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## PVT AND PHASE EQUILIBRIA OF SIMPLE AND NOT-SO-SIMPLE LIQUID SYSTEMS

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Although I am not supposed to be an impartial judge, let me begin by stating that I think this Conference has been very successful. We had two very good poster sessions, St. Peter answered quite positively to our prayers for good weather and, above all, there were four fine and authoritative plenary lectures, that covered most of the fields of interest of the participants.

The very success of this Conference, however, is my problem today. What am I going to say after all this? So I am afraid you will be soon to realize that my lecture is a typical case of last and... least.

Most of what I shall be reporting to you today are results obtained in the development of a project to obtain thermodynamic properties of relatively simple liquid mixtures, over extended ranges of temperature and pressure. When it started, several years ago, some important problems of liquid state physics were being solved. Noticeably, the repulsive part of the intermolecular potential had been identified as the essential cause of the structure of a non-hydrogen bonded liquid, the old van der Waals' ideas had been revived and successfully applied to liquid mixtures [1] and extensive computer simulations had fostered the development of perturbation theories.

This progress in our understanding of the liquid state called for suitable experimental results as, even in this age of computers, agreement with experiment must still be a measure of the success of a theory. Experimental data on liquid mixtures were, at the time, mostly measurements of excess thermodynamic properties of binary mixtures of condensed gases, as functions of composition, at one temperature (usually close to the triple point of the less volatile component of the mixture) and at the saturation vapour pressure (essentially zero pressure).

A theory of mixtures usually contains one or two adjustable parameters, supposedly characteristic of the potential between two unlike molecules in a mixture. These parameters can be obtained for instance, by fitting to the values of one or two excess functions for the equimolar mixture. As has already been pointed out in this Conference [2], this procedure does not leave much to be compared between theory and experimental results of the type described above. Moreover, as pointed

out by SOARES *et al.* [3], agreement at one temperature does not warrant that the same will happen at other temperatures.

An example of what was thought to be a thorough understanding of simple liquid mixtures was the paper of LEE *et al.* [4] on the system Ar+Kr. When it was published, the available experimental data on this important system was limited to excess volumes  $V^E$  at 116 K and excess Gibbs energies  $G^E$  at 104 K and 116 K [5]. The perturbation theory calculations of LEE *et al.* agree very well with these results. They also calculated excess enthalpies  $H^E$ . Although there were no experimental results to compare with, they stated that their values should be very reliable, because the experimental  $G^E$  were accurately predicted at two different temperatures.

More recently, STAVELEY and coworkers [6] published the first available experimental excess enthalpies. Comparison with the Barker-Henderson theory calculations of LEE *et al.* is shown in fig. 1. There is a striking disagreement, especially in what concerns the symmetry about the  $x=0.5$  axis.

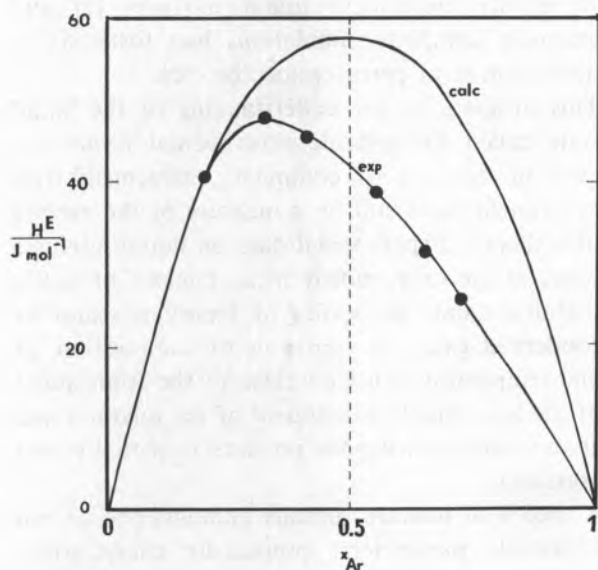


Fig. 1

Excess enthalpies  $H^E$  of argon+krypton liquid mixtures at 116 K: —●— experimental results reference [6]; — calculated results, reference [4]

This proves how difficult it is to devise meaningful tests of a theory with limited experimental data. Results over a wide range of conditions

(composition, temperature, pressure) would provide the best possible situation. For the important argon+krypton system, we have recently performed measurements of (p,V,T) properties [7] at several temperatures, up to the freezing pressure of krypton. Available results were therefore extended, so that most of the overlapping liquid ranges of argon and krypton have been covered. The dependence on pressure of the excess volumes  $V^E$  of an approximately equimolar mixture is shown in fig. 2. The main features of this dependence may be summarized as follows:

- The first 20 MPa of applied pressure exert a remarkably strong effect on  $V^E$ .
- At the highest pressures,  $V^E$  is essentially constant (independent of pressure and temperature) and approximately zero.

