



THE IMPACT OF LIONEL STAVELEY'S RESEARCH ON THE THEORY OF LIQUID MIXTURES

A brief survey is presented of the impact of Lionel Staveley's work on the theory of liquid mixtures. Starting in the 1950's with experiments on mixtures of carbon monoxide and methane, his work on liquids has been closely tied to the needs of theory. His studies of simple liquids of spherical molecules played a crucial role in the development of theories of such simple liquids in the period from the mid-1950's to the 1970's. His more recent work on mixtures of molecular liquids is now proving of great value in evaluating theories for liquids of nonspherical molecules. Several examples are presented of this interplay between theory and experiment.

I first met Lionel Staveley in 1974 on a visit to Oxford. At that time our interests had turned to the development of perturbation theory for nonspherical molecules. There was a wealth of experimental data on liquid mixtures at room temperature and pressure, but for the most part these involved rather large and often flexible molecules that were not well suited to testing the theories that we were working on. We needed accurate data on mixtures of relatively small, rigid molecules, such as N_2 , CH_4 , HCl , CF_4 , C_2H_4 , N_2O , etc., and it was soon clear to us that Lionel would be the best man to help us. Our initial meeting nearly ten years ago led to a rewarding and most pleasant collaboration. Our discussions were made much easier for me by Lionel's ability to concentrate on the main scientific goals — to "leave out the sordid details of the experiment" as he would put it; these "details" were far from trivial, and involved dealing with a variety of problems of corrosion, toxicity, high pressures, etc. Since the mid-1950's Lionel Staveley's work on liquid mixtures has been remarkable in that it has focussed on those mixtures of greatest interest to theorists working in this area. In a review of mixture data suitable for testing theories published in 1972 by Mc DONALD [1], almost 40% of the papers were from Staveley's laboratory. Of more importance, in cases where there were discrepancies between Staveley's and earlier work, Staveley's measurements were usually judged to be the more accurate [2,3]. His recent work on molecular liquids has provided a wealth of data that will provide a challenge to theorists for some years to come.

1 — EARLY WORK ON LIQUIDS; BEFORE 1955

Lionel's initial work was in the area of kinetics. His first papers [4] were published 50 years ago when he was only 18, with Hinshelwood and Moelwyn-Hughes. His first work in thermodynamics was in 1938, when he spent a year (on a Goldsmith's scholarship) in the laboratory of Professor K. Clusius* in Munich. There he carried out experiments on the effect of isotopic composition on the triple point of various cryogenic liquids, including argon and xenon. This work was published [5,6] in 1941,

* Clusius was a student of Eucken, who was in turn a student of Nernst. Thus the "genealogy" is Nernst → Eucken → Clusius → Staveley.

during World War II. During the next 14 years there were a series of studies on hydration and hydrogen bonding — particularly the solubility of water in various solvent mixtures (benzene + alcohols and benzene + various organic liquids); these studies continued up to 1949 [7-12]. There were also studies of entropy of vaporization [13] and of heat capacities [14,15], but no further work on cryogenic liquids.

During this early period the theory of Scatchard and Hildebrand (later called regular solution theory by Hildebrand) was influential, and qualitative discussions of experimental results often referred to this theory. The regular solution theory [16] assumes a zero excess entropy, i.e. a mixture in which the molecules surrounding a central A molecule, say, are randomly distributed among other A's, B's, etc. The excess volume is also taken to be zero, and the excess Gibbs energy is given by

$$G^E = v\phi_A\phi_B(\delta_A - \delta_B)^2 \quad (1)$$

where v is the molal volume of the mixture, ϕ_α is the volume fraction of α , and δ_α is the solubility parameter. The regular solution theory is an extension of the theory of van Laar, and is restricted to mixtures in which G^E is positive (and hence H^E also), while V^E and S^E are small.

