Thermodynamics of Some Binary Liquid Mixtures Containing Aliphatic Amines

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Excess molar quantities of mixing (volumes, refractions, enthalpies, and Gibbs free energies) have been measured for most binary systems generated by benzene, chlorobenzene, *n*-heptane, *n*-butylamine, diethylamine, and triethylamine. Antoine equations for the vapor pressures of the pure components have also been determined. Improved values are reported for the physical constants of diethylamine and *n*-butylamine.

The purpose of this work is to accumulate complete thermodynamic data suitable for later use in an evaluation of the molecular origin and theories of so-called strong interactions in liquid mixtures. Despite the large amount of published material on the thermodynamics of liquid mixtures, there are few data suitable for the above purpose.

EXPERIMENTAL

Materials. The three amines—*n*-butylamine, diethylamine, and triethylamine (British Drug Houses)—were allowed to stand over sodium hydroxide pellets for several days. They were then twice distilled using a reflux ratio of 5 to 1 through a 3-m straight column (internal diameter 30 mm) packed with borosilicate glass pieces. The middle fractions were retained. There is a confusion in the literature on the physical constants of diethylamine and *n*-butylamine. In this work the criterion of purity was concurrent constancy of boiling point, density, and refractive index. The densities of diethylamine and *n*-butylamine recorded after the first distillation were higher than the literature values, but after a second and third distillation, the values become lower. These lower values are given in Table I.

Benzene (May and Baker) was recrystallized six times, dried over sodium hydroxide pellets for several days, and twice distilled using the above column. *n*-Heptane (standard samples were from the local Shell and Mobil refineries) was dried over sodium hydroxide and distilled, but no change in density or refractive index was detected. Chlorobenzene (May and Baker) was dried over phosphoric oxide for several days and twice distilled using the above column.

The physical properties of the liquids are shown in Table I.

METHODS AND RESULTS

Temperature. To establish the temperature scale, a platinum resistance thermometer (Tinsley) was calibrated by the CSIR Standards Laboratory, Pretoria, in conjunction with a Muller bridge (Rubicon, Philadelphia) according to the 1948 temperature scale. Throughout the temperature range used in this work, the precision of calibration was better than 0.01° C. All temperatures quoted are according to the 1948 scale. The various thermometric devices used in the parts of this work were referred to this thermometer in thermostats controlling to better than 0.005° C, and a precision of 0.01° C was achieved.

Sample Analysis. The liquid samples were analyzed by one of the following methods: density, refractive index, and, for amines, nonaqueous titration against perchloric acid. The density and refractive index methods involved reference to large-scale graphs. The composition of samples could always be estimated to within 0.005 mole fraction by using one or another of these methods.

Density. Densities of pure liquids and mixtures were obtained using Sprengel-Ostwald pycnometers (capacity ca. 20 cm^3) fitted with capillary arms of internal diameter 0.5 mm. The temperature was controlled at 25.00° ± 0.01° C. The weights of the pycnometers and flasks were corrected for buoyancy and residual vapors. The pycnometers were calibrated using distilled water. The accuracy and precision of the measurements are within ±0.0001 and are referred to water at 4° C.

Table I. Physical Properties

	Normal bp, ° C			Relative density, d_4^{25}			Refractive index, n_D^{25}		
	Our value	Lit. value	Ref.	Our value	Lit. value	Ref.	Our value	Lit. value	Ref.
n-Heptane	98.42	98.43	(*16*)	0.67952	0.67951	(*16*)	1.3851	1.3851	(*16*)
Benzene	80.11	80.10	(*15*)	0.87365	0.87370	(*15*)	1.4979	1.49792	(*15*)
Chlorobenzene	131.72	131.72	(3)	1.1011	1.10118 1.101121	(*11*)	1.52185	1.5219	(3)
n-Butylamine	76.97	77.4	(*19*)	0.73310	0.7346	(*19*)	1.3987	1.3987	(*19*)
Diethylamine	55.33	55.45	(*17*)	0.6990	0.7016	(*17*)	1.3820	1.3825	(*17*)
Triethylamine	89.20	89.5	(*18*)	0.72305	0.7230	(*20*) (*18*)	1.3980	1.3980	(*18*)

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The density measurements on the mixtures were fitted to polynomials of the form:

$$d_4^{25} = A + Bx + Cx^2 + Dx^3 \quad (1)$$

by a method of least squares (IBM library program 1620.07.0.002) using an IBM 1620 computer. At least 18 points were used in each curve fit. The results and the standard deviations, σ, are presented in Table II. This presentation carries all the experimental results in a compact way and shows the precision obtained.

