equal (*3*, *7*), the above explanation is satisfactory for *m*-methoxy phenol.

Only 50 cal./mole of 310 cal./mole difference in ΔF_1° values for phenol and *p*-methoxy phenol are accounted for by ΔH_1° values. We therefore conclude that the ΔH_{int} effect related to resonance stabilization of un-ionized *p*-methoxy phenol is obscured by effects of solute-solvent interactions on ΔH_{ext} and ΔS°. We may separate all these contributions to the free energy of ionization by following earlier work (*2*, *3*) and considering a reaction:

$$\text{HAx(aq.)} + \text{A}^-\text{(aq.)} = \text{Ax}^-\text{(aq.)} + \text{HA(aq.)} \qquad (1)$$

for which the equation:

$$\Delta H_{\text{int}} = \Delta H_1^\circ - 280\,\Delta S_1^\circ$$

has been obtained (*2*, *3*). Using data for phenol and *p*-methoxy phenol from Table IV in this equation gives $\Delta H_{\text{int}} = +300$ cal./mole for *p*-methoxy phenol in reaction (*1*), thus showing that resonance stabilization makes it energetically "harder" to remove a proton from *p*-methoxy phenol than from phenol.

The free energy change ΔF_1° for *p*-methoxy phenol in reaction (*1*) is 310 cal./mole, so $\Delta F_1^\circ \cong \Delta H_{\text{int}}$ because of the almost equal contributions of ΔH_{ext} and $T\Delta S_1^\circ$ to $\Delta F_1^{\circ 2}$. Similarly, ΔF_1° equals −440 and +20 cal./mole while ΔH_{int} equals −450 and +30 cal./mole for *m*-methoxy phenol and *o*-methoxy phenol, respectively, in reaction (*1*).

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Thermodynamics of Solutions XI. Heats of Mixing of Hydrocarbons

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A calorimeter, designed to combine convenience and quick operation with reasonable accuracy, allows the measurements of four heats of mixing in a single run. The comparison of some of the results with good literature values indicates that the probable error is less than 1%. Data for 27 binary hydrocarbon systems at 25° and 50° C. are better represented as a function of the volume fraction than as a function of the mole fraction.

AN EXTENSIVE, SYSTEMATIC BODY of heats of mixing data is an essential precursor to the formulation of any precise rules for predicting solution behavior. Hydrocarbon mixtures have been chosen as the first step in a program designed to contribute to this growing body of data.

In addition to accuracy, the critical design requirements for a mixing calorimeter are the amount of material used and the time required for the operation. Since it was necessary to cover a wide field, operation time was important. The calorimeter, therefore, allows the determination of the heat of mixing at four concentrations (0–50%) in a single run. A total volume of 45 ml. was considered tolerable since neither work with expensive materials nor unusually difficult purifications was anticipated. Except for accidental failure, two sets of measurements (two fillings, two days of work) are sufficient to describe the excess heat content of a mixture at a single temperature over the whole concentration range, except for possible anomalies at high dilutions. A few measurements with large amounts of materials are believed to be better than numerous determination with small amounts. With a volume of 45 ml., the vaporization correction, if properly computed, is not believed to depress the upper limit of the temperature range excessively. The uncertainty of this correction of 50° C. is less than the desired limits of error (about 1%).

CALORIMETER

The stirrer, *k*, (Figure 1) contains four compartments of 5 ml. each. They are formed by a shell of the shape of an inverted cup (cylinder and cone), and by four vertical dividers. A thin metal foil (usually tin, 0.02 mm.), secured at the bottom of the four compartments by a ring and crossbars pressing on the dividers, closes the compartments. One turn of a screw thread at the outside of the cylindrical part stiffens the shell and assists in stirring.

When the stirrer is depressed by means of the knurled knob, *b*, the foil isolating the appropriate compartment is ruptured against the sawblade, *n*, and the components are allowed to mix. Normally, the stirrer with its four compartments rotates at 200 r.p.m. and it is necessary to stop stirring in order to rupture the foil. This takes about five seconds. Fortuitously, the heat of rupture is for all