2 — THEORY FOR MIXTURES OF SPHERICAL MOLECULES: 1950 — THE 1970's

Starting in the early 1950's a number of theories were developed for mixtures in which the molecules are spherical. These theories used statistical mechanics as a starting point and solved the equations by introducing well-defined approximations (lattice models, random mixing, etc.), in contrast to the older work of Hildebrand. Much of the work in the 1950's and 1960's stemmed from the idea of a random mixture. Although the early work was carried out in the framework of cell models, the theories do not require this and the central ideas are more transparent if the cell model is avoided [1-3]. If we consider the configurational energy U_C , it is given for a mixture of spherical molecules by

$$U_C = 2\pi N \rho \sum_{\alpha\beta} x_\alpha x_\beta \int_0^\infty dr r^2 u_{\alpha\beta}(r) g_{\alpha\beta}(r) \quad (2)$$

where $\rho = N/V$ is the number density, x_α is mole fraction of α , $u_{\alpha\beta}(r)$ is the intermolecular pair potential energy, and $g_{\alpha\beta}(r)$ is the radial distribution function for an $\alpha\beta$ pair ($g_{\alpha\beta}$ is proportional to the probability of finding an α molecule at distance r from a β molecule). For a random binary mixture these probabilities are the same for all pairs, i.e.

$$g_{AA}(r) = g_{AB}(r) = g_{BB}(r) = g_x(r) \quad (3)$$

and (2) becomes the energy of a pure fluid,

$$U_C = 2\pi N \rho \int_0^\infty dr r^2 u_x(r) g_x(r) \quad (4)$$

where

$$u_x(r) = \sum_{\alpha\beta} x_\alpha x_\beta u_{\alpha\beta}(r) \quad (5)$$

is the (composition-dependent) intermolecular potential energy for a hypothetical pure fluid, so that the mixture properties are equal to those of an *equivalent pure substance*.

The random mixture theory was actively pursued by PRIGOGINE and his coworkers in Brussels [17-19]. Clearly, the approximation (3) will only be suitable if the molecules are equal or almost equal in size — otherwise the peaks in $g(r)$ will occur at different r values for the various pairs. When the molecules are the same size, and the energy parameter ϵ_{AB} obeys the Berthelot rule,

$$\epsilon_{AB} = (\epsilon_{AA}\epsilon_{BB})^{1/2} \quad (6)$$

the theory predicts that G^E is positive while V^E is negative. This prediction was in contrast to that of the regular solution theory and its modifications, and also to the conformal solution theory of Longuet-Higgins; these theories predicted that G^E and V^E should have the same sign. At the time this prediction was made there were no suitable experimental data available to test these ideas, however — such data as existed were for relatively large and complex molecules (neopentane, cyclohexane, etc.). It was at this point, in 1951, that Prigogine sent one of his co-workers, Victor Mathot, to Oxford. The original plan called for Mathot to work with Fritz Simon on low temperature physics, but after some initial discussions it was decided that he would work in Staveley's laboratory instead, making careful measurements to test the predictions of the current

theories. Molecules of equal size were needed; Kr/CH₄ was considered but rejected because of the expense of krypton, and CO/CH₄ was chosen as a suitable alternative. At that time the Glastonbury Abbey kitchen served as the laboratory in the Inorganic Chemistry Laboratory. Victor Mathot recounts that his apparatus grew higher and higher on top of the bench (the vapour pressure of CO/CH₄ at 90K is of the order 2 atm.) and he eventually had to use a ladder. One day, before leaving, he placed a small Belgian flag at the top of the apparatus. The next day he arrived in the lab to find a Union Jack placed above the Belgian flag. The originator of the Union Jack was never discovered, although Mathot had his own suspicions about this! The experimental work on CO/CH₄ was completed in 1954, and an initial account of the work was published [22] in 1955; this was followed by a more extensive account [23] of the work in 1956. The experiments showed that for this mixture G^E was positive while V^E was negative, as required by the random mixture theory; moreover quantitative agreement between theory and experiment was fairly good (fig. 1). This was a considerable step forward at the time.

