Enthalpy of Gaseous Mixtures of Methane + Ethane + Carbon Dioxide under Pressure

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The residual enthalpies of two mixtures of CH_4 + C_2H_6 + CO_2 have been determined from isothermal throttling measurements at temperatures between −10 and 90 °C at pressures up to 137 bar. The results were compared with currently used methods of prediction based on equations of state and the principle of corresponding states.

Enthalpy data for mixtures of hydrocarbons and nonhydrocarbons are needed for the design of gas processing equipment. As well, experimental data can be used to test methods of prediction of enthalpies and to improve correlations. A number of methods can be used to determine the effect of pressure on the enthalpy of mixtures. A direct measure of this effect is obtained from measurements of the isothermal throttling coefficient, ϕ

$$\phi \equiv \left(\frac{\partial H}{\partial P}\right)_T \qquad (1)$$

Integration of the experimental values of ϕ with respect to pressure yields the residual enthalpy

$$(H^\circ - H)_T = -\int_0^P \phi \, dP \qquad (2)$$

Experimental Section

The experimental apparatus and procedure have been described previously (*11*) and only a summary is presented here. The mixture is brought to the experimental conditions of pressure and temperature using a recycle system employing a diaphragm compressor. The fluid enters the calorimeter, which consists of a capillary coil about 3 m in length. Depending upon the flow rate, the pressure drop caused by the capillary is 10–15 bar. This pressure drop would usually cause a drop in temperature of the flowing fluid. An insulated Nichrome wire placed coaxially inside the capillary is used to dissipate electrical energy and to match the outlet temperature with that of the inlet. Duplicate multijunction differential thermopiles are employed to indicate temperature equality. The pressure drop is measured by a calibrated pressure transducer and the electrical energy supplied determined by voltage measurements using standard resistors. The flow rate of the mixture is measured by a calibrated orifice meter located in the recycle system.

The compositions of the two mixtures are given in Table I. The error in the isothermal throttling coefficient is directly dependent upon errors in the determination of the mass flow rate, the power input, and the pressure drop. Errors in the absolute pressure, temperature, and compositions result in uncertainty in the state at which the measurement was made. The present results are estimated to be accurate to ±1.2% considering errors in the mass flow rate (0.5%), power input (0.1%), and pressure drop (0.6%). This estimate depends somewhat on the pressure level.

Results and Discussion

Measurements of the isothermal effect of pressure on enthalpy were made along six isotherms between −10 and 90 °C. The pressure range of these measurements was 20–140 bar.

Table I. Compositions of the Mixtures

	Mole fraction	
	A	B
Methane	0.340	0.514
Ethane	0.325	0.242
Carbon dioxide	0.335	0.244
	1.000	1.000

The raw data are available in a thesis (*13*) and Figure 1 shows the results for mixture A. The bars, shown on the 0 °C isotherm, indicate the average value of ϕ over the pressure range of the experiment. A smooth curve is drawn through the bars so that the area under the curve is equal to the area underneath the bar. For data containing error, the spline fit technique of Klaus and Van Ness (*7*) was used to prepare the smooth curves. The curves have been extended to zero pressure to agree with the value of ϕ° estimated from second virial coefficients. The second virial coefficients for the pure components were obtained from Dymond and Smith (*3*), while values of the interaction virial coefficient B_{ij} for CH_4–CO_2 and C_2H_6–CO_2 were obtained from Ng (*12*); for CH_4–C_2H_6, B_{ij} were taken from Hoover et al. (*5*), Gunn (*4*), and Dantzler et al. (*2*). The smoothed values of ϕ for the two mixtures are presented in Tables II and III. The smoothed values of ϕ obtained from the spline fit were integrated with respect to pressure using Simpson's rule to obtain residual enthalpies. Residual enthalpies for mixture A are compared with the results of Peterson and Wilson (*14*) in Figure 2. Although their data are for an equimolar mixture, the present data for mixture A are seen to be in good agreement with their results.

The values of ϕ for mixture A at the lowest temperatures are relatively large. This is a result of the proximity of the two-phase region and, at high pressures, the critical point for this mixture. All experimental values were obtained in the single phase gaseous region because two-phase flow results in severe pressure fluctuations in the calorimeter. The isothermal throttling coefficients for mixture B are much lower than those for mixture A because the increased methane concentration shifts the phase envelope to lower temperatures.

Comparison of Methods of Prediction

In a recent comparison of enthalpy prediction methods, Tarakad and Danner (*18*) chose six methods for detailed evaluation: 1. the Curl-Pitzer (*1*) tables with the mixing rule of Kay (*6*) (CPK), 2. the Curl-Pitzer (*1*) tables with the mixing rule of Stewart, Burkhardt, and Voo (*17*) (CPSBV), 3. the equation of state of Lee, Erbar, and Edmister (*8*), 4. the Soave (*15*) modification of the Redlich-Kwong equation of state (SRK), 5. the Starling (*16*) modification of the Benedict-Webb-Rubin equation (BWRS), 6. the Lee and Kesler (*9*) three parameter corresponding states correlation (LK).