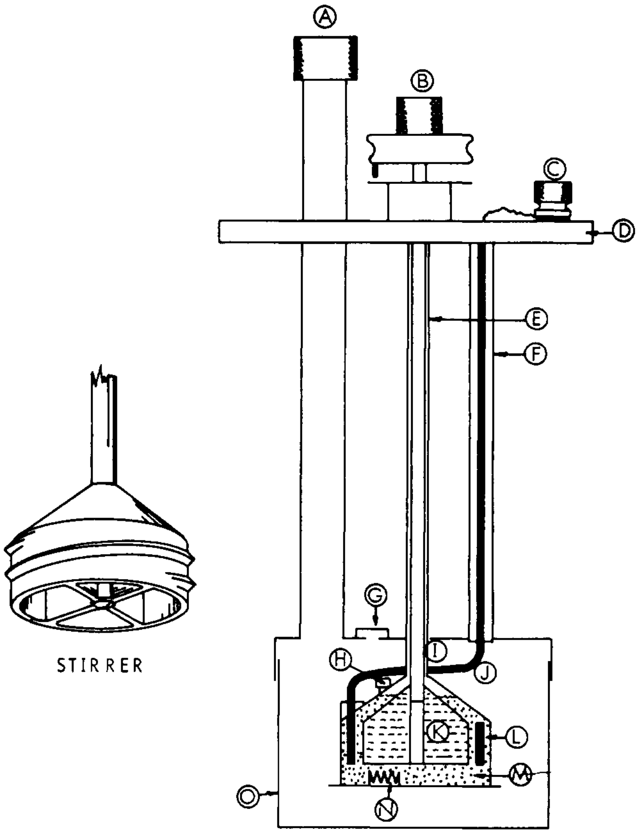

Figure 1. Schematic sketch of the calorimeter

practical purposes balanced by the five second loss in the stirring heat. The stirrer is easily removed from the calorimeter and, as it nets only 90 grams, the hydrocarbons can be weighed directly into the compartments. By filling these compartments to overflowing through small holes located hear the top of the stirrer, and then plugging the holes with teflon rods, the vapor space is eliminated except for possible degassing of the hydrocarbons.

The weights are recorded to 0.1 mg. and corrections for buoyancy made. Any small volume change due to the thermal expansion of the liquid is taken up by the deformation of the metal foil.

This stirrer, designed by W.H. Husing, solves a difficult problem of achieving thermal equilibrium rapidly. After the first compartment has been opened, about one-third of the total liquid content stays in the remaining three compartments and is not directly stirred. The compartments are, however, separated from the stirred outside liquid by a large area of thin copper sheet so that heat transfer is good even under these conditions. The mixing of the opened compartment with the outside liquid is enhanced by the radial arrangement of punches; a circulation is forced by the gradient of the centrifugal force.

The stirrer was machined from a copper rod. All exposed parts are plated with rhodium.

The mixing chamber, *m*, containing about 30 ml., is also rhodium plated copper. The conical top section is designed to reduce the vapor volume. The bottom of the chamber is flanged and the baseplate can be removed for disassembly and cleaning. The mixing chamber is filled through a port, *h*, provided near the top of the conical section. A matching port is in the jacket, *g*. The thermometer and heater, *l*, are mounted between the stirrer and the cylindrical section of the mixing chamber. The thermometer consists of 27 ohms of 2 mil platinum wire, silver soldered to three fine copper leads. It is insulated by fiber glass sleeving and protected by stainless steel hypodermic tubing. The tubing is coiled to fit snuggly against spacers in the mixing chamber. The ends of the tubing, containing the leads, pass out of the calorimeter through holes at the top of the cylindrical section, detour somewhat in the intervening space between the calorimeter and the jacket, *j*, to increase the length of the heat path, and leave the jacket through the three support tubes, *f*. An epoxy resin is used to make the vacuum seals. The heater (10 ohm, Manganin wire) has the same design except that the potential leads join the current leads at points halfway between the calorimeter and the jacket. To reduce thermal leakage, the stirrer shaft is thin-walled stainless steel tubing and the hollow calorimeter support, *i*, is made of nylon.

The jacket material is highly polished, nickel plated brass. The two sections are sealed with an 0 ring. Five tubes (three of which are shown) support the jacket.

The terminal lugs, *c*, for the leads are mounted on a glass-impregnated teflon plate. The stirrer drive assembly, *b*, also mounted on this plate, can be depressed against a spring about ¼ inch in order to rupture the foil isolating the stirrer compartments. A pin in the stirrer pulley with corresponding guides in the mount insures proper positioning of the stirrer during rupture. An 0 ring seal at the base of the stirrer drive can be used to prevent evaporation from the calorimeter and precisely define the vapor volume. The stirrer shaft is guided by a loose teflon bearing located directly above the jacket.

