P = vapor pressure
P_i = partial vapor pressure of component i
μ_i^E = excess partial molar free energy of component i in liquid mixture referred to the pure component as standard state
y_i = mole fraction of component i in vapor phase
G^E = excess free energy of one mole of liquid mixture
β_i = second virial coefficient of component i at pressure P_i
β_{12} = mixed second virial coefficient (cross-term) between components 1 and 2 in the vapor
σ = standard deviation

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Enthalpies of Cyclohexane and Mixtures of *n*-Pentane and Cyclohexane

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A flow calorimeter was used to measure enthalpy for cyclohexane and four mixtures of *n*-pentane with cyclohexane. The results are presented from 75° to 680° F, with pressures to 1400 psia.

This experimental study was undertaken to determine the enthalpy of a mixture of two commonly encountered hydrocarbons with one component a naphthene and the other a paraffin. The heat of vaporization of pure cyclohexane has been measured by Osborne and Ginnings (*9*) and by Kozicki and Sage (*4*) and presented by Graue, Berry, and Sage (*3*). Enthalpy values do not appear to have been reported prior to 1969 for pure cyclohexane, nor for mixtures of *n*-pentane with cyclohexane. Pentane has been measured using the apparatus used for the cyclohexane and pentane-cyclohexane mixtures (*6*).

The measurements were made by flowing cyclohexane or the cyclohexane-containing mixtures through a thermally insulated flow calorimeter, which operates isobarically. In operation, the entering hydrocarbon cools from an initially measured temperature to 75° F, giving up its enthalpy by transferring heat to surrounding Freon-11 maintained at its boiling point temperature. The measurement of both the hydrocarbon flow rate and the rate of evolution of Freon-11 allows computation of the enthalpy difference between the inlet temperature and 75° F. Temperatures were measured by calibrated Chromel-Constantan thermocouples that develop 0.04 mv per ° F, resulting in a precision uncertainty of 0.25° F. Heise gages were used to measure the pressure. The details of the calorimeter have been discussed (*6*). Besides making measurements with cyclohex-

ane and its mixtures, the calorimeter has been used at intervals to measure the enthalpy of pure *n*-pentane and liquid water as a means of checking the measurement validity. These measurements on pure components showed an average deviation of 1.5 Btu per pound when compared with published enthalpy values for *n*-pentane (2) and water (8).

The cyclohexane and *n*-pentane were obtained from the Phillips Petroleum Co. The cyclohexane was stated to have a purity of 99.5 mole %, and was used as received. The *n*-pentane was examined by chromatography and contained only a trace of isopentane (2-methylbutane), indicating a purity of 99.9%. The mixtures were prepared by weighing the pure pentane and cyclohexane to make a 5000-gram sample. The composition so determined was used to describe the mixture composition with an accuracy believed better than 1.0%. In addition, as the measurements proceeded, small samples were removed from the calorimeter and the refractive index was determined to ensure that gradual change in composition was not taking place.

A total of 771 measurements were made on the cyclohexane and cyclohexane-pentane mixtures. These measurements, showing the enthalpy relative to 75° F and the pressure of measurement, are deposited with the American Society of Information Science (ASIS). About half of these results were obtained in an initial group of measurements, followed one year later by a second group. Although the results of the first partial study were previously reported (5), these earlier measurements are included in the deposited

Table I. Properties of Liquid Phase at 75° F and 1-Atm Pressure

Material	Wt %, *n*-pentane	Liquid density, g/cm³	Heat of mixing, Btu/lb	Enthalpy to add, Btu/lb
100 % cyclohexane	0	0.7749	0	84.0
19.7 moles % pentane	17.4	0.7431	0.50	92.4
38.5 moles % pentane	34.9	0.7138	0.86	100.7
61.2 moles % pentane	57.5	0.6815	1.19	111.2
79.3 moles % pentane	76.6	0.6631	0.82	119.6
100 % pentane	100	0.6219	0	129.4

