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

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A flow calorimeter was used to measure the enthalpy of *n*-hexadecane and mixtures of *n*-hexadecane with *n*-pentane. The results are presented for pressures up to 1400 p.s.i.a. and temperatures from 75° to 600° F.

THE ENTHALPY VALUES of *n*-hexadecane and mixtures containing 16.7, 38.6, 58.7, and 79.4 mole % *n*-pentane with hexadecane have been measured between 117° and 625° F., with pressures ranging up to 1400 p.s.i.a. The data were obtained using a flow calorimeter previously described (*5*), capable of measuring enthalpy differences with an average uncertainty of 1.5 B.t.u. per pound. Briefly, the calorimeter functions by passing the hydrocarbon at constant flow rate into the calorimeter, where first the inlet hydrocarbon temperature is measured. The hydrocarbon is then cooled to 75° F., giving up its enthalpy to Freon-11 at its boiling point. By measuring the rate of evolution of Freon-11 and the hydrocarbon flow rate, the enthalpy change at the pressure of measurement is evaluated by the relation

$$\Delta H = \frac{\rho_{\text{F-11}}\ \Delta H_{\text{F-11}}\ V_{\text{F-11}}}{\rho_{\text{HC}}\ V_{\text{HC}}}$$

The accuracy of the measurements was checked by using the calorimeter to determine enthalpy differences for pure liquid water and for *n*-pentane. The statistical deviation of the results was 1.2 B.t.u. per pound, compared with the published values for water of Meyer, McClintock, Silvestri, and Spencer (*7*), and 1.48 B.t.u. per pound, when checked against published values of *n*-pentane (*2, 3, 4*). The precision of measurement was 0.9 B.t.u. per pound. The measurement of inlet temperature by thermocouples had an uncertainty of 0.5° F., and introduced a variation of 0.4 B.t.u. per pound in the measurements. Pressure was measured to ±1 p.s.i.a., and caused a variation of about 0.1 B.t.u. per pound.

The *n*-pentane was supplied by the Phillips Petroleum Co. It was found to analyze better than 99.0 mole % *n*-pentane with a chromatograph. The hexadecane was purchased from the Humphrey Chemical Co., and was stated to have a purity of 99.0%. It was used as received.

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

Material	Wt. % Pentane	Liquid Density, G./Cm.³	Heat of Mixing, B.t.u./Lb.	Enthalpy to Add, B.t.u./Lb.
100 % hexadecane	0	0.7696	0	93.7
16.7 mole % pentane	6.0	0.7613	0.28	96.0
38.6 mole % pentane	16.8	0.7436	0.39	100.0
58.7 mole % pentane	31.2	0.7184	0.35	105.2
79.4 mole % pentane	55.0	0.6829	0.19	113.5

Mixtures of 5000-gram size were prepared by weighing the pure pentane and hexadecane. The precision of composition measurement was 0.1%. During operation the constancy of composition was monitored by refractive index measurements.

The measured enthalpy differences between 75° F. and

Table II. Smoothed Values of Enthalpy for Hexadecane

Units. B.t.u. per lb.
Base level. Saturated liquid at −200° F.

Temp., ° F.	P.S.I.A. 0	25	32	40	200	1400
75	246.9	93.7	93.7	93.8	94.2	97.5
200					161.2	165.9
220					172.9	177.7
240					185.0	189.4
260					197.4	201.0
280					209.9	213.1
300					223.2	225.5
320					235.9	237.7
340					249.7	250.7
360					262.3	264.2
380					275.4	277.7
400	405.5				289.8	291.8
420	417.0				304.0	305.7
440	428.6				317.7	319.7
460	440.4				332.2	333.7
480	452.4				346.4	347.8
500	464.6	360.6	360.6	360.6	360.7	361.9
520	477.0	375.2	375.2	375.2	375.2	375.5
540	489.5	389.9	389.9	389.9	389.9	389.7
560	502.3	404.7	404.7	404.7	404.6	404.2
580	515.2	419.5	419.5	419.5	419.4	418.9
590	521.7	426.9	426.9	426.9	426.7	426.2
596.5		432.0[a]				
596.5		518.0[a]				
600	528.2	520.7	434.7	434.6	434.5	433.8
610	534.7	527.9	443.9	443.7	443.2	441.5
619.1			451.8[a]			
619.1			529.8[a]			
620	541.4	535.2	530.7	452.7	451.8	449.2
630	548.1	541.9	538.2	461.7		
640	554.8	548.9	545.7	471.2		
641				472.6[a]		
641				541.7[a]		
650	561.6	556.2	553.5	549.9		
660	568.4	563.5	561.0	558.4		