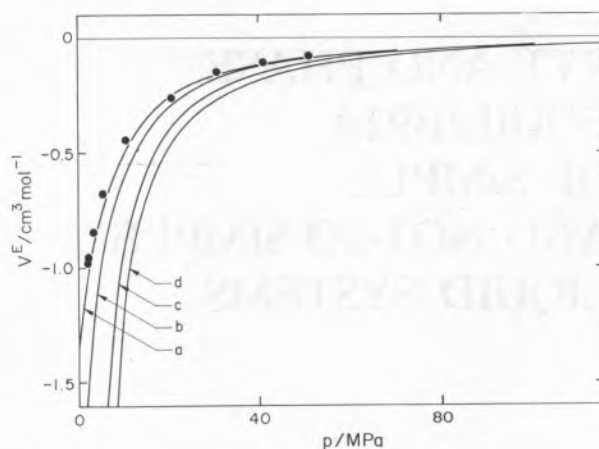


Fig. 2

Dependence on pressure of the excess volume  $V^E$  of an approximately equimolar mixture of liquid argon+krypton, at the following temperatures: (a) 129.32 K; (b) 134.32 K; (c) 142.68 K; (d) 147.08 K. ● data of reference [8], at 129.31 K

Fig. 3 shows the pressure effect on the composition dependence of  $V^E$ . At low pressures, the  $V^E$  vs. mole fraction  $x$  curves are quite obviously skewed to the side of the more volatile component, argon-rich mixtures yielding more negative  $V^E$ . This is a common feature for simple liquid mixtures. When pressure is raised, the curves become more symmetric up to about 20 MPa. When pressure is further increased, asymmetry is restored, but now in the opposite direction: argon-rich mixtures yield more positive  $V^E$ . As the

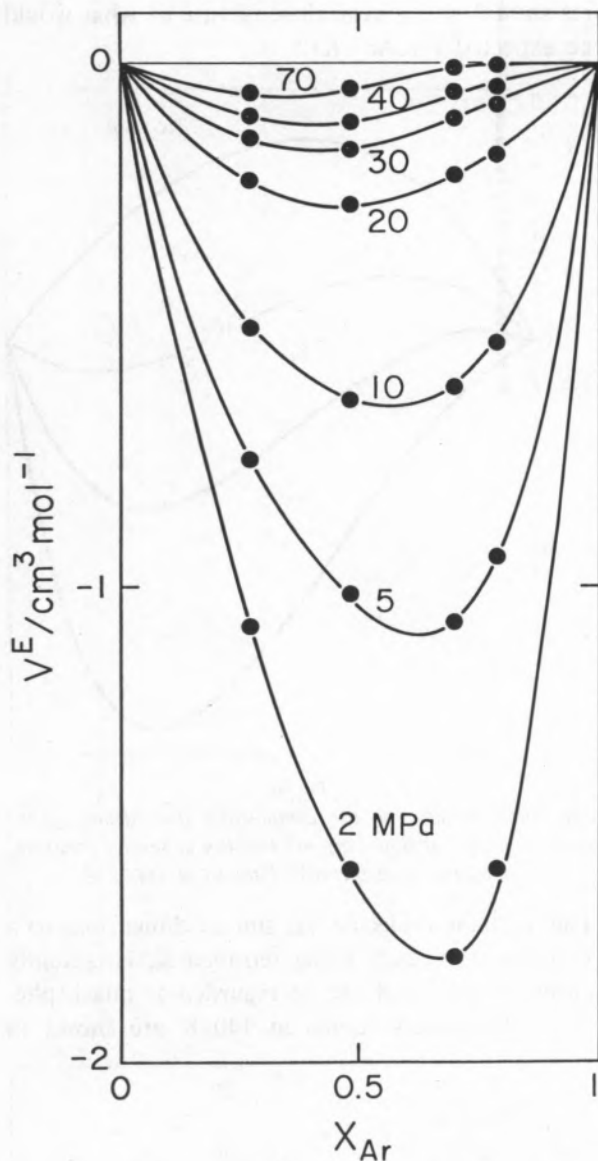


Fig. 3

Experimental excess volumes  $V^E$  for argon+krypton liquid mixtures, as function of composition, at several pressures and at 134.32 K

pressure approaches the freezing pressure of krypton, the  $V^E$  vs.  $x$  curves become almost S-shaped.

