LENNARD-JONES LECTURE

Recent Experimental and Theoretical Work on Molecularly Simple Liquid Mixtures*

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1 Introduction

The thermodynamic properties of liquid mixtures 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, since they can save the time and money which would be needed to determine the required properties experimentally.

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

$$\mu_i = \mu_i^0 + RT\ln x_i, \tag{1}$$

where x_i is the mole fraction of component i, and 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 equation (1) that the partial vapour pressure p_i of component i is given by the equation

$$p_i = p_i^0 x_i, \tag{2}$$

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

We are concerned in this review with real, and hence non-ideal, liquid mixtures, and we shall confine ourselves to mixtures of only two components. If x_1 moles of

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a liquid 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

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

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

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

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

$$\Delta G_m(\text{id}) = RT[x_1 \ln x_1 + (1 - x_1) \ln(1 - x_1)] \tag{5}$$

Another consequence of equation (1) is that if two liquids mix to form an ideal solution, they do so with no enthalpy change 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 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 at a fixed temperature, but also (for a given concentration of the mixture) 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. Without wishing to decry the value of theories which seek to do this semi-empirically, for example by assuming some particular equation of state, we shall only be concerned with theories which attempt the prediction of the excess functions of a given system on the most fundamental basis possible, namely in terms of the intermolecular forces which operate between the molecules involved in that 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, 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 for a pair of molecules as a function of their separation and mutual orientation. Meanwhile, however, information on intermolecular forces between small molecules was increasing in quantity and quality, and has continued to do so. So it was clear that these new statistical–mechanical theories of liquid mixtures should first be 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 described in this review.

One of the first of the more fundamental theoretical approaches to the liquid mixture problem was based on the cell model pioneered by Lennard-Jones and Devonshire,[1] who used it to calculate the properties of molecularly simple liquids such as liquid argon. In more recent years, increasing use has been made of perturbation treatments, which start from a suitable reference system. For this a frequent choice is the 12–6 fluid, that is a liquid for which the potential energy between any two molecules depends only on their separation and is adequately represented by the famous Lennard-Jones 12–6 potential. The popularity of this choice is largely due to its suitability for computer simulation calculations of the properties of such a fluid. Again, one method of handling the problem of anisotropy presented by non-spherical molecules such as those of nitrogen and ethane is to regard the intermolecular forces as forces operating from *two* centres within a molecule which can be represented by isotropic Lennard-Jones potentials. So, one way and another, the influence of Lennard-Jones in the theoretical field with which we are concerned has indeed been far-reaching.

2 Experimental Methods

A. The Determination of G^E.—G^E is found 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 (6).

$$G^E = ARTx\,(1-x)\,[1 + B(2x-1) + C(2x-1)^2 \ldots] \qquad (6)$$

and the experimental results are then used to determine A, B, C, ... If the composition of the vapour in equilibrium with the liquid mixture is also measured, G^E can be evaluated without having to assume any particular form of equation connecting G^E and x. But in either case, 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.

The importance of correcting for the non-ideality of the vapour phase is strikingly demonstrated by Figure 1, which shows the dependence on composition of the total vapour pressure of liquid mixtures of argon and krypton.[2] It will be seen that the deviations from ideality (*i.e.* from Raoult's law) are small, but also that they are apparently negative at higher argon concentrations. When, however, allowance is made for the non-ideality of the vapour phase (which is tantamount to converting the partial pressures into fugacities), it is then found that the deviations from Raoult's law are positive over the whole composition range.

B. The Determination of V^E.—Most of the published V^E values have been obtained by the straightforward method of measuring the amount of each gas needed to fill

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[1] J. E. Lennard-Jones and A. F. Devonshire, *Proc. R. Soc. London, Ser. A*, 1937, **163**, 53; 1938, **165**, 1.

[2] R. H. Davies, A. G. Duncan, G. Saville, and L. A. K. Staveley, *Trans. Faraday Soc.*, 1967, **63**, 855.

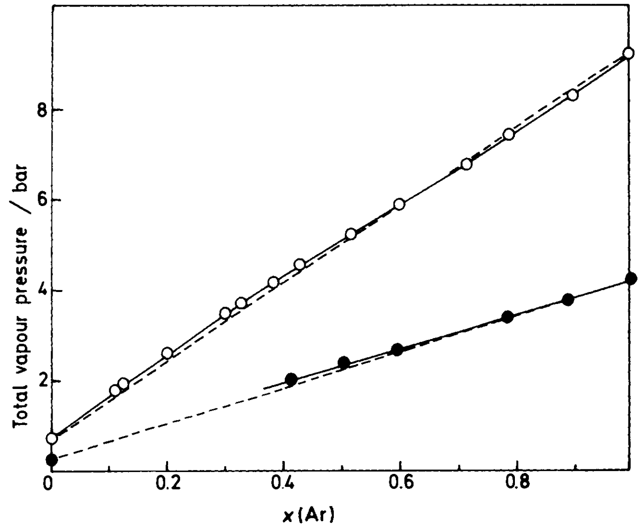

Figure 1 *Total vapour pressure for the* Ar + Kr *system. Upper curve, at* 115.77 K, *the triple-point temperature of krypton; lower curve, at* 103.94 K

a pyknometer of known volume at a known low temperature with a mixture, the composition of which is of course given by the amounts of the two components used to form it. The actual mixing therefore takes place in the pyknometer. The determination of the amount of a component condensed into the pyknometer depends on accurate pressure measurements, which give the pressure drop on removing the gaseous component from a reservoir of known volume maintained in a thermostat near room temperature. V^E values obtained in this way are those for mixing at the saturation vapour pressure of the system at the chosen temperature. Since the liquid level in the stem of the pyknometer has to be seen, the apparatus is made of glass, and generally is not used at vapour pressures above $\sim$ 1.5 MPa. However, this relatively simple technique can be supplemented by studies of the equation of state of pure and mixed liquefied gases to which reference will be made later (Section 2D). The value of such studies is that they enable one to estimate the change with pressure of the excess functions. They can be used to give V^E at a chosen temperature and at the saturation vapour pressure of a particular mixture by extrapolating the p,V isotherm for the mixture back to the saturation vapour pressure. It becomes more difficult to perform this extrapolation accurately, the higher the temperature, owing to the increasing steepness of the p,V isotherms, while at low temperatures near the triple-point of one of the components the liquid range over which p,V measurements can be made will be limited by the onset of solidification at a comparatively low applied pressure.

Recently, Haynes *et al.*[3, 4] have described a magnetic method for determining

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[3] W. M. Haynes, M. J. Hiza, and N. V. Frederick, *Rev. Sci. Instrum.* 1976, **47**, 1237.

[4] W. M. Haynes, *Rev. Sci. Instrum.*, 1977, **48**, 39.

the densities of pure and mixed liquefied gases in which the quantity measured is the magnetic field required to balance the gravitational force on a barium ferrite cylinder immersed in the liquid. By carrying out experiments without any liquid (*i.e.* with the barium ferrite cylinder in a vacuum), the technique can be made to give absolute densities. This method can be used to ~5 MPa, and while it is much more sophisticated than the pyknometric technique it clearly has considerable potential.

