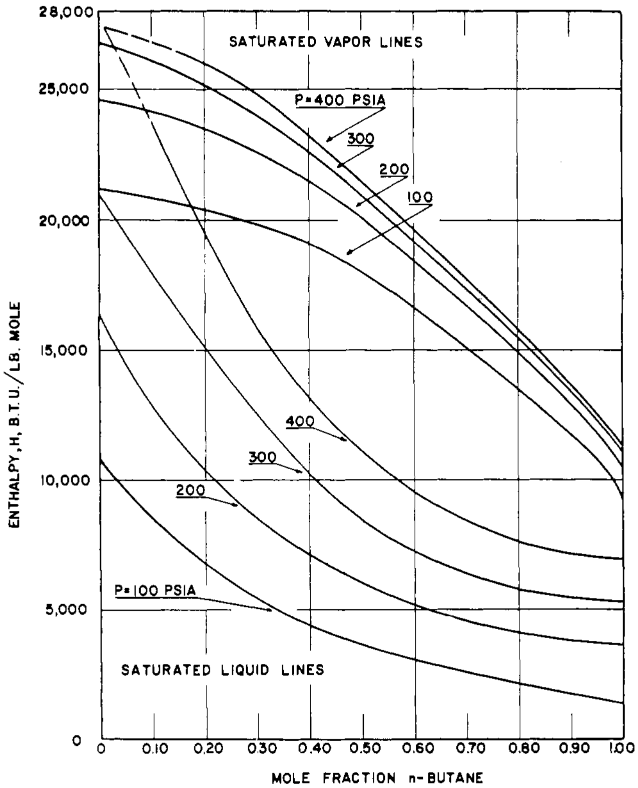

Figure 2. Enthalpy *vs.* composition diagram for *n*-butane–*n*-heptane system

was used to calculate the enthalpies of the saturated and superheated vapors of *n*-butane–*n*-heptane mixtures. The necessary values of H^0 were obtained from (*1*).

With these calculated data and the available information on pure *n*-butane, the term $(\partial H_G/\partial y)_{T,P}$ could be evaluated graphically. The slope data were smoothed by plotting $(y - x)\,(\partial H_G/\partial y)_{T,P}$ *vs.* y for each pressure. Again, four parabolic shaped curves were obtained. The enthalpy, H_b, of the saturated liquid mixtures can now be calculated by Equation 3. As the enthalpy values at points $x = 0$ and $x = 1$ are known, the H_b *vs.* x curve can be completed by repeating the series of calculations for a number of different compositions in the vapor phase.

RESULTS AND CONCLUSIONS

Using the data for the pure components available in the literature (*5*, *7*), the Benedict-Webb-Rubin equation of state (2) and the method of calculation described above, enthalpy *vs.* composition diagrams at 100, 200, 300, and 400 pounds per square inch absolute, were constructed for the system *n*-butane–*n*-heptane. The final results are presented in Table I and in graphical form in Figure 2. The tabulated values are believed to be accurate within ± 3% and are reported to four or five significant figures for consistency. Although these data cannot be used directly to obtain partial enthalpy data, they can be used to check enthalpies of mixtures obtained through the use of partial enthalpies or any other method.

ACKNOWLEDGMENT

The authors wish to acknowledge the help of Donald F. Weitzel with the calculations involved in this study.

NOMENCLATURE

H = enthalpy, B.t.u./lb. mole. $H = 0$ for a pure component in the ideal gas state at unit fugacity and 0°R.
H^0 = enthalpy of a component in the ideal gas state and unit fugacity, B.t.u./lb. mole
ΔH_c = differential heat of condensation, B.t.u./lb. mole
P = pressure, pounds per square inch absolute
R = gas law constant, 1.987 B.t.u./lb. mole-°R.
T = absolute temperature, °R.
V = molal volume, cu. ft./lb. mole
d = density, lb. mole/cu. ft.
x = mole fraction in liquid phase
y = mole fraction in vapor phase
A_0, B_0, C_0, a, b, c, α and γ = empirical constants of Benedict-Webb-Rubin equation of state

Subscripts

G = vapor phase
b = bubble point
d = dew point
i = a component
j = total number of components

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Phase Equilibria in Hydrocarbon Systems

Volumetric Behavior of Cyclohexane

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Little experimental information is available concerning the influence of pressure and temperature upon the molal volume of cyclohexane. Rossini (*12*) reviewed the available information concerning the physical properties of cyclohexane at atmospheric pressure and these data are used as the basis for establishing the purity of the cyclohexane used in this investigation. Geist and Cannon (*4*), as well as Parks and coworkers (*8*), determined a number of the properties of cyclohexane at atmospheric pressure. The critical temperature and pressure were reported by

Table I. Experimental Volumetric Measurements for Cyclohexane[a] in Liquid Phase

Pressure Specific, Lb./Sq. Inch Volume, Absolute Cu. Ft./Lb.

