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Enthalpies for Ethylbenzene, Isooctane, and Ethylcyclohexane in the Fluid State

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An electrical-matching, flow calorimeter was used to measure the enthalpies of ethylbenzene (349-551 K, 1.5-200 bar), isooctane (358-520 K, 20-100 bar), and ethylcyclohexane (335-576 K, 20-100 bar). Water/steam calibration measurements show the apparatus capable of 0.1-0.2% precision with no detectable systematic bias. The present measurements are shown to be accurate to ±0.25% in enthalpy and ±2% in heat capacity. Literature vapor pressures, heats of vaporization, and perfect gas state enthalpies, consistent with the present hydrocarbon enthalpies, are used with our results to provide pressure/enthalpy diagrams for both the liquid and vapor states.

Introduction

This Gas Processors Association project was begun in 1981 to provide total enthalpy measurements for three C8 hydrocarbons—one alkane, one cycloalkane, and one aromatic. Only liquid heat capacity and heat of vaporization data, mostly near ambient temperature, exist for these compounds. Experimental difficulties, such as sample decomosition resulting in partial plugging of capillary tubing, precluded enthalpy measurements planned to 700 K including the critical region of each compound. Nevertheless, the present results to about 550 K are valuable for the design of heat-transfer and separation equipment processing natural gas condensate and petroleum fractions.

Experimental Apparatus

Complete experimental details for this investigation are given in the dissertation of Johnson (*1*) whereas previous experimental summaries (*2*, *3*) outline the general method. Here, we provide a brief description followed by several important changes in operation of the apparatus over that previously reported (*2*, *3*).

The Freon-11, boil-off calorimeter of Figure 1 measures the difference between the enthalpy of a fluid or fluid mixture, at some pressure and elevated temperature, and the enthalpy of the same fluid in the liquid state near 25 °C and at the same pressure. During steady-state operation, Freon is boiled off near 25 °C in the inner calorimeter, the vapor flow rate is measured by an orifice meter, the Freon is condensed then at about 21 °C, and the liquid is returned to the inner calorimeter. The Freon, thermosyphon system is driven by a constant power input to the inner calorimeter. With no experimental fluid flowing through the calorimeter, an electrical-matching heater supplies the total power level as monitored by the orifice meter. Then, the hot experimental fluid, which is pumped at a known, constant flow rate, enters the calorimeter supplying a power level that is measured as the difference between the original electrical power input and that now required to maintain the same orifice meter reading. The electrical-matching technique (1) avoids actual measurement of the Freon, boil-off rate, (2) nearly cancels the already small heat leaks, and (3) eliminates the need for an accurate, independent value for the heat of vaporization of Freon-11.

Previously, we measured the Freon boil-off rate with a turbine meter (*2*, *3*). Careful measurement (±1 mK) of the boil-off temperature (T4 of Figure 1) and the condenser temperature (T6, not shown) fix the pressure drop $P_4 - P_6$ between the inner calorimeter and condenser. In the vapor flow tube between these vessels, essentially all the pressure drop occurs at the Freon vapor inlet valve of Figure 1. This valve, which can be adjusted externally, prevents precondensation in the entrance section of the tube. For a given valve setting, $P_4 - P_6$ is a function of flow rate as in a standard orifice. Thus, constancy of T4 and of T6 provides constancy of the mass flow rate regardless of whether boil-off is due to the electrical-matching heater or hot experimental fluid.

The micro-PRT denoted T1B in Figure 1 was found during water/steam calibration to provide the proper inlet temperature for the experimental fluid regardless of its mass flow rate or temperature level.

Chemical Purity

Water and three C8 hydrocarbons were used in this research as experimental samples with Freon-11 as the reference fluid. A chromatographic analysis of the hydrocarbons showed major peak areas of more than 99.9%. The source and specifications of the samples are described below. Each sample was degassed sufficiently (usually for half hour) prior to charging. The sensitivity of many of the thermophysical properties of pure liquid samples to small amounts of dissolved air is often unappreciated (*4*). For example at 410 K, the bubble-point curve of water is elevated roughly 15 kPa/ppm of air whereas for the C8 hydrocarbons this figure is roughly 0.1 kPa/ppm of air or 1 bar for 0.1% air based upon literature Henry's constants. The corresponding percent errors in enthalpy are difficult to estimate in the liquid but in the vapor are of the order of the percent impurity itself.

***Water*.** Deionized water was distilled four times to obtain an ultrapure sample before it was used. The measured conductivity of water was 8.5 $(\mathrm{M\Omega \cdot cm})^{-1}$ at 298 K.

***Ethylbenzene*.** Ethylbenzene was purchased from Phillips Chemical Co., research grade, in half-gallon bottles. The minimum purity claimed by the producer was 99.9%.

***Ethylcyclohexane*.** Research grade (99.9% minimum purity) was obtained from Wiley Organics in half-gallon bottles. Ethylcyclohexane was the most expensive of the three hydrocarbons used in this investigation.

***Isooctane*.** Isooctane (2,2,4-trimethylpentane) was supplied by Phillips in one-liter bottles and a single five-gallon container. The minimum purity claimed by Phillips was 99.9%.

***Trichlorofluoromethane*.** Freon-11, trichlorofluoromethane, was used as a reference fluid in this apparatus. It was obtained from Du Pont Inc. in 100-pound containers with a minimum purity of 99%.