Another method, developed by Singh and Miller,[5] depends on measurements of the dielectric constant ε (permittivity). The connection between ε, the molar volume V, and the Mosotti–Clausius function M (the total polarization) is given for a pure species i by equation (7).

$$M_i = V_i(\varepsilon_i - 1)/(\varepsilon_i + 2). \tag{7}$$

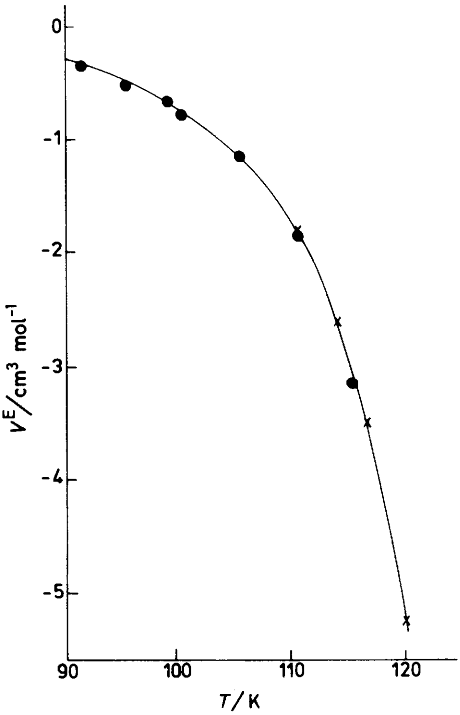

Figure 2 *Excess volume for the mixture* $0.503\,N_2 + 0.497\,CH_4$ *at the saturation vapour pressure. Circles, refs.* 6 *and* 7; *crosses, ref.* 8
(Reproduced by permission from *J. Chem. Thermodyn.*, 1978, **10**, 151)

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[5] S. P. Singh and R. C. Miller, *J. Chem. Thermodyn.*, 1972, **4**, 85; 1973, **5**, 207.
[6] Y.-P. Liu and R. C. Miller, *J. Chem. Thermodyn.*, 1972, **4**, 85.
[7] D. R. Massengill and R. C. Miller, *J. Chem. Thermodyn.*, 1973, **5**, 207.
[8] M. Nunes da Ponte, W. B. Streett, and L. A. K. Staveley, *J. Chem. Thermodyn.*, 1978, **10**, 151.

It is assumed that M for a mixture is the mole-fraction average of the pure component values (*i.e.* that the excess of the function, M^{E}, is zero). On this assumption, V^{E} can be calculated from equation (8).

$$V^{E} = \sum x_{i}M_{i}\{(\varepsilon + 2)/(\varepsilon - 1) - (\varepsilon_{i} + 2)/(\varepsilon_{i} - 1)\} \qquad (8)$$

This method readily lends itself to measurements over a range of temperature and pressure.

All of the methods mentioned above are capable of a precision of a few parts in 10^{4}. For binary mixtures of condensed gases, $V^{E}_{\frac{1}{2}}$ is often of the order of one per cent of the molar volume, and for such systems the experimental values of $V^{E}_{\frac{1}{2}}$ (*i.e.* V^{E} for the equimolar mixture) should be reliable to 1 to 2 per cent. Figure 2 is a plot of V^{E} at the saturation vapour pressure against temperature for an approximately equimolar mixture of nitrogen and methane which incorporates results obtained in two laboratories. It will be seen that there is satisfactory agreement between the two sets of measurements.

C. The Determination of H^{E}.—This proved to be more difficult than the determination of G^{E} and V^{E}. H^{E} can be deduced from measurements of G^{E} at more than one temperature, using the relation

$$(\partial G^{E}/\partial T)_{p} = -H^{E}/T^{2} \qquad (9)$$

but to obtain reliable values in this way requires exceptionally good G^{E} data, and a direct calorimetric method is to be preferred. A series of calorimeters for measuring the enthalpy of mixing of two liquefied gases has been constructed in Oxford.[9–12] Known amounts of the pure components are liquefied into separate cavities. These cavities are separated in the earlier models by a metal diaphragm, and in the later versions by a valve, and together form a closed system. Mixing is accomplished by puncturing the diaphragm or by opening the valve and shaking the whole cryostat. Provision is made for monitoring the temperature of the vessel in which mixing takes place, and for supplying it with a known amount of energy. The mixing is almost always an endothermic process, and the measurement of H^{E} becomes, in effect, a measurement of the energy which has to be supplied to counterbalance the temperature drop on mixing. An idea of the performance of such calorimeters is given by the results for the argon + methane system plotted in Figure 3. The accuracy is believed to be ~1 to 2 per cent.

More recently, a calorimeter has been constructed by Professor Streett and his collaborators at Cornell University (see *ref.* 35). This instrument is similar in many respects to the Oxford models, but it is more completely automated and the mixing of the two liquids is effected by a rotating stirrer. Figure 4 embodies what are thought to be all the H^{E} results for the nitrogen + oxygen system. For certain types

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[9] R. A. H. Pool and L. A. K. Staveley, *Trans. Faraday Soc.*, 1957, **53**, 1186.

[10] R. A. H. Pool, G. Saville, T. M. Herrington, B. D. C. Shields, and L. A. K. Staveley, *Trans. Faraday Soc.*, 1962, **58**, 1692.

[11] K. L. Lewis G. Saville, and L. A. K. Staveley, *J. Chem. Thermodyn.*, 1975, 7, 389.

[12] K. L. Lewis and L. A. K. Staveley, *J. Chem. Thermodyn.*, 1975, 7, 855.

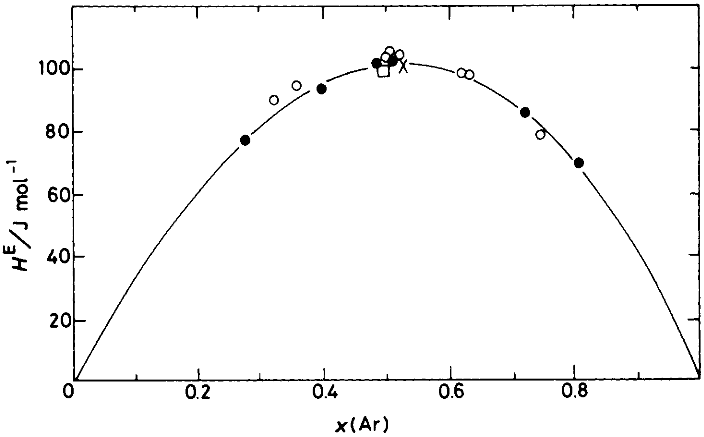

Figure 3 *Enthalpy of mixing for the* Ar + CH_4 *system at* 91.5 K. *Full circles, ref.* 11; *open circles, ref.* 13; *square, ref.* 14; *cross, ref.* 15
(Reproduced by permission from *J. Chem. Thermodyn.*, 1975, **7**, 855)

of calorimeter—for example, combustion calorimeters, and those intended for the measurement of the enthalpy of mixing of liquids at or near room temperature—certain substances or systems on which careful experiments have been carried out in several laboratories are now generally recognized to be suitable for standardizing a new calorimeter or for checking its performance. In the field of liquefied gas mixtures, a standard system with which to check H^E measurements would also seem to be desirable, and the nitrogen + oxygen system would appear to be a good candidate for this. The two substances are readily available in a state of high purity, and the H^E measurements can conveniently be made at or near the normal boiling-point of nitrogen.

In the low-temperature calorimeters just described, the vapour phase cannot be wholly eliminated, whereas this can of course be done in those operating at or near room temperature. Corrections therefore have to be made for the transference of material between the vapour and liquid phases. There is no objection to this so long as the corrections can convincingly be made with adequate precision. If the vapour pressures are not too high, these corrections do not present a serious problem in H^E determinations. But as the temperature rises and the critical region is approached, the corrections become ever larger and more difficult to make accu-

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[13] M. Lambert and M. Simon, *Physica*, 1962, **28**, 1191.
[14] V. Mathot, *Nuovo Cimento*, 1958, **9** *Suppl.* 1, 356.
[15] J. Jeener, *Rev. Sci. Instrum.*, 1957, **28**, 263.