Excess Molar Volume. Volume changes of mixing were calculated from the individual density data (not from the

Table II. Relative Densities of Liquid Mixtures

$$d_4^{25} = A + Bx + Cx^2 + Dx^3$$

x is the mole fraction of the first-named component, and σ the standard deviation

	A	$100\,B$	10^3C	10^3D	$10^4\sigma$
Benzene + *n*-heptane	0.67936	11.663	13.60	63.69	2.6
Chlorobenzene + *n*-heptane	0.67945	29.776	78.66	45.17	0.9
n-Butylamine + *n*-heptane	0.67944	2.102	24.53	8.06	0.7
Diethylamine + *n*-heptane	0.67961	0.320	6.4	9.8	0.6
Triethylamine + *n*-heptane	0.67950	3.921	4.35		0.5
n-Butylamine + benzene	0.87349	−16.902	36.39	−7.64	1.2
Diethylamine + benzene	0.87376	−20.734	41.05	−8.47	1.1
Triethylamine + benzene	0.87357	−23.439	118.55	−34.8	0.7
n-Butylamine + chlorobenzene	1.10114	−35.260	−15.41		1.2
Diethylamine + chlorobenzene	1.1009	−38.153	−24.50	3.99	2.0
Triethylamine + chlorobenzene	1.10109	−47.938	122.13	−20.75	0.9
Chlorobenzene + benzene	0.87356	25.987	−36.76	4.42	0.6
Diethylamine + triethylamine	0.72310	−1.929	−4.72		0.6
Triethylamine + *n*-butylamine	0.73311	−1.145	1.38		0.4
Diethylamine + *n*-butylamine	0.73319	−3.224	−1.99		0.2

Table III. Excess Molar Volumes of Mixing

$$V^E/\text{cm}^3 = x(1 - x)[A + B(1 - 2\,x) + C\,(1 - 2\,x)^2 + D\,(1 - 2\,x)^3]$$

x is the mole fraction of the first-named component, and σ the standard deviation

	No. of points	A	B	C	D	$10^3\sigma/\text{cm}^3$
Benzene + heptane (*4*)	15	2.3648	−0.3177	0.15316		7
Benzene + heptane	17	2.31396	−0.5905	0.1996	0.8204	14
Chlorobenzene + heptane	20	−0.91162	0.35067	−0.2616		14
n-Butylamine + heptane	25	2.7892	0.5258	0.3419	0.6557	16
Diethylamine + heptane	19	2.6325	−0.3153	−0.1692	0.4043	11
Triethylamine + heptane	21	0.4335	−0.0380	−0.0287	0.2389	7
Chlorobenzene + benzene	21	0.0331	−0.0178	0.0308		9
n-Butylamine + benzene	23	1.1217	0.2060	0.0831		9
Diethylamine + benzene	17	0.1244	0.3669	−0.2550		4
Triethylamine + benzene	21	0.0232	0.3573	−0.1874		5
n-Butylamine + chlorobenzene	18	−0.6481	0.1636	0.0033		7
Diethylamine + chlorobenzene	18	−3.1641	0.3627	0.3661	0.3532	19
Triethylamine + chlorobenzene	20	−3.6480	0.2858	0.2867		13
Diethylamine + *n*-butylamine	17	−0.5199	0.0031	−0.0033		3
Triethylamine + *n*-butylamine	23	−0.2214	0.0228	−0.1378		5
Diethylamine + triethylamine	17	0.3987	0.0560	−0.1028		5

Table IV. Refractive Indexes, n_D^{25}, and Maximum Excess Molar Refractions, $[R^E]_{\text{max}}$, of Mixtures

$$n_D^{25} = A + Bx + Cx^2 + Dx^3$$

x is the mole fraction of the first-named component, and σ the standard deviation

