



RECENT EXPERIMENTAL AND THEORETICAL WORK ON THE THERMODYNAMIC PROPERTIES OF MOLECULARLY SIMPLE LIQUID MIXTURES

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1 — INTRODUCTION

The thermodynamic properties of mixtures of liquids have interested chemists for many years. An enormous amount of experimental information has been amassed, and a great deal of effort has been devoted to developing theories which seek to account for the observed behaviour of such mixtures. These theories have more than academic interest and importance, for the better our understanding of liquid mixtures, the better are the chances of successfully predicting the properties of a particular mixture. Reliable predictions of this kind may have considerable technological value.

The thermodynamic properties of a liquid mixture are generally considered with reference to the corresponding properties of an ideal liquid mixture. The ideal solution, like the ideal gas, is a convenient fiction. In an ideal liquid mixture, the chemical potential μ_i of a component i at a temperature T must obey the equation

$$\mu_i = \mu_i^0 + RT \ln x_i, \quad (1)$$

where x_i is the mole fraction of component i . μ_i^0 is the chemical potential (or Gibbs energy per mole) of the pure liquid i at the temperature T . (Strictly speaking, μ_i^0 is a function of the pressure acting on the system, but most of the experimental work on liquid mixtures has been carried out at low pressures, of the order of one atmosphere, and moderate pressure changes in this region have almost no effect on μ_i^0). If the mixture of the vapours in equilibrium with the liquid mixture can be regarded as a mixture of ideal gases, it follows from eqn. (1) that the partial vapour pressure p_i of component i is given by the equation

$$p_i = p_i^0 x_i, \quad (2)$$

where p_i^0 is the vapour pressure of pure liquid i at the same temperature.

We are concerned in this lecture with real, and hence non-ideal, liquid mixtures, and we shall confine ourselves to mixtures of only two components. If x_1 moles of a liquid component 1 and $(1-x_1)$ moles of a liquid 2 are mixed to give one mole of a solution at a temperature T , then for

any extensive thermodynamic function X , the change ΔX_m in this function is

$$\Delta X_m = X_m - x_1 X_1^0 - (1 - x_1) X_2^0, \quad (3)$$

where X_m , X_1^0 and X_2^0 are respectively the values of X for a mole of the mixture, a mole of pure component 1 and a mole of pure component 2. ΔX_m can also be written as

$$\Delta X_m = X_m(\text{id}) + X^E, \quad (4)$$

where X^E is the excess function. For the Gibbs energy, it readily follows from eqn. (1) that

$$\Delta G(\text{id}) = RT[x_1 \ln x_1 + (1 - x_1) \ln(1 - x_1)]. \quad (5)$$

$\Delta S(\text{id})$ is given by $-R[x_1 \ln x_1 + (1 - x_1) \ln(1 - x_1)]$. From the above criteria of ideality, it follows that if two liquids mix to form an ideal solution, they do so with no enthalpy change (i.e. athermally), and with no volume change. So for a real mixture, we have $\Delta H_m = H^E$, the enthalpy of mixing, and $\Delta V_m = V^E$, the volume increase on mixing. S^E , of course, is given by $(H^E - G^E)/T$. In this review, values of the four excess functions G^E , H^E , V^E and S^E all refer to the formation of one mole of mixture.

G^E , H^E and V^E can all be determined by experiment. Of interest is not only their composition dependence, but also their temperature dependence (at constant pressure) and their pressure dependence (at a constant temperature). The aim of a theory is to calculate these excess functions for particular mixtures. We shall be concerned only with those theories which attempt to do this on the most fundamental basis possible, namely in terms of the intermolecular forces which operate between the molecules involved in a particular system. When such theories began to be advanced — essentially in the years following the Second World War — almost all the experimental data on the excess functions of binary liquid systems then available referred to mixtures of substances which are liquid at ordinary temperatures, involving therefore such compounds as benzene, cyclohexane, tetrachloromethane, *n*-hexane and so on. While the molecules of such substances may be simple to, say, an organic chemist, they are complex and difficult when it is a matter of finding a quantitative expression for the intermolecular energy of a pair of molecules as a function of their

separation. So it at once became clear that these new statistical-mechanical theories of liquid mixtures could only be fairly and usefully tested on mixtures of the simplest and smallest molecules, or in other words on mixtures of liquefied gases. This was the primary consideration which prompted the initiation and development of the kind of experimental cryogenic work discussed in this lecture.

2 — EXPERIMENTAL METHODS

We shall not give a detailed account of the experimental methods for measuring G^E , V^E and H^E for liquid mixtures, but simply indicate the nature of these methods and draw attention to one or two salient points. G^E is determined by measuring the vapour pressure of mixtures of known composition. An equation connecting G^E with the mole fraction x of one component is assumed, such as the Redlich-Kister equation

$$G^E = ARTx(1-x)[1 + B(2x-1) + C(2x-1)^2 \dots] \quad (6)$$

and the experimental results are then used to determine A, B, C, \dots . If the composition of the vapour in equilibrium with a liquid mixture is also measured, G^E can be evaluated without having to assume any specific form of equation connecting G^E and x . But in either event, it is essential to allow for the imperfection of the vapour phase. To deal adequately with this for pressures up to a few atmospheres it is not necessary to proceed beyond the second virial coefficient. There is, however, a serious shortage of experimental data on even the second virial coefficients of gas mixtures at low temperatures, and indeed even for some of the pure gases themselves, and work to remedy this deficiency would be valuable.

