Smoothed Experimental Enthalpy Data for Four Mixtures: Three Methane–Ethane Binary Mixtures and a Ternary Mixture with Propane

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Experimental enthalpy determinations made on three methane–ethane binaries and one methane–ethane–propane ternary have been interpreted and smoothed. The resulting enthalpy values are thermodynamically self-consistent over the experimental range roughly −240 to +300 °F at pressures up to 2000 psia. Smoothed enthalpy values are presented in tabular form at the temperatures and pressures of measurement. Values of smoothed derivative functions are also given in the tables: C_p values corresponding to isobaric determinations and $\phi \equiv (\partial H/\partial P)_T$ values derived from both isothermal and isenthalpic experiments. The smoothed values are probably accurate to ±1% which makes them adequate to test most engineering correlations. The derivative properties are somewhat less accurate, ±2%, with larger deviations near the critical point of the mixtures. The most firmly established enthalpy values are included in Table I. These extend over the greater portion of the range of temperatures and pressures investigated and should be particularly suited to testing methods of predicting enthalpy both because of their accuracy and because of their scope. The original experimental data have been placed on file in the microfilm edition.

Introduction

The prediction of enthalpy differences for mixtures plays a vital role in the design of processing equipment. For identical conditions, various methods of prediction may yield values that differ markedly and it is valuable to have accurate experimental values against which to test the various methods of prediction. The calorimetric facilities in the Thermal Properties of Fluids Laboratory at the University of Michigan were developed to meet this need under the combined sponsorship of the National Science Foundation, the Petroleum Research Fund, and the Gas Processors Association. The methods that were developed to process the data combined with the fact that the basic data were taken with considerable care served to yield values of enthalpy and associated derivative properties that are thermodynamically self-consistent and appear to be quite accurate. These data for pure compounds (*8*, *11*, *13*, *16*, *33*, *36*) as well as binary (*3*, *8*, *14*, *15*, *17*, *34*, *35*, *37*) and ternary (*8*, *9*) mixtures have been used to test prediction methods (*1*, *2*, *4*, *5*, *8*, *10*, *18*, *19*, *22*, *24–29*, *31–34*, *37*, *38*) and it was thought desirable to obtain additional results of this type. Mixtures of particular interest to the natural gas processing industry were selected for study to ensure immediate applicability of the results.

Experimental Section

Equipment and Procedure. The basic principles and detailed description of equipment and procedures have been presented in detail elsewhere (*8*, *15*, *33*). The basic measurements center around flow calorimeters through which the fluid under investigation is passed. One calorimeter operates with very low pressure drops (the isobaric mode) whereas the other is designed to produce significant pressure drops (isothermal or isenthalpic operation). Electrical energy is supplied to the calorimeter and inlet and outlet temperatures and pressures are measured together with the mass flow rate. Such data are sufficient to permit determination not only of enthalpy differences but also of derivative properties as well.

Table I. Enthalpy Values at the Points of Thermodynamic Consistency[a]

Ia. Mixture 1 (52.3% C_2)

P, psia	−228.4 °F	−99.0 °F	1.75 °F	101.5 °F	252.5 °F
0		301.4	351.4	395.8	472.3
250		155.2	336.4		
500		122.2	307.9		
750		122.2	242.2		
978		122.4	214.6	348.0	
1250			206.3	331.2	
1500	38.1	123.2	203.3	316.4	433.9
2500			200.1	295.4	

Ib. Mixture 2 (22.3% C_2)

P, psia	−253.2 °F	−150.6 °F	−58.4 °F	79.0 °F	255.0 °F
0		291.7	332.4	397.1	490.8
250		129.9		388.5	
500		99.6			
1000	23.2	100.2	193.8	358.9	471.2
1500			182.8	337.8	
2000			179.1	319.4	403.3

Ic. Mixture 3 (5.55% C_2)

P, psia	−242 °F	−150 °F	−97 °F	−47 °F	79 °F	200 °F
0			319.4	343.7	407.2	
250			302.8	331.4	400.4	
500	(36.8)	115.5	279.1	316.8		
700		115.0		302.8		
800		115.0	194.9	294.7		
1000	36.1	114.5	175.6	276.3	376.8	(455.3)
1200		114.3	170.7	256.1		
1500		114.2	166.5	233.6		
2000	(36.4)	114.5	163.4	217.3	346.3	

Id. Mixture 4 (Ternary)

P, psia	−243 °F	−150 °F	−47 °F	1.5 °F	158.5 °F	300 °F
0			335.8	358.4	436.9	
250			320.0			
500	(29.8)	102.3	291.8	333.3	423.6	(508.4)
750		102.6	262.3	317.8		
1000		102.9	233.3	299.5		
1200			211.9	284.2		
1500	(34.0)	103.8	198.6	263.0	395.0	(490.8)
2000			191.7	242.5		

[a] Note: Values in parentheses are "best" values but *not* the result of duplicate determinations.

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Table II

Compositions of Standard Mixtures Used to Calibrate the Chromatograph

component	composition, mol %			
	1 (52.3%)	2 (22.3%)	3 (5.55%)	4 (ternary)
nitrogen, N_2	0.05	0.08	*a*	*a*
carbon dioxide, CO_2	0.03	0.03		
methane, CH_4	47.90	77.71		
ethane, C_2H_6	51.70	22.10		
propane, C_3H_8	0.03	0.03		
propylene, C_3H_6	0.29	0.05		
	100.00	100.00		

Nominal Compositions of the Mixtures Investigated

component	composition, mol % 1	2	3	4
methane	47.7	77.7	94.45	85.3
ethane	52.3	22.3	5.55	9.00
propane				5.70
	100.0	100.0	100.00	100.00

a Not available.

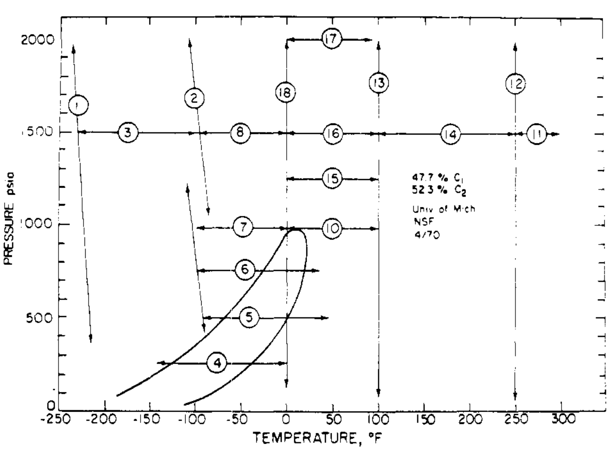

Figure 1. Pressures and temperatures of measurements for a 52.3 mol % ethane in methane mixture.

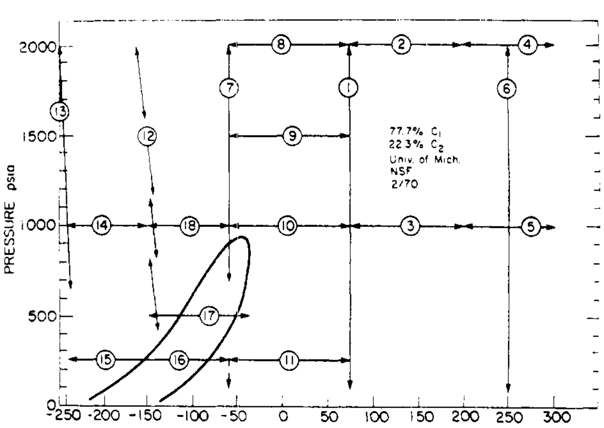

Figure 2. Pressures and temperatures of measurements for a 22.3 mol % ethane in methane mixture.

Composition. In addition to the basic data mentioned in the previous paragraph, it is essential that the composition of the mixture be known for each experiment and that the composition remains reasonably constant over the period of investigation for

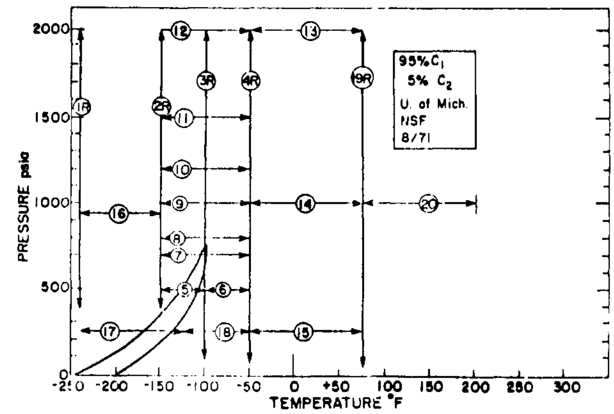

Figure 3. Pressures and temperatures of measurements for a 5 mol % ethane in methane mixture.

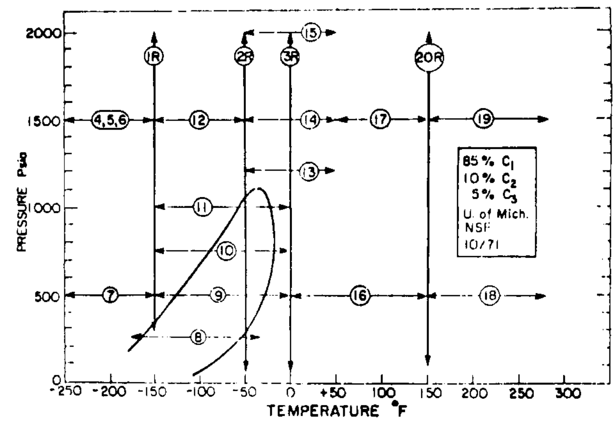

Figure 4. Pressures and temperatures of measurements for a methane–ethane–propane mixture.

Table III. Zero Pressure Enthalpy Values Based on Published Data

	mixture no. 1 (51.2% C_2)	2 (22.3% C_2)	3 (5.55% C_2)	4 (ternary)
Temp, °F	252.5	255.0	79.0	158.5
$H°_M$,[a] Btu/lb	472.3	490.8	407.2	437.6

[a] These values are based on $H = 0$ for pure methane, ethane, and propane as saturated liquids at −280 °F.

Table IV. Estimated Values of Enthalpies of Liquid Mixtures to be Used as Checks on Calorimetric Determinations

mixture no.	T, °F	P, psia	enthalpies of pure components,[a] Btu/lb CH_4	C_2H_6	C_3H_8	H^E, Btu/lb	H_M,[a] Btu/lb
1 (52.3% C_2)	−220	1500	54.0	37.7		0.6	43.5
2 (22.3% C_2)	−240	1000	34.7	26.4		1.0	32.8
3 (5.55% C_2)	−240	1000	34.7	26.4		0.3	34.2
4 (ternary)	−243	1500	35.0	25.0	21.2	0.3	32.0

[a] Based on $H = 0$ for pure components as saturated liquids at −280 °F.

each mixture. Samples taken from the recycle flow system at frequent intervals were analyzed by chromatograph utilizing direct comparison against samples from four tanks each containing a standard mixture. The composition of each standard tank was analyzed for trace components in addition to methane, ethane, and propane. The results of the analyses of the standard mixtures are given in Table II. Analyses for individual runs are

Table V. Thermodynamic Properties at the Pressures of Isobaric Determinations. Binary Mixture Containing Approximately 52.3 mol % Ethane in Methane[a]

				P = 978 psia			P = 1250 psia			P = 1500 psia			P = 2000 psia		
temp, °F	H, Btu/lb (P = 250 psia)	H, Btu/lb (P = 500 psia)	H, Btu/lb (P = 750 psia)	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb
−250.0										0.6419	0.6352	24.39			
−240.0										0.6427	0.6360	30.75			
−230.0										0.6440	0.6372	37.11			
−220.0										0.6457	0.6389	43.50			
−210.0										0.6475	0.6407	49.90			
−200.0										0.6490	0.6422	56.31			
−190.0										0.6500	0.6432	62.74			
−180.0										0.6527	0.6458	69.19			
−170.0										0.6560	0.6491	75.66			
−160.0										0.6596	0.6527	82.17			
−150.0										0.6640	0.6570	88.72			
−140.0										0.6688	0.6618	95.32			
−130.0	99.45									0.6755	0.6684	101.97			
−120.0	120.35									0.6850	0.6778	108.70			
−110.0	137.65			0.7252	0.7245	114.43				0.6960	0.6887	115.54			
−100.0	153.45	121.05	121.56	0.7352	0.7345	121.72				0.7080	0.7006	122.48			
−90.0	170.85	127.85	129.26	0.7451	0.7444	129.11				0.7220	0.7143	129.59			
−80.0	190.55	134.95	136.66	0.7601	0.7594	136.62				0.7363	0.7284	136.79			
−70.0	211.85	149.55	144.26	0.7789	0.7782	144.30				0.7550	0.7469	144.19			
−60.0	235.55	167.55	152.76	0.8047	0.8039	152.20				0.7725	0.7642	151.69			
−50.0	263.35	185.55	161.76	0.8333	0.8325	160.37				0.7910	0.7825	159.49			
−40.0	299.05	204.55	170.96	0.8773	0.8765	168.90				0.8110	0.8023	167.39			
−30.0	320.35	224.05	182.76	0.9451	0.9442	177.97				0.8345	0.8256	175.49			
−20.0	325.05	245.55	201.76	1.0385	1.0375	187.80				0.8600	0.8508	183.89			
−10.0	330.35	272.05	220.26	1.1947	1.1936	198.90				0.8969	0.8873	192.59			
0.0	335.35	302.65	239.01	1.4500	1.4486	212.01				0.9420	0.9319	201.69	0.8730	0.8730	198.42
10.0		318.55	264.26	1.8773	1.8591	228.52	1.1873	1.1715	215.75	1.0044	0.9929	211.29	0.8846	0.8846	207.20
20.0		324.85	289.76	2.1461	2.1253	249.01	1.3258	1.3082	228.16	1.0709	1.0587	221.59	0.8980	0.8980	216.12
30.0		332.55	304.06	1.8349	1.8171	268.99	1.4572	1.4378	241.93	1.1497	1.1366	232.59	0.9128	0.9128	225.17
40.0		339.05	316.96	1.5338	1.5189	285.58	1.5340	1.5136	256.77	1.2295	1.2155	244.09	0.9301	0.9301	234.38
50.0		344.05		1.3246	1.3117	299.57	1.4774	1.4577	271.74	1.2821	1.2675	256.69	0.9487	0.9487	243.78
60.0				1.1509	1.1397	311.86	1.3511	1.3331	285.74	1.2760	1.2615	269.29	0.9786	0.9786	253.40
70.0				0.9945	0.9849	322.45	1.2288	1.2125	298.46	1.2164	1.2025	281.69	1.0270	1.0270	263.40
80.0				0.8658	0.8574	331.64	1.1166	1.1017	310.05	1.1548	1.1416	293.39	1.0990	1.0990	274.01
90.0				0.7782	0.7707	339.73	1.0080	0.9946	320.53	1.0830	1.0707	304.49			
100.0				0.7028	0.6960	347.03	0.8979	0.8860	329.91	1.0204	1.0088	314.89			
110.0				0.6407	0.6345	353.62	0.7881	0.7776	338.29	0.9625	0.9527	324.69			
120.0				0.5755	0.5699	359.72				0.9152	0.9059	333.99			
130.0										0.8736	0.8647	342.79			
140.0										0.8345	0.8260	351.29			
150.0										0.8046	0.7964	359.39			
160.0										0.7817	0.7737	367.19			
170.0										0.7636	0.7558	374.89			
180.0										0.7498	0.7422	382.39			
190.0										0.7397	0.7322	389.69			
200.0										0.7301	0.7227	396.99			
210.0										0.7217	0.7143	404.19			
220.0										0.7133	0.7060	411.29			
230.0										0.7059	0.6987	418.29			
240.0										0.7005	0.6934	425.29			
250.0										0.6957	0.6886	432.19			

260.0	0.6913	0.6842	439.09
270.0	0.6883	0.6813	445.89
280.0	0.6862	0.6792	452.69
290.0	0.6850	0.6780	459.49
300.0	0.6855	0.6785	466.29
310.0	0.6860	0.6790	472.99

[a] C_p values at 250, 500 and 750 psia are not reported as most of the data lie in the two-phase region.

