# EQUILIBRIA BETWEEN FLUID PHASES IN MIXTURES OF NON-ELECTROLYTES

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## ABSTRACT

At low temperatures gas–liquid and liquid–liquid phase equilibria are determined by the balance between the like and unlike intermolecular potentials in a mixture. For molecularly simple systems it is now clear that the unlike characteristic energies are weaker than the geometric means of the like energies, and there is evidence that this difference increases with difference of molecular size. In mixtures of aliphatic fluorocarbons and hydrocarbons the energy difference is large enough to lead to liquid–liquid equilibria and to upper critical solution temperatures (UCST).

If the molecules are more complicated, by virtue of either their polarity or their ability to form charge-transfer complexes, then the effective unlike interactions can be smaller or larger than the geometric mean. The former case is understood, at least semiquantitatively, and can lead again to UCST. The latter can lead, in special circumstances, to lower critical points (LCST). Here our understanding is less satisfactory since only lattice models have been studied theoretically.

At higher temperatures and pressures, both simple and complicated systems have critical lines, some of which can unambiguously be called gas–liquid lines and some liquid–liquid, but many of which defy such simple classification. The exploration of the kinds of critical line which can occur has recently been an active field of experimental research, and it is probable that there is now little really new to be discovered for binary mixtures. However, the precise behaviour of the thermodynamic functions on critical lines is a field which is ripe for further study since Griffiths and Wheeler have set up a classical thermodynamic scheme of classification. This leads to many precise predictions which now await confirmation or disproof.

Our attempts to understand the critical behaviour of mixtures in terms of the intermolecular forces has proceeded along two lines. First, the great variety of critical lines has proved surprisingly easy of at least semiquantitative interpretation. Even van der Waals' equation, with suitable choice of the parameters, can represent most of the phenomena, and one can do better by using more accurate equations. On the other hand, the nature of the singularities at critical points in both one- and two-component systems has proved one of the most formidable problems in statistical thermodynamics. Such progress as has been made is reviewed.

## INTRODUCTION

We may have several objects in mind in studying the equilibria between the fluid phases of mixtures. We may be interested in the differences of composition between gas and liquid or between liquid and liquid because we wish to exploit these differences in order to separate substances by distillation or by liquid–liquid extraction. We may wish to explore the field in order to map out the large number of different kinds of phase diagram which can be found even in binary mixtures, and to examine their thermodynamic properties. Or we may wish to relate the observed differences in composition, the topology of the phase diagrams and the behaviour of the thermodynamic functions to the forces between the constituent molecules.

In this review I do not discuss the practical side but attempt to summarize briefly some of the recent advances in the second and third aspects of this subject, and to indicate where I think there are still substantial gaps in our understanding in spite of the large volume of work in the last twenty years. I confine myself to binary mixtures since most work has been done on these systems. Moreover, since intermolecular forces are at least approximately pairwise additive, the study of these systems leads most directly to the measurement of the strength of the forces between the unlike molecules.

## MOLECULARLY SIMPLE SYSTEMS

The theory of liquids (of one component) owes much of its recent progress to the study of the simplest possible systems, namely those composed of hard spheres and studied, not in the laboratory, but by computer simulation. Next in complexity come simulated liquids with strictly pairwise additive potentials of the Lennard–Jones form, with characteristic energy $\varepsilon$ and distance $\sigma$,

$$u(r) = \varepsilon f(\sigma/r) \tag{1}$$

where

$$f(x) = 4(x^{-12} - x^{-6}) \tag{2}$$

The 'experimental' results for these model systems[1,2] have proved in many ways to be more satisfactory data for testing statistical theories than the results for even the simplest and best-studied real liquid, namely argon. When we compare theory and experiment we have always three tasks: first, create an accurate theory, second, make accurate measurements, and third, ensure that the premises of the theory are satisfied by the system whose properties have been measured. The use of model systems absolves us from the third of these tasks, and so increases the precision with which theories can be tested.

We now know enough of the forces between a pair of argon atoms to know that the potential is not of the Lennard–Jones form, but has a deeper and narrower potential well[3,4]. The value of $\varepsilon/k$ is probably $(142 \pm 1)$ K. Nevertheless, the properties of the dense liquid argon on and near the saturation line at temperatures near the normal boiling point are surprisingly well simulated[2] by a Lennard–Jones fluid with a well depth of $\varepsilon/k = 118$ K. The difference is accounted for by the presence in the liquid of multibody potentials, of which the most important is the three-body dipole potential

of Axilrod and Teller. This leads to the reduction of $\varepsilon$ observed in the effective pair potential.

Argon and the other heavy inert gases, krypton and xenon, conform mutually to a principle of corresponding states with a surprisingly high accuracy. Such agreement implies detailed conformation of both pair and three-body forces in a way which has not yet been worked out in detail. Again, the use of effective Lennard–Jones potentials provides a convenient expression of this agreement, if one which is over-simplified to the point of impropriety.