V^E is most commonly determined by the straightforward method of measuring the amount of each gas needed to fill a pycnometer at a known low temperature with a mixture of known composition. Recently, HAYNES and HIZA (1976, 1977), have described a magnetic method in which the quantity measured is the magnetic field required to balance the gravitational force on a barium ferrite cylinder immersed in the liquefied gas mixture. This method can be used to 50 atmos-

pheres, and clearly has considerable potential. Another method, developed by SINGH and MILLER (1978), depends on measurements of the dielectric constant (permittivity) of the pure and mixed liquids, assuming the Mosotti-Clausius correlation between this property and the molar volume. All of these methods are capable of a precision of a few parts in 10^4 .

The determination of H^E has proved to be more difficult. It can be deduced from measurements of G^E at more than one temperature, using the relation

$$(\partial G^E / \partial T)_p = -H^E / T^2, \quad (7)$$

but a direct calorimetric method is to be preferred. My collaborators and I have constructed a series of calorimeters for measuring the enthalpy of mixing of two liquefied gases (see, e.g., LEWIS *et al.*, 1975). Known amounts of each pure component are liquefied into separate cavities. The two cavities are separated by a valve, and together form a closed system. Mixing is accomplished by opening the valve and shaking the whole cryostat. An indication of the sort of results obtained is shown for the system argon-methane in fig. 1.

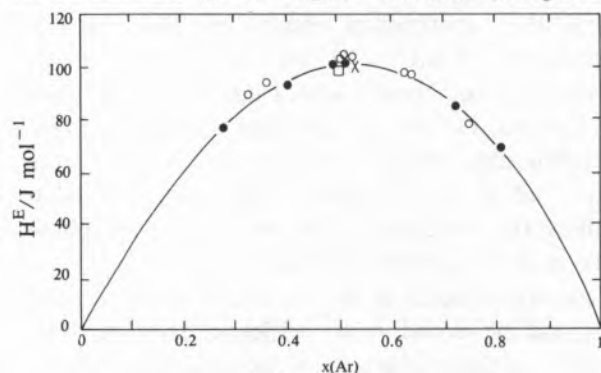


Fig. 1

Excess enthalpy H^E for the $\text{Ar} + \text{CH}_4$ system at 91.5K. Full circles, LEWIS, SAVILLE, STAVELEY (1975); open circles, LAMBERT and SIMON (1962); square, MATHOT (1958); cross, JEENER (1957)

The accuracy is ~ 1 to 2 per cent. A similar calorimeter has been more recently constructed by Professor W.B. Streett at Cornell University. This is more completely automated, and the mixing of the two liquids is effected by a rotating stirrer. This instrument is already giving results of higher precision. However, the vapour phase cannot be wholly eliminated from such calorimeters (unlike those operating at room temperature), and the corrections which have to be made on this

account become increasingly more serious as the critical region is approached. Eventually it is necessary to change to a different type of calorimeter such as a flow calorimeter, even though these require considerably larger amounts of substance (see, e.g., MOSEDALE and WORMALD, 1977). The effort required to obtain reliable values of H^E has undoubtedly been worthwhile. In the first place, H^E (and likewise S^E) can be described as a more sensitive function than G^E . As just one example of what is meant by this, we may cite a result arising from studies of the equation of state of pure and mixed liquefied gases to which we shall refer later (Section 6(c)). From such studies on a system for which the excess functions are known for some low (effectively almost zero) pressure, it is possible to calculate how these excess functions will change with increasing applied pressure. A typical result is shown in fig. 2

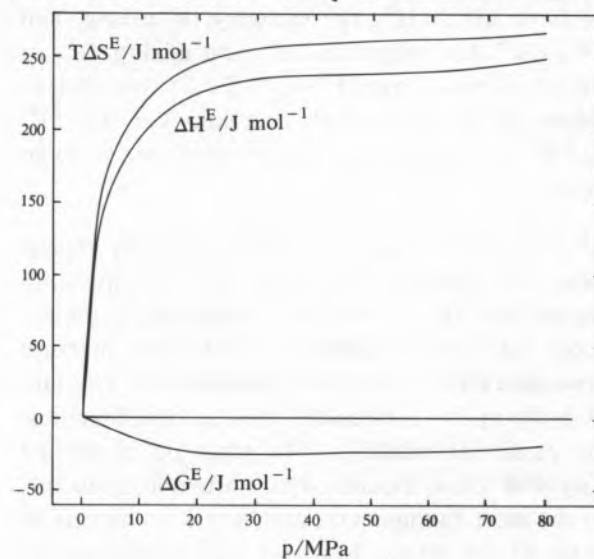


Fig. 2

The effect of pressure on the excess functions of an approximately equimolar mixture of $\text{N}_2 + \text{CH}_4$ at 115K (NUNES DA PONTE *et al.*, 1978)

for the nitrogen-methane system. It will be seen that the changes with pressure in H^E and TS^E are altogether larger than those in G^E . In theoretical predictions of these functions, if a theory gives an expression from which G^E can be calculated, to estimate H^E and S^E it is necessary to go further and evaluate $(\partial G^E / \partial T)_p$, which clearly makes a reasonably successful prediction of H^E and S^E a more exacting undertaking than the prediction of G^E . Another reason which makes H^E data

