Heats of Mixing of Liquids.

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Heats of mixing of some substituted benzenes have been measured.

THIS work is a continuation of that of Cheesman and Whitaker (*Proc. Roy. Soc.*, 1952, *A*, **212**, 406). Measurements with the same calorimeter have been made at 24·33° of the heats of mixing of the six combinations in pairs of benzene, toluene, chlorobenzene, and bromobenzene. Several of these pairs have been reported as ideal on the basis of liquid–vapour equilibrium measurements, but this merely means that the measurements were too crude to detect deviations from ideality (Guggenheim, *Trans. Faraday Soc.*, 1937, **33**, 151). For all these mixtures the heat of mixing per mole was expected and found to be small compared with $\boldsymbol{R}T$.

EXPERIMENTAL

The experimental procedure followed closely that described by Cheesman and Whitaker (*loc. cit.*), using a small copper vessel in which the two liquids were separated by a tinfoil diaphragm. This diaphragm was broken at the moment of mixing by a steel armature which also acted as a magnetic stirrer. The vessel was supported in an evacuated housing in a thermostat, and the temperature difference between the calorimeter and the surrounding bath was recorded by copper–constantan thermojunctions connected to a galvanometer.

The cylinder consisted of two vessels; one was fixed permanently to its supports and carried the calibrating winding and thermocouple. The second vessel, which screwed on to the first and clamped the breakable diaphragm, carried a glass capillary in which an air bubble served to cushion any change of volume. Several interchangeable vessels of this type (" caps ") having different capacities enabled different molar ratios of mixing to be attained.

The course of each experiment was similar to that described by Cheesman and Whitaker, but whereas all the pairs of liquids previously studied mixed endothermically, three of the six new mixtures were found to mix exothermically. Consequently the plot of the galvanometer scale reading against time was of a different shape. Examples of such plots are shown in Fig. 1*a* for a typical endothermic mixture and in Fig. 1*b* for a typical exothermic mixture. In both cases the essential assumption is that the ratio of the enthalpy increase of mixing (ΔH) to the input of electrical energy (VIt) during the calibration period is equal to the ratio of FA to CG where F and G are determined by extrapolation of CB and of ED respectively. Owing to induction effects, galvanometer readings could not be taken during operation of the magnetic stirrer, and extrapolation was necessary during this period.

Initially it was found that the reproducibility of the results on the system bromobenzene–toluene was much worse than expected. This was due to inadequate mixing, probably owing to the widely differing densities of the two components. Thereafter the rate of stirring was doubled, and a correction applied for the temperature increase produced by the stirring. This correction was found to be constant for each cap and in each case equivalent to a galvanometer deflection of less than 1 mm. Corrections were applied to all results for the mixtures chlorobenzene–bromobenzene, bromobenzene–toluene, and bromobenzene–benzene. The variation in ΔH produced by including this correction decreases as ΔH increases, and is much smaller for exothermic than for endothermic mixtures since in the former case both FA and CG are increased, whilst in the latter case FA is decreased and CG increased in magnitude. The maximum change in the value of ΔH occasioned by this correction is 2% for the mixture bromobenzene–toluene, 10% for chlorobenzene–bromobenzene, and about 15% for bromobenzene–benzene. The volume change on mixing was too small in every case to be measured by observation of movement of the meniscus in the capillary tube.

FIG. 1*a*.

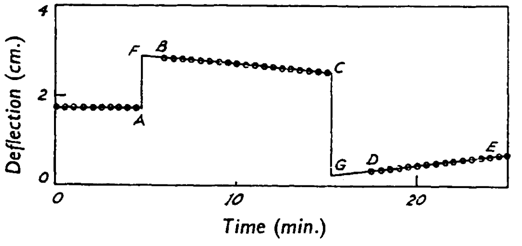


FIG. 1*b*.