Table II. Smoothed Values of Enthalpy for Cyclohexane

Units. Btu per lb
Base level. Saturated liquid at −200° F

Temp, ° F	Psia										
	0	100	200	300	400	500	588	700	800	1000	1400
75		84.6			85.3				86.3		87.7
100		95.9			96.6				97.5		98.8
120		105.2			105.9				106.8		108.0
140		114.7			115.4				116.3		117.5
160		124.3			125.0				125.9		127.1
180		134.4			135.0				135.9		137.0
200		145.0			145.5				146.1		147.0
220		156.1			156.5				157.0		157.6
240		167.3			167.6				167.9		168.4
260		178.5			178.7				179.0		179.5
280		189.8			190.0				190.2		190.4
300	338.1	202.0	202.1		202.3				202.7		203.3
320	347.4	214.0	214.1		214.3				214.7		215.3
324		216.5[a]									
324		339.9[a]									
340	356.7	347.5	226.1		226.3				226.8		227.3
360	366.4	358.0	238.6		238.9				239.4		240.1
380	376.7	368.3	251.8		252.0				252.2		252.6
396			263.8[a]								
396			368.1[a]								
400	387.3	378.8	370.3	265.7	265.8				266.0		266.2
420	398.0	389.5	381.5	279.3	279.3				279.4		279.4
440	408.4	400.8	393.0	293.6	293.6				293.4		293.3
443				296.3[a]							
443				385.1[a]							
460	419.4	412.2	404.8	395.8	308.1				307.5		306.7
480	430.8	424.0	416.6	408.0	324.3				322.7		320.4
481					325.1[a]						
481					396.3[a]						
500	442.3	435.8	428.8	420.8	413.2	339.1	338.4		337.7	336.3	334.3
507						345.3[a]			45		
507						400.4[a]					
520	453.5	447.7	441.5	434.3	427.3	412.0	355.4	353.1	352.6	351.8	348.3
530	459.7	454.2	447.8	441.0	434.3	420.5	367.4	362.0	360.7	359.1	356.0
534							377.3				
536							396.0				
540	466.0	460.6	454.1	447.9	441.2	429.1	411.2	371.0	369.4	366.9	363.8
560	477.9	472.8	467.0	461.6	455.1	444.8	434.5	399.8	390.2	384.2	379.2
580	490.5	485.5	480.2	474.9	468.9	460.5	451.3	434.4	418.3	402.3	395.0
600	503.3	497.5	493.6	488.4	483.1	476.2	468.8	457.6	442.1	421.2	411.2
620	516.3	511.9	507.5	502.4	497.3	491.7	485.5	475.0	462.5	440.8	425.8
640	529.3	525.3	521.4	516.5	511.7	506.4	501.5	491.7	481.8	461.6	445.1
660	542.6	538.8	535.7	530.6	526.2	521.3	516.5	507.9	500.3	482.5	462.5
680	555.8	552.5	549.3	544.9	540.7	535.7	530.7	524.1	518.3	504.5	480.2

[a] Enthalpy values on two-phase boundary.

data as a convenience. The second study was made to fill in gaps in the measurements and get more definitive results, especially around the dew and bubble points. Where the two sets of measurements overlap, no significant differences in the results were observed. All of the data have now been evaluated in this presentation.

The results have been placed upon a common basis of zero enthalpy at −200° F and the saturated liquid state of the pure components. A two-step procedure is used to do this. The measured values are first corrected to a base level of 75° F and the saturated liquid condition by using the thermodynamic equation of state as described previously (*6*). This correction for pressure change in the liquid phase is small, amounting to a maximum of 3 to 4 Btu per pound at the 1400-psia level. For the cyclohexane, the addition of the heat of vaporization, 168.1 Btu per pound (*3*), gives the enthalpy of the saturated vapor at 75° F, at a pressure of 1.85 psia. The enthalpy difference for the vapor between 1.85 psia and zero pressure was computed by the thermodynamic equation of state to be 0.3 Btu per pound, an enthalpy difference smaller than the accuracy of measurement of the calorimeter. The API data book (*1*) shows the vapor state at zero pressure to have an enthalpy value relative to −200° F of 252.4 Btu per pound. Subtracting the heat of vaporization plus 0.3 from the API value gives 84.0, the number of Btu per pound needed to add to the values of enthalpy based on the saturated liquid at 75° F. This is also the enthalpy difference between 75° and −200° F for saturated liquid cyclohexane. The similar enthalpy difference for *n*-pentane was previously determined to be 129.4 Btu per pound (*6*). For the mixtures, the needed value of enthalpy to add to the measurements relative to 75° F and the saturated liquid mixture is a weight average of the values for the pure components, plus the heat of mixing at 75° F. Mathiesen and Thynne (*7*) show heats of mixing for cyclohexane with

