

HEATS OF MIXING

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One of the most important requirements of a calorimeter for measuring the heats of mixing of liquids is the elimination of any vapour phase. For example in some of the measurements described here, in which about 1 cm^3 quantities of each liquid were mixed, a vapour space of only 1 cm^3 would have given rise to an error of 50 per cent or more in the heat of mixing.

In our previous calorimeter¹ the vapour phase was successfully eliminated but there remained a number of weak points in the design:

(1) The mercury used as confining liquid was in contact with the air so that heat exchanges with the surroundings were neither very small nor reproducible.

(2) There were rather large heat exchanges between the "mixing vessel" and the "reference vessel" caused by conduction along the thermopile between the two vessels.

(3) There was necessarily a heat effect due to breaking the glass seal which initially separated the two liquids. This effect was usually small but since no two seals were identical it was not reproducible.

(4) The quantity of mercury in the calorimeter (about 350 g), and hence the heat capacity (about $50 \text{ J/}^\circ\text{C}$), were larger than desirable.

These disadvantages have been largely overcome in the new calorimeter described below. In particular:

- (1) during measurements the calorimeter was completely enclosed in a vacuum jacket;
- (2) a thermistor was used instead of the thermopile without loss of sensitivity but with a considerable decrease in heat losses;
- (3) mixing was effected by inverting the calorimeter instead of by breaking a glass seal; and
- (4) the heat capacity of the new calorimeter was about $15 \text{ J/}^\circ\text{C}$.

The calorimeter was tested by making measurements on mixtures of $\text{CCl}_4 + \text{CHCl}_3$. The results agreed well with previous work¹⁻³, and showed a useful gain in reproducibility. For example, in our measurements of the very small heats of mixing of $\text{CCl}_2(\text{CH}_3)_2 + \text{CCl}_3(\text{CH}_3)$, the actual quantity of heat measured varied between 0.036 J and 0.074 J and was usually reproducible to within 0.001 J .

New measurements have been made on mixtures of pairs of the compounds $\text{SiCl}_n(\text{CH}_3)_{4-n}$ and of pairs of the compounds $\text{CCl}_n(\text{CH}_3)_{4-n}$. These measurements are being continued, but a preliminary account is given here of the results so far obtained. These substances were chosen because the molecules though roughly spherical in *shape* are by no means spherical in their *force fields*.

THE CALORIMETER

The calorimeter is shown in *Figure 1*. It consisted of a glass vessel with inner and outer cylindrical compartments A and B and a capillary tube C,

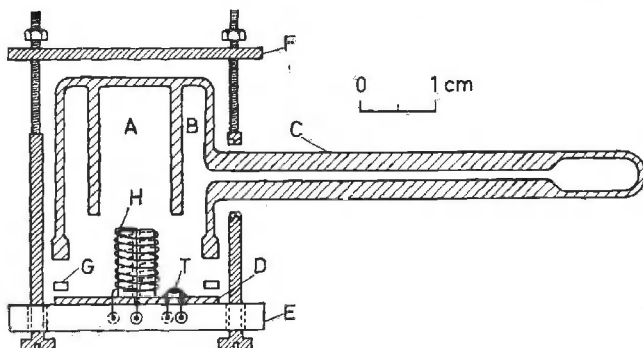


Figure 1

which could be held tightly against a flat glass plate D mounted on a Perspex plate E and carrying an electrical heating coil H and a thermistor T, any leakage being prevented by a neoprene gasket G. The heating coil H and thermistor T were cemented into place and insulated with Araldite.

The calorimeter was loaded as follows. The vessel was inverted under mercury and a thread of mercury a few centimetres long was introduced