highly desirable relates to the so-called combining rules. The intermolecular energy curve for a pair of molecules is often characterized by the parameters ϵ and σ , ϵ being the depth of the potential well and σ the separation at which the energy is zero. Since in a mixture of two components 1 and 2, the three pair interactions 1-1, 2-2 and 1-2 have to be considered, the problem arises of the relation between ϵ_{12} and σ_{12} for the unlike pair and the corresponding parameters for the two like pairs. It has been recognized for some time that the original Lorentz-Berthelot combining rules, namely

$$\sigma_{12} = 1/2(\sigma_{11} + \sigma_{22}) \text{ (Lorentz)} \quad (8)$$

and

$$\epsilon_{12} = (\epsilon_{11} \epsilon_{22})^{1/2} \text{ (Berthelot)} \quad (9)$$

are not adequate, and must be modified by introducing parameters j_{12} and k_{12} , such that

$$\sigma_{12} = 1/2(1 + j_{12})(\sigma_{11} + \sigma_{22}), \quad (10)$$

and

$$\epsilon_{12} = (1 - k_{12})(\epsilon_{11} \epsilon_{22})^{1/2} \quad (11)$$

It transpired that the calculated excess functions are sensitive to the values of j_{12} and k_{12} (especially the latter), small though these values may appear to be. In the absence of a general reliable method for estimating j_{12} and k_{12} , one is forced to sacrifice two pieces of experimental information to fix these parameters, for example one value of G^E (for a certain concentration and temperature), and similarly one value of V^E . If, therefore, the experimental data available for testing the theory are limited to G^E and V^E , there is little left to test. There remain only the concentration dependence of G^E and V^E (which is often almost symmetrical anyway, at least for G^E), and their values at other temperatures. If H^E is also known, however, the situation is much improved.

3 — SOME OBSERVATIONS ON CURRENT MOLECULAR THEORIES OF SOLUTIONS

It would need considerable space to do justice to all the theories relevant to our subject, and our comments here must necessarily be brief. There are

two systems of absolutely fundamental importance on account of their extreme molecular simplicity, namely Ar + Kr and Kr + Xe. Considerable quantitative success has now been achieved in the theoretical treatment of these two systems, as was described by Professor Calado in his plenary lecture delivered at the conference held in 1979 at Santiago de Compostela (CALADO, 1983). Two other very basic systems are Ar + CH₄ and Kr + CH₄, since the methane molecule, while not of course monatomic, is compact, highly symmetrical, and has no dipole or quadrupole moment. In recent years, my own experimental interest has been in studying systems the molecules in which, while remaining small, have dipoles, quadrupoles or octupoles. Such studies can be regarded as forming a planned programme through stages of increasing molecular complexity, which should eventually link up with the more complex molecules of substances liquid at ordinary temperatures. In the early stages of this experimental programme, Gubbins and Gray and their collaborators developed a perturbation theory of solutions designed to examine the effect on the excess functions of dipoles, quadrupoles and octupoles in the molecules of one or both components, and also of anisotropy in the dispersion and repulsive forces (TWU *et al* and FLYTZANI-STEPHANOPOULOS *et al.*, 1975). Their theory has now been tested in a series of joint publications on several of the systems which we have investigated experimentally.

The types of system which have been studied experimentally, with examples of the actual systems chosen, are the following: — non-polar — dipole (Xe + HCl; Xe + HBr); dipole-dipole (HCl + HBr); non-polar-quadrupole (Xe + N₂O; Ar + N₂; Ar + O₂); non-polar-octupole (Xe — CF₄); dipole-quadrupole (HCl + N₂O); quadrupole-quadrupole (N₂O + C₂H₄); dipole-octupole (HCl + CF₄).

A perturbation theory, such as that developed by Gubbins and Gray, treats the real system by starting with a simpler system as a reference, and then converting this into the real system, as it were, by introducing a suitable kind of perturbation. Thus, the reference system might be a mixture of hard spheres, or of molecules such as argon and krypton for which the intermolecular pair potentials are functions only of the intermole-

cular separation (*i.e.* there are no orientational factors involved), and can be adequately represented by some relatively simple expression, such as a Lennard-Jones potential (12-6 potential). The perturbation then takes the form of the introduction into the molecules of one or both components of a dipole, a quadrupole or an octupole, and it also becomes necessary even for a simple diatomic molecule like nitrogen to allow for the angular dependence of the dispersion and repulsive (overlap) forces. Here it must be pointed out that a dipolar molecule like HCl also has a quadrupole moment, and it is found that the influence of this quadrupole moment is by no means negligible. It is of paramount importance to construct intermolecular potential functions for the molecules involved which are as good as possible, that is which give the best representation of, or the best consistency with, the bulk properties of the pure polar components. It might be thought that we are dealing with substances which are so simple and so well-known that all the necessary information on their bulk properties would be available. But this is by no means always the case. For HCl, for example, it would be invaluable to have *p*-*V*-*T* data on the liquid up to, say, 1000 bar, from which the configurational energy could be calculated as a function of volume. So here is a field in which the experimentalist can make a valuable contribution.