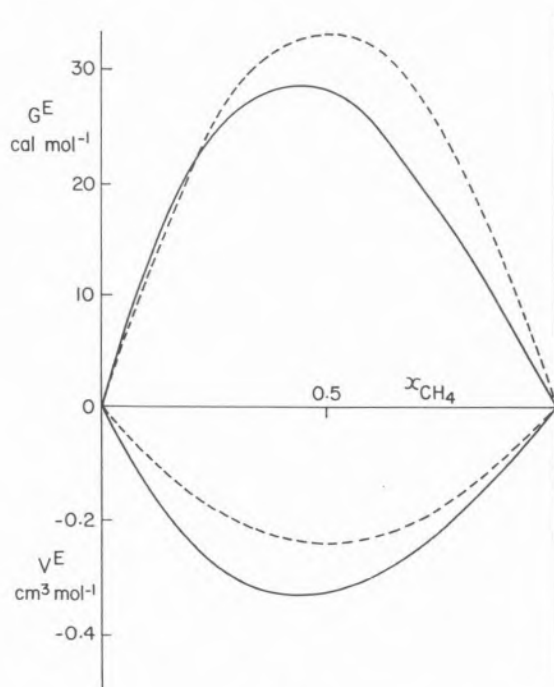
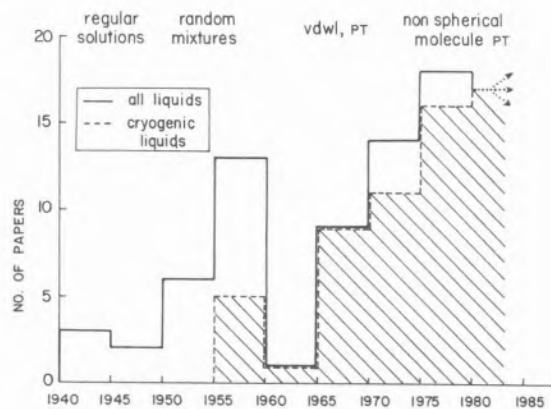


Fig. 1

Comparison of experiment (solid lines) and random mixture theory with ϵ_{AB} given by (6) (dashed lines) for G^E and V^E of CO/CH₄ mixtures at 90.67K (from MATHOT et al. [22])

The work with Mathot marked the beginning of Lionel's work on cryogenic liquid mixtures, and the development of his very precise cryogenic techniques. Over subsequent years the emphasis of his liquid phase research shifted more and more to the study of simple cryogenic liquids (see fig. 2).



PAPERS ON LIQUID PHASE THERMODYNAMICS: L.A.K. STAVELEY

Fig. 2

Research papers on liquid phase thermodynamics authored by Lionel Staveley and collaborators, averaged over 5 year intervals

Although the random mixture theory works fairly well for G^E and V^E of CO/CH₄ (fig. 1), later measurements of H^E for this system by POOL and STAVELEY [24] were not even in qualitative agreement with the theory. In particular, the experimental S^E is negative in CO-rich mixtures but positive in CH₄-rich mixtures. This cubic behaviour was not predicted by any of the existing theories in 1957. The initial work on CO/CH₄ was followed by studies of the excess properties of a variety of cryogenic mixtures of spherical or nearly spherical molecules [25-40], including Ar/N₂, Ar/O₂, O₂/N₂, CO/N₂, Ar/CO, Ar/Kr, Kr/CH₄, Kr/Xe and Ar/CH₄. In many of the earlier papers (see e.g. refs. 25-32) comparisons of the experimental data are made with the random mixture theory, and also with related theories of the time such as the average potential model (a 2-fluid theory) [19,41] and with Scott's three-fluid theory [41]. In the average potential model eq. (3) is replaced by

$$g_{AB}(r) = \frac{1}{2}[g_{AA}(r) + g_{BB}(r)] \quad (7)$$

Physically, this leads to an approximation in which the properties of the real mixture are equated to

those of an ideal solution composed of two pseudo-components A' and B', whose potentials are given by

$$u_{x\alpha} = \sum_{\beta} x_{\beta} u_{\alpha\beta}(r) \quad \alpha = A', B' \quad (8)$$

Comparisons with experiment showed that none of these theories gave good agreement. Later comparisons with computer simulation results [1,2] showed that the theories themselves were at fault (and not just the potential models used). These theories are particularly poor when the molecules differ in size; the peaks in $g_{\alpha\beta}(r)$ for the various pairs then occur at different locations, so that eq. (3) will be a very poor approximation. Much of the early work was reviewed by PARSONAGE and STAVELEY [42] (see also refs. 1-3).