The temperature dependence of  $V^E$ , at several pressures, for  $x=0.5$ , is shown in fig. 4. Steep curves indicate a strong effect of pressure on the excess enthalpy, given by:

$$\Delta H^E = H^E(p) - H^E(p_0) = \int_{p_0}^p [V^E - T(\frac{\partial V^E}{\partial T})_p] dp \quad (1)$$

At low pressures, the entropy term  $[-T(\partial V^E/\partial T)_p]$  is dominant and very strong effects are obtained. Fig. 5 compares  $\Delta H^E$  with  $\Delta G^E$ , the effect of pressure on the excess Gibbs energy

$$\Delta G^E = G^E(p) - G^E(p_0) = \int_{p_0}^p V^E dp$$

It shows, as has already been said in this Conference [2], that  $H^E$  is a very sensitive thermodynamic function; the very steep increase of  $H^E$  with pressure should be compared with the figure given in reference [6]:

$$H^E(x=0.5, 116 \text{ K}, p=0) = 42.7 \text{ J mol}^{-1}$$

On the other hand,  $V^E$  changes more rapidly with pressure for the argon-rich mixtures than for the krypton-rich ones. It is reasonable to expect that the same will also be true for the change of  $V^E$  with temperature,  $(\partial V^E/\partial T)_p$ , and from equation (3),  $\Delta H^E$  at low pressures should therefore be larger for argon-rich mixtures. And so, although no measurements of  $H^E$  function of pressure have been performed yet for argon+krypton mixtures, we may predict that the  $H^E$  vs.  $x$  curves should be very asymmetric at least for some ranges of pressure.

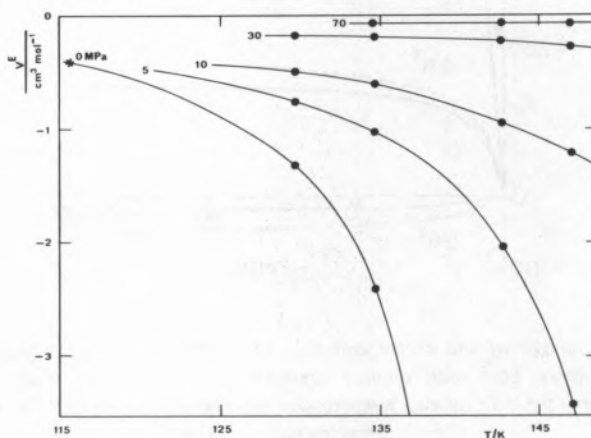


Fig. 4

Experimental excess volumes for an approximately equimolar mixture of liquid argon+krypton as a function of temperature, at several pressures: \* reference [5]; ● reference [7]

Some years ago, McDONALD [9], draw, from extensive computer simulations of simple liquid mixtures, the conclusion that "the  $G^E$  and the  $H^E$  dependence on composition is rather uninteresting". Although experiment proved him to be

right about  $G^E$ , it does not certainly seem to be the case for  $H^E$ .

To examine how theory predicted excess enthalpies, we used the simple, but successful van der Waals-one fluid theory [1]. The excess enthalpies of argon+krypton mixtures were calculated using the equation of state of argon given by GOSMAN *et al.* [10], to characterize the reference fluid. The experimental pressure dependence of  $H^E$ , for an equivalent molar mixture, was very well reproduced by theory, as shown in fig. 5. This is a remarkable success for such a simple theory. As to the  $H^E$  vs.  $x$  curves, the theory gives very asymmetric curves at low pressures, symmetry about the  $x=0.5$  increasing with applied pressure, as

