666. *A New Calorimeter for Heats of Mixing. The Heat of Mixing of Benzene with Carbon Tetrachloride.*

By J. A. LARKIN and M. L. McGLASHAN.

A new calorimeter for measuring heats of mixing has been made and tested. It is believed to be capable of higher precision, and to be more convenient, than any previous design. The new calorimeter has been used to make an extensive series of measurements, with a probable error of about ± 0.3 J mole^{-1}, on benzene + carbon tetrachloride at 25°. The results are about 4 J mole^{-1} higher than was expected after consideration of several sets of previous measurements. It is believed that the discrepancies are due to incomplete mixing to varying degrees in all the previous calorimeters.

WE have made and tested a new calorimeter for measuring the heats of mixing of liquids and believe it to be capable of higher precision, and to be more convenient, than any previous design. The liquids are mixed out of any contact with vapour spaces which, even when they are very small, can lead [1,2] to large errors in measurements of heats of mixing. Completeness of mixing is easily achieved, and can easily be confirmed in the course of an experiment by making use of the fact that when mixing is complete the heat of stirring (stirring in this case by inversion of the mixing vessel) is reproducible. The new calorimeter is an improved version of one tentatively described elsewhere.[3] A troublesome gasket has been eliminated so that the liquids can now be mixed without danger of leakage from the calorimeter (which would of course lead to large errors due to cooling when even an otherwise negligible quantity of liquid evaporated from the surface into the surrounding vacuum), and without the liquids ever coming into contact with gasket material or grease with which they might interact. The arrangement of the calorimeter thermometer has been improved; it now consists of four thermistors connected in parallel and distributed over the surface of the calorimeter.

Several pairs of liquids have been used to prove new calorimeters.[1] The choice of a suitable pair of liquids should be governed by the following criteria: (a) they should be easily purified; (b) they should be at least as difficult to mix (*e.g.*, they should have widely different densities) as any pair which it is proposed to study in the calorimeter; (c) if vapour spaces are present over the liquids in the calorimeter (but see below) they should be chosen (*e.g.*, they should have widely different vapour pressures) so as to lead to errors at least as large as those which would occur with any pair which it is proposed to study; and (d) the heat of mixing should be of the same sign as, and of comparable magnitude to, the heats of mixing which it is proposed to measure. Finally, any such pair should have

[1] McGlashan, " Experimental Thermochemistry," Vol. II, ed. Skinner, Interscience Publ. Inc., New York, to be published in 1961, Chapter 15: " Heats of Mixing."

[2] McGlashan and Morcom, *Trans. Faraday Soc.*, 1961, **57**, 581.

[3] Das, Diaz-Peña, and McGlashan, *Pure Appl. Chem.*, 1961, **2**, 141.

5 U

been studied carefully in more than one laboratory and preferably at several different temperatures.

A great majority of the pairs of liquids so far studied mix endothermally with heats of mixing [1] of a few tens or a few hundreds of J mole^{-1}. We decided to recommend the pair benzene–carbon tetrachloride for proving a calorimeter which is to be used in that range, and with this in mind, to make some measurements on that pair with the new calorimeter. (The pair carbon tetrachloride–chloroform, which has been used more often than any other for this purpose,[1] has the disadvantages that chloroform is difficult to keep pure, and that the densities differ by only 0·1 g. ml.$^{-1}$.) Benzene and carbon tetrachloride are easily purified and the densities differ by as much as 0·7 g. ml.$^{-1}$. The vapour pressures are nearly identical but this will not matter if future calorimeters are designed, as we hope they always will be, with no vapour spaces, however small, in contact with the liquids. The heat of mixing of benzene with carbon tetrachloride had been studied at 25° in several laboratories [4–10] but even after some selection the results scattered over a range of about 10 J mole^{-1}, or about 10% of the heat of mixing of about 110 J mole^{-1} for an equimolar mixture. We were confident that we could improve the accuracy with which the heat of mixing was known by a factor of about ten and expected that the older data would scatter more or less uniformly about ours, though we already suspected that some of them were systematically too low because of incomplete mixing. We have found, however, that the heat of mixing is systematically higher by about 4 J mole^{-1} than we expected. Our measurements are certainly reproducible at worst to about ±0·5 J mole^{-1} and we believe them to be free from systematic errors greater than 0·2 J mole^{-1}. We are convinced that the discrepancies arise from incomplete mixing to varying degrees in all the previous calorimeters, and that our measurements are as accurate as we claim. In view of this conclusion, however, the pair benzene–carbon tetrachloride cannot be recommended for proving a new calorimeter until it has " been studied carefully in more than one laboratory." In the meantime we shall be even more sceptical than we were before of calorimeters " proved " with carbon tetrachloride–chloroform or some such pair, which are easy to mix, and then used to study a pair of liquids which are difficult to mix.