ACCESSORIES

The calorimeter is immersed in a water bath of typical construction. By means of a sensitive thermoregulator the bath can be held within 0.001° C. of the set temperature for several hours. A single stage oil diffusion pump is used to reduce the jacket pressure to 0.00005 mm. Hg. The stirring speed is accurately maintained by a variable speed drive using a feedback circuit.

The resistance of the calorimeter's platinum thermometer is measured with a Mueller bridge. The unbalanced voltage from this bridge is amplified and permanently recorded on a strip chart recorder. Noise in this circuit is equivalent to an input signal of 5×10^{-9} volt corresponding to a temperature change of 0.00003° C. At maximum gain, the sensitivity at the recorder is approximately 10 cm./millidegree.

Current for the heater circuit is supplied by three parallel six volt storage batteries. Voltages from the heater and standard resistor are reduced by the factor 0.001 so that they can be measured with a White double potentiometer. All critical resistors and the standard cell used with the potentiometer have been calibrated by the National Bureau of Standards. The heating time is present and measured with a tuning fork controlled millisecond timer.

EXPERIMENTAL TECHNIQUE AND COMPUTATION

In most of the experiments the calorimeter temperature was kept slightly below that of the bath to prevent the condensation of vapor along the stirrer shaft. After recording the temperature drift for about 10 minutes at a relatively high sensitivity (1 cm./millidegree), the foil isolating the first stirrer compartment was ruptured and the resulting temperature drop followed at a lower sensitivity. When the temperature had again stabilized, the Mueller bridge was balanced, the sensitivity increased, and the drift recorded for 10 to 15 minutes. The calorimeter was then heated to its original temperature while recording the voltage drops across the heater and the standard resistor. After heating, the temperature drift was again recorded for 10 to 15 minutes. This total process was repeated for the remaining compartments.

Since the thermometer had been calibrated against a

N.B.S. certified platinum resistance thermometer, the heating step after mixing was simply a heat capacity measurement for the filled calorimeter; it was treated as such. From the knowledge of the total heat capacity of the calorimeter and the temperature change due to mixing, the enthalpy change was calculated. Corrections for the vapor space were then applied. The temperature change was found by a linear extrapolation of the "fore" and "after" thermal drifts to the midpoint of the heating or mixing period.

As the bookeeping for the calculation with its accumulative character was tedious and time consuming, a Bendix G-15D computer was programmed to handle the computation. Only raw data, such as weights, densities, Antoine coefficients, activity coefficients, resistance, and voltage readings, etc. were fed to the computer. This same computer was used to find the coefficients for the analytical expressions of the heats of mixing.

PERFORMANCE

There is as yet no definitive test for the reliability of a heat of mixing calorimeter. The use of standard systems for this purpose is still in its development; however, Larkin and McGlashan (*2*) have tentatively suggested benzene-carbon tetrachloride as a suitable standard. Their very precise measurements are in serious disagreement with earlier measurements. Nevertheless, their data appear to be reliable and are probably the best available for this purpose; hence, benzene-carbon tetrachloride was chosen as a test for the reliability of our instrument. Larkin and McGlashan find the following equation fits their 26 data points with a standard error of 0.2%.

$$H_{25}^{M} = x_1x_2[462.6 + 16(x_1 - x_2) + 25(x_1 - x_2)^2 + 10(x_1 - x_2)^3] \text{ joules/mole}$$

They estimate the probable error of their measurements at 0.3%. A least squares fit to our data yields:

$$H_{25}^{M} = x_1x_2[455.9 + 11.5(x_1 - x_2) + 34.9(x_1 - x_2)^2 - 11.3(x_1 - x_2)^3] \text{ joules/mole}$$

with a standard error of 0.1%. At the equimolar concentration, the disagreement is 1.4% as compared to the 4% average disagreement with the earlier measurements. While satisfactory, the disagreement exceeds somewhat the estimated accuracy of both instruments. Since no great effort was made to purify our reagents, impurities could possibly account for part of this difference; traces of water dissolved in carbon tetrachloride may have such an effect since on mixing, hydrogen bonds would be formed with benzene.

In the course of our work, another frequently measured system, cyclohexane-benzene, was measured. Mrazek and Van Ness (*3*) have compared several sets of data by different authors. Their smoothed results appear to be in excellent agreement with these data. Our results are somewhat lower than theirs, the differences ranging smoothly with increasing benzene concentration from 0 to 1.6%.

