are T_{in} to correct for the conditions not being exactly at the isotherm 298.15K, T_{rad} for radiation, and T_{ke} for kinetic energy effects. dT is the difference between ΔT and the value given by the polynomial whose coefficients are given in Table II.

Table II. Regression Coefficients for Joule-Thomson Throttling Effect, ΔT, for Methane When Expanded from T and p to Atmosphere Pressure (1.0132 bar)[a]

T, K	No. of points	Mean dev T, K	p_{max}, bar	a	b	$c \times 10^4$	$d \times 10^6$	$e \times 10^8$
366.70	12	0.02_6	100	−0.27416	0.27159	1.05962	−1.24527	....
333.25	12	0.01_9	100	−0.34432	0.34019	2.34839	−1.64100	....
298.15	13	0.01_4	100	−0.44166	0.43461	4.27312	0.70131	−1.98714
273.15	13	0.01_5	100	−0.52636	0.51829	8.82472	0.60135	−2.66419
247.50	12	0.02_0	80	−0.64256	0.63278	11.36580	12.33009	−7.53303
224.00	15	0.05_2	85	−0.78261	0.77073	9.25119	58.49603	−24.05202

[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.

Table III. Values of Ideal Gas Heat Capacity, $C_p°$, Second and Third Virial Coefficients, Atmospheric Heat Capacity, C_{pA}, and Atmospheric Enthalpies Used in This Work

T, K	$C_p°$, R	−B, cc mol^{-1}	C (cc mol^{-1})^2	C_{pA}, R	$\{H(p_A, T) - H(0, 273.15K)\}$, J mol^{-1}
150	4.002	181	4736	4.065	−4206
200	4.018	105	3932	4.055	−2521
250	4.120	65.7	2957	4.140	−821
273.15	4.195	53.5	2637	4.210	−17
300	4.301	42.0	2340	4.311	933
350	4.552	26.1	1950	4.557	2774
400	4.865	14.9	1692	4.872	4732

Table IV. Regression Coefficients Describing Enthalpy of Methane at p and T Relative to Ideal Gas at 273.15K[a]

T, K	p_{max}, bar	a	b	$c \times 10^2$	$d \times 10^4$	$e \times 10^6$
367.70	100	3423.80	−10.5213	−0.2015	0.4554	. . .
333.25	100	2158.20	−12.6461	−0.5908	0.5783	. . .
298.15	100	882.41	−15.5526	−1.2232	−0.1667	0.6468
273.15	100	0.70	−18.1433	−2.7348	−0.0819	0.8340
247.50	80	−884.94	−21.7460	−3.5816	−3.9462	2.3718
224.00	85	−1683.20	−26.1351	−3.1366	−18.7209	7.1046

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

Table V. Comparison Between Values of Enthalpy, in J mol^{-1}, of Methane for This Work, Denoted D, and Those Computed from Equation of State of Vennix et al. (*20*), Denoted V[a]

		T, K					
p, bar		224.00	247.00	273.15	298.15	333.25	366.70
		$\{H(0, 273.15K) - H(0, T)\}$/J mol^{-1}					
0.0		1683	885	0	−882	−2158	−3424
		$\{H(0, 273.15K) - H(p_A, T)\}$/J mol^{-1}					
1.013		1710	907	17	−867	−2146	−3413
		$\{H(p_A, T) - H(p, T)\}$/J mol^{-1}					
1.013	D	0	0	0	0	0	0
	V	0	0	0	0	0	0
10	D	240	199	166	141	115	95
	V	230	194	164	142	117	97
20	D	522	430	356	301	243	200
	V	506	420	352	303	248	204
30	D	830	671	551	462	370	307
	V	809	657	545	465	378	313
40	D	1170	924	750	626	500	410
	V	1143	907	743	629	508	420
50	D	1548	1189	954	791	628	515
	V	1516	1170	947	794	638	525
60	D	1967	1466	1156	956	775	618
	V	1936	1446	1152	960	766	630
70	D	2428	1754	1369	1123	882	720
	V	2407	1733	1361	1125	895	733
80	D	2932	2052	1579	1289	1008	821
	V	2914	2031	1571	1291	1021	834
90	D	. . .	. . .	1788	1453	1131	920
	V	3403	2329	1781	1454	1145	933
100	D	. . .	. . .	1995	1614	1253	1016
	V	3809	2624	1989	1615	1267	1031