	A	$100\,B$	10^3C	10^3D	$10^4\sigma$	$[R^E]_{\text{max}}$, cm^3 mol^{-1}
Benzene + *n*-heptane	1.38485	6.457	6.71	41.57	2.8	0.01
Chlorobenzene + *n*-heptane	1.38519	9.565	28.71	12.28	0.9	0.09
n-Butylamine + *n*-heptane	1.38512	0.372	2.79	7.01	1.1	0.03
Diethylamine + *n*-heptane	1.38521	1.01	6.85		0.9	0.03
Triethylamine + *n*-heptane	1.38516	1.065	2.18		0.7	0.00
n-Butylamine + benzene	1.49793	−12.172	31.07	−8.63	1.4	0.03
Diethylamine + benzene	1.49805	−13.726	24.26	−3.01	1.2	0.05
Triethylamine + benzene	1.49781	−15.984	83.63	−23.67	0.8	−0.01
n-Butylamine + chlorobenzene	1.52196	−11.683	−6.30		2.0	0.08
Diethylamine + chlorobenzene	1.52176	−12.677	−14.78	1.86	0.9	0.08
Triethylamine + chlorobenzene	1.52183	−15.159	32.29	−4.52	0.7	0.04
Chlorobenzene + benzene	1.49800	2.836	−4.50		1.1	0.01
Diethylamine + triethylamine	1.3980	−1.284	−3.0		0.6	0.00
Triethylamine + *n*-butylamine	1.3987	−0.07			0.6	−0.02
Diethylamine + *n*-butylamine	1.3986	−1.55	−0.0011		1.0	0.00

density polynomials) and fitted to:

$$V^E = x(1 - x)\left[\sum_{r=0}^{m} A_r(1 - 2x)^r\right] \qquad (2)$$

where x is the mole fraction of the first-named compound in Table III. To determine A_r, the least-squares program minimized

$$\sum_i (\delta V_i^E)^2/(n - m) \quad (=\sigma^2)$$

where n is the number of data points. The parameters A_r were rounded off, and σ was recalculated. In the worst case the recalculated value differed from the original by 0.0001 cm^3 which is within the experimental precision. The rounded parameters are given in Table III.

Refractive Index. Refractive indexes were determined using a thermostated calibrated Bellingham and Stanley type 60 Abbe refractometer. Effects due to evaporation and contamination by moisture were avoided by reducing the time required to transfer samples to the refractometer and to take measurements. Conditions were established by studying the effect of using various time intervals and various conditions.

To avoid interpolation of density results in the calculation of molar refractions, aliquots were drawn from the same batch of mixture for both refractive index and density determinations. These refractive index measurements were reproducible to within ±0.0001.

The results in polynomial form are given in Table IV, and the explanatory comments under the heading Density apply.

Excess Molar Refraction. The same treatment was applied to molar refractions,

$$(n^2 - 1)/(n^2 + 2)V \quad (=[R]^E),$$

as to the molar volumes, V, to obtain the excess quantities. These quantities are, however, very small, though significant. The precision of measurement does not justify fitting to a polynomial in composition, but the maximum values (all occurring in the region near $x = 0.5$) are significant and are listed in column 7 of Table IV.

To permit discussion of the significance of these results, we have made a survey of published $[R^E]$ values and of results where both density and refractive index have been measured on the same mixture, and $[R]^E$ values have been calculated for these. This collection is given in Table V.

Calorimetry. Heats of mixing were determined at 25° and 45° ± 0.01°C in an insulated all-glass U-tube calorimeter similar to types in the literature (*14, 15*). This cell was mounted in a sealed evacuable brass cylinder immersed in a water bath set at the correct temperature.

The two liquids to be mixed (total charge ca. 17 cm^3) were separated by mercury (300 grams) in the U-tube which, on inversion, caused mixing to take place. Gentle rocking of the metal cylinder ensured good mixing.