The first thermodynamic function to be calculated is the Helmholtz energy *A*, which is expanded in terms of the perturbing potential — not as a series, which generally converges too slowly, but as the Padé approximation

$$A = A_0 + A_2 \left[\frac{1}{1 - A_3/A_2} \right], \quad (12)$$

where *A*₀ is the value of this function for the reference potential. (The term *A*₁ vanishes with a suitable choice of the reference potential). The required excess functions of the mixture are derived from *A* using standard thermodynamic relations.

4 — COMPARISON OF THEORY AND EXPERIMENT FOR SOME SELECTED SYSTEMS

As our first example, we take the system Xe + HCl (CALADO *et al.*, 1975, 1978). Generally,

the comparison of theory and experiment is made by comparing the actual and calculated values of the excess functions, but in fig. 3 the predicted

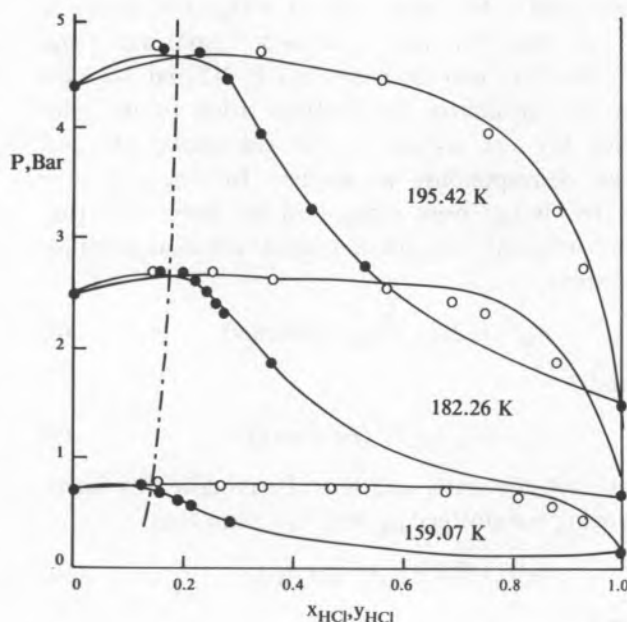


Fig. 3

Vapour — liquid equilibria for the system Xe + HCl from theory (lines) and experiment (points). The dash-dot line is the azeotropic locus. The open circles and *x*_{HCl} refer to the liquid phase, the full circles and *y*_{HCl} to the vapour phase. (CALADO *et al.*, 1978)

and measured behaviour of this very non-ideal system is shown on a different basis, namely as plots of the total vapour pressure against the composition of liquid and vapour phases at three different temperatures. The problem of the indeterminate parameter in the cross-interaction potential (in effect, the *k*₁₂ of eqn. (11)) was resolved by assuming the experimental value of the vapour pressure for the equimolar mixture at the highest temperature. The agreement between the calculated and experimental curves in fig. 3 is impressive, and the same is true for *V*^E. When, however, the comparison is made for the function *H*^E (which earlier was described as being more “sensitive”), the outcome is rather different. Two calculated curves are shown in fig. 4, neither in close agreement with experiment (LOBO *et al.*, 1980). As already pointed out, the HCl molecule has both a dipole moment (*μ*) and a quadrupole moment (*Q*). Curve (a) in fig. 4 was calculated by incorporating the four terms *μμ*, *μQ*, *Qμ* and *QQ* in the intermo-

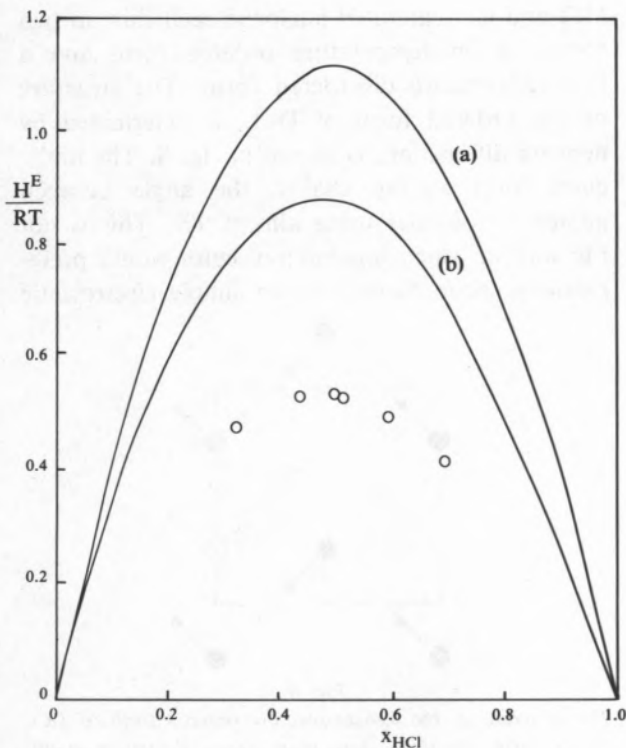


Fig. 4

Comparison of experimental values of H^E for the system $\text{Xe} + \text{HCl}$ at 182.32K (open circles) with those calculated using two potential models (a) and (b) (LOBO *et al.*, 1980)

lecular potential, but ignoring the anisotropy of the dispersion and overlap terms, whereas in the calculations leading to curve (b) this anisotropy was allowed for. This is an example of the sensitivity of a calculated H^E to the details of a theoretical treatment. The HCl molecule, in fact, has a deceptive simplicity, a point to which we will return later.