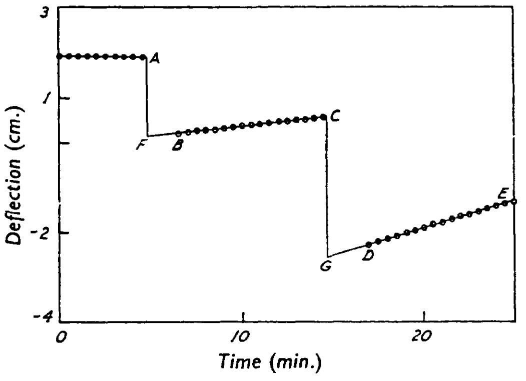
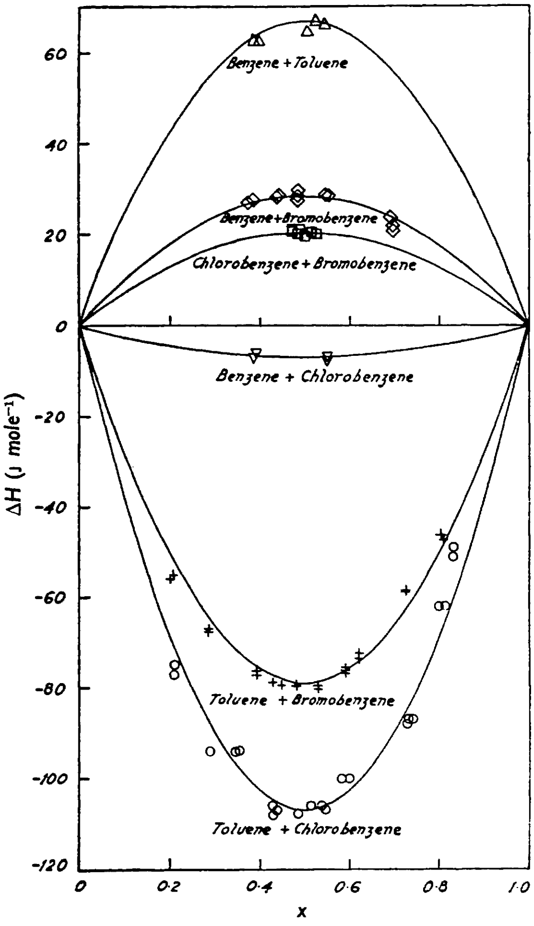


FIG. 2.



Materials.—All distillations were carried out in a fractionating column having an efficiency of 27 theoretical plates and a reflux ratio of 10 : 1.

Benzene. B.D.H. crystallisable benzene was shaken with concentrated sulphuric acid (4 times), water, 10% sodium carbonate solution and water successively. It was then distilled once and fractionally crystallised.

Toluene. Two batches were used. The first was purified by shaking a good commercial product with Raney nickel followed by drying it over sodium and distillation twice. It was then fractionally crystallised five times. Since this toluene had an unexpectedly low density we also made measurements with a sample of specially purified toluene kindly supplied to us by Dr. Tompa at Courtaulds' Research Laboratories. This had been prepared by distillation of the commercial product through a 100-plate column packed with 1/16″ gauge Dixon rings, with a reflux ratio of 100 : 1. Our toluene was used in the measurements on mixtures with chlorobenzene and with bromobenzene; when Dr. Tompa's material was received some of these measurements were repeated but the heats of mixing were not significantly different. Dr. Tompa's material was used for all the measurements here reported of mixtures of benzene and toluene, as the low-density material gave an appreciably higher heat of mixing.

Bromobenzene. B.D.H. bromobenzene was fractionally distilled once and dried (P_2O_5).

Chlorobenzene. B.D.H. chlorobenzene was dried ($CaCl_2$) and distilled once.

A comparison of the densities of the purified liquids with published values (Timmermans, " Physico-chemical constants of pure organic compounds," Elsevier, Amsterdam, 1950) is given below ($T = 24{\cdot}33°$).

	Benzene	Toluene	Toluene (Tompa)	Bromobenzene	Chlorobenzene
Obs.	0·8743	0·8592	0·8626	1·4892	1·1015
Publ.	0·8744	0·8628	0·8628	1·4889	1·1018

Results.—As Cheesman and Whitaker's calorimeter had been completely reconstructed for this work, a number of measurements were first made on the mixtures of chloroform and carbon tetrachloride, and the results agreed well with those already published. The results for the six new pairs of liquids are given in Table 1. In this Table the first column gives the mole fraction (x) of the liquid named second and the second column gives the measured value of the enthalpy increase (ΔH). The values in the third column are those calculated from the formula $\Delta H = x(1 - x)U$. The values assigned to the " interchange energy " U are given in the second column of Table 2.

