

benzene-octane mixtures. Table II shows smoothed enthalpies for pure benzene, from 380° to 700° F. Table III shows saturated liquid and vapor enthalpies from 70 psia to the critical pressure of 714 psia. Figure 1 illustrates graphically the enthalpy behavior for the mixture with 58.8 wt % benzene. Table IV shows the predicted enthalpy difference at 560° F between the real gas enthalpy and that of the ideal gas as shown by this work, and by three other sources (1, 5, 11). The temperature of 560° F is only 8° F higher than the critical temperature, and represents an isotherm where considerable nonideality exists in the gas phase. The discrepancies are moderate, but become somewhat larger at higher pressures, showing a maximum deviation of 5.3 Btu/lb.

Tables V-X show smoothed enthalpies for the 90.1, 80.3, 69.7, 58.8, 35.6, and 20.2 wt % benzene in octane mixtures. These include saturated enthalpies and also denote the enthalpy at the critical point, obtained from the measurements of Kay and Hissong (10) on the benzene-*n*-octane system.

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## Enthalpies of Mixtures of Benzene and Cyclohexane

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**Measured enthalpy values are reported on the -200° F basis for mixtures of 80.0, 59.5, 31.7, and 19.9 wt % benzene in cyclohexane. The results are shown from 460° to 590° F with pressures from 0 to 1400 psia.**

Enthalpy measurements have been made on four mixtures of benzene and cyclohexane, a close-boiling nonideal system that exhibits a minimum critical temperature at about 22 wt % benzene (6). The measurements were obtained with a flow calorimeter that operates isobarically and obtains enthalpy differences relative to 75° F and the liquid phase at the pressure of measurement. This calorimeter has previously been described with its constructional and operational characteristics (9). Over a three-year operating period, the calorimeter has been shown to measure enthalpies with an average deviation of 1.5 Btu/lb, established by making measurements at periodic intervals with liquid water and *n*-pentane, and comparing the results with literature values (2, 12). These measurements on water and pentane were made during the study of the benzene-cyclohexane systems, assuring the maintenance of the established accuracy of measurement.

The benzene used had a density at 75° F of 0.8730 gram/

cc, with refractive index  $n_D^{20} = 1.50030$ . It was obtained from the Phillips Petroleum Co., with stated purity exceeding 99.0%. The cyclohexane was also received from the Phillips Petroleum Co. with purity of 99.5%, a density at 75° F of 0.7749 gram/cc, and a refractive index of 1.42604. The American Petroleum Institute data book shows values of density of 0.8749 gram/cc with  $n_D^{20} = 1.50112$  for benzene, and 0.7750 gram/cc, and refractive index of 1.4262 for cyclohexane. The mixtures were prepared by weighing pure benzene and cyclohexane for a sample of 5000 grams. The precision of weighing was 2.5 grams, representing an uncertainty in the mixture composition due to weighing of less than 0.1%. While the calorimeter was operating, refractive index measurements were made of the mixtures to ensure that the composition remained constant.

A total of 651 measurements were made of enthalpies relative to 75° F and the pressure of measurement. These measurements have been tabulated and deposited with ASIS (3). The measured enthalpies have also been converted to a zero enthalpy basis of -200° F and the saturated liquid condition of the pure components to conform to the American Petroleum Institute data book basis (1). The enthalpy

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

Material	Benzene, wt %	Density, g/cc	Heat of mixing, Btu/lb	$\Delta H$ needed for -200° F basis, Btu/lb
Benzene	100	0.8730	0	88.1
81.2 mole % benzene	80.0	0.8491	2.7	90.1
61.3 mole % benzene	59.5	0.8263	4.1	90.5
33.4 mole % benzene	31.7	0.7988	3.7	89.0
21.1 mole % benzene	19.9	0.7893	2.7	88.1
Cyclohexane	0	0.7749	0	84.0

difference required to convert the enthalpies from 75° F to the -200° F basis has been previously established as 88.1 Btu/lb for pure benzene (7), and 84.0 Btu/lb for pure cyclohexane (8). Both cyclohexane and benzene exist in the solid state at -200° F. Because of this a zero enthalpy state represents a hypothetical supercooled state. The enthalpy needed to correct the measured enthalpy values for benzene or cyclohexane based on 75° F and the liquid phase to the -200° F basis was determined previously by plotting isotherms of the measurements and obtaining the extrapolated zero pressure ideal gas enthalpies. Comparison with the ideal gas enthalpies presented in Table 7A1.3 of the American Petroleum Institute data book determined the enthalpy values needed for conversion to the -200° F basis. For mixtures, the number required is a weight average of the pure components, plus the heat of mixing at 75° F and the liquid phase. The heat of mixing of benzene-cyclohexane mixtures has been well established by many investigators (4, 5, 10, 11, 13-17).

