

# CALORIMETRY OF NON-REACTING SYSTEMS WITH PARTICULAR EMPHASIS ON SOLUTION AND MIXING PROCESSES

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## INTRODUCTION

I suppose that chemists who make calorimetric measurements divide themselves into two more or less distinct groups according as to whether they are interested primarily (a) in making a contribution to the building of thermochemical tables, or (b) in the study of intermolecular forces.

Those belonging to the first group, traditionally called "thermochemists", measure enthalpies of chemical reactions (including enthalpies of solution), as steps in reaction sequences leading to standard enthalpies of formation of single substances. They also make calorimetric measurements on pure substances of the heat capacity as a function of temperature, and of the enthalpies of transition, of fusion, of vaporization, and of gas imperfection, leading to standard entropies of single substances. Non-calorimetric measurements such as vapour pressure,  $pVT$ , and infrared spectroscopic measurements, are also often used to supplement calorimetric measurements for this purpose. The end results of such studies are thermochemical tables from which equilibrium constants of chemical reactions can be calculated. Reaction calorimetry has of course been fully dealt with in the first two Sessions of this Symposium. One paper in Session III, however, belongs properly to that group. This is Paper III: 2 by Murgulescu and Tomus on the enthalpies of solution of anhydrous and of hydrated barium bromate leading to enthalpies of formation of these two substances. There appear to be no papers whether in Session III or elsewhere which deal with the calorimetry of single substances from the point of view of the thermochemist.

Those belonging to the second group, interested primarily in intermolecular forces, subdivide themselves in turn according as they study single substances or mixtures. Since there is only one paper in Session III on the calorimetry of single substances, and since that one comes from our laboratory, I shall talk only briefly about the study of single substances from the point of view of the intermolecular forces, and shall then spend the rest of this lecture talking about the calorimetry of mixtures, and particularly about enthalpies of mixing which are the subject of eight of the fourteen papers in Session III.

## SINGLE SUBSTANCES

One of the most important unsolved problems in physical science is that of finding out precisely how the interaction energy of a pair of molecules depends on the separation and on the relative orientations of the two molecules. The

most direct method of studying this interaction energy is by measurements on the dilute gas of the temperature dependence of the second virial coefficient

$$B = \lim_{V \rightarrow \infty} \left\{ \frac{V}{n} \left( \frac{pV}{nRT} - 1 \right) \right\} \quad (1)$$

which is related to the pair interaction energy  $u(r, \theta_1, \theta_2, \phi_2 - \phi_1)$  by the equation

$$B = (L/4) \int_0^\infty \int_0^{2\pi} \int_{-1}^1 \int_{-1}^1 \{1 - \exp(-u/kT)\} d \cos \theta_1 d \cos \theta_2 d(\phi_2 - \phi_1) r^2 dr \quad (2)$$

which for spherically symmetrical molecules becomes

$$B = 2\pi L \int_0^\infty \{1 - \exp(-u/kT)\} r^2 dr \quad (3)$$

Values of  $B$  are usually derived from  $pVT$  measurements<sup>1</sup>, or occasionally by combining enthalpies of vaporization with vapour pressures<sup>2, 3</sup>. In the latter connexion precise measurements of the enthalpy of vaporization are urgently needed over wide ranges of temperature for many simple substances. Values of  $(B - TdB/dT)$  can be derived from flow-calorimetric measurements of the isothermal Joule-Thomson coefficient  $(\partial H/\partial p)_T$ <sup>4, 5</sup>, or by combining ordinary (isenthalpic) Joule-Thomson coefficients  $(\partial T/\partial p)_H$  with heat capacities  $C_p$ <sup>6</sup>. Values of  $T^2 d^2 B/dT^2$  can be derived from flow-calorimetric measurements of the pressure dependence  $(\partial C_p/\partial p)_T$  of the heat capacity<sup>7, 8</sup>.

Flow-calorimetric measurements are thus most useful for establishing precisely how the second virial coefficient depends on the temperature, and particularly so at temperatures below say the critical temperature, where values of  $B$  derived from  $pVT$  measurements become progressively less reliable because of adsorption of the gas on the walls of the apparatus. It is a pity that there are so few flow calorimeters being used for this kind of work. In Paper III: 12 Francis, McGlashan, and Wormald describe a new flow calorimeter built primarily for measurements of  $(\partial H/\partial p)_T$  and hence of  $(B - TdB/dT)$ , but also suitable for measurements of  $(\partial T/\partial p)_H$  or of  $(\partial H/\partial T)_p = C_p$ , and discuss their results for benzene vapour.

