Thermodynamics of Hydrocarbon Mixtures. Part I. The Heats of mixing of the Binary and Ternary Systems formed by Benzene, cyclo*Hexane, and* n-*Heptane.*

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The heats of mixing of the systems benzene–*cyclo*hexane, benzene–*n*-heptane, *cyclo*hexane–*n*-heptane, and benzene–*cyclo*hexane–*n*-heptane have been determined at 20°. The results for the binary systems show deviations from the theory of strictly regular solutions. The determined heats of mixing are compared with those calculated from vapour-pressure data, and the interchange energies estimated at different temperatures. The solubility parameters calculated from the heats of mixing are not in agreement with those given by Hildebrand. The results for the ternary system are quite well represented by the equations of Scatchard, Goates, Ticknor, and Macartney (*J. Amer. Chem. Soc.*, 1952, **74**, 3724) and Redlich and Kister (*Ind. Eng. Chem.*, 1948, **40**, 341) which relate the heats of mixing in ternary and binary systems.

A KNOWLEDGE of the thermodynamic properties of multicomponent hydrocarbon mixtures is important in many large-scale industrial processes, but detailed experimental investigation of the very large number of complex systems involved is clearly impossible. The prediction of the properties of a multicomponent system from the behaviour of its constituent binary mixtures would be a very significant advance. Scatchard, Wood, and Mochel (*J. Amer. Chem. Soc.*, 1940, **62**, 712) suggested an equation to predict the free energies of ternary mixtures from their constituent binary mixtures, which was modified by Redlich and Kister (*Ind. Eng. Chem.*, 1948, **40**, 341) and later tested experimentally by Scatchard, Goates, Ticknor, and Macartney (*J. Amer. Chem. Soc.*, 1952, **74**, 3724) for the system methanol–carbon tetrachloride–benzene. Tsao and Smith ("Applied Thermodynamics," Chem. Eng. Prog. Symp. Series No. 7, 1953, **49**, 107) have recently measured the heats of mixing of the ternary system methanol–*n*-heptane–toluene and the appropriate binary systems and suggested a method for predicting ternary heats of mixing data from binary systems. None of these results refers to a mixture of non-polar hydrocarbons.

Further data are needed to test the recent theories of liquid mixtures, and non-polar hydrocarbon mixtures which show relatively small deviations from ideality are very suitable for this purpose. Consequently, measurements of the heats of mixing and the vapour pressures of selected binary and ternary hydrocarbon mixtures should be of practical and theoretical interest. This paper reports the heats of mixing of the binary and ternary systems formed by benzene–*cyclo*hexane–*n*-heptane. The volume changes on mixing and the vapour pressures are also being measured, and the work is being extended to include other systems.

EXPERIMENTAL

An apparatus designed to measure small heats of mixing accurately must incorporate efficient mixing and stirring and accurate temperature measurement; the vapours must not be allowed to mix, for, even if data are available to make corrections, this reduces the accuracy of the results (van der Waals and Hermans, *Rec. Trav. chim.*, 1950, **69**, 949). Many previous workers ignored this, for instance Hirobe (*J. Fac. Sci. Tokyo Univ.*, 1925, **1**, 155), Vold (*J. Amer. Chem. Soc.*, 1937, **59**, 1515), and Tsao and Smith (*loc. cit.*), but the mixing vessels used by Cheesman and Whitaker (*Proc. Roy. Soc.*, 1952, *A*, **212**, 406) and Scatchard, Goates, *et al.* (*loc. cit.*) both overcome this difficulty.

Calorimeter.—This consists of three concentric Dewar vessels, the innermost containing carbon tetrachloride (250 ml.) surrounding the mixing vessel itself, a platinum resistance thermometer, and an electric heating coil. The middle Dewar vessel holds alcohol which is kept within ±2° of the temperature of the inner Dewar vessel by means of a heating coil and a

12-junction copper–constantan thermocouple. The outer Dewar vessel contains lagging, and the whole calorimeter rests in a lagged metal cylinder, 90 × 36 cm. The inner Dewar vessel is closed by a rubber stopper and the other two by wooden lids with rubber gaskets. The electrical leads and the ebonite stirrer shaft pass through the lids in air-tight sleeves.