100° F.		160° F.		220° F.		280° F.		340° F.		400° F.		460° F.	
4111.7	0.020365	9421.2	0.020402	9872.2	0.020951	9708.4	0.021570	9935.8	0.022148	9824.8	0.022815	9804.6	0.023487
2094.8	0.020677	8897.6	0.020456	9133.8	0.021062	9498.1	0.021611	9507.4	0.022210	9463.0	0.022923	9478.4	0.023564
955.8	0.020881	7828.2	0.020587	8071.3	0.021234	9060.4	0.021684	9019.4	0.022312	9072.2	0.023036	8997.0	0.023695
459.0	0.020962	6063.1	0.020843	7153.8	0.021363	8143.8	0.021857	8094.1	0.022516	8062.6	0.023312	8083.3	0.023961
53.2	0.021081	4033.2	0.021157	6135.6	0.021546	7091.6	0.022071	7149.0	0.022737	7006.5	0.023608	7092.8	0.024304
		2226.3	0.021518	5036.3	0.021754	6095.2	0.022271	6121.2	0.022997	6054.0	0.023865	6101.8	0.024666
		1036.7	0.021757	4067.6	0.021952	5048.6	0.022531	5103.6	0.023283	5042.8	0.024199	5093.8	0.025131
		446.1	0.021868	3073.0	0.022178	4025.6	0.022798	4085.0	0.023675	3990.0	0.024662	5011.1	0.025752
		107.9	0.021970	2023.4	0.022503	3043.1	0.023116	3044.3	0.024097	2958.4	0.025194	2981.3	0.026495
				996.8	0.022787	1974.9	0.023479	1966.3	0.024654	2048.0	0.025863	1997.1	0.027540
				479.4	0.022969	921.5	0.023931	877.2	0.025321	1066.6	0.026827	1175.7	0.028740
				89.9	0.023104	511.3	0.024139	513.6	0.025623	561.3	0.027468	776.6	0.029694
						93.2	0.024424	200.1	0.025931	303.2	0.027935	474.7	0.030922

[a] Sample weight for 100° F. = 0.23370 lb.; all other temperatures, 0.22291 lb.

Meissner and Redding (*7*) based in part upon experimental information for substances of similar chemical nature. Vapor pressures were reported by Rossini and coworkers (*12*, *16*), Nagornov and Rotinjanz (*10*), Scatchard (*14*), Aston (*1*), Kay and Albert (*6*), and Young (*17*). Data are unavailable concerning the effect of pressure on the volume of this compound.

The molal volume of cyclohexane was measured at temperatures between 100° and 460°F. and for pressures up to 10,000 pounds per square inch. The vapor pressure was also measured for the entire temperature interval.

METHODS AND APPARATUS

The methods and equipment employed were the same as used in earlier studies of *n*-nonane (*3*), *n*-heptane (*11*), and *n*-hexane (*15*). In principle the method involved the introduction of a known weight of cyclohexane into a stainless steel chamber, the effective volume of which could be changed by the introduction or withdrawal of mercury. The stainless steel chamber was located in an agitated liquid bath in order to maintain constant temperature. A detailed description of the methods of measurement and equipment employed is available (*13*).

The volume of the system occupied by cyclohexane was established with a probable error of 0.25% at pressures below 5000 pounds per square inch and 0.4% at the higher pressures. Weighing bomb techniques (*13*) permitted the quantity of cyclohexane employed to be determined within 0.03%. Pressures were measured with a balance involving a piston-cylinder combination which was calibrated against the vapor pressure of carbon dioxide at the ice point (*2*). Pressures were known within 0.1% or 0.2 pound per square inch, whichever was the larger uncertainty. Temperature of the stainless steel vessel confining the sample was determined by a platinum resistance thermometer of the strain-free type (*9*). This thermometer was compared with a reference instrument calibrated at the National Bureau of Standards. Temperature of the sample was related to the international platinum scale with a probable error of 0.02° F.