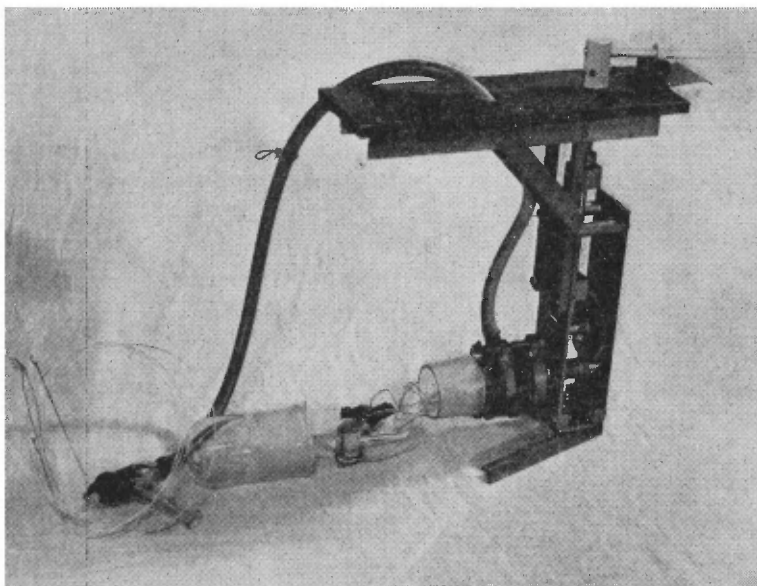


Figure 2

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into C. The vessel, still under mercury, was then turned right way up. A weighed quantity (0.1 — 1.0 g) of one of the two liquids was then introduced into A by means of a hypodermic syringe with a bent needle. A weighed quantity of the other liquid was similarly introduced into B. The base plate was then carefully brought into position and the whole screwed tightly together as indicated in *Figure 1*. The loaded calorimeter was then lifted carefully (so as to prevent premature mixing) from the bowl of mercury in which these operations had been carried out and was fitted into a vacuum jacket made from a large ground-glass joint as shown in *Figures 2 and 3*. This jacket was arranged so that it could be turned over, so as to invert the calorimeter and bring about mixing, without detaching it from the vacuum line and without seriously disturbing the electrical connections from the heating coil and thermistor. The complete apparatus as shown in *Figure 3* was placed in a precision thermostat, evacuated, and left overnight to come to thermal equilibrium. The thermistor was made one arm of a Wheatstone bridge arranged so that the current passing through the thermistor was as small as possible. Since all the liquids studied absorbed heat on mixing, the heat of mixing was compensated as nearly as possible by the simultaneous liberation of a measured quantity of heat in the electrical heating coil¹.

RESULTS AND DISCUSSION

We were interested to see how far, if at all, a lattice theory allowing for preferred orientations would account for the results of mixing pairs of

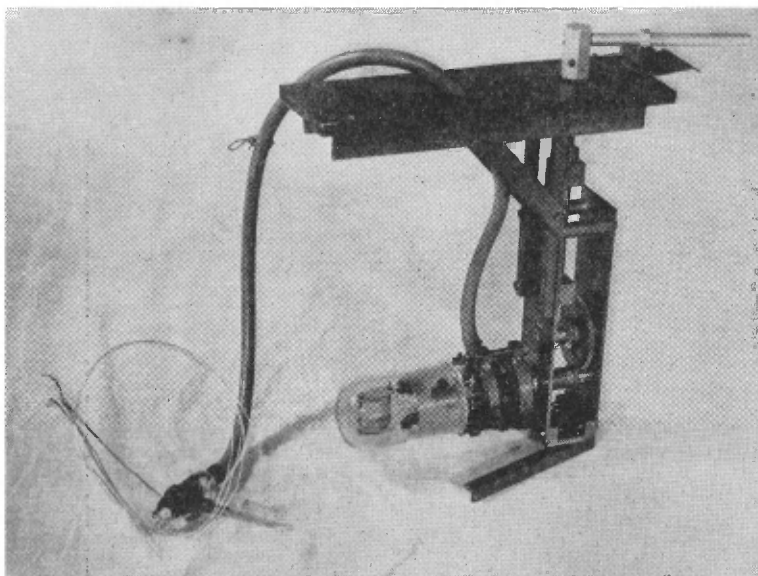
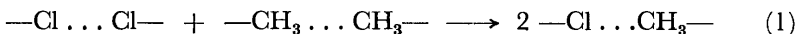


Figure 3

substances $MCl_n(CH_3)_{4-n}$ with, for given $M(= Si \text{ or } C)$, a single value for the energy of "interchange of contacts":



Similar theories have been discussed by Münster⁴, Tompa⁵, Barker⁶, Barker, Brown and Smith⁷ and Guggenheim⁸.

Let N_A, N_B molecules of A, B each occupy r_A, r_B sites on a lattice of co-ordination number z . Let $q_X z = r_X z - 2r_X + 2$ be the total number of points of contact of a molecule of type X with other molecules. Of these points of contact of a molecule X let a fraction α_X be of type a (e.g. Cl), and let a fraction $1 - \alpha_X$ be of type b (e.g. CH_3). We define a quantity γ by the relation

$$\gamma = [(1 - x)\alpha_A q_A + x\alpha_B q_B] / [(1 - x)q_A + xq_B] \quad (2)$$

where x is the mole fraction, $N_B / (N_A + N_B)$, of substance B in the mixture. We further define an energy parameter $2u/z$ equal to the energy of the interchange of contacts shown in equation (1).