In both cases the vapor pressures of the components are about equal and errors due to the presence of the vapor space are insignificant. A rough calculation of the maximum error attributable to the vapor space is easily made. The total volume of the calorimeter is 51.0 ± 0.3 cc. A normal filling leaves about a five cc. vapor volume. Assuming the molal heat of vaporization to be 40,000 joules, we have a maximum heat absorption or evolution of about nine joules. If the vapor volume is known within 10%, the error is about one joule. In actual practice, however, the error is considerably less than this since the vapor pressures of the hydrocarbons measured do not exceed 0.2 atmosphere at 25° C. (0.4 atm. at 50° C.) and the concentration does not ordinarily change by more than 50 mole per cent on mixing. The 25° error is thus about a tenth of a joule. Since the calorimeter holds approximately a third of a mole, the error due to changes in the vapor composition is certainly less than 0.5 joules/mole at 25° C. and less than one joule/mole at 50° C.

If the calorimeter is completely isolated from the atmosphere, an error is generated due to the change in pressure associated with any excess volume of mixing (*4*). This will generally not exceed −0.2 joules/mole for the hydrocarbon mixtures. Usually the calorimeter was not isolated. But even when the calorimeter was closed because of the high vapor pressure of a component, the correction for the change of the total pressure was considered to be negligible.

Materials. Commercial hydrocarbons were further purified by treating with silica gel to remove water and aromatics. They were then distilled under a nitrogen blanket using a 40-plate Oldershaw column at a 10/1 reflux ratio. Reduced pressure was used for the higher boiling hydrocarbons. Octene-1 was not treated with silica gel, and the cetane, was not distilled but was further purified by fractional crystallization. Care was taken to prevent any absorption of water while handling and transferring the chemicals.

A mass spectroscopic analysis of the hydrocarbons found no impurities other than 1.5% $C_{11}H_{14}$ in the tetralin. The refractive index and the source for each hydrocarbon are given in Table I. Unless otherwise mentioned, the decalin contains 64% of the cis and 36% of the trans isomers.

EXPERIMENTAL RESULTS

It has become customary to represent heats of mixing data with the following expression:

$$B = H^M/x_1x_2 = B_o + B_1(x_1 - x_2) + B_2(x_1 - x_2)^2 + \ldots\ldots \quad (1)$$

Table I. Refractive Index and Source of Materials

Hydrocarbon	Source	Refractive Index n_D^{20} Measured	Refractive Index n_D^{20} Reference
n-Heptane	Phillips Petroleum Co.	1.38773	1.38764(*1*)
n-Octane	Phillips Petroleum Co.	1.39762	1.39743(*1*)
iso-Octane	Phillips Petroleum Co.	1.39150	1.39145(*1*)
Octene-1	Phillips Petroleum Co.	1.40849	1.40870(*1*)
n-Hexadecane	Humphrey-Wilkinson, Inc.	1.43438	1.43453(*1*)
Cyclohexane	Shell Chemical Co.	1.42572	1.42673(*1*)
Methylcyclohexane	Phillips Petroleum Co.	1.42290	1.42312(*1*)
Decalin[a]	Eastman Organic Chemicals	1.47690	
Benzene	J.T. Baker Chemical Co.	1.50087	1.50112(*1*)
Toluene	Mallinckrodt Chemical Works	1.49680	1.49693(*1*)
m-Xylene	J.T. Baker Chemical Co.	1.49700	1.49722(*1*)
Tetralin	Eastman Organic Chemicals	1.54176	1.54135(*1*)
Carbon Tetrachloride	Allied Chemical Co.	1.4603	1.4576 (7)

[a] 64% cis and 36% trans decalin.