MATERIALS

The research grade cyclohexane was purchased from the Phillips Petroleum Co. and was reported to contain 0.0005 mole fraction impurity. It was deaerated by prolonged refluxing at reduced pressure and stored in stainless steel containers until used. The specific weight of the sample of deaerated cyclohexane at 77° F. was 48.302 pounds per cubic foot as compared to 48.311 pounds per cubic foot for air-saturated material at the same temperature reported by Rossini (*12*). The index of refraction at 77° F. relative to the *D* lines of sodium for the deaerated sample was 1.4238 as compared to 1.42354 reported for the same conditions for an air-saturated sample (*12*). The freezing point in air at atmospheric pressure was 43.45° F. as compared to a critically chosen value of 43.80° F. (*12*). A change in molal volume from 1.902 to 3.890 cubic foot per pound mole resulted in 0.20 pound per square inch decrease in the two-phase pressure at 100° F. At 280° F., an increase in molal volume from 2.189 to 5.309 cubic foot per pound mole

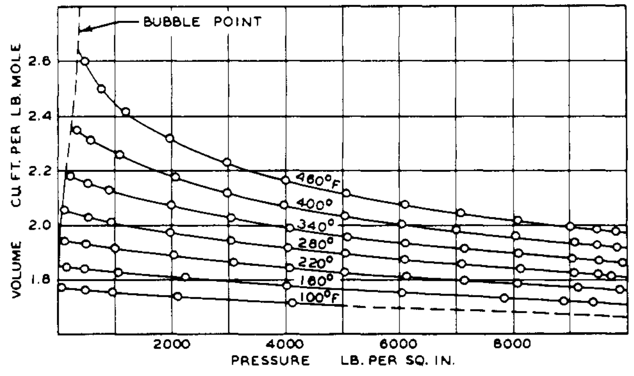

Figure 1. Molal volume of cyclohexane in liquid phase

Table II. Molal Volumes of Cyclohexane in Liquid Phase

Pressure, Lb./Sq. Inch, Absolute

	100° F.	160° F.	220° F.	280° F.	340° F.	400° F.	460° F.
	(3.2)[a]	(10.9)[a]	(28.4)[a]	(62.0)[a]	(120)[a]	(210)[a]	(341)[a]
B.P.	1.775	1.851	1.945	2.055	2.190	2.360	2.648
200	1.768[b]	1.845	1.940	2.048	2.182	...	...
400	1.764	1.840	1.934	2.038	2.165	2.335	2.627
600	1.761	1.837	1.928	2.028	2.150	2.307	2.553
800	1.758	1.833	1.923	2.019	2.136	2.284	2.493
1,000	1.755	1.830	1.917	2.010	2.124	2.265	2.450
1,250	1.751	1.827	1.911	2.001	2.110	2.242	2.410
1,500	1.747	1.825	1.906	1.993	2.096	2.220	2.373
1,750	1.744	1.820	1.900	1.984	2.084	2.200	2.344
2,000	1.740	1.815	1.895	1.976	2.074	2.181	2.318
2,250	1.737	1.810	1.887	1.969	2.061	2.163	2.295
2,500	1.734	1.806	1.881	1.960	2.050	2.145	2.270
2,750	1.730	1.803	1.875	1.953	2.040	2.132	2.250
3,000	1.727	1.798	1.870	1.946	2.030	2.119	2.230
3,500	1.720	1.790	1.859	1.933	2.012	2.095	2.196
4,000	1.715	1.780	1.848	1.920	1.995	2.074	2.167
4,500	1.710	1.774	1.840	1.908	1.979	2.055	2.141
5,000	1.705	1.767	1.832	1.896	1.964	2.037	2.119
6,000	1.70	1.755	1.815	1.876	1.937	2.005	2.080
7,000	1.69	1.744	1.800	1.857	1.915	1.978	2.046
8,000	1.68	1.733	1.788	1.841	1.898	1.957	2.019
9,000	1.67	1.721	1.774	1.827	1.881	1.937	1.995
10,000	1.66	1.710	1.760	1.811	1.863	1.917	1.975

[a] Values in parentheses represent vapor pressure, in pounds per square inch.

[b] Volume expressed in cubic feet per pound mole. Mol. wt. taken as 84.156.