Mixing Vessel.—This is made of brass, in two parts (Fig. 1). The lower cylinder, 3 × 8 cm., has three spikes (*I*) projecting upward from the base, and three vertical vanes (*G*) inside and outside to facilitate stirring. It has an external liquid-tight thread (*F*) at the top. The upper part consists of the lid, which has a Polythene gasket (*K*) and bears the vertical plunger sheath and a threaded sealed metal capillary tube (*D*) which can be removed to fill the vessel. The plunger (*C*) moves vertically in its sheath, and is liquid-tight when lubricated with Silicone grease.

Mixing and Stirring.—One liquid fills a thin glass ampoule which rests in the mixing vessel on the points *I*. The second liquid surrounds the ampoule and completely fills the mixing vessel. The point of the plunger rests on the ampoule, and breaking is effected by slightly depressing the plunger with a screw outside. The plunger also functions as an internal stirrer, since the plunger sheath is connected at the top by two metal strips (*A*) and a universal joint (*B*) to the ebonite stirrer shaft. The mixing vessel itself rotates and stirs the liquids both inside and outside it.

FIG. 1. *The mixing vessel.*

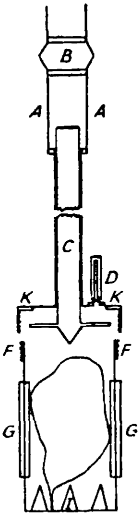
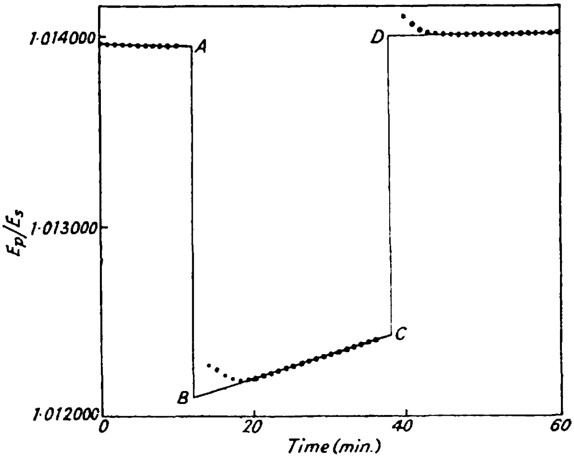


FIG. 2. *Typical mixing experiment for the system benzene–*n*-heptane. Mole fraction of benzene* = 0·878. ΔH_m = 511 J/*mole.*



Electrical Circuits.—The sheath of the platinum resistance thermometer is of German silver, and the thermometer was calibrated at four fixed points, the carbon dioxide sublimation point, 0°, the transition temperature of sodium sulphate decahydrate, and 100°. The potential difference across the thermometer (E_p) is compared with that across a standard resistance (E_s) (27·6230 ω at 25°) by means of a Precision Vernier Potentiometer (Messrs. Pye Ltd.). A current of 5 mA flows through the circuit.

The heating coil consists of 170 cm. of constantan wire wound non-inductively on a mica former, with two copper leads from each end spot-welded to the constantan, and held in a flattened German silver tube filled with dry nitrogen at a pressure of $\frac{2}{3}$ atm. Current, which generally was allowed to flow for 2 min., is supplied for thermal calibration by four accumulators and the voltage drop across the coil is compared with that across a standard resistance (6·874 ω) at 25° by means of a Tinsley potentiometer.

Procedure.—The apparatus is assembled and allowed at least 3 hr. to attain thermal equilibrium. The temperature is measured every minute for 10—15 min. before mixing, the ampoule is then broken, and readings taken for a further 25 min. Mixing is complete in a matter of seconds. Current is passed through the heating coil for 2 min., having previously passed through an equal resistance for 2 hr., and the temperature measured every minute for a further period of 25 min. The temperature drop on mixing was always less than 0·6°, and the rise on heating was always about 0·4°. Fig. 2 shows a typical mixing experiment, in which *AB* represents the temperature fall on mixing, and *CD* the rise on thermal calibration.