Table VI. Thermodynamic Properties at the Pressures of Isobaric Determinations. Binary Mixture Containing Approximately 22.3 mol % Ethane in Methane[a]

	P = 250 psia		P = 500 psia	P = 1000 psia			P = 1500 psia			P = 2000 psia		
temp, °F	C_p,[b] Btu/(lb °F)	H, Btu/lb	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb
−260.0				0.7247	0.7207	18.26						
−250.0	0.7209	22.54		0.7304	0.7264	25.49						
−240.0	0.7305	29.80		0.7343	0.7303	32.78						
−230.0	0.7400	37.15		0.7377	0.7336	40.09						
−220.0	0.7495	44.60		0.7412	0.7371	47.44						
−210.0	0.7590	52.14		0.7465	0.7424	54.84						
−200.0	0.7685	59.78		0.7526	0.7485	62.29						
−190.0	0.7780	67.51		0.7588	0.7546	69.80						
−180.0	0.7872	75.34		0.7665	0.7623	77.38						
−170.0	0.7967	83.26		0.7767	0.7724	85.03						
−160.0	0.8058	91.27		0.7903	0.7860	92.91						
−150.0		131.37	99.87	0.8070	0.8031	100.65						
−140.0		170.67	108.87	0.8248	0.8208	109.08						
−130.0		196.37	117.37	0.8471	0.8430	117.37						
−120.0		215.87	126.67	0.8798	0.8756	125.96						
−110.0		233.87	145.87	0.9240	0.9196	134.86						
−100.0		252.77	185.37	0.9865	0.9818	144.36						
−90.0		274.27	209.37	1.0582	1.0531	154.56						
−80.0		296.57	231.27	1.1458	1.1403	165.46						
−70.0		308.87	252.87	1.2836	1.2774	177.46						
−60.0	0.5730	315.10	273.87	1.5582	1.5507	191.36				0.9154	0.9110	178.11
−50.0	0.5410	320.66	294.57	2.1819	2.1695	209.97	1.1234	1.1220	192.07	0.9526	0.9480	186.96
−40.0	0.5532	326.12	306.37	2.3519	2.3385	233.08	1.1902	1.1887	203.60	0.9885	0.9837	196.62
−30.0	0.5445	331.61	312.37	1.9485	1.9374	254.79	1.2769	1.2753	215.88	1.0246	1.0197	206.63
−20.0	0.5317	337.02		1.4988	1.4903	271.79	1.3945	1.3927	229.29	1.0596	1.0545	217.01
−10.0	0.5272	342.34		1.1940	1.1872	285.10	1.4115	1.4097	243.37	1.0897	1.0844	227.71
0.0	0.5224	347.59		1.0170	1.0112	296.00	1.3487	1.3470	257.20	1.1008	1.0955	238.62
10.0	0.5199	352.80		0.9188	0.9136	305.61	1.2510	1.2494	270.20	1.1028	1.0975	249.59
20.0	0.5186	357.99		0.8639	0.8590	314.51	1.1423	1.1408	282.18	1.0917	1.0864	260.51
30.0	1.5174	363.17		0.8203	0.8156	322.81	1.0496	1.0483	293.13	1.0677	1.0626	271.27
40.0	0.5169	368.34		0.7839	0.7794	330.82	0.9755	0.9743	303.19	1.0376	1.0326	281.70
50.0	0.5169	373.51		0.7522	0.7479	338.42	0.9252	0.9240	312.65	1.0055	1.0007	291.88
60.0	0.5169	378.68		0.7225	0.7184	345.72	0.8865	0.8854	321.71	0.9700	0.9653	301.75
70.0	0.5169	383.85		0.6950	0.6910	352.83	0.8480	0.8469	330.38	0.9330	0.9285	311.23
80.0	0.5169	389.02		0.6785	0.6741	359.60	0.8160	0.8150	338.64	0.9000	0.9009	320.32
90.0				0.6680	0.6637	366.28				0.8729	0.8738	329.17
100.0				0.6597	0.6554	373.00				0.8464	0.8472	337.82
110.0				0.6531	0.6489	379.59				0.8205	0.8213	346.17
120.0				0.6477	0.6435	386.09				0.8005	0.8013	354.32
130.0				0.6427	0.6385	392.54				0.7826	0.7834	362.17
140.0				0.6385	0.6345	398.97				0.7678	0.7686	370.01
150.0				0.6356	0.6315	405.25				0.7518	0.7526	377.56
160.0				0.6335	0.6294	411.53				0.7403	0.7410	385.10

Table VI (*Continued*)

	P = 250 psia		P = 500 psia	P = 1000 psia			P = 1500 psia			P = 2000 psia		
temp, °F	C_p,[b] Btu/(lb °F)	H, Btu/lb	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb
170.0				0.6319	0.6278	417.79				0.7333	0.7340	392.45
180.0				0.6310	0.6269	424.04				0.7274	0.7281	399.79
190.0				0.6305	0.6264	430.29				0.7227	0.7234	407.03
200.0				0.6307	0.6266	436.53				0.7186	0.7193	414.28
210.0				0.6320	0.6279	442.78				0.7147	0.7154	421.42
220.0				0.6345	0.6304	449.05				0.7112	0.7119	428.56
230.0				0.6373	0.6332	455.34				0.7080	0.7087	435.65
240.0				0.6400	0.6358	461.67				0.7048	0.7055	442.75
250.0				0.6426	0.6384	468.02				0.7033	0.7040	449.79
260.0				0.6450	0.6408	474.39				0.7018	0.7025	456.83
270.0				0.6476	0.6434	480.79				0.7003	0.7010	463.87
280.0				0.6510	0.6468	487.22				0.6988	0.6995	470.91
290.0				0.6542	0.6499	493.66				0.6972	0.6979	477.85
300.0				0.6575	0.6532	500.17				0.6960	0.6967	484.90
310.0				0.6598	0.6555	506.70						
320.0				0.6610	0.6567	513.24						

[a] C_p values at 500 psia are not reported as most of the data lies in the two-phase region. [b] C_p values at 250 psia are not reported in the two-phase region.

Table VII. Thermodynamic Properties at the Pressures of Isobaric Determinations. Binary Mixture Containing Approximately 5.5 mol % Ethane in Methane

	P = 250 psia			P = 500 psia			P = 700 psia		P = 800 psia		
temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H(A), Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	C_p, Btu/(lb °F)	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H(A), Btu/lb
−240.0	0.8227	0.8029	39.0								
−230.0	0.8252	0.8053	47.1								
−220.0	0.8315	0.8115	55.2								
−210.0	0.8418	0.8215	63.3								
−200.0	0.8579	0.8372	71.6								
−190.0	0.8872	0.8658	80.1								
−180.0	0.9420	0.9193	89.0								
−170.0	1.1580	1.1301	98.9								
−160.0			154.1								
−150.0			216.2			115.54		115.0	0.9721	0.9721	114.8
−140.0			262.2			126.3		124.9	1.0319	1.0319	124.8
−130.0			276.8			139.2		136.2	1.1326	1.1326	135.6
−120.0			288.6			219.63		149.4	1.2901	1.2901	147.8
−110.0			295.0	2.0540	2.0540	259.8		166.4	1.6132	1.6132	162.1
−100.0			301.1	1.2500	1.2500	275.6		223.8	3.2542	3.2542	183.3
−90.0	0.5904	0.5881	307.0	0.9460	0.9626	286.5		256.1	4.2824	4.2811	230.8
−80.0	0.5771	0.5749	312.8	0.7830	0.7967	295.2		271.5	1.8179	1.8174	256.3
−70.0	0.5688	0.5666	318.5	0.6730	0.6848	302.3		282.9	1.2712	1.2708	271.2
−60.0	0.5635	0.5613	324.5	0.6086	0.6193	309.1		292.1	1.0294	1.0291	282.5
−50.0	0.5591	0.5570	329.8	0.5730	0.5831	315.06		300.1	0.8895	0.8892	292.1
−40.0	0.5554	0.5553	335.3								
−30.0	0.5524	0.5523	340.9								
−20.0	0.5502	0.5501	346.37								
−10.0	0.5485	0.5484	351.9								
0.0	0.5472	0.5471	357.3								
10.0	0.5458	0.5457	362.8								

20.0	0.5446	.5445	368.3
30.0	0.5431	.5430	373.7
40.0	0.5416	.5415	379.1
50.0	0.5408	.5407	384.5
60.0	0.5398	0.5397	389.9
70.0	0.5385	0.5384	395.34
80.0	0.5374	0.5374	400.7

	P = 1000 psia			P = 1200 psia			P = 1500 psia			P = 2000 psia		
temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H(A), Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H(A), Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H(A), Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H(A), Btu/lb
−240.0	0.8072	0.8072	37.7									
−230.0	0.8137	0.8137	45.8									
−220.0	0.8202	0.8202	54.0									
−210.0	0.8268	0.8268	62.23									
−200.0	0.8352	0.8352	70.5									
−190.0	0.8471	0.8471	78.9									
−180.0	0.8632	0.8632	87.5									
−170.0	0.8820	0.8820	96.2									
−160.0	0.9122	0.9122	105.2	0.9180	0.9180	105.6	0.8930	0.8930	105.2	0.8239	0.8239	106.2
−150.0	0.9512	0.9512	114.5	0.9438	0.9322	114.3	0.9060	0.9072	114.2	0.8460	0.8533	114.5
−140.0	1.0043	1.0043	124.3	0.9777	0.9657	123.8	0.9269	0.9281	123.4	0.8697	0.8772	123.2
−130.0	1.0681	1.0681	134.7	1.0190	1.0065	133.6	0.9550	0.9563	132.8	0.8950	0.9028	132.1
−120.0	1.1540	1.1540	145.7	1.0750	1.0618	144.0	0.9879	0.9892	142.5	0.9226	0.9306	141.2
−110.0	1.2802	1.2802	157.9	1.1540	1.1398	155.0	1.0300	1.0314	152.6	0.9504	0.9586	150.7
−100.0	1.4851	1.4851	170.9	1.2680	1.2525	166.7	1.0850	1.0865	163.2	0.9783	0.9868	160.4
−90.0	2.1021	2.1044	188.5	1.4310	1.4497	180.4	1.1357	1.1070	174.0	1.0043	1.0062	170.4
−80.0	2.8528	2.8559	214.2	1.6650	1.6867	196.0	1.2244	1.1934	185.5	1.0391	1.0410	180.6
−70.0	2.1772	2.1796	240.1	2.1960	2.2246	215.0	1.3348	1.3011	198.0	1.0760	1.0780	191.18
−60.0	1.5936	1.5953	258.5	1.7910	1.8144	235.0	1.4965	1.4587	212.5	1.1178	1.1199	202.2
−50.0	1.2633	1.2647	272.6	1.4080	1.4264	251.9	1.7410	1.6970	228.5	1.1597	1.1619	213.8
−40.0	1.0920	1.1019	284.4							1.2061	1.2089	225.7
−30.0	0.9700	0.9788	294.8							1.1791	1.1818	237.6
−20.0	0.8900	0.8980	304.0							1.1441	1.1468	249.3
−10.0	0.8360	0.8436	312.8							1.1071	1.1097	260.6
0.0	0.7960	0.8032	321.6							1.0712	1.0737	271.5
10.0	0.7580	0.7648	328.9							1.0352	1.0376	282.2
20.0	0.7260	0.7326	336.3							1.0012	1.0035	292.3
30.0	1.7060	0.7124	343.5							0.9672	0.9695	302.2
40.0	0.6920	0.6983	350.6							0.9353	0.9375	311.7
50.0	0.6780	0.6841	357.5							0.9075	0.9096	320.9
60.0	0.6660	0.6720	364.3							0.8806	0.8827	329.9
70.0	0.6540	0.6600	370.9							0.8573	0.8593	338.6
80.0	0.6441	0.6441	377.4							0.8403	0.8396	347.1
90.0	0.6370	0.6370	383.9							0.8386	0.8379	355.4
100.0	0.6320	0.6320	390.2							0.8233	0.8227	363.5
110.0	0.6280	0.6280	392.5									
120.0	0.6270	0.6270	402.8									
130.0	0.6320	0.6320	409.1									
140.0	0.6310	0.6310	415.4									
150.0	0.6420	0.6420	421.8									
160.0	0.6567	0.6567	428.3									
170.0	0.6650	0.6650	434.8									
180.0	0.6752	0.6752	441.8									
190.0	0.6870	0.6870	448.3									
200.0	0.7020	0.7020	455.3									

Table VIII. Thermodynamic Properties at the Pressures of Isobaric Determination. Ternary Mixture Containing Methane, Ethane, and Propane

temp, °F	P = 250 psia		P = 500 psia			P = 750 psia		P = 1000 psia		P = 1200 psia			P = 1500 psia			P = 2000 psia		
	C_p, Btu/(lb °F)	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	C_p, Btu/(lb °F)	H, Btu/lb	C_p, Btu/(lb °F)	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb
−240.0			0.7360	0.7360	32.05								0.7325	0.7325	36.17			
−230.0			0.7419	0.7419	39.44								0.7345	0.7345	43.50			
−220.0			0.7494	0.7494	46.89								0.7370	0.7370	50.86			
−210.0			0.7584	0.7584	54.43								0.7404	0.7404	58.24			
−200.0			0.7684	0.7684	62.06								0.7449	0.7449	65.67			
−190.0			0.7798	0.7798	69.80								0.7506	0.7506	73.14			
−180.0			0.7933	0.7933	77.66								0.7578	0.7578	80.69			
−170.0		89.09	0.8103	0.8103	85.68								0.7668	0.7668	88.31			
−160.0		97.69	0.8326	0.8326	93.89								0.7770	0.7770	96.03			
−150.0		166.57	0.8566	0.8566	102.34		102.57		102.92				0.7892	0.7892	103.85			
−140.0		195.79	0.8844	0.8938	111.13		110.63		110.98				0.8040	0.8065	111.85			
−130.0		217.39	0.9604	0.9706	120.33		118.79		119.45				0.8218	0.8244	120.00			
−120.0		234.79			130.23		126.95		128.51				0.8429	0.8456	128.33			
−110.0		250.19			178.34		135.11		137.96				0.8662	0.8689	136.95			
−100.0		263.39			205.93		143.47		147.92				0.8938	0.8966	145.78			
−90.0		275.09			225.94		161.48		158.37				0.9240	0.9269	154.81			
−80.0		286.19			244.04		195.91		169.03				0.9590	0.9620	164.34			
−70.0		297.19			259.80		220.49		180.28				1.0000	1.0032	174.07			
−60.0		307.99			275.16		240.00		203.28				1.0550	1.0583	184.40			
−50.0		317.69			289.01		257.01		226.47				1.1170	1.1205	195.34			
−40.0		323.89			303.89		271.60		248.43	1.751	1.733	223.24	1.2060	1.1971	206.79	1.0348	1.0251	198.85
−30.0					318.26		284.09		262.33	1.705	1.687	241.09	1.3190	1.3092	219.30	1.0460	1.0362	209.15
−20.0					325.50		295.49		274.64	1.475	1.459	249.64	1.4500	1.4393	233.00	1.0590	1.0491	219.58
−10.0					328.05		306.20		286.36	1.297	1.283	270.45	1.4450	1.4343	247.79	1.0730	1.0630	230.14
0.0			0.6355		333.98		316.02		297.58	1.138	1.126	282.45	1.2680	1.2586	260.99	1.0900	1.0798	240.05
10.0			0.6188	0.6183	340.42					1.013			1.1700	1.1762	273.23	1.0930		
20.0			0.6036	0.6031	346.53					0.943			1.0830	1.0888	284.49	1.0700		
30.0			0.5908	0.5903	352.49					0.904			1.0090	1.0144	295.05	1.0520		
40.0			0.5810	0.5805	358.35					0.886			0.9490	0.9541	304.90	1.0360		
50.0			0.5726	0.5722	364.11					0.877			0.8909	0.8956	314.15	1.0220		
60.0			0.5657	0.5653	369.80					0.872			0.8410	0.8455	322.79			
70.0			0.5608	0.5604	375.42					0.867			0.8010	0.8053	331.04			
80.0			0.5597	0.5593	381.02					0.865			0.7717	0.7758	338.98			
90.0			0.5610	0.5606	386.61								0.7500	0.7540	346.62			
100.0			0.5636	0.5632	392.23								0.7325	0.7364	354.06			
110.0			0.5662	0.5658	397.88								0.7160	0.7198	361.30			
120.0			0.5689	0.5685	403.54								0.7032	0.7069	368.43			
130.0			0.5717	0.5713	409.25								0.6924	0.6961	375.47			
140.0			0.5744	0.5740	414.97								0.6830	0.6866	382.41			
150.0			0.5768	0.5764	420.72								0.6736	0.6772	389.25			
160.0			0.5797	0.5797	426.51								0.6661	0.6661	395.98			
170.0			0.5822	0.5822	432.35								0.6616	0.6616	402.58			
180.0			0.5849	0.5849	438.15								0.6590	0.6590	409.18			
190.0			0.5875	0.5875	444.05								0.6572	0.6572	415.78			
200.0			0.5902	0.5902	449.95								0.6570	0.6570	422.28			
210.0			0.5927	0.5927	455.85								0.6590	0.6590	428.88			
220.0			0.5953	0.5953	461.75								0.6620	0.6620	435.48			
230.0			0.5980	0.5980	467.75								0.6650	0.6650	442.18			