The temperature change was determined from a graphical extrapolation of resistance values obtained from a calibrated thermistor (Standard Telephone and Cables type F23) conveniently mounted in the U-tube. This is the technique used by Brown and Fock (*5*). The temperature change was calibrated against potentiometrically measured energy by electrically heating the cell using nichrome wire (75 cm) wound outside its glass walls.

The metal cylinder was not evacuated since an asbestos paper insulation surrounding the cell was sufficient to allow temperature changes to be measured to within 0.01°C.

To check the technique and apparatus, reliable results from the literature were repeated. The systems were benzene + carbon tetrachloride (*6*), benzene + methanol (*10*), and benzene + n-heptane (*8*).

Excess Enthalpy. The individual enthalpy results are given in Table VI. The estimated accuracy of the measurements was ±20 J or ±5%, whichever is the greater.

The data in Table VI were fitted to equations like Equation 2. The standard deviation was of the same form as that already explained, and the same rounding off procedure was used and justified in the same way. The rounded parameters are given in Table VII.

Equilibrium Still Measurements. The excess free energy measurements were made using an Othmer-type vacuum-jacketed equilibrium still, designed to measure both liquid and vapor concentrations (*13*). The boiling temperature was kept constant to within 0.02°C measured by a precision

Table V. Excess Molar Refractions of Mixing

		$[R]^E_{max}$, cm^3 mol^{-1}	Ref.
Carbon tetrachloride	Ethyl acetate	0.015	(*1*)
Methyl cyclohexane	Heptane	0.00	(*21*)
Carbon tetrachloride	Cyclohexane	0.01	(*22*)
Carbon tetrachloride	Cyclohexane	0.02	(*1*)
Carbon tetrachloride	Dioxane	0.00	(*23*)
Carbon tetrachloride	Methyl acetate	0.00	(*24*)
n-Butyl alcohol	Isobutyl alcohol	0.00	(*25*)
n-Butyl alcohol	Isopropyl alcohol	0.00	(*26*)
n-Butyl alcohol	Isoamyl alcohol	0.02	(*27*)
Methanol	Dioxane	−0.01	(*28*)
Ethanol	Dioxane	0.00	(*29*)
n-Butyl alcohol	Dioxane	0.00	(*30*)
s-Butyl alcohol	Dioxane	0.02	(*30*)
Isobutyl alcohol	Dioxane	0.00	(*30*)
t-Butyl alcohol	Dioxane	0.02	(*30*)
Ethanol	Methyl cyclohexane	0.01	(*31*)
Isopropyl alcohol	n-Hexane	0.01	(*2*)
Benzene	Cyclohexane	0.02	(*32*)
Benzene	Dioxane	0.02	(*33*)
Benzene	Cyclopentane	0.01	(*1*)
Benzene	n-Hexane	0.04	(*2*)
Benzene	n-Heptane	0.01	(*3*)
Toluene	Methyl cyclohexane	−0.02	(*34*)
Bromobenzene	2,2,4-trimethyl pentane	0.10	(*35*)
Chlorobenzene	n-Hexane	0.07	(*2*)
Benzene	Butyl bromide	−0.02	(*36*)
Benzene	Methanol	0.04	(*47*)
Benzene	Isopropyl alcohol	0.04	(*37*)
Benzene	Carbon tetrachloride	0.06	(*12, 47*)
Chlorobenzene	Carbon tetrachloride	0.09	(*47*)
Benzene	Chlorobenzene	0.00	(*9*)
Benzene	Chlorobenzene	0.01	(*12*)
Benzene	Anisole	0.00	(*9*)
Benzene	Bromobenzene	0.02	(*9*)
Benzene	Benzonitrile	0.03	(*9*)
Benzene	Phenol	0.00	(*9*)
Benzene	Aniline	0.01	(*9*)
Benzene	Aniline	−0.01	(*38*)
Dimethyl aniline	Benzene	−0.03	(*9, 39*)
o-Chlorophenol	Aniline	−0.06	(*40*)
Acetic acid	o-Toluidine	−0.12	(*41*)
Acetic acid	Aniline	−0.09	(*42*)
Acetic acid	Dioxane	−0.08	(*43*)
Ethanol	Carbon tetrachloride	0.01	(*44*)
Ethanol	Carbon tetrachloride	−0.01	(*1*)
Chloroform	Carbon tetrachloride	−0.05	(*1*)
Dichloromethane	Carbon tetrachloride	0.14	(*1*)
Chloroform	Pentachloroethane	0.13	(*1*)
Carbon tetrachloride	Pentachloroethane	0.04	(*1*)
Dichloromethane	Chloroform	0.20	(*1*)
Acetone	Chloroform	0.10	(*45*)
Dioxane	Water	−0.05	(*1, 46*)
Dimethyl formamide	Water	0.04	(*1*)
Dimethyl sulfoxide	Water	1.3	(*1*)
Diethylamine	Water	−0.07	(*1*)