The concentration of the mixture is determined after the mixing experiment by measurement of its refractive index with an Abbé refractometer (Messrs. Hilger & Son, Ltd.), calibration curves of refractive index against mole fraction (x) having previously been determined. The ampoule and its contents are weighed before the experiment, and the broken glass is weighed afterwards. In conjunction with the refractive-index measurement, this enables the total mass of liquid to be determined.

Errors.—The reproducibility of the results for the heat of mixing, obtained from repeated experiments at the same concentration, was 0·7%. This is in agreement with the estimated total error due to the various factors involved, which is shown in Table 1. The rate of stirring had only a very small influence on the temperature, and it was maintained always at a constant rate which allowed the appropriate correction to be made by linear extrapolation.

TABLE 1. *Estimated errors.*

	Max. error (%)		Max. error (%)
Potential drop across platinum resistance thermometer	±0·004	Concentration measurement	±0·2
Potential drop across heating coil	±0·02	Non-mixing in the capillary	±0·002
Timing	±0·1	Stirring, always 80 r.p.m.	Negligible
Extrapolation of curves	±0·3	Evaporation	Negligible

Maximum total error ±0·626

Purity of Materials.—Benzene, of " AnalaR " grade, was shaken with concentrated sulphuric acid several times, washed with aqueous sodium carbonate and then with water, and dried ($CaCl_2$). It was fractionated through a 1½-m. column packed with glass helices. It was shown to be free from thiophen. *cyclo*Hexane, of B.P. quality, was treated with nitrating acid, then washed with aqueous sodium carbonate and water, dried ($CaCl_2$), and fractionated through the 1½-m. column. *n*-Heptane (Hopkin and Williams synthetic grade) was dried ($CaCl_2$) and fractionated through the 1½-m. column. Carbon tetrachloride was washed with alcoholic potassium hydroxide at 50—60° several times, shaken with water, and then shaken again with alcoholic potassium hydroxide three times. It was washed again with water, then with concentrated sulphuric acid, water, and alcoholic potassium hydroxide, and finally with water. It was dried (KOH), and fractionated in the 1½-m. column, the fraction which came over in the range 76·60—76·63° being collected.

TABLE 2. *Properties of the liquids.*

	B. p. (760 mm.)	F. p.	n_D^{25}	d^{25}
Benzene	80·10° (80·103°)	5·43° (5·506°)	1·4986 (1·49790)	0·87315 (0·87368)
*cyclo*Hexane	80·57 (80·738)	—	1·4237 (1·42354)	0·77382 (0·77389)
n-Heptane	98·40 (98·426)	—	1·3854 (1·38517)	0·67924 (0·67949)
Carbon tetrachloride	76·61 (76·71)	—	1·4587 (1·4573)	—

Values in parentheses are by Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 129, except for CCl_4 which are from Grimm, *Z. phys. Chem.*, 1929, **2**, *B*, 181.

The properties of the liquids are shown in Table 2.

RESULTS AND DISCUSSION

Benzene–Carbon Tetrachloride at 25°.—A few experiments were made on this system to compare the results given by our apparatus and technique with those of Cheesman and Whitaker (*loc. cit.*) and of Hirobe (*loc. cit.*). Table 3 shows that the new results are in excellent agreement with the earlier figures.

TABLE 3. *Heat of mixing* (ΔH_m) *of benzene–carbon tetrachloride at* 25° *in joules per mole.*

Mole fraction of benzene (x_1)	0·318	0·736	0·817
Present value	96	82	64
Cheesman and Whitaker	95	84	65
Hirobe	98	84	64

Benzene–cyclo*Hexane at* 20°.—The heats of mixing (ΔH_{12}) per mole of mixture, expressed in absolute joules, are shown in Table 4.