240.0	0.6003	0.6003	473.75	0.6710	0.6710	448.78
250.0	0.6027	0.6027	479.75	0.6791	0.6791	455.58
260.0	0.6051	0.6051	485.75	0.6884	0.6884	462.38
270.0	0.6076	0.6076	491.85	0.6980	0.6980	469.38
280.0	0.6101	0.6101	497.95	0.7096	0.7096	476.38
290.0	0.6127	0.6127	504.05	0.7224	0.7224	483.48
300.0	0.6155	0.6155	510.15	0.7360	0.7360	490.78

presented as part of the basic data available elsewhere. The individual analyses were averaged to give the nominal compositions listed in Table II. In obtaining the average values reported in Table II, added weight was given to the composition of runs made across the two-phase region and near the critical point.

Experimental Data. Isobaric, isothermal, and isenthalpic measurements were made on each mixture from about −240 to +250 °F (300 °F for two systems) at pressures between 100 and 2000 psia. The actual conditions of measurements for each mixture are presented on pressure–temperature diagrams as Figures 1-4. Each associated group of experiments is identified by a number within a circle. A group of isobaric measurements in the single-phase region included from 3 to 9 experiments with the same inlet temperature. Power input was adjusted to yield outlet temperatures increasing in increments of about 20 °F. In regions where C_p varied significantly (such as near the critical point) smaller temperature rises were used (as small at 5 °F). Isobaric determinations were made across the two-phase region to establish bubble- and dew-point temperatures in addition to yielding isobaric heats of vaporization and enthalpy values within the two-phase region. Isothermal determinations were made mainly in the single-phase region. Pressure drops were usually between 100 and 500 psi. A limited number of isenthalpic determinations were made at low temperatures in the liquid phase.

The basic experimental results obtained under sponsorship of the National Science Foundation are filed in the microfilm edition.

Experimental Difficulties. During the course of time required to make extensive calorimetric determinations on four different systems, a number of operational difficulties are usually encountered. Nothing unusual occurred during these investigations but in the process of checking out the equipment after completion of the determinations involving mixtures 1 and 2, several small leaks were noted in the all-important section between the calorimeter and flowmeter and later it was found that a short in the battery used to power the potentiometer probably caused somewhat erroneous readings.

It is impossible to determine whether any of these operational problems (which were only detected after completion of the investigation of mixtures 1 and 2) influenced the results to any appreciable degree but, at a minimum, the possibility of systematic error must be taken into account. It should be noted that leaks between the calorimeter and flowmeter will tend to yield property values that are too high.

Selection of Bases and Use of Other Published Data

In presenting enthalpy data for mixtures it is sufficient to select one reference state for each of the components in the mixture. The bases $H = 0$ for pure methane, pure ethane, and pure propane as saturated liquids at −280 °F were chosen so as to be consistent with prior analysis of calorimetric data for these pure components (*8*, *11*, *13*, *16*, *33*, *36*) and a number of mixtures (*3*, *8*, *9*, *15*, *17*, *34*, *35*, *37*).

Published data for pure methane, pure ethane, and pure propane served two purposes in the process of obtaining reliable enthalpy values for mixtures under investigation. Whereas operation of the equipment was limited in lower value to about 100 psia, excellent published data for the pure compounds are available at pressures of 1 atm and below (*7*, *12*, *30*) so that the experimental results were readily extended to the lower pressures. In addition, when used in connection with estimates based on published values of excess enthalpy of mixing for liquid hydrocarbon mixtures, a valuable check on the validity of the mixture data was obtained (*6*).

The procedures employed to utilize published data on the pure components to obtain enthalpy values for the individual mixtures

Table IX. Thermodynamic Properties at the Pressures of Isobaric Determinations in the Regions of Rapid Change (High $(\partial C_P/\partial T)_P$) for Mixture 1 (52.3% C_2)

P = 978 psia				P = 1250 psia				P = 1500 psia			
temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb
5.00	1.6682	1.6520	219.73	15.00	1.2581	1.2414	221.79	30.00	1.1497	1.1366	232.59
10.00	1.8773	1.8591	228.52	17.50	1.2914	1.2742	224.93	40.00	1.2295	1.2155	244.09
15.00	2.0835	2.0633	238.41	20.00	1.3258	1.3082	228.16	41.00	1.2407	1.2266	245.29
15.50	2.0996	2.0792	239.51	22.50	1.3622	1.3441	231.48	42.00	1.2497	1.2355	246.59
16.00	2.1178	2.0973	240.51	25.00	1.3965	1.3779	234.89	43.00	1.2588	1.2444	247.79
16.50	2.1340	2.1133	241.61	27.50	1.4268	1.4078	238.37	44.00	1.2659	1.2515	249.09
17.00	2.1451	2.1243	242.61	30.00	1.4572	1.4378	241.93	45.00	1.2720	1.2575	250.29
17.50	2.1501	2.1292	243.71	30.62	1.4642	1.4447	242.83	46.00	1.2760	1.2615	251.59
18.00	2.1532	2.1323	244.81	31.25	1.4703	1.4507	243.74	47.00	1.2790	1.2644	252.89
18.50	2.1552	2.1343	245.81	31.88	1.4774	1.4577	244.66	48.00	1.2801	1.2655	254.09
19.00	2.1542	2.1333	246.91	32.50	1.4844	1.4647	245.56	49.00	1.2811	1.2665	255.39
19.50	2.1522	2.1313	248.01	33.13	1.4905	1.4707	246.48	50.00	1.2821	1.2675	256.69
20.00	2.1461	2.1253	249.01	33.75	1.4956	1.4757	247.40	51.00	1.2831	1.2685	257.89
20.50	2.1380	2.1173	250.11	34.38	1.5006	1.4806	248.33	52.00	1.2841	1.2695	259.19
21.00	2.1279	2.1073	251.10	35.00	1.5067	1.4867	249.26	53.00	1.2841	1.2695	260.49
21.50	2.1148	2.0943	252.20	25.62	1.5117	1.4916	250.17	54.00	1.2841	1.2695	261.69
22.00	2.0996	2.0792	253.20	36.25	1.5168	1.4966	251.12	55.00	1.2831	1.2685	262.99
22.50	2.0824	2.0622	254.30	26.87	1.5218	1.5016	252.05	56.00	1.2821	1.2675	264.29
23.00	2.0663	2.0463	255.30	37.50	1.5259	1.5056	253.00	57.00	1.2811	1.2665	265.49
23.50	2.0491	2.0292	256.30	38.13	1.5279	1.5076	253.95	58.00	1.2801	1.2655	266.79
24.00	2.0329	2.0132	257.30	38.75	1.5299	1.5096	254.88	59.00	1.2790	1.2644	268.09
24.50	2.0188	1.9992	258.30	39.38	1.5319	1.5115	255.83	60.00	1.2760	1.2615	269.29
25.00	2.0077	1.9882	259.30	40.00	1.5340	1.5136	256.77	61.00	1.2720	1.2575	270.59
30.00	1.8349	1.8171	268.99	40.63	1.5340	1.5136	257.73	62.00	1.2659	1.2515	271.89
35.00	1.6763	1.6600	277.58	41.25	1.5340	1.5136	258.67	63.00	1.2598	1.2454	273.09
40.00	1.5338	1.5189	285.58	41.87	1.5340	1.5136	259.60	64.00	1.2528	1.2385	274.39
45.00	1.4166	1.4029	292.87	42.50	1.5329	1.5125	260.56	65.00	1.2467	1.2325	275.59
				43.13	1.5299	1.5096	261.51	66.00	1.2407	1.2266	276.79
				43.75	1.5279	1.5076	262.45	67.00	1.2346	1.2205	277.99
				44.38	1.5249	1.5046	263.39	68.00	1.2285	1.2145	279.29
				45.00	1.5208	1.5006	264.33	69.00	1.2225	1.2086	280.49
				45.63	1.5158	1.4956	265.27	70.00	1.2164	1.2025	281.69
				46.25	1.5117	1.4916	266.20	80.00	1.1548	1.1416	293.39
				46.88	1.5067	1.4867	267.14				
				47.50	1.5016	1.4816	268.06				
				48.12	1.4956	1.4757	268.98				
				48.75	1.4895	1.4697	269.91				
				49.38	1.4834	1.4637	270.83				
				50.00	1.4774	1.4577	271.74				
				50.63	1.4703	1.4507	272.65				
				51.25	1.4632	1.4437	273.55				
				51.88	1.4561	1.4367	274.46				
				52.50	1.4501	1.4308	275.35				
				53.13	1.4440	1.4248	276.25				
				53.75	1.4369	1.4178	277.13				
				54.38	1.4289	1.4099	278.02				
				55.00	1.4198	1.4009	278.90				
				57.50	1.3844	1.3660	282.35				
				60.00	1.3511	1.3331	285.74				
				62.50	1.3187	1.3012	289.03				
				65.00	1.2874	1.2703	292.24				

at zero pressure are described in detail elsewhere (*21*). In brief, for each pure component, one utilizes accurate published data on the heat capacity of saturated liquid, C_{pl}, and the enthalpy change on vaporization, ΔH_{vap}, together with an estimate of the enthalpy change from the pressure at which ΔH_{vap} is known to zero pressure to estimate the enthalpy of the pure compound as an ideal gas at the temperature of vaporization relative to the *reference* state of saturated liquid at −280 °F. Further, by using the properties of the ideal gas as calculated from theoretically based analyses of spectroscopic and calorimetric data (*23*), one can calculate the enthalpy of all of the pure components at zero pressure at any temperature of interest. At low pressure the gases form ideal mixtures and therefore the enthalpy of any of the investigated mixtures can be calculated using the relation

$$H^\circ_M = \sum y_i H^\circ_i \quad (1)$$

where the subscripts M and i refer to the mixture and the individual components respectively and y_i refers to the mole or mass fractions of the individual components in the mixture. Details of the calculations are presented elsewhere (*21*). The applicable results are summarized in Table III.

In addition to the uses made of published data mentioned above, enthalpy data for the pure components (utilizing the same bases) can be used together with estimates of the enthalpy change on mixing to calculate the mixture enthalpy where such data are available. The procedure provides valuable check points in the liquid region for the mixture data. The results of calculations described in detail elsewhere (*21*) are presented in Table IV.

Analysis of Experimental Data

In an attempt to obtain the most accurate and thermody-

Table X. Thermodynamic Properties at the Pressures of Isobaric Determinations in the Regions of Rapid Change (High $(\partial C_P/\partial T)_P$) for Mixture 2 (22.3% C_2)

P = 1000 psia				P = 1500 psia				P = 2000 psia			
temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb	temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb
-60.00	1.5582	1.5507	191.36	-30.00	1.2769	1.2753	215.88	-30.00	1.0246	1.0197	206.63
-59.00	1.6185	1.6107	192.96	-27.50	1.3108	1.3091	219.12	-25.00	1.0426	1.0376	211.78
-58.45	1.6528	1.6449	193.76	-25.00	1.3437	1.3420	222.44	-20.00	1.0596	1.0545	217.01
-58.00	1.6809	1.6713	194.56	-22.50	1.3736	1.3718	225.83	-15.00	1.0767	1.0715	222.33
-57.00	1.7443	1.7344	196.26	-20.00	1.3945	1.3927	229.29	-10.00	1.0897	1.0844	227.71
-56.00	1.8067	1.7964	198.06	-18.75	1.4015	1.3997	231.03	-5.00	1.0957	1.0904	233.15
-55.00	1.8680	1.8574	199.86	-17.50	1.4055	1.4037	232.78	0.0	1.1008	1.0955	238.62
-54.00	1.9304	1.9194	201.76	-16.25	1.4095	1.4077	234.55	5.00	1.1028	1.0975	244.10
-53.00	1.9938	1.9824	203.66	-15.00	1.4125	1.4107	236.31	10.00	1.1028	1.0975	249.59
-52.00	2.0581	2.0464	205.66	-13.75	1.4135	1.4117	238.07	15.00	1.0987	1.0934	255.07
-51.00	2.1205	2.1084	207.77	-12.50	1.4145	1.4127	239.83	20.00	1.0917	1.0864	260.51
-50.00	2.1819	2.1695	209.97	-11.25	1.4135	1.4117	241.61	25.00	1.0807	1.0755	265.92
-49.00	2.2422	2.2294	212.17	-10.00	1.4115	1.4097	243.37	30.00	1.0677	1.0626	271.27
-48.00	2.2855	2.2725	214.37	-7.50	1.4015	1.3997	246.88				
-47.00	2.3116	2.2984	216.67	-5.00	1.3876	1.3858	250.36				
-46.00	2.3378	2.3245	218.97	-2.50	1.3706	1.3688	253.81				
-45.00	3.3519	2.3385	221.27	0.0	1.3487	1.3470	257.20				
-44.50	2.3589	2.3455	222.47	2.50	1.3228	1.3211	260.54				
-44.00	2.3650	2.3515	223.67	5.00	1.3028	1.3011	263.82				
-43.50	2.3690	2.3555	224.87	7.50	1.2769	1.2753	267.04				
-43.00	2.3710	2.3575	225.97	10.00	1.2510	1.2494	270.20				
-42.50	2.3720	2.3585	227.17								
-42.00	2.3710	2.3575	228.37								
-41.50	2.3690	2.3555	229.57								
-41.00	2.3650	2.3515	230.68								
-40.50	2.3589	2.3455	231.88								
-40.00	2.3519	2.3385	233.08								
-39.00	3.3378	2.3245	235.38								
-38.00	2.3116	2.2984	237.68								
-37.00	2.2855	2.2725	239.98								
-36.00	2.2503	2.2375	242.28								
-35.00	2.2080	2.1954	244.48								
-34.00	2.1607	2.1484	246.68								
-33.00	2.1105	2.0985	248.78								
-32.00	2.0561	2.0444	250.88								
-31.00	2.0018	1.9904	252.88								
-30.00	1.9485	1.9374	254.79								
-27.50	1.8157	1.8053	259.49								
-25.00	1.6920	1.6824	263.89								
-22.50	1.5894	1.5803	267.89								
-20.00	1.4988	1.4903	271.79								

namically consistent property values from the experimental data, a sequence of processing steps was employed. (1) A generalized correlation (*20*) was used to adjust experimental values to normalized values of composition, pressure level, and temperatures. (2) The normalized values were then smoothed to obtain consistency between data from different runs and to determine numerical values for the derivative properties and integral values of enthalpy differences. (3) The values so obtained were carefully checked for thermodynamic self-consistency and adjusted as necessary. (4) The adjusted values were checked for consistency with published data of superior quality and again adjusted as required. The resulting values should be reasonably accurate over the entire region of investigation. Further information with regard to each step outlined above is presented in the following paragraphs.