Table II. Heats of Mixing of Hydrocarbons

25° C.		50° C.	
x_1	H^M j./mole	x_1	H^M j./mole
Benzene + *n*-Heptane			
0.2522	635	0.2814	631
0.4031	859	0.4391	821
0.5034	936	0.5409	869
0.5743	948	0.6107	861
0.6599	895		
0.7213	829		
0.7950	703		
0.8860	465		
Benzene + *n*-Hexadecane			
0.4015	1088	0.4388	968
0.4333	1128	0.6101	1112
0.5739	1296	0.7018	1096
0.6049	1302	0.7583	1038
0.6693	1300		
0.6972	1280		
0.7295	1248		
0.7544	1212		
0.7837	1129		
0.8285	1015		
0.8790	828		
0.9354	526		
Benzene + *i*-Octane			
0.2651	698	0.3040	719
0.2802	729	0.4654	907
0.4200	931	0.5677	940
0.4406	958	0.6366	918
0.5207	1000		
0.5419	1011		
0.5909	1003		
0.6110	1003		
0.6868	939		
0.7042	921		
0.7449	862		
0.7602	836		
0.8145	716		
0.8261	690		
0.8975	467		
0.9047	442		
Benzene + Octene-1			
0.2550	427.4	0.2952	437.6
0.4067	583.7	0.4552	567.7
0.5069	642.1	0.5572	599.4
0.5782	656.1	0.6266	593.0
0.6946	622.0		
0.7520	570.7		
0.8196	478.7		
0.9009	301.7		
Cyclohexane + *i*-Octane			
0.2297	117.4	0.2647	125.9
0.2413	121.4	0.4183	161.4
0.3737	162.7	0.5200	172.9
0.3879	164.2	0.5912	172.1
0.4724	179.0	0.6151	171.4
0.4871	179.4	0.6806	161.5
0.5441	182.5	0.7624	138.5
0.5588	181.6	0.8649	92.1
0.6512	169.8		
0.7135	155.0		
0.7888	128.0		
0.8823	80.6		
Cyclohexane + Octene-1			
0.2201	145.6	0.2574	140.9
0.3614	211.1	0.4093	193.9
0.4589	240.3	0.5106	213.7
0.5307	252.5	0.5818	218.0
0.6503	248.8		
0.7124	235.6		
0.7879	204.9		
0.8811	140.6		
Cyclohexane + *m*-Xylene			
0.1891	320.8	0.2114	323.9
0.3188	471.0	0.3488	459.6
0.4128	542.0	0.4466	517.8
0.4839	571.9	0.5182	536.3
0.5621	575.6		
0.6312	561.0		
0.7205	505.2		
0.8368	362.7		
Cyclohexane + Decalin			
0.2201	36.1	0.2538	35.0
0.3607	41.5	0.4047	40.5
0.4584	37.8	0.5061	38.2
0.5301	31.8	0.5774	34.1
0.6557	15.9	0.6008	25.1
0.7173	8.7	0.6668	19.9
0.7917	1.3	0.7512	12.6
0.8834	−4.0	0.8585	4.1
Cyclohexane + 90% trans-Decalin			
0.6507	9.3		
0.7130	3.4		
0.7882	−3.2		
0.8814	−7.1		
Cyclohexane + 99% *cis*-Decalin			
0.6440	20.7		
0.7070	1.35		
0.7836	6.2		
0.8784	−0.0		
n-Heptane + Tetralin			
0.1514	268.8	0.1802	282.0
0.2659	395.1	0.3051	397.8
0.3519	457.0	0.3981	443.2
0.4200	484.7	0.4686	458.2
0.5397	482.2	0.4924	453.9
0.6098	461.4	0.5634	444.4
0.7008	407.5	0.6610	402.8
0.8241	284.6	0.7962	291.6
i-Octane + *n*-Hexadecane			
0.2615	174.2	0.2934	115.6
0.4146	223.2	0.4533	142.6
0.5149	233.5	0.5553	143.2
0.5860	229.9	0.6248	139.6
0.6942	203.5		
0.7517	181.6		
0.8196	146.4		
0.9009	90.7		
Octene-1 + *n*-Hexadecane			
0.2656	120.0	0.3070	84.3
0.4201	155.5	0.4692	103.0
0.5212	163.8	0.5708	104.0
0.5921	160.8	0.6395	100.3
0.7015	136.7		
0.7581	121.7		
0.8244	98.1		
0.9036	60.1		
Toluene + *n*-Hexadeacane			
0.3494	603.4	0.3954	548.9
0.3732	609.8	0.5667	657.8
0.5229	750.3	0.6632	662.2
0.5428	750.7	0.7242	633.7
0.6237	771.4		
0.6395	767.5		
0.6893	752.2		
0.7031	744.3		
0.7663	679.6		
0.8138	610.9		
0.8674	500.2		
0.9291	316.1		
Benzene + Cyclohexane			
0.2014	505.6	0.2243	496.8
0.3354	704.3	0.3665	667.3
0.4310	780.4	0.4641	717.9
0.5026	800.5	0.5359	723.7
0.5936	780.0	0.5607	726.1
0.5963	775.6	0.5612	728.2
0.6603	732.6	0.6294	693.7
0.6629	725.8	0.6300	694.9
0.7448	629.7	0.7186	609.1
0.7481	619.8	0.7193	610.8
0.8539	422.5	0.8362	422.4
0.8561	414.2	0.8370	423.0
Benzene + Decalins			
0.2762	578.5	0.2896	526.6
0.4338	747.2	0.4504	671.4
0.5340	791.7	0.5530	700.0
0.6046	787.6	0.6229	686.5
0.6909	714.4		
0.7488	649.5		
0.8172	537.3		
0.8995	343.7		
Benzene + *cis*-Decalin			
0.6862	689.3		
0.7447	627.2		
0.8140	522.0		
0.8978	334.6		
Benzene + Tetralin			
0.2314	99.2	0.2651	84.3
0.3748	140.0	0.4188	113.4
0.4734	156.0	0.5205	122.1
0.5452	160.8	0.5914	122.5
0.6602	149.6		
0.7214	139.2		
0.7953	117.3		
0.8859	77.0		
Cyclohexane + *n*-Heptane			
0.2236	146.5	0.5878	207.6
0.3658	209.0	0.6553	203.1
0.4639	236.2	0.7412	184.1
0.5356	245.7	0.8513	133.8
0.6186	242.1		
0.6838	232.6		
0.7639	207.0		
0.8662	146.0		
Cyclohexane + *n*-Hexadecane			
0.3456	412.2	0.3931	309.6
0.5138	508.9	0.5637	365.5
0.6134	523.1	0.6603	363.1
0.6788	509.6	0.7217	344.4
0.7466	459.2		
0.7971	415.9		
0.8560	341.8		
0.9222	219.0		
Cyclohexane + Tetralin			
0.1971	279.0	0.2286	288.3
0.3294	406.2	0.3718	399.4
0.4240	464.3	0.4713	440.0
0.4953	488.4	0.5432	450.4
0.6155	485.8		
0.6814	459.6		
0.7622	396.6		
0.8653	270.5		
n-Heptane + *n*-Hexadecane			
0.2625	73.9	0.2722	33.4
0.4175	92.6	0.3219	37.7
0.5191	95.7	0.4205	40.7
0.5907	92.9	0.4870	42.3
		0.5168	41.1
		0.5881	39.8
		0.5882	39.3
		0.6554	35.8
n-Heptane + Octene-1			
0.1727	22.1	0.2019	25.0
0.2938	32.6	0.3357	34.8
0.3846	37.8	0.4321	38.6
0.4545	39.7	0.5038	39.6
0.5804	39.8		
0.6478	38.3		
0.7338	32.9		
0.8463	22.2		
n-Heptane + Toluene			
0.1238	276.6	0.1467	298.3
0.2206	418.7	0.2560	433.2
0.2980	494.9	0.3407	496.2
0.3610	534.0	0.4075	522.1
0.5493	538.6	0.4329	524.5
0.5941	518.7	0.5038	522.8