The second virial coefficient  $B$  is not very sensitive to the precise details of the form of the pair-interaction energy  $u(r)$ . Nevertheless, accurate enough values of  $B$  are now known for argon<sup>9-11</sup> and for krypton<sup>10, 11</sup> over wide enough temperature ranges to show conclusively that the commonly assumed "12-6" form

$$u(r) = \epsilon \{ (r_0/r)^{12} - 2(r_0/r)^6 \} \quad (4)$$

is seriously wrong. (There is also a good deal of other evidence<sup>12</sup> for this conclusion.)

It has become clear that a detailed knowledge of the form of the pair-interaction energy can be gained only by piecing together information about different small segments of the curve<sup>12, 13</sup>. In particular measurements of the equilibrium properties of the crystals, such as, for example, the beautiful heat capacity measurements of Morrison and his colleagues<sup>14</sup> on argon and krypton, lead<sup>13</sup> to information about the pair-interaction energy in the immediate neighbourhood of its minimum. More calorimetric measurements of heat

capacities, and of enthalpies of fusion and of vaporization, are urgently needed on substances like argon, krypton, and xenon, simple enough to allow theoretical interpretation. Even more urgently needed are  $pVT$  measurements on the crystals of such substances. In principle at least such measurements could be done calorimetrically by studies of the pressure dependence of the enthalpy; I wonder whether this would be feasible in practice?

### MIXTURES

The simplest kind of mixture is a dilute gaseous one. The second virial coefficient  $B(T, x)$  of a binary gas mixture is given exactly as a function of the mole fraction  $x$  of the second substance by the relation

$$B(T, x) = (1 - x)^2 B_{11}(T) + 2x(1 - x)B_{12}(T) + x^2 B_{22}(T) \quad (5)$$

so that each of the  $B_{ij}$ 's can be measured and is related to the corresponding  $u_{ij}(r)$  by a relation having the same form as equation (3). For the most part only  $pVT$  measurements have so far been used to study  $B(T, x)$  and hence  $B_{12}(T)$ . It is a pity that so few flow-calorimetric measurements have yet been made on dilute-gas mixtures<sup>6</sup>. For flow-calorimetric measurements on the vapours of substances liquid at room temperature most workers have used a vapour stream generated by boiling the liquid. In order to extend such work to mixtures it will be necessary to avoid fractional distillation by use of two independent boilers, or a single flash-boiler, or by use of a gas-circulating pump in the absence of any liquid. Another challenging possibility is that of direct measurement of the enthalpy of mixing of gases for example by generating two separate streams of vapour and mixing them in a flow calorimeter. The molar enthalpy of mixing  $H^E$  is given for dilute gases by the relation

$$H^E = x(1 - x)(\delta_{12} - Td\delta_{12}/dT)p \quad (6)$$

where  $\delta_{12}$  is defined by

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (7)$$

The properties of dense gaseous or liquid mixtures still of course depend on the same three pair-interaction energies  $u_{11}(r)$ ,  $u_{12}(r)$ , and  $u_{22}(r)$ , but in a way which is only just beginning to be understood and which is probably much more complicated than for dilute gaseous mixtures. Recent theories<sup>15-17</sup> of such fluid mixtures form a family depending on the assumption of the principle of corresponding states, and so should apply best to mixtures of the Group 0 elements, and other simple gases like methane and nitrogen having nearly central force-fields. These theories have inspired a whole lot of splendid new experimental work on the thermodynamic mixing properties of binary liquid mixtures of the substances Ar, Kr (but not Xe yet), CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub>, and CO, at temperatures round 90°K near their normal boiling points. This work has been reviewed in several places<sup>18, 19, 12</sup>. Calorimetric measurements of the enthalpies of mixing of these substances will be briefly discussed later on in this lecture.

So far work on mixtures of these substances has been confined almost entirely to pressures of 1 atm or less. There is an urgent need for  $pVTx$  measurements on such mixtures at higher pressures and especially over the region of gas-liquid coexistence including of course the critical region<sup>20</sup>. Flow calorimetry could make a valuable contribution here but has as yet rarely been used for such studies. An exception is the work of J. M. Smith and his colleagues<sup>21</sup>

who have used a flow calorimeter to measure the enthalpy as a function of pressure through the coexistence region for mixtures of more complex molecules such as benzene + ethanol.

