



THERMODYNAMICS AND STATISTICAL MECHANICS OF THE FLUID STATE

This paper is an edited version of the one delivered at the Symposium held in Oxford on 25th June, 1982 to mark the retirement of Dr. Lionel Staveley.

The behaviour of a substance in its gaseous or liquid state tends to be dominated by the fact that the molecules within it exert forces upon one another. We do, of course, have the concept of a perfect gas, for which $PV = RT$, an equation which results when all intermolecular forces are set to zero, but real substances only approximate to this in the gaseous state at low pressures. At higher pressures, generally above a few bars, the influence of the intermolecular forces becomes increasingly important until at about 100 bars pressure they may even dominate. In the case of liquids, there is no such thing as a perfect liquid, and intermolecular forces are important at all times. Indeed, were it not for the existence of intermolecular forces, liquids would not exist. The task facing anyone conducting research into the fluid state is therefore twofold: (1) to quantify the forces which molecules exert on one another and (2) to supply the link between these intermolecular forces and the observable, macroscopic, properties of the fluid phase.

This is an enormous task made particularly difficult by the fact that the two questions are closely coupled. Normally we have to make experimental measurements on some macroscopic systems and infer from these measurements what the intermolecular forces might be, by assuming a particular link between the microscopic and the macroscopic quantities involved. In a few cases, this link is well known, but usually it is not.

For example, if we make measurements of the P - V - T properties of a monatomic gas at low pressures, we find that we can represent the behaviour as

$$PV/RT = 1 + B/V$$

and statistical mechanics allows us to write, rigorously,

$$B(T) = -2\pi N \int_0^{\infty} [\exp(-U(r)/kT) - 1] r^2 dr$$

where B is the second virial coefficient and $U(r)$ is the potential energy of a pair of atoms a distance r apart. It has the general functional form shown in fig. 1 for argon-argon and krypton-krypton interactions.

LIONEL STAVELEY has contributed substantially to the body of knowledge on this subject by a series of precision measurements of B , particularly for the rare gases argon, krypton and xenon [7, 15]. These

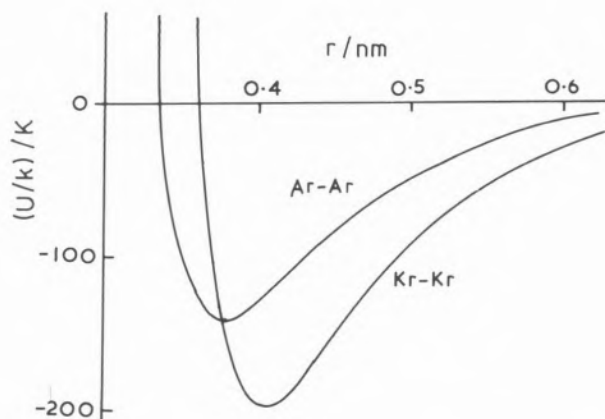


Fig. 1

Intermolecular potential energy curves for argon-argon and krypton-krypton interactions

have then formed the basis of various inversion procedures to obtain $U(r)$.

For other fluid states one does not have this simplification and the problem is more intractable. However, in recent years, computer simulation has improved things considerably, and more about this will be found in the later papers at this meeting.

LIQUID MIXTURES

Much of LIONEL STAVELEY's work has been concerned with liquid mixtures and I would like to illustrate the importance of these measurements by describing a common chemical engineering situation.

A chemical process plant rarely handles pure substances. Thus, for example, a petroleum refinery will have as its feed, a complex multicomponent mixture of hydrocarbons which it will endeavour to split into a number of smaller streams each containing a rather more restricted range of the same hydrocarbons. This separation process is usually based on distillation and in the distillation column shown in fig. 2, each tray is a plate with holes through which vapour from the lower stage can pass, bubbling through the liquid trapped on each tray, excess liquid flowing down to the tray beneath. Clearly, the composition of the liquid on each tray is different, being richer in the more volatile components as one goes higher up the column.

Faced with the design of such a column, one clearly needs the relevant thermodynamic information, both for the liquid and vapour phases, from which the liquid-vapour equilibrium can be calculated.