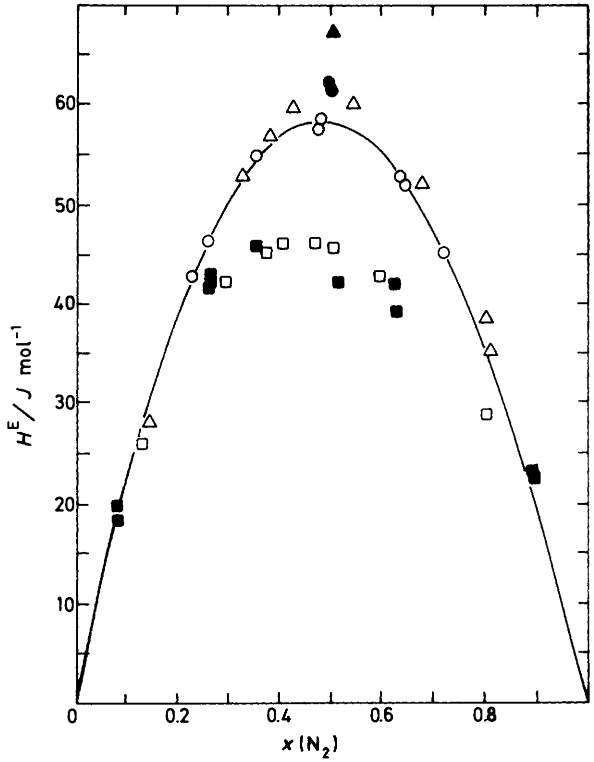

Figure 4 *Enthalpy of mixing for the* $N_2 + O_2$ *system. Open circles,* 80.5 K, *ref.* 6; *filled circles,* 77.7 K, *ref.* 19; *open triangles,* 80.3 K, *ref.* 11; *filled squares,* 77 K, *ref.* 17; *open squares,* 77.5 K, *ref.* 18; *solid triangle, value for* 74 K *derived from* G^E, *ref.* 16

rately, and eventually it is necessary to change to a different type of calorimeter, such as the flow calorimeter.[20]

D. Equation of State Studies.—In recent years, an increasing amount of work has been carried out on the effect of pressure on the excess functions of liquefied gas mixtures, which has already added considerably to the useful data on these systems which is available for contemplation by theoreticians. It is now known that these functions can present a very different appearance at, say, 100 MPa from that given by the low-pressure values. From the molecular point of view, the effect of applying

[16] A. G. Duncan and L. A. K. Staveley, *Trans. Faraday Soc.*, 1966, **62**, 548.

[17] C. M. Knobler, R. J. J. van Heijningen, and J. J. M. Beenakker, *Physica*, 1961, **27**, 296.

[18] W. Kohler, Ph.D. Dissertation, University of Göttingen, 1964.

[19] W. B. Streett, J. A. Zollweg, and K. P. Wallis, unpublished results, privately communicated.

[20] S. E. Mosedale and C. J. Wormald, *J. Chem. Thermodyn.*, 1977, **9**, 483.

pressure is to change the balance between the forces of attraction and repulsion. As the liquid is compressed, the forces of repulsion become increasingly dominant, in that they have to oppose not only the intermolecular forces of attraction but also the externally applied pressure.

The first experiments of this kind were made in the Soviet Union by Blagoi and Sorokin,[21, 22] who studied mixtures of argon + krypton and of krypton + methane to about 50 MPa. Since then, similar studies have been made to rather higher pressures at Oxford, and more recently still at the Instituto Superior Tecnico in Lisbon and at the School of Chemical Engineering at Cornell University. The technique used in all these laboratories consists essentially in finding the amount of liquid which fills a metal cell of known volume at a known temperature under a measured applied pressure. (An alternative technique, briefly described in Section 2B, is that depending on permittivity measurements). Experiments must of course be done on the pure components as well as on at least one mixture of known composition. Given values of G^E and H^E at a low (or zero) pressure, their values at higher pressures can at once be obtained from the equation of state results by using them to calculate the *changes* in the excess functions from the relations given in equations (10) and (11).

$$(\partial G^E/\partial p)_T = -V^E \tag{10}$$

$$\text{and } (\partial H^E/\partial p)_T = V^E - T(\partial V^E/\partial T)_p \tag{11}$$

It will be seen from equation (11) that the calculation of the change of H^E with pressure requires a knowledge of the temperature coefficient of V^E, so that the p,V,T studies must be made over a range of temperature.

To illustrate the kind of results obtained, we show in Figure 5 the effect of pressure on V^E for an approximately equimolar mixture of liquid nitrogen and methane,[8] in Figure 6 the pressure dependence of H^E, S^E, and G^E for the same solution, and in Figure 7 the pressure dependence of H^E and G^E for the argon + krypton system.[23] Certain features at once emerge from these figures which are common to all the systems so far studied in this way. First, it will be seen that the applied pressure has its greatest effect over about the first 20 MPa. Secondly, there are much larger changes in H^E and S^E than in G.^{E} Also, V^E becomes numerically very small at high pressures. It will also be noted that for the nitrogen + methane system V^E eventually becomes positive, so that at high pressures the molecules behave in the mixture as if they are slightly larger than they are in the pure liquids.

One cannot therefore claim that a system has been comprehensively investigated until its behaviour under pressure has been investigated. But it is also necessary that it should be studied over as wide a temperature range as possible. Figure 2

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[21] Yu. P. Blagoi and V. A. Sorokin, *Sb. Nauchn. Tr. Fiz.-Tekh. Inst. Nizk Temp. Akad. Nauk Ukr. SSR*, 1969, **5**, 5.

[22] Yu. P. Blagoi, A. E. Butko, S. A. Michailenko, and V. A. Sorokin, *Akad. Sci. Ukr. SSR, Phys. Tech. Inst. Low Temps.*, 1975, UDK 534.22, 538.34.

[23] S. F. Barreiros, J. C. G. Calado, P. Clancy, M. Nunes da Ponte, and W. B. Streett, *J. Phys. Chem.*, 1982, **86**, 1722.

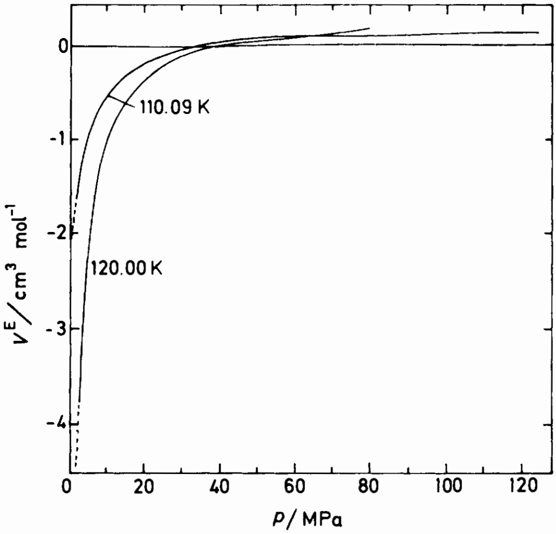

Figure 5 *Dependence on pressure of the excess volume for the mixture* 0.503 N_2 + 0.497 CH_4, *ref.* 8
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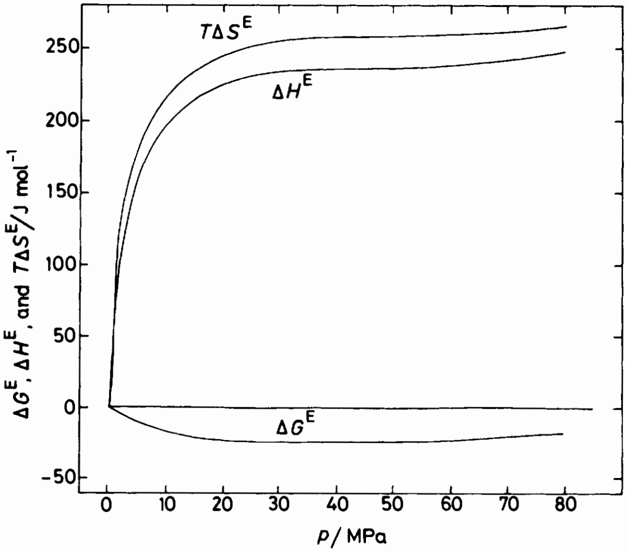