For comparison with the present experimental values, we have deleted Lee-Erbar-Edmister and instead considered the corresponding states correlation of Mollerup (*10*), together with the other five methods. The Lee-Erbar-Edmister equation was not considered since it was found to be inaccurate by Tarakad and Danner. The residual enthalpies obtained from the experimental results are compared with those of the six methods of prediction in Tables IV and V for mixtures A and B, respectively.

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Table II. Isothermal Throttling Coefficients for Mixture A

Pressure, bar	$-\phi$, J mol^{-1} bar^{-1}					
	−10 °C	0 °C	20 °C	40 °C	60 °C	90 °C
0[a]	41.80	40.20	34.60	30.40	26.80	22.60
10	46.83	42.87	36.39	31.39	27.55	22.92
20	52.83	47.40	38.99	32.96	28.46	23.41
30	63.32	54.16	42.18	34.74	29.55	23.93
38	77.29					
40		64.55	46.22	36.66	30.67	24.42
50		80.96	51.50	39.01	31.82	24.86
60		114.5	58.09	41.64	32.97	25.25
70		142.2	65.04	44.16	34.06	25.59
80		99.01	70.61	46.13	34.91	25.83
90		48.30	70.55	47.17	35.34	25.90
100		29.57	60.75	46.76	35.19	25.77
110		19.19	46.50	44.34	34.46	25.43
120		14.30	34.92	39.75	33.29	24.89
130		10.94	26.25	34.36	31.38	24.15
137		8.86	21.67	30.83	29.31	23.52

[a] $B - T(\mathrm{d}B/\mathrm{d}T)$.

Table III. Isothermal Throttling Coefficients for Mixture B

Pressure, bar	$-\phi$, J mol^{-1} bar^{-1}					
	−10 °C	0 °C	20 °C	40 °C	60 °C	90 °C
0[a]	36.20	32.80	28.80	25.20	22.30	18.68
10	38.62	35.15	30.25	26.18	22.86	19.12
20	41.83	37.85	31.67	27.21	23.52	19.39
30	46.46	41.24	33.26	28.11	24.10	19.67
40	53.62	45.52	35.31	29.09	24.66	19.95
50	64.00	51.01	37.77	30.13	25.20	20.21
60	79.37	58.01	40.32	31.18	25.71	20.40
70	94.67	66.39	42.60	32.12	26.14	20.49
80	90.73	70.53	44.28	32.80	26.43	20.48
90	61.32	64.61	44.89	33.09	26.51	20.37
100	37.81	52.58	43.74	32.85	26.32	20.19
110	26.03	39.36	40.45	31.96	25.86	19.95
120	18.30	27.82	35.70	30.34	25.12	19.62
130	13.35	20.13	30.33	28.15	24.05	19.14
137	11.45	17.41	26.67	26.47	23.08	18.68

[a] $B - T(\mathrm{d}B/\mathrm{d}T)$.

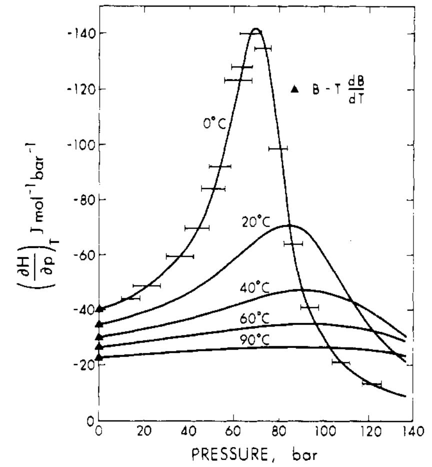

Figure 1. Isothermal throttling coefficients for mixture A.

The BWRS, SRK, and Mollerup methods are equivalent in their ability to predict the residual enthalpies of these mixtures of methane, ethane, and carbon dioxide. One surprising result is the relatively large deviations of the LK method. Tarakad and Danner (*18*) found that it was the best in their comparison with hydrocarbon systems.