Table III. Experimental Values of Vapor Pressure

Temp., °F.	Pressure, Lb./Sq.Inch Abs.	Volume, Cu.Ft./Lb.	Temp., °F.	Pressure, Lb../Sq.Inch Abs.	Volume, Cu.Ft./Lb.
100	3.41[a]	0.021092	340	120.5[a]	0.026035
	3.58	0.046219		121.14	0.050625
	3.64	0.032783		122.60	0.033377
	3.68	0.033016			
	3.78	0.022605			
160	10.86[a]	0.021995	400	209.6[a]	0.028043
	11.19	0.057210		210.78	0.064024
	11.49	0.024757		212.61	0.040837
				216.48	0.028821
220	28.22[a]	0.023100	460	341.6[a]	0.031501
	28.49	0.040814		343.78	0.053921
	28.87	0.026515		345.82	0.041491
				349.34[b]	0.033339
280	62.14[a]	0.024431			
	62.76	0.063088			
	63.25	0.040211			
	64.97	0.026016			

[a] Chosen value of vapor pressure taken at 0.90 for each temperature.
[b] Pressure determined after remaining at 460° F. for 6 hours.

resulted in a decrease in two-phase pressure of 0.23 pound per square inch. Prolonged refluxing of the sample at reduced pressure did not decrease this variation. Mass spectrographic analysis and change in vapor pressure with increase in molal volume indicate that the sample in the present measurements probably contained less than 0.002 mole fraction of material other than cyclohexane. The freezing point data indicated less than 0.001 mole fraction impurities. The impurities are probably hydrocarbons of closely related structure. The variation in two-phase pressure with volume was greater than expected from the purity established by spectrographic analysis. The markedly lower freezing point at atmospheric pressure also indicates that the purity is not as high as that reported by spectrographic analysis.

EXPERIMENTAL RESULTS

Experimental volumetric measurements of cyclohexane are recorded in Table I for the condensed liquid regions. The experimental results (Figure 1), show the distribution of the data obtained. The standard deviation of the experimental points from the smooth curves was 0.0014 cubic foot per pound mole. Smoothed values of the molal volume of cyclohexane in the liquid phase are in Table II. Experimentally measured vapor pressures in Table III are a function of the specific volume. The unusually large change in vapor pressure with volume experienced in this study decreases confidence in these vapor pressure measurements. The pressure of approximately 0.90 was used to represent the present vapor pressure measurements (Table III).

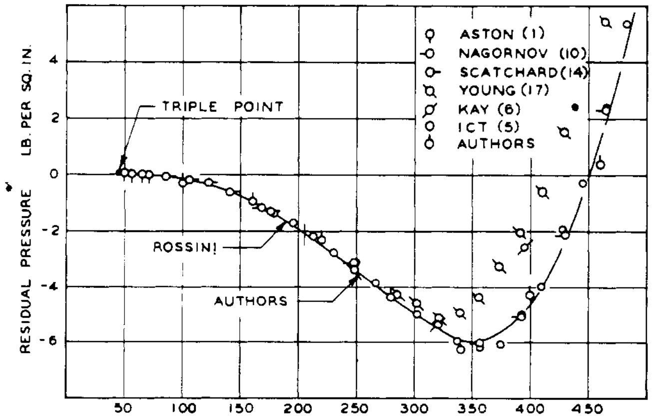

Figure 2. Residual vapor pressures of cyclohexane

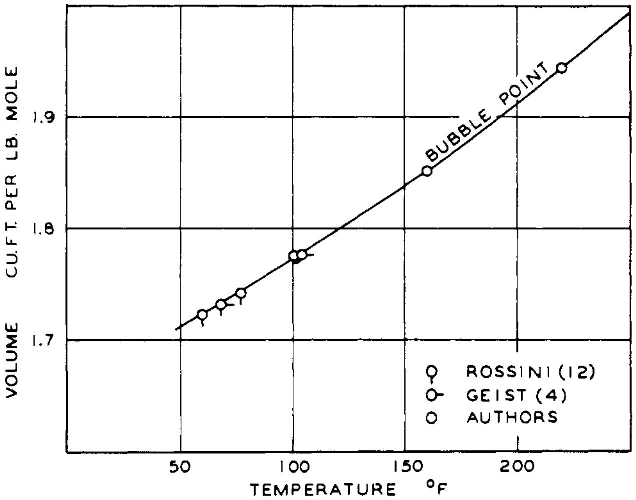

Figure 3. Deviation of present volumetric measurements of bubble point from other investigators