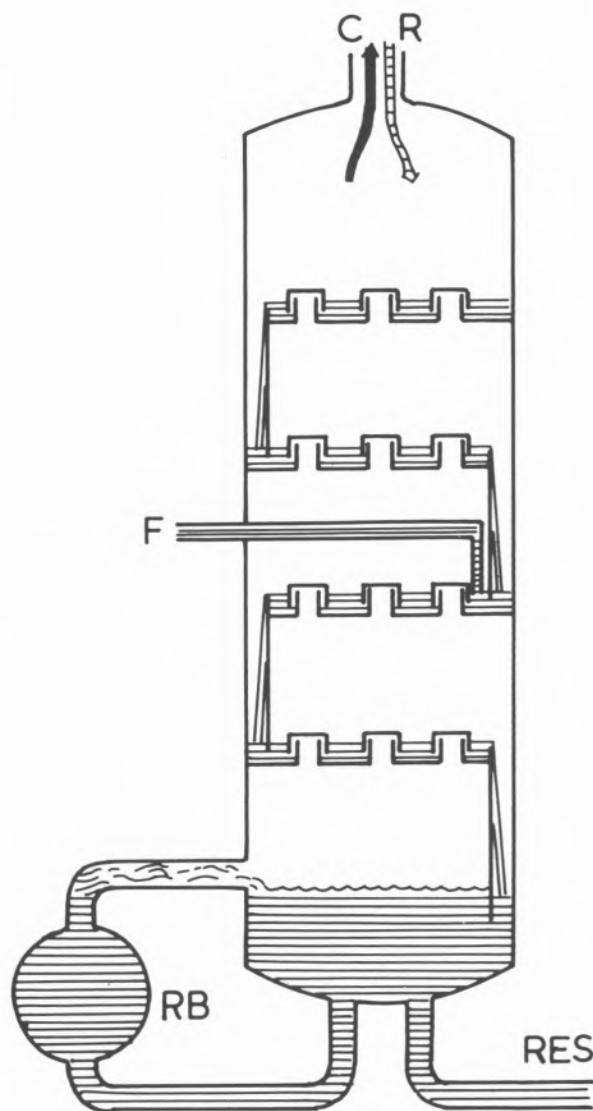


Fig. 2

Distillation column showing: the feed F , the reboiler RB , the residue RES , the vapour stream to the condenser C and the liquid reflux stream from the condenser R

Usually it is information about the liquid phase which is lacking, since one often has adequate approximations for the vapour phase.

One can see why this information is likely to be lacking; there is hope of our being able to measure the thermodynamic properties of each pure substance present in the mixture; there is no hope of our ever being able to measure the same properties for every possible mixture which can be formed from them. We therefore need a means of predicting liquid mixture properties, perhaps from a knowledge of the

properties of the pure components. But however we do it, it is more likely to be reliable if the method is soundly based on theory rather than being a purely empirical averaging procedure.

Liquid mixture properties are usually expressed in terms of the so-called excess functions. If we mix two liquids together at a given pressure and temperature, the volume of the resulting mixture is very often close to the sum of the two original volumes. We therefore write

$$V^E = V_{\text{mix}} - V_1 - V_2$$

where V_{mix} is the volume of the mixture and V_1 and V_2 are the volumes of the two unmixed liquids, with the expectation that V^E will be small. A similar situation holds for the excess enthalpy of a mixture

$$H^E = H_{\text{mix}} - H_1 - H_2$$

The excess Gibbs free energy is particularly important when studying liquid-vapour equilibrium. In this case the definition is, per mole of mixture of composition (x_1, x_2),

$$G^E = G_{\text{mix}} - x_1 G_1 - x_2 G_2 - x_1 RT \ln x_1 - x_2 RT \ln x_2$$

Once we have a complete set of the values (V^E , H^E and G^E) as a function of pressure, temperature and composition, then we have completely determined the thermodynamics of the system. We note also that for an ideal mixture, all excess functions are zero.

Dr. STAVELEY began his experimental work on liquid mixtures around 1950. Initially he investigated mixtures in which the components are liquids at normal temperatures — alcohols, benzene, cyclohexane, etc. He found that the excess functions varied enormously in magnitude, the alcohols with their hydrogen bonds tending to form very non-ideal solutions whereas the less polar molecules formed mixtures which were much closer to ideal [1-4].

This early work led him to conclude that the non-ideality of a liquid mixture was very sensitive to the molecular species involved. Molecular shape and specific interactions were having a very large influence on the excess functions, thus making it very difficult to make any sensible test of the mole-

cular theories of liquids then available. The whole situation was just too complicated.