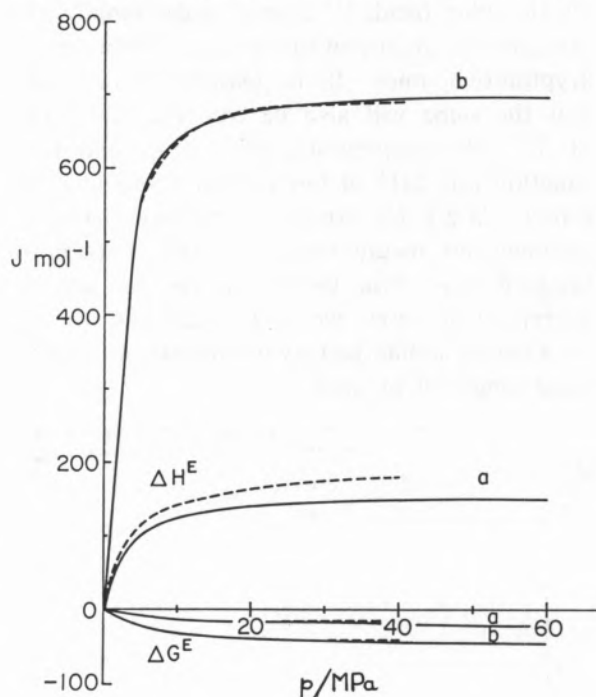


Fig. 5

Changes of the excess enthalpy  $\Delta H^E$  and the excess Gibbs energy  $\Delta G^E$  with applied pressure, for the mixture 0.485 Ar + 0.515 Kr, at two temperature: (a) 134.32 K; (b) 142.68 K. (— experiment; ---- theory)

shown in fig. 6. The larger pressure effect on argon-rich mixtures referred to above is correctly predicted.

WORMALD and collaborators made extensive measurements of enthalpies of mixing of simple liquids [11-13]. Although the system Ar + Kr was not included, the results obtained for Ar + CH<sub>4</sub> mixtu-

res should give a very close picture of what would be expected for Ar + Kr.

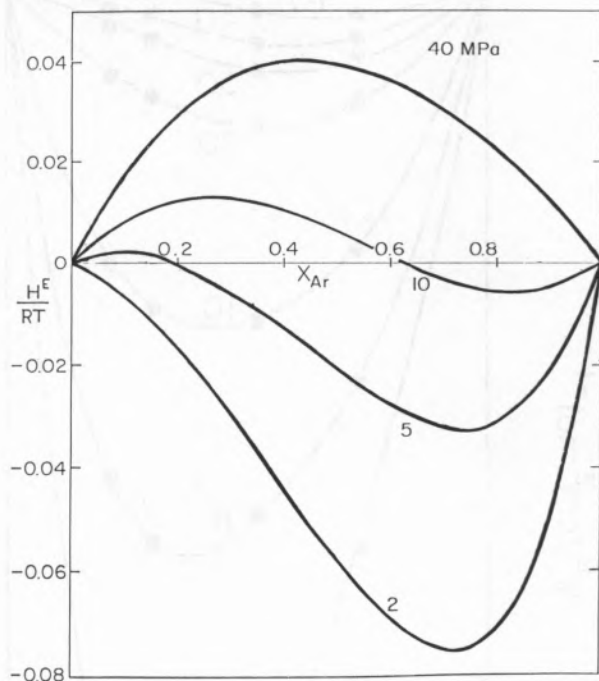


Fig. 6

Theoretical results for the composition dependence of the excess enthalpy of liquid argon + krypton at several pressures, calculated with the vdW-1 model at 134.32 K

The methane molecule has similar dimensions to a krypton atom and, being tetrahedral, is certainly quite compact and can be regarded as quasi-spherical. Wormald's results at 140 K are shown in

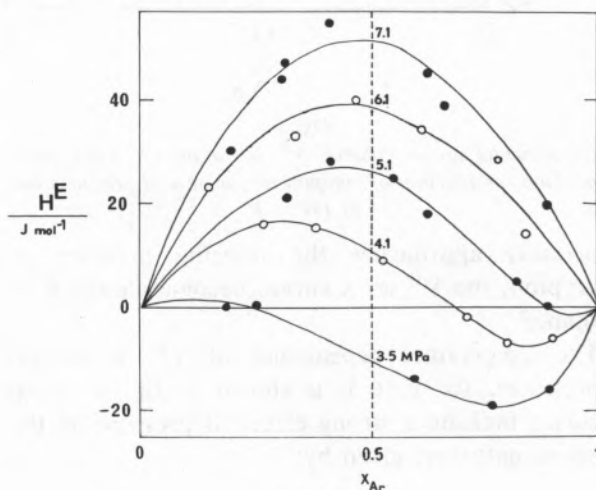


Fig. 7

Experimental excess enthalpies  $H^E$  for liquid argon + methane, as a function of composition at several pressures at 140.00 K, given in reference [13]

fig. 7 and give a qualitatively very similar picture to the vdW-1 calculations of fig. 6.

Wormald's results are complemented by several sets of results on vapour-liquid equilibrium and (p,V,T) properties, which make argon + methane mixtures one of the best studied of the simple liquid systems.

Vapour-liquid equilibrium data were reviewed by KIDNAY *et al.* [14] (p,V,T) properties were measured by SOROKIN and BLAGOI [15], LIU and MILLER [16], SINGH and MILLER [17,18], and NUNES DA PONTE *et al.* [19,20]. Good agreement was obtained between the results of different authors, and the available data extend from the triple point of methane up to close to the critical point of argon.