Normalization and Correction of Experimental Data. The basic data (included in the microfilm edition) are in terms of experimentally determined differences in enthalpy for a particular experimental mixture, x_i, corresponding to values of temperature and pressure measured at the inlet, j, and the outlet, k, of the calorimeter:

$$\Delta H_M = [H_{T_k,P_k} - H_{T_j},P_j]x_i \qquad (2)$$

As mentioned previously, periodic checks were made of the composition of the experimental mixture and variations as extreme as 1.2% ethane from the nominal values were noted. (Actually, variations were generally much less than that.) Similarly, during any series of isobaric runs, the system pressure ranged as much at ±3 psi and the inlet temperature varied as much as ±1.5 °F in extreme cases. Final interpretation of the data is both simplified and made more meaningful by adjusting the basic calorimetric data to the composition listed in Table II, normalizing all isobaric determinations obtained at one pressure level to a convenient value (such as 1000 psia), and adjusting to an average value all inlet temperatures for one set of isobaric determinations. The sum total of all such corrections was usually less than 0.1% with a maximum adjustment of 3%. Such large corrections occurred only for the run made through the critical point for mixture 1 (run 10). For all other runs the corrections did not exceed 1.5%. Details of this normalization procedure are presented elsewhere (*8*).

In addition to the minor corrections to normalized values mentioned above, small corrections were made to account for the small measured pressure drop in the isobaric calorimeter and the fact that small differences in temperature normally existed between the inlet and outlet of the calorimeter during isothermal runs. These corrections were made in a rigorous manner as described elsewhere (*35*) and in extreme cases such corrections amounted to 0.3% of the experimentally determined enthalpy difference.

Table XI. Thermodynamic Properties at the Pressures of Isobaric Determinations in the Regions of Rapid Change (High $(\partial C_p/\partial T)_p$) for Mixture 3 (5.55% C_2)

P = 800 psia

temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb
−120.0	1.2901	1.2901	147.8
−119.0	1.3101	1.3101	149.2
−118.0	1.3340	1.3340	150.5
−117.0	1.3579	1.3579	151.8
−116.0	1.3839	1.3839	153.2
−115.0	1.4128	1.4128	154.6
−114.0	1.4447	1.4447	156.0
−113.0	1.4915	1.4915	157.5
−112.0	1.5284	1.5284	159.0
−111.0	1.5683	1.5683	160.5
−110.0	1.6132	1.6132	162.1
−109.0	1.6650	1.6650	163.8
−108.0	1.7308	1.7308	165.5
−107.0	1.8096	1.8096	167.2
−106.0	1.9003	1.9003	169.1
−105.0	2.0040	2.0040	171.0
−104.0	2.1196	2.1196	173.1
−103.0	2.2871	2.2871	175.3
−102.0	2.4576	2.4576	177.7
−101.0	2.7926	2.7926	180.3
−100.0	3.2542	3.2542	183.3
−99.5	3.4716	3.4716	185.0
−99.0	3.6481	3.6481	186.8
−98.5	3.3405	3.8405	188.6
−98.0	4.0588	4.0588	190.6
−97.5	4.2562	2.2562	192.7
−97.0	4.5005	4.4991	194.9
−96.5	4.7531	4.7517	197.2
−96.0	4.9970	4.9955	199.6
−95.5	5.2170	5.2154	202.2
−95.0	5.3868	5.3852	204.8
−94.5	5.4337	5.4321	207.5
−94.0	5.4247	5.4231	210.2
−93.5	5.4267	5.4251	213.0
−93.0	5.4247	5.4231	215.7
−92.5	5.4127	5.4111	218.4
−92.0	5.3868	5.3852	221.1
−91.5	5.1359	5.1344	223.7
−91.0	4.8221	4.8207	226.2
−90.5	4.5603	4.5589	228.6
−90.0	4.2824	4.2811	230.8
−89.0	3.5878	3.5867	234.7
−88.0	3.1081	3.1072	238.1
−87.0	2.7583	2.7575	241.0
−86.0	2.5385	2.5377	243.6
−85.0	2.3636	2.3629	246.1
−84.0	2.1487	2.1481	248.3
−83.0	2.0638	2.0632	250.4
−82.0	2.0048	2.0042	252.5

P = 800 psia (continued)

temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb
−81.0	1.9348	1.9342	254.4
−80.0	1.8179	1.8174	256.3
−79.0	1.7220	1.7215	258.1
−78.0	1.6330	1.6325	259.8
−77.0	1.5561	1.5556	261.4
−76.0	1.5181	1.5176	262.9
−75.0	1.4591	1.4587	264.4
−74.0	1.4072	1.4068	265.8
−73.0	1.3702	1.3698	267.2
−72.0	1.3332	1.3328	268.6
−71.0	1.3002	1.2998	269.9
−70.0	1.2712	1.2708	271.2

P = 1000 psia

temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb
−100.0	1.4851	1.4851	170.9
−99.0	1.5214	1.5214	172.4
−98.0	1.5588	1.5588	174.1
−97.0	1.6153	1.6153	175.6
−96.0	1.6657	1.6675	177.3
−95.0	1.7337	1.7356	179.0
−94.0	1.7988	1.8008	180.7
−93.0	1.8669	1.8689	182.6
−92.0	1.9409	1.9430	184.5
−91.0	2.0220	2.0242	186.4
−90.0	2.1021	2.1044	188.5
−89.0	2.1712	2.1736	190.6
−88.0	2.2673	2.2698	192.8
−87.5	2.3283	2.3308	194.0
−87.0	2.3924	2.3950	195.2
−86.5	2.4564	2.4591	196.4
−86.0	2.5145	2.5172	197.6
−85.5	2.5726	2.5754	198.9
−85.0	2.6276	2.6305	190.2
−84.5	2.6737	2.6766	201.5
−84.0	2.7067	2.7097	202.9
−83.5	2.7067	2.7097	204.2
−83.0	2.7848	2.7878	205.6
−82.5	2.8148	2.8179	207.0
−82.0	2.8348	2.8379	208.4
−81.5	2.8428	2.8459	209.8
−81.0	2.8458	2.8489	211.4
−80.5	2.8525	2.8559	212.8
−80.0	2.8528	2.8559	214.2
−79.5	2.8558	2.8589	215.6
−79.0	2.8638	2.8670	217.1
−78.5	2.8428	2.8459	218.5
−78.0	2.8168	2.8199	219.9
−77.5	2.7948	2.7979	221.3
−77.0	2.7868	2.7898	222.7
−76.5	2.7708	2.7738	224.1
−76.0	2.7407	2.7437	225.4
−75.5	2.6887	2.6916	226.8
−75.0	2.6046	2.6074	228.1
−74.0	2.4895	2.4922	230.7
−73.0	2.4284	2.4311	233.1
−72.0	2.3423	2.3449	234.5
−71.0	2.2602	2.2627	237.8
−70.0	2.1772	2.1796	240.0
−69.0	2.0871	2.0894	242.2
−68.0	2.0080	2.0102	244.2
−67.0	1.9449	1.9470	246.2
−66.0	1.8849	1.8870	248.1
−65.0	1.8218	1.8238	249.9

P = 1000 psia (continued)

temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb
−64.0	1.7638	1.7657	251.7
−63.0	1.7107	1.7126	253.5
−62.0	1.6637	1.6655	255.2
−61.0	1.6326	1.6344	256.8
−60.0	1.5936	1.5953	258.5

P = 1200 psia

temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb
−85.0	1.5360	1.5560	187.9
−84.0	1.5570	1.5773	189.5
−83.0	1.5780	1.5986	191.0
−82.0	1.6050	1.6259	192.7
−81.0	1.6340	1.6553	194.3
−80.0	1.6650	1.6867	196.0
−79.0	1.6950	1.7171	197.7
−78.0	1.7270	1.7495	199.4
−77.0	1.7640	1.7870	201.2
−76.0	1.8070	1.8306	203.0
−75.0	1.8540	1.8782	204.8
−74.0	1.9000	1.9248	206.8
−73.0	1.9510	1.9765	208.7
−72.0	2.0240	2.0504	210.7
−71.0	2.1090	2.1365	212.8
−70.0	2.1960	2.2246	215.0
−69.5	2.2160	2.2449	216.1
−69.0	2.2260	2.2550	217.2
−68.5	2.2280	2.2571	218.3
−68.0	2.2260	2.2550	219.5
−67.5	2.2210	2.2500	220.6
−67.0	2.2140	2.2429	221.8
−66.5	2.2000	2.2287	222.9
−66.0	2.1780	2.2064	224.0
−65.5	2.1450	2.1730	225.1
−65.0	2.1010	2.1284	226.1
−64.5	2.0630	2.0899	227.2
−64.0	2.0250	2.0514	228.2
−63.5	1.9940	2.0200	229.2
−63.0	1.9580	1.9835	230.3
−62.5	1.9230	1.9481	231.2
−62.0	1.8940	1.9187	232.2
−61.5	1.8670	1.8914	233.1
−61.0	1.8400	1.8640	234.1
−60.5	1.8150	1.8387	235.0
−60.0	1.7910	1.8144	235.9
−59.0	1.7410	1.7637	237.7
−58.0	1.6940	1.7161	239.5
−57.0	1.6510	1.6725	241.1
−56.0	1.6130	1.6340	242.8
−55.0	1.5770	1.5976	244.4
−54.0	1.5430	1.5631	246.0
−53.0	1.5050	1.5246	247.5
−52.0	1.4710	1.4902	249.0
−51.0	1.4380	1.4568	250.5
−50.0	1.4080	1.4264	251.9

P = 1500 psia

temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb
−60.0	1.4965	1.4587	212.5
−59.5	1.5034	1.4654	213.3
−59.0	1.5132	1.4749	214.0
−58.5	1.5241	1.4856	214.7
−58.0	1.5379	1.4990	215.5
−57.5	1.5517	1.5125	216.2
−57.0	1.5675	1.5279	217.0
−56.5	1.5842	1.5441	217.8
−56.0	1.6010	1.5605	218.6
−55.5	1.6187	1.5778	219.3
−55.0	1.6355	1.5941	220.1
−54.5	1.6522	1.6104	221.0
−54.0	1.6710	1.6288	221.7
−53.5	1.6857	1.6431	222.6
−53.0	1.6996	1.6566	223.4
−52.5	1.7104	1.6672	224.2
−52.0	1.7203	1.6768	225.0
−51.5	1.7272	1.6835	225.9
−51.0	1.7350	1.6911	226.7
−50.5	1.7390	1.6950	227.6
−50.0	1.7410	1.6970	228.5
−49.5	1.7419	1.6979	229.3
−49.0	1.7419	1.6979	230.1
−48.5	1.7419	1.6979	231.0
−48.0	1.7410	1.6970	231.8
−47.5	1.7380	1.6941	232.7
−47.0	1.7321	1.6883	233.5

P = 2000 psia

temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H, Btu/lb
−50.0	1.1597	1.1619	213.8
−49.5	1.1617	1.1639	214.4
−49.0	1.1647	1.1669	215.0
−48.5	1.1677	1.1699	215.5
−48.0	1.1697	1.1719	216.1
−47.5	1.1716	1.1738	216.7
−47.0	1.1736	1.1758	217.3
−46.5	1.1791	1.1818	217.9
−46.0	1.1811	1.1839	218.5
−45.5	1.1831	1.1859	219.1
−45.0	1.1851	1.1879	219.7
−44.5	1.1881	1.1909	220.3
−44.0	1.1911	1.1939	220.9
−43.5	1.1941	1.1969	221.3
−43.0	1.1971	1.1999	232.0
−42.5	1.1991	1.2019	222.6
−42.0	1.2011	1.2039	223.2
−41.5	1.2031	1.2059	223.8
−41.0	1.2041	1.2069	224.5
−40.5	1.2051	1.2079	225.1
−40.0	1.2061	1.2089	225.7
−39.5	1.2071	1.2099	226.2
−39.0	1.2071	1.2099	226.9
−38.5	1.2071	1.2099	227.5
−38.0	1.2061	1.2089	228.1
−37.5	1.2051	1.2079	228.7
−37.0	1.2031	1.2059	229.3
−36.5	1.2011	1.2039	229.9
−36.0	1.1981	1.2009	230.5
−35.5	1.1951	1.1979	231.1
−35.0	1.1931	1.1959	231.7
−34.5	1.1911	1.1939	232.3
−34.0	1.1911	1.1939	232.9
−33.5	1.1911	1.1939	233.5
−33.0	1.1901	1.1929	234.1
−32.5	1.1891	1.1919	234.6
−32.0	1.1881	1.1909	235.2
−31.5	1.1871	1.1899	235.8
−31.0	1.1851	1.1879	236.3
−30.5	1.1811	1.1839	237.0
−30.0	1.1791	1.1818	237.5

Table XII. Thermodynamic Properties at the Pressures of Isobaric Determinations in the Regions of Rapid Changes (High $(\partial C_P/\partial T)_P$) in Mixture 4 (Ternary)