It was at about this time that substantial progress was being made in the theory of liquid mixtures and in particular, relating the excess properties directly to the intermolecular forces. These theories drew heavily on the assumed structure of the liquid phase, whether pure or mixed. An early example was the cell theory in which each molecule is presumed to move in a cell or cage formed by the others. In the case of a mixture, the cell wall could be made up of molecules chosen randomly and so in the case of a binary mixture, would contain molecules of both species. This theory is not particularly accurate, but it does illustrate the problems encountered in developing a theory of liquid mixtures.

Fig. 3 shows a "wanderer" molecule in a cell formed by other molecules. The motion of this wanderer molecule depends on the forces exerted on it by all of the molecules in the wall of the cell. If these molecules are not spherical, or if the wanderer molecule is not spherical, one has great difficulty in describing the force quantitatively. Even if all of the molecules are spherical, problems still remain; the cell is a dynamic entity, not a static one, so one needs some sort of time average; the cell is complicated in shape but can one approximate it as a spherical cavity?

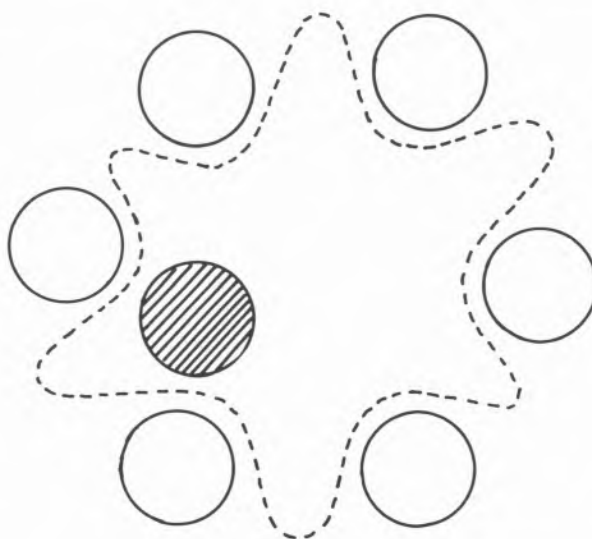


Fig. 3
Caging of the "wanderer" particle (shaded) in a cell formed by its nearest neighbours (open circles). The dashed line shows the approximate shape of the cell

Clearly, many approximations must go into a theory of liquid mixtures and it is desirable to choose to examine systems which require as few approximations as possible. From an experimental point of view we can begin by avoiding molecules of complex shape and examine only spherical molecules such as the rare gases argon, krypton and xenon. To this rather short list we can add the almost spherical oxygen, nitrogen, carbon monoxide, methane and carbon tetrafluoride.

All of these substances exist in the liquid phase only at low temperatures, generally around 100 K. LIONEL STAVELEY was the first person to grasp this nettle and measure experimentally V^E , H^E and G^E at these cryogenic temperatures. Experimentally, this is an order of magnitude more difficult than making the same measurements at room temperature. It is greatly to his credit that he showed that not only was it possible, but also obtained values of the quantities concerned which were of a precision that would have been considered remarkably good had they been determined at room temperature.

The first system investigated in this way was carbon monoxide-methane [5,6]. This choice might seem a little surprising, but was made for a number of reasons. First, as a purely practical one, the overlap of the two liquid ranges is such that measurements are possible at 90 K with pressures which do not exceed 2.5 bar. Secondly, it provides an excellent system with which to test the cell theory since this theory suggests that where two molecular species in a mixture are of essentially the same size, as are carbon monoxide and methane, V^E will be negative and G^E positive. This was to be compared with all other theories then current which predicted that both V^E and G^E would be positive. Fig. 4 shows what a triumph the cell theory appeared to have.

From this early success, Dr. STAVELEY moved on to increase the precision of his measurements and the range of substances covered, investigating most of the binary systems which can be formed from argon, nitrogen, oxygen, carbon monoxide, methane, krypton and xenon [7-15]. In many respects, argon-krypton and krypton-xenon should be ideal for testing theories of mixing since all three molecules involved are truly spherical and there is no possibility of molecular shape entering the argument. All three molecules obey the principle of corresponding states, i.e. they all have the same shape for the intermolecular potential energy curve,