### ENTHALPIES OF MIXING OF LIQUIDS

The enthalpy of mixing of a liquid mixture arises, like the other thermodynamic excess functions, from the usually subtle effects of replacing some of the 1-1 and some of the 2-2 interactions in the unmixed liquids by 1-2 interactions in the mixture. Here, as elsewhere in this paper, it seems rather artificial to be prevented by the title from more than a surreptitious glance at non-calorimetric measurements. However, an excuse is provided by the inclusion in Session III of Paper III: 13 by Murgulescu and Vilcu on the elevation of the boiling point of water by small quantities of mannitol. In the study of liquid mixtures enthalpies of mixing are of course important, but no more so than say volumes of mixing. Many of the most interesting measurements of enthalpies of mixing have in fact been published as parts of wide-ranging studies of the excess functions of particular mixtures<sup>22</sup>, and it is to be hoped that this practice will continue to spread. The temperature derivative  $\partial H^E/\partial T = C_p^E$  of the enthalpy of mixing  $H^E$  is at least as interesting as  $H^E$  itself, and it is good to report an enormous increase in our knowledge of this quantity<sup>23</sup> since the present author plotted almost all that was then known about the temperature dependence of  $H^E$  about three years ago<sup>24</sup>. Several papers in Session III make further contributions to our knowledge of  $C_p^E$ . The pressure derivative  $\partial H^E/\partial p = (V^E - T\partial V^E/\partial T)$  of  $H^E$  is also very interesting, but has never yet been measured calorimetrically (and for that matter  $\partial V^E/\partial T$  has only rarely been measured by any other method), though it should not be much more difficult to measure  $H^E$  at given temperature and several pressures, than it is to measure it at given (low) pressure and several temperatures. As an example, the enthalpy of mixing of n-hexane + n-hexadecane at 35° and 1 atm is about 80 J mole<sup>-1</sup> while at 35° and 100 atm it would be<sup>25</sup> about 110 J mole<sup>-1</sup>.

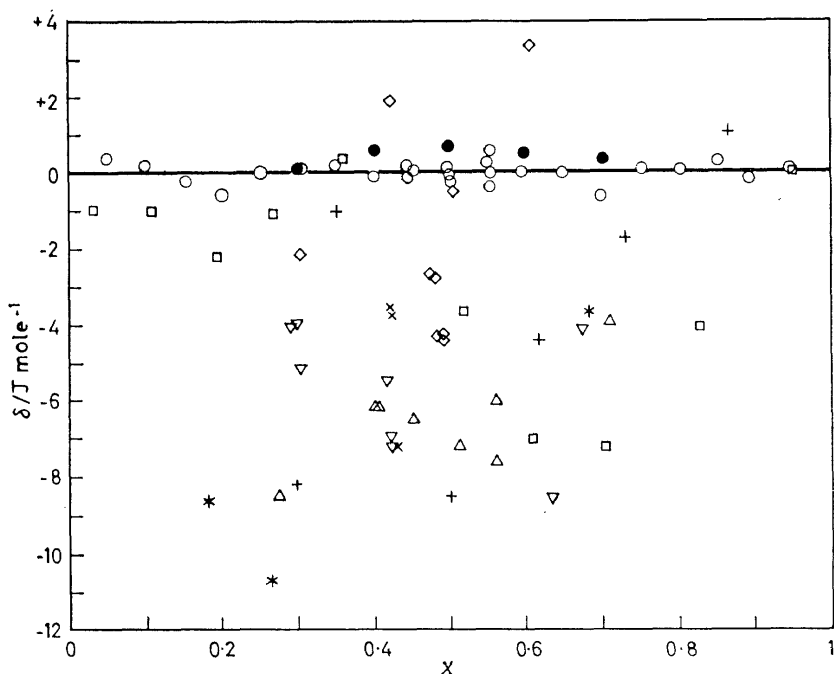
In principle, values of  $H^E$  can be obtained by use of the Gibbs-Helmholtz relation

$$H^E = G^E - T\partial G^E/\partial T \quad (8)$$

from values of the excess Gibbs function  $G^E$  calculated from the results of vapour-pressure measurements (corrected for deviations of the vapour phase from a perfect gas) at several temperatures. Even in the few cases where allowance for gas imperfection can be accurately made to vapour-pressure results of the highest precision, however, values of  $H^E$  obtained by use of equation (8) are notoriously inaccurate, and the temperature derivative  $C_p^E$  of  $H^E$  often does not even have the right sign. This reason for the importance of direct calorimetric measurements of  $H^E$  has been emphasized again by Swinton in Paper III: 11 in connexion with the extremely precise vapour-pressure measurements of Everett and Swinton<sup>26</sup> on mixtures of cyclohexane + bicyclohexyl. When  $G^E$  and  $H^E$  have both been measured over a range of temperatures the results should be analysed<sup>27</sup> by integration of  $H^E$  rather than by differentiation of  $G^E$ . Indeed it is doubtful whether it is ever worth while to measure  $G^E$  at more than one temperature.