Fig. 8 shows results of several authors for the pressure dependence of the excess volume  $V^E$  of an equimolar mixture of argon + methane. At high pressures,  $V^E$  reaches a limiting value, as for argon + krypton, but positive ( $\sim +0.15 \text{ cm}^3 \text{ mol}^{-1}$ ), not zero.

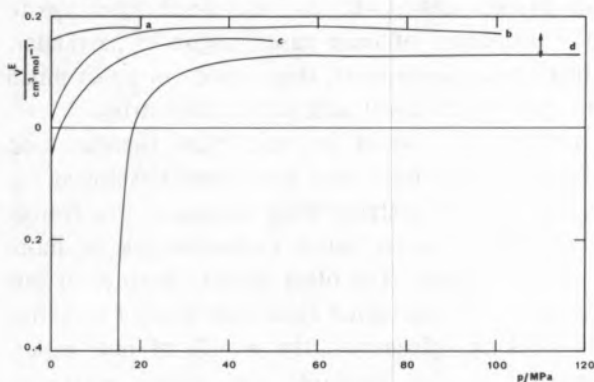


Fig. 8

Experimental excess volumes  $V^E$  for approximately equimolar mixtures of liquid argon + methane as a function of pressure, at the following temperatures: (a) 100.00 K, reference [17]; (b) 116.30 K, reference [19]; (c) 119.98 K, reference [15]; (d) 142.68 K, reference [20]

This effect may be interpreted in terms of the non-sphericity of the methane molecule. Fig. 9 shows a model for the interaction distance of two methane molecules. Collisional configurations where one hydrogen atom in one molecule fits the "hole" between three hydrogen atoms in the other one result in small carbon to carbon distances than in other configurations. An argon atom, however, has no protrusions that could give the same effect, and, therefore methane behaves

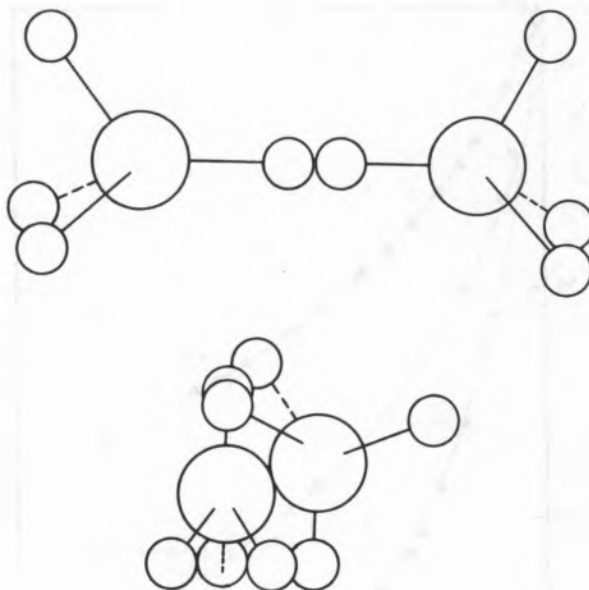


Fig. 9

Two possible relative orientations of two colliding methane molecules

on average as a bigger molecule in a methane-argon collision than in a methane-methane one. In fig. 10 we compare (p,V) isotherms of methane, argon and an equimolar mixture of both substances, with calculations based on a perturbed hard-sphere equation method due to OELLRICH *et al.* [21]. Agreement with experiment is rather good, except for argon near the vapour pressure. Shortcomings of these perturbation methods near the critical point are well known, and as argon is only 8K from its critical temperature, those discrepancies were to be expected. However, at high pressures, the experimental molar volumes of the equimolar mixture are higher than the calculated values. This is because the equation of state of hard-sphere mixtures given by MANSOORI *et al.* [22] and used in these calculations admits the additivity of the hard-sphere diameters:

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22}) \quad (3)$$

As methane behaves differently in 1-1 and 1-2 collisions, a deviation parameter  $j_{12}$  to the arithmetic rule can be introduced:

$$\sigma_{12} = \frac{1}{2}(1 + j_{12})(\sigma_{11} + \sigma_{22}) \quad (4)$$

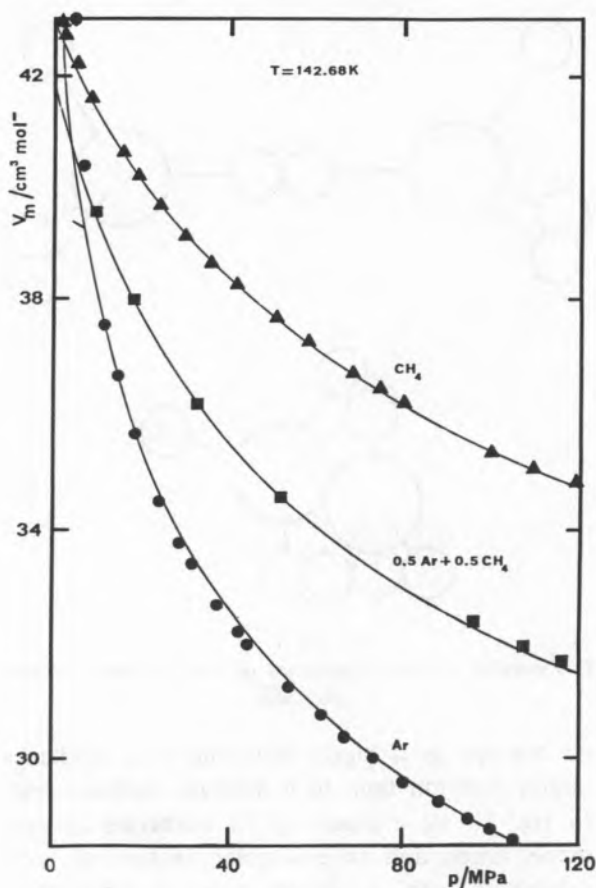


Fig. 10

( $p, V$ ) isotherms of liquid argon, methane and an equimolar mixture. ● ▲ ■, experimental; — theory, reference [21], ( $T = 142.68$  K)

Calculation of  $j_{12}$  was performed for several methane containing mixtures, as well as for argon + krypton. We fitted ( $p, V, T$ ) results for argon + krypton [7], argon + methane [19,20], nitrogen + methane [23], carbon monoxide + methane [24], and krypton + methane [25] by the equation of state of the [6,12] Lennard-Jones fluid given by NICOLAS *et al.* [26]. This gave us the distance and energy parameters  $\sigma$  and  $\epsilon$  for each pure substance and equimolar mixture, and then, using the van der Waals-one fluid theory [1] mixing rules, we calculated  $j_{12}$  and also  $k_{12}$ , the deviation parameter for the geometric mean rule:

$$\epsilon_{12} = (1 - k_{12}) (\epsilon_{11} \epsilon_{22})^{1/2} \quad (5)$$

Table 1 shows the results obtained with this procedure. Except for krypton + methane mix-

tures, the  $k_{12}$  values are all very similar. The trend in  $j_{12}$  is consistent with the high pressure values of the excess volumes,  $V_{\text{lim}}^E$ , obtained for each equimolar mixture.

These values can be compared with the results of SINGH and MILLER [27], that used several van der Waals-like equations.

For krypton + methane, the geometric and arithmetic mean rules are essentially valid. Although there are obvious differences between a spherical krypton atom and a tetrahedral methane molecule, they are of about the same size, and intermolecular potentials are actually rather similar. This explains why these mixtures are very nearly ideal, as shown by measurements of their excess functions [8,25,28,29].

The work I have been describing is concerned with simple liquid mixtures. This kind of work is sometimes looked at with some contempt by application minded scientists and engineers, and referred to as "argonitis". This is supposed to be a disease that has struck theoretists and experimentalists alike, who pay too much attention to the properties of inert gases, argon in particular. Inert gases being inert, they could not be of much interest to chemical and related industries.

However it should be said that theories and prediction methods that have been developed for simple liquid systems have provided the framework for a much better understanding of more complex liquids. The other plenary lectures of this Conference have given good examples of how this is working. Moreover, the wealth of new experimental results available for simple mixtures, make it likely that new fruitful theoretical efforts could be undertaken in this field. On the other

Table 1

Deviation parameters to the arithmetic mean rule,  $j_{12}$  (equation 4), and to the geometric mean rule,  $k_{12}$  (equation 5), and high pressure limit of the excess volume,  $V_{\text{lim}}^E$ , for several equimolar mixtures

	$j_{12}$	$k_{12}$	$\frac{V_{\text{lim}}^E}{\text{cm}^3 \text{ mol}^{-1}}$
Ar + Kr	-0.0002	0.029	0.
Ar + CH <sub>4</sub>	0.0056	0.025	0.15
N <sub>2</sub> + CH <sub>4</sub>	0.0031	0.026	0.12
CO + CH <sub>4</sub>	0.0015	0.026	0.02
Kr + CH <sub>4</sub>	0.0000	-0.003	0.

hand, "argonitis" has proved to be a lot of fun for many people working in this field, including myself. As JORGE CALADO once said [30], argonitis would be a very applied science in planet Venus, where the atmosphere seems to be much richer in argon than on Earth. And Krypton, of course, is the planet of Superman. So, if you think of such a typical simple mixture as argon + krypton as Venus + Superman, it is quite clear that "argonitis" can make your imagination wander.