Table II. Heats of Mixing of Hydrocarbons (*Continued*)

25° C.		50° C.		25° C.		50° C.		25° C.		50° C.	
	H^M		H^M		H^M		H^M		H^M		H^M
x_1	j./mole	x_1	j./mole	x_1	j./mole	x_1	j./mole	x_1	j./mole	x_1	j./mole
n-Heptane + Toluene				*n*-Heptane + Decalin				Tetralin + *n*-Hexadecane			
0.6466	483.8	0.6045	486.5	0.7314	57.3			0.8378	464.5		
0.7844	345.7	0.7534	365.4	0.8450	36.7			0.9118	300.5		
n-Heptane + *m*-Xylene				Decalin + *n*-Hexadecane				*i*-Octane + *n*-Octane			
0.1599	232.7	0.1656	229.4	0.2691	149.5	0.3062	90.7	0.1533	13.2	0.1898	10.7
0.2745	335.8	0.2844	328.3	0.4227	199.7	0.4709	118.8	0.2649	19.8	0.3189	15.4
0.3634	383.1	0.3739	371.7	0.5236	215.5	0.5735	126.5	0.3486	23.3	0.4135	17.0
0.4322	401.2	0.4428	387.7	0.5946	217.8	0.6421	126.3	0.4171	24.6	0.4847	17.5
0.4862	401.4	0.4664	388.0	0.6895	205.4			0.5657	25.3		
0.5574	393.2	0.5377	383.6	0.7474	189.6			0.6331	23.8		
0.6550	356.1	0.6363	352.4	0.8162	160.6			0.7198	20.5		
0.7918	256.0	0.7782	259.8	0.8987	106.0			0.8341	14.1		
n-Heptane + Decalin				Tetralin + *n*-Hexadecane				Methylcyclohexane + *n*-Heptane			
0.1717	52.6	0.2010	41.7	0.3080	497.2	0.3384	475.5	0.1911	18.0	0.5478	19.1
0.2932	71.3	0.3342	54.0	0.4713	641.8	0.5059	491.2	0.3209	27.6	0.6179	18.9
0.3834	78.5	0.4304	56.8	0.5719	675.4	0.6068	606.8	0.4147	32.3	0.7086	17.2
0.4532	80.3	0.5021	56.4	0.6405	669.6	0.6728	589.6	0.4860	34.6	0.8293	12.3
0.5768	75.1			0.7208	619.0			0.5721	33.9		
0.6450	68.9			0.7750	562.4			0.6422	32.5		
								0.7287	29.2		
								0.8425	21.3		