TABLE 1.

x	ΔH (J mole^{-1}) (exp.)	ΔH (J mole^{-1}) (calc.)
Benzene–toluene; $U = 268$ J mole^{-1}.		
0·385	62·4	63
0·396	62·4	64
0·505	64·8	67
0·524	67·1	67
0·542	66·3	67
Benzene–chlorobenzene; $U = -\ 28$ J mole^{-1}.		
0·386	−6·5	−6·6
0·391	−6·1	−6·7
0·551	−7·2	−6·9
0·552	−6·9	−6·9
Benzene–bromobenzene, $U = 114$ J mole^{-1}.		
0·374	27·0	27
0·385	27·8	27
0·440	28·3	28
0·442	28·7	28
0·484	27·7	28
0·486	29·9	28
0·486	28·3	28
0·549	29·1	28
0·552	28·9	28
0·690	23·9	24
0·694	21·0	24
0·695	21·9	24

x	ΔH (J mole^{-1}) (exp.)	ΔH (J mole^{-1}) (calc.)
Chlorobenzene–bromobenzene; $U = 82$ J mole^{-1}.		
0·472	21·2	20
0·473	20·8	20
0·486	20·3	20
0·487	20·3	20
0·490	21·2	20
0·500	19·8	20
0·514	20·6	20
0·526	20·3	20
Toluene–bromobenzene; $U = -\ 316$ J mole^{-1}.		
0·200	−55·8	−51
0·205	−55·1	−52
0·284	−67·6	−64
0·286	−67·2	−65
0·393	−76·4	−76
0·393	−77·2	−76
0·428	−78·9	−77
0·445	−79·6	−78
0·480	−79·5	−79
0·529	−80·2	−79
0·530	−79·8	−79
0·589	−76·3	−77
0·589	−76·5	−77
0·591	−75·9	−76
0·619	−73·4	−75
0·619	−72·6	−75
0·725	−58·6	−63
0·726	−59·1	−63
0·805	−46·6	−50
0·808	−47·5	−49

x	ΔH (J mole^{-1}) (exp.)	ΔH (J mole^{-1}) (calc.)
Toluene–chlorobenzene; $U = -\ 428$ J mole^{-1}.		
0·209	−75	−71
0·211	−77	−71
0·291	−94	−88
0·298	−94	−90
0·301	−94	−90
0·304	−94	−91
0·430	−108	−105
0·431	−106	−105
0·434	−107	−105
0·486	−108	−107
0·487	−108	−107
0·512	−106	−107
0·538	−106	−106
0·546	−107	−106
0·582	−100	−104
0·600	−100	−103
0·727	−88	−85
0·730	−87	−84
0·732	−87	−84
0·741	−87	−82
0·800	−62	−68
0·812	−62	−65
0·832	−49	−60
0·832	−51	−60

TABLE 2.

Mixture	U (J mole^{-1}) exp.)	U (J mole^{-1}) (Hildebrand)	Mixture	U (J mole^{-1}) (exp.)	U (J mole^{-1}) (Hildebrand)
Benzene–toluene	268	29	Chlorobenzene–bromobenzene...	82	17
Benzene–chlorobenzene	−28	49	Toluene–bromobenzene	−316	71
Benzene–bromobenzene	114	9	Toluene–chlorobenzene	−428	159

DISCUSSION

All the measurements and the calculated parabolic curves are shown in Fig. 2. For the two most exothermic mixtures (toluene–chlorobenzene and toluene–bromobenzene) the deviations between the experimental points and the parabolæ seem to be systematic. These deviations are however neither large enough nor sufficiently firmly established to warrant more detailed analysis at this stage. The formulæ used for calculating ΔH are probably not accurate to within ± 5 joules mole^{-1}; the maximum observed deviation does not exceed twice this value and for the majority of the experimental points it is much less.

A comparison of the experimental values of U with those calculated by Hildebrand's (cf. Hildebrand and Scott, "The solubility of non-electrolytes," Reinhold, New York, 1950) well-known formula is given in the 3rd column of Table 2. There is, of course, no correlation. It is only fair to mention that Hildebrand himself did not claim his formula to be applicable to such small values of U. He put forward this formula to obtain rough estimates of values of U, in cases where it is not small. The formula has been much misused by many workers, especially in the field of polymer solutions. The smallness of the heats of mixing in all these mixtures may be gauged by comparison with $\boldsymbol{R}T \simeq 2{\cdot}5$ kJ mole^{-1}, so that the numerically greatest value of U is only about one sixth of $\boldsymbol{R}T$. In the present state of our knowledge of molecular interactions it is not possible to make any predictions about such values except to foresee their smallness.

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