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Table I. Enthalpy Data for Water

T_{in},[a] K	P, bar	T_{out}, K	ΔH_{st}, J/g	ΔH_{exp}, J/g	% diff
354.553	249.3	300.587	222.91	222.66	-0.11
374.064	76.0	300.849	305.46	306.10	0.21
374.084	76.0	300.820	305.66	306.06	0.13
394.197	100.3	300.386	391.87	391.28	-0.15
399.088$^{\nu}$	1.50	300.381	2609.3	2603.8	-0.21
410.400	70.3	301.213	457.58	457.39	-0.04
412.709	51.0	300.933	469.49	469.26	-0.05
423.200$^{\nu}$	2.98	300.632	2645.6	2645.1	-0.02
423.984$^{\nu}$	1.60	300.630	2658.1	2658.9	0.03
423.345	66.0	300.913	527.50	527.80	0.06
426.591	70.0	300.948	528.29	529.42	0.21
429.587	70.0	300.669	542.34	542.45	0.02
430.531	70.0	300.715	546.22	545.86	-0.07
431.893	56.2	301.445	549.51	549.69	0.03
431.926	30.0	300.658	553.68	552.60	-0.20
432.024	75.2	301.435	549.38	549.87	0.09
432.954	71.7	300.660	556.84	556.45	-0.07
439.165$^{\nu}$	1.50	300.499	2689.8	2686.0	-0.14
439.370	51.2	300.287	586.38	586.34	0.00
448.171	78.9	301.209	620.39	620.38	0.00
449.003	72.0	300.598	626.55	625.87	-0.11
452.548	36.9	300.635	643.48	643.82	0.05
452.599	76.9	300.622	642.16	640.92	-0.19
455.314$^{\nu}$	4.70	300.798	2702.6	2702.4	-0.01
455.568	51.3	300.006	658.76	660.40	0.25
455.705$^{\nu}$	2.84	300.655	2714.8	2714.8	-0.00
456.360$^{\nu}$	7.77	300.653	2683.8	2683.5	-0.01
456.454$^{\nu}$	5.77	300.734	2697.8	2697.9	0.01
456.714$^{\nu}$	7.91	300.692	2684.5	2679.3	-0.19
463.189$^{\nu}$	35.7	300.293	692.45	693.46	0.15
463.461	73.4	301.010	688.35	686.79	-0.22
464.420	50.7	301.448	696.15	698.01	0.27
464.798	52.1	300.360	698.19	698.94	0.11
465.160	64.3	300.923	696.68	695.87	-0.11
467.664$^{\nu}$	7.98	300.683	2710.1	2714.4	0.16
473.478	50.0	300.643	735.49	736.08	0.08
480.498$^{\nu}$	9.01	300.743	2744.4	2742.5	-0.07
491.873	100.3	300.587	815.86	816.68	0.10
494.593$^{\nu}$	7.98	300.518	2771.6	2777.7	0.22
496.346$^{\nu}$	20.0	300.759	2712.4	2714.8	0.09
508.271	80.3	301.438	893.71	895.10	0.15
514.656	100.3	301.016	919.24	920.99	0.19
518.772$^{\nu}$	9.01	300.763	2827.3	2832.4	0.18
520.896	150.0	300.892	945.20	946.43	0.13
528.905	50.0	300.838	983.01	983.39	0.14
533.820$^{\nu}$	20.0	300.701	2810.2	2812.4	0.08
539.391	150.0	301.039	1033.2	1032.3	-0.09
549.463$^{\nu}$	20.0	300.954	2848.4	2844.4	-0.14
549.761	150.0	301.010	1084.7	1083.9	-0.07
555.010$^{\nu}$	6.05	300.941	2906.3	2907.5	0.04
555.331	245 8	301.013	1101.5	1103.4	0.17

[a] ν indicates vapor state.

Experimental Results

Table I presents the experimental results for water/steam. Throughout this article,

$$\Delta H_{exp} \equiv H(P,T) - H(\text{liquid at } P,T_{out}) \qquad (1)$$

is the actual enthalpy difference for the isobaric calorimeter. In Table I, ΔH_{st} is the corresponding value from the NBS-NRC Steam Tables (*5*).

Table II provides the experimental enthalpies for ethylbenzene while Table III presents these data smoothed and referenced to the liquid state at 1 bar and 298.15 K (25 °C):

$$H_r \equiv H(P,T) - H(\text{liquid at 1 bar, 298.15 K}) \qquad (2)$$

The data were smoothed along isobars to provide consistent values of the isobaric heat capacity C_p, given in parentheses in Table III.

Table II. Raw Enthalpy Data for Ethylbenzene

P, bar	T_{in}, K	ΔH_{exp}, J/g	T_{out}, K
	Liquid State		
100.70	348.416	87.61	300.624
101.68	372.916	135.12	300.613
100.40	401.054	193.10	300.610
100.00	424.031	241.54	300.627
100.00	462.271	326.02	300.597
100.00	497.135	410.42	300.800
99.26	520.316	467.37	300.701
200.13	348.927	85.28	300.621
200.00	373.011	131.73	300.605
200.00	400.978	188.43	300.683
200.13	424.293	238.07	300.677
199.86	446.324	285.99	300.658
200.00	461.982	320.87	300.598
200.13	497.423	403.78	300.785
200.13	522.796	465.15	300.733
199.86	551.238	537.01	300.791
19.94	348.784	88.49	300.617
20.00	372.351	134.41	300.599
20.00	400.707	192.99	300.729
20.00	424.665	245.21	300.651
20.00	446.221	293.56	300.652
20.00	459.181	324.08	300.567
20.08	498.001	415.66	300.704
20.11	522.582	478.46	300.755
50.31	349.038	89.13	300.628
49.62	372.885	135.90	300.615
50.00	400.925	193.14	300.729
50.10	424.170	242.39	300.690
50.00	446.582	293.05	300.647
50.00	460.135	323.65	300.615
49.30	461.252	326.31	300.604
50.00	496.456	409.89	300.802
50.00	519.665	468.76	300.760
	Vapor State		
1.510	440.996	602.66	300.651
1.496	455.230	628.34	300.635
1.496	475.435	666.09	300.539
1.482	492.782	699.43	300.633
1.510	515.932	745.20	300.649
1.496	524.524	762.68	300.618
2.013	446.793	611.96	300.716
2.013	459.460	635.18	300.631
1.999	468.685	652.04	300.817
2.013	476.411	666.92	300.680
2.020	494.461	701.78	300.650
1.999	523.187	759.21	300.679
3.151	468.276	648.87	300.728
3.157	476.478	664.32	300.640
3.151	491.764	693.84	300.669
3.151	506.511	723.01	300.625
3.144	515.701	741.68	300.603
3.157	525.084	760.77	300.660
5.495	496.884	696.01	300.613
5.495	502.294	706.68	300.840
5.426	506.704	716.16	300.639
5.564	507.657	717.08	300.681
5.495	515.467	732.87	300.596
5.495	525.021	753.85	300.692
5.564	536.516	777.23	300.742