Table III. Coefficients for Equations 1 and 2 at 25° C.; Temperature Dependence

Mixture					S.E.,[a]						
(1)	(2)	B_o	B_1	B_2	%	dB_o/dt	A_o	A_1	A_2	S.E.,[a] %	dA_o/dt
Benzene	*n*-Heptane	3709	848	359	0.62	−12.3	33.27	−0.42	1.11	0.44	−0.147
Benzene	*n*-Hexadecane	4835	1885	2754	2.4	−28.6	34.34	−1.96	2.11	0.43	−0.210
Benzene	iso-Octane	3968	969	483	0.63	−10.3	33.53	−1.36	1.68	0.13	−0.130
Benzene	Octene-1	2552	814	417	0.26	−8.4	22.67	1.08	0.75	0.30	−0.105
Benzene	Cyclohexane	3196	177	140	0.11	−11.1	32.47	−1.28	1.32	0.08	−0.150
Benzene	Decalin[b]	3107	605	291	0.77	−13.9	26.77	−1.93	1.16	0.83	−0.155
Benzene	Tetralin	628	141	31	1.1	−10.0	5.82	0.07	0	0.91	−0.060
Cyclohexane	*n*-Heptane	960	284	156	0.82	−5.5	7.850	1.209	0.653	0.52	−0.054
Cyclohexane	*n*-Hexadecane	1991	676	620	2.1	−24.5	12.01	−1.10	0.95	0.91	−0.147
Cyclohexane	iso-Octane	724.0	95.1	−34.8	0.30	−1.3	5.40	−0.51	−0.27	0.86	−0.013
Cyclohexane	Octene-1	985	333	164	0.77	−5.8	7.895	1.228	0.477	0.33	−0.057
Cyclohexane	*m*-Xylene	2296	418	161	0.38	−6.7	20.00	2.40	1.05	0.30	−0.078
Cyclohexane	Decalin[b]	136	−176	−72	1.69	+0.4	0.78	−1.46	0	10.0	+0.004
Cyclohexane	Tetralin	1955	393	134	0.29	−6.8	16.30	1.46	0.53	0.22	−0.072
n-Heptane	*n*-Hexadecane	383	4	0	. . .	−8.6	1.71	−0.77	0	. . .	−0.040
n-Heptane	Octene-1	162.3	12.7	0	0.61	−0.1	1.066	0.047	0	0.61	−0.002
n-Heptane	Toluene	2208	−351	123	0.20	−4.4	17.81	−0.05	0.47	0.10	−0.054
n-Heptane	*m*-Xylene	1610	−137	64	0.27	−2.3	11.98	0.01	0.38	0.28	−0.030
n-Heptane	Decalin[b]	316.5	−64.9	19.7	0.47	−3.8	2.071	−0.486	0.156	0.65	−0.026
n-Heptane	Tetralin	1960	−81	115	0.60	−5.4	13.81	−0.08	0.77	0.63	−0.041
iso-Octane	*n*-Hexadecane	930	72	38	0.43	−14.0	4.140	−0.821	0.288	0.25	−0.065
Octene-1	*n*-Hexadecane	645	50	0	1.4	−9.4	2.94	−0.69	0	1.50	−0.044
Toluene	*n*-Hexadecane	2925	1260	782	0.90	−14.4	18.32	−0.54	0.77	1.05	−0.109
Decalin[b]	*n*-Hexadecane	846	253	169	0.78	−14.7	4.156	0.050	0.280	0.21	−0.072
Tetralin	*n*-Hexadecane	2596	846	584	1.50	−11.1	13.87	−0.26	0.54	0.34	−0.067
iso-Octane	*n*-Octane	102.1	0	0	. . .	−1.2	0.620	0	0	0.50	−0.008
Methylcyclohexane	*n*-Heptane	136	33	0	. . .	−2.4	0.987	0.144	0	. . .	−0.017

[a] S.E. % = 100 S/B_o or 100 S/A_o, where S = the standard error of approximation. [b] 64% cis, 36% trans.