## CALORIMETRY OF NON-REACTING SYSTEMS

During the last three years or so there has been a striking increase in the annual crop of  $H^E$  measurements<sup>23</sup>. The accuracy of many of the published measurements, however, still leaves much to be desired. Whereas values of the enthalpy of combustion of benzoic acid measured in several different laboratories agree within one or two hundredths of one per cent<sup>28</sup>, there is probably still no pair of liquids for which values of the enthalpy of mixing measured in several different laboratories agree even within one or two per cent. Far too many calorimeters have been "proved" by the agreement of measurements with one particular previous set of measurements on some pair for which the various sets of apparently reputable measurements spread over a range of as much as ten per cent of  $H^E$  (see, for example, *Figure 1*). I wonder whether some of us should not join forces in a thorough study of  $H^E$  for one or



*Figure 1.* The excess  $\delta$  of the molar enthalpy of mixing  $H^E$  over the value calculated according to the equation  $H^E/[J \text{ mole}^{-1}] = x(1-x)\{462.6 + 16(1-2x) + 25(1-2x)^2 + 10(1-2x)^3\}$  plotted against the mole fraction  $x$  of carbon tetrachloride at  $25^\circ$

$\circ$ ,  $\bullet$  Ref. 30; the filled circles are the results of a second series of measurements made with different samples.

$\triangle$  G. H. Cheesman and A. M. B. Whitaker. *Proc. Roy. Soc. (London)* **A212**, 406 (1952); corrected from  $24.7$  to  $25.0^\circ$

$\nabla$  G. H. Cheesman and W. R. Ladner. *Proc. Roy. Soc. (London)* **A229**, 387 (1955); corrected from  $24.4$  to  $25.0^\circ$

$\diamond$  M. L. McGlashan and K. W. Morcom. Unpublished measurements made using the calorimeter described by D. S. Adcock and M. L. McGlashan, *Proc. Roy. Soc. (London)* **A226**, 266 (1954), which we now regard as obsolete

$\square$  W. Schulze. *Z. Physik. Chem. (Leipzig)* **197**, 105 (1951).

$\times$  I. Brown and W. Fock. *Australian J. Chem.* **8**, 361 (1955).

$*$  C. P. Brown, A. R. Mathieson, and J. C. J. Thynne. *J. Chem. Soc. (London)* **1955**, 4141.

$+$  H. Hirobe. *J. Fac. Sci. Univ. Tokyo* **1**, 155 (1925).

more carefully chosen pairs of liquids so as to provide a goal for the less ambitious to aim at and for the more ambitious to improve upon. Some of the criteria for the choice of a suitable pair are as follows:

(i) the vapour pressures should be different enough to reveal errors due to the presence of vapour spaces<sup>24</sup>;

(ii) the densities should be different enough to reveal errors due to incomplete mixing<sup>24</sup>;

(iii) the liquids should be easily purified and easily kept pure (*e.g.* not chloroform);

(iv) the temperature coefficient  $C_p^E$  should not be so great as to require measurement of the absolute temperature to better than say  $0.05^\circ\text{K}$ ; and

(v) pairs should be chosen having values of  $H^E$  ( $25^\circ$ ,  $x = 0.5$ ) of say about  $+100$ ,  $-100$ ,  $+1000$ , and  $-1000$  J mole<sup>-1</sup> roughly in order of importance.

The standardizing measurements should be made on the same samples of the chosen liquids interchanged among the several laboratories. The measurements should be made at  $25^\circ$  and at several other selected temperatures. Apart from considerations which apply to any kind of calorimetry, special care should be taken (*a*) to ensure that there are no vapour spaces however small in contact with the liquids, (*b*) that mixing is complete, (*c*) that the process which takes place in the calorimeter is precisely known: for example, the pressure in the calorimeter before and after mixing must be known, and (*d*) that the liquids are not contaminated, for example by exposure to damp air, during the loading of the calorimeter. Neglect of one or more of these considerations has certainly led to serious errors in the past.

The importance of eliminating vapour spaces can be illustrated by reference to a recent controversy<sup>29</sup> about the *sign* of  $H^E$  for an equimolar mixture of n-hexane + n-hexadecane at  $100^\circ$ . According to one view  $H^E$  should have been about  $+10$  J mole<sup>-1</sup> and according to the other (which turned out to be right) about  $-100$  J mole<sup>-1</sup>. For many liquids at room temperature such a controversy could have been settled in a few minutes with two test-tubes and an ordinary thermometer. Let us suppose that we were to try to settle just the sign of  $H^E$  for n-hexane + n-hexadecane at  $100^\circ$  by use of a calorimeter of the kind made from a Dewar flask which has commonly been used in the past to measure enthalpies of mixing. Suppose that  $0.5$  mole (*ca.*  $75$  cm<sup>3</sup>) of n-hexane, and an ampoule containing  $0.5$  mole (*ca.*  $160$  cm<sup>3</sup>) of n-hexadecane, were placed in the flask, and that the space between the liquid surface and the stopper was  $100$  cm<sup>3</sup>. The measured enthalpy change  $\Delta H$  on breaking the ampoule and mixing would then consist of two parts:

$$\Delta H = H^E + \Delta H_{\text{vap}} \quad (9)$$

where  $H^E$  is the required molar enthalpy of mixing and  $\Delta H_{\text{vap}}$  is the enthalpy change due to a change in the composition of the vapour which saturates the air-space. We can evaluate<sup>24</sup>  $\Delta H_{\text{vap}}$  roughly by assuming that the vapour is a perfect gas, that n-hexadecane is completely involatile, that the liquid mixture obeys Raoult's law, and that n-hexane obeys Trouton's rule. Then on mixing, exactly half the n-hexane in the air-space will condense so that

$$\Delta H_{\text{vap}} \simeq -0.5(p_6^\circ V^g/RT)\Delta_e H_6^\circ \simeq -0.5(p_6^\circ V^g/RT)10RT \simeq -5p_6^\circ V^g \quad (10)$$

where  $p_6^\circ$  is the vapour pressure of pure n-hexane,  $V^g$  is the volume of the

air-space, and  $\Delta_e H_6^\circ$  is the enthalpy of vaporization of pure n-hexane. The vapour pressure of n-hexane at  $100^\circ$  is  $2.4 \text{ atm} \simeq 0.24 \text{ J cm}^{-3}$  and  $V^g = 100 \text{ cm}^3$  so that

$$\Delta H_{\text{vap}} \simeq -5 \times 0.24 \times 100 \text{ J} = -120 \text{ J} \quad (11)$$

If the n-hexane had been in the ampoule rather than the n-hexadecane then  $\Delta H_{\text{vap}}$  would have been about  $+120 \text{ J}$  instead of  $-120 \text{ J}$ . In principle of course a correction could be made for  $\Delta H_{\text{vap}}$  if the volume of the air-space were accurately known<sup>24</sup>. In practice, however, the air-space does not come to equilibrium after mixing in the usually short time of a calorimetric experiment and the correction cannot be accurately calculated.

The presence of vapour spaces has no doubt also led to serious errors in measurements of heats of solution which are usually made in calorimeters in which the solvent is in contact with a large air-space.

When I wrote on Heats of Mixing for *Experimental Thermochemistry*, Vol. 2<sup>24</sup>, I had hoped to be able to recommend the widely studied pair benzene + carbon tetrachloride ( $H^E = 116 \text{ J mole}^{-1}$  at  $x = 0.5$  and  $25^\circ$ ) for proving new calorimeters intended for use in that range. Even after some selection the several sets of published results on this pair scattered over a range of about  $10 \text{ J mole}^{-1}$  or 10 per cent of  $H^E$ . We were confident that we could improve on the precision of any previous set of measurements by a factor of about ten, and expected that the older results 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 found<sup>30</sup>, however, as is shown in *Figure 1*, that our values were higher by about  $4 \text{ J mole}^{-1}$  than we had expected. It seems likely that incomplete mixing is responsible for the low values, and no doubt also for some of the scatter, obtained by previous workers. This view has since been largely confirmed by a series of measurements by Lundberg and Redlich<sup>31</sup>. Their results are still systematically lower than ours but only by  $1.5 \text{ J mole}^{-1}$  or less depending on the composition. The remaining discrepancy is almost certainly due to differences in the samples. The moral of this story is that much more attention should be paid to completeness of mixing even when the difference in density is much less than for benzene ( $0.87 \text{ g cm}^{-3}$ ) + carbon tetrachloride ( $1.58 \text{ g cm}^{-3}$ ).

The precise nature of the process occurring in a mixing calorimeter, and the relation of the required enthalpy of mixing  $H^E$  to the quantity of electrical energy needed just to restore the temperature of the calorimeter to its initial value after mixing (corrected of course for thermal leaks and for the work of stirring), have been discussed elsewhere<sup>24</sup>. It will be sufficient here to make three remarks. First, the quantity actually measured in calorimeters such as that of Larkin and McGlashan<sup>30</sup>, which has also been used by Diaz-Peña and Martín (Paper III: 14) and by Swinton (Paper III: 11), and that described by Holleman in Paper III: 6, is  $U^E$  rather than  $H^E$ . Even when there is no change in pressure on mixing, and even when the pressure is only 1 atm, the difference  $pV^E$  may be as large as  $0.1 \text{ J mole}^{-1}$ . It is to be hoped that such a difference will soon be too large to be neglected. Second, and much more important, when there is a change of pressure on mixing there will be a further error which for ordinary liquids at room temperature will usually be at least  $3 \text{ J mole}^{-1} \text{ atm}^{-1}$ . Third, even if the pressure is the same before and

after mixing it is necessary to know what it is, since  $\partial H^E/\partial p$  is for example about  $0.3 \text{ J mole}^{-1} \text{ atm}^{-1}$  for n-hexane + n-hexadecane<sup>25</sup>, and may well be larger for other pairs of substances.