TABLE 4. *Heat of mixing of benzene*–cyclo*hexane at* 20°.

Mole fraction of benzene (x_1) ...	0·100	0·215	0·245	0·250	0·300	0·595	0·700	0·785	0·870
ΔH_{12} (J/mole)	188	413	485	520	634	841	712	556	378

They fall on a smooth curve which is very slightly asymmetrical, the maximum value of ΔH_{12} occurring at $x_1 = 0{\cdot}535$. The best equation to fit the results is

$$\Delta H_{12} = x_1x_2[3350 + 590(x_1 - x_2) - 912(x_1 - x_2)^2] \quad . \quad . \quad . \quad . \quad (1)$$

where x_1 and x_2 are the mole fractions of benzene and *cyclo*hexane respectively.

Benzene–n-*Heptane at* 20°.—Table 5 shows the heat of mixing (ΔH_{13}) for this system. The plot of x_1 against ΔH_{13} is somewhat asymmetrical, the maximum value of ΔH_{13} occurring at $x_1 = 0{\cdot}560$. Equation (2) represents these data

$$\Delta H_{13} = x_1x_3[3841 + 1046(x_1 - x_3)] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where x_3 is the mole fraction of *n*-heptane.

TABLE 5. *Heat of mixing of benzene*–n-*heptane at* 20°.

Mole fraction of benzene (x_1)	0·150	0·210	0·220	0·300	0·324	0·376	0·441
ΔH_{13} (J/mole)	436	546	584	742	772	823	902
Mole fraction of benzene (x_1)	0·511	0·588	0·650	0·715	0·828	0·878	
ΔH_{13} (J/mole)	945	948	928	857	629	511	

cyclo*Hexane*–n-*Heptane at* 20°.—The heat of mixing (ΔH_{23}) for this system is shown in Table 6. The plot is rather more asymmetrical than the others, the maximum value of ΔH_{23} occurring at $x_2 = 0{\cdot}590$.

TABLE 6. *Heat of mixing of* cyclo*hexane*–n-*heptane at* 20°.

Mole fraction of *cyclo*hexane (x_2)	0·230	0·310	0·378	0·444	0·480	0·540	0·617	0·730	0·830	0·893
ΔH_{23} (J/mole)	152	206	227	262	273	287	293	229	158	107

These results are best represented by equation (3):

$$\Delta H_{23} = x_2x_3[1121 + 268(x_2 - x_3) - 335(x_2 - x_3)^2] \quad . \quad . \quad . \quad . \quad (3)$$

Discussion of the Binary Systems: Comparison with the Theory of Regular Solutions.—The three binary systems all show small positive heats of mixing, which is to be expected from the nature of the components. The observed variation of the heats of mixing with composition is in only approximate agreement with the theory of strictly regular solutions proposed by Guggenheim (*Proc. Roy. Soc.*, 1935, *A*, **148**, 304). In this theory the "zero-th approximation" leads to an expression for the heat of mixing

$$\Delta H_m = x(1 - x)Nw \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

(where w is the interchange energy) which is of the same form as the first term in equations (1)—(3). The "quasi-chemical approximation" (Guggenheim, *loc. cit.*; Rushbrooke, *Proc. Roy. Soc.*, 1938, *A*, **166**, 296) and Kirkwood's accurate series expansion (*J. Chem. Phys.*, 1938, **6**, 70) lead to equations of the form of (5) when only three terms are considered:

$$\Delta H_m = x(1 - x)Nw\left[[1 - x(1 - x)\frac{2w}{zkT} - x(1 - x)\,(1 - 2x)^2\left(\frac{w}{zkT}\right)^2\right] \quad . \quad (5)$$

where z is the co-ordination number of the quasi-lattice. These equations result in symmetrical ΔH_m–x curves, but the experimental equations (1)—(3) are somewhat asymmetrical. A tentative interpretation of this departure from strictly regular behaviour might be made in terms of a possible variation of w with composition, *i.e.*,

$$w_{x,1} = w_{0{\cdot}5} + p_1\,(x_1 - x_2) + p_2(x_1 - x_2)^2 + \ldots \qquad (6)$$

(where p_1, p_2 are constants) which might be due to the differences in the molar volumes of the components.