Pressures in the heterogeneous region were measured after the sample had been maintained at 460° F. for several hours and were markedly higher for the same molal volume than the data of Table III. These data indicate that increasing significant thermal rearrangement occurs at temperatures above 280° F. For this reason the vapor pressure data (Table II) for the higher temperatures are not as reliable as those for temperatures below 340° F. and may involve errors as large as 3 pounds per square inch. Figure 2 compares the residual basis of the present vapor pressure measurements with the critically chosen values of Rossini (*12*) and other experimental data (*1, 5, 6, 10, 14, 17*). The residual vapor pressure (Figure 2) was established from the following equations:

$$\log P_r = 5.70715 - \frac{2918.29}{T} \tag{1}$$

$$P = P_r - P'' \tag{2}$$

where P_r is the reference pressure, P the residual pressure, and P'' the vapor pressure, all expressed in pounds per square inch, and T is the absolute temperature in degrees Rankine. Reasonable agreement between the several sets of data was found throughout the temperature range investigated. The purity of the sample used by Young (*17*) seemingly was open to some question. Apparently for this reason the International Critical Tables (*5*) followed the measurements of Nagornov (*10*) at the higher temperatures. Except for the data of Young (*17*) and information reported by Kay (*6*) the present measurements follow the accepted vapor pressure data within the experimental uncertainty of the observations with the present sample. Because variations in vapor pressure with volume are near bubble point and dew point, the pressure measured at 0.9 was used to establish the vapor pressure data in Table III. Values in Table II were based upon the full curve of Figure 2, which corresponds closely to the entire temperature range reported by Rossini. The standard deviation of the values from the present experimental data from the full curve of Figure 2 was 0.13 pound per square inch.

Figure 3 shows the agreement of the present volumetric data at bubble point from the values reported by Rossini (*12*) and Geist (*4*). The indicated differences between the three sets of data are within the probable errors of measurement involved.

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Vapor-Liquid Equilibria of Naphthalene-*n*-Dodecane, *n*-Dodecane-Butyl Carbitol, and Naphthalene-Butyl Carbitol Systems at Subatmospheric Pressure

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This investigation is another in a series undertaken to determine vapor-liquid equilibrium characteristics of the heavy hydrocarbon systems under vacuum. Vapor-liquid equilibrium data were determined for the naphthalene–*n*-dodecane, *n*-dodecane–butyl carbitol, and naphthalene–*n*-butyl carbitol systems at a pressure of 100 mm. of mercury absolute, using a modified Colburn still.

MATERIALS

The naphthalene used was C.P. grade material, of the same quality as that used by Ward (*14*) and Martin (*9*). Experimental values of physical properties of the naphthalene are compared with literature values in Table I. The vapor pressure data for the naphthalene reported in Table I were determined as a function of temperature by boiling the material under fixed subatmospheric pressures in the Colburn still.

The *n*-dodecane was obtained in a relatively pure state and was further purified by fractionation at 100 mm. of mercury pressure in a 1-inch, vacuum-jacketed, glass column packed with 1/4-inch glass helices for 5 feet of its length. Only the constant boiling heart cut was used. Refractive index, vapor pressure, and density data for the purified dodecane agreed closely with literature values

Table I. Properties of Naphthalene, *n*-Dodecane, and Butyl Carbitol

	Naphthalene		*n*-Dodecane		Butyl Carbitol	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
Refractive index	$n_D^{99.6}$ 1.5826	1.5822 (*5*)	n_D^{25} 1.4203	1.4195 (*2*)	n_D^{27} 1.4290	1.4290 (*7*)
Density	...	...	d_4^{20} 0.750	0..751 (*7*)	d_{20}^{20} 0.952	0.9536 (*6*)
	Temperature, °C.					
At Vap. Press., Mm. Hg						
50	124.60	124.90 (*12*)	127.50	127.54 (*12*)	142.4	141.4 (*13*)
.80	137.90	137.81	139.75	139.90	154.2	153.3
100	144.35	144.31	146.20	146.14	160.7	159.8
150	156.25	156.81	157.50	158.10	173.2	172.3
200	166.40	166.27	167.40	167.14	181.9	181.2

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