Table I shows the compositions studied in both mole and weight percent, the density, the heat of mixing, and the enthalpy needed to shift the data from the 75° to

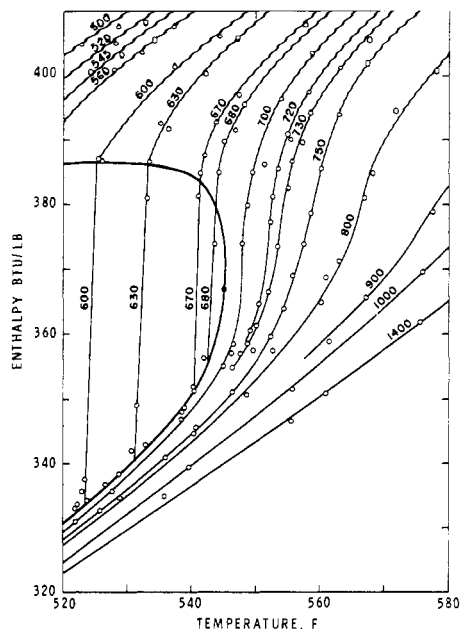


Figure 1. Enthalpy of 80 wt % benzene with cyclohexane

-200° F basis. Before making this conversion, the measurements were placed upon a preliminary base level of 75° F and the saturated liquid state by using the thermodynamic equation of state, and the liquid densities measured at 70°, 75°, and 80° F. This is a small correction evaluated with high preciseness, as previously discussed (9).

By crossplotting procedures, smoothed values of enthalpy have been developed, and are presented in Tables II to V using the -200° F basis. These smoothed values deviate from measured enthalpies by a standard error of estimate of 0.96 Btu/lb. Figure 1 illustrates the measurements for

Table II. Smoothed Values of Enthalpy for Mixture 80.0 Wt % Benzene and 20.0 Wt % Cyclohexane

Base level: pure saturated liquid components at -200° F

Temp, ° F	Psia											
	0	400	500	600	630	680	700	750	800	900	1000	1400
460	411.0	291.6										
469.4		298.2 <sup>a</sup>										
472.0		381.7 <sup>a</sup>										
480	420.0	391.4	305.6									302.2
490	424.8	400.2	312.8									308.7
497.7			318.6 <sup>a</sup>									
499.7			389.2 <sup>a</sup>									
500	429.5	406.7	389.6	320.2				318.5			316.1	315.2
510	434.0	412.5	400.9	327.9			326.7	325.7			322.9	321.7
520	438.9	418.2	408.3	335.9			334.6	333.3	332.4		329.8	328.3
523.2				338.6								
525.4				391.9								
530	443.7	423.8	415.2	398.5	344.7		343.2	341.2	340.2		337.1	334.9
531.1					345.8 <sup>a</sup>							
533.2					391.5 <sup>a</sup>							
540	448.7	429.6	421.6	408.5	403.6	355.7	353.9	349.9	348.6		344.8	341.7
542.2						359.9 <sup>a</sup>						
543		431.1	423.4	410.8	406.9	370.9	357.8	352.7	351.3		347.1	343.8
543.8						385.4 <sup>a</sup>						
545		432.3	424.6	412.5	409.1	393.7	360.6	354.9	353.2		348.7	345.2
547		433.4	425.9	414.0	410.9	398.6	366.5	357.2	355.1		350.1	346.6
550	453.4	435.1	427.7	416.2	413.5	403.4	391.7	361.2	358.2		352.6	348.8
555		437.7	430.6	419.9	417.4	409.3	403.5	371.1	364.1		356.7	
560	458.2	440.5	433.4	423.5	420.9	413.7	409.7	389.7	369.6	364.0	360.9	355.9
570	463.1	446.0	439.2	430.2	428.1	421.6	418.8	410.1	395.1	374.2	369.6	363.1
580	468.0	450.4	444.7	437.0		428.9	426.2	418.6	408.7	388.1	378.7	370.4
590	472.9	456.6	450.4	443.5		436.1	433.3	426.1	417.5	399.1	389.2	377.8

<sup>a</sup> On saturated locus. Estimated critical condition:  $t = 545.1$ ,  $p = 680.5$ ,  $h = 367.0$ .