Comparison with Vapour-pressure Data.—Vapour-pressure data are available for the systems benzene–*n*-heptane (Brown and Ewald, *Austral. J. Sci. Res.*, 1951, **4**, 198; 1952, **5**, 530) and benzene–*cyclo*hexane (Scatchard, Wood, and Mochel, *J. Phys. Chem.*, 1939, **43**, 119). The heat of mixing at 70° calculated from the vapour-pressure data is

$$\Delta H_{13} = x_1x_3[3005{\cdot}07 + 954{\cdot}89(x_1 - x_3) + 170{\cdot}15(x_1 - x_3)^2] \qquad (7)$$

which is similar to equation (2) which refers to 20°. For benzene–*cyclo*hexane the corresponding equation, referring to 40°, is

$$\Delta H_{12} = x_1x_2[2929 - 97(x_1 - x_2) - 125{\cdot}5(x_1 - x_2)^2] \qquad (8)$$

and at 70°

$$\Delta H_{12} = x_1x_2[2427 + 113(x_1 - x_2) + 25{\cdot}4(x_1 - x_2)^2] \qquad (8a)$$

which may be compared with equation (1) at 20°.

The interchange energy w varies with temperature (Guggenheim, " Mixtures," Oxford Univ. Press, 1952, p. 83) and should be replaced by $[w - T\,\mathrm{d}w/\mathrm{d}T - T^2\,\mathrm{d}^2w/\mathrm{d}T^2]$ in all the equations. The second differential coefficient allows for the variation of ΔH_m with temperature which has been observed (van der Waals, Thesis, Gröningen, 1950; Cheesman and Whitaker, *loc. cit.*). The values of w, and average values of $\mathrm{d}w/\mathrm{d}T$ and $\mathrm{d}^2w/\mathrm{d}T^2$ calculated from equations (1)—(8), are shown in Table 7.

TABLE 7. *Interchange energy at* $x = 0{\cdot}5$ (J/*mole*).

	w (20°)	w (40°)	w (70°)	$\mathrm{d}w/\mathrm{d}T$	$\mathrm{d}^2w/\mathrm{d}T^2$ (42·5°
Benzene–*cyclo*hexane ...	3350	2929	2427	−21·05 (30°); −16·73 (55°)	−0·173
Benzene–*n*-heptane	3841	—	3005	−16·72 (45°)	—
*cyclo*Hexane–*n*-heptane	1121	—	—	—	—

Solubility Parameters.—According to Vold (*loc. cit.*),

$$\Delta\delta_{13} = \Delta\delta_{23} + \Delta\delta_{12} \qquad (9)$$

where the δ's are the solubility parameters, and

$$\Delta\delta_{12}{}^2 = \left[\left(\frac{\Delta E_1}{V_1}\right)^{\frac{1}{2}} - \left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}}\right]^2$$

where ΔE_1, ΔE_2 are energies of vaporisation and V_1, V_2 molar volumes. Table 8 shows the values of Δδ calculated from the heats of mixing, together with those obtained by Hildebrand and Scott (" The Solubility of Nonelectrolytes," Reinhold, New York, 1950) from vapour-pressure measurements.

TABLE 8. *Solubility parameters.*

	Δδ (experimental)	Δδ (Hildebrand and Scott)
Benzene–*cyclo*hexane	2·85	0·95
Benzene–*n*-heptane	2·84	1·70
*cyclo*Hexane–*n*-heptane	1·46	0·75

For the three systems the experimental values are the larger. This is in conformity with the results of Cheesman and Whitaker (*loc. cit.*) and Vold (*loc. cit.*) on different systems. Equation (9) does not fit our data.