Figure 6 *Dependence on pressure of* G^E, H^E, *and* TS^E *for the mixture* 0.503 N_2 + 0.497 CH_4 *at* 115 K, *ref.* 8
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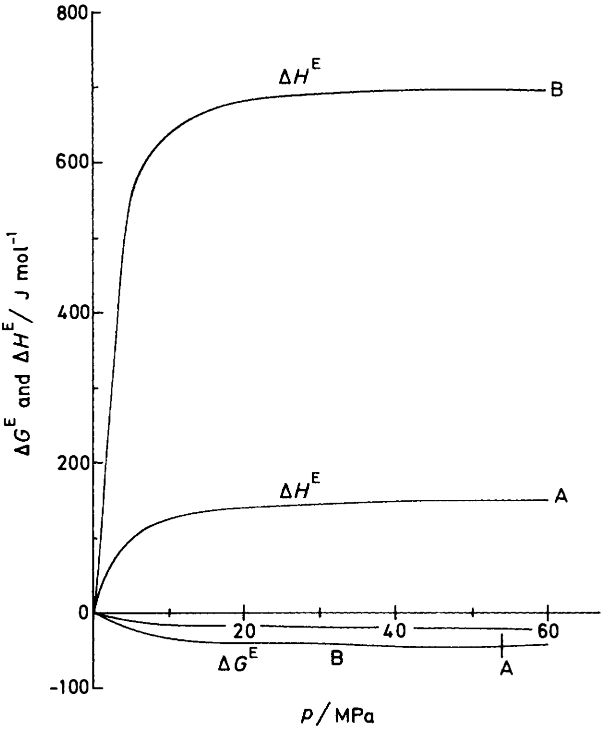

Figure 7 *Dependence on pressure of* G^E *and* H^E *for the mixture* 0.485 Ar + 0.515 Kr, *at* 134.3 K *(A) and* 142.7 K *(B), ref.* 23
(Reproduced by permission from *J. Phys. Chem.*, 1982, **86**, 1722)

illustrates the very marked effect which a rise in temperature can have on V^E. The influence of temperature on H^E can be still more striking. Figure 8 presents results for H^E in the argon + methane system at the saturation vapour pressure, those at the lower two temperatures having been obtained using a calorimeter of the type described above,[24] and those at the higher three temperatures with a flow calorimeter.[20] It will be seen that H^E decreases with rising temperature and changes sign well before the critical temperature (151 K) of argon, the more volatile component, is reached.

Figure 9 for the argon + krypton system once again shows that V^E is strongly temperature-dependent at low pressures, but it also demonstrates that at sufficiently high pressures, V^E (now small) is almost unaffected by a change in temperature.

3 The Importance of the Enthalpy of Mixing (H^E)

The effort required to obtain reliable values of H^E has undoubtedly been worth-

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[24] A. J. Kidnay, K. L. Lewis, J. C. G. Calado, and L. A. K. Staveley, *J. Chem. Thermodyn.*, 1975, **7**, 847.

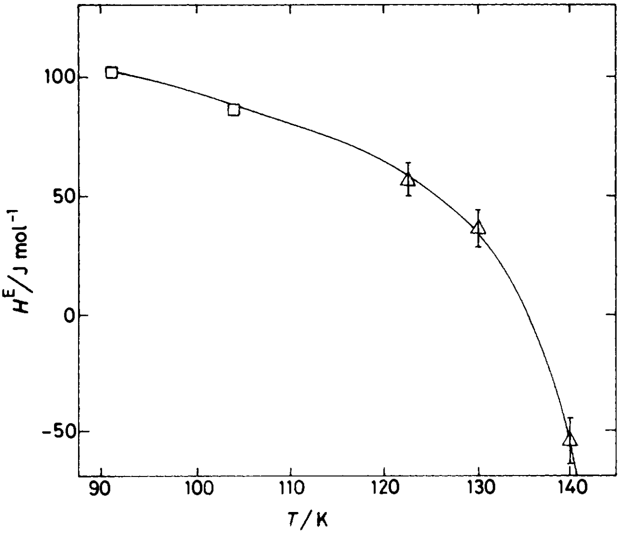

Figure 8 *Temperature dependence of the enthalpy of mixing for an equimolar* Ar + CH_4 *mixture at the saturation vapour pressure. Squares, refs.* 11 *and* 24; *triangles, ref.* 20 (Reproduced by permission from *J. Chem. Thermodyn.*, 1977, **9**, 483)

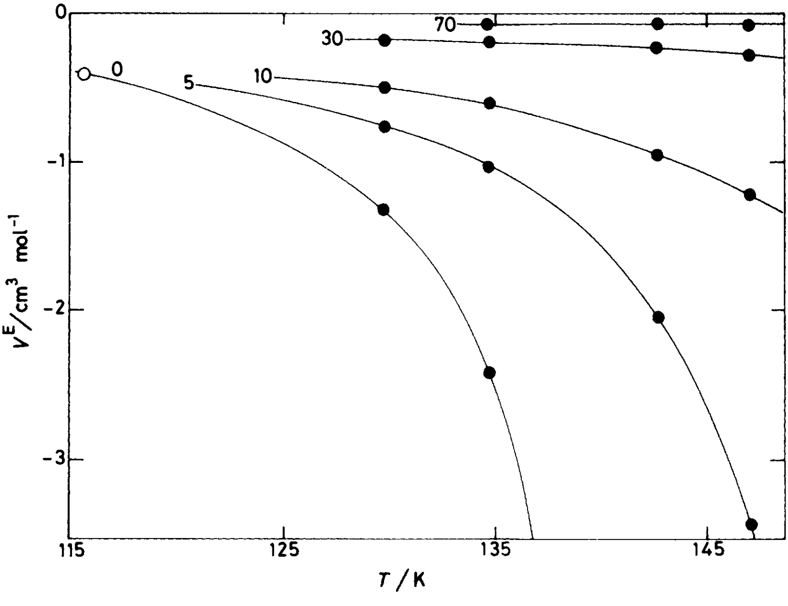

Figure 9 *Showing the effect of temperature on* V^E *for the mixture* 0.485 Ar + 0.515 Kr *at the constant pressures given in* MPa *by the figure at the left-hand end of each curve, plotted from the results of Barreiros et al., ref.* 23

while. In the first place, H^E (and likewise S^E) can be described as a more sensitive function than G^E. Some experimental evidence which supports this statement has just been presented in Figures 6 and 7. Later, in comparing theoretical predictions with experiment, we shall see that calculated values of H^E are much affected by the assumptions and approximations made in the theory. The reason for this is that if a theory gives an expression from which G^E can be calculated, then 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 calculation of H^E and S^E a more exacting undertaking than the prediction of G^E.

But there is another reason which puts a premium on H^E data, and this relates to the so-called combining rules. The intermolecular potential energy 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 equations (12) and (13).

$$\sigma_{12} = \tfrac{1}{2}(\sigma_{11} + \sigma_{22}) \text{ (Lorentz)} \tag{12}$$

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{\frac{1}{2}} \text{ (Berthelot)} \tag{13}$$

are not adequate, and so they are commonly modified by introducing parameters j_{12} and k_{12}, such that

$$\sigma_{12} = \tfrac{1}{2}(1 + j_{12})(\sigma_{11} + \sigma_{22}) \tag{14}$$

$$\text{and} \quad \varepsilon_{12} = (1 - k_{12})(\varepsilon_{11}\varepsilon_{22})^{\frac{1}{2}} \tag{15}$$

Equations (14) and (15)—or relations effectively equivalent to them—have been widely used in theoretical work. It was soon found 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. We shall later refer to an attempt which has been made to improve on equation (13), and so eliminate the parameter k_{12}. But in most of the comparisons so far carried out between theoretical and experimental values of the excess functions for particular systems, to derive numerical values from the theory it has been necessary to sacrifice two pieces of experimental information to fix j_{12} and k_{12}, usually one value of G^E (for a certain concentration and temperature) and 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 then 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 (if available) at other temperatures. If H^E is also known, however, the situation is much improved, and the addition of experimental values of the 'sensitive' function H^E to those of G^E and V^E must therefore be rated much more highly than merely as a fifty per cent increase in the available information.

4 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 indeed to just one type of theory, and our comments here must necessarily be brief. There are two systems of absolutely fundamental importance on account of their extreme molecular simplicity, namely argon + krypton and krypton + xenon. The intermolecular potentials in these systems are a function of the molecular separation only, there being no question of any angular dependence, and they have been very thoroughly studied. Two other very basic systems are argon + methane and krypton + methane, since the methane molecule is compact, highly symmetrical, and has no dipole or quadrupole moment. In testing earlier theories, it was often assumed that small diatomic molecules like those of nitrogen, oxygen and carbon monoxide could be regarded as being spherical, but clearly it is better to avoid this approximation and to recognize the anisotropic character of the field of force around such molecules. In any case, one of the objectives of the experimental work has been to obtain data for systems of molecules which, while simple, have characteristics such that the system would generate information of value in the interpretation of the properties of mixtures of substances which have larger molecules and which are liquid at ordinary temperatures. It was clearly desirable, therefore, to make a systematic study of the effect of polarity in the molecules of one or both components of a mixture.