P = 1200 psia				P = 1500 psia				P = 2000 psia			
temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H(A), Btu/lb	temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H(A), Btu/lb	temp, °F	C_p(S), Btu/(lb °F)	C_p(A), Btu/(lb °F)	H(A), Btu/lb
−45.0	1.595	1.578	214.99	−40.0	1.206	1.1971	206.79	−5.0	1.082	1.072	235.51
−44.5	1.608	1.591	215.78	−39.0	1.217	1.208	207.98	−4.5	1.083	1.073	236.04
−44.0	1.621	1.604	216.58	−38.0	1.227	1.218	209.17	−4.0	1.083	1.073	236.58
−43.5	1.635	1.618	217.38	−37.0	1.238	1.229	210.46	−3.5	1.084	1.074	237.12
−43.0	1.650	1.633	218.20	−36.0	1.249	1.240	211.65	−3.0	1.085	1.075	237.66
−42.5	1.665	1.647	219.02	−35.0	1.261	1.252	212.94	−2.5	1.086	1.076	239.19
−42.0	1.681	1.663	219.85	−34.0	1.271	1.262	214.14	−2.0	1.087	1.077	238.73
−41.5	1.698	1.680	220.68	−33.0	1.283	1.273	215.43	−1.5	1.088	1.078	238.27
−41.0	1.715	1.697	221.53	−32.0	1.295	1.285	216.72	−1.0	1.089	1.079	239.81
−40.5	1.732	1.714	222.38	−31.0	1.307	1.297	218.01	−0.5	1.089	1.079	240.35
−40.0	1.751	1.733	223.24	−30.0	1.319	1.309	219.30	0.0	1.090	1.080	240.89
−39.5	1.771	1.752	224.11	−29.0	1.331	1.321	220.69	0.5	1.091	1.081	241.43
−39.0	1.775	1.756	224.99	−28.0	1.344	1.334	221.98	1.0	1.092	1.082	241.97
−38.5	1.796	1.777	225.87	−27.0	1.357	1.347	223.27	1.5	1.092	1.082	242.51
−38.0	1.819	1.800	226.76	−26.0	1.358	1.348	224.66	2.0	1.093	1.083	243.05
−37.5	1.843	1.824	227.67	−25.0	1.359	1.349	225.95	2.5	1.094	1.084	243.59
−37.0	1.861	1.841	228.59	−24.0	1.375	1.365	227.34	3.0	1.095	1.085	244.14
−36.5	1.875	1.855	229.52	−23.0	1.393	1.383	228.73	3.5	1.096	1.086	244.68
−36.0	1.881	1.861	230.45	−22.0	1.412	1.402	230.12	4.0	1.096	1.086	245.23
−35.5	1.875	1.855	231.38	−21.0	1.429	1.418	231.51	4.5	1.097	1.087	245.77
−35.0	1.861	1.841	232.30	−20.0	1.450	1.439	233.00	5.0	1.098	1.088	246.31
−34.5	1.843	1.824	233.22	−19.5	1.459	1.448	233.69	5.5	1.099	1.089	246.85
−34.0	1.821	1.802	234.12	−19.0	1.468	1.457	234.38	6.0	1.100	1.090	247.40
−33.5	1.802	1.783	235.02	−18.5	1.476	1.465	235.08	6.5	1.101	1.091	247.95
−33.0	1.788	1.769	235.91	−18.0	1.484	1.473	235.87	7.0	1.101	1.091	248.50
−32.5	1.781	1.762	236.79	−17.5	1.491	1.480	236.57	7.5	1.100	1.090	249.04
−32.0	1.764	1.745	237.67	−17.0	1.497	1.486	237.36	8.0	1.099	1.089	249.58
−31.5	1.750	1.732	238.53	−16.5	1.502	1.491	238.06	8.5	1.097	1.087	250.13
−31.0	1.735	1.717	239.40	−16.0	1.506	1.495	238.85	9.0	1.095	1.085	250.67
−30.5	1.720	1.702	240.25	−15.5	1.510	1.499	239.55	9.5	1.094	1.084	251.22
−30.0	1.705	1.687	241.09	−15.0	1.513	1.502	240.34	10.0	1.093	1.083	251.75
−29.5	1.690	1.672	241.93	−14.5	1.514	1.503	241.03	10.5	1.091	1.081	252.29
−29.0	1.676	1.658	242.77	−14.0	1.514	1.503	241.83	11.0	1.090	1.080	252.83
−28.5	1.662	1.644	243.60	−13.5	1.513	1.502	242.62	11.5	1.089	1.079	253.37
−28.0	1.648	1.631	244.42	−13.0	1.512	1.501	243.32	12.0	1.088	1.078	253.91
−27.5	1.635	1.618	245.23	−12.5	1.511	1.500	244.11	12.5	1.088	1.078	254.45
−27.0	1.623	1.606	246.03	−12.0	1.510	1.499	244.81	13.0	1.087	1.077	245.99
−26.5	1.612	1.595	246.83	−11.5	1.504	1.493	245.60	13.5	1.086	1.076	255.53
−26.0	1.602	1.585	247.62	−11.0	1.493	1.482	246.30	14.0	1.085	1.075	256.07
−25.5	1.591	1.574	248.41	−10.5	1.474	1.463	247.09	14.5	1.084	1.074	256.60
−25.0	1.580	1.563	249.21	−10.0	1.445	1.434	247.79	15.0	1.083	1.073	257.14
				−9.5	1.405	1.395	248.48				
				−9.0	1.400	1.390	249.17				
				−8.5	1.377	1.367	249.87				
				−8.0	1.357	1.347	250.56				
				−7.5	1.340	1.330	251.26				
				−7.0	1.327	1.317	251.85				
				−6.5	1.318	1.308	252.55				
				−6.0	1.353	1.343	253.24				
				−5.5	1.344	1.334	253.84				
				−5.0	1.336	1.326	254.53				
				−4.5	1.328	1.318	255.23				
				−4.0	1.320	1.310	255.82				
				−3.5	1.312	1.302	256.52				
				−3.0	1.305	1.295	257.11				
				−2.5	1.298	1.288	257.81				
				−2.0	1.291	1.281	258.40				
				−1.5	1.285	1.275	259.10				
				−1.0	1.279	1.270	259.70				
				−0.5	1.273	1.264	260.39				
				0.0	1.268	1.259	260.99				
				1.0	1.258	1.249	262.28				
				2.0	1.248	1.255	263.49				
				3.0	1.238	1.245	264.79				
				4.0	1.230	1.237	266.00				
				5.0	1.222	1.229	267.21				
				6.0	1.212	1.218	268.41				
				7.0	1.203	1.209	269.62				
				8.0	1.189	1.195	270.83				
				9.0	1.179	1.185	272.03				
				10.0	1.170	1.176	273.23				

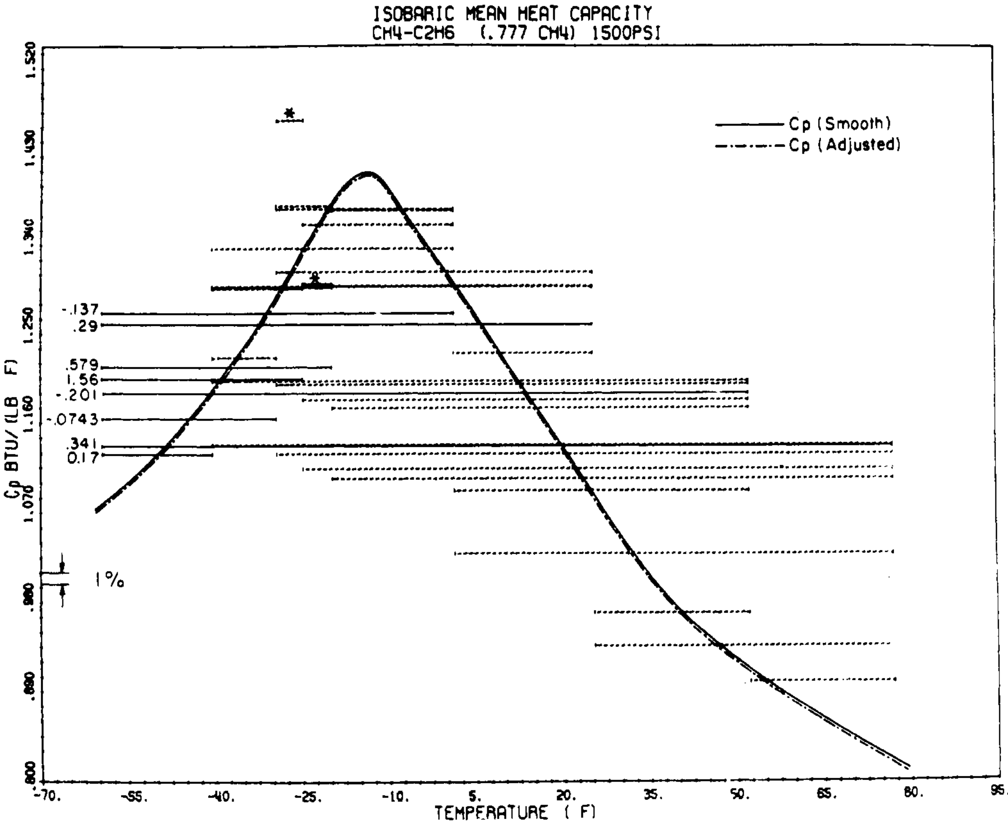

Figure 5. Isobaric heat capacity curve for a 22.3 mol % ethane in methane mixture at 1500 psia.

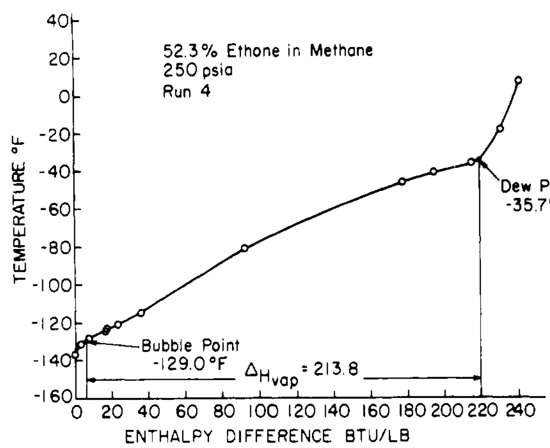

Figure 6. Isobaric enthalpy traverse through the two-phase region at 250 psia for a 52.3 mol % ethane in methane mixture.

Smoothing of Normalized Calorimetric Data. The isobaric, isothermal, and isenthalpic data obtained in the single-phase region were analyzed to yield values of the derivative functions $C_p \equiv (\partial H/\partial T)_P$, $\phi \equiv (\partial H/\partial P)_T$, and $\mu \equiv (\partial T/\partial P)_H$, respectively. In this process it is a relatively easy matter to identify individual points with considerably greater than average experimental error and therefore the smoothed values are probably of improved accuracy compared to the individual data points. Integration of the smoothed derivative functions yield provisional values of enthalpy differences which must then be checked for thermodynamic consistency.

Data taken within and near the two-phase region are generally not interpreted in terms of derivative functions but are merely smoothed graphically to yield values of enthalpy differences in this important region.

Details of the analyses have been presented elsewhere (*38*). Brief summaries of the procedures employed are given below.

Isobaric Data. Single Phase. The normalized and corrected values of isobaric differences in enthalpy and temperature were used to calculate mean values of $\hat{C}_p$.

$$\hat{C}_p \equiv \frac{[H_{T_k} - H_{T_j}]_P}{T_k - T_j} \tag{3}$$

Values thus calculated apply over the temperature interval $T_j \rightarrow T_k$ and are plotted as solid horizontal lines as illustrated on Figure 5. Prior adjustment of T_j to an average value for any isobaric set of runs permits calculation of additional isobaric enthalpy differences and therefore additional values of $\hat{C}_p$. Typical values obtained by difference are plotted as dashed horizontal lines in Figure 5.

Point values of the derivative function, C_p, are determined to satisfy the constraint

$$[H_{T_k} - H_{T_j}]_P = \int_{T_j}^{T_k} C_p \, dT_p \tag{4}$$

i.e., "equal area" requirements were met. Computer-aided graphical procedures were used as described in detail elsewhere

Table XIII. Empirical Data Obtained from Interpretation of Isobaric Enthalpy Traverses

mixture no.	pressure, psia	bubble point, °F	dew point, °F	ΔH_{vap}, Btu/lb
1. (52.3% C_2)	250	−129.0	−35.7	213.80
	500	−76.5	2.7	173.40
	750	−33.25	14.2	102.30
2. (22.3% C_2)	250	−154.2	−77.2	204.2
	500	−112.5	−46.8	166.5
3. (5.55% C_2)	250	−168[a]		
	500	−127.5[a]	−112[a]	113[a]
	700	−102[a]	−98[a]	59[a]
4. (ternary)	250	−159.5	−48[a]	227[a]
	500	−119	−40[a]	168[a]
	750	−89		
	1000	−67[a]		

[a] Not well defined by the data.

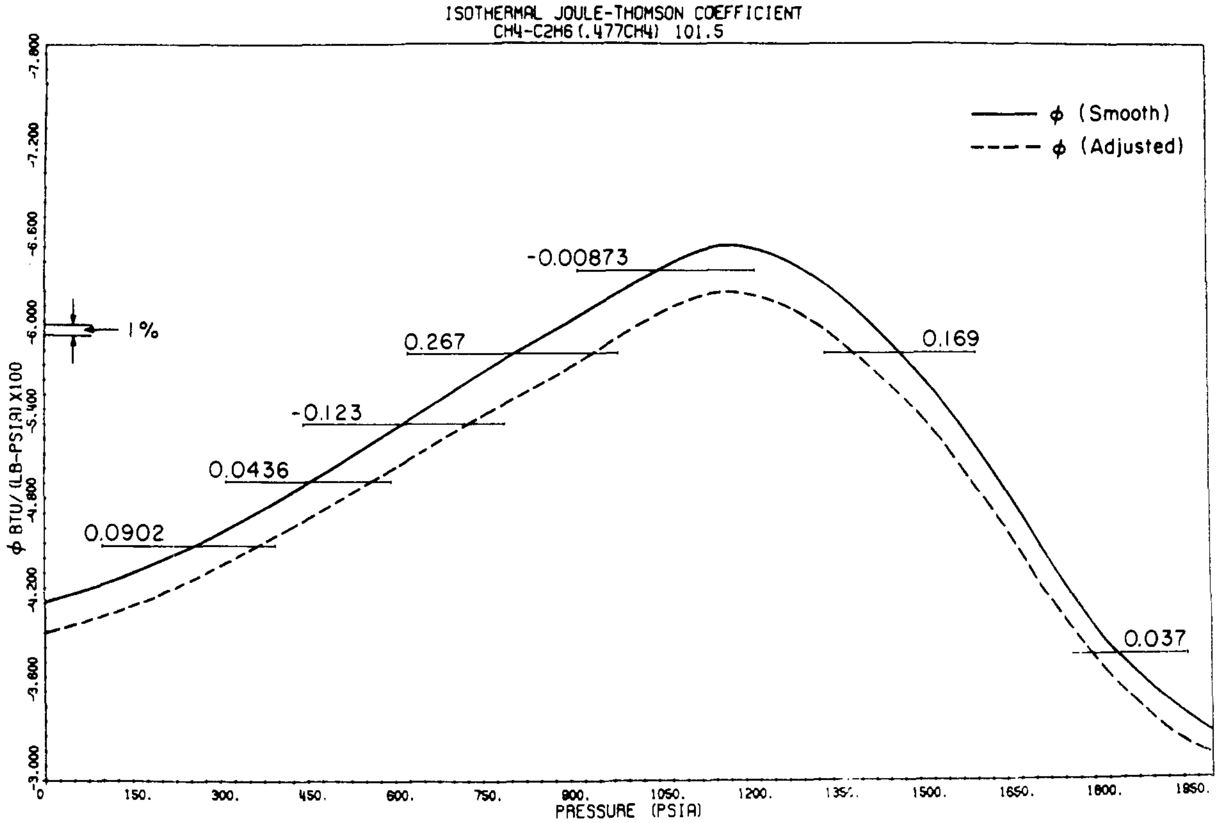

Figure 7. Isothermal throttling coefficient for a 52.3 mol % ethane in methane mixture at 101.5 °F.

(*8*). After each trial curve for $C_p = f(T)$ was established, integration of eq 4 was carried out over the temperature interval of each individual data point and difference point. The integration was carried out by computer using the Gauss–Legendre technique. Values of percentage error are listed on Figure 5 for each of the original data points used to generate the curve. One point has an indicated error of 1.56%. Note also that several values of $\hat{C}_p$ obtained by differences involving this point (indicated by asterisks) deviate markedly from the curve. It was thus concluded that this point was in error and it was given little weight in determining the final curve.

All isobaric data obtained in the single phase were interpreted in this way. The values of C_p so obtained are reported as C_p(S) (for smoothed) in Tables V–XII. In general, the differences between the experimental data and values calculated by numerical integration of the smoothed values of C_p showed random variation in sign and agreement was on the order of ±0.2% or better.

The smoothed values of $C_p(T)$ were also integrated to obtain isobaric enthalpy differences between temperatures of the experimental isothermal determinations. These differences were used in checking the thermodynamic consistency of the data as described subsequently.

Two Phase (Enthalpy Traverse). The calorimetric determinations within and through the two-phase region were obtained with a constant inlet temperature. Plots of temperature vs. enthalpy difference were made as illustrated in Figure 6.

Interpretation of such plots yielded not only smoothed values of enthalpy within and near the two-phase region but also the isobaric heat of vaporization and values of the bubble and dew points (Table XIII).

Isothermal Data. Interpretation of the isothermal data to yield smooth values of ϕ is very similar to the interpretation of the isobaric data. Figure 7 is a plot of

$$\hat{\phi} = \frac{[H_{P_k} - H_{P_j}]_T}{P_k - P_j} \qquad (5)$$

as represented by horizontal lines extending over the experimentally measured pressure interval. The solid curve results from use of an iterative, computer-aided, graphical-numerical procedure described elsewhere (*8*). Percentage deviations between the experimental data and values calculated by Gauss–Legendre integration of ϕ

$$[H_{P_k} - H_{P_j}]T = \int_{P_j}^{P_k} \phi \, dP_T \qquad (6)$$

are presented as applicable for the individual points on the figure.