EXPERIMENTAL

The Calorimeter.—The calorimeter (I) is shown drawn to scale in Fig. 1. It consists of a glass mixing vessel with two compartments A and B in its upper half, and a side-arm, with capillary C and bulb D, which can be attached to the vessel through the ground-glass joint E–F. When the calorimeter is loaded and the side-arm attached, the liquids to be mixed are confined separately, and in the complete absence of vapour spaces, in the compartments A and B by mercury which fills the rest of the vessel and the capillary C (but not the bulb D). Mixing can then be brought about by inverting the vessel. This can be done without allowing the liquids ever to come near the greased joint E–F or the air in the bulb D, by turning the calorimeter several times over and back, through 180° only, in a clockwise direction about an axis through the mixing vessel and perpendicular to the plane of the side view shown in Fig. 1. The capillary C and bulb D provide an air-space in D which, while remaining out of contact with the liquids, ensures that the volume change on mixing causes no appreciable change of pressure [1] in the calorimeter. Four thermistors T (Messrs. Standard Telephones and Cables Ltd., Footscray, Sidcup, Kent: Type M52) connected in parallel were distributed over the outer surface of the vessel and fixed in place with " Araldite " (Messrs. Ciba Ltd., Duxford, Cambs: Type 103 with Hardener 951). At 25° c the combined resistance of the four thermistors was about 100 Ω with a temperature coefficient of about −3 Ω °K^{-1}. A heating coil H with a resistance of about

[4] Cheesman and Whitaker, *Proc. Roy. Soc.*, 1952, *A*, **212**, 406.

[5] Cheesman and Ladner, unpublished measurements; Ladner, Ph.D. Thesis, 1955, University of Reading.

[6] McGlashan and Morcom, unpublished measurements.

[7] Schulze, *Z. phys. Chem. (Leipzig)*, 1951, **197**, 105.

[8] Brown and Fock, *Austral. J. Chem.*, 1955, **8**, 361.

[9] Brown, Mathieson, and Thynne, *J.*, 1955, 4141.

[10] Hirobe, *J. Fac. Sci. Univ., Tokyo*, 1926, **1**, 155.

40 Ω was made by winding 150 cm. of 38 s.w.g. constantan wire on a glass post. The coil was insulated with " Araldite," and the post was sealed through the bottom of the vessel with " Araldite." [Six of the measurements reported below were made with a calorimeter (II) which differed from (I) only in that the post carrying the heating coil H was inserted into a thin-walled glass pocket which was an integral part of the mixing vessel. Calorimeter (II) was made because " Araldite " appears to be attacked by some of the methylchlorosilanes which we are at present studying.]

The calorimeter was loaded as follows. With the side-arm detached, the mixing vessel was roughly evacuated (to ensure that no air bubbles were trapped by the mercury), completely filled with mercury, and clamped right way up in a trough filled with enough mercury to reach just above the level of the open socket F. A weighed (± 0.0002 g.) quantity (0.05—2.5 g.) of one of the liquids to be mixed was then introduced through F into compartment A by means of a hypodermic syringe with a bent needle. A weighed quantity of the other liquid was similarly introduced into compartment B. The side-arm, with the joint E greased, was then immersed in mercury in the trough, the capillary C was filled with mercury, and the side-arm was inserted into the socket F and secured with a spring which passed round the body of the