Table VI. Excess Enthalpies of Mixing ($J\ Mol^{-1}$)

Mole fractions x refer to the first-named component

x	H^E_{298}	x	H^E_{318}	x	H^E_{298}	x	H^E_{318}	x	H^E_{298}	x	H^E_{318}
Benzene + *n*-Heptane				Chlorobenzene + *n*-Heptane				*n*-Butylamine + *n*-Heptane			
0.307	702	0.508	857	0.166	228	0.315	491	0.335	1254	0.325	1200
0.355	773	0.553	848	0.315	489	0.502	606	0.374	1296	0.442	1281
0.602	946	0.572	872	0.338	488	0.549	607	0.402	1305	0.484	1275
0.610	955	0.667	797	0.547	635	0.585	603	0.552	1311	0.516	1241
0.616	911	0.689	809	0.548	665	0.662	556	0.621	1151	0.549	1225
0.648	889	0.695	752	0.579	665	0.672	555	0.628	1156	0.688	1003
0.691	863	0.795	620	0.614	628	0.752	451	0.732	907		
0.885	467			0.865	313			0.741	868		
Diethylamine + *n*-Heptane				Triethylamine + *n*-Heptane				*n*-Butylamine + Benzene			
0.162	280	0.324	555	0.165	19	0.303	78	0.185	376	0.301	648
0.266	549	0.411	628	0.492	82	0.462	96	0.239	460	0.427	720
0.421	699	0.562	670	0.532	110	0.535	94	0.278	516	0.492	689
0.466	728	0.572	652	0.573	86	0.555	91	0.395	607	0.512	709
0.576	722	0.606	630	0.653	64	0.656	82	0.422	686	0.515	698
0.621	701	0.612	625	0.786	46	0.710	74	0.544	674	0.563	696
0.762	483	0.643	573	0.914	18			0.648	562	0.651	600
0.859	290	0.686	548					0.799	409		
Diethylamine + Benzene				Triethylamine + Benzene				*n*-Butylamine + Chlorobenzene			
0.207	236	0.233	240	0.123	151	0.209	225	0.269	269	0.370	393
0.366	335	0.301	277	0.213	237	0.251	263	0.298	285	0.418	374
0.469	333	0.396	315	0.317	309	0.321	324	0.332	315	0.472	394
0.622	294	0.462	320	0.395	326	0.399	350	0.485	331	0.504	403
0.764	232	0.492	319	0.479	318	0.523	363	0.505	341	0.521	392
0.799	180	0.556	305	0.502	331	0.705	306	0.588	276	0.748	250
		0.731	224	0.731	250	0.837	189	0.629	260		
				0.777	225			0.667	257		
Diethylamine + Chlorobenzene				Triethylamine + Chlorobenzene							
0.167	−73	0.210	−64	0.123	−51	0.285	−64				
0.251	−90	0.305	−92	0.370	−103	0.348	−60				
0.401	−121	0.471	−115	0.511	−93	0.358	−81				
0.586	−124	0.486	−110	0.512	−100	0.362	−71				
0.592	−120	0.508	−108	0.533	−106	0.517	−80				
0.618	−113	0.531	−117	0.846	−62	0.621	−58				
0.856	−64	0.771	−72								

Table VII. Excess Molar Enthalpies of Mixing

$$H^E/J\ \mathrm{mol}^{-1} = x(1 - x)\ [A + B(1 - 2\ x) + C(1 - 2\ x)^2 + D(1 - 2\ x)^3]$$

x is the mole fraction of the first-named component, and σ is the standard deviation