Table IV provides the experimental enthalpies for isooctane while Table V presents these data smoothed and referenced to 1 bar and 298.15 K. Likewise, Table VI presents the experimental enthalpies for ethylcyclohexane while Table VII provides these data smoothed and referenced to 1 bar and 298.15 K.

Accuracy and Precision Data

The water/steam data of Table I shows our apparatus to be *accurate* to about ±0.25% because the NBS-NRC Steam Tables (*5*) are considered accurate to better than 0.5 J/g for the vapor (or ~0.05%) and 0.03% for the liquid for the present temperatures. Under these conditions involving both the liquid and vaporous state, water is presently the *only* calibration fluid for accurate calorimetry. Our data of Table I show little sys-

Table III. Smoothed Enthalpy (H_r) and Heat Capacity (C_p) Data for Ethylbenzene

T, K	H_r (C_p) at various P (bar)[a] 1.5[v]	2.0[v]	3.15[v]	5.50[v]	20	50	100	200
350					96.4 (1.933)	99.3 (1.922)	103.3 (1.909)	110.5 (1.905)
375					145.8 (2.025)	148.4 (2.006)	152.0 (1.992)	159.1 (1.987)
400					197.6 (2.117)	199.7 (2.093)	202.9 (2.078)	209.8 (2.069)
425					251.7 (2.208)	253.1 (2.182)	256.0 (2.167)	262.6 (2.151)
450	622.1 (1.816)				308.0 (2.298)	308.8 (2.274)	311.3 (2.258)	317.3 (2.233)
475	668.5 (1.893)	667.5 (1.897)	665.1 (1.899)		366.6 (2.386)	366.8 (2.367)	368.9 (2.353)	374.2 (2.315)
500	716.8 (1.970)	715.9 (1.978)	713.6 (1.981)	705.9 (1.995)	427.3 (2.474)	427.1 (2.462)	428.9 (2.457)	433.1 (2.397)
525	767.0 (2.047)	766.4 (2.058)	764.1 (2.063)	756.9 (2.086)	490.3 (2.561)	489.9 (2.559)	491.5 (2.551)	494.0 (2.479)
550								557.1 (2.562)

[a] Units: H_r, J/g; C_p, J/g·K. ν indicates vapor state.

Table IV. Raw Enthalpy Data for Isooctane in the Liquid State

P, bar	T_{in}, K	ΔH_{exp}, J/g	T_{out}, K
19.97	358.223	135.02	300.641
20.04	365.857	153.22	300.611
19.97	379.344	186.36	300.653
19.63	393.875	222.80	300.514
20.04	402.297	244.57	300.518
19.97	423.886	300.99	300.548
20.04	438.760	341.69	300.561
19.97	450.002	372.65	300.694
19.97	467.533	423.55	300.655
20.32	480.751	463.67	300.793
20.04	494.128	506.29	300.864
20.32	520.075	592.15	301.740
100.30	359.233	135.74	300.622
99.95	366.494	152.65	300.678
100.09	374.121	171.52	300.504
99.61	392.240	216.31	300.485
100.09	401.663	240.00	300.522
99.61	422.961	295.09	300.513
99.95	437.546	333.57	300.698
100.30	449.398	366.06	300.652
100.30	450.682	369.91	300.521
100.30	466.078	412.91	300.637
99.61	479.307	450.86	300.755
99.95	493.948	494.55	300.669
100.30	502.697	520.90	300.788
100.09	513.753	554.90	301.210
100.09	519.441	572.53	301.100

Table V. Smoothed Enthalpy (H_r) and Heat Capacity (C_p) Data for Isooctane

T, K	P (bar)[a] 20	100
360	147.2 (2.408)	152.3 (2.399)
380	195.9 (2.472)	200.9 (2.465)
400	246.2 (2.556)	250.9 (2.538)
420	298.3 (2.658)	302.5 (2.618)
440	352.6 (2.779)	355.7 (2.705)
460	409.5 (2.918)	410.7 (2.799)
480	469.5 (3.076)	467.7 (2.901)
500	532.7 (3.253)	526.8 (3.010)
520	599.7 (3.449)	588.1 (3.125)

[a] Units: H_r, J/g; C_p, J/g·K.