[a] Enthalpy values on two-phase boundary.

Table III. Smoothed Values of Enthalpy for Mixture of 16.7 Mole % Pentane and 83.3 Mole % Hexadecane

Units. B.t.u. per lb.
Base level. Pure saturated liquid components at −200° F.

Temp., °F.	P.S.I.A. 0	25	40	1400
75	249.3	96.0	96.1	100.0
200		163.5	163.5	168.5
220		175.5	175.5	180.2
240		187.5	187.5	191.8
260		200.0	200.1	203.7
274.5		209.8[a]		
280		213.1	213.0	216.0
300		226.1	225.9	228.2
320		239.1	238.8	241.2
340		252.3	252.0[a]	254.2
360		266.3	266.0	267.8
380		280.3	279.9	281.6
400	408.1	294.9	293.5	294.3
420	419.6	309.0	307.5	308.0
440	431.2	323.8	321.9	322.0
460	443.1	339.5	336.7	336.0
480	455.0	355.2	352.0	349.9
500	467.3	371.0	367.9	364.0
520	479.8	388.0	384.3	378.2
540	492.1	406.6	402.1	393.0
560	505.0	430.2	421.2	408.0
580	518.0	468.2	444.0	422.8
588	523.1	487.2	454.7	428.8
599.5		525.0[a]		
600	531.0	525.2	472.2	438.0
620	544.2	539.0	497.0	

[a] Enthalpy values on two-phase boundary.

Table IV. Smoothed Values of Enthalpy for Mixture of 38.6 Mole % Pentane and 61.4 Mole % Hexadecane

Units. B.t.u. per lb.
Base level. Pure saturated liquid components at −200° F.

Temp., °F.	P.S.I.A. 0	25	40	70	200	460	1400
75	253.9	100.0	100.1	100.2	100.5	101.2	103.7
180		156.0					
192		162.9[a]					
200		168.2	167.9				172.8
220		182.0	180.1				184.5
234.5			189.3[a]				
240		196.0	193.9	193.0			196.1
260		210.2	207.9	205.5			208.5
280		225.7	222.1	218.0			220.4
290				224.8[a]			
300		241.3	237.0	232.2			232.0
320		256.2	252.0	247.0			245.0
340		272.1	266.2	262.0			258.5
360		288.2	282.0	278.0			272.0
380		304.5	297.5	294.0			285.2
400	412.8	320.5	316.0	312.0			298.8
420	424.3	334.5	328.0	323.5			312.7
440	436.1	349.3	342.2	338.1			326.5
460	448.1	365.0	357.5	353.5			341
480	459.1	382.0	373.5	368.7			355
500	472.2	401.8	390.2	384.0	373.0	369.2	368
520	484.6	429.0	410.9	400.0	388.7	384.7	383.5
540	497.1	464.0	433.2	416.8	404.5	400.2	399.0
556.5		502.2[a]					
560	510.0	504.8	458.0	436.0	420.5	416	414
580	523.0	519.0	491.0	457.0	437.0	431.5	429.5
600	536.1	532.2	528.5[a]	480.1	455.8	446.5	444.7
620	549.4	545.5	542.6	509.0	475.9	462.1	460.0

[a] Enthalpy values on two-phase boundary.