FIG. 1. *The calorimeter.*
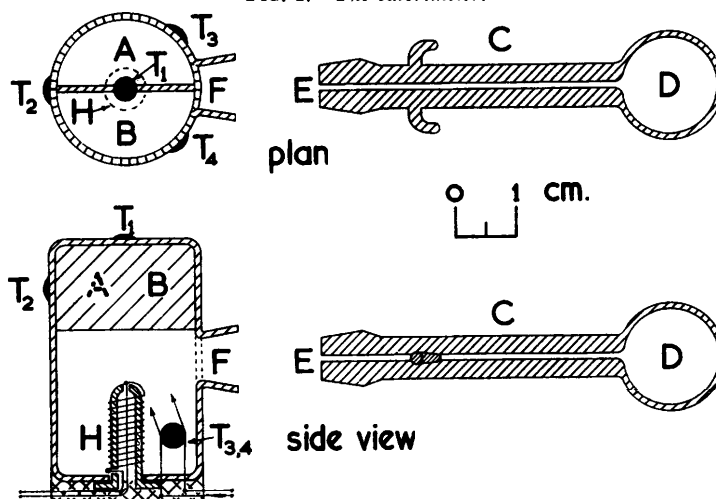
mixing vessel and was hooked on to the two lugs attached to C. The loaded calorimeter was then lifted carefully (so as to prevent premature mixing) from the trough and fitted into a vacuum jacket as shown in Fig. 2.

The vacuum jacket was made in two parts from 75 mm. glass tubing. Each part was joined to an FG75 flat flange glass joint at one end and was closed at the other end. The larger part had a tube K sealed into its closed end, and an opening L. Each part was fitted with a brass collar M made in two halves, seated on cork, and bolted together at N (only one of the two joints N is shown on each collar in Fig. 2). Each collar also carried two projecting pieces P (only one is shown on each collar in Fig. 2) fitted with spring-loaded (Q) bolts R by means of which the (greased) flanges could be held tightly together. The collar M on the larger part was fitted through the shaft S to a stand on which the calorimeter and jacket could be immersed in a thermostat. The stand was fitted with a lever, operated from above the thermostat and acting through an arrangement of gears, by means of which the calorimeter and jacket could be turned over and back through 180° in a clockwise direction about the shaft S. Photographs of a similar stand have been published elsewhere.[3] A length of thick-walled rubber tubing attached to the opening L served both as a flexible connexion to vacuum and as a conduit for the electrical leads allowing the calorimeter to be turned over without detaching it from the vacuum line and without seriously disturbing the electrical leads.

The loaded calorimeter was fitted by means of a rubber sleeve U into the tube K against the rubber seating V. The thermistor and heater leads were connected to the external circuits through the terminal block W. The jacket was bolted together and the whole apparatus

was immersed in a precision thermostat (better than $\pm 0.001°$ c), evacuated (to about 10^{-4} mm. Hg), and left overnight to come to thermal equilibrium.

Electrical Circuits.—The heating circuit and clock were as previously described.[2] As previously, a small correction was made for the resistance of the leads of the heating coil. The standard cell and the standard resistance were checked against N.P.L.-certificated Laboratory standards. The stop-watch was checked against B.B.C. time signals.

The thermistor circuit was a Wheatstone's bridge, as shown in Fig. 3, consisting of two arms with fixed resistances of 10Ω and 100Ω, the four thermistors with a combined resistance of about 100Ω, a 0—9999.9Ω five decade resistance box with a resistance of about 1000Ω actually in the circuit, and a galvanometer (Messrs. Tinsley: Type 4500 LS) with a resistance of 33Ω and a maximum current sensitivity of 100 cm. μA^{-1} at a scale-distance of 1 m. The bridge was supplied with current from an accumulator in series with a milliammeter (0—10 mA) and a resistance box X. Before use the accumulator was stabilised by bleeding through a resistance box Y a current adjusted to the same value as would be carried by the bridge. The resistances in the bridge, and the galvanometer, were chosen so as to make the heating effect of the current

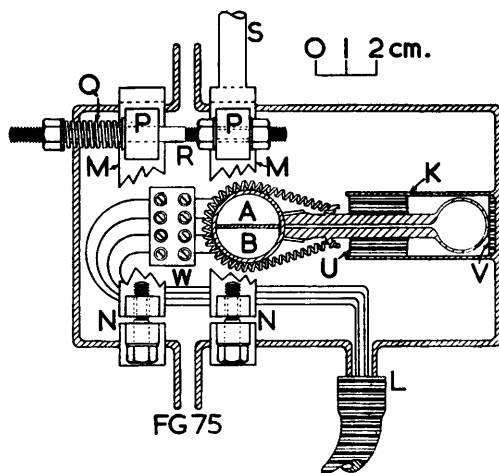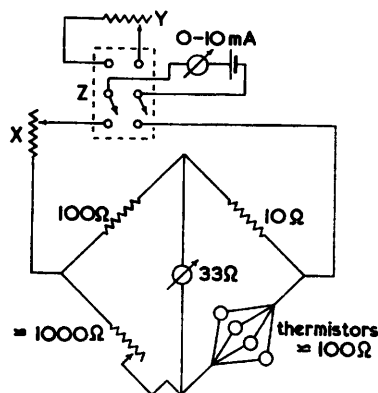Fig. 2. *The vacuum-jacket viewed from above and showing the calorimeter in position.*