In the 60's there were two significant developments in liquid theory which moved away from the older concept of a random mixture; these were the van der Waals 1-fluid conformal solution theory, and the hard sphere perturbation theory. The van der Waals 1-fluid (vdW1) theory [43-46] attempts to account for nonrandomness due to molecular size differences. In this theory (3) is replaced by

$$g_{AA}(r/\sigma_{AA}) = g_{AB}(r/\sigma_{AB}) = g_{BB}(r/\sigma_{BB}) = g_X(r/\sigma_X) \quad (9)$$

Eq. (4) again holds for the internal energy, with the potential parameters of the pure reference fluid given by the vdW1 mixing rules:

$$\epsilon_X \sigma_X^3 = \sum_{\alpha\beta} x_{\alpha} x_{\beta} \epsilon_{\alpha\beta} \sigma_{\alpha\beta}^3 \quad (10)$$

$$\sigma_X^3 = \sum_{\alpha\beta} x_{\alpha} x_{\beta} \sigma_{\alpha\beta}^3 \quad (11)$$

In the hard sphere perturbation theory the reference molecules have repulsive forces only, and the configurational energy is written as a reference plus a first order term:

$$U_c = U_0 + U_1 \quad (12)$$

The reference fluid properties are equated to those of a fluid of hard spheres through a second expansion. Three versions of the theory exist [47-49], which differ only in detail. The form due to WEEKS, CHANDLER and ANDERSEN [49], and extended to mixtures by LEE and LEVESQUE [49], is usually the

most accurate. Around 1970 the first extensive computer simulations of Lennard-Jones mixtures were carried out, and were used to test these and the earlier theories [1,2]. These tests showed that the vdW1 and hard sphere perturbation theories were much more accurate than the earlier random mixture theories. The vdW1 theory breaks down for molecules that are much different in size, but the hard sphere perturbation theory does not suffer from this defect because size difference effects are included in the reference fluid [50].

The experimental work of Staveley and his collaborators provided much of the data needed to test these theories, and many of their papers from about 1971 onwards have included comparisons with the more recent theories (see, for example, references 32,33,37,38 and 40). Mixtures of spherical molecules are most suitable for such tests, and typical comparisons with the experimental data of Staveley *et al.* are shown in Table 1 and fig. 3. Agreement with experiments is quite good. In these comparisons ϵ_{AB} and σ_{AB} are given by