An example — and it is not the only one — where the theory of Gubbins and his collaborators achieves a notable success is with the non-polar-octupole system $\text{Xe} + \text{CF}_4$ (fig. 5, LOBO *et al.*, 1981). Here the agreement between the experimental and calculated H^E results is excellent. Once again, the value of G^E for the equimolar mixture has had to be sacrificed to deal with the indeterminate intermolecular energy parameter.

Systems of two quadrupolar molecules can be of two kinds, depending on whether the quadrupoles of species 1 and 2 have the same sign, or opposite signs. The way two quadrupolar molecules tend to associate is different, according to whether the signs of the two quadrupoles are the same or not

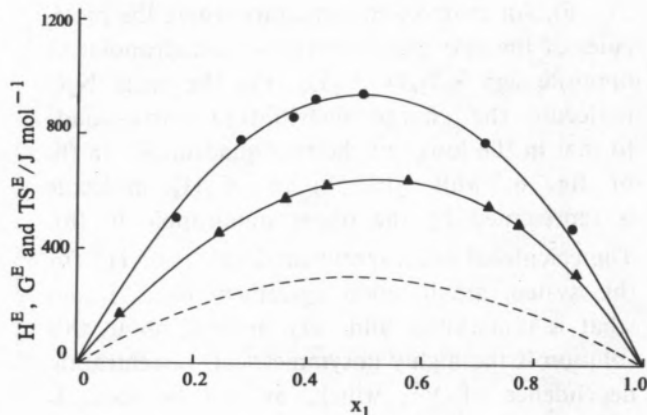


Fig. 5

G^E at 159.01K (triangles) and H^E at 163.01K (circles) for $\text{Xe} + \text{CF}_4$ plotted against x_1 , the mole fraction of xenon. Points are experimental results, the solid lines are calculated. The dashed line is TS^E . (LOBO *et al.*, 1981)

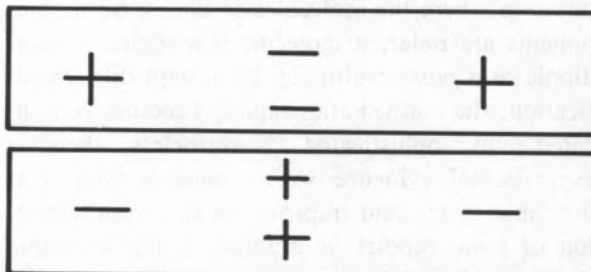
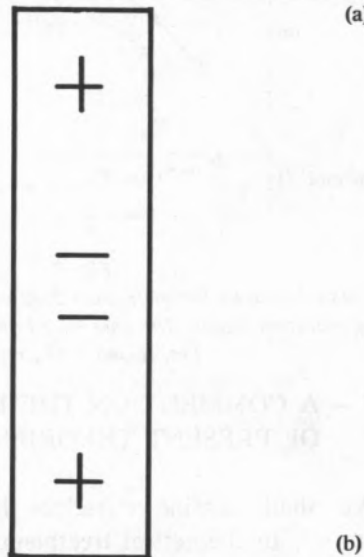
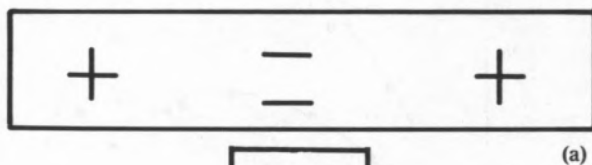


Fig. 6

Showing the preferred orientation for two quadrupoles of (a) the same sign, (b) of opposite sign

(fig. 6). An example of a mixture where the molecules of the two components have quadrupoles of opposite sign is $\text{N}_2\text{O}-\text{C}_2\text{H}_4$. For the linear N_2O molecule the charge distribution corresponds to that in the lower of the two quadrupoles in (b) of fig. 6, while that in the C_2H_4 molecule is represented by the upper quadrupole in (b). The calculated and experimental values of H^E for this system are in good agreement (fig. 7), but what is remarkable and very unusual about this solution is the highly unsymmetrical concentration dependence of V^E , which, as will be seen, is not reproduced by the theoretical calculations (LOBO, STAVELEY, CLANCY and GUBBINS, unpublished work, reference [27]).

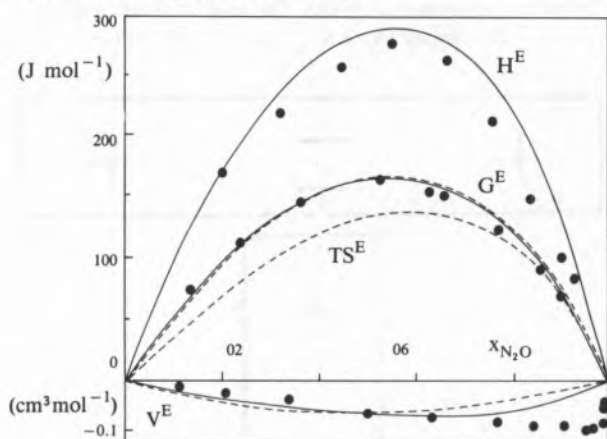


Fig. 7

Excess functions for the system $\text{N}_2\text{O}+\text{C}_2\text{H}_4$. The points are experimental results. The lines have been obtained by calculation. (LOBO et al., ref. [27])