Table III. Smoothed Values of Enthalpy for Mixture of 19.7 Moles % Pentane and 80.3 Moles % Cyclohexane

Units. Btu per lb
Base level. Pure saturated liquid components at −200° F

Temp,	Psia											
° F	0	100	150	200	300	400	500	600	700	800	1000	1400
75		92.5				93.5				94.5		95.9
100		103.7				104.9				105.9		107.3
120		113.8				115.0				116.0		117.4
140		123.7				124.9				125.9		127.4
160		133.8				135.0				136.0		137.4
180		143.9				145.1				146.1		147.5
200		154.5				155.7				156.7		158.0
220		165.3				166.5				167.5		168.8
240		176.7		177.4		177.9				178.8		180.2
260		187.8		188.4		189.0				189.9		191.2
280		199.6		200.2		200.6				201.5		202.6
300			213.1	213.1		213.5				214.1		215.1
320			226.2	226.2		226.4				227.1		227.9
335.6			236.5[a]									
340			272.4	239.1		239.3				239.8		240.5
350.5			357.8[a]									
360	376.7	368.8	364.9	253.0		253.0				253.0		253.5
366.4				255.4[a]								
370				286.2								
380	387.5	380.4	377.1	368.0		265.6				265.9		266.3
381				377.0[a]								
400	397.8	392.2	389.5	386.5	279.5	279.5		279.6		279.6		279.8
413.4					289.1[a]							
420	408.7	402.4	399.9	396.6	341.0	293.3		293.3		293.4		293.6
425.7					389.4[a]							
440	419.2	412.7		406.8	398.7	308.0		308.0		308.1		308.2
449.5						315.6[a]						
450						322.5						
460	430.6	424.5		418.2	410.4	394.0	323.9	323.6		323.3		323.1
461.4						400.2[a]						
477.7							332.7[a]					
480	441.8	436.1		429.8	422.3	413.8	348.2	339.3		338.8		337.8
485						417.3	371.0					
492.3							405.0[a]					
500	453.1	447.9		441.9	434.7	427.3	411.2	359.0		358.0	356.0	352.3
505							415.1	366.5				
510							419.2	377.5				
515							423.0	395.3				
520	464.9	459.5		453.8	447.2	439.8	426.8	407.0	382.0	376.8	372.8	367.4
540	477.2	471.7		466.0	459.9	452.7	443.3	432.5	415.0	400.4	389.9	382.7
560	489.3	484.2		478.8	472.7	466.0	459.2	449.7	436.3	424.9	408.9	398.9
580	502.1	496.9		491.7	485.8	479.3	473.7	465.2	455.7	447.0	428.1	415.7
600	515.0	509.8		504.5	498.8	493.0	488.0	480.4	473.2	466.8	448.0	433.0
620	528.1	523.6		518.6	513.2	507.3	502.8	496.2	490.2	484.9	468.1	450.3
640	541.2	537.2		532.3	527.5	521.8	517.8	511.9	506.7	501.9	488.0	468.0
660	554.6	551.1		547.0	541.9	536.5	532.5	527.7	523.6	518.2	507.4	486.2
680	567.9	564.5		561.0	556.5	551.6	547.5	543.2	539.5	535.2	525.0	504.7

[a] Enthalpy values on two-phase boundary.