$$\epsilon_{AB} = \zeta_{AB}(\epsilon_{AA}\epsilon_{BB})^{1/2} \quad (13)$$

$$\sigma_{AB} = 1/2 \eta_{AB}(\sigma_{AA} + \sigma_{BB}) \quad (14)$$

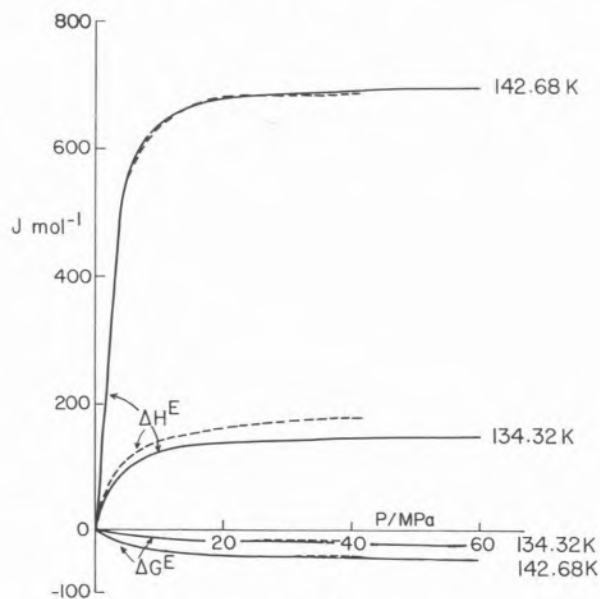


Fig. 3

Changes of the excess enthalpy and Gibbs energy with pressure for mixtures of argon and krypton at $x_{Ar} = 0.485$. Solid lines are from experimental data, dashed lines are calculated from vdW1-fluid theory. In the theoretical calculations eqn. (13) and (14) were used for ϵ_{AK} and σ_{AK} , with ζ_{AK} taken from Monte Carlo data and η_{AK} fitted to excess volume data (from BARREIROS *et al.* [40])

when $\zeta_{AB} = \eta_{AB} = 1$ these equations reduce to the usual Lorentz-Berthelot rules.

Table 1
Results for Ar/Kr mixtures, $T = 116\text{K}$, $P = 0$
(From McDONALD [1] and HENDERSON and LEONARD [2] *)

	$G_{1/2}^E/\text{J mol}^{-1}$		$H_{1/2}^E/\text{J mol}^{-1}$		$V_{1/2}^E/\text{cm}^3 \text{mol}^{-1}$	
	$\zeta_{AB}=1$	$\zeta_{AB}\neq 1$	$\zeta_{AB}=1$	$\zeta_{AB}\neq 1$	$\zeta_{AB}=1$	$\zeta_{AB}\neq 1$
Monte Carlo	+ 46	+ 84	- 29	+ 29	-0.69	-0.60
RM	+ 203	—	+ 254	—	+ 0.42	—
VDW1	+ 46	+ 84	- 30	+ 24	-0.68	-0.66
PERT (LHB)	+ 39	+ 84	- 28	+ 32	-0.62	-0.57
EXPT.[29,39]		+ 84		+ 42.7		-0.52

* In these calculations $\eta_{AB}=1$ in eqn. (14). $G_{1/2}^E$, $H_{1/2}^E$, and $V_{1/2}^E$ are the excess properties for the equimolar solution; RM=random mixture theory, VDW1=van der Waals 1-fluid theory, PERT (LHB)=the hard sphere perturbation theory of Leonard, Henderson and Barker; ζ_{AB} is defined by eqn. (13). For the cases where $\zeta_{AB}\neq 1$ the ζ_{AB}^E value is adjusted to make theory and experiment match for $G_{1/2}^E$.

3 — THEORY FOR MIXTURES OF NONSPHERICAL MOLECULES: 1974 — THE 1980'S

Lionel and his collaborators realised at an early stage that the assumption of central isotropic intermolecular forces was likely to lead to error even for such relatively simple molecules as CO, CO₂, etc. In 1957 POOL and STAVELEY [24] wrote:

“For CO...there is evidence that the rotational movement in the pure liquid is restricted... The chief need on the theoretical side is for further consideration to be given to the effect of directional forces. On the experimental side, almost all the systems suitable for study should be investigated, since their number is very limited”.

The same concern was expressed in the 1959 review by PARSONAGE and STAVELEY [42]:

“Even a (symmetric) diatomic molecule will have a quadrupole moment...It is now realized that quadrupole forces can have a more important influence on the physical properties...than was at one time supposed (as shown by Buckingham)”.

However, it was not until the early 1970's that serious attempts were made to include the noncentral nature of the intermolecular forces in theoretical calculations of thermodynamic properties [51].