Table V. Smoothed Values of Enthalpy for Mixture of 58.7 Mole % Pentane and 41.3 Mole % Hexadecane

Units. B.t.u. per lb. Base level. Pure saturated liquid components at −200° F.

Temp., °F.	P.S.I.A. 0	25	40	70	100	200	400	630	1400
75	259.9	105.2	105.3	105.4	105.5	105.7	106.3	106.8	108.8
140		140.2							
60		150.7[a]							
180		174.2	162.2						
197.5			172.4[a]						
200		195.2	176.7	174.4	174.5	175.0	176.0	176.7	178.2
220		212.4	201.1	186.7	186.9	187.4	188.2	188.8	190.0
240		228.0	221.2	199.3	199.5	199.9	200.5	201.1	202.4
245.2				202.5[a]					
260		242.2	238.4	216.2	212.0	212.5	213.2	213.9	214.9
280		256.7	254.1	235.9	225.5	225.7	226.2	226.6	227.3
283					227.5[a]				
300		270.7	268.0	255.0	245.4	239.4	239.8	240.1	240.2
320		284.2	281.2	271.2	264.2	253.0	253.0	253.0	253.0
340		299.1	295.2	287.2	281.0	266.0	266.0	266.0	266.0
360		314.2	309.8	303.0	297.2	279.4[a]	279.1	279.1	279.1
380		329.4	324.7	318.0	313.2	297.2	293.2	292.7	292.2
400	419.2	345.4	340.0	332.2	328.2	315.2	307.2	306.2	305.5
420	430.9	363.2	355.3	347.2	343.0	333.2	321.3	320.2	319.3
440	442.5	382.2	371.2	362.6	358.7	350.2	336.2	334.3	333.2
460	454.4	404.2	388.2	378.2	375.0	367.0	351.2	349.0	347.3
480	466.5	431.2	407.2	395.2	391.2	383.4	366.5	363.5	362.0
500	478.9	464.2	429.7	413.9	406.5	399.9	382.4	379.1	376.7
520	491.2	488.2	459.5	433.4	426.2	417.0	399.9	394.4	391.6
527		492.8[a]							
540	503.9	501.2	485.4	455.4	445.0	433.5	418.7	410.4	407.2
560	516.9	514.7	509.7	477.2	463.2	451.2	435.2	426.4	423.9
563.5			513.6[a]						
580	529.9	527.3	524.7	500.7	483.2	469.0	451.7	442.9	439.2
600	542.9	540.7	537.9	525.6	505.2	486.7	468.2	459.6	455.9
612				543.0[a]					
620	556.1	553.6	551.2	549.2	527.2				

[a] Enthalpy values on two-phase boundary.

Table VI. Smoothed Values of Enthalpy for Mixture of 79.4 Mole % Pentane and 20.6 Mole % Hexadecane

Units. B.t.u. per lb.
Base level. Pure saturated liquid components at −200° F.