Table VI. Raw Enthalpy Data for Ethylcyclohexane in the Liquid State

P, bar	T_{in}, K	ΔH_{exp}, J/g	T_{out}, K
20.181	335.336	68.47	300.482
19.974	343.401	85.75	300.580
19.974	356.735	114.98	300.405
20.043	378.113	162.31	300.630
19.974	391.268	192.55	300.537
20.043	399.004	210.49	300.504
19.629	431.846	289.82	300.381
19.284	476.777	402.44	300.470
19.974	495.318	450.43	300.626
20.181	513.343	499.18	300.748
20.181	525.274	530.25	300.733
19.974	551.012	600.65	300.769
19.974	573.556	664.61	300.881
99.953	335.247	73.03	300.478
100.30	356.614	119.52	300.402
99.953	377.861	167.19	300.594
98.229	401.969	222.51	300.484
99.953	419.130	262.15	300.618
99.608	433.391	296.31	300.375
100.30	455.511	349.33	300.628
99.263	476.809	403.11	300.464
100.30	496.266	448.02	300.576
99.953	513.578	496.46	300.783
99.953	524.613	525.28	300.751
99.953	550.532	597.68	300.999
99.953	576.169	665.78	300.701

Table VII. Smoothed Enthalpy (H_r) and Heat Capacity (C_p) Data for Ethylcyclohexane

T, K	H_r (C_p) at P (bar)[a] 20	100
380	174.2 (2.271)	185.7 (2.262)
400	220.4 (2.343)	231.4 (2.313)
420	267.9 (2.412)	278.2 (2.364)
440	316.8 (2.476)	326.0 (2.417)
460	366.9 (2.537)	374.9 (2.470)
480	418.3 (2.594)	424.8 (2.524)
500	470.7 (2.647)	475.8 (2.578)
520	524.1 (2.696)	527.9 (2.634)
540	578.5 (2.741)	581.2 (2.690)
560	633.7 (2.783)	635.6 (2.747)
580		691.1 (2.805)

[a] Units: H_r, J/g; C_p, J/g·K.

tematic bias with the Steam Tables so our ±0.25% uncertainty is essentially from random errors.

For the C8 hydrocarbon data presented in this report, Tables II–VII, we expect an accuracy of ±0.25 in enthalpy and ±2% for the heat capacities. These claims are supported by (1) harmony with other, independent properties used in preparation of the pressure/enthalpy diagrams of the next section and (2) agreement with literature heat capacity measurements.

Correlation with Literature Measurements

Our smoothed measurements of Tables III, V, and VII were used to prepare pressure/enthalpy diagrams for ethylbenzene, isooctane, and ethylcyclohexane, respectively. For subcritical temperatures, the isotherms were constructed as follows:

(A) Nearly vertical isotherms are drawn through the compressed liquid enthalpies.

(B) These lines intersect the best literature vapor pressure curves to provide saturated liquid enthalpies, H_L^σ.

(C) The saturated vapor enthalpies, H_V^σ, are calculated with use of an equation for the heat of vaporization, $\lambda \equiv H_V^\sigma - H_L^\sigma$, based upon an accurate literature measurement of λ at 25 °C and the empirical equation (*6*)

$$(\lambda/\lambda_{298}) = [(1 - \mathrm{Tr})/(1 - \mathrm{Tr}|_{298})]^n \tag{3}$$