Accordingly, in the last decade a number of systems have been investigated, the molecules in which, while small, have dipoles, quadrupoles, or octopoles. Hydrogen chloride and hydrogen bromide were chosen to represent dipolar molecules, though we shall see that the apparent simplicity of these molecules is probably deceptive. Dinitrogen oxide (nitrous oxide, N_2O) and ethene (C_2H_4) have been used to provide quadrupolar molecules. (Dinitrogen oxide has a dipole moment, but this is so small that its influence is negligible. It was preferred to carbon dioxide, since the relatively high melting-point and triple-point pressure of carbon dioxide create experimental difficulties). Symmetrical diatomic molecules such as those of nitrogen and oxygen also have quadrupole moments, but no dipole moment. Tetrafluoromethane, CF_4, has been used as a component whose molecules are octopoles, but not dipoles or quadrupoles. It should be noted that polar diatomic molecules like those of hydrogen chloride and hydrogen bromide have a quadrupole moment as well as a dipole moment.

The types of system which have now been studied experimentally, with examples of the actual systems chosen, include the following: non-polar + dipolar ($Xe + HCl$; $Xe + HBr$); dipolar + dipolar ($HCl + HBr$); non-polar + quadrupolar ($Xe + N_2O$; $Ar + N_2$; $Xe + C_2H_6$); non-polar + octopolar ($Xe + CF_4$); dipolar + quadrupolar ($HCl + N_2O$); quadrupolar + quadrupolar) ($N_2O + C_2H_4$); dipolar + octopolar ($HCl + CF_4$). In the early stages of this experimental programme, Gubbins and Gray and their collaborators[25-27] developed a perturbation theory of solutions designed to examine the effect on the excess

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[25] C.-H. Twu, K. E. Gubbins, and C. G. Gray, *Mol. Phys.*, 1975, **29**, 713.

[26] M. Flytzani-Stephanopoulas, K. E. Gubbins, and C. G. Gray, *Mol. Phys.*, 1975, **30**, 1649.

[27] C.-H. Twu, K. E. Gubbins, and C. G. Gray, *J. Chem. Phys.*, 1976, **64**, 5186.

functions of dipoles, quadrupoles, and octopoles in the molecules of one or both components, and also of anisotropy in the dispersion and repulsive forces. Much of the rest of this review will be a consideration of some of the systems just mentioned, in which the experimental results (often obtained in Oxford) will be compared with the results of theoretical calculations carried out by Gubbins and his co-workers.

A perturbation theory 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.[28] Here the perturbation takes the form of introducing into the molecules of one or both components a dipole, quadrupole, or octopole, and it also becomes desirable even for diatomic molecules like those of nitrogen and hydrogen chloride to allow for the angular dependence of the dispersion and repulsive (overlap) forces.

It is advisable to choose as the reference system one which approaches as closely as possible to the real system to be treated. In recent theoretical studies of the effect of polarity, the fluid chosen as the reference has been one for which an n–6 potential operates between the centres of a pair of molecules. If $n = 12$, we have the Lennard-Jones 12–6 fluid, the properties of which have been thoroughly studied by computer simulation methods. As shown by Rowlinson,[29] the properties of an n–6 fluid can be determined by relating them to those of the 12–6 fluid. To deal with a reference mixture of these idealized molecules, use is made of the well-tried van der Waals-1 conformal solution theory,[30] which equates the reference mixture with a pure fluid for which the σ and ε parameters are given by equations (16) and (17).

$$\sigma^3 = \sum_{12} x_1 x_2 \sigma_{12}^3 \tag{16}$$

$$\varepsilon\sigma^3 = \sum_{12} x_1 x_2 \varepsilon_{12} \sigma_{12}^3 \tag{17}$$

Since these equations require expressions for σ_{12} and ε_{12}, it is at this stage that the problem of the combining rules arises, and at which, if equations (14) and (15) are used, as is generally the case, the parameters k_{12} and j_{12} (or quantitities equivalent to them) enter the calculations.

As regards the introduction of perturbation terms, we may illustrate this by considering the Xe + HCl system, where the perturbation concerns the two pair potentials involving HCl, namely HCl–HCl and Xe–HCl.[31] The HCl–HCl potential is obtained by adding to the central n–6 expression the terms for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interaction, plus terms to allow for the anisotropy in the dispersion and overlap forces. So even for such simple

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[28] J. A. Pople, *Proc. R. Soc. London, Ser. A*, 1954, **221**, 498.

[29] J. S. Rowlinson, *Mol. Phys.* 1964, **8**, 107.

[30] J. S. Rowlinson and F. L. Swinton, Liquids and Liquid Mixtures, 3rd edn., Butterworths, London, 1982, chapter 8.

[31] J. C. G. Calado, C. G. Gray, K. E. Gubbins, A. M. F. Palavra, V. A. M. Soares, L. A. K. Staveley, and C.-H. Twu, *J. Chem. Soc. Faraday Trans. 1*, 1978, **74**, 893.

molecule the expression for the potential energy has already become quite elaborate. The Xe–HCl potential is not so complex, consisting of an n–6 expression supplemented by terms for anisotropy and for the attraction resulting from the dipole induced in the zenon atom by the dipole and quadrupole of a hydrogen chloride molecule.

It is, of course, important that the intermolecular potential functions adopted for the two pairs of like molecules involved in the treatment of a binary mixture should give the best representation of, or consistency with, the bulk properties of the pure 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 hydrogen chloride, for example, it would be invaluable to have $p.V.T$ data on the liquid up to, say, 100 MPa, from which the configurational energy could be calculated as a function of volume. So here is another field in which the experimentalist can make a valuable contribution.

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

$$A = A_0 + A_2\left[\frac{1}{1 - A_3/A_2}\right] \tag{18}$$

where A_0 is the value of the Helmholtz function for the reference system. (The term A_1 vanishes as a result of the choice of the reference potential). Once an expression for A has been obtained, the required excess functions for the mixture are derived from this using standard thermodynamic relations. For example, use of the equation

$$(\partial A/\partial V)_T = -p \tag{19}$$

leads at once to an equation of state for the mixture from which V^E can be calculated.

5 Comparison of Theory and Experiment for some Selected Systems

A. Xenon + Hydrogen Chloride.—The comparison of theory and experiment is usually made by comparing the actual and calculated values of the excess functions, but in Figure 10 the predicted 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 equation (15)] was resolved by assuming the experimental value of the vapour pressure for the equimolar mixture at the highest temperature. For this system, the value of j_{12} in equation (14) proves to be virtually zero. The agreement between the calculated curves and the experimental points in Figure 10 is impressive. The asymmetry of the dependence of V^E on composition is also found to be reproduced reasonably well. When, however, the comparison

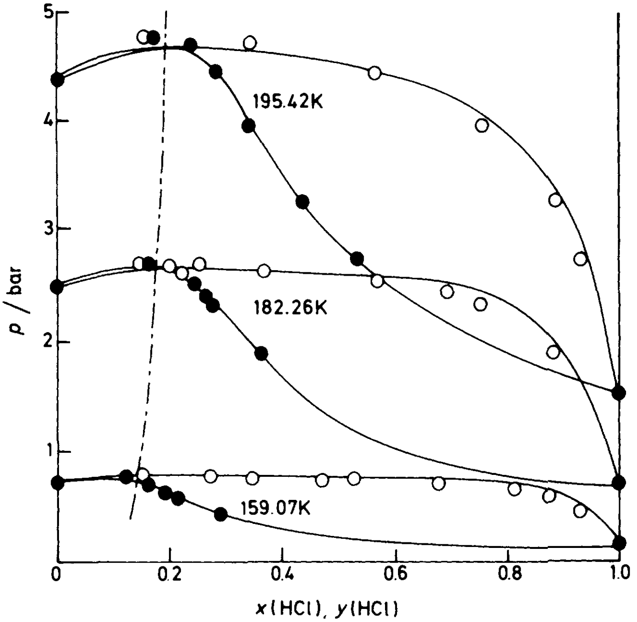

Figure 10 *Total vapour pressure for the system* Xe + HCl *at three temperatures.* x(HCl) *and* y(HCl) *are the mole fractions of* HCl *in the liquid phase (open circles) and the vapour phase (filled) circles respectively. The curves are calculated*[31]

is made for H^E, the outcome is rather different.[32] Two calculated curves are shown in Figure 11, neither of which is in close agreement with experiment. Curve A was calculated using an HCl–HCl potential which omitted terms to deal with the anisotropy of the dispersion and overlap forces, whereas for the calculated curve B these terms were included. It will be seen that their inclusion makes a considerable difference, and brings the calculated H^E values nearer to, but still not into agreement with, the experimental results. On the other hand, inclusion of the anisotropy terms makes very little difference to the calculated G^E and V^E values. This is another illustration of what we have called the sensitivity of the function H^E.