The lower limit of pressure which could be attained in the course of isothermal experiments was about 100 psia. At lower pressures, values of $\phi(P)$ in the gas phase were estimated by several prediction methods (*8*) and used together with the experimental values to produce a smoothed curve extending the calorimetric data down to zero pressure. Thus the curve drawn on Figure 7 between 0 and 350 psia is in good agreement with the experimental data between 100 and 350 psia (0.09% deviation) and is of a shape in agreement with predictions made at low pressures. Several isothermal runs were made completely in the liquid region, i.e., at low temperatures above the two-phase region as indicated in Figures 1–4.

All isothermal data were interpreted in the manner described above and illustrated in Figure 7. The values of ϕ so obtained are reported as ϕ(S) in Tables XIV–XIX.

The numerical integration procedure was applied to yield values of isothermal enthalpy differences between the pressures of isobaric determinations for use together with similar isobaric integrations to check the thermodynamic consistency of the data.

Isenthalpic Data. Isenthalpic determinations were made with no energy added to the calorimeter when a drop in pressure through the calorimeter resulted in an increase in temperature of the flowing fluid. Experimental constraints did not permit isenthalpic determinations to be made from the highest to the lowest pressure. Instead, one run consisted of a series of relatively small pressure drops made with the same inlet

Table XIV. Thermodynamic Properties at the Temperatures of Isothermal and Isenthalpic Determinations, Binary Mixture Containing Approximately 52.3 mol % Ethane in Methane

	T = −228.45 °F			T = −99.05 °F			T = 1.75 °F			T = 101.5 °F			T = 252.5 °F		
pressure, psia	$10^4\mu$, °F/in.^{2}	$10^4\mu$, Btu/(lb in.$^{-2}$)	H, Btu/lb	$10^4\mu$, °F/in.^{2}	$10^4\mu$, Btu/(lb in.$^{-2}$)	H, Btu/lb	ϕ(S), Btu/(lb in.$^{-2}$)	ϕ(A), Btu/(lb in.$^{-2}$)	H, Btu/lb	ϕ(S), Btu/(lb in.$^{-2}$)	ϕ(A), Btu/(lb in.$^{-2}$)	H, Btu/lb	ϕ(S), Btu/(lb in.$^{-2}$)	ϕ(A), Btu/(lb in.$^{-2}$)	H, Btu/lb
0.0										−0.0420	−0.0400	395.80	−0.0268	−0.0249	472.30
50.0										−0.0425	−0.0405	393.79	−0.0268	−0.0249	471.06
100.0										−0.0433	−0.0412	391.75	−0.0269	−0.0250	469.81
150.0										−0.0440	−0.0419	389.68	−0.0270	−0.0251	468.56
200.0										−0.0449	−0.0427	387.56	−0.0270	−0.0251	467.30
250.0										−0.0457	−0.0435	385.41	−0.0271	−0.0252	466.04
300.0										−0.0467	−0.0444	383.21	−0.0272	−0.0253	464.78
350.0										−0.0477	−0.0453	380.97	−0.0273	−0.0254	463.51
400.0				−2.70	1.99	122.126				−0.0487	−0.0464	378.67	−0.0274	−0.0255	462.24
450.0										−0.0499	−0.0475	376.32	−0.0275	−0.0255	460.97
500.0	−24.10	15.50	37.186	−4.00	3.02	122.150				−0.0511	−0.0486	373.93	−0.0276	−0.0256	459.68
550.0										−0.0523	−0.0498	371.46	−0.0277	−0.0257	458.40
600.0	−21.80	14.00	37.341	−5.50	4.05	122.184				−0.0535	−0.0509	368.94	−0.0277	−0.0258	457.12
650.0										−0.0548	−0.0521	366.37	−0.0278	−0.0258	455.83
700.0	−19.70	12.60	37.474	−7.00	5.08	122.229				−0.0560	−0.0533	363.74	−0.0279	−0.0259	454.54
750.0										−0.0573	−0.0545	361.03	−0.0280	−0.0260	453.24
800.0	−17.60	11.30	37.594	−8.70	6.44	122.287				−0.0585	−0.0556	358.28	−0.0280	−0.0260	451.94
850.0										−0.0596	−0.0567	355.48	−0.0281	−0.0261	450.63
900.0	−15.60	10.00	37.701	−10.80	8.10	122.359				−0.0608	−0.0578	352.61	−0.0281	−0.0261	449.32
950.0										−0.0620	−0.0590	349.69	−0.0281	−0.0261	448.02
1000.0	−13.60	8.80	37.795	−13.40	9.87	122.440				−0.0632	−0.0601	346.72	−0.0281	−0.0261	446.71
1050.0							−0.0272	−0.0272	210.87	−0.0643	−0.0612	343.68	−0.0281	−0.0261	445.41
1100.0	−11.80	7.65	37.877	−15.75	11.56	122.547	−0.0243	−0.0243	209.58	−0.0653	−0.0621	340.60	−0.0280	−0.0260	444.11
1150.0							−0.0213	−0.0213	208.44	−0.0659	−0.0627	337.47	−0.0279	−0.0259	442.81
1200.0	−10.20	6.60	37.948	−18.20	13.32	122.673	−0.0187	−0.0187	207.44	−0.0659	−0.0627	334.34	−0.0278	−0.0258	441.52
1250.0							−0.0169	−0.0169	206.55	−0.0655	−0.0623	331.21	−0.0277	−0.0257	440.23
1300.0	−8.60	5.55	38.009	−20.50	15.09	122.815	−0.0154	−0.0154	205.75	−0.0646	−0.0614	328.11	−0.0275	−0.0256	438.95
1350.0							−0.0137	−0.0137	205.02	−0.0633	−0.0602	325.07	−0.0274	−0.0255	437.67
1400.0	−7.10	4.55	38.059	−22.80	16.79	122.975	−0.0121	−0.0121	204.38	−0.0617	−0.0587	322.09	−0.0272	−0.0253	436.40
1450.0							−0.0108	−0.0108	203.80	−0.0599	−0.0570	319.20	−0.0270	−0.0251	435.15
1500.0	−5.70	3.65	38.100	−25.25	18.59	123.154	−0.0097	−0.0097	203.29	−0.0579	−0.0551	316.39	−0.0268	−0.0249	433.89
1550.0							−0.0089	−0.0089	202.83	−0.0555	−0.0528	313.69	−0.0266	−0.0247	432.65
1600.0	−4.40	2.90	38.132	−27.70	20.35	123.349	−0.0082	−0.0082	202.40	−0.0527	−0.0501	311.12	−0.0264	−0.0245	431.42
1650.0							−0.0075	−0.0075	202.01	−0.0495	−0.0471	308.69	−0.0261	−0.0242	430.21
1700.0	−3.50	2.15	38.157	−30.10	22.16	123.560	−0.0069	−0.0069	201.65	−0.0462	−0.0440	306.41	−0.0258	−0.0240	429.00
1750.0							−0.0063	−0.0063	201.32	−0.0429	−0.0408	304.29	−0.0255	−0.0237	427.81
1800.0	−2.10	1.35	38.174	−32.50	23.93	123.790	−0.0058	−0.0058	201.02	−0.0402	−0.0383	302.32	−0.0251	−0.0234	426.63
1850.0							−0.0052	−0.0052	200.75	−0.0379	−0.0360	300.47	−0.0248	−0.0230	425.48
1900.0	−1.00	0.65	38.184	−35.00	25.77	124.038	−0.0047	−0.0047	200.50	−0.0360	−0.0342	298.66	−0.0243	−0.0226	424.33
1950.0							−0.0043	−0.0043	200.27	−0.0344	−0.0327	297.04	−0.0239	−0.0222	423.21
2000.0	0.20	−0.15	38.187	−37.60	27.68	124.305	−0.0039	−0.0039	200.07	−0.0331	−0.0315	295.42	−0.0234	−0.0218	422.11

Table XV. Thermodynamic Properties at the Temperatures of Isothermal and Isenthalpic Determinations. Binary Mixture Containing Approximately 22.3 mol % Ethane in Methane

	$T = -253.2$ °F			$T = -150.55$ °F			$T = -58.45$ °F			$T = 79.0$ °F			$T = 255.0$ °F		
pressure, psia	$10^4\mu$, °F/in.^{2}	$10^4\phi$, Btu/(lb in.$^{-2}$)	H, Btu/lb	$10^4\mu$, °F/in.^{2}	$10^4\phi$, Btu/(lb in.$^{-2}$)	H, Btu/lb	ϕ(S), Btu/(lb in.$^{-2}$)	ϕ(A), Btu/(lb in.$^{-2}$)	H, Btu/lb	ϕ(S), Btu/(lb in.$^{-2}$)	ϕ(A), Btu/(lb in.$^{-2}$)	H, Btu/lb	ϕ(S), Btu/(lb in.$^{-2}$)	ϕ(A), Btu/(lb in.$^{-2}$)	H, Btu/lb
0.0										-0.0346	-0.0333	397.10	-0.0212	-0.0197	490.80
50.0										-0.0350	-0.0336	395.43	-0.0212	-0.0197	489.81
100.0										-0.0356	-0.0342	393.74	-0.0212	-0.0197	488.83
150.0										-0.0361	-0.0347	392.01	-0.0212	-0.0197	487.84
200.0										-0.0367	-0.0353	390.27	-0.0212	-0.0198	486.85
250.0										-0.0373	-0.0358	388.49	-0.0212	-0.0198	485.86
300.0										-0.0379	-0.0364	386.68	-0.0212	-0.0198	484.88
350.0										-0.0385	-0.0370	384.85	-0.0212	-0.0197	483.89
400.0				-23.50	18.76	99.387				-0.0391	-0.0375	382.98	-0.0212	-0.0197	482.90
450.0										-0.0396	-0.0381	381.10	-0.0212	-0.0197	481.92
500.0				-21.40	17.10	99.565				-0.0401	-0.0386	379.18	-0.0212	-0.0197	480.93
550.0										-0.0406	-0.0391	377.24	-0.0211	-0.0197	479.95
600.0	-98.60	71.80	20.547	-19.40	15.46	99.727				-0.0411	-0.0395	375.28	-0.0211	-0.0196	478.96
650.0										-0.0415	-0.0399	373.29	-0.0211	-0.0196	477.99
700.0	-94.30	68.60	21.246	-17.35	13.85	99.873				-0.0418	-0.0402	371.29	-0.0210	-0.0195	477.00
750.0										-0.0422	-0.0406	369.27	-0.0210	-0.0195	476.03
800.0	-90.00	65.60	21.917	-15.40	12.30	100.003				-0.0426	-0.0409	367.23	-0.0209	-0.0194	475.06
850.0										-0.0429	-0.0412	365.18	-0.0208	-0.0194	474.08
900.0	-85.80	62.60	22.558	-13.57	10.82	100.118				-0.0432	-0.0415	363.11	-0.0207	-0.0193	473.12
950.0										-0.0435	-0.0418	361.02	-0.0206	-0.0192	472.16
1000.0	-82.20	59.80	23.170	-11.80	9.43	100.220				-0.0437	-0.0420	358.93	-0.0205	-0.0191	471.20
1050.0							-0.0345	-0.0345	191.95	-0.0440	-0.0423	356.82	-0.0204	-0.0190	470.25
1100.0	-78.70	57.30	23.755	-10.22	8.18	100.308	-0.0312	-0.0312	190.31	-0.0441	-0.0424	354.70	-0.0203	-0.0189	469.30
1150.0							-0.0276	-0.0276	188.84	-0.0443	-0.0426	352.58	-0.0202	-0.0188	468.36
1200.0	-75.50	55.00	24.316	-8.70	6.99	100.383	-0.0241	-0.0241	187.55	-0.0443	-0.0426	350.44	-0.0202	-0.0187	467.42
1250.0							-0.0207	-0.0207	186.43	-0.0443	-0.0426	348.32	-0.0200	-0.0186	466.49
1300.0	-72.60	53.00	24.857	-7.20	5.75	100.447	-0.0177	-0.0177	185.47	-0.0441	-0.0424	346.20	-0.0199	-0.0185	465.56
1350.0							-0.0152	-0.0152	184.65	-0.0438	-0.0421	344.08	-0.0198	-0.0184	464.64
1400.0	-69.80	51.00	25.378	-5.70	4.55	100.498	-0.0132	-0.0132	183.94	-0.0435	-0.0418	341.99	-0.0196	-0.0182	463.72
1450.0							-0.0116	-0.0116	183.32	-0.0430	-0.0414	339.90	-0.0195	-0.0181	462.81
1500.0	-67.30	49.20	25.878	-4.20	3.35	100.538	-0.0105	-0.0105	182.77	-0.0425	-0.0408	337.84	-0.0194	-0.0180	461.91
1550.0							-0.0097	-0.0097	182.27	-0.0419	-0.0403	335.82	-0.0192	-0.0179	461.01
1600.0	-64.90	47.30	26.360	-2.40	2.24	100.566	-0.0092	-0.0092	181.79	-0.0412	-0.0396	333.82	-0.0191	-0.0178	460.12
1650.0							-0.0085	-0.0085	181.35	-0.0405	-0.0389	331.86	-0.0189	-0.0176	459.24
1700.0	-62.80	45.70	26.825	-1.45	1.16	100.583	-0.0079	-0.0079	180.94	-0.0396	-0.0381	329.93	-0.0188	-0.0174	458.36
1750.0							-0.0073	-0.0073	180.56	-0.0387	-0.0372	328.05	-0.0186	-0.0173	457.49
1800.0	-60.70	44.20	27.274	-0.19	0.12	100.589	-0.0067	-0.0067	180.21	-0.0376	-0.0362	326.22	-0.0184	-0.0171	456.64
1850.0							-0.0062	-0.0062	179.89	-0.0365	-0.0351	324.43	-0.0182	-0.0169	455.78
1900.0	-58.70	42.70	27.708	1.10	-0.92	100.585	-0.0057	-0.0057	179.59	-0.0353	-0.0340	322.71	-0.0180	-0.0167	454.94
1950.0							-0.0052	-0.0052	179.32	-0.0342	-0.0329	321.04	-0.0176	-0.0164	454.12
2000.0	-56.75	41.30	28.128	2.35	-1.88	100.571	-0.0049	-0.0049	179.07	-0.0331	-0.0318	319.41	-0.0172	-0.0160	453.31

Table XVI. Thermodynamic Properties at the Temperatures of Isothermal and Isenthalpic Determinations. Binary Mixture Containing Approximately 5.5 mole % Ethane in Methane