When this equation is fitted to our data (Table II) using three or even four coefficients, the calculated values of the heat contents at infinite dilution are questionable in many cases. However, the expression:

$$A = H^M/V\phi_1\phi_2 = A_o + A_1(\phi_1 - \phi_2) + A_2(\phi_1 - \phi_2)^2 + \ldots\ldots \qquad (2)$$

is quite satisfactory with two or three coefficients and the predicted limiting heats are perfectly reasonable. Table III lists the coefficients at 25° C. for Equations 1 and 2 as found by the method of least squares. Equation 1 is not, however, to be relied upon outside the range of the experimental data.

A comparison of the coefficients in Table III indicates that the equation of Scatchard and Hildebrand ($H^M/V\phi_1\phi_2$ = const.) is generally more suitable as a first approximation of the concentration dependence than the simple assumption that H^M/x_1x_2 is constant. A notable exception is the system *n*-heptane + *n*-hexadecane where H^M/x_1x_2 is very close to being constant. This appears to be characteristic of *n*-paraffin mixtures (*5, 6*).

Within the experimental accuracy, the curves for 50° are simply downward displacements of the curves for 25°. Assuming the temperature dependence to be linear, columns 7 and 12 of Table III give the differential coefficients for the constant terms.

CYCLOHEXANE-DECALIN

The most striking system measured was cyclohexane + decalin (Figure 2). The heats of mixing changed sign at high cyclohexane concentrations. Some measurements were made at 25° C. with decalin having cis-decalin concentrations of 10%, 64%, and 99%. The results were consistent; the heats of mixing changed signs at cyclohexane concentrations of 75, 81, and 88 mole per cent respectively. However, the calorimeter used is not well suited for these measurements. The very small heats of mixing (maximum 42 joules/mole) and the great differences in the vapor pressures of the components make the relative corrections for the vapor space undesirably large.

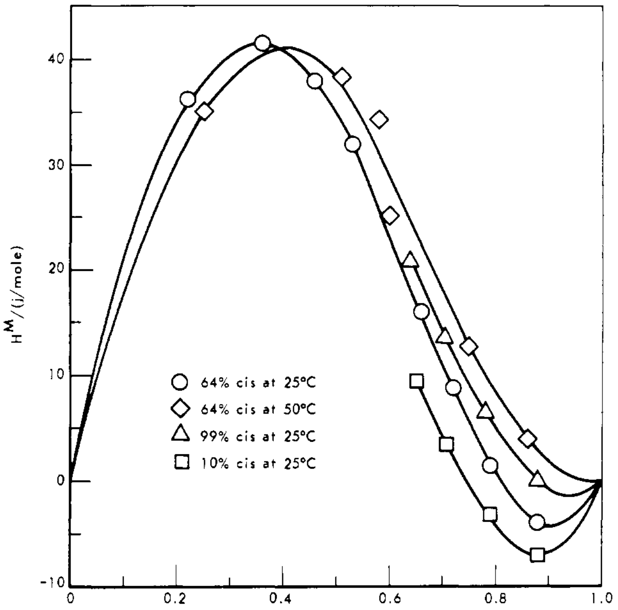

Figure 2. Heats of mixing of cyclohexane + decalin

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NOMENCLATURE

A = $H^M/V\phi_1\phi_2$
A_j = coefficients in Equation 2
B = H^M/x_1x_2
B_j = coefficients in Equation 1
H^M = excess heat content in j./mole
x_i = mole fraction of component i
V = Volume of one mole of the components of the mixture in ml.
V_i = molar volume of component i in ml.
ϕ_1 = volume fraction of component i

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Thermodynamic Properties of Pu^{239} as an Ideal Gas

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THERE IS INSUFFICIENT published information on the plutonium spectrum to permit an accurate calculation of the thermodynamic properties of this element as an ideal monatomic gas. The values presented in this paper can be considered only as estimates because they are based on only the 32 levels listed in Table II. The 9179.05 cm.$^{-1}$ and 10,238.24 cm.$^{-1}$ levels were supplied by Dr. Jean Blaise in a private communication; the others are from Tableau XXIII of Gerstenkorn (*1*), the only published values known to the author at the time these calculations were performed.

The highest energy level in Table II is 27,651.22 cm.$^{-1}$ There are certainly large numbers of higher levels to be expected and there already exists evidence of additional lower levels which have not been published because of some unresolved questions. These factors make it difficult to select an upper temperature at which to terminate the calculations. The paucity of spectroscopic data does

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