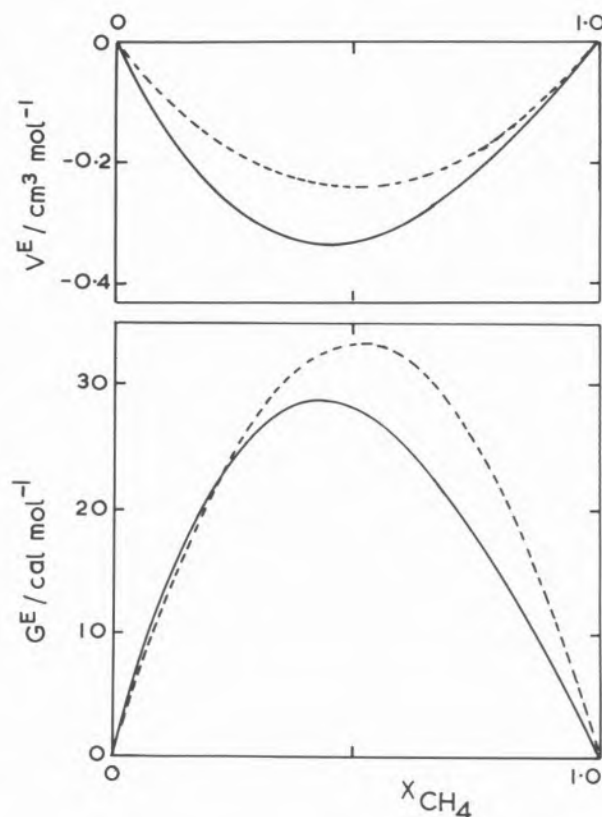


Fig. 4

Excess volume and Gibbs free energy for binary mixtures of carbon monoxide and methane at 90 K. The full lines are from experimental measurements, the dashed lines are calculated from cell theory

only the scales are different (fig. 1). However, there are severe experimental problems. The minimum temperature at which argon and krypton co-exist as liquids involves working with pressures of up to 10 bar. Development of experimental methods to deal with these conditions took some time and it was only five years ago that H^E for this system was finally measured [15].

Unfortunately, all of this work showed that the early success of the cell theory could not be maintained. Measurements on the argon-oxygen system resulted in values for V^E , H^E and G^E which were an order of magnitude greater than those predicted by the theory. The same was true for carbon monoxide-nitrogen. For argon-krypton the theory leads to a value for G^E which is only one half of that observed experimentally (fig. 5); for V^E the calculation fails completely.

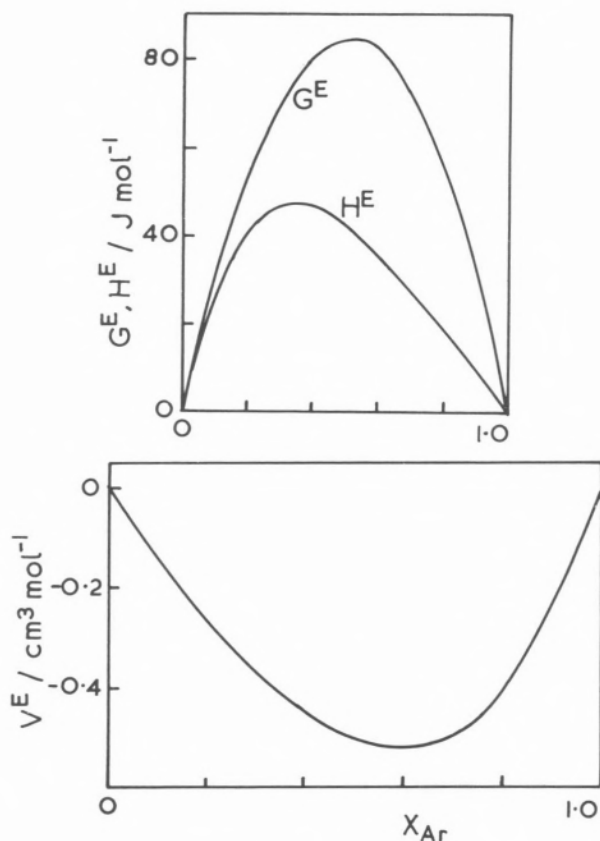


Fig. 5

Experimental measurements of the excess Gibbs free energy, enthalpy and volume for binary mixtures of argon and krypton at 116 K

As a result of Dr. STAVELEY'S efforts over the years, the scientific world now has in its possession an extensive body of experimental information on

cryogenic liquid mixtures. It has shown the old cell theory to be inadequate for describing liquid mixtures but it has also paved the way for the more modern theories which will be described in the following paper.

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