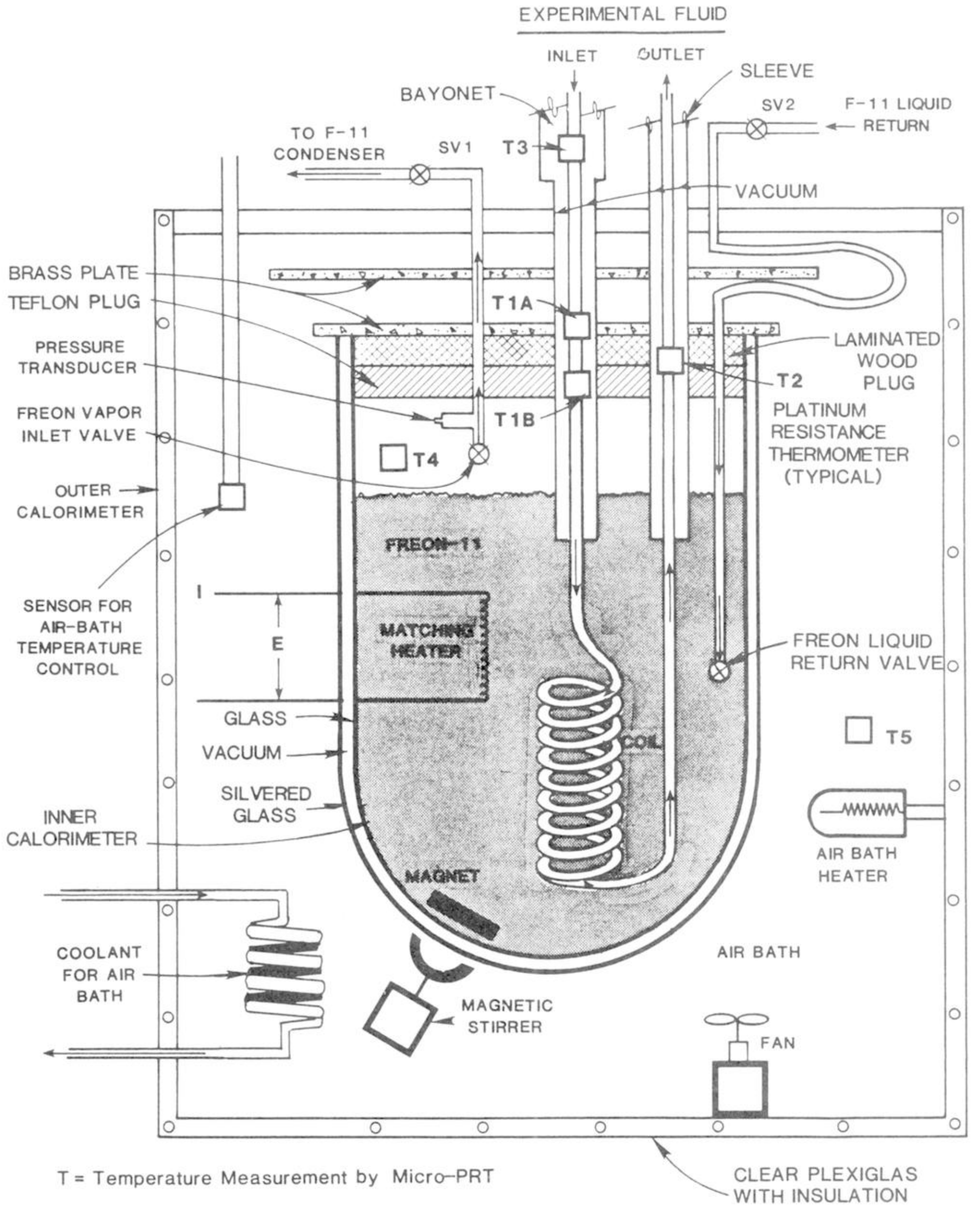

Figure 1. Calorimeter detail.

where Tr ≡ (T/T_c) is the reduced temperature. When λ measurements exist also at temperatures above 25 °C, eq 3 can be further tested and the exponent n, normally 0.38, adjusted. In cases where accurate saturated vapor and liquid volumes exist, the Clapeyron equation

$$dP^\sigma/dT = \lambda/T(V_V^\sigma - V_L^\sigma) \qquad (4)$$

can be invoked to provide λ.

(D) The literature ideal gas state heat capacities C_p^* are integrated from 25 °C to the higher temperatures, and the literature heat of vaporization at 25 °C is added to the integrals to provide H_r^*, the ideal gas state enthalpy referenced to liquid at 25 °C.

(E) For each isotherm, H_r^* should be somewhat greater than H_V^σ with the difference increasing with T because of the increased vapor pressure. A straight line on the P/H diagram can be drawn between H_V^σ and H_r^*, but the true vapor isotherms should possess negative curvature with the absolute curvature decreasing with increasing T. Direct vapor enthalpy measurements should thus lie slightly above the straight line and provide the proper curvature. If they fail to do so, they are inconsistent with either H_V^σ or H_r^*, or both.

The above outline will be used to describe correlation of each of the three C8 hydrocarbons, and the above sections will be denoted as step A, step B, etc.

Ethylbenzene. We used the Wagner vapor pressure equation (*7*)

$$\ln (P^\sigma/P_c) = (Ax + Bx^{1.5} + Cx^3 + Dx^6)/(1 - x) \qquad (5)$$

with $x \equiv 1 - \text{Tr}$, $A = -7.48645$, $B = 1.45488$, $C = 3.37588$, and $D = -2.23048$ from fit to literature measurements. For ethylbenzene, $T_c = 617.20$ K, $P_c = 36.1$ bar, $V_c = 3.52 \times 10^{-3}$ m^3/kg, NBP = 409.34 K (NBP = normal boiling point), and MW = 106.17.

For step C, Osborne and Ginnings (*8*) measured λ(25 °C) = 397.89 J/g whereas Hossenlopp and Scott (*9*) later determined the following heats of vaporization: 371.56 (345.958 K), 365.85 (356.446 K), 361.44 (364.365 K), 354.65 (376.271 K), 349.43 (385.301 K), 341.55 (398.945 K), 335.17 (409.343 K), 325.11 (425.132 K), and 317.38 J/g (437.224 K). Equation 3 with n = 0.385 provides a good representation (±1 J/g) of ref 9 data. However, above 500 K (where no λ data exist), eq 3 provides higher values of λ than does a more comprehensive equation of Hossenlopp and Scott. Above 500 K, we thus used the equation of Hossenlopp and Scott to compose Figure 2.

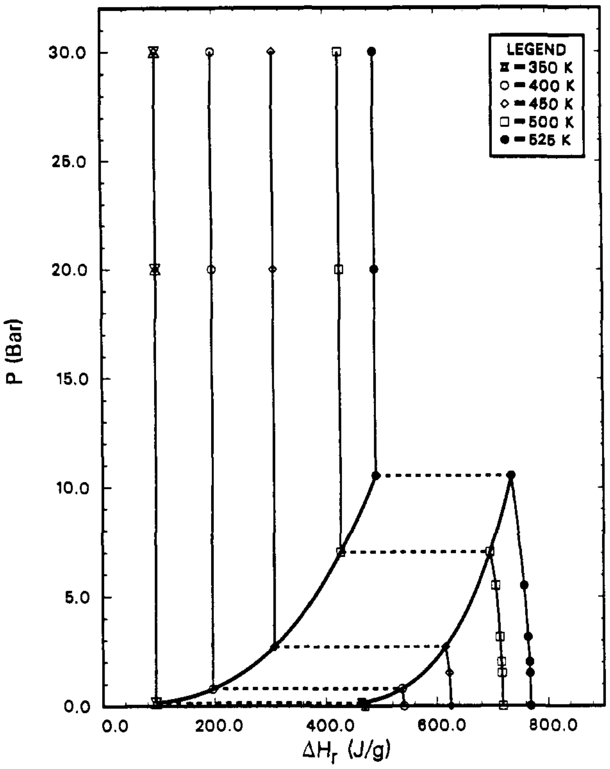

Figure 2. Pressure/enthalpy diagram for ethylbenzene.