I shall now mention some of the more welcome trends in recent measurements of enthalpies of mixing, and shall then discuss these trends with illustrations taken where possible from papers in Session III. These trends include measurements on "condensed gases" at temperatures far below room temperature, measurements on fused salts and on liquid metals at temperatures far above room temperature, increased attention to the temperature dependence of enthalpies of mixing, increased attention to the study of particular mixtures or families of mixtures chosen because of their suitability for the testing of various theories, and some attention to the enthalpies of mixing of electrolyte solutions.

Ingenuous new calorimeters have been designed and used for measurements of the enthalpy of mixing of "condensed gases" at temperatures far below room temperature by Jeener and others at Brussels<sup>32</sup>, by Staveley and his colleagues at Oxford<sup>33</sup>, and (at temperatures as low as  $20^\circ\text{K}$ ) by Beenakker and his colleagues at Leiden<sup>34</sup>. The results of these measurements have been used to test the family of theories already mentioned above, which depend on the assumption of the principle of corresponding states<sup>35</sup>. This important but difficult field, in which much has been achieved in the last five years but in which much still remains to be done, is unfortunately not represented in this Symposium.

Measurements of the enthalpy of mixing for "ordinary" liquids at ordinary temperatures have of course also been used to test the corresponding-states theories<sup>36</sup>, but more measurements, like those on the tetrachlorides of the Group IV elements<sup>37</sup>, are urgently needed on liquids which can plausibly be regarded as being composed of molecules with spherical force fields. In this connexion we have begun a study at Reading of the thermodynamic excess functions, including the enthalpy of mixing and its temperature dependence, for mixtures of the tetramethyl compounds of some of the Group IV elements.

At the other extreme of temperature there has recently been a vigorous drive, unfortunately as yet unmatched by theoretical advances, into the field of enthalpies of mixing of fused salts and of liquid metals at temperatures far above room temperature. Calorimeters suitable for such work have been designed and used notably by Kleppa and his colleagues at Chicago (up to  $800^\circ$ )<sup>38</sup>, and by Wittig and his colleagues at Munich (up to  $975^\circ$ )<sup>39</sup>. In Paper III: 1 Murgulescu and Marchidan present results, obtained in a calorimeter similar to that of Wittig, for the enthalpies of mixing of lead bromide + lead chloride at  $560$  and  $650^\circ$ , and for potassium chloride + potassium bromide at  $810$  and  $890^\circ$ , and discuss a classification<sup>40</sup> according to the sign and magnitude of  $H^E$  of fused salt mixtures having a common ion. In Paper III: 4 Kleppa, Hersh, and Toguri present some new results for the enthalpies of mixing of sodium chloride + potassium chloride at  $810^\circ$ , sodium bromide + potassium bromide at  $770^\circ$ , and sodium iodide + potassium iodide at  $700^\circ$ , as well as preliminary results for eight alkali halide mixtures with a common cation. They also fully review the enthalpies of mixing of fused salt mixtures having either a common anion or a common cation, in the light of qualitative theoretical arguments about the changes on mixing of the interaction energy of an ion with its next-nearest neighbours. In Paper III: 5 Yokokawa and Kleppa present new results



for the enthalpies of mixing of liquid rubidium + caesium at 112° which they have measured as part of a systematic study of all the binary liquid mixtures formed from sodium, potassium, rubidium, and caesium. For rubidium + caesium  $H^E$  is negative in striking contrast to the positive values found for all the other alkali-metal mixtures.

Several new calorimeters have been designed for measurements of enthalpies of mixing of ordinary liquids over wide ranges of temperature on either side of room temperature<sup>41</sup>. One of the most notable of these is that of Schäfer and Rohr<sup>42</sup> which was used to make the measurements discussed by Schäfer in Paper III: 9. Two other outstanding new calorimeters are described in this Symposium. That of Holleman (Paper III: 6) can be used at temperatures far above the normal boiling points of the liquids. That of Savini and Van Ness (Paper III: 15) has been used to make a prodigious series of measurements on ethanol + n-heptane at 25, 40, and 60°. Their reproducibility ( $\pm 4$  J mole<sup>-1</sup> in values of  $H^E$  of up to about 1200 J mole<sup>-1</sup>) has probably never been surpassed, and has perhaps only been equalled by that claimed by Larkin and McGlashan<sup>30</sup> ( $\pm 0.3$  J mole<sup>-1</sup> in values of  $H^E$  of up to about 100 J mole<sup>-1</sup>). Savini and Van Ness's calorimeter is, however, capable of producing results of this precision in a small fraction of the time needed with any previous calorimeter of comparable precision. It will be interesting to know how successfully this calorimeter can be used at temperatures above the normal boiling point of one (or both) of the components.