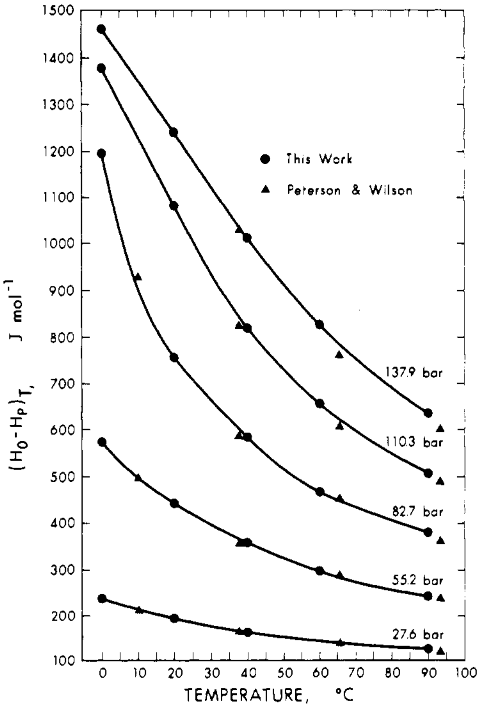

Figure 2. Comparison of residual enthalpies for mixture A with the data of Peterson and Wilson.

Glossary

B	second virial coefficient, cm^3 mol^{-1}
H	enthalpy, J mol^{-1}
$H°$	ideal gas enthalpy, J mol^{-1}
P	pressure, bar

Table IV. Residual Enthalpies for Mixture A Compared with Methods of Prediction

		$(H^\circ - H)_T$/J mol^{-1}						
T/K	P/bar	This work	CPK (*1, 6*)	CPSBV (*1, 17*)	M (*10*)	SRK (*15*)	BWRS (*16*)	LK (*9*)
363.15	30	722	648	652	693	725	699	730
	70	1715	1690	1698	1683	1739	1709	1798
	100	2489	2570	2581	2453	2504	2497	2654
	130	3242	3420	3424	3194	3223	3252	3497
	137	3409	3596	3602	3358	3373	3416	3682
333.15	30	841	795	799	838	865	852	886
	70	2113	2147	2157	2115	2156	2162	2279
	100	3163	3308	3324	3165	3188	3241	3484
	130	4175	4397	4399	4172	4146	4239	4630
	137	4388	4621	4617	4386	4332	4440	4859
313.15	30	967	938	943	965	983	989	1025
	70	2534	2637	2647	2548	2565	2622	2778
	100	3924	4207	4207	3946	3924	4051	4443
	130	5174	5523	5494	5223	5095	5224	5802
	137	5402	5763	5723	5456	5290	5430	6032
293.15	30	1135	1163	1165	1128	1131	1169	1207
	70	3227	3478	3500	3255	3219	3373	3655
	100	5285	5822	5805	5399	5221	5395	6174
	130	6528	6998	6946	6643	6389	6518	7327
	137	6695	7163	7105	6797	6529	6680	7474
273.15	30	1373	1451	1452	1353	1327	1419	1461
	70	4961	6218	6089	5142	4956	5224	6866
	100	7299	7930	7859	7525	7162	7334	8344
	130	7827	8441	8370	7984	7733	7871	8674
	137	7896	8507	8431	8048	7787	7941	8720
263.15	30	1515	1654	1661	1502	1453	1587	1633
$\|(H^\circ - H)_{\mathrm{exptl}} - (H^\circ - H)_{\mathrm{calcd}}\|$			286	268	56	52	56	466

Table V. Residual Enthalpies for Mixture B Compared with Methods of Prediction

		$(H^\circ - H)_T$/J mol^{-1}						
T/K	P/bar	This work	CPK (*1, 6*)	CPSBV (*1, 17*)	M (*10*)	SRK (*15*)	BWRS (*16*)	LK (*9*)
363.15	30	577	561	562	577	605	579	590
	70	1384	1381	1377	1377	1424	1388	1424
	100	1996	2067	2059	1981	2024	2001	2067
	130	2588	2724	2711	2560	2585	2585	2694
	137	2720	2866	2852	2688	2702	2713	2833
333.15	30	696	643	641	694	720	700	711
	70	1703	1687	1679	1701	1741	1723	1767
	100	2495	2574	2562	2493	2518	2526	2619
	130	3257	3386	3366	3247	3241	3282	3445
	137	3422	3564	3543	3411	3388	3443	3622
313.15	30	801	738	735	794	815	806	816
	70	2006	1997	1986	2006	2032	2041	2093
	100	2991	3075	3055	2998	2998	3049	3180
	130	3921	4038	4006	3934	3879	3963	4195
	137	4112	4234	4202	4130	4047	4145	4396
293.15	30	930	881	877	921	930	943	950
	70	2443	2470	2449	2447	2443	2503	2573
	100	3770	3893	3849	3787	3730	3849	4075
	130	4905	5030	4969	4957	4794	4912	5265
	137	5104	5230	5172	5161	4964	5096	5466
273.15	30	1099	1095	1088	1088	1084	1126	1129
	70	3179	3343	3317	3204	3131	3290	3438
	100	5143	5396	5327	5275	5027	5180	5663
	130	6172	6382	6315	6279	6014	6142	6646
	137	6302	6513	6450	6404	6127	6278	6773
263.15	30	1214	1219	1214	1195	1177	1244	1243
	70	3886	4341	4274	3921	3778	4013	4364
	100	6098	6357	6270	6291	5934	6075	6713
	130	6779	7063	6985	6913	6648	6787	7310
	137	6865	7141	7069	6993	6720	6880	7385
$\|(H^\circ - H)_{\mathrm{exptl}} - (H^\circ - H)_{\mathrm{calcd}}\|$			125	93	39	60	30	230