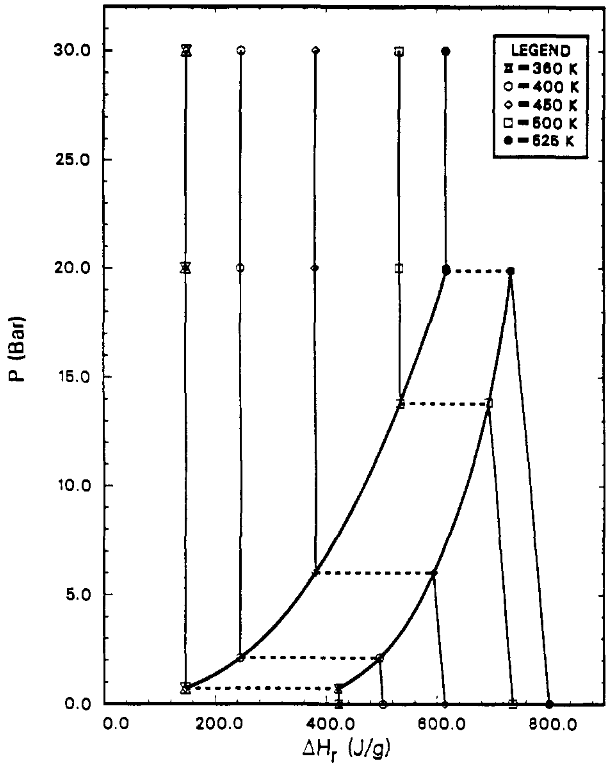

Figure 3. Pressure/enthalpy diagram for isooctane.

For step D, the ideal gas state enthalpies of Miller and Scott (*10*) agree with the TRC Tables (*11*) to within 0.15 J/g over the temperature range of the present vapor data. Some values of H_r^* are 400.13 (300 K), 540.77 (400 K), 625.46 (450 K), 718.65 (500 K), and 819.66 J/g (550 K). The check of step E is perfectly fulfilled for ethylbenzene with our vapor enthalpies being slightly above the straight line between H_V^σ and H_r^* and showing the proper curvature as seen on Figure 2.

Isooctane (2,2,4-Trimethylpentane). For isooctane the constants are T_c = 543.9 K, P_c = 25.6 bar, V_c = 4.10 × 10^{-3} m^3/kg, NBP = 372.4 K, and MW = 114.23. In the Wagner vapor pressure equation, A = -7.388 90, B = 1.252 94, C = -3.166 06, and D = -2.220 01. Again, Osborne and Ginnings (*8*) have measured λ(25 °C) = 307.48 J/g. While no other experimental values of λ were found initially, earlier *PVT* investigations by Sage and Lacey (*12*) and McMicking and Kay (*13*) allowed the following estimates of λ through the Clapeyron equation: 189.52 (478.15 K), 116.88 (523.15 K), and 88.58 J/g (533.15 K) from ref 13. These two sources are in good agreement, and their heats of vaporization are well calculated by eq 3 with n = 0.38. This equation was thus used to construct the *P*/*H* diagram for isooctane, Figure 3. Later, we found that Svoboda et al. (*14*) had measured λ from 298 to 368 K. These values are fit to ±1 J/g by eq 3 with n = 0.38.

Ideal gas state enthalpies H_r^* were calculated from the TRC Tables (*11*). Some values are 394.46 (360 K), 476.14 (400 K), 587.85 (450 K), 710.23 (500 K), and 843.29 J/g (550 K).

Figure 3 shows the values of H_V^σ to align well with H_r^*. Our liquid enthalpies are thus harmonius with the literature and allow construction of Figure 3.

Ethylcyclohexane. For ethylcyclohexane the constants are T_c = 609.0 K, P_c = 30.3 bar, V_c = 4.01 × 10^{-3} m^3/kg, NBP = 404.9 K, and MW = 112.22. In the Wagner vapor pressure equation, A = -6.681 07, B = 0.523 014, C = -3.244 464, and D = 0. Little vapor pressure data exist between about 2 bar and the critical point; however, the Wagner equation is known to provide a good interpolation for this region when it is well fit to the low-pressure measurements and the critical point. Again, Osborne and Ginnings (*8*) have measured λ(25 °C) = 360.7 J/g. Recently, Svoboda et al. (*15*) measured heats of vaporization of 354.2 (313.15 K), 346.4 (328.15 K), 337.7 (343.15 K) 329.7 (358.15 K), and 323.7 J/g (368.15 K). These measurements are fit within ±2 J/g by eq 3 and the single value of ref 8 with n = 0.38. We used this equation for interpolation of λ to higher temperatures for Figure 4 although Svoboda et al. (*15*) present a more accurate and complex empirical equation to represent their data.