Fig. 3. *The Wheatstone's bridge circuit.*

through the thermistors unimportant compared with the quantities of energy being measured. With the arrangement shown and a bridge current of 6 mA the galvanometer deflexion caused by a change in the temperature of the thermistors was about 700 cm. $°K^{-1}$. The loaded calorimeter had a heat capacity of about 35 J $°K^{-1}$ so that the galvanometer deflexion caused by the introduction of energy into the calorimeter was about 20 cm. J^{-1}. The dissipation of energy by the thermistors had the satisfactorily small value 2×10^{-3} J min.$^{-1}$.

Details of a Typical Experiment.—Galvanometer deflexions Δ plotted against time t are shown for a typical experiment in Fig. 4. In this experiment 0·8686 g. (0·011120 mole) of benzene and 2·0939 g. (0·013612 mole) of carbon tetrachloride were mixed at 25·0° c to give 0·024732 mole of a mixture containing mole fraction $x = 0.5504$ of carbon tetrachloride. The complete apparatus was left overnight in the thermostat to come to thermal equilibrium. Just before the experiment the zero reading of the galvanometer was taken. Current (6 mA) was then switched from the bleeding resistance Y to the bridge by throwing the switch Z (see Fig. 3). Galvanometer readings were then taken for 14 min. At 14 min. a current of 0·06220 A was switched to the calorimeter heater and passed for a time $\tau_1 = 19.00$ sec. (the clock was started and stopped electrically by the same switch which started and stopped the heating current; details may be found elsewhere [2]). The calorimeter was turned over and back four times beginning a few seconds after 14 min., and twice more at each of the times 15, 16, 17, and 18 min. Galvanometer readings were taken at 0·5 min. intervals from 14 min. until they were again steady (*i.e.*, Δ slowly increasing at a constant rate because of the energy dissipated by the thermistors). This part of the experiment is called the " mixing." At 27 min., when the galvanometer had been steady for several minutes, the calorimeter was

turned over and back twelve times to measure the thermal effect of stirring. This part of the experiment is called the " stirring correction." At 34 min., when the galvanometer had again been steady for several minutes, the current of 0·06220 A was again switched to the calorimeter heater and was passed for a time $\tau_3 = 7·89$ sec. Galvanometer readings were again continued until they had been changing linearly with time for several minutes. This part of the experiment is called the " calibration." Finally the galvanometer zero was checked.

The molar heat of mixing $\Delta_m H$ is given by the formula

$$\Delta_m H = i_H{}^2 R_H \{\tau_1 - (\Delta_1/\Delta_3)\tau_3 + (\Delta_2/\Delta_3)\tau_3\}/(n_1 + n_2) \qquad (1)$$

where i_H ($= 0·06220$ A) is the current passed through the calorimeter heater, R_H ($= 38·64\Omega$) is the resistance of the heater corrected for the resistance of the leads, τ_1 ($= 19·00$ sec.) and τ_3 ($= 7·89$ sec.) are the times for which current was passed through the heater in the " mixing "