Temp., °F.	P.S.I.A.										
	0	25	40	70	100	200	400	600	740	1000	1400
75	269.9	113.5	113.6	113.7	113.8	114.1	114.7	115.2	115.6	116.4	117.6
120		137.4									140.5
139.4		148.8[a]									
140		156.5	149.0								152.0
160		211.3	160.5								163.5
171.8			167.1[a]								
180		233.0	193.5	172.0							175.2
200		249.6	229.5	183.5	183.6	184.3	185.3	186.1	186.5	187.0	187.5
214.2				192.0[a]							
220		262.7	250.0	205.0	195.5	195.9	196.7	197.4	197.8	198.5	199.0
240		274.5	267.0	244.0	209.0	209.2	209.5	209.9	210.1	210.6	211.4
244					211.0[a]						
260		286.9	281.6	268.0	241.0	222.2	222.5	222.9	223.2	223.7	224.5
280		299.5	295.7	285.5	273.6	235.4	235.5	235.7	235.9	236.1	236.5
300		313.5	310.5	301.5	292.0	248.6	249.0	249.1	249.2	249.3	249.4
308						254.4[a]					
320		326.5	323.7	316.8	307.6	271.5	263.5	263.2	263.1	262.9	262.8
340		340.0	335.7	332.1	323.5	297.5	277.5	277.3	277.2	277.1	277.0
360		355.0	352.3	347.5	339.3	321.5	291.6	291.4	291.2	290.9	290.5
380		370.5	367.5	361.5	355.0	341.5	305.6	305.3	305.1	304.7	304.2
400	429.9	387.6	383.5	375.5	370.5	358.2	320.0	319.8	319.6	319.0	318.5
408							326.0[a]				
420	441.4	406.2	400.0	390.7	385.6	373.4	341.5	334.6	334.4	334.0	333.5
440	453.2	427.5	418.3	406.0	401.0	388.5	364.5	350.5	349.8	348.6	348.0
460	465.1	454.5	437.8	422.5	417.5	403.5	379.7	367.0	365.8	364.0	362.7
469		468.0[a]									
480	477.2	475.1	462.5	440.2	435.0	419.5	396.1	383.8	381.5	379.2	377.7
500	489.8	488.0	486.0[a]	461.0	453.1	435.5	416.5	402.0	98.5	394.5	393.0
520	502.1	500.5	499.5	485.5	472.5	454.5	433.5	421.6	417.1	411.1	408.2
540	514.8	513.7	512.8	505.5	493.3	473.5	453.5	441.5	435.5	427.6	424.6
560	527.8	526.8	525.9	522.0	512.8	493.5	474.5	461.5	454.4	445.3	441.0
568.4				529.5[a]							
580	540.9	539.7	539.0	537.9	530.6	513.6	493.5	483.0	474.5	462.5	457.5
592									486.5		
600	554.0	552.9	552.1	551.0	546.5	531.3	511.7	501.3	493.6	481.0	474.0
608					554.8[a]						
620	567.4	566.2	565.5	564.1	562.5	548.4	529.5	520.5	511.5	500.2	490.8

[a] Enthalpy values on two-phase boundary.

the temperature of measurement at a constant pressure have been tabulated and deposited with ASIS. These 330 tabulated values were computed directly from the calorimeter measurements. Evaluation of the enthalpy values depends on determination of the liquid phase density at 75° F. Table I shows the densities for hexadecane and the four mixtures at 75° F. and 14.7 p.s.i.a. as measured by hydrometer.

The API data book (*1*) uses the saturated liquid at −200° F. as the datum level for tabulating enthalpy values. At 75° F., the API data book shows a zero pressure vapor phase enthalpy of 246.9 B.t.u. per pound for *n*-hexadecane. Subtracting the latent heat of vaporization of 153.2 B.t.u. per pound at 75° F., as measured by Parks and Moore (*8*), establishes an enthalpy of 93.7 B.t.u. per pound for the liquid phase of hexadecane at its saturated pressure of less than 1 p.s.i.a. In the liquid phase, the enthalpy differences for 25 p.s.i.a. is negligible; thus, the liquid phase enthalpy at 25 p.s.i.a. and 75° F. is also 93.7 B.t.u. per pound, referred to the −200° F. base level. As a check, the values of enthalpy at zero pressure were extrapolated from the measured enthalpy differences at 640°, 630°, and 620° F. at zero pressure and compared with the zero pressure API values. For the mixtures, the zero pressure enthalpy curves were computed as a weighted average of the zero pressure enthalpies of pentane and hexadecane, with the subtraction of a small heat of mixing in the liquid phase at 75° F. Table I shows heats of mixing at 75° F. for the five materials studied, as determined from the measurements of McGlashan and Morcom (*6*) and Van der Waals and Hermans (*9*). Table I also shows the additional enthalpy needed to convert the data of the saturated liquid phase at 75° F. to the −200° F. basis. As well as shifting for datum level, the measured enthalpy values need to be adjusted by the thermodynamic procedure previously described (*5*) to allow for changes in pressure at 75° F. in the liquid phase. Table II shows smoothed values of enthalpies for *n*-hexadecane with the −200° F. basis. The average deviation of the measured values from the smoothed enthalpies is 1.1 B.t.u. per pound with a plus trend of 0.07 B.t.u. per pound. The statistical deviation is 1.5 B.t.u. per pound. No particular difference in deviation was observed for the various pressure levels. Tables III, IV, V, and VI show the enthalpies for the mixtures. Figures 1, 2, and 3 show enthalpy as a function of temperature in the high-temperature range. The dashed curves represent estimated two-phase boundaries. Figure 3 shows enthalpy values for the mixture with 79.4 mole % pentane over a temperature range from 150° to 620° F., illustrating the very wide temperature range of the two-phase zone.