	$T = -242.0\ °F$		$T = -150.0\ °F$		$T = -97.0\ °F$		
pressure, psia	$\phi \times 10^4$, Btu/(lb in.$^{-2}$)	H, Btu/lb	$\phi \times 10^4$, Btu/(lb in.$^{-2}$)	H, Btu/lb	$-\phi(S) \times 10^2$, Btu/(lb in.$^{-2}$)	$-\phi(A) \times 10^2$, Btu/(lb in.$^{-2}$)	H, Btu/lb
0.0					6.067	5.704	319.4
50.0					6.438	6.053	316.4
100.0	43.75	38.2			6.810	6.403	313.3
150.0					7.200	6.770	310.0
200.0	38.40	37.8			7.625	7.169	306.6
250.0					8.100	7.616	302.8
300.0	33.30	37.4			8.640	8.123	298.9
350.0					9.437	8.872	294.7
400.0	28.70	37.1			10.400	9.778	290.0
450.0					11.530	10.840	284.9
500.0	24.25	36.8	−35.50	115.5	12.970	12.194	279.1
550.0					15.370		272.1
600.0	19.90	36.6	−28.00	115.2	20.420		263.4
650.0					34.400		249.7
700.0	16.00	34.4	−20.00	115.0	42.230		230.0
750.0					41.840		208.8
800.0	12.20	36.3	−17.20	114.8	30.320	30.32	194.9
850.0					15.130	13.57	184.8
900.0	9.00	36.2	−14.2	114.6	7.360	6.60	180.0
950.0					4.780	4.29	177.5
1000.0	5.80	36.0	−11.8	114.5	3.440	3.09	175.6
1050.0					2.800	2.7440	174.1
1100.0	3.20	36.1	−8.8	114.4	2.420	2.3716	172.8
1150.0					2.1600	2.1168	171.7
1200.0	1.00	36.0	−6.6	114.3	1.8800	1.8424	170.7
1250.0					1.6610	1.7015	169.8
1300.0	−1.00	36.0	−4.0	114.2	1.4800	1.5161	169.0
1350.0					1.3480	1.3809	168.3
1400.0	−2.80	36.1	−1.4	114.2	1.2400	1.2702	167.6
1450.0					1.1330	1.1606	167.0
1500.0	−4.00	36.0	1.0	114.2	1.0300	1.055	166.5
1550.0					0.9210	0.8652	166.0
1600.0	−4.50	36.0	2.8	114.2	0.8220	0.7722	165.6
1650.0					0.7486	0.7032	165.3
1700.0	−5.00	36.1	5.0	114.3	0.6900	0.6482	164.9
1750.0					0.6430	0.6040	164.6
1800.0	−5.50	36.2	7.7	114.3	0.6000	0.5636	164.3
1850.0					0.5498	0.5165	164.0
1900.0	−5.80	36.3	9.0	114.4	0.5000	0.4697	163.8
1950.0					0.4534	0.4259	163.5
2000.0	−5.90	36.4	11.0	114.5	0.4130	0.3880	163.4

	$T = -47.0\ °F$			$T = 79.0\ °F$		
pressure, psia	$-\phi(S) \times 10^2$, Btu/(lb in.$^{-2}$)	$-\phi(A) \times 10^2$, Btu/(lb in.$^{-2}$)	$H(A)$, Btu/lb	$-\phi(S) \times 10^2$, Btu/(lb in.$^{-2}$)	$-\phi(A) \times 10^2$, Btu/(lb in.$^{-2}$)	$H(A)$, Btu/lb
0.0	4.828	4.568	343.7	2.944	2.768	407.2
50.0	4.953	4.686	341.4	2.968	2.791	405.8
100.0	5.100	4.825	339.0	2.995	2.816	404.4
150.0	5.266	4.982	336.6	3.024	2.843	403.0
200.0	5.451	5.157	334.0	3.055	2.872	401.6
250.0	5.650	5.346	331.4	3.088	2.903	400.1
300.0	5.853	5.503	328.7	3.124	2.937	398.7
350.0	6.075	5.712	325.9	3.161	2.971	397.2
400.0	6.320	5.942	323.0	3.199	3.007	395.7
450.0	6.606	6.211	320.0	3.239	3.045	394.2
500.0	6.900	6.488	316.8	3.277	3.080	392.7
550.0	7.169	6.737	313.49	3.307	3.109	391.1
600.0	7.450	7.002	310.1	3.333	3.133	389.6
650.0	7.772	7.304	306.5	3.354	3.153	388.0
700.0	8.130	7.641	302.8	3.371	3.169	386.4
750.0	8.541	8.021	298.9	3.387	3.184	384.8
800.0	8.970	8.424	294.7	3.401	3.197	383.2
850.0	9.378	8.814	290.4	3.413	3.208	381.6
900.0	9.800	9.211	285.9	3.422	3.217	380.0
950.0	10.250	9.634	281.2	3.430	3.224	378.4
1000.0	10.620	9.981	276.3	3.435	3.229	376.8
1050.0	10.810	10.161	271.2	3.438	3.231	375.2
1100.0	10.880	10.227	266.2	3.438	3.231	373.6
1150.0	10.750	10.104	261.0	3.436	3.230	372.0
1200.0	10.290	9.672	256.1	3.432	3.225	370.4
1250.0	9.610	8.896	251.5	3.424	3.217	368.8
1300.0	8.940	8.275	247.2	3.413	3.207	367.2

Table XVI (*Continued*)

	$T = -47.0$ °F			$T = 79.0$ °F		
pressure, psia	$-\phi$(S) × 10^2, Btu/(lb in.$^{-2}$)	$-\phi$(A) × 10^2, Btu/(lb in.$^{-2}$)	H(A), Btu/lb	$-\phi$(S) × 10^2, Btu/(lb in.$^{-2}$)	$-\phi$(A) × 10^2, Btu/(lb in.$^{-2}$)	H(A), Btu/lb
1350.0	8.227	7.615	243.2	3.401	3.195	365.6
1400.0	7.420	6.868	239.6	3.381	3.176	364.1
1450.0	6.566	6.078	236.3	3.357	3.154	362.5
1500.0	5.740	5.313	233.6	3.331	3.129	360.9
1550.0	5.042	4.751	231.0	3.300	3.100	359.4
1600.0	4.450	4.193	228.8	3.266	3.067	357.9
1650.0	3.970	3.741	226.8	3.232	3.036	356.4
1700.0	3.567	3.361	225.0	3.198	3.004	354.9
1750.0	3.225	3.039	223.4	3.163	2.971	353.4
1800.0	2.930	2.761	222.0	3.128	2.938	351.9
1850.0	2.688	2.533	220.6	3.092	2.904	350.5
1900.0	2.480	2.337	219.4	3.055	2.870	349.1
1950.0	2.292	2.160	218.3	3.017	2.834	347.6
2000.0	2.110	1.988	217.3	2.977	2.796	346.3

Table XVII. Thermodyanmic Properties at the Temperatures of Isothermal and Isenthalpic Determinations. Ternary Mixture Containing Methane, Ethane, and Propane

	$T = -150.0$ °F		$T = -47.0$ °F			$T = 1.5$ °F			$T = 158.5$ °F		
pressure, psia	$10^4\phi$, Btu/(lb in.$^{-2}$)	H, Btu/lb	ϕ(S), Btu/(lb in.$^{-2}$)	ϕ(A), Btu/(lb in.$^{-2}$)	H, Btu/lb	ϕ(S), Btu/(lb in.$^{-2}$)	ϕ(A), Btu/(lb in.$^{-2}$)	H, Btu/lb	ϕ(S), Btu/(lb in.$^{-2}$)	ϕ(A), Btu/(lb in.$^{-2}$)	H, Btu/lb
0.0						−0.0442	−0.04256	358.4	−0.02630	−0.0254	436.90
50.0						−0.04593	−0.04422	356.23	−0.02665	−0.02571	435.62
100.0						−0.04754	−0.04577	353.98	−0.02696	−0.02600	434.33
150.0						−0.04907	−0.04724	351.65	−0.02724	−0.02627	433.02
200.0						−0.05054	−0.04866	349.26	−0.02749	−0.02652	431.70
250.0						−0.05200	−0.05006	346.79	−0.02773	−0.02675	430.37
300.0						−0.05347	−0.05148	344.25	−0.02796	−0.02697	429.03
350.0						−0.05496	−0.05291	341.64	−0.02819	−0.02719	427.67
400.0	3.68	102.29				−0.05660	−0.05449	338.95	−0.02835	−0.02734	426.31
450.0						−0.05835	−0.05618	336.19	−0.02848	−0.02747	424.94
500.0	6.32	102.34				−0.06020	−0.05796	333.34	−0.02859	−0.02758	423.56
550.0						−0.06216	−0.05915	330.28	−0.02870	−0.02922	422.10
600.0	8.85	102.42				−0.0642	−0.06109	327.42	−0.02874	−0.02926	420.65
650.0						−0.06629	−0.06308	324.32	−0.02873	−0.02925	419.18
700.0	10.94	102.51				−0.06840	−0.06509	321.11	−0.02869	−0.02921	417.72
750.0						−0.07050	−0.06867	317.81	−0.02866	−0.02918	416.26
800.0	12.68	102.63				−0.07256	−0.07067	314.32	−0.02860	−0.02912	414.80
850.0						−0.07454	−0.07260	310.74	−0.02853	−0.02905	413.35
900.0	14.20	102.77				−0.07640	−0.07441	307.07	−0.02845	−0.02897	411.89
950.0						−0.07810	−0.07607	303.31	−0.02835	−0.02886	410.46
1000.0	15.60	102.92				−0.07960	−0.07753	299.46	−0.02825	−0.02876	409.01
1050.0						−0.08000	−0.07723	295.61	−0.02814	−0.02865	407.57
1100.0	16.88	103.08				−0.07980	−0.07703	291.75	−0.02802	−0.02853	406.15
1150.0						−0.07887	−0.07613	287.91	−0.02789	−0.02840	404.72
1200.0	18.10	103.25				−0.07710	−0.07443	284.15	−0.02776	−0.02826	403.31
1250.0			−0.05100	−0.06179	208.85	−0.07504	−0.07626	280.28	−0.02762	−0.02812	401.89
1300.0	19.28	103.44	−0.04140	−0.05016	206.07	−0.07280	−0.07399	276.53	−0.02748	−0.02798	400.50
1350.0			−0.03460	−0.04192	206.96	−0.07008	−0.07122	272.89	−0.02732	−0.02782	399.10
1400.0	20.50	103.64	−0.03000	−0.03635	201.83	−0.06700	−0.06809	269.40	−0.02714	−0.02763	397.71
1450.0			−0.02620	−0.03174	200.13	−0.06343	−0.06446	266.09	−0.02695	−0.02744	396.33
1500.0	21.60	103.85	−0.02280	−0.02280	198.65	−0.05980	−0.06078	262.96	−0.02674	−0.02723	394.97
1550.0			−0.01990	−0.01990	197.59	−0.05609	−0.05568	260.08	−0.02653		393.64
1600.0	22.76	104.07	−0.01757	−0.01757	196.65	−0.05227	−0.05189	257.40	−0.02630		392.32
1650.0			−0.01590	−0.01590	195.81	−0.04840	−0.04805	254.92	−0.02607		391.01
1700.0	23.96	104.31	−0.01452	−0.01452	195.06	−0.04450	−0.04418	252.64	−0.02583		389.71
1750.0			−0.01335	−0.01335	194.36	−0.04059	−0.04029	250.45	−0.02558		388.42
1800.0	25.16	104.55	−0.01216	−0.01216	193.72	−0.03680	−0.03653	248.57	−0.02533		387.15
1850.0			−0.01105	−0.01105	193.14	−0.03342	−0.03318	246.78	−0.02508		385.89
1900.0	26.35	104.81	−0.01005	−0.01005	192.61	−0.03027	−0.03005	245.19	−0.02484		384.64
1950.0			−0.00915	−0.00915	192.13	−0.02732	−0.02712	243.80	−0.02460		383.41
2000.0	27.60	105.08	−0.00836	−0.00836	191.70	−0.02450	−0.02432	242.51	−0.02436		382.18

temperature. These data, when used in conjunction with results of isobaric experiments, permitted rigorous calculation of isothermal enthalpy changes over the same pressure interval as explained in detail elsewhere (*34*). These isothermal values were analyzed as described in the preceding section to yield smoothed values of ϕ(S). These values together with C_p(S) values yielded μ(S) according to the rigorous relation

$$\mu = -\phi / C_p \tag{7}$$

The values thus calculated are included in the skeleton tables where applicable.

Adjustment to Ensure Thermodynamic Consistency. The individual enthalpy differences calculated by numerical integration of smoothed values of C_p and ϕ obtained as described in the

Table XVIII. Thermodynamic Properties at the Temperatures of Isothermal Determinations, in the Regions of Rapid Change (High $(\partial\phi/\mu\rho)_T$) for Mixture 3 (5.55% C_2)

$T = -47.0$ °F				$T = 79$ °F			
pressure, psia	$-\phi$(S) × 10^2, Btu/(lb in.$^{-2}$)	$-\phi$(A) × 10^2, Btu/(lb in.$^{-2}$)	H, Btu/lb	pressure, psia	$-\phi$(S) × 10^2, Btu/(lb in.$^{-2}$)	$-\phi$(A) × 10^2, Btu/(lb in.$^{-2}$)	H, Btu/lb
900.0	9.800	9.211	285.9	1000.0	3.435	3.229	376.8
910.0	9.891	9.296	285.0	1010.0	3.436	3.229	376.5
920.0	9.983	9.383	284.0	1020.0	3.436	3.229	376.2
930.0	10.070	9.464	283.1	1030.0	3.437	3.230	375.8
940.0	10.160	9.549	282.2	1040.0	3.438	3.231	375.5
950.0	10.250	9.634	281.2	1050.0	3.438	3.231	375.2
960.0	10.330	9.709	280.2	1060.0	3.438	3.231	374.9
970.0	10.410	9.784	279.2	1070.0	3.438	3.231	374.6
980.0	10.500	9.869	278.3	1080.0	3.438	3.231	374.2
990.0	10.560	9.925	277.3	1090.0	3.438	3.231	373.9
1000.0	10.620	9.981	276.3	1100.0	3.438	3.231	373.6
1010.0	10.670	10.029	275.3	1110.0	3.438	3.231	373.2
1020.0	10.710	10.067	274.3	1120.0	3.437	3.230	373.0
1030.0	10.750	10.104	273.3	1130.0	3.437	3.230	372.6
1040.0	10.780	10.133	272.3	1140.0	3.437	3.230	372.3
1050.0	10.810	10.161	271.2	1150.0	3.436	3.229	372.0
1060.0	10.840	10.189	270.2	1160.0	3.435	3.228	371.6
1070.0	10.860	10.208	269.2	1170.0	3.435	3.228	371.3
1080.0	10.880	10.227	268.2	1180.0	3.434	3.227	371.0
1090.0	10.880	10.227	267.2	1190.0	3.433	3.226	370.7
1100.0	10.880	10.227	266.2	1200.0	3.432	3.225	370.4
1110.0	10.870	10.217	265.1				
1120.0	10.850	10.198	264.1				
1130.0	10.830	10.180	263.1				
1140.0	10.790	10.142	262.1				
1150.0	10.750	10.104	261.0				
1160.0	10.690	10.048	260.0				
1170.0	10.610	9.973	260.0				
1180.0	10.520	9.888	258.1				
1190.0	10.410	9.785	257.1				
1200.0	10.290	9.672	256.1				

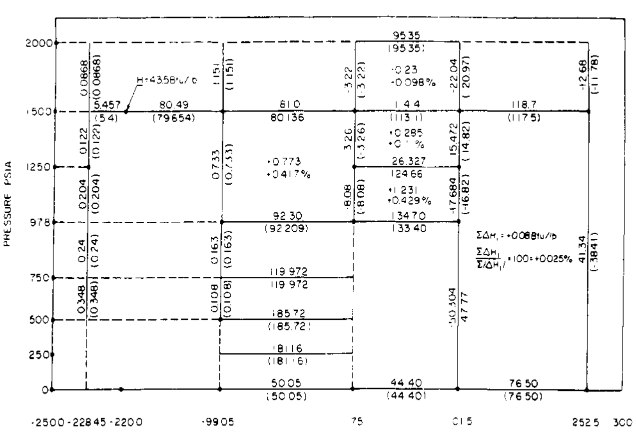

Figure 8. Summary of consistency checks, 52.3 mol % ethane in methane mixture.

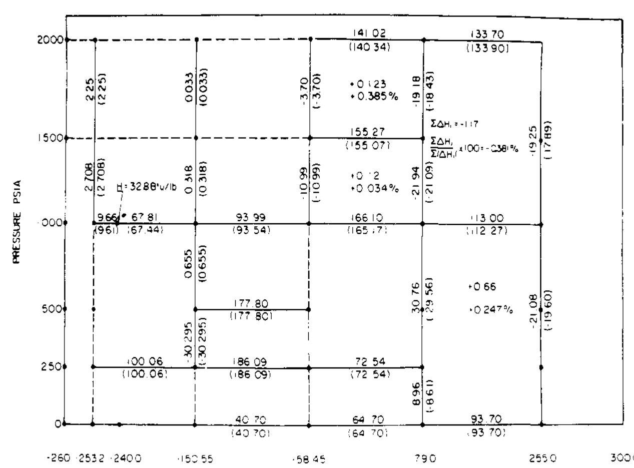

Figure 9. Summary of consistency checks, 22.3 mol % ethane in methane mixture.

preceding section are summarized on P–T diagrams as Figures 8–11. These values are represented by numbers that are *not* included in parentheses.