5 — A COMMENT ON THE LIMITATIONS OF PRESENT THEORIES

We shall confine ourselves here to just one matter. In theoretical treatments of binary liquid mixtures where the molecules of one or both components are polar, a molecule is assigned a *point* dipole or a *point* multipole. Even with this simplification, the mathematics rapidly becomes complicated and sophisticated. Nevertheless, there is experimental evidence which suggests that it is desirable to try and improve on this approximation of *point* dipoles or multipoles. For example, the way in which two or more HCl molecules associate suggests hydrogen bonding rather than simple electrostatic attraction. In the solid state,

HCl and its deuterated analogue each exist in two forms, a low-temperature ordered form and a high-temperature disordered form. The structure of the ordered form of DCl , as determined by neutron diffraction, is shown in fig. 8. The molecules form zig-zag chains, the angle between adjacent molecules being almost 90° . This is not the way in which dipolar molecules would preferentially group themselves on simple electrostatic

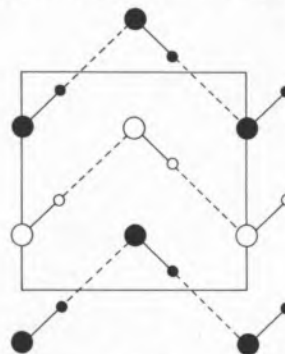


Fig. 8

The structure of the low-temperature ordered form of DCl . Large circles, chlorine atoms, small circles, deuterium atoms. The chains lie in the ab planes, the spacing between the planes for the open and full circles being $c/2$. (after SÁNDOR and FARROW, 1967)

grounds. The structure does, however, strongly suggest that the real ordering force is attraction between the proton or deuteron and the negative charge offered by a pair of unshared electrons in a p-orbital of the chlorine atom.

In the low-temperature ordered form of HCl and DCl the orientational ordering is of course long-range. The high-temperature cubic form is orientationally disordered, and the liquid no doubt still more so, but neutron scattering studies have indicated that the same kind of ordering persists on a *local* scale even above the melting-point (BOUTIN and SAFFORD, 1964). It therefore seems that an intermolecular potential for $\text{HCl}-\text{HCl}$ interaction which is to be used to treat the properties of liquid HCl and its mixtures should be based on a model which does not simply assign a point dipole to the molecule, but has charges so distributed within it as to simulate the tendency to form a hydrogen bond between a proton and a pair of p electrons. Perhaps the cause (or part of the cause) of the discrepancy between the experimental and calculated H^E values for the $\text{HCl}-\text{Xe}$ system (fig. 4) is to be found here.

As a second example of the point under discussion we may cite the remarkable results obtained by CALADO and his coworkers for the system Xe-C₂H₆ — remarkable, in that all four excess functions G^E , H^E , S^E and V^E are negative. Thermodynamically, this is an indication of some special kind of attraction or association between a xenon atom and an ethane molecule. The ethane molecule has a quadrupole moment, and the xenon atom is the most polarisable of the rare gas atoms, so inevitably quadrupole — induced dipole attraction must be an important term in the Xe-C₂H₆ potential. But it is doubtful if any of the present theories could or would predict negative values for all four excess functions. The implication of the experimental results is that there is some especially favourable factor giving attraction between Xe and C₂H₆ molecules. Perhaps the spatial charge distribution in the ethane molecule happens to be particularly effective in relation to the size of the xenon atom, in which case once again a more detailed model will be required to do justice to the situation.

6 — POSSIBILITIES FOR FURTHER EXPERIMENTAL WORK

In this Section some suggestions are advanced for further work. The number of binary systems composed only of relatively simple molecules is of course limited by the number of suitable substances available. From what has been said in previous Sections it will be clear that for any one system, through the necessity of having to use some of the thermodynamic data to fix otherwise indeterminate parameters in theoretical expressions for the excess functions, it is desirable to make the experimental study as complete as possible. Some developments in the experimental field which might prove fruitful will be considered under four headings.

6.1 — MORE DETAILED STUDIES OF SYSTEMS FOR WHICH NOT ALL THE PRIMARY EXCESS FUNCTIONS HAVE SO FAR BEEN DETERMINED

The function for which information is most commonly lacking is H^E . It is still not available, for example, for the very important system Kr-Xe.

Moreover, H^E can have a sensitive dependence on temperature (see (b.2) below), and therefore if possible it should be measured at more than one temperature.

An interesting system for which at present only G^E is available is Kr-NO. The importance of this mixture is that the NO molecule, having one unpaired electron, can associate with another molecule to form a dimer, but not any higher aggregate. It is therefore perhaps the simplest liquid mixture of two components one of which can associate to a dimer, and the best therefore on which to test a theoretical treatment of such association. CALADO and STAVELEY (1979) measured the vapour pressure of Kr-NO mixtures, which depart strongly from ideality, and in interpreting their results took into consideration both the dimerisation and what might be called the more general causes of non-ideality. They concluded that the latter were responsible for about 40 per cent of the observed non-ideality, and the dimerisation for the rest. Comparison of the calculated total vapour pressure with the experimental values is shown in fig. 9. It would be useful to have H^E and V^E data as well, since this could provide more information about the dimerisation, and a study of the similar system CH₄-NO would also be worthwhile.