It can then be shown (for a general method see Guggenheim⁸) that the molar energy of mixing, ΔU_m , is given by

$$\Delta U_m / Lu = [(1 - x)q_A + xq_B]y(x) - (1 - x)q_A y(0) - xq_B y(1) \quad (3)$$

with $y = y(x)$ given by the "quasi-chemical" formula

$$(\gamma - y)(1 - \gamma - y) = y^2 \eta^2 \quad (4)$$

where η^{-2} is the "equilibrium constant" of process (1) according to the

Table 1. Molar heats of mixing at 25°C

n_A	n_B	ΔH_m (J/mole) for $M = Si, x = 0.5$		
		<i>Exp.</i>	Calc. for $\eta^2 = 1,$ $Lu = 2160$ J/mole	Calc. for $\eta^2 = 3,$ $Lu = 2510$ J/mole
2	3	38	101	73
2	4	405	405	405
3	4	140	101	148
		ΔH_m (J/mole) for $M = C, x = 0.5$		
		<i>Exp.</i>	Calc. for $\eta^2 = 1,$ $Lu = 710$ J/mole	Calc. for $\eta^2 = 25,$ $Lu = 1570$ J/mole
2	3	6	33	16
2	4	133	133	133
3	4	103	33	70
1	2	11	33	16
1	3	2.4	133	63
1	4	49	299	212
0	4	300*	532	391

* From the measurements at 0°C of Englert-Chwoles⁹.

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quasi-chemical theory, γ is given by equation (2), and L is Avogadro's number.

To compare the theory with our experimental results we make the reasonable assumptions that $r = 5$ and $z = 4$ so that $q = 3$ throughout. Then for mixtures of $A = MCl_{n'}(CH_3)_{4-n'}$ + $B = MCl_{n''}(CH_3)_{4-n''}$, identifying a with Cl and b with CH_3 , we have $\alpha_A = n'/4$ and $\alpha_B = n''/4$.

In *Table 1* we give our experimental results for the molar heat of mixing ΔH_m at $x = 0.5$ and $25^\circ C$ for three pairs with $M = Si$ and for seven pairs with $M = C$. In the third column we give values calculated from formula (3) with $\eta^2 = 1$, that is to say for the "zeroth approximation" corresponding to random mixing of contacts in spite of a finite energy of interchange. The values in the fourth column were calculated from formula (3) with $\eta^2 = 3$ for the silicon compounds, and $\eta^2 = 25$ for the carbon compounds.

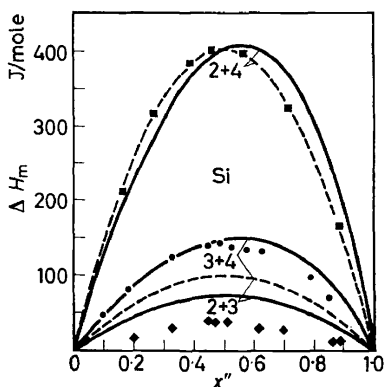


Figure 4

This is the so-called "quasi-chemical approximation" and the values chosen for η^2 imply that in the silicon compounds there is a slight preference, and in the carbon compounds a stronger preference, for contacts between like groups rather than between unlike groups. For each set of compounds the formula was fitted to the result for the mixture ($n' = 2$) + ($n'' = 4$).

Dealing first with the results for $M = Si$ we see that the zeroth approximation correctly predicts that for both $Si_2 + Si_3$ and $Si_3 + Si_4$, ΔH_m is smaller than for $Si_2 + Si_4$, but that this approximation fails to distinguish between the first two. The quasi-chemical approximation, however, correctly predicts the order, and very roughly the relative magnitudes, for all three pairs. In *Figure 4* the results are shown plotted against the mole fraction x'' of the component with the larger value of n . We see that while the zeroth approximation implies that all the curves should be symmetrical about $x = 0.5$, which is in close agreement with experiment, the quasi-chemical approximation implies in each case a greater or lesser displacement of the maximum towards higher values of x'' .

When we turn to the results for $M = C$ we see that for the three corresponding pairs the entries in *Table 1* lead to similar conclusions as in the case of $M = Si$. However, in this case, as we can see in *Figure 5*, the

quasi chemical approximation not only leads to a much better prediction of the relative magnitudes but also correctly predicts displacements of the maxima in the curves from $x'' = 0.5$.

Unfortunately, when we turn to the results of measurements with *tert*-butyl chloride as one of the components, the situation is much less satisfactory. The theory implies much bigger values for C1 + C3 and for C1 + C4 than those actually found. We propose to repeat these measurements with a new sample of *tert*-butyl chloride, and also to extend the Si

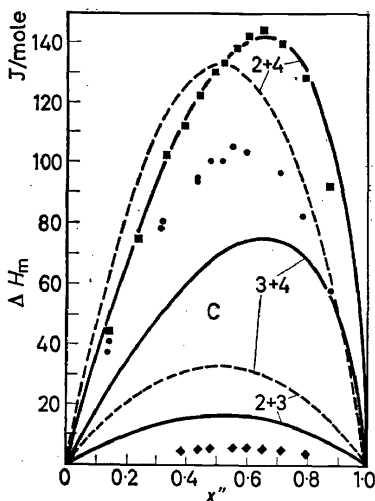


Figure 5

measurements so as to include $\text{SiCl}(\text{CH}_3)_3$ (at the moment we are worried about an apparent reaction of this substance with mercury), and $\text{Si}(\text{CH}_3)_4$. We also hope soon to begin vapour pressure measurements on some of these systems.

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