Until now I have been talking about what may be considered simple liquid systems. Strictly speaking, only the condensed rare gases should be classified as such. However highly compact, small molecules, like nitrogen and methane, can be included in the list.

Many other liquids can be classified as "not-so-simple", this expression meaning, of course, that larger size and/or permanent multipole make the description of the intermolecular potential somewhat more complicated than in the case of spherically symmetric inert gases.

A significant share of the latest work on these liquids has been carried out in Oxford [31] and in Lisbon [32,33], and I will refer only to a small part I have been involved in.

We have recently concluded an experimental study of the equation of state of liquid carbon monoxide [34]. This is a small and compact molecule, with a small dipole and a large quadrupole: 0.112 Debye and  $-2.5 \times 10^{-26}$  e.s.u. cm<sup>2</sup>, following STOGRYN and STOGRYN [35]. Although it is of great theoretical and practical importance, experimental studies of its properties in the liquid phase are scarce, corresponding states methods being used in attempts to calculate them, with nitrogen as reference fluid [36].

Reduced second virial coefficients of nitrogen [37] and carbon monoxide [38,39] are plotted in fig. 11. At the higher temperatures the corresponding states principle is closely followed but at low temperatures there seems to be discrepancies, although definite conclusions can not be reached, because there is only one value for  $B(\text{CO})$ .

In the liquid phase, calculation based on a corresponding states correlation with nitrogen [36] depart somewhat from our experimental results. The influence of pressure on these deviations is

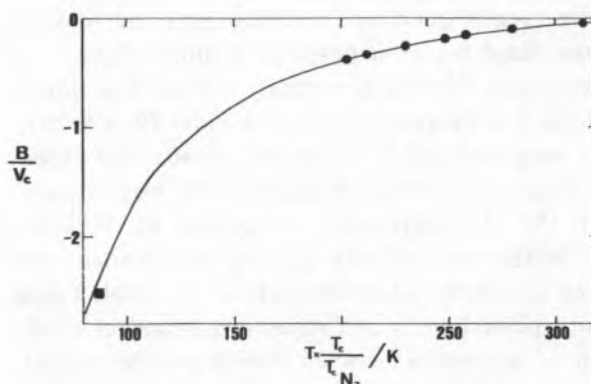


Fig. 11

Reduced second virial coefficients of nitrogen (—, reference [37]) and carbon monoxide (●, reference [39]; ■, reference [38])

shown in fig. 12. Although they increase with increasing pressure, they remain below one percent, indicating a reasonably successful application of the principle of corresponding states. At the freezing line, available results seemed to indicate until recently strong departures from corresponding states with nitrogen. FUKUSHIMA *et al.* [40] measured the melting pressure of carbon monoxide and their results departed considerably from those of MILLS and GRILLY [41] for nitrogen. However, our results [42] agree well with an extrapolation of the earlier ones of CLUSIUS *et al.* [43] and VERSCHOYLE [44] and are much closer to the nitrogen melting line than those of FUKUSHIMA *et al.*

So, the available evidence is that despite its small dipole and large quadrupole, carbon monoxide

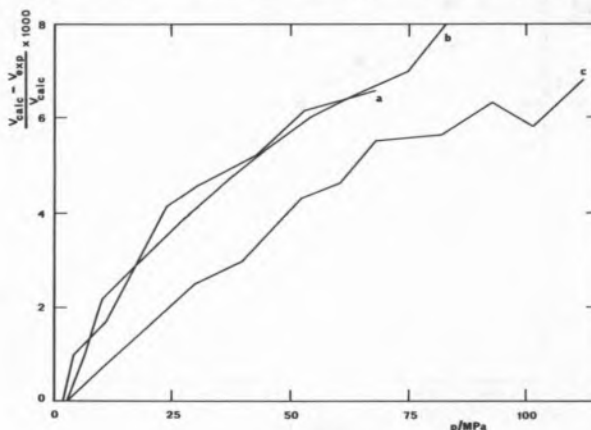


Fig. 12

Deviations between experimental [34] and calculated [36] molar volumes of carbon monoxide, as a function of pressure at: (a) 82 K; (b) 100 K; (c) 120 K