Until a few years ago the variation of the enthalpy of mixing with temperature had been little studied, and was tacitly assumed to be small and uninteresting. We now know that  $H^E$  sometimes decreases and sometimes increases with increasing temperature, and that the temperature coefficient is sometimes small and sometimes large<sup>24</sup>. For n-hexane + n-hexadecane we found<sup>29</sup>, in agreement with our prediction<sup>43</sup>, that  $H^E$  decreased from +129 J mole<sup>-1</sup> at 20° through zero at 64° to -95 J mole<sup>-1</sup> at 100°. This finding has now been confirmed by Holleman<sup>44</sup> (and in Paper III: 6) who has also found similar changes of sign for other pairs of n-alkanes. The negative values of  $H^E$  for mixtures of n-alkanes at high temperatures are implied by the existence of lower consolute temperatures which have recently been found<sup>45</sup> for such mixtures at temperatures near the critical temperature of the more volatile component.

Measurements of  $H^E$  for a number of mixtures of n-alkanes have been used<sup>46, 25, 47</sup> to test the lattice theory of mixtures of molecules of different sizes<sup>48</sup>. The lattice theory implies zero volume change on mixing. When values of the excess volume  $V^E$  for these mixtures, and values of the expansivities and compressibilities of the pure n-alkanes, are used to calculate values of the energy  $U_V^E$  of mixing with zero volume change from the measured values of  $H^E$ , it is found that there is close agreement with the predictions of the lattice theory with a single value of the "energy of interchange" for all the mixtures, and also in agreement with the theory that  $U_V^E$  is independent of temperature for a given mixture (compare the strikingly large temperature coefficient and the change of sign of  $H^E$ ). The measurements reported by Swinton in Paper III: 11 on cyclohexane + bicyclohexyl are part of a similar test of the lattice theory of mixtures of molecules of different sizes, in this case with substances chosen to simulate "monomers" and "dimers".

Measurements of  $H^E$  for n-alkanes have also been used to test the principle of congruence<sup>49</sup> according to which there exists a single valued function  $f(n)$  of  $n$  such that at given temperature and pressure any excess function such as  $H^E$  is given for any values of the chain lengths  $n_A$  and  $n_B$  of two n-alkanes A and B, and for any mole fraction  $x$  of B, by the relation

$$H^E(n_A, n_B, x) = f([1 - x]n_A + xn_B) - (1 - x)f(n_A) - xf(n_B) \quad (12)$$

The principle appears to hold quite well for the enthalpies of mixing of n-alkanes at 20°<sup>46, 47</sup>. However, Holleman now shows in Paper III: 6 (and see ref. 44) that it certainly does not hold at 76°, a conclusion which is in strange contrast to that<sup>50</sup> for the volumes of mixing which conform well with the principle at temperatures over the range 20 to 126°. In Paper III: 14 Diaz-Peña and Martín show that the enthalpies of mixing of methanol with five n-alkan-1-ols (C<sub>4</sub> to C<sub>12</sub>) at 25° conform strikingly well with the principle. This extension of the principle to compounds other than n-alkanes points the way to many other such applications. It would be interesting, for example, to know whether the n-perfluoroalkanes obey the principle. It would also be interesting to know with regard to the n-alkan-1-ols whether the agreement is less good, as appears to be the case for the n-alkanes<sup>44, 47</sup>, when both, rather than just one, of the components are changed.

Enthalpies of mixing, and particularly their temperature dependence, are potentially a rich source of information about the formation of complexes in liquid mixtures. Such complexes may be formed by hydrogen bonding or by charge transfer or by dipole-dipole association, and may be of AA or AB types. Paper III: 9 by Schäfer is an excellent example of such a study. He has considered mixtures of a polar substance A with a non-polar substance B and has interpreted his results in terms of dipole-dipole association of the A molecules. In particular he accounts as follows for the positive temperature coefficient of  $H^E$  for methyl bromide + propene between 200 and 238°K, and for the zero temperature coefficient for methyl chloride + propene between 185 and 250°K. At low temperatures  $H^E$  is positive because some of the A molecules, which are bound together by dipole-dipole association, are partly desegregated by the addition of B molecules (which are supposed to have no tendency to segregate unless forced to do so by the segregation of the A molecules). At a higher temperature more of the A molecules are desegregated by the addition of B molecules and so  $H^E$  is larger. At a sufficiently high temperature the A molecules are completely desegregated by the addition of B molecules and so  $H^E$  ceases to increase with further increase of temperature. At a higher temperature still the "normal" decrease of  $H^E$  with increasing temperature takes over, so that  $H^E$  passes through a maximum. An alternative explanation of these results is the assumption that AA dimers are formed in equilibrium with A monomers, and that the three species A, AA, and B form a ternary ideal mixture. The curve in the upper part of *Figure 2* was calculated according to this theory which is thus seen to account for the maximum in  $H^E$  without any assumption about "normal" behaviour.