T temperature, K
ϕ isothermal throttling coefficient, J mol^{-1} bar^{-1}

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Solubility of Hydrogen in α-Methylstyrene

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Prior studies of the solubility of hydrogen in α-methylstyrene at atmospheric pressure give results that differ by 30 to 40%. In an attempt to resolve this deviation, solubilities were measured from 15 to 74 °C. The results, which were reproducible within 3%, fall about midway between the earlier data.

The liquid-phase, catalytic hydrogenation of α-methylstyrene to cumene is often used as a model reaction for reactor studies, for example, in fixed (*1*, *2*, *4*) and in trickle beds (*5*). An accurate value of the hydrogen concentration in the liquid styrene is necessary for quantitative interpretation of such reactor investigations. However, reported solubilities (*3*, *5*) differ by 30–40% possibly because such low concentrations are difficult to measure accurately. In an attempt to resolve this uncertainty, we have carefully measured the solubility at atmospheric pressure of hydrogen over the temperature range 15–74 °C.

Experimental Section

The saturated solutions were prepared from α-methylstyrene (Dow Chemical Co.) with a stated purity of 99.2% and hydrogen (Liquid Carbonic Corp.) with a stated purity of 99.99%. The liquid was saturated at atmorpheric pressure by bubbling pure H_2 for at least 10 h through 800 cm^3 of styrene contained in a 1000-cm^3 Pyrex flask. The flask was immersed in a water bath whose temperature could be controlled to ±0.1 °C. To test the assumption of saturation, measurements were made first at successively higher temperatures and then at successively lower temperatures, with 10 h allowed for saturation at each temperature. Since the solubility was found to increase continuously with temperature, this procedure provided a means of approaching saturation first by absorption and then by desorption. The hydrogen concentration was determined by analyzing liquid samples in gas chromatographs using a 6 m long, 0.63 cm o.d. column packed with 20–40 mesh, 5A molecular sieve particles. Nitrogen was used as the carrier gas. The purity of the nitrogen (liquid Carbonation Corp.) was given as 99.996%.

A special, gastight, 50-μL Hamilton syringe was employed to withdraw 30-μL samples from the absorber. These samples were withdrawn slowly and carefully in order to avoid desorption of hydrogen. They were then immediately injected into a Model 1420 (Varian Instrument Co.) chromatograph operated at conditions also shown in Table I. The calibration procedure in this case consisted of injecting into the chromatograph 30–150-μL samples of a gas mixture containing 5.00 ± 0.03% H_2 in nitrogen, using a 500-μL, gastight Hamilton syringe. The mixture was prepared by evacuating a steel vessel, originally flushed with nitrogen, to 2 mmHg. Then hydrogen was introduced until the pressure reached 14.7 psia. Finally, nitrogen was added to bring the pressure to 294 psia.

Table I. Gas Chromatograph Operating Conditions

GC Model	1420
Column temp, °C	100
Injector temp, °C	170
Detector temp, °C	160
Detector current, mA	100
Carrier gas flow rate,[a] cm^3/min	25
Attenuator setting	2

[a] At 25 °C, 1 atm.

Table II. Experimental Results, Individual Solubility Measurements

Hydrogen Solubility, (g-mol/cm^3) × 10^6						
14.8 °C	33.8 °C	41.0 °C	48.5 °C	58.5 °C	65.5 °C	73.5 °C
2.39	2.74	2.79	3.08	3.09	3.18	3.29
2.43	2.74	2.86	3.10	3.12	3.17	3.26
2.45	2.78	2.82	3.06	3.09	3.16	3.24
2.43	2.78	2.83	3.06	3.16	3.16	3.27
	2.70	2.88	3.08	3.11	3.16	
			3.04	3.09		

Results and Discussion

In the calibration procedure, the moles of hydrogen in the gas samples were calculated by supposing ideal-gas behavior at 25 °C and 1 atm. This assumption introduced less than 0.1% error. The calibration curve was obtained by plotting moles of hydrogen vs. the area of the response peak. It is estimated that the resulting curve could be in error by a maximum of 2%. Peak area values for the samples of liquid α-methylstyrene saturated with hydrogen were then compared with the calibration curves to establish the solubility.

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