	Temp, °C	A	B	C	D	σ/cm^3
Benzene +	25	3676	−1012			14
heptane	45	3414	−576			14
Chlorobenzene +	25	2592	−757	−932		10
heptane	45	2441	−282	−507		6
n-Butylamine +	25	5284	1174	−711		13
heptane	45	5047	1120	305		7
Diethylamine +	25	2969	−215	−1442		13
heptane	45	2684	−25	−1327		12
Triethylamine +	25	335	−68	−316		6
heptane	45	379	17	−88		2
n-Butylamine +	25	2671	58	−536		10
benzene	45	2829	580	118		15
Diethylamine +	25	1329	268			9
benzene	45	1258	200			5
Triethylamine +	25	1318	126	91		8
benzene	45	1479	−27	−226		7
n-Butylamine +	25	1283	806	12	−3271	7
chlorobenzene	45	1580	−508	1493	7157	10
Diethylamine +	25	−498	1			4
chlorobenzene	45	−453	1	159		4
Triethylamine +	25	−406	−11	−145		7
chlorobenzene	45	−303	−108	340		7

platinum resistance thermometer. The pressure was maintained constant by an electronically regulated dry air leak into a continuously pumped line connected to a 20-liter ballast bottle. This pressure could be maintained to within 0.1 torr for an indefinite period. The vapor from the still was trapped from the rest of the line by condensers through which iced water was circulated. The charge in the still was ca. 160 cm^3. The recycling rate was estimated to be between 2 and 4 cm^3 per minute depending on the volatility of the mixture. In all cases measurements were taken only after the boiling temperature had remained constant for at least 2 hr.

The only difficulty we had with this still was poor mixing between the liquid in the receiver and that in the still when one was very much more volatile than the other. This was particularly noticeable with certain chlorobenzene mixtures and restricted the range of composition used. The apparatus was checked by repeating the results of Brown and Ewald (*4*) for the benzene + *n*-heptane system at 60° and 80° C. The excess free energy curve obtained for this system was always within 10 J mole^{-1} of the quoted values.

As the Othmer still is known to produce results of poor quality for certain mixtures, all our results were tested using the Redlich-Kister thermodynamic consistency test. The experimental values of $RT \ln \gamma_1$ and $RT \ln \gamma_2$ were plotted separately against x_1, and the difference between the areas under the two curves was measured. This amounted to 6% in the worst case. Experimental errors in $RT \ln \gamma_1$, and $RT \ln \gamma_2$ could cause a difference of 12% between these areas.

Table VIII. Constants for Antoine Equations

$\log_{10}[P/\text{torr}] = A - [B/(C + t/°\text{C})]$

Measurements are spaced equally through the temperature range indicated

	A	B	C	σ, torr	Number of points	Range of temperature, °C
Chlorobenzene	7.0338	1464.638	221.03	0.1	15	62 to 114
Benzene	6.9784	1254.734	226.120	0.3	21	52 to 80
n-Heptane	6.8662	1246.43	214.35	0.3	15	60 to 98
n-Butylamine	7.1386	1258.745	218.66	0.2	22	40 to 77
Triethylamine	7.1512	1398.54	238.30	0.2	17	51 to 84
Diethylamine	6.84312	1058.538	211.819	0.2	29	29 to 55

The temperature range over which good results can be obtained depends on the boiling points of the components of any one mixture. The most favorable temperature range for each system was chosen, and afterward the values were adjusted to a common temperature.

VAPOR PRESSURE OF COMPONENTS

Vapor pressures were determined in the equilibrium still at fourteen or more temperatures and the results were fitted by computer (IBM 1620) to the Antoine equation:

$$\log P = A - [B/(C + t)] \qquad (3)$$

A damped least-squares regression technique based on a method of Law and Bailey (7) was used. The values of the constants and the standard deviations, σ, of the pressures are given in Table VIII.