Table III. Smoothed Values of Enthalpy for the Mixture 59.5 Wt % Benzene and 40.5 Wt % Cyclohexane

Base level: pure saturated liquid components at -200° F

Temp, ° F	Psia											
	0	400	500	543	600	630	654	670	700	800	1000	1400
460	413.5											295.7
473.7		307.8 <sup>c</sup>										
476.3		387.8 <sup>c</sup>										
480	423.0	392.3	312.4									308.8
490	427.9	402.4	320.0 <sup>c</sup>						318.7			315.7
498.4			326.7 <sup>c</sup>									
500	432.8	410.0	374.0	327.8					326.3			322.3
500.6			393.7 <sup>c</sup>									
509.7				335.7 <sup>c</sup>								
510	438.0	416.5	404.3	339.0	335.9				334.8			329.2
512.2				395.3 <sup>c</sup>								
520	442.7	422.7	412.7	404.5	344.7			343.4	342.4	340.3	337.5	335.9
524.0					348.6 <sup>c</sup>							
527.1					395.0 <sup>c</sup>							
530	448.0	428.5	419.9	413.6	399.3	354.4		352.8	351.4	348.6	345.3	342.7
530.7						354.8 <sup>c</sup>						
534.3						393.1 <sup>c</sup>						
538			425.2	420.1	409.8	404.2	367.4	363.2	360.6	355.7	351.8	
539.8							376.7 <sup>b</sup>					
540	453.2	434.3	426.4	421.7	411.9	407.1	390.5	366.8	363.3	357.6	353.4	349.7
542			427.8	423.2	413.9	409.7	399.6	383.0	366.3	359.6	355.1	
545			429.6	425.4	416.7	412.8	406.0	399.2	371.4	362.4	357.6	
550	458.4	440.3	432.7	429.2	421.1	417.3	413.0	408.4	394.0	367.4	361.7	356.6
560	463.2	446.2	438.9	435.7	428.7		422.6		414.5	379.4	370.3	363.6
570	468.8	452.0	444.9	441.8	435.7		430.5		423.5	398.3	379.2	370.9
580	473.9	457.7	450.7	447.8	442.6		437.7		431.6	412.2	388.7	378.5
590	479.0	463.2	456.6	453.7	449.4				439.1	420.3	398.5	386.4

<sup>c</sup> On saturated locus. <sup>b</sup> At critical point.

Table IV. Smoothed Values of Enthalpy for the Mixture 31.7 Wt % Benzene and 68.3 Wt % Cyclohexane

Base level: pure saturated liquid components at -200° F

Temp, ° F	Psia											
	0	400	500	540	600	625	640	660	700	800	1000	1400
460	416.7	304.8										299.7
469.9		312.1 <sup>c</sup>										
473.1		391.0 <sup>c</sup>										
480	426.9	397.3	319.6							315.8	314.7	313.8
490	432.0	405.3	327.2							323.2	321.9	320.8
500	437.3	412.8	336.2							330.8	329.3	327.8
501.4			336.1 <sup>c</sup>									
504.1			398.7 <sup>c</sup>									
510	442.7	420.0	406.5	343.2						338.7	336.8	334.9
512.3				345.2 <sup>c</sup>								
515.2				399.8 <sup>c</sup>								
520	448.0	426.7	415.5	407.6	352.2		351.3		350.0	346.7	344.5	342.2
527.0					359.7 <sup>c</sup>							
529.7					399.1 <sup>c</sup>							
530	453.7	433.2	423.5	417.6	399.4	363.8	361.8	360.2	359.4	354.8	352.4	349.6
535		436.5	427.1	421.7	408.2	373.1	368.9	365.8	364.2	359.3	356.5	
536.5						382.5 <sup>c</sup>						
538		438.4	429.2	424.1	412.0	401.2	375.3	370.1	367.1	361.9	358.9	
540	459.4	439.7	430.5	425.5	414.2	405.7	394.5	373.4	369.1	363.8	360.5	357.1
545		442.7	433.9	429.2	425.2	413.1	410.1	394.5	374.9	368.5	364.8	
550	464.9	445.9	437.3	432.8	423.5	418.5	416.5	409.0	382.4	373.5	369.2	364.6
560	470.0	452.1	444.1	440.0	432.1				414.7	387.5	377.9	372.2
570	475.9	458.2	450.7	446.8	440.0				425.3	405.0	387.0	379.7
580	481.8	464.3	457.3	453.5	447.8				434.9	416.3	396.1	387.5
590	487.7	470.6	463.8	460.3	455.3				443.8	425.7	405.0	395.7

