

Table VI. (Continued)

Temp, °F	Psia												
	0	100	150	200	300	400	500	600	700	800	1000	1400	
418.1							397.8 ^a						
420	446.0	440.5		433.3	425.1	416.3	400.4	352.0		348.4	345.1	343.8	
440	457.6	452.1		446.2	438.5	430.5	418.1	373.5		368.4	364.2	360.1	
460	469.6	464.5		459.1	452.1	444.7	435.3	421.0		389.6	379.8	376.6	
480	481.7	477.1		472.0	465.9	458.9	451.0	441.3	425.7	412.0	398.6	391.8	
500	494.4	490.0		484.9	479.5	473.0	466.0	458.2	447.0	433.5	418.3	408.3	
520	506.7	502.5		498.1	493.1	486.9	480.8	474.5	465.3	453.5	439.7	424.0	
540	519.1	515.5		511.5	506.8	501.0	495.5	490.1	482.1	472.8	460.4	441.8	
560	532.0	528.7		524.8	520.4	515.1	510.0	504.5	497.7	490.2	479.7	460.2	
580	545.0	541.9		538.2	534.1	529.3	524.1	519.1	513.0	516.9	497.5	478.1	
600	558.2	555.3		551.8	547.7	543.7	538.6	533.7	528.4	523.4	514.7	496.3	
620	571.4			565.8		557.5	553.2	548.8		539.4	531.0	515.1	
640	584.8			579.8		572.2	568.0	564.0		555.3	548.1	532.3	
660	598.4			593.6		586.5	582.5	578.5		571.2	564.3	549.0	
680	611.4			607.8		601.4	597.5	593.5		587.0	580.3	565.5	

^a Enthalpy values on two-phase boundary.

n-pentane. Table I shows the compositions of the mixtures studied, the liquid density at 75° F and 1-atm pressure, the heat of mixing, and the enthalpy needed to convert from the 75° F basis to the -200° F basis.

After conversion to the -200° F basis, the data were plotted on large scale cartesian coordinate graph paper, and smoothing was performed by visually drawing an appropriate average curve through the plotted values. The average deviation of the smoothed values from the experimental was 1.3 Btu per pound. A statistical deviation of 1.8 Btu per pound was found. The final smoothed enthalpy values are presented in five tables. Table II shows the results for pure cyclohexane, and Tables III, IV, V, and VI show results for the mixtures.

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Enthalpies of Mixtures of Benzene and Hexadecane

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Experimental measurements of enthalpy are reported for five binary mixtures of benzene and *n*-hexadecane from 120° to 600° F with pressures up to 1400 psia.

Calorimetric measurements have been obtained to determine the enthalpy behavior of a relatively low boiling point aromatic, benzene, with a high boiling point paraffin, hexadecane. This mixture apparently has not been studied previously. Enthalpy values for pure benzene have been reported by Connolly and Kandalic (5), Gilliland and Lukes (6), Kemp (7), Lindsay and Brown (10), and Osborne and Ginnings (14). Organick and Studhalter (13) presented computed enthalpies of benzene, and Canjar and Manning (4) recently published a tabular listing of pure benzene enthalpies. Parks and Moore (15) show the latent heat of vaporization of pure hexadecane at room temperature. Enthalpies for pure *n*-hexadecane were previously presented (8) from measurements made with the same calorimeter used for this series of measurements.

The flow calorimeter determines the difference in enthalpy between the hydrocarbon mixture at a measured inlet temperature state, and a fixed base state of 75° F and the liquid phase. Both states are at the pressure of measurement. The design and operation of the calorimeter has been described (9). The accuracy of measurement was determined by measuring the enthalpy for water and *n*-pentane, and comparing the results with the published values of Meyer et al. (12), and the tabulations of the API Research Project 44 (2). The average deviation between measured and published values of water and pentane was found to be 1.5 btu/pound, a difference maintained for three years of calorimeter operation. During the measurements of the benzene and hexadecane mixtures, the calorimeter accuracy was checked twice by measuring pure water and *n*-pentane.