FIG. 4. *Galvanometer deflexions Δ plotted against time t for a typical experiment. (The ordinate scale has been reduced by a factor of five for the " calibration " part of the experiment.)*
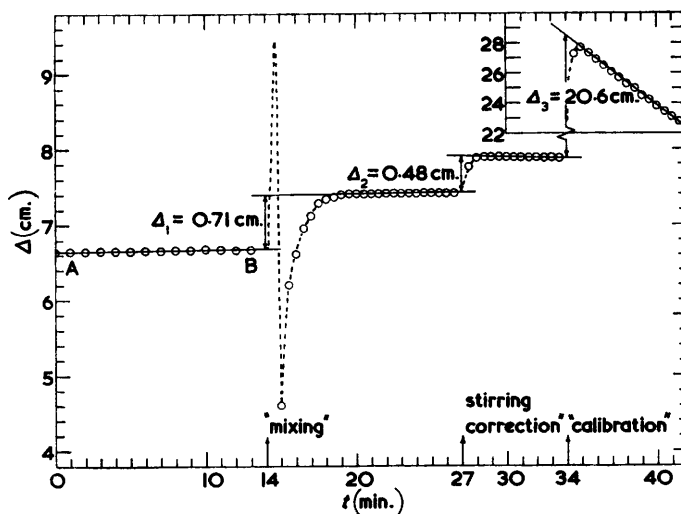
and " calibration " parts of the experiment respectively, Δ_1 ($= +0·71$ cm.), Δ_2 ($= +0·48$ cm.), and Δ_3 ($= +20·6$ cm.) have the meanings shown in Fig. 4, and $n_1 + n_2$ ($= 0·024732$ mole) is the total number of moles of the two liquids which were mixed. The numerical values given in parentheses relate to the particular experiment described above. Substituting these numerical values in equation (1) we obtain for that experiment

$$\Delta_m H \text{ (J mole}^{-1}) = 0·06220^2 \times 38·64 \text{ } (19·00 - 0·27 + 0·18)/0·024732 = 114·3$$

Discussion of Errors.—Reasonable estimates of the upper limits of error in the quantities occurring on the right-hand side of equation (1) are 2×10^{-5} A in i_H, $0·02\Omega$ in R_H, $0·03$ sec. in τ_1 and in τ_3, $0·05$ cm. in Δ_1 and in Δ_2 (including possible shifts in the galvanometer zero), $0·5$ cm. in Δ_3, and 10^{-5} mole in $(n_1 + n_2)$. The overall probable error in $\Delta_m H$ calculated from these individual errors is $0·2_5\%$.

When the (endothermal) heat of mixing is compensated as nearly as possible by the simultaneous introduction of electrical energy [11,12] the error arising from heat losses in the " mixing " part of the experiment is proportional to the difference between the areas above and below the base line (AB in Fig. 4) corresponding to thermostat temperature. In our experiments errors from this source never amounted to more than $0·1_5\%$ of the heat of mixing and were usually considerably less. This was so in spite of the rather high value $0·037$ min.$^{-1}$ of the coefficient $-$ d ln Δ/dt of Newton's law of cooling for our calorimeter. The value of this

[11] van der Waals, Thesis, 1950, University of Groningen; van der Waals and Hermans, *Rec. Trav. chim.*, 1949, **68**, 181; 1950, **69**, 949; van der Waals, *ibid.*, 1951, **70**, 101.
[12] Adcock and McGlashan, *Proc. Roy. Soc.*, 1954, A, **226**, 266.

coefficient could be reduced by improving the vacuum in the calorimeter jacket and by reducing the losses due to radiation, but such improvements were not thought worth while. The errors arising from heat losses in the " stirring correction " and " calibration " parts of the experiment were negligible.

Incomplete mixing has probably (see below) led to serious errors in some previous measurements of heats of mixing especially when the liquids which were mixed differed markedly in density as is the case for benzene (0·87 g. ml.$^{-1}$) + carbon tetrachloride (1·58 g. ml.$^{-1}$). The reproducibility of the " stirring correction," which we often repeated several times before doing the " calibration " (see Fig. 4), together with the reproducibility of the measurements themselves, made it certain that no errors arose from incomplete mixing in our experiments.

The presence of vapour spaces over the liquids has led to serious errors [1] in many previous measurements of heats of mixing, though in the particular case of benzene (94 mm. Hg at 25° c) + carbon tetrachloride (114 mm. Hg at 25° c) such errors were probably small because of the similarity of the vapour pressures. Since there were no vapour spaces over the liquids in our calorimeter no errors can in any case arise from this source.

Our final estimate of about 0·3% error in $\Delta_m H$ is borne out in the experiments reported below.