[a] The comparison is between the value at atmospheric pressure and that at the high pressure, i.e., $\{H(p_A, T) - H(p, T)\}$. Also included are the values of the enthalpy at zero pressure and atmospheric pressure relative to the standard state for this work, the ideal gas at 273.15K, i.e., $\{H(0, 273.15K) - H(0, T)\}$ and $\{H(0, 273.15K) - H(p_A, T)\}$

have been calculated from Equations 1 and 4 and the values of ΔT calculated from the regression coefficients of Table II. These values have been fitted to polynomials in pressure, which reproduce the measurements to within 0.08 J mol^{-1}, i.e., with no loss in precision. The regression coefficients for these polynomials are given in Table IV, and selected enthalpies along the isotherms are given in Table V. All the polynomial equations give entirely satisfactory results for interpolation but should not be used outside the ranges indicated. Some caution is necessary in differentiating the expressions [e.g., to obtain $(\partial H/\partial P)_T$], since the aim here has been to minimize deviations from the primary variable. Other numerical methods should be considered to obtain derived quantities.

The uncertainties in the enthalpies presented are due to errors in the polynomials representing the Joule-Thomson measurements given in Table II and also inaccuracies in the atmospheric pressure enthalpy relationship of Equation 4. An error of 0.05K in the observed temperature difference would cause an error of approximately 2 J mol^{-1} in the enthalpy, and an error of 0.1 bar in pressure would cause an error of approximately 3 J mol^{-1}.

Thus, with our experimental equipment it is believed that the enthalpies in this work have a precision of better than 5 J mol^{-1} but have a potential inaccuracy arising from Equation 4. Any inaccuracies in Equation 4 cannot be quantified until further experimental determinations of the atmospheric heat capacity of methane have been made, but their effects on the absolute accuracy of the enthalpies reported here can be approximately assessed.

For example, if there were a constant error in the atmospheric heat capacity values used in this work of 0.1 J mol^{-1} K^{-1} (about 0.2%), and if ΔT/K = 40.0, then the error in the high-pressure enthalpy values relative to the standard state of 273.15K owing to this cause will be 6 J mol^{-1}, 4 J mol^{-1}, and 9 J mol^{-1} at inlet temperatures of 373.15, 273.15, and 223.15K, respectively. However, the precision in the data reported here is ±5 J mol^{-1}, and should Equation 4 be found to be inaccurate, the enthalpy values obtained from the Joule-Thomson throttling data of Table II can readily be revised. The enthalpies calculated from equations of state give only isothermal effects of pressure on the enthalpy (the so-called residue enthalpy) and also need heat capacity data as a function of temperature along one isochore or isobar to complete the H-p-T diagram. Thus, the absolute accuracy of these tables derived from p-V-T data are also doubtful until further heat capacity values are measured.

Comparison with Other Studies

Table V compares our values with those computed from the equation of state of Vennix et al. (*20, 21*) along our isotherms, with the reference state being atmospheric pressure at the isotherm temperature. There is good agreement. The experimental data of Jones et al. (*13*) have also been compared, but owing to the impurities in

Table VI. Comparison Between Results of This Work Calculated from Polynomials Given in Table IV and Those of Harrison et al. (*11*), Corrected to Same Units as Those Used in This Work. Values Compared Are Residual Enthalpies $\{H(0, T) - H(p, T)\}$

$\{H(0, T) - H(p, T)\}$/J mol^{-1}					
273.15K			298.15K		
p, bar	Dawe	Harrison	p, bar	Dawe	Harrison
16.38	304	304	18.02	284	284
21.56	403	403	23.79	377	377
31.54	599	597	35.00	559	558
41.05	789	787	45.61	737	736
50.14	974	972	56.27	910	908
58.84	1154	1152	66.42	1079	1076
67.22	1329	1327	76.31	1244	1240
75.31	1498	1498	86.00	1403	1399
83.16	1663	1664	95.52	1558	1554
90.80	1822	1825			
98.32	1978	1981			

the methane used by these workers, and since they reported their data along different isotherms, a detailed comparison cannot be very fruitful. However, where the data overlap, on the average their values of $\{H(p, T_1) - H(0, T_1)\}$ when compared with ours are often some 2–3% smaller. A fuller comparison has been given by Vennix et al. (*21*), but no mention is made in their report of whether they took account of the impurities.

Table VI compares our values with those presented by Harrison et al. (*11*) at 273.15 and 298.15K, which have been calculated from the accurate p-V-T data of Douslin et al. (*6*). The agreement is excellent, being always within 4 J mol^{-1}. A comparison at other temperatures using suitable graphical interpolations also shows excellent agreement throughout the range of overlap of this work and that of Harrison et al.

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