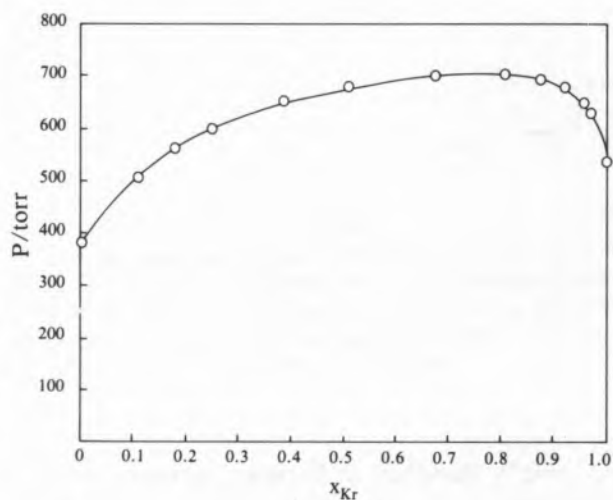


Fig. 9

Total vapour pressure of the system Kr+NO as a function of the krypton mole fraction x_{Kr} . The curve is calculated, and the points are the experimental results. (CALADO and STAVELEY, 1979)

6.2 — EXTENSION OF THE TEMPERATURE RANGE

In principle, a complete study of any one binary system would start at the lowest possible temperature (set by the melting-points of the components), and cover a sufficient range of temperature to pass through the critical region, so that finally the mixture would be one of two gases. Some of the systems considered in this review have been studied at two temperatures and a few at three, but for many the information on the excess functions still relates to just one temperature. Striking changes can take place as the critical region of one component is approached. Two illustrations may be given, one relating to H^E for the Ar-CH₄ system (fig. 10) and the other to V^E for the N₂-CH₄ system (fig. 11). Fig. 10 combines results obtained with a calorimeter of the

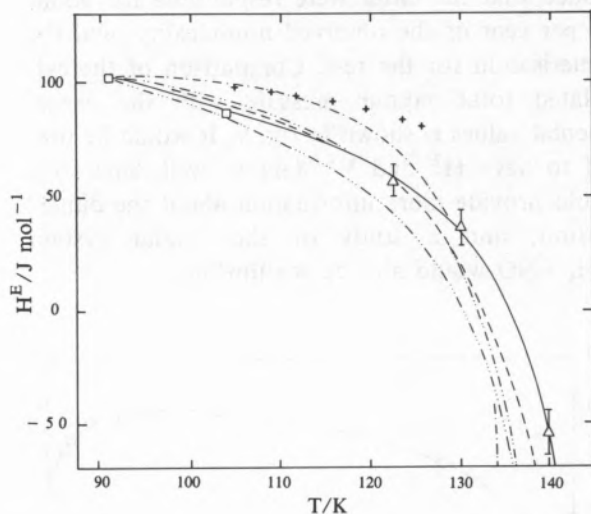


Fig. 10

Showing the effect of temperature on H^E for equimolar mixtures of Ar + CH₄. Squares, experimental results of LEWIS *et al.* (1975); triangles, experimental results of MOSEDALE and WORMALD (1977). The crosses and the various curves have been obtained by calculation

type briefly described in Section 2 (LEWIS *et al.*, 1975) with results produced by flow calorimetry (MOSEDALE and WORMALD, 1977). It will be seen that before the critical temperature of argon (151K) is reached, H^E has changed sign and the mixing process has become exothermic. As for V^E

for N₂-CH₄ mixtures, as the critical temperature of nitrogen (126K) is approached, the contraction on mixing the two components increases considerably. However, it must be pointed out that when the vapour pressure of the mixed liquids exceeds ~ 10 atmospheres, the determination of G^E becomes ever more difficult owing to the increasing importance of the non-ideality of the vapour phase and the difficulty in adequately allowing for this.