Table IV. Smoothed Values of Enthalpy for Mixture of 38.5 Moles % Pentane and 61.5 Moles % Cyclohexane

Units. Btu per lb
Base level. Pure saturated liquid components at −200° F

Temp, °F	Psia											
	0	100	150	200	300	400	500	600	700	800	1000	1400
75		100.9				101.7				102.8		104.3
100		112.2				113.6				114.6		116.1
120		122.8				124.2				125.2		126.6
140		133.1				134.6				135.5		136.8
160		143.5				145.0				145.9		147.2
180		154.0				155.5				156.4		157.7
200		164.7				166.2				167.1		168.4
220		175.9				177.4				178.3		179.6
240		187.5	188.3	188.4		188.9				189.8		191.0
260		199.4	200.2	200.3		200.7				201.5		202.6
280			212.4	212.5		212.9				213.6		214.6
300	357.3		225.5	225.5		225.8				226.4		227.4
313			234.4[a]									
320	367.0		277.7	238.9		239.2				239.7		240.4
330			344.7									
332.7			359.9[a]									
340	377.1	369.4	364.2	252.9		252.7				253.1		253.6
343				255.0[a]								
350			370.2	294.4								
355				324.6								
360	387.6	380.2		354.6	266.6	266.6		266.6		266.8		267.1
363.3				372.8[a]								
370				376.9	274.4	274.4						
380	398.5	391.4		383.2	281.8	281.6		281.2		280.8		280.4
385				386.3	285.4	285.2						
390.2					289.3[a]							
400	409.3	402.9		395.4	342.4	296.6		296.6		295.6		294.3
405					371.6	300.6						
408.6					389.6[a]							
420	420.4	414.4		407.5	398.0	312.6	312.5	312.4		311.0		309.0
425.6						317.1[a]						
430						336.2	320.6					
435						364.0	324.7					
440	431.2	426.1		419.6	411.0	395.6	329.0	328.8		326.6		325.4
440.6						399.2[a]						
450						406.1	336.9					
453.5							339.8[a]					
460	442.5	437.9		432.0	424.2	413.6	363.6	345.5		342.1		340.4
469							403.2[a]					
480	454.2	449.7		444.4	437.1	428.7	413.6	370.3		358.4		354.6
500	466.1	461.9		456.7	450.2	443.0	433.0	416.5	387.1	379.4	374.2	369.7
520	477.9	474.3		469.3	463.3	457.2	449.0	438.3	416.3	403.0	393.0	384.6
540	490.5	486.5		482.2	476.5	470.8	464.7	455.6	440.7	426.8	413.6	401.4
560	502.7	499.3		494.8	489.4	484.7	479.4	471.9	460.8	449.0	434.8	418.1
580.	515.2	512.1		507.8	502.5	498.4	493.6	487.0	478.7	469.6	455.4	435.8
600	528.4	524.9		520.9	516.1	512.3	507.5	501.8	495.6	488.8	475.0	454.3
620	541.3			534.4	529.7	526.1	521.5	516.5	510.8	505.3	493.8	472.4
640	554.9			548.1	543.9	540.2	535.6	531.0	525.8	521.0	511.0	490.3
660	568.4			562.2	558.2	554.3	550.2	545.4	541.1	536.3	527.9	508.0
680	581.5			575.9	572.2	568.5	564.5	560.1	555.5	550.9	554.0	525.2

[a] Enthalpy values on two-phase boundary.

Table V. Smoothed Values of Enthalpy for Mixture of 61.2 Moles % Pentane and 38.8 Moles % Cyclohexane

Units. Btu per lb
Base level. Pure saturated liquid components at −200° F

Temp, °F	Psia											
	0	100	150	200	300	400	500	600	700	800	1000	1400
75		111.4				112.3				113.3		114.9
100		123.1				124.9				126.0		127.5
120		134.1				135.9				136.9		138.4
140		145.2				146.9				147.9		149.3
160		156.0				157.8				158.7		160.0
180		167.0				168.7				169.6		170.9
200		178.0		179.2		179.7				180.5		181.7
220		189.9		191.1		191.5				192.2		193.3
240		202.0		203.2		203.6				204.3		205.3
260				215.8		216.1				216.5		217.2

(*Continued on next page*)

Table V. (*Continued*)