Materials.—The benzene was some of that used previously,[13] the purity of which had been established [14] by precise measurements of vapour pressure. Before use it was redistilled through a 27-plate fractionating column and dried over sodium. " AnalaR " carbon tetrachloride was fractionally distilled three times through the same column. A reflux ratio of 10 : 1 was used and the middle fractions only were retained. In the third fractionation the sample was distilled from potassium hydroxide pellets. The product was stored over anhydrous sodium sulphate, small portions being distilled off as required. The density of the carbon tetrachloride was 1·58465 g. ml.$^{-1}$ at 25·0° c; compare 1·58452 which is the mean of the more recent of the values quoted at 25° c by Timmermans.[15]

RESULTS

The results of twenty-six measurements of the heat of mixing of benzene (1) + carbon tetrachloride (2) at 25·0$_0$° c are given in the Table. The first and second columns give the masses

Heats of mixing for mixtures of benzene (1) + *carbon tetrachloride* (2) *at* 25·0° c.

w_1 (g.)	w_2 (g.)	x	ΔH (J)	$\Delta_m H$ (J mole^{-1})	δ (J mole^{-1})
1·2402	0·1272	0·0495	0·405	24·2	+0·4
1·2294	0·2696	0·1002	0·788	45·0	+0·2
1·2119	0·4319	0·1532	1·157	63·2	−0·2
1·1644	0·5723	0·1997	1·427	76·6	−0·6
1·3685	0·9068	0·2517	2·108	90·0	0·0
1·3982	1·1975	0·3031	2·572	100·1	+0·1
1·3911	1·4570	0·3472	2·914	106·8	+0·2
1·1792	1·5409	0·3989	2·810	111·9	−0·1
1·0591 *	1·6653	0·4440	2·801	114·9	+0·2
1·2083	1·9246	0·4471	3·206	114·6	−0·2
1·1716 *	1·9050	0·4522	3·150	115·0	0·0
1·0776	2·0966	0·4970	3·176	115·8	+0·1
1·0487 *	2·0642	0·4999	3·100	115·5	−0·1
0·9729 *	1·9180	0·5003	2·876	115·4	−0·2
0·8686	2·0939	0·5504	2·828	114·3	+0·2
0·7707 *	1·8837	0·5538	2·531	114·5	+0·5
0·8617	2·1076	0·5540	2·808	113·5	−0·4
0·8486 *	2·0776	0·5542	2·775	113·9	0·0
0·7075	2·0439	0·5946	2·480	111·0	0·0
0·5704	2·0634	0·6475	2·173	104·9	0·0
0·5594	2·5320	0·6968	2·280	96·5	−0·6
0·3764	2·2305	0·7505	1·665	86·2	+0·1
0·2825	2·2478	0·8016	1·334	73·2	+0·1
0·2029	2·2763	0·8507	1·021	58·7	+0·3
0·1304	2·1743	0·8944	0·685	43·4	−0·1
0·0592	2·1220	0·9479	0·333	22·9	+0·1

* Measurement made in calorimeter II; all other measurements were made in calorimeter I.

[13] McGlashan and Wingrove, *Trans. Faraday Soc.*, 1956, **52**, 470.
[14] McGlashan and Williamson, *Trans. Faraday Soc.*, 1961, **57**, 588.
[15] Timmermans, " Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publ. Co., Inc., Amsterdam, 1950.

w_1 of benzene and w_2 of carbon tetrachloride and the fourth column gives the measured heat of mixing ΔH. The third column gives the mole fraction x of carbon tetrachloride in the final mixture, and the fifth column gives the heat of mixing $\Delta_m H$ per mole of final mixture. The last column will be discussed below.

DISCUSSION

Our measurements have been fitted by the equation

$$\Delta_m H \text{ (J mole}^{-1}) = x(1-x)\{462\cdot6 + 16(1-2x) + 25(1-2x)^2 + 10(1-2x)^3\} \quad (2)$$

Values of the excess δ of the measured value of $\Delta_m H$ over that calculated from equation (2) are shown in the sixth column of the Table. The root mean square value $\langle \delta^2 \rangle^{\frac{1}{2}}$ of δ is $0\cdot2_6$ J mole^{-1}, in good agreement with the value calculated above for the probable experimental error. For only five of the twenty-six measurements is $|\delta|$ greater than $0\cdot3$ J mole^{-1}.