If we turn now to mixtures of argon with other molecularly simple liquids such as krypton, xenon, nitrogen, oxygen, carbon monoxide or methane, then we are faced with the same choice of using our best estimates of both two- and three-body potentials, or of managing in a less rigorous way with effective pair potentials, often of Lennard–Jones form. In practice, we make the second choice, for several reasons which we now consider.

The theories of mixtures of molecules are, like the theory of pure liquids, best tested by comparison with the properties of computer-simulated systems, and these have all had pairwise additive potentials[5, 6]. The best of current theories are now accurate enough for these tests to be the only certain way of distinguishing between them. All the theories are ultimately based on the physical truth that the structure of dense liquids is, to a large degree, determined by the repulsive forces between the molecules and that the effects of the attractive forces can be obtained by calculating a perturbation average over this structure. This statement is most obviously true for those theories which use directly the perturbation theorems of statistical mechanics, but it is equally true of those based on Percus–Yevick or van der Waals approximations[7]. A full discussion of these theories is beyond the scope of this review; it is sufficient to say that the more refined of them can now give a substantially correct account of the thermodynamic properties of dense fluid mixtures of molecules between which there are two-body conformal potentials.

There would be little real difficulty in extending some, at least, of these perturbation theories to non-conformal potentials and in adding three-body potentials. The reason we do not usually do this is not the difficulty of the statistical mechanics, but our ignorance of the details of the intermolecular forces in even the simplest of the real liquid mixtures. In a binary mixture of molecules with conformal two-body potentials, we have six parameters, $\varepsilon_{11}$, $\sigma_{11}$, $\varepsilon_{12}$, $\sigma_{12}$, $\varepsilon_{22}$, $\sigma_{22}$. If we admit three-body potentials we need further parameters to characterise 111, 112, 122 and 222 interactions. Although both theory and experiment are now in a tolerably satisfactory condition, they cannot achieve the extremely high accuracy that would be necessary to determine so many parameters. We therefore fall back on the simpler interpretation of the thermodynamic properties in terms of effective two-body conformal potentials.

We describe the cross energies and diameters by the parameters $\xi_{12}$ and $\eta_{12}$, defined by

$$\varepsilon_{12} = \xi_{12}(\varepsilon_{11}\varepsilon_{22})^{1/2} \tag{3}$$

$$\sigma_{12}^3 = \eta_{12}(\tfrac{1}{2}\sigma_{11} + \tfrac{1}{2}\sigma_{22})^3 \tag{4}$$

so that the departures of $\xi_{12}$ and $\eta_{12}$ from unity are the departures of $\varepsilon_{12}$ and $\sigma_{12}$ from the familiar geometric and arithmetic means. The parameters can, in principle, be evaluated from measurements of very many physical properties of the mixture. Those most commonly used in practice are the excess thermodynamic functions $G^E$, $H^E$ and $V^E$, the dependence on composition of the critical constants, particularly $T^C$, and of the second virial coefficient of the gas, $B$.

The first are easy to measure with an accuracy that suffices to determine $\xi_{12}$ at least to 1%. (Since we use, in practice, only three independent excess functions it is prudent not to attempt to determine both $\xi_{12}$ and $\eta_{12}$ but to hope that the latter can be equated to unity without distorting the comparison of theory and experiment.) Theory is now sufficiently reliable for meaningful values of $\xi_{12}$ to be derived from these excess functions.

The second, the critical temperature, can be measured with great accuracy, often better than 0.1%, but the theory is not so adequate, for reasons to be discussed later. In practice, we are restricted to systems for which $\varepsilon_{11}/\varepsilon_{22}$ and $\sigma_{11}/\sigma_{22}$ are close to unity[8].

The third, the second virial coefficient of the gas mixture, is difficult to measure with sufficient accuracy, but the theory is perfect.

The results of these comparisons are usually expressed as values of $\xi_{12}$ with the implication that $\eta_{12}$ is unity, either because of the paucity of independent measurements on one system (as with the excess functions above) or because there is a greater interest in predominantly 'energetic' properties such as $G^E$, $H^E$ and $T^C$ than in 'volumetric' properties such as $V^E$ or $V^C$. The consensus of many comparisons of theory and experiment is as follows.

(1) $\xi_{12}$ lies between 1.00 and 0.96 for mixtures of the simplest substances, Ar, Kr, Xe, $N_2$, $O_2$, CO and $CH_4$. These values are the best-established[7, 8].

(2) $\xi_{12}$ is between 0.99 and 1.01 for mixtures of aliphatic hydrocarbons of about the same size[9], e.g. $CH_4 + C_2H_6$, $C_2H_6 + C_3H_8$, or for mixtures of cycloalkanes[10, 11] such as cyclopentane + cyclohexane. Interactions between hydrocarbons of different sizes are harder to interpret but lead generally to $\xi_{12}$ substantially less than unity, e.g. $CH_4 + n\text{-}C_4H_{10}$, $C_2H_6 + n\text{-}C_5H_{12}$. Clearly, for molecules of this complexity the concept of conformal pair potentials is a gross approximation, and so the values of $\xi_{12}$ are only measures of an apparent energy. Nevertheless, the agreement of values measured in different ways, and interpreted by different theories, gives one some confidence that they represent underlying molecular realities[9, 12].