The benzene was obtained from the Phillips Petroleum Co. A refractive index of 1.50030 n_D^{20} and a density of

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Table I. Properties of Liquid Phase at 75° F and 1 Atm *n*-Hexadecane with Benzene

Composition	Wt % hexadecane	Liq density, g/cc	Heat of mixing, btu/lb	Enthalpy to add, btu/lb
100 % <i>n</i> -Hexadecane	100.0	0.7696	0.00	93.7
58.1 mole % Hexadecane	80.1	0.7847	2.92	95.5
33.0 mole % Hexadecane	58.8	0.8034	4.40	95.8
18.6 mole % Hexadecane	39.9	0.8226	4.30	94.6
8.0 mole % Hexadecane	20.2	0.8460	2.66	91.8
3.7 mole % Hexadecane	10.0	0.8585	1.43	90.1
100 % Benzene	0.0	0.8731	0.00	88.1

0.8730 grams per cc at 75° F and 1 atm pressure were measured. Published values (1) were 1.50112 for the refractive index and 0.8737 for the density. The *n*-hexadecane was obtained from the Humphrey Chemical Co. with measured refractive index of 1.43459 and a density of 0.7696. The API data book (1) shows values of 1.43453 and 0.7718. Both materials were stated to have a purity greater than 99.0 mole percent, and were used as received. The mixtures were prepared by weighing the pure benzene and hexadecane for a sample of 5000 grams. The precision of weighing was 2.5 grams, representing better than 0.1% in the determining composition. While the calorimeter was operating, the constancy of composition was monitored by refractive index measurements taken at random intervals.

Table I shows the compositions studied, the liquid density at 75° F, the heat of mixing at 75° F [obtained from the results of Lundberg (11)], and the enthalpy needed to convert the enthalpy relative to 75° F and the saturated liquid condition to the enthalpy basis at -200° F recommended by the API data book (1). The number for this conversion for benzene was determined by comparing the zero pressure enthalpies determined from the measurements with the ideal enthalpy values presented in API Project 44 (2). These Project 44 enthalpy values require the addition of 198.2 btu/lb to be placed on the -200° F liquid basis. The comparison showed that 88.1 btu/lb needs to be added to the measured values to match the ideal enthalpies presented

Table II. Smoothed Values of Enthalpy for the Mixture 80.1 Wt % Hexadecane, 19.9 Wt % Benzene; Units Btu/lb, Base Level Pure Saturated Liquid Components at -200° F

Temp, ° F	Psia						
	0	100	150	200	300	800	1400
75		95.7	95.9	96.0	96.3	97.6	99.3
120		117.7					121.9
160		137.6					142.5
200		159.2					163.3
240		182.1					185.4
280		206.1					208.5
320		230.9					232.8
360		256.1					258.5
400		282.0					284.7
440	423.0	308.2					311.3
440.2		308.3 ^a					
460	433.4	327.5	321.6				324.5
480	445.5	342.8	335.1				338.1
500	457.0	359.3	348.7				351.8
502.4			350.3 ^a				
520	468.7	376.5	366.2	362.8			365.7
540	480.4	394.2	384.4	377.8			379.3
546.0				384.3 ^a			
560	492.5	412.3	402.5	395.8	393.3	393.5	393.5
580	504.5	431.5	421.1	412.0	408.9	409.5	408.0
600	516.9	453.8	438.4	428.3	425.6	425.7	422.0

^a Enthalpy values at bubble point.

by API Project 44 using the -200° F basis. The zero pressure enthalpies were obtained by plotting measured enthalpies of benzene dependent on pressure at 460, 540, 580, and 660° F isotherms, and extrapolating to zero pressure. Since measurements were made at 20 psia, the range of extrapolation is small. Presumably the hypothetical supercooled saturated liquid benzene at -200° F has 88.1 btu/lb less enthalpy than at 75° F. The number 88.1 is considered to be a value that puts the measured enthalpies for benzene on a consistent basis with the API data book. For hexadecane, the amount of enthalpy needed to correct to the -200° F basis was previously determined to be 93.1 btu/lb (8).