In 1957, Kohler[33] proposed an alternative to equation (13) (the Berthelot rule), based on London's formula for dispersion energy. Kohler's expression for ε_{12} is

$$\varepsilon_{12}\sigma_{12}^6 = 2\frac{\varepsilon_{11}\sigma_{11}^6\varepsilon_{22}\sigma_{22}^6}{\varepsilon_{11}\sigma_{11}^6\alpha_2^2 + \varepsilon_{22}\sigma_{22}^6\alpha_1^2}\alpha_1\alpha_2 \tag{20}$$

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[32] L. Q. Lobo, L. A. K. Staveley, P. Clancy, and K. E. Gubbins, *J. Chem. Soc., Faraday Trans 1*, 1980, **76**, 174.

[33] F. Kohler, *Monatsh. Chem.*, 1957, **88**, 857. (See also F. Kohler, J. Fischer, and E. Wilhelm, *J. Mol. Struct.*, 1982, **84**, 245).

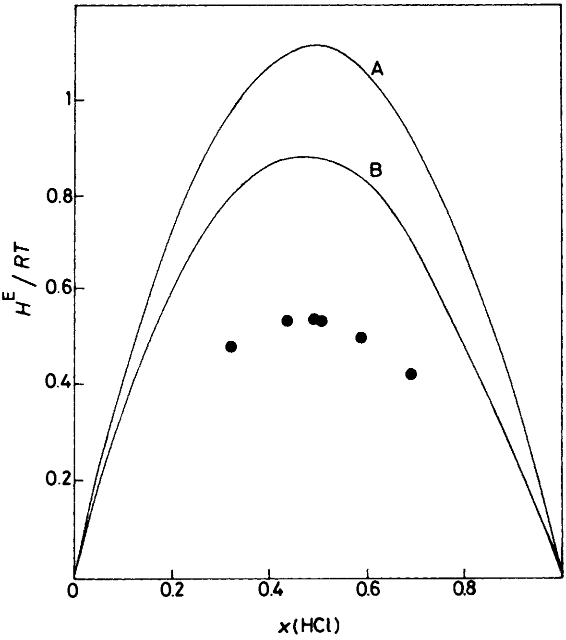

Figure 11 *Enthalpy of mixing for the* Xe + HCl *system. Circles, experimental values. A and B are calculated curves (see text)*[32]

where α_1 and α_2 are the polarizabilities of molecules 1 and 2. Moser *et al.*[34] have applied equation (20) to the Xe + HCl system. Using the Lorentz and Berthelot relations and an HCl–HCl potential similar to, but not identical with that used for the calculations we have just summarized, the phase diagram shown by the broken lines in Figure 12 was obtained. When Kohler's equation (20) was substituted for the Berthelot relation, but no other changes made, calculation gave the full lines in Figure 12, which now correctly show that the system has a positive azeotrope. This is a striking demonstration of the importance of the combining rules.

It seems likely that increasing use will be made of Kohler's equation. It has recently been applied in calculations on the system carbon dioxide + ethane. The Lorentz equation (12) was also used, so that no experimental values of the excess functions had to be sacrificed. Excellent agreement between theory and experiment was obtained for H^E and V^E, though the agreement for G^E, perhaps surprisingly, was rather less good.[35]

When we have spoken of a molecule having a dipole, quadrupole, or octopole, in theoretical treatments these have been taken to be a *point* dipole or a *point* multipole. Even with this simplification, the mathematics rapidly becomes complicated and sophisticated. Nevertheless, there is evidence which suggests that it may

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[34] B. Moser, K. Lucas, and K. E. Gubbins, *Fluid Phase Equilibria*, 1981, 7, 153.

[35] K. P. Wallis, P. Clancy, J. A. Zollweg, and W. B. Streett, paper submitted to *J. Chem. Thermodyn.*

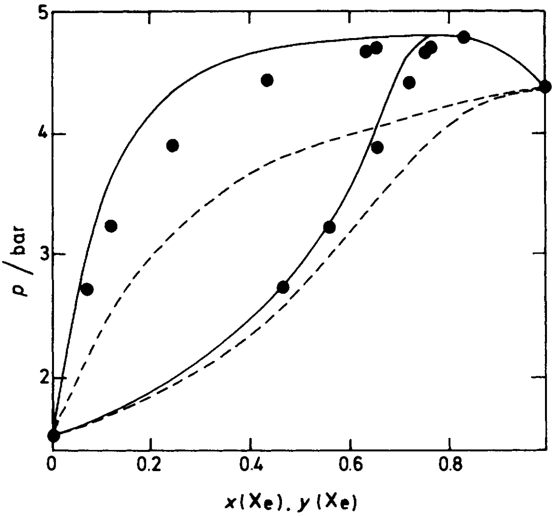

Figure 12 *Vapour pressure–composition diagram for the* Xe + HCl *system. Circles, experimental values; broken curves, calculated using equation* (13); *continuous curves, calculated using equation* (20)[34]
(Reproduced by permission from *Fluid Phase Equilibria*, 1981, 7, 153)

be desirable to try and improve on this approximation. For example, the way in which two hydrogen chloride molecules associate suggests hydrogen-bonding rather than simple electrostatic attraction. In the solid state, hydrogen chloride and its deuterated analogue each exist in two forms, a low-temperature orientationally ordered orthorhombic form and a high-temperature orientationally disordered cubic form. The structure of the ordered form of deuterium chloride, as determined by neutron diffraction,[36] is shown in Figure 13. The molecules form zigzag 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 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 form of hydrogen chloride and deuterium chloride, the orientational ordering is of course long-range. While the high-temperature form is orientationally disordered, and the liquid no doubt still more so, neutron scattering studies have indicated that the same kind of ordering persists on a local scale even above the melting-point.[37] It therefore seems that ideally an intermolecular potential for HCl–HCl interaction which is to be used to treat the properties of the pure liquid and its mixtures should be based on a model that does not simply assign a

[36] E. Sàndor and R. F. C. Farrow, *Nature (London)*, 1967, **215**, 1265.

[37] H. Boutin and G. J. Safford, Proc. Symposium on Inelastic Scattering of Neutrons, Bombay, 1964, II, 393.

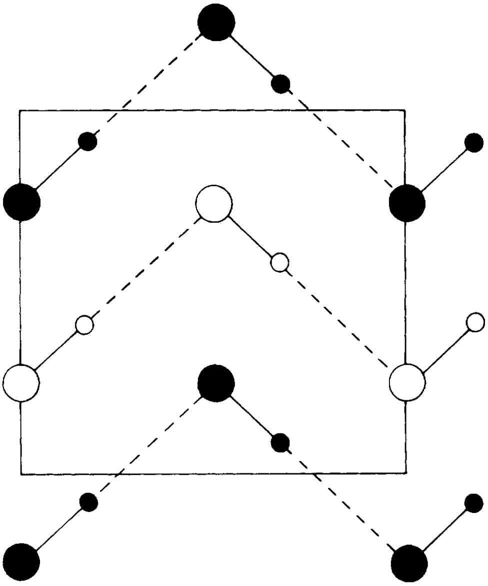

Figure 13 *Structure of ordered phase of solid* DCl.[36] *Smaller circles, deuterium atoms; larger circles, chlorine atoms. Planes containing molecules shown as open circles are separated from those composed of molecules shown as filled circles by half the unit cell dimension in the direction perpendicular to the paper*

point dipole and a point quadrupole to the molecule, but has charges so distributed within it as to be consistent with 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 values of H^E for the HCl + Xe system is to be found here.