Temp, °F	Psia 0	100	150	200	300	400	500	600	700	800	1000	1400
280	360.2		229.1	229.1	228.7	228.8				229.1		229.6
290			236.8[a]									
300	369.8		298.5	241.9	242.0	242.0				242.2		242.5
310			360.8[a]	250.8								
318.7				258.6[a]								
320	380.0		366.9	265.9	255.7	255.8				256.0		256.3
330			372.8	328.3								
337.8				374.1[a]								
340	390.2	382.5	378.9	374.5	269.8	269.8				269.9		270.1
360	400.8	394.1	390.4	385.7	284.8	284.7				284.5		284.1
365.2					288.6[a]							
370					321.4							
380	412.0	405.6	411.9	397.1	388.1[a]	300.3	299.3	298.7		298.6		298.2
390					394.1							
398.6						314.8[a]						
400	422.9	417.1		408.8	400.3	322.6	314.7	314.6		314.4		312.9
410						352.4						
412.3						396.7[a]						
415					409.3	399.3						
420	434.1	428.7		420.7	412.2	402.8	331.3	331.2		329.9		328.5
425.7							336.4[a]					
430							354.9					
440	445.4	439.9		433.4	425.3	416.6	399.1[a]	351.0		346.4		345.3
445						420.2	404.1					
460	456.9	451.8		446.0	438.5	430.4	418.4	378.7	369.4	363.9		361.1
480	469.0	468.9		458.6	451.6	444.8	434.9	422.0	404.0	386.5		376.1
500	481.4	476.3		471.0	465.3	458.6	450.7	441.9	431.1	411.0	396.1	391.5
520	493.8	488.8		483.5	479.9	472.3	465.7	460.0	448.9	432.8	416.5	406.5
540	506.1	501.9		496.7	492.6	486.0	480.7	474.8	466.2	454.6	437.5	424.5
560	518.7	514.9		510.4	506.4	500.5	495.6	490.1	482.6	473.5	458.2	442.7
580	532.0	528.4		523.5	520.3	514.7	510.3	504.9	498.9	491.7	478.1	460.7
600	544.7	541.5		537.8	534.3	529.1	526.5	520.0	515.3	508.9	496.2	478.9
620	557.6			551.5	548.0	543.2	539.1	534.8	529.9	524.7	513.0	496.6
640	570.4			565.3	561.7	557.9		559.7		539.9	529.2	514.2
660	584.4			579.2	575.7	572.0		564.7		555.1	544.9	531.5
680	598.0			593.5	589.7	586.3		579.4		570.4	560.7	548.7

[a] Enthalpy values on two-phase boundary.

Table VI. Smoothed Values of Enthalpy for Mixture of 79.3 Moles % Pentane and 20.7 Moles % Cyclohexane

Units. Btu per lb. Base level. Pure saturated liquid components at −200° F

Temp, °F	Psia 0	100	150	200	300	400	500	600	700	800	1000	1400
75		119.6				121.0				122.2		124.1
100		128.9				130.6				131.8		133.6
120		142.8				144.4				145.6		147.2
140		154.0				155.5				156.6		158.1
160		165.7				167.1				168.0		169.2
180		177.5		178.3		178.7				179.3		180.2
200		189.5		190.4		190.6				191.1		191.8
220		201.6		202.4		202.7				203.1		203.8
240		214.3		215.0		215.2				215.5		216.0
260	359.2		228.3	227.5		227.6				227.9		228.2
273.5			237.2[a]									
280	369.4		291.6	240.5	240.5	240.5				240.7		240.9
288.5			358.4[a]									
300	380.3	370.7	366.5	254.6	254.7	254.7				254.9		255.1
301.5				255.7[a]								
320	391.0	381.5	376.8	358.1	269.1	269.1				269.1		269.1
323				374.1[a]								
340	401.1	393.1	389.2	384.7	283.5	283.5		283.4		283.3		283.2
347.2					293.3[a]							
359.2					385.4							
360	411.6	404.9	401.2	397.0	386.1	298.9		298.5		297.8		297.2
380	422.4	416.6	412.8	408.2	398.3	319.2	314.9	314.9		314.5		312.6
381						320.0[a]						
385						345.6						
390						385.6						
391						394.6						
400	434.6	428.5		421.0	411.8	492.2	333.8	332.8		330.4	328.4	328.1
409							343.3					

(*Continued on next page*)

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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