In the most widely used perturbation theory approach, the reference fluid is one of spherical molecules with intermolecular potential $u_0(r)$ defined by

$$u_0(r) = \langle u(r\omega_1\omega_2) \rangle_{\omega_1\omega_2} \quad (15)$$

where $\langle \dots \rangle_{\omega_1\omega_2}$ means an unweighted average over the orientations ($\omega_i = \theta_i\phi_i$ or $\phi_i\theta_i\chi_i$ for linear or nonlinear molecules, respectively), $u(r\omega_1\omega_2)$ is the pair potential in the fluid of interest, and r is the vector from the centre of molecule 1 to the centre of molecule 2. In practice the Lennard-Jones (n,6) model is often used as the reference potential, and the potential for the full system is written as a sum of multipole, induction, overlap (shape) and dispersion terms:

$$u(12) = u_0(r) + u_{\text{mult}}(12) + u_{\text{ind}}(12) + u_{\text{ov}}(12) + u_{\text{dis}}(12) \quad (16)$$

where $(12) \equiv (r\omega_1\omega_2)$. The Helmholtz energy A is then given by (the A_1 term vanishes in this series)

$$A = A_0 + A_2 + A_3 + \dots \approx A_0 + A_2 \left(\frac{1}{1 - A_3/A_2} \right) \quad (17)$$

where A_0 is the free energy of the reference system and A_2 and A_3 are the second- and third-order perturbation terms. General expressions have been worked out [52-53] for A_2 and A_3 , and involve two- and three-body correlation functions for the reference fluid. The second form of eqn. (17) is a Padé approximant to the series proposed by STELL *et al.* [54], and is found to agree remarkably well with computer simulation results even when strong electrostatic forces are present, provided that the molecules are not too nonspherical in shape. Calculations based on (17) show that the electrostatic forces have a very large effect on the thermodynamics properties [55], whereas the effect of nonspherical shape is smaller [53].

The more recent studies of molecular liquid mixtures by Staveley and coworkers have been designed to elucidate the role of electrostatic and other anisotropic forces. This can be achieved by comparing the data with eq. (17) and similar theories. This work has now resulted in a substantial body of data on G^E , V^E and H^E for mixtures involving the inert gas liquids and such small rigid molecules as CO,

NO, N₂O, C₂H₆, C₂H₄, NF₃, HCl, HBr, CH₄, CF₄, etc. Much of this data has been compared [56-60] with the predictions of eq. (17), and these tests throw considerable light on the relative importance of the various kinds of intermolecular forces. In these comparisons it is usual to fit the three (n, ϵ , σ) potential parameters (n, ϵ , σ) to the pure fluid data, and to fit the unlike pair parameters ζ_{AB} and η_{AB} in eqns. (13) and (14) to G^E and V^E at a single temperature. The ability of the theory to fit G^E and V^E at that temperature is then only a weak test; a much stronger test is that provided by H^E and by G^E and V^E at temperatures other than the temperature of fit. The excess enthalpy is particularly sensitive to details of the intermolecular forces.

For Xe/N₂O [58] and Xe/CF₄ [59] mixtures the theory and experiment are found to be in essentially quantitative agreement for all three excess properties, using the lowest order spherical harmonic terms to represent the multipolar, dispersion and overlap potential terms in eq. (16). The multipolar forces have a much larger influence on the thermodynamics than the anisotropic dispersion or overlap forces in these systems; for CF₄ the leading multipole term is the octopole-octopole, and for N₂O the main contribution is from quadrupole-quadrupole forces, the dipolar terms being negligible in this case.

For the mixtures Xe/HCl, Xe/HBr and HCl/HBr the situation is more complex. Using intermolecular potentials that include the leading multipole (dipole and quadrupole), induction, dispersion and overlap terms it is possible to describe G^E and V^E for these systems quite well, and also the vapor-liquid equilibria and azeotropic compositions (for Xe/HCl) [56]. This is shown in fig. 4 and 5. It is interesting that the theory correctly predicts the "cubic" behaviour of V^E for Xe/HBr, such behaviour is quite common in polar/nonpolar mixtures [3]. However, the same intermolecular potential models give H^E values that are too large by 60-100%, depending on the precise details of the model used [57] (see fig. 6). the reason for this discrepancy is not yet understood. It may be due to an improper treatment of the electrostatic or induction forces. The latter are now known [61] to be very poorly represented by the isotropic pair term used in these calculations; both anisotropy of the polarisability and multibody effects are known to be important.