Enthalpy is a point function of state and therefore these independently determined values of differences in enthalpy can be tested against the rigorous thermodynamic requirement that the sum of all differences around a closed loop must equal zero, theoretically. Practically, the values of the actual sums (taken in the clockwise direction with proper attention to sign), $\sum \Delta H_j$, and the percentage deviations,

$$\text{percentage deviation} \equiv \frac{\sum \Delta H_j}{\sum |\Delta H_j|} \times 100 \qquad (8)$$

provide a quantitative measure of the internal thermodynamic consistency of the smoothed data and are included within each closed loop. Consideration of the values presented in Figures 8–11 reveals that the data are indeed self-consistent to about 1.0% in most cases.

Unfortunately, this important consistency check does not eliminate the possibility of experimental error. For example, if the flow determinations for all runs are in error by a constant percentage, all experimental results will incorporate this same percentage error and the results will be thermodynamically consistent but inaccurate. As mentioned previously, leaks were found in the system after completion of the investigation. Note that it is highly improbable to have leaks of the same percentage of flow for both isobaric and isothermal determinations because two different calorimeters were used. Nevertheless, it was decided to make additional adjustments to ensure not only internal thermodynamic consistency but also agreement with

Table XIX. Thermodynamic Properties at the Temperatures of Isothermal Determinations, in the Regions of Rapid Change (High $(\partial\phi/\mu p)_T$) for Mixture 4 (Ternary)

T = 158.5 °F				T = 1.5 °F			
pressure, psia	$-\phi(S) \times 10^2$, Btu/(lb in.$^{-2}$)	$-\phi(A) \times 10^2$, Btu/(lb in.$^{-2}$)	H, Btu/lb	pressure, psia	$-\phi(S) \times 10^2$, Btu/(lb in.$^{-2}$)	$-\phi(A) \times 10^2$, Btu/(lb in.$^{-2}$)	H, Btu/lb
900.0	7.640	7.441	307.07	400.0	2.835	2.734	426.31
910.0	7.675	7.475	306.32	410.0	2.838	2.737	426.04
920.0	7.710	7.509	305.57	420.0	2.841	2.740	425.76
930.0	7.744	7.543	304.82	430.0	2.843	2.742	425.49
940.0	7.777	7.575	304.07	440.0	2.846	2.745	425.22
950.0	7.810	7.607	303.31	450.0	2.848	2.747	424.94
960.0	7.844	7.640	302.54	460.0	2.850	2.749	424.67
970.0	7.877	7.672	302.07	470.0	2.853	2.752	242.39
980.0	7.908	7.702	301.01	480.0	2.855	2.754	424.12
990.0	7.936	7.730	300.24	490.0	2.857	2.756	423.84
1000.0	7.960	7.753	299.46	500.0	2.859	2.758	423.56
1010.0	7.975	7.698	298.69	510.0	2.861	2.913	423.27
1020.0	7.986	7.709	297.93	520.0	2.864	2.916	422.99
1030.0	7.994	7.717	297.15	530.0	2.866	2.918	422.69
1040.0	7.998	7.721	296.38	540.0	2.868	2.920	422.40
1050.0	8.000	7.723	295.61	550.0	2.870	2.922	422.10
1060.0	8.001	7.724	294.84	560.0	2.871	2.923	421.81
1070.0	8.000	7.723	294.06	570.0	2.872	2.924	421.52
1080.0	7.996	7.719	293.29	580.0	2.873	2.925	421.28
1090.0	7.989	7.712	292.52	590.0	2.874	2.926	420.93
1100.0	7.980	7.703	291.75	600.0	2.874	2.926	420.65
1110.0	9.968	7.692	290.97	610.0	2.874	2.926	420.35
1120.0	7.952	7.676	290.21	620.0	2.874	2.926	420.06
1130.0	7.934	7.659	289.44	630.0	2.874	2.926	419.76
1140.0	7.912	7.638	288.68	640.0	2.874	2.926	419.48
1150.0	7.887	7.613	287.91	650.0	2.873	2.925	419.18
1160.0	7.857	7.585	287.15	660.0	2.872	2.924	418.89
1170.0	7.823	7.552	286.40	670.0	2.872	2.924	418.59
1180.0	7.787	7.517	285.65	680.0	2.871	2.923	418.31
1190.0	7.749	7.480	284.89	690.0	2.870	2.922	418.01
1200.0	7.710	7.443	284.15	700.0	2.869	2.921	417.72
1210.0	7.671	7.796	283.37	710.0	2.868	2.920	417.43
1220.0	7.630	7.754	282.58	720.0	2.868	2.920	417.14
1230.0	7.589	7.713	281.81	730.0	2.867	2.919	416.84
1240.0	7.547	7.670	281.05	740.0	2.867	2.919	416.56
1250.0	7.504	7.626	280.28	750.0	2.866	2.918	416.26
1260.0	7.462	7.584	279.53	760.0	2.865	2.917	415.96
1270.0	7.418	7.539	278.76	770.0	2.864	2.916	415.68
1280.0	7.374	7.494	278.01	780.0	2.863	2.915	415.38
1290.0	7.328	7.448	277.27	790.0	2.861	2.913	415.09
1300.0	7.280	7.399	276.53	800.0	2.860	2.912	414.80
				810.0	2.859	2.911	414.51
				820.0	2.857	2.909	414.22
				830.0	2.856	2.908	413.92
				840.0	2.854	2.905	413.63
				850.0	2.853	2.905	412.35
				860.0	2.852	2.904	413.05
				870.0	2.850	2.902	412.77
				880.0	2.848	2.900	412.47
				890.0	2.847	2.899	412.19
				900.0	2.845	2.897	411.89

other published data of acceptable accuracy.

Utilization of Published Data. As discussed under the section entitled, Selection of Bases and Use of Other Published Data, accurate data for pure methane (*11*, *33*), ethane (*8*), and propane (*33*, *36*) were used to establish enthalpy values for the mixture in the gaseous state at zero pressure as listed in Table III. Similarly, estimates of the excess enthalpy of mixing of liquid methane, ethane, and propane served to establish enthalpy values for one set of conditions in the liquid region for each binary and ternary mixture as summarized in Table IV. These "check points" serve to establish values of enthalpy differences for comparison with the experimentally obtained values. The comparisons are summarized in Table XX. The discrepancies [up to 6.7 Btu/lb (1.5%) in one case] are much larger than had been expected as similar comparisons made with other data (*3*, *8*, *15*, *33*–*37*) had yielded remarkable agreement. Therefore, it was decided to adjust all values in accordance with several goals and limitations: (1) obtain agreement with the values of enthalpy differences between pairs of check points based on other published data (Table XX); (2) utilize estimates of the isothermal effect of pressure on enthalpy based on volumetric data at high temperatures where such estimations have proven to be accurate (*8*); (3) make adjustments in the derivative functions C_p and ϕ such that integration yields thermodynamic consistency. Further, these adjustments should not be excessive, i.e., in keeping with corrections made for similar determinations on the same equipment.

With the exception that it was necessary to make corrections to both the isobaric and isothermal data somewhat in excess of those applied in the analysis of data for similar systems, it was possible to satisfy all other conditions by a laborious trial-and-error procedure. The resulting thermodynamically consistent values of enthalpy differences are listed in parentheses on Figures 8–11. In some cases, it was necessary to make adjustments to isothermal determinations by as much

Table XX. Comparison of Enthalpy Differences as Estimated from Published Data (Tables III and IV) with Those Determined from Calorimetric Measurements

	mixture no.							
	1 (52.3% C_2)		2 (22.3% C_2)		3 (5.55% C_2)		4 (ternary)	
	°F	psia	°F	psia	°F	psia	°F	psia
pairs of check points	252.5	0	255	0	79	0	158.5	0
	−220	1500	−240	1000	−242	1000	−243	1500
enthalpy diff	Btu/lb		Btu/lb		Btu/lb		Btu/lb	
published data	429.2		458.7		373.0		404.9	
exptl value	435.9		462.0		371.1		402.9	
diff %	−6.7 (1.5)		−3.3 (0.7)		+1.9 (0.5)		+2.0 (0.5)	

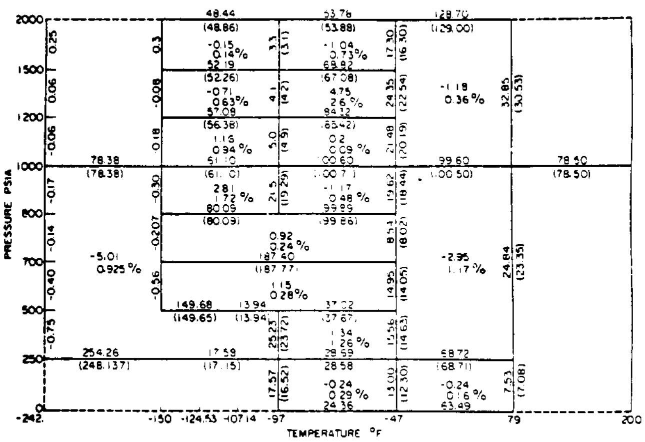

Figure 10. Summary of consistency checks, 5.55 mol % ethane in methane mixture.

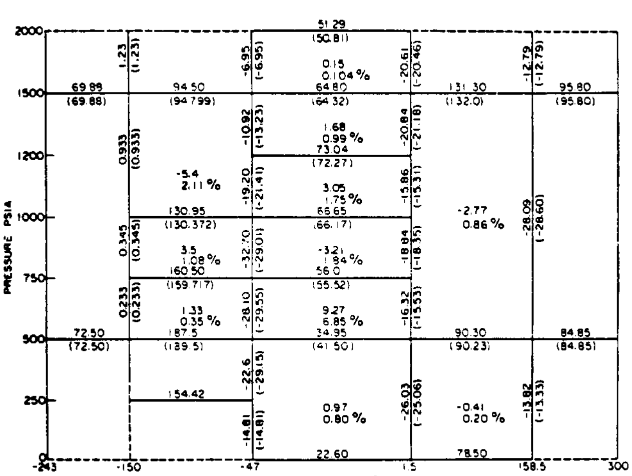

Figure 11. Summary of consistency checks, methane–ethane–propane

as 7.1% as indicated by the dashed curve in Figure 7. Corrections as large as 1.3% were made on the isobaric values (center-line on Figure 5). Thus, these data, although thermodynamically consistent to about 1% were judged to be in error by somewhat larger amounts. Taking into account the possibility of systematic errors during the experiment, unusually large adjustments were made in preparing the skeleton tables of thermodynamic data. The values so adjusted are listed as C_p(A) and ϕ(A) together with values of H which are consistent with the adjusted values of the derivative functions.

Skeleton Tables of Thermodynamic Data

Table I contains selected values of thermodynamic properties for the three methane–ethane binaries and the ternary. These values were obtained as described in preceding sections. These tables include only those values of enthalpy at intersections of isobaric and isothermal determinations; i.e., the values are, in effect, measured twice (except as otherwise indicated). These values are probably the better known of all enthalpy values included in this manuscript and, since they cover the entire range of experimental investigation, should serve well to test prediction methods.

Values of C_p, ϕ, and H reported in Tables VI and VIII comprise the major contribution of this investigation. Both smooth and adjusted values of C_p and ϕ are listed as discussed previously. The enthalpy values are consistent with the adjusted values of the derivative functions C_p(A) and ϕ(A).

Table VI contains values of C_p and H at the pressures of measurement over a temperature range from −260 to +320 °F at temperature intervals of 10 °F. At pressures below the critical, values of C_p are not reported within or near the two-phase region except for the 250 psia isobar in Table VIa.

Similarly, Table VIII consists of values of ϕ and H at the temperatures of isothermal determinations and μ, ϕ, and H at temperatures of isenthalpic determinations. Results of isothermal determinations are reported at intervals of 50 psi and those corresponding to isenthalpic determinations at intervals of 100 psi.

Data obtained from enthalpy traverses across the two-phase region are reported in Table VIII.

Near the critical point of the mixture, C_p attains a maximum. In this region C_p is a strong function of temperature (as well as pressure), i.e., $(\partial C_p/\partial T)_p$ is large and consequently thermodynamic properties change very rapidly. Therefore, it was felt necessary to report C_p and H at closer intervals of temperature in this region. Table VI contains these values. The format of this table is the same as VI. Similarly, Table IX contains values of ϕ and H at closer intervals of pressure at pressures near the critical point of the mixture.

Acknowledgment

The data presented in this report were obtained by Joseph C. Golba and he is commended for his patience and attention to detail so necessary to obtain precise calorimetric data.

Glossary

C_p	isobaric heat capacity ≡ $(\partial H/\partial T)_P$, Btu/(lb °F)
C_p(A)	values of C_p adjusted to ensure thermodynamic consistency
C_p(S)	smoothed C_p values before thermodynamic consistency checks
H	specific enthalpy, Btu/lb
H_i	specific enthalpy of ith component, Btu/lb
H_M	specific enthalpy of mixture, Btu/lb
H^E	excess enthalpy, Btu/lb
P	pressure, psia
T	temperature, °F
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase

Greek Notation

ΔH_i	change in H of pure component i between two states, Btu/lb
ΔH_P	change in H between two temperatures at constant pressure, Btu/lb
ΔH_T	change in H between two pressures at constant temperature, Btu/lb
ΔH_{vap}	specific enthalpy of vaporization, Btu/lb
μ	Joule–Thomson coefficient $\equiv (\partial T/\partial P)_H$, °F/psia
ϕ	isothermal throttling coefficient $\equiv (\partial H/\partial P)_T$, Btu/lb-psia
ϕ(A)	values of ϕ adjusted to ensure thermodynamic consistency
ϕ(S)	smoothed ϕ values before thermodynamic consistency checks

Subscripts

i	component in a mixture
j, k	identify specific experimental values of temperature or pressure
l	saturated liquid
M	mixture
P	property at pressure P, psia
T	property at temperature T, °F
1,2	component number in a mixture

Superscripts

E	excess property
°	designates ideal gas property mean property

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Supplementary Material Available: Tables of isobaric, isothermal, and isenthalpic data (8 pages). Ordering information is given on any current masthead page.

A Refractometric Study of Trialkyl Borates†

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Refractive indices at wavelengths of 5893, 5461, and 4358 Å have been observed for the following trialkyl borates: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. The measurements, which were made at temperatures between 5 and 60 °C for methyl borate and from 5 to 90 °C for the remaining homologues, were then correlated with temperature and wavelength. Thermal coefficients of the refractive indices and of the Lorentz–Lorenz molar refractions were calculated, and structural interpretations were offered whenever possible.

Since the amount of physical data for the trialkyl borates is somewhat meager and scattered throughout the literature, studies have been undertaken in this laboratory in order to obtain systematic and extensive measurements for the following series of homologues: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. These studies have thus far yielded data on the vapor pressures (*1*), densities and absolute viscosities (*2*), and surface tensions (*3*), as functions of temperature up to the normal boiling point. A further search of the literature has revealed a paucity of information with regard to the refractometric properties of this class of compounds. Individual refractive indices have been reported (for the D line), at a few different temperatures (*4*, *5*), and one reference (*6*) offered a temperature correlation of the form, $n_D^t = A - Bt$, with constants A and B being given for the D line at temperature t °C; since the data which served as the

† This work was abstracted from the M.Eng. thesis of Stephen Frimpong, University of Louisville, Louisville, Ky., 1977.