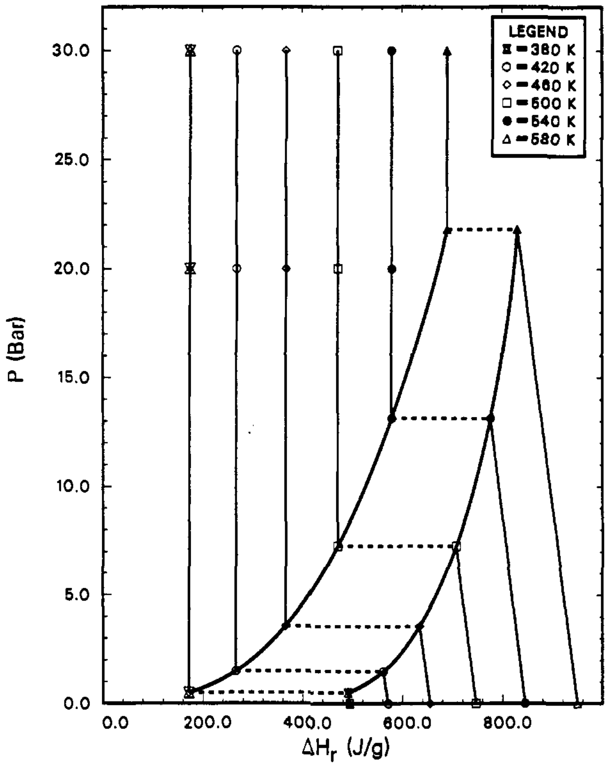

Figure 4. Pressure/enthalpy diagram for ethylcyclohexane.

Ideal gas state enthalpies H_r^* were calculated from the TRC Tables (*11*). Some values are 363.34 (300 K), 531.52 (400 K),

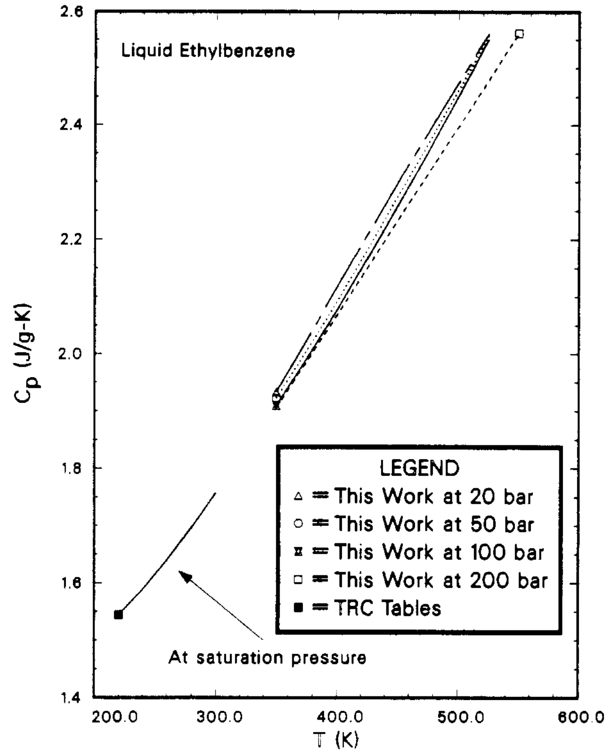

Figure 5. Comparison of the heat capacity values for liquid ethylbenzene.

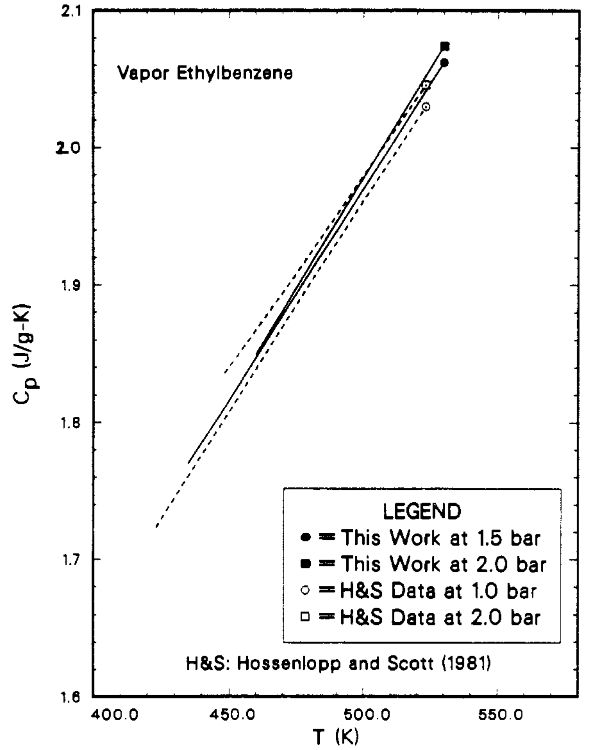

Figure 6. Comparison of the heat capacity values for vapor ethylbenzene.

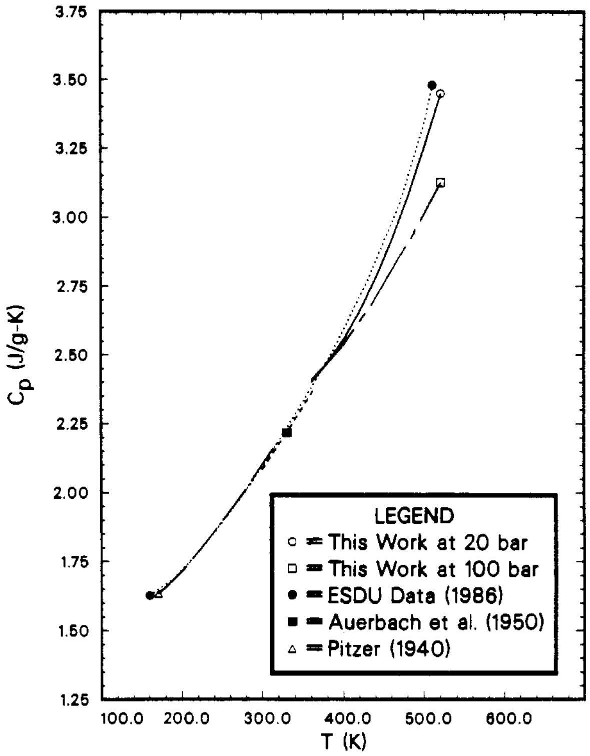

Figure 7. Comparison of the heat capacity values for liquid isooctane.