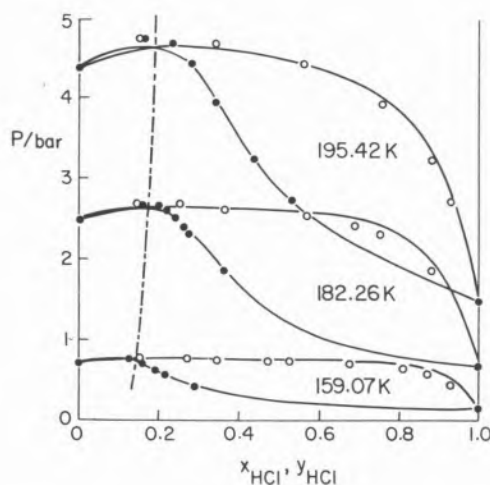


Fig. 4

Vapour-liquid equilibria for HCl + Xe from experiment (points) and theory of eqn. (17) (lines). The dash-dot line is the azeotropic locus (from CALADO et al. [56])

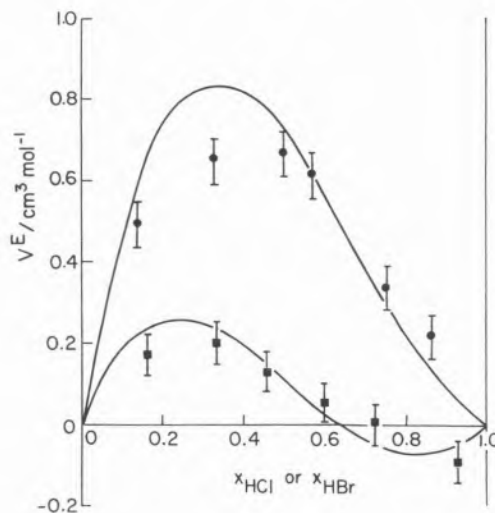


Fig. 5

Excess molar volumes for HCl + Xe (●) and HBr + Xe (■) at 195.42 K compared with theory of eqn. (17) (lines) (from CALADO et al. [56])

Mixtures containing ethylene are interesting in that ethylene is the simplest example of a molecule with a nonaxial quadrupole [62] — i.e. in contrast to such highly symmetrical molecules as HCl, CO₂ and NH₃, ethylene has two independent quadrupole moments Q_{xx} and Q_{zz} (where z is along the C=C axis); similarly the dispersion and overlap forces are nonaxial for this fluid. Early calculations neglected the nonaxial nature of the molecule and used an "effective axial" approximation — i.e. a single