The lower curve in *Figure 2* shows the temperature dependence of  $H^E$  similarly calculated for an ideal mixture of A, AB, and B. The theory thus accounts for the negative value of  $H^E$ , and for the large positive temperature

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coefficient for such mixtures as chloroform + ether which form hydrogen-bonded complexes<sup>51</sup>. Benzene + carbon tetrachloride are now known<sup>52</sup> to form a charge-transfer complex. Hildebrand and Scott wonder<sup>53</sup> why this does not show up in the thermodynamic excess functions. The answer is that although  $H^E$  is as far as we know positive at all accessible temperatures for

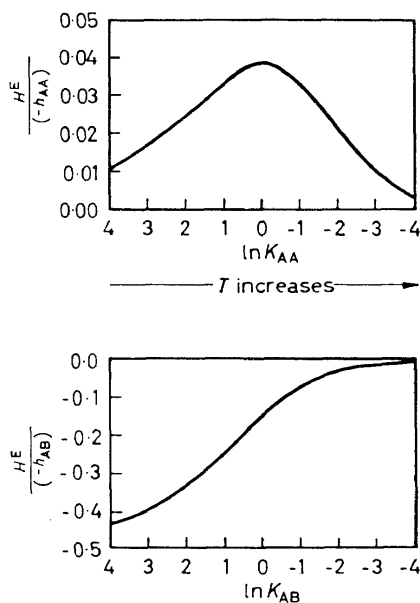


Figure 2. Enthalpy of mixing  $H^E$  for an equimolar mixture of A + B calculated on the assumption that:

(Upper part):  $2A \rightleftharpoons AA$  with equilibrium constant  $K_{AA}$  and enthalpy change  $h_{AA}$ , and the three species A, AA, and B, form a ternary ideal mixture;

(Lower part):  $A + B \rightleftharpoons AB$  with equilibrium constant  $K_{AB}$  and enthalpy change  $h_{AB}$ , and the three species A, AB, and B, form a ternary ideal mixture.

If  $(-h_{AA})$  and  $(-h_{AB})$  are positive, that is if the complexes are formed exothermally, then the temperature increases from left to right in the figure since in each case  $d \ln K/dT = h/RT^2$

this pair, the formation of the complex does show up in the strikingly large positive temperature coefficient of  $H^E$ . The positive value of  $H^E$  results when we add a positive contribution varying only slowly with temperature to take account of the fact that the mixture of the three species A, AB, and B is not really ideal but "regular" in Hildebrand's sense. In this connexion Watts and the present author are at present measuring  $H^E$  as a function of temperature for carbon tetra chloride + benzene, + toluene, + *p*-xylene, and + mesitylene.

Enthalpies of mixing of electrolyte solutions have been studied by Young and his colleagues<sup>54</sup> but by few others. The field is a potentially interesting one which should be further explored. Measurements of enthalpies of dilution of electrolyte solutions are more common and, at least for dilute solutions, more amenable to theoretical treatment<sup>55</sup>. Enthalpies of solvation derived

from measurements of enthalpies of solution of salts by subtraction of the lattice enthalpy have been commonly measured and discussed for aqueous solutions but only rarely for non-aqueous solutions. In Paper III: 10 Somsen presents new results for the enthalpy of solution of eighteen alkali halides in the solvent formamide. He has calculated the enthalpies of solvation and has discussed them in terms of Born's theory according to which the energetics of solvation can be completely accounted for by considering the transfer of the ions from a medium having a dielectric constant of unity to a medium having the dielectric constant of the solvent.

### ENTHALPIES OF SORPTION

In Paper III: 7 Gregg describes four calorimeters suitable for the measurement of the enthalpy of immersion of a solid in a liquid, the most sensitive of them having a precision of 0.02 J. He presents a large number of results for calcined oxides in various liquids and suggests that measurements of the enthalpy of immersion provide a convenient method for the determination of the specific surface of a solid.

In Paper III: 3 Burgess, Duffett, and Minkoff discuss the variation with chain length of the enthalpy of sorption of n-alkanes in molecular sieves, the enthalpy being that derived from their measurements of sorption made at several temperatures with a sorption balance.

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