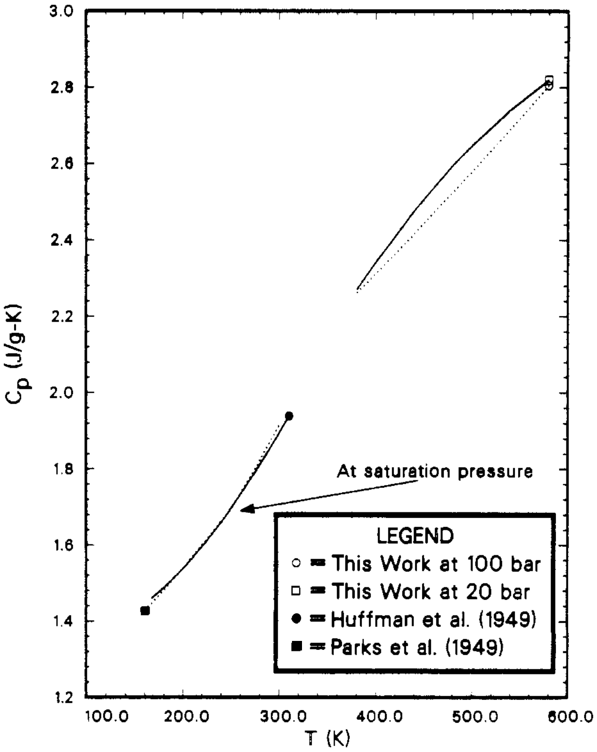

Figure 8. Comparison of the heat capacity values for liquid ethylcyclohexane.

655.29 (460 K), 746.64 (500 K), 844.67 (540 K), and 949.05 J/g (580 K).

Figure 4 shows the values of H^{σ}_{V} to align well with H_r^*. As with isooctane, our liquid enthalpies are harmonious with the literature and allow construction of Figure 4.

Heat Capacity Comparisons. Figure 5 shows our liquid ethylbenzene C_p values to align well with the TRC Tables (*11*) values below 310 K. No literature C_p measurements were found at temperatures above 310 K. Figure 6 compares our vapor ethylbenzene C_p values with those of Scott and Hossenlopp (*9*). While there is some disagreement concerning trends with pressure and temperature, the agreement is generally within 2%.

Figure 7 illustrates the comparison for liquid isooctane with three literature sources taken at the vapor pressure: (1) Engineering Sciences Data Unit (ESDU) correlation (*16*), (2) Auerbach et al. (*17*), and (3) Pitzer (*18*). The agreement is excellent considering particularly that pressure has an important effect above about 440 K. The lower critical temperature of isooctane of 544 K means that our highest temperature data near 525 K will show the effect of an increasingly compressible liquid. This effect, which is barely discerned on an enlarged version of Figure 3, is pronounced in Figure 7.

Finally, Figure 8 compares our liquid ethylcyclohexane measurements with those of Huffman et al. (*19*) and of Parks et al. (*20*) below 320 K. While our measurements are at higher temperatures, the alignment appears reasonable with our 20-bar line.

Acknowledgment

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Isobaric Heat Capacity Data for Liquid HFC-134a

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The isobaric heat capacity, C_p, of liquid HFC-134a, which is a prospective alternative to CFC-12, has been measured by using a flow calorimeter. The values of 31 C_p have been determined at temperatures from 276 to 356 K and pressures from 1.0 to 3.0 MPa. The uncertainty was estimated to be within ±10 mK in temperature, ±3 kPa in pressure, and ±0.3% in C_p, respectively. The C_p of saturated liquid, C_p', has been determined on the basis of the data measured in the compressed liquid phase, and a correlation of C_p' has also been developed.

Introduction

Chlorofluorocarbons (CFCs) have been widely used as working fluids for heat pump systems and refrigerators. The ozone depletion and global warming by CFCs is becoming a very important issue, and it is our urgent task to develop and apply stratospherically safe CFC alternatives. Tetrafluoroethane, CH_2FCF_3 (HFC-134a), is one of the prospective alternatives to CFC-12, which has been widely used as a blowing agent and working fluid of domestic refrigeration systems.

This paper reports the isobaric heat capacity data of liquid HFC-134a and a correlation for the heat capacity of the saturated liquid. The purity of HFC-134a used in this study was 99.97 wt %.

Experimental Section

The detailed description regarding the flow calorimeter has been reported in our previous papers (*1-3*). The special features are its highly adiabatic performance, the flow stability of the sample liquid in the closed circulation system, and the reliability of automatically measuring of mass-flow rate.

The isobaric heat capacity, C_p, is defined as follows:

$$C_p = \dot{Q}/(\dot{m}\Delta T) \quad (1)$$

Flow calorimetry consists of three simultaneous measurements: measurement of energy, $\dot{Q}$, supplied by a microheater to the sample liquid; measurement of the temperature increment, ΔT, which is the difference $T_{out} - T_{in}$, the temperatures of sample liquid before and after heating by the microheater; and measurement of the mass-flow rate, $\dot{m}$. The energy supplied to the sample liquid was determined from the voltage and heating current through the microheater.

The temperature and temperature increment were measured with two 100-Ω platinum resistance thermometers (PRT) calibrated by a standard PRT in accordance with IPTS-68. The mass-flow rate was determined as the mass difference of a vessel before and after a sampling by means of a digital mass balance. The vessel was placed on the digital mass balance and connected to the circulation lines with small-diameter

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