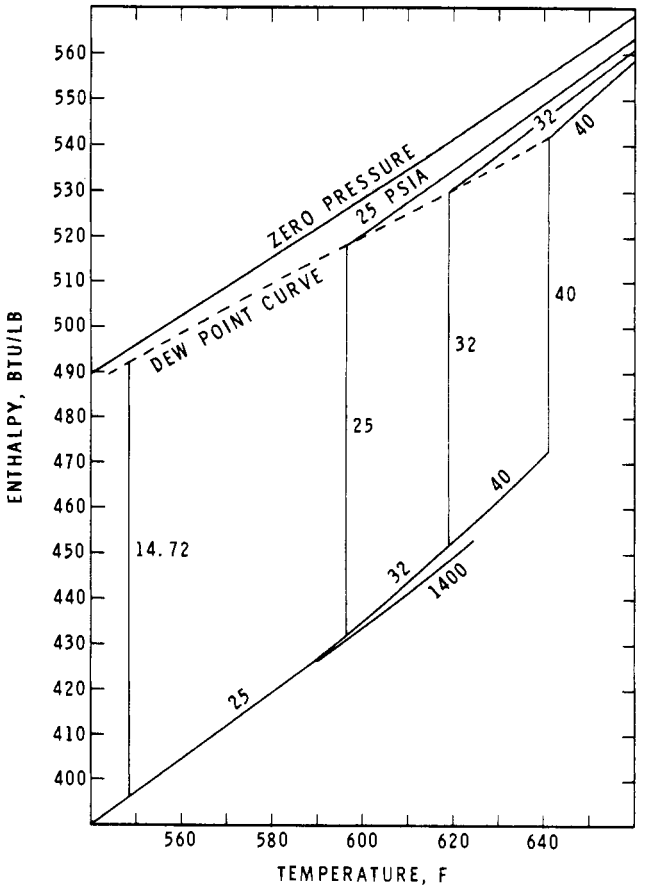

Figure 1. Enthalpy of *n*-hexadecane
Base level. Saturated liquid at −200° F.