(3) Silanes heavily substituted with methyl groups behave substantially as aliphatic hydrocarbons[9, 13]. Thus tetraethylsilane + cycloalkane, and octamethylcyclotetrasilane + cycloalkane, lead to values of $\xi_{12}$ of $1.00 \pm 0.01$ when the volume differences of the pure components is small. The parameter $\xi_{12}$ falls to about 0.94 when the difference $|\sigma_{11}^3 - \sigma_{22}^3|/\frac{1}{2}(\sigma_{11}^3 + \sigma_{22}^3)$ reaches about 1.1. If this increasing volume difference is the correct parameter with which to correlate the fall of $\xi_{12}$, then we have a parallel to the fall in the hydrocarbon series noted above. However, the substituted silanes are more nearly spherical molecules and, in that respect at least, the values of $\xi_{12}$ may be taken to be more reliable.

(4) Aromatic and aliphatic hydrocarbons have $\xi_{12}$ consistently less than unity[8], probably about 0.96.

(5) Aliphatic fluorocarbons and aliphatic hydrocarbons are the best-known case of non-polar molecules having values of $\xi_{12}$ substantially below unity, generally around 0.90–0.92. The simplest system is $CH_4 + CF_4$, which has been discussed on several occasions[7,8], since here both excess liquid properties[14] and the second virial coefficient[15] have been measured.

## MOLECULARLY MORE COMPLEX LIQUIDS

All but the first group of mixtures discussed above are straining considerably our belief that a set of spherical conformal two-body potentials is an adequate model. If we are to discuss intelligibly most of the liquids of interest to chemists and chemical engineers, then we must develop our model further to admit the following complications. First, molecules have 'shape', that is, the repulsive part of the potential depends on mutual orientation. Secondly, the polarizability is not isotropic, and so the attractive potential is a function of orientation. Thirdly, molecules are polar, that is, they have a permanent electric anisotropy which leads to additional orientationally dependent forces. Those that arise from the permanent anisotropy directly are two-body forces: those that arise from inductive effects are not. So far all effects can be included in a description by classical mechanics and electrostatics, but if the electric anisotropy is extreme and localized, then it can be discussed adequately only by quantal methods. Hydrogen bonding is the best-known example. Fourthly, we have complexing which is not primarily electrostatic in origin, such as charge-transfer between iodine and many other substances, or the now well-known complexes between aromatic hydrocarbons and aromatic fluorocarbons. Fifthly, and finally, molecules may be flexible so that the phase integral of classical statistical mechanics cannot be cleanly factorized into a molecular part and a configurational part. This problem arises particularly with alkane mixtures and, in extreme form, with polymer solutions.

Some of these complications lead to effects that are qualitatively easy to understand. Thus if one component only is polar, then the effective cross energy is lower than would be otherwise expected, and so the apparent value of $\xi_{12}$ (if the effect is expressed in this way) will be less than unity. This leads to large positive values of $G^E$ and so, in a way which needs no explanation here, to the appearance of upper critical solution temperatures (UCST). Any system for which $\xi_{12}$ is less than unity can be expected to have a UCST if it can be cooled far enough for the liquid separation to occur before the eutectic temperature is reached. Separation has been found in mixtures of methane with both longer-branched alkanes[16] and alkenes[17], and there are indications[18] that it lies not far below the solidification temperature for $CH_4 + n\text{-}C_6H_{14}$.

Complexing between the unlike molecules leads to apparent values of $\xi_{12}$ greater than unity, but these do not generally lead to any qualitatively unusual phase behaviour, unless the strong interaction can occur only over a restricted range of molecular orientations. Then lower critical solution temperatures (LCST) may be observed as in many hydrogen-bonded aqueous systems. It is not so easy to give a simple qualitative explanation of these as of the UCST, but it can be done in terms of a balance of energy and entropy

effects[19]. Statistical theories of this phenomenon are confined to lattice models in which the molecules are constrained to a small number of fixed orientations[20]. Such models have now been abandoned in the rest of the theory of the liquid state, and there is here a field where more theoretical work is obviously needed.

Qualitatively we can, therefore, understand some of the thermodynamic consequences of molecular complexity. How much farther should we go in trying to achieve quantitative explanations? It is, I think, worth pausing here and asking what we hope to achieve by such work before the overwhelming number of possible experiments, computer simulations and statistical theories overcome us. Presumably, we do not want a quantitative account of the interaction of every possible pair of molecules of interest, and a means of calculating its thermodynamic consequences at all pressures and temperatures. If we had, it would avail us little. Presumably, therefore, we seek to formulate general principles and treat in detail only interactions of particular importance. My own proposals, with which I expect few to agree fully, are that we should concentrate our efforts on the following.

First, we have those systems whose complexity is so mild that it can be treated within the scope of orientational perturbation theory[8, 21