corresponds quite well with nitrogen and may be considered for most purposes a simple fluid. Hydrogen chloride is certainly a much less simple fluid. It is however as simple a polar fluid as may be imagined and therefore of considerable experimental and theoretical interest. The measurement of the thermodynamic properties of HCl-Xe, HCl-HBr and HBr-Xe [45,46] was perhaps the first systematic study of mixtures of simple liquid with polar liquids and remains a beautiful example of agreement between theory and experiment. POWLES, GUBBINS and collaborators [47] published results of a computer simulation on liquid HCl. They used a site-site [6-12] Lennard-Jones intermolecular potential, with parameters taken from previous results on  $\text{Cl}_2$ ,  $\text{N}_2$  and  $\text{H}_2$ , nitrogen being used for extrapolation to obtain the parameters for the H-H interaction. The potential thus obtained added to the dipolar and quadrupolar interactions, was proposed as a suitable approximation to the true potential for HCl molecules. However a much simpler potential was actually used in their computations, by taking only the site-site interactions but with parameters scaled by two factors  $f_\epsilon$  and  $f_\sigma$ . These factors were chosen to give a best fit to the experimental liquid density and vapour pressure along the entire coexistence line. Then calculated values of the internal energy were compared with experimental data, as shown in fig. 13. At the time of publication there was

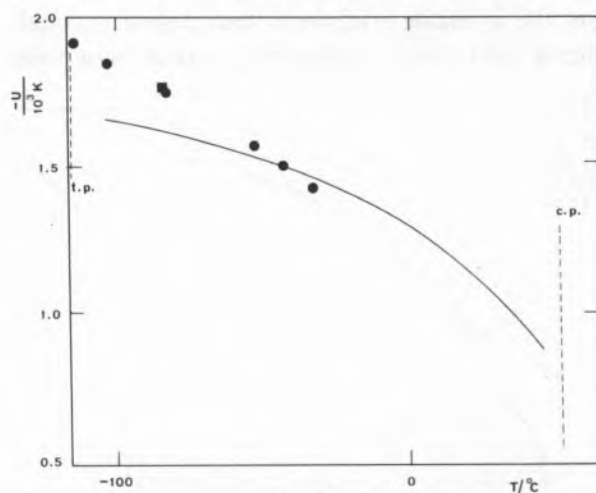


Fig. 13

Configurational internal energy of orthobaric liquid HCl, as a function of temperature: —, computer simulation, reference [47]; ■, experimental, reference [48]; ●, experimental, reference [49]

only the value given by GIAUQUE [48] to compare with, in the liquid phase. More recent work [49], in good agreement with Giauque's, gave the other values of  $U$  plotted in the figure. They show that at low temperatures discrepancies between experimental and computation increase. POWLES *et al.* stated in their paper that it would be valuable to have values of  $U$  at several temperatures, which would allow for a fit of the factor  $f_\epsilon$  independently of  $f_\sigma$ . We hope our values may lead in turn to a refining of their model.

I said most of what I intended to, but before I finish let me go back in time. Fig. 14 shows the excess functions,  $V^E$ ,  $G^E$ ,  $H^E$  and  $T.S^E$  for carbon monoxide + methane liquid mixtures. It is taken from a paper by POOL and STAVELEY [46] that reported the first comprehensive thermodynamic study of a mixture of condensed gases. As I went through it, I realized that it had been received by the editor on the 26th of March 1957, that is, twenty five years tomorrow. It was a fortunate coincidence that this Conference was scheduled for this occasion, thus commemorating what may be described as the silver wedding of thermodynamics of simple liquid mixtures. And even more fortunately, we were able to start in this Conference the Lionel Staveley Lecture Series and had Lionel Staveley himself giving us the first. All this make it a great honour for me to have participated in this event and given this lecture today.

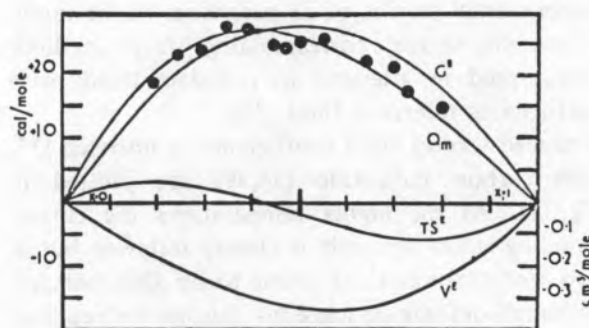


Fig. 14

Excess thermodynamic functions for the system  $\text{CO} + \text{CH}_4$  at 90.67 K, against mole fraction of carbon monoxide. The points are the experimental values of  $H^E$  (Qm). The figure is taken from reference [46]

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