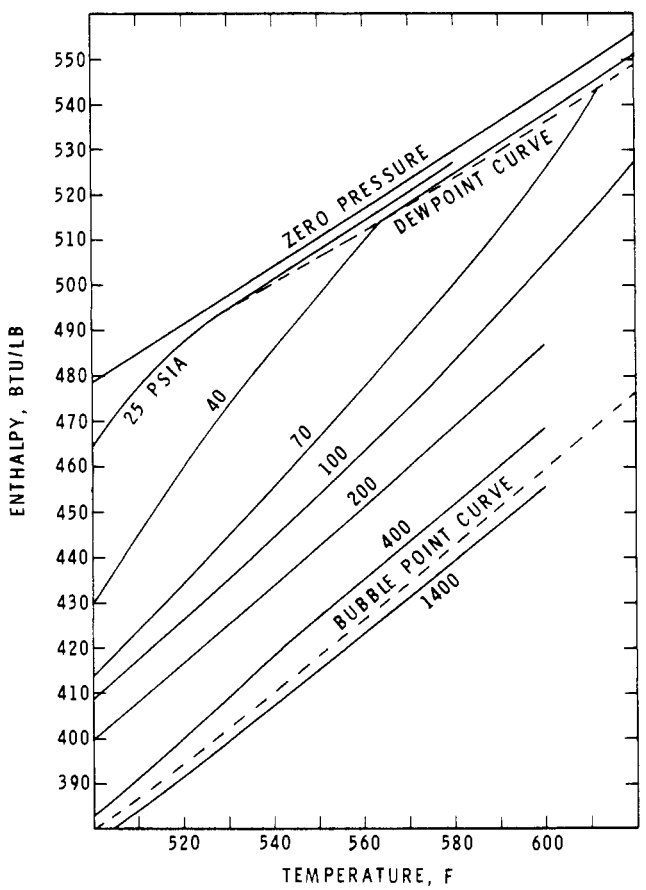

Figure 2. Enthalpy of mixture of 58.7 mole % pentane with 41.3 mole % hexadecane
Base level. Saturated pure liquid components at −200° F.

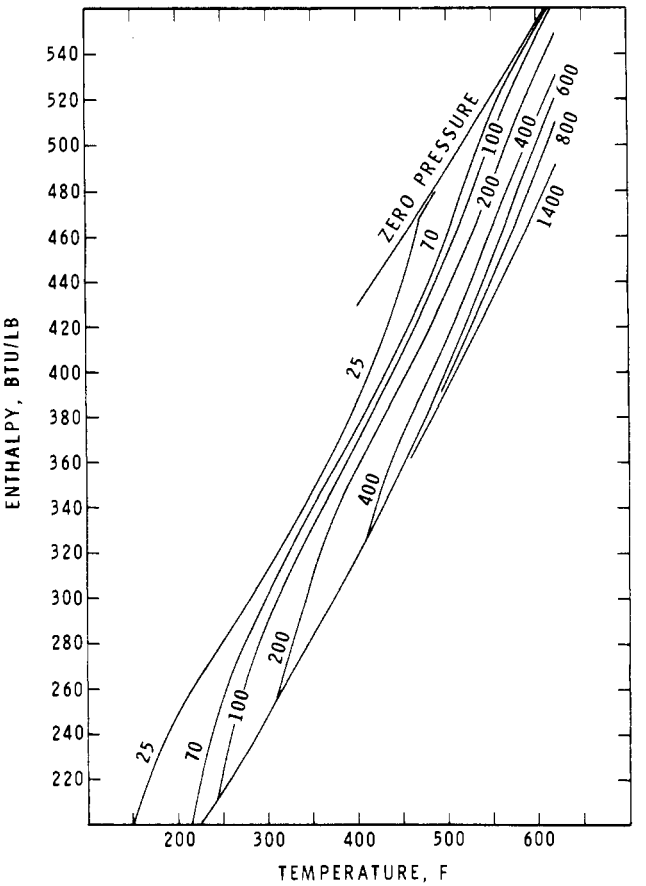

Figure 3. Enthalpy of mixture of 79.4 mole % pentane and 20.6 mole % hexadecane, showing large range of two-phase enthalpy

NOMENCLATURE

ΔH = measured enthalpy difference relative to 75° F. and pressure of measurement, B.t.u. per lb.
$\Delta H_{F\text{-}11}$ = latent heat of vaporization of Freon-11, B.t.u. per lb.
$V_{F\text{-}11}$ = volumetric flow rate of Freon-11, cm.^{3} per second
V_{HC} = volumetric flow rate of hydrocarbon, cm.^{3} per second
$\rho_{F\text{-}11}$ = density of Freon-11, grams per cm.^{3}
ρ_{HC} = density of hydrocarbon, grams per cm.^{3}

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