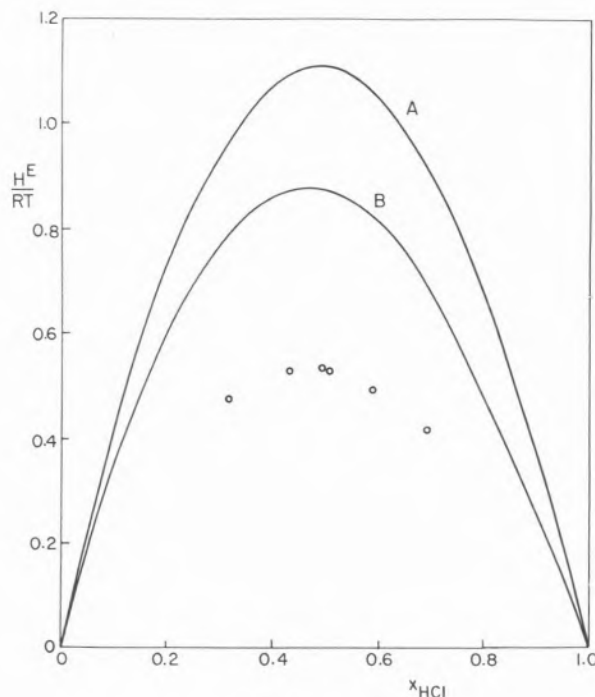


Fig. 6

Comparison of the theory of eqn. (17) for HCl-HCl potential models A and B (lines) with experiment (points) for H^E of HCl+Xe at 182.32K. In model A the potential consists of an $(n,6)$ term plus multibody terms (dipole and quadrupole). In model B anisotropic overlap and dispersion terms are also included. In both calculations the two-body induction potential between Xe and HCl is included (from LOBO et al. [57])

“effective” quadrupole moment. However, the values of Q_{xx} , Q_{yy} and Q_{zz} and also of the polarisabilities, are accurately known for ethylene, so that it should be possible to determine the magnitude of the nonaxial effects from eqn. (17). It is found that for ethylene the effects are small for the pure fluid [62,63], but are large in mixtures. Careful studies for mixtures of nitrous oxide + ethylene, carried out by Lélío Lobo and Lionel Staveley at Oxford, show clearly the importance of such effects. The nonaxial nature of the molecule affects all three excess properties, but the excess enthalpy is especially sensitive, as seen from fig. 7. Although the fit between theory and experiment is rather poor in this case, the calculation shows clearly the importance of correctly accounting for the nonaxial nature of the intermolecular forces. The fit to experiment can be improved in this case by modifying the N_2O - N_2O potential.

Much of the most interesting experimental data is yet to be compared with theory, including the mix-

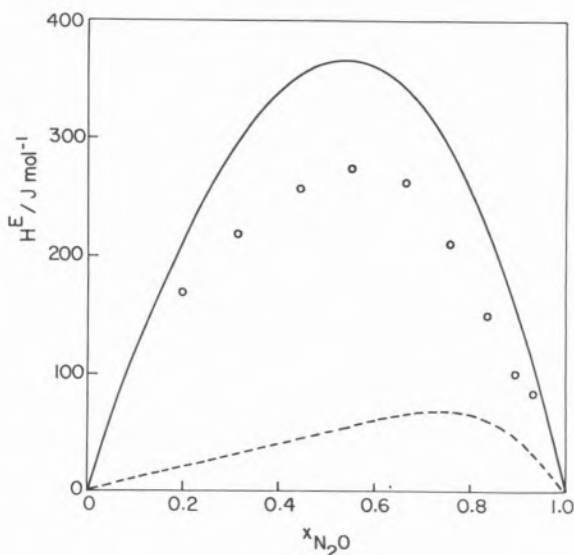


Fig. 7

The excess enthalpy of $N_2O + C_2H_4$ at 184.01K from experiment (points) and theory (lines); — correct nonaxial treatment; - - - approximate effective axial treatment (from LOBO et al. [60])

tures HCl + N_2O and HCl + CF_4 studied by Lobo and Staveley, while Lobo was at Oxford; the latter mixture exhibits liquid-liquid separation, and should provide a challenge to the theorists. In addition, new and more powerful forms of perturbation theory are now being developed, based on nonspherical reference molecules. These have yet to be compared to experiment, but such comparisons will probably be made in the next few years.

4 — CONCLUSION

Starting in the 1950's with his work with Victor Mathot on CO/CH_4 mixtures, Lionel's experiments on liquids have been closely tied to the needs of current theoretical studies. Because of the perception he has shown in choosing the most suitable systems for study, the interplay between experiment and theory has been especially strong and effective. His measurements on simple liquids of spherical molecules played a crucial role in the development of the simple liquid theories during the period from the 1950's to the 1970's. His more recent studies of nonspherical molecules are now playing a similar role in developing theories for more complex liquids. These data are likely to serve as a standard for testing theoretical ideas for many years to come.

His work will also continue to have great impact through the work of his many students and collaborators, several of whom have set up flourishing laboratories of their own.

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