FIG. 5. *The excess δ of the molar heat of mixing $\Delta_m H$ over the value calculated according to equation* (2), *plotted against the mole fraction x of carbon tetrachloride for benzene + carbon tetrachloride at* 25·0° c.
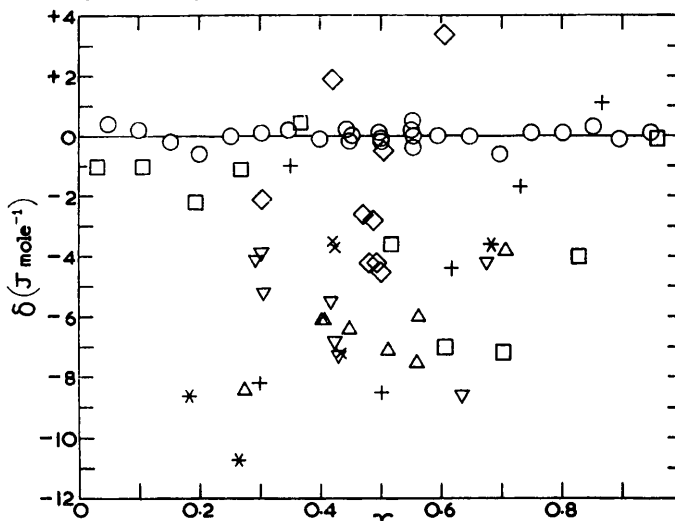
○ This work; △ Cheesman and Whitaker [4] (corrected from 24·7° to 25·0° c); ▽ Cheesman and Ladner [5] (corrected from 24·4° to 25·0° c); ◇ McGlashan and Morcom [6] (corrected from 24·8° to 25·0° c); □ Schulze; [7] × Brown and Fock; [8] ✳ Brown, Mathieson, and Thynne; [9] + Hirobe. [10]

A comparison of our results with those of previous workers is shown in Fig. 5 where δ is plotted against the mole fraction x of carbon tetrachloride. Three of the previous sets of measurements (see the legend to Fig. 5) were made at temperatures a few tenths of a degree below 25° c. They have been corrected to 25·0° c with amply sufficient accuracy by assuming [4,7,16] that $d\Delta_m H/dT = 5\cdot8x(1-x)$ J °K^{-1} mole^{-1}.

The scatter of our measurements is much less than that of any of the previous sets. Much more striking, however, is the fact that our values of $\Delta_m H$ are higher, in some cases by as much as 8% or more, than nearly all previous values, and higher by about 4 J mole^{-1} than we had expected after consideration of the previous values. We are convinced that the discrepancies are due mainly to incomplete mixing in previous calorimeters. Canning and Cheesman, [17] using the same calorimeter and technique as Cheesman and Whitaker, [4] found that benzene (0·87 g. ml.$^{-1}$) + bromobenzene (1·49 g. ml.$^{-1}$) did not mix completely. If this was so it is difficult to believe that benzene (0·87 g. ml.$^{-1}$) + carbon tetrachloride (1·58 g. ml.$^{-1}$) were completely mixed in Cheesman and Whitaker's experiments. Cheesman and Ladner mentioned the possibility that incomplete mixing had led to hidden

[16] Boissonas and Cruchaud, *Helv. Chim. Acta*, 1944, **27**, 994.
[17] Canning and Cheesman, *J.*, 1955, 1230.

errors in their published measurements [18] on pairs of liquids with density differences less than 0·02 g. ml.$^{-1}$. If this was so it is difficult to believe that there were not much bigger errors from this source in their unpublished measurements [5] on benzene + carbon tetrachloride. McGlashan and Morcom's measurements,[6] made in a calorimeter [12] which we now regard as superseded, are in better agreement with our present measurements in spite of a scatter about ten times as great. Schulze's measurements [7] are in fair agreement with ours for mixtures rich in benzene.

We hope that benzene + carbon tetrachloride will soon be studied somewhere else in a calorimeter capable of a precision similar to or better than ours and in which it is certain that mixing is complete.

[*Added in proof*: We have now made five further measurements with a different sample of benzene (supplied by the National Chemical Laboratory with a certified purity of 99·990 ± 0·002 moles %), and a different sample of carbon tetrachloride (kindly given to us by Mr. L. A. K. Staveley; we find 1·58462 g. ml.$^{-1}$ for its density at 25·0°). The results, namely:

x	0·3007	0·4002	0·4983	0·5993	0·6999
δ(J mole^{-1})	+0·1	+0·6	+0·7	+0·5	+0·4

are systematically higher than those given in the Table but by an amount which is only just outside our experimental error.]

DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY, READING.

[18] Cheesman and Ladner, *Proc. Roy. Soc.*, 1955, A, **229**, 387.