<sup>c</sup> On two-phase boundary. <sup>b</sup> At critical point.

the mixture with 80 wt % benzene and delineates the region around the critical zone. The critical point is denoted by the darkened point along the saturated locus. The mixtures were selected to be at composition intervals of 20 wt %. In the case of the mixture at 31.7 wt % benzene, a numerical error was made on first preparing the sample. After

measuring the enthalpy for this mixture, it was apparent that an inconsistency existed. A re-computation showed that the composition was 31.7 wt % benzene and not the 40% initially intended. The tables indicate critical enthalpies, established with the help of the measurements of Kay and Hissong (6) for the benzene-cyclohexane system.

Table V. Smoothed Values of Enthalpy for Mixture 19.9 Wt % Benzene and 80.1 Wt % Cyclohexane

Base level: pure saturated liquid components at -200° F

Temp, ° F	Psia											
	0	400	500	538	600	613	650	700	750	800	1000	1400
460	417.3											304.8
473.0		316.6 <sup>a</sup>										
475.5		395.2 <sup>a</sup>										
480	428.1	399.8	321.8					321.3				317.7
490	433.8	407.8	329.7					328.6				324.3
500	439.2	414.8	337.5					336.3		334.2		330.9
503.1			339.9 <sup>a</sup>									
508.5			402.8 <sup>a</sup>									
510	445.0	421.7	404.7	345.6				344.2		342.2		388.1
514.2				349.3 <sup>a</sup>								
518.9				403.4 <sup>a</sup>								
520	450.5	428.1	415.0	405.7	354.7			352.7		350.3	348.0	345.3
527.4					363.4 <sup>a</sup>							
530	456.1	434.7	423.8	419.3	390.3	367.2	365.3	362.0	360.4	358.4	356.4	352.6
531.3					400.2 <sup>a</sup>							
534		437.3	427.2	423.2	407.8	374.9	371.3	366.2	364.4	362.5	359.8	
536.5						385.8 <sup>b</sup>						
538		439.8	430.4	426.7	414.0	409.4	277.3	370.3	368.4	366.1	363.3	
540	462.0	441.2	432.0	428.4	416.6	412.7	380.7	372.6	370.5	367.9	365.0	360.1
545		443.3	435.6	432.5	422.1	419.3	402.4	379.7	376.5	372.6	369.5	
550	467.5	447.4	439.0	436.3	426.7	424.7	413.8	390.2	382.0	377.3	373.7	367.5
560	472.9	453.8	445.8	443.3	435.2	433.6	426.2	412.8	395.7	388.2	382.2	375.2
570	478.8	460.0	452.8	450.2	443.1	442.0	435.8	427.8	414.8	403.0	391.1	382.8
580	484.9	466.4	459.6	456.9	451.0		444.8	437.6	426.5	417.5	400.2	390.7
590	490.9	472.7	466.3	463.7	458.8		453.4	446.4	436.3	427.8	410.0	399.0

<sup>a</sup> On saturated locus. <sup>b</sup> At critical point.

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## CORRECTION

We refer to the article "Adsorption of Methane on Carbon at Temperatures to 121° C and Pressures to 650 Atmospheres" by T. Don Stacy, Eldred W. Hough, and William D. McCain, Jr. (*J. Chem. Eng. Data*, **13** (1), 74 (1968)). The total dead-space volume of the cell and connected tubing of 66.4 cc reported in this paper is incorrect. The

correct value of dead-space volume was 65.0 cc. This was an error in the preparation of the paper. The correct value was used in all calculations; therefore, the results given in Table I are not in error. We are indebted to P. G. Menon of the Regional Research Laboratory, Hyderabad-9, India, for calling this error to our attention.