These considerations raise the question whether one could choose a better representative of compounds whose molecules have a dipole moment than hydrogen chloride. Unfortunately, there are very few substances which are liquid at sufficiently low temperatures for their mixtures with, say, liquid xenon to be investigated, and which at the same time have small molecules that are incapable of hydrogen-bonding but nevertheless have a sufficiently large dipole moment. One possibility is ClF, though apart from experimental difficulties which might arise from the chemical reactivity of this compound, some of the information on its physical properties which is needed to apply the kind of theory we are discussing may not be available at present.

B. Xenon + Dinitrogen Oxide.—This system was chosen as a model for a mixture of non-polar molecules and molecules with a quadrupole moment.[38] The linear

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[38] J. R. S. Machado, K. E. Gubbins, L. Q. Lobo, and L. A. K. Staveley, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 2496.

molecule of N_2O has, in fact, a dipole moment, but this is very small (0.166 D, = 0.55×10^{-30} C m), and although terms for the dipole were included in the N_2O–N_2O potential in the perturbation treatment, their effect on the calculated excess functions is trivial. In an early perturbation study of the influence of polarity, Chambers and McDonald[39] examined this by considering the excess Gibbs energy of an equimolar mixture of a non-polar liquid with one having molecules of dipole moment μ. The result they obtained using the Padé approximant is shown graphically in Figure 14. If one compares on this basis two imaginary cases, one having $\mu = 0.5$ D and the other $\mu = 1$ D, the dipoles of the less polar molecules would only have about one-tenth of the effect produced by the more polar molecules. For molecules with $\mu = 0.166$ D, the effect would be negligible.

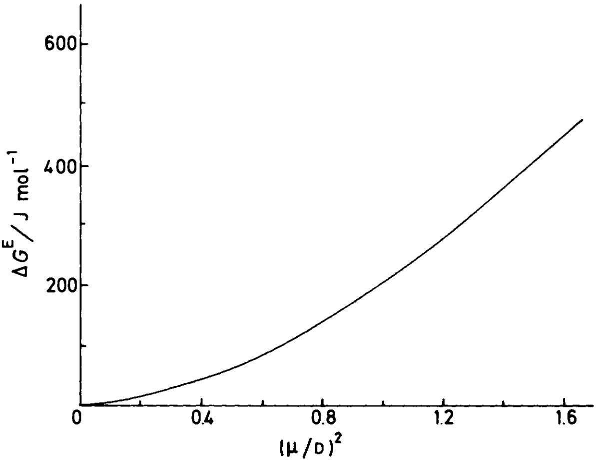

Figure 14 *Showing the calculated effect on G^E for an equimolar mixture of a dipole moment μ in the molecules of one component*[39]
(Reproduced by permission from *Mol. Phys.*, 1975, **29**, 1053)

In the theoretical treatment of the Xe + N_2O system, the parameters were given values to fit the experimental results for G^E and V^E for the equimolar mixture. The calculated H^E is in excellent agreement with experiment (Figure 15). Initially, anisotropic dispersion and overlap terms were included in the N_2O–N_2O potential, but it was found that virtually no difference was made to the calculated H^E values if the anisotropy of the dispersion and overlap forces was ignored. This is in contrast to the position for the Xe + HCl system, where allowance for anisotropy substantially improves the calculated H^E values (Figure 11).

C. Xenon + Tetrafluoromethane.—For this system, chosen as a model for a mixture

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[39] M. V. Chambers and I. R. McDonald, *Mol. Phys.*, 1975, **29**, 1053.

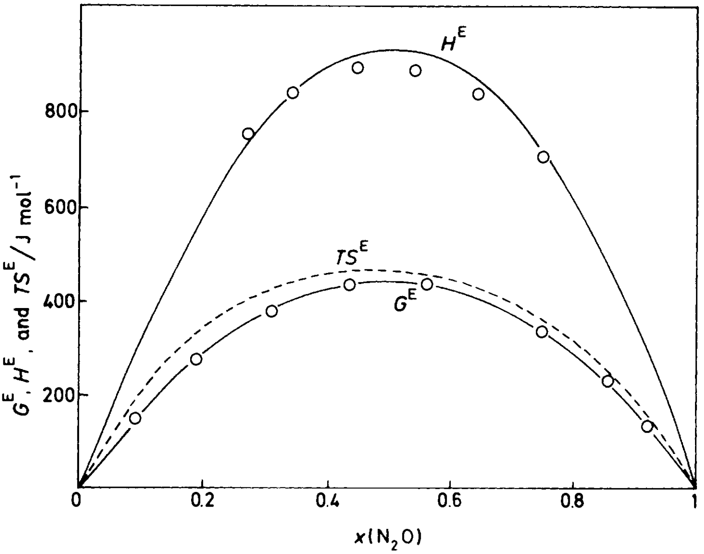

Figure 15 *Excess functions for the system* Xe + N_2O. *The points and the broken line are experimental, and the continuous curves are calculated*[38]

of non-polar molecules and molecules having an octopole but no dipole or quadrupole, the calculated values of H^E are again in excellent agreement with experiment[40] (Figure 16).

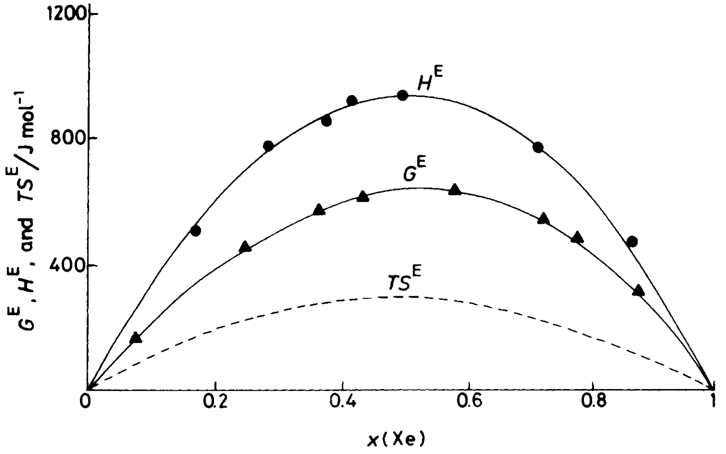

Figure 16 *Excess functions for the system* Xe + CF_4. *The points and the broken line are experimental, and the continuous curves are calculated*[40]

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[40] L. Q. Lobo, D. W. McClure, L. A. K. Staveley, P. Clancy, K. E. Gubbins, and C. G. Gray, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 425.

D. Dinitrogen Oxide + Ethene.—Systems of two quadrupolar molecules can be of two kinds, depending on whether the quadrupoles of the two species 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 (Figure 17). An example of a mixture where the molecules of the two components have quadrupoles of opposite sign is $N_2O + C_2H_4$. For the linear N_2O molecule the charge distribution corresponds to that in the lower of the two quadrupoles in B of Figure 17, while that in the C_2H_4 molecule is represented by the upper quadrupole in B.

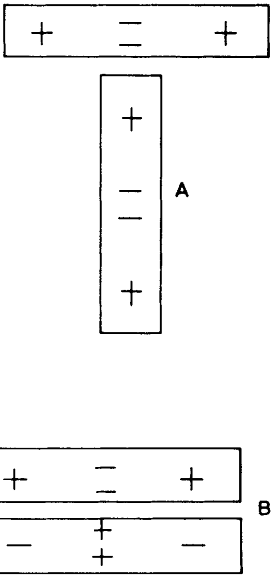

Figure 17 *Showing the mode of association of two molecules with quadrupoles of the same sign* (A), *and of opposite sign* (B)

The experimental values of G^E, H^E, and V^E are plotted against composition in Figure 18.[41] The values of V^E are numerically small, but what is very unusual about this system is the extremely unsymmetrical concentration-dependence of V^E. This is not reproduced by the perturbation theory applied to the previous systems we have discussed, and indeed it is doubtful if any current theory of solutions could do this.