Excess Free Energy. The excess free energy was determined for each system at two temperatures using the following equation in which the usual meanings are given to the symbols:

$$\mu_i^E = RT \ln V_i = RT \ln Py_i/P_ix_i + (V_i - \beta_i)(P_i - P) \qquad (4)$$

where i = 1,2 (components)

$$G^E = x_1\mu_1^E + x_2\mu_2^E$$

The vapor pressure values required (P_1, P_2) were calculated from Equation 3. The second virial coefficients were calculated from critical constants obtained from the literature using the Berthelot equation. The densities of the liquids at the various temperatures were determined from experimental density values measured at 25° C, and coefficients of cubic expansion were obtained from the literature.

Table IX. Example of Excess Free Energy Results

Mole fractions x_1, y_1, refer to the liquid and vapor phases, respectively, of the first-named component. The detailed results for the remaining systems have been deposited with ASIS. See note at the end of this article

x_1	y_1	P, torr	G^E (60° C) J, mole^{-1}	x_1	y_1	P, torr	G^E (80° C) J, mole^{-1}
0.000	0.000	210.35	0.0	0.00	0.00	428.2	0.0
0.034	0.077	221.5	37.9	0.024	0.049	440.7	18.6
0.056	0.125	228.6	57.2	0.150	0.268	507.4	119.8
0.160	0.293	258.7	157.8	0.165	0.288	515.1	134.6
0.220	0.379	275.1	194.8	0.201	0.343	533.3	151.6
0.272	0.446	289.4	227.1	0.232	0.380	548.8	179.4
0.315	0.493	299.1	241.8	0.288	0.444	572.9	205.7
0.476	0.640	333.6	291.3	0.383	0.544	612.8	239.8
0.565	0.701	348.4	299.1	0.383	0.544	613.0	240.7
0.609	0.731	355.0	293.0	0.550	0.678	670.2	271.7
0.716	0.795	369.1	266.6	0.621	0.725	689.9	268.8
0.901	0.911	387.0	131.2	0.711	0.788	712.8	242.4
1.000	1.000	391.8	0.0	1.000	1.000	757.9	0.0

Table X. Excess Molar Gibbs Free Energies of Mixing

$G^E/J\ \text{mole}^{-1} = x(1 - x)[A + B(1 - 2x) + C(1 - 2x)^2 + D(1 - 2x)^3]$

x is the mole fraction of the first-named component, and σ is the standard deviation

	Temp, °C	A	B	C	D	σ
Benzene +	60	1181	−199	214		3
heptane	80	1073	−228	88		3
Chlorobenzene +	80	1571	−344	221		4
heptane	100	1481	−242	253	−274	4
n-Butylamine +	55	1938	−85	195	478	5
heptane	75	1694	44	143	217	5
Diethylamine +	35	993	−10	290		4
heptane	55	819	127	182	−149	3
Triethylamine +	60	63.5	−31.3	−7.1		0.5
heptane	80	50.4	−5.5	7.5		0.6
n-Butylamine +	50	596.3	98.5	141.4	−117.2	0.8
benzene	70	522	110	65		3
Diethylamine +	35	291	−12	117	−222	2.4
benzene	55	249	−49	162		2
Triethylamine +	60	489	147	−42	−99	1
benzene	80	438	205	−112	−182	1
n-Butylamine +	60	647	−106	270	199	3
chlorobenzene	80	607	−47	377	−124	3
Diethylamine +	60	420	−181	290		4
chlorobenzene	40	409	−245	248		4
Triethylamine +	70	658	−85	273	−242	4
chlorobenzene	90	706	−55	67	−258	4

Equation 4 may be written with a term in β_{12}. This term was not included as it was considered negligible compared to the experimental error.

The estimated precision of the results was ±10 *J*.

An example of the equilibrium still measurements of free energies of mixing is given in Table IX, and the full table covering all systems is deposited with the American Society for Information Science (*7a*). The equations for the excess molar free energies as a function of concentration were computed using the program that was used to calculate the heats of mixing equations. The parameters of the excess free energy equation for all systems are given in Table X.

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NOMENCLATURE

d_4^{25} = relative density at 25° C referred to water at 4° C
x_i = mole fraction of component i in liquid phase
V^E = excess molar volume of mixing
n = refractive index
$[R]^E$ = excess molar refraction of mixing
γ = mole fractional activity coefficient referred to pure component as standard state

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-