Table III. Smoothed Values of Enthalpy for the Mixture 58.8 Wt % Hexadecane, 41.2 Wt % Benzene; Units Btu/lb, Base Level Pure Saturated Liquid Components at -200° F

Temp, ° F	Psia							
	0	100	150	200	300	400	800	1400
75		96.0	96.2	96.3	96.6	96.8	97.9	99.6
120		117.9						120.5
160		137.4						140.4
200		157.8						160.7
240		179.0						181.9
280		201.6						204.2
320		225.4						227.1
360		250.4						251.2
374.5		259.4 ^a						
380		268.7	263.0					263.9
400		294.1	275.6					276.7
416.8			286.4 ^a					
420		313.7	290.6	288.5				289.4
440	396.4	332.0	313.2	301.4				302.4
458.5				313.8 ^a				
460	427.5	349.5	333.6	316.1	314.6			315.5
480	438.1	364.4	352.7	339.1	327.6			328.7
500	448.9	380.9	369.9	358.8	341.2			341.9
520	459.8	397.4	386.6	377.2	354.4			354.9
521					355.4 ^a			
540	470.9	417.2	404.7	394.9	375.9	369.2	367.6	368.2
560	482.1	437.4	423.2	413.1	395.0	384.2	382.6	381.7
563.5						386.9 ^a		
580	489.4	458.4	442.2	431.2	411.9	400.7	396.8	395.4
600	504.9	480.4	462.1	449.7	428.1	417.4	411.2	409.6

^a Enthalpy values at bubble point.

Table IV. Smoothed Values of Enthalpy for the Mixture 39.9 Wt % Hexadecane, 60.1 Wt % Benzene; Units Btu/lb, Base Level Pure Saturated Liquid Components at -200° F

Temp, ° F	Psia									
	0	100	150	200	300	400	500	600	800	1400
75		94.8	94.9	95.9	95.3	95.6	95.9	96.1	96.6	98.2
120		115.4								118.3
160		134.2								136.7
200		153.4								155.9
240		123.7								176.0
280		195.9								197.3
320		218.8								219.9
341.5		230.6 ^a								
360		274.9	242.6							243.4
380		302.3	254.9							255.4
382.5			256.2 ^a							
400		321.3	290.4	266.8						267.5
419.2				278.6 ^a						
420	401.3	337.7	318.6	281.3	279.0					279.5
440	411.8	353.8	339.6	316.6	291.8					291.8
460	420.8	370.7	358.8	341.6	305.0					304.1
471.8					312.8 ^a					
480	431.5	387.3	376.8	362.2	326.3	318.6				316.6
500	441.5	403.6	392.9	380.1	354.3	332.0				329.6
518.3						344.4 ^a				
520	451.8	419.9	409.1	397.0	377.0	346.8	345.4		344.1	342.6
540	462.3	438.2	427.0	413.3	397.6	374.6	359.4		357.8	355.5
560	472.8	461.2	446.4	429.9	416.2	397.6	373.4	372.8	371.5	368.8
562.3		465.1 ^b								
564.8							376.6 ^a			
580	483.5	476.6	469.6	448.3	433.2	417.2	399.8	388.4	385.9	382.4
582.8			473.4 ^b							
598.7								403.0 ^a		
600	494.2	488.0	483.8	471.8	452.3	436.1	420.4	405.0	401.1	396.4

^a Enthalpy values at bubble point. ^b Enthalpy values at dew point.

Table V. Smoothed Values of Enthalpy for the Mixture 20.2 Wt % Hexadecane, 79.8 Wt % Benzene; Units Btu/lb, Base Level Pure Saturated Liquid Components at -200° F

Temp, ° F	Psia									
	0	100	150	200	300	400	500	600	800	1400
75		92.0	92.1	92.3	92.5	92.7	93.0	93.2	93.7	95.2
120		111.4								114.3
160		129.8								132.4
200		148.9								151.8
240		168.7								171.7
280		189.2								192.1
320		211.1								213.1
325		213.9 ^a								
360		317.2	233.9							235.1
364.5			236.4 ^a							
380		336.1	295.9	245.6						246.6
397.5				256.0 ^a						
400	387.5	350.9	331.1	266.9	257.5					258.6
420	396.8	363.4	350.7	326.9	269.5					270.4
440	406.3	375.9	365.9	352.7	281.9					282.4
448.5					286.9 ^a					
460	415.2	389.9	381.9	369.9	324.9	294.2				294.4
480	424.6	404.9	395.9	386.2	359.4	307.2				306.6
484.7						310.2 ^a				
495.5		420.4 ^b								
500	433.9	423.9	411.5	402.2	381.6	348.9	320.1			318.7
518.3							332.9 ^a			
520	443.6	436.7	428.6	418.7	400.9	382.9	336.7	334.0		331.1
520.2			428.9 ^b							
537.2				434.9 ^b						
540	453.4	447.5	443.1	436.9	419.1	404.1	378.9	348.9		343.9
553.5								359.6 ^a		
560	463.2	457.9	455.5	450.5	435.2	422.9	404.7	376.7	362.1	356.7
566.8					441.9 ^b					
580	468.0	468.1	465.9	462.3	453.3	440.9	426.5	407.7	375.9	369.7
583						443.9 ^b				
600	483.0	478.3	475.7	473.7	468.7	459.4	446.4	432.5	389.7	383.2