We shall see that for this system the incorporation of anisotropic overlap and dispersion terms *does* give improved calculated values of H^E. But first a further complication in handling this system must be mentioned, which arises from the fact that the ethene molecule lacks axial symmetry, so that the quadrupole tensor has

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[41] L. Q. Lobo, L. A. K. Staveley, P. Clancy, K. E. Gubbins, and J. R. S. Machado, *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**, 1399.

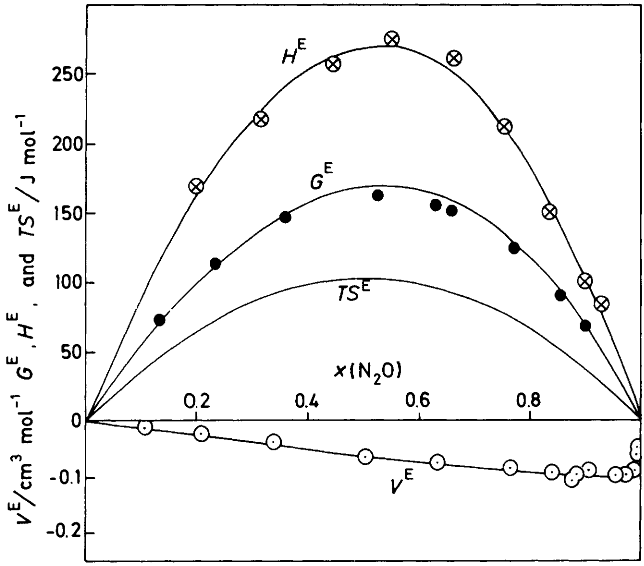

Figure 18 *Experimental results for the excess functions for the system* $N_2O + C_2H_4$[41]

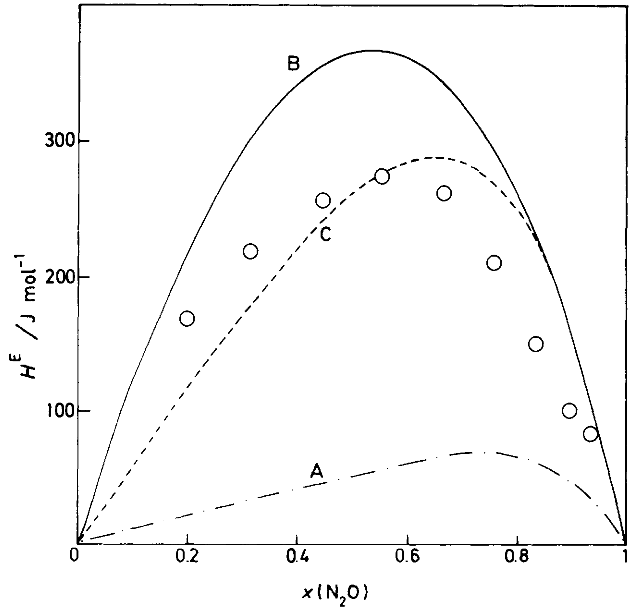

Figure 19 *Enthalpy of mixing for the system* $N_2O + C_2H_4$. *The points are the experimental values, and the three curves are calculated (see text)*[41]

two principal components, and not just the one which suffices for a linear molecule like N_2O. This can be dealt with either by making an 'effective axial approximation', or by introducing the correct non-axial representation of the two independent components of the quadrupole moment. It is interesting that the 'effective axial approximation' gives good results for the properties of pure ethene, but inferior results for the $N_2O + C_2H_4$ mixture. Figure 19 sumarizes the results of three calculations of H^E. For curve A, the 'effective axial approximation' was assumed, and the anisotropic corrections were omitted from the N_2O–N_2O potential. In obtaining curve B, these corrections were still omitted, but the non-axial treatment of the quadrupole was adopted, while for curve C this treatment was combined with the inclusion of the anisotropic terms in the N_2O–N_2O potential. Clearly, curve C gives the best, though not perfect, agreement with the experimental results.

E. Krypton + Nitrogen Oxide.—The reason for including this system in this review is rather different. Chemists have long been interested in liquid mixtures in which one component tends to associate. An example of such a system, provided by familiar substances, is benzene + acetic acid. Kr + NO may lay claim to be, from the molecular point of view, the simplest system of this kind. Nitrogen oxide, by virtue of the one unpaired electron in its molecule, forms a dimer. Molecules of acetic acid, which associate by hydrogen-bonding, undoubtedly form cyclic dimers, but they can in principle produce larger aggregates in more concentrated solutions or in the pure liquid, whereas with nitrogen oxide the association must presumably stop at the dimer stage. Accordingly, the system Kr + NO is well suited for adoption as a model system for a study of the effects of dimerization by one component. So far, only G^E and V^E at one temperature have been determined,[42] and further work could be profitably undertaken. The system is strongly non-ideal, having a positive azeotrope, and the dependence of V^E on composition is somewhat asymmetric. It has been possible to make an analysis of G^E to estimate how much of this function is due to the dimerization, and how much to what one might call the general causes of non-ideality. This led to the conclusion that roughly 60 per cent of the observed G^E for the equimolar mixture can be ascribed to the monomer–dimer equilibrium.

F. Argon, Krypton, or Xenon + Ethane.—The long liquid range of ethane makes it possible to study the binary mixtures of this substance with each of the rare gases argon, krypton, and xenon. The $Ar + C_2H_6$ system is strongly non-ideal, with $G^E_{\frac{1}{2}}$, the value for the equimolar mixture, equal to $374\,J\,mol^{-1}$ at 90.2 K.[12] For $Kr + C_2H_6$, $G^E_{\frac{1}{2}}$ is much less, being $80\,J\,mol^{-1}$ at 117 K. The system $Xe + C_2H_6$ was found to show *negative* departures from Raoult's Law, with $G^E_{\frac{1}{2}} = -29\,J\,mol^{-1}$ at 163 K.[43] Furthermore, liquid ethane and xenon were found to mix exothermically. In short, for this system, all the four excess functions G^E,

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[42] J. C. G. Calado and L. A. K. Staveley, *Fluid Phase Equilibria*, 1979, 3, 153.

[43] J. C. G. Calado, E. F. S. Gomes de Azevedo, and V. A. M. Soares, *Chem. Eng. Commun.*, 1980, **5**, 149.

H^E, S^E, and V^E are negative. This implies some special kind of attraction or association between a xenon atom and an ethane molecule, though the reason for this is by no means obvious. The ethane molecule has a quadrupole moment, and the xenon atom is the most polarizable of the rare gas atoms, so inevitably quadrupole-induced dipole attraction must enter into the Xe–C_2H_6 potential. But it is doubtful if any of the current theories would or could predict negative values for all four excess functions. 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 a more detailed model will be required to do justice to the system.

6 Conclusions

It is fair to say that perturbation theory has achieved notable successes in accounting quantitatively for the observed thermodynamic properties of molecularly simple binary liquid mixtures in terms of the intermolecular forces involved. Where agreement between theory and experiment is less impressive, it would seem that the reason for this must be sought in the inadequacy of the potentials used rather than in any shortcomings of the theory as such. The reader unfamiliar with this field of physical chemistry may have been surprised by the complexity of the intermolecular potentials already used for pairs of like molecules as simple as those of hydrogen chloride and dinitrogen oxide. Nevertheless, it begins to appear that there are limitations to what can be achieved if the polarity of a molecule is dealt with by assigning it a *point* dipole, *point* quadrupole, or higher multipole. It may prove necessary to move to point charge models which represent more realistically the electronic structure of the molecules, though calculations which are already lengthy and complicated will no doubt become still more so.

The work surveyed in this review can be regarded as belonging to the first stage of an approach to the problem of the molecular interpretation of the thermodynamic properties of liquid mixtures. Proceeding from the simplest systems, the experimental work should deal with mixtures of molecules of increasing size and complexity, and so ultimately lead to an understanding on a molecular basis of the properties of mixtures of important and familiar substances which are liquid at ordinary temperatures. Few would question the desirability of achieving this goal, but it must be admitted that it still seems a long way off.