Benzene–cyclo*Hexane*–n-*Heptane at* 20°.—The ternary heats of mixing (ΔH_{123}) were determined by mixing the third component with binary mixtures at two or three different concentrations. Table 9 shows the experimental results for ΔH_{123} (J/mole of mixture) at 20° (column 4).

Equations have been suggested to allow the calculation of the heats of mixing of a ternary mixture from the heats of mixing of the three binary mixtures involved. Scatchard, Wood, and Mochel (*loc. cit.*) suggested an equation which was modified by Redlich and Kister (*loc. cit.*) to give

$$\begin{aligned}\Delta H_{123} \equiv\; & x_1'x_2'\,[H_{12}' + H_{12}''(x_1' - x_2') + H_{12}'''(x_1' - x_2')^2 + \ldots .] \\ & + x_1'x_3'\,[H_{13}' + H_{13}''(x_1' - x_3') + H_{13}'''(x_1' - x_3')^2 + \ldots] \\ & + x_2'x_3'\,[H_{23}' + H_{23}''(x_2' - x_3') + H_{23}'''(x_2' - x_3')^2 + \ldots] \quad . \quad (10)\end{aligned}$$

in which $\Delta H_{12} \equiv x_1x_2\,[H_{12}' + H_{12}''(x_1 - x_2) + H_{12}'''(x_1 - x_2)^2 + \ldots]$ etc.

TABLE 9. *Ternary heats of mixing.*

x_1' (C_6H_6)	x_2' (C_6H_{12})	x_3' (C_7H_{16})	ΔH_{123} obs.	ΔH_{123} calc. from equation		
				10	11	12
0·312	0·392	0·296	816	895	820	1064
0·369	0·363	0·268	912	941	877	1064
0·270	0·418	0·311	737	828	767	1024
0·327	0·387	0·286	880	901	838	1069
0·270	0·555	0·175	765	761	709	884
0·335	0·505	0·160	818	851	800	938
0·302	0·530	0·168	798	809	756	917
0·818	0·138	0·044	553	547	547	407
0·774	0·172	0·054	628	651	645	502
0·752	0·188	0·060	697	697	690	544
0·809	0·145	0·046	582	568	567	423
0·817	0·139	0·044	570	557	549	423
0·810	0·070	0·120	649	637	632	459
0·843	0·058	0·099	542	550	547	386
0·843	0·058	0·099	547	550	547	386
0·791	0·120	0·088	673	648	637	472
0·856	0·083	0·061	489	482	479	320
0·836	0·095	0·069	548	539	533	360
0·480	0·228	0·292	954	936	894	992
0·501	0·195	0·304	946	1003	965	962
0·461	0·259	0·280	923	999	952	1031
0·595	0·250	0·155	904	946	918	835
0·639	0·195	0·166	856	916	894	765
0·616	0·223	0·161	904	934	909	802
0·298	0·280	0·422	819	895	809	1038
0·316	0·237	0·447	828	881	828	1018
0·232	0·191	0·577	715	724	682	867
0·462	0·380	0·158	949	971	919	967
0·415	0·342	0·243	957	972	917	1053
0·197	0·684	0·119	616	568	531	670
0·206	0·169	0·625	645	660	624	794

Scatchard, Goates, *et al.* (*loc. cit.*) further modified equation (10) by replacing both $(x_1 - x_2)$ and $(x_1 - x_3)$ by $(2x_1 - 1)$. This modified equation (11) was originally intended to apply to mixtures containing one polar component, or for mixtures in which one component differs markedly in some way from the other two. Tsao and Smith (*loc. cit.*) suggested a slightly different equation (12) in which $x_1'x_2'$ is replaced by $x_2'/(x_2' + x_3')$, $x_1'x_3'$ by $x_3'/(x_2' + x_3')$, and $x_2'x_3'$ by $(1 - x_1')$ in equation (10).

Table 9 shows values of ΔH_{123} calculated from the binary data by equations (10), (11), and (12). Both equations (10) and (11) represent the ternary data quite well, showing average deviations of +2·1% and −1·9% respectively. Equation (12) gives a much poorer fit.

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