^a Enthalpy values at bubble point. ^b Enthalpy values at dew point.

Table VI. Smoothed Values of Enthalpy for the Mixture 10.0 Wt % Hexadecane, 90.0 Wt % Benzene; Units Btu/lb, Base Level Pure Saturated Liquid Components at -200°F

Temp, $^{\circ}\text{F}$	Psia									
	0	100	150	200	300	400	500	600	800	1400
75		90.4	90.5	90.6	90.8	91.0	91.2	91.5	92.0	93.4
120		109.6								111.8
160		127.4								129.7
200		146.3								148.8
240		166.2								168.4
280		186.5								188.8
300		196.6								199.2
320		207.2 ^a								209.7
340		319.7	218.1							220.4
360	364.1	339.8	229.7 ^a	229.5						230.8
380	375.2	354.9	330.4	241.6						241.4
391.2				248.2 ^a						
400	385.1	367.0	353.0	315.7	253.3					252.4
420	394.4	378.2	368.6	354.3	265.8	265.4				263.9
435		386.5 ^a								
439.8					276.7 ^a					
440	403.4	390.4	381.7	373.9	279.2	277.8				275.6
459.7			394.7 ^b							
460	412.0	402.8	395.0	388.2	360.6	290.0				287.4
475						298.6 ^a				
477.5				400.2 ^b						
480	421.1	413.6	409.2	401.6	383.5	328.4	302.9	302.5		299.4
500	430.1	424.1	420.1	414.6	401.0	379.0	315.4	315.3		311.5
507.3							320.9 ^a			
511					409.7 ^b					
520	439.3	433.9	430.9	426.8	417.7	400.7	374.8	330.0	325.4	323.9
535.2								341.7 ^a		
537						417.0 ^b				
540	448.6	443.9	441.4	438.2	431.3	420.0	404.4	365.2	339.3	337.0
553							419.2 ^b			
560	458.1	454.0	451.4	448.8	442.8	434.2	424.9	406.5	355.0	350.8
570								420.0 ^b		
580	467.4	463.5	461.4	459.0	453.7	446.7	439.4	429.2	375.3	364.0
600	477.2	473.2	471.3	468.9	464.4	458.7	452.5	443.7	409.4	377.9

^a Enthalpy values at bubble point. ^b Enthalpy values at dew point

For the mixtures, the needed conversion enthalpy is a weight average of the values for the pure components plus the heat of mixing in the liquid phase at 75°F . Besides adding the enthalpy values listed in the last column of Table I, conversion to the -200°F basis requires the addition of the enthalpy difference at 75°F and the liquid phase between the pressure of measurement and the saturated liquid state, a value that never exceeds 3.5 btu/lb. This was computed using the thermodynamic equation of state, as described (9). Since 75°F is far below the critical temperature, the computation of enthalpy difference in the liquid phase is made with more certainty than the accuracy of measurement.

A total of 705 enthalpy measurements was obtained. The uncorrected measurements have been tabulated and deposited with ASIS (17), showing enthalpy values relative to 75°F and the pressure of measurement. These measured values have been adjusted to the -200°F basis, plotted, and smoothed, resulting in Tables II through VI showing enthalpy dependent upon temperature and pressure. These smoothed enthalpies deviate from the measured values by an arithmetic average of 0.96 btu/lb.

To aid in programming the measurements for the mixture containing 60.1 wt % benzene, Berkstresser and Rebert (3) measured some bubble points, using the apparatus described by Rebert and Hayworth (16). The critical point was determined to be 678.4°F and 729 psia. Bubble points occurred for 500, 600, and 700 psia at 564.8, 598.7, and 639.4°F , respectively.

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