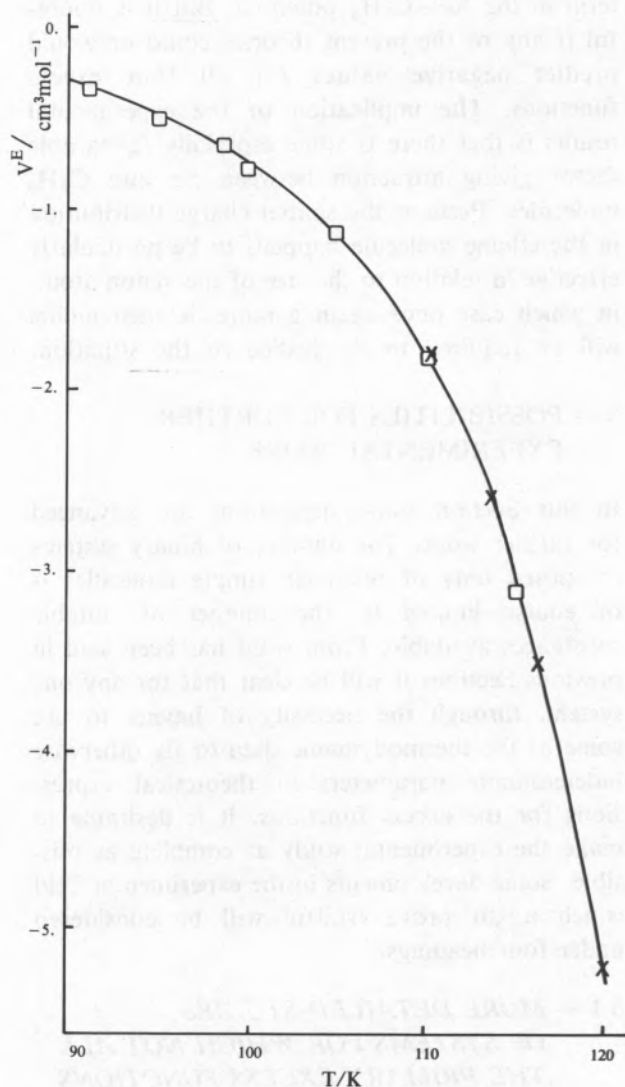


Fig. 11

Temperature dependence of V^E at the saturation vapour pressure for equimolar mixtures of N₂ + CH₄. Squares, LIU and MILLER, 1972; crosses, NUNES DA PONTE *et al.*, 1978

6.3 — STUDIES OF THE EFFECT OF PRESSURE ON THE EXCESS FUNCTIONS

p-V-T studies have now been made on a few mixtures of liquefied gases up to pressures of the order of 10^3 atmospheres, and are being actively pursued both in Lisbon and at Cornell University. The first experiments of this kind were made in the USSR. The systems which have been studied so far include Ar+Kr (BLAGOI and SOROKIN, 1969; BARREIROS *et al.*, 1982), and $N_2 + CH_4$ (NUNES DA PONTE *et al.*, 1981). An example has already been given in fig. 2 of the sort of information which has emerged from this work. From the molecular point of view the consequence of applying pressure to a liquid mixture is to change the balance between the intermolecular forces of attraction and repulsion, the latter becoming increasingly important. The value of V^E at sufficiently high pressures tends to approach a fairly constant, small limiting positive value, which is rather a direct way of getting information about the parameter j_{12} modifying the Lorentz rule (eqn. (10)). In more general terms, the data resulting from these equation of state studies of pure and mixed liquefied gases really add another dimension to the material available for testing theories, and such studies are undoubtedly very valuable.

6.4 — SOME POSSIBLE "NEW" SYSTEMS

It has already been pointed out that the apparent simplicity of the HCl molecule as a small molecule with a dipole moment may be deceptive, in that the attraction between these molecules should be considered as a case of hydrogen bonding rather than as simply involving the electrostatic attraction of two dipoles. For a model system on which to test the consequences of the molecules of one component having a dipole moment, it would be better if this component is not a hydride. Its dipole moment must not, however, be too small, since the excess functions have a rather sensitive dependence on the moment μ , G^E , for example, increasing more rapidly than μ^2 (CHAMBERS and McDONALD, 1975). The choice, therefore, of a "good" dipolar molecule is very limited. A possible candidate is ClF, which has a dipole moment

of 0.88 Debye and a reasonably long liquid range, the melting-point being 117K and the normal boiling-point 173K. Systems which would appear to be worth investigating are $Cl_2 + ClF$ and $Xe + ClF$, and also $Xe + Cl_2$. (All three systems could be studied at the same temperature).

H_2S is a fairly simple polar molecule, but in the low-temperature form of the crystal the molecules are again arranged in a way implying hydrogen-bonding, so that the disadvantages associated with HCl probably apply to H_2S too. Nevertheless, systems like $Xe + H_2S$ and $HCl + H_2S$ would be worth studying.

Another respect in which the availability of suitable molecules proves to be rather frustrating is in attempts to make systematic studies of the effect of changing the relative sizes of the molecules of the two components. This is not surprising, of course, since compounds which are gaseous at ordinary temperatures do not have very large molecules. SF_6 is a possibility worth considering for providing a relatively large molecule, the molar volume of the liquid at its melting-point being about 75 per cent greater than that of xenon at its triple-point. A practical disadvantage of SF_6 is its comparatively high melting-point and triple-point pressure (222K and 2.2 atmospheres respectively). The SF_6 molecule is interesting in that it is of such high symmetry that it has no dipole, quadrupole or octupole, the first moment being a hexadecapole. Another relatively large molecule, somewhat similar to that of SF_6 , is that of PF_5 . This substance has a rather more accommodating range (melting-point 190K, normal boiling-point 198K).

Carbon dioxide, having a molecule with no dipole but with a large quadrupole, could be a useful component of a mixture, though again the high melting-point (with which is associated a high triple-point pressure) considerably reduces the useful liquid range — hence the preference for N_2O in our work as an example of a substance with quadrupolar molecules. The molecule COS is worth attention, as having a dipole as well as a quadrupole.

Systems involving the polar pyramidal molecules PH_3 and PF_3 might yield interesting results. The molecule NF_3 , however, although pyramidal, has almost no dipole moment or basic (i.e.

electron donating) properties. NF_3 , moreover, has a long liquid range (melting-point 66K, normal boiling-point 144K). It should therefore be possible to study binary systems of NF_3 and a variety of other substances, e.g. Ar, Kr, Xe, N_2 , O_2 , CO, CH_4 , CF_4 .

Finally, I should like to express my deep appreciation of the honour done to me by the organizers of the International Conference on the Thermodynamics of Mixtures of Non-Electrolytes in giving my name to one of the plenary lectures, and in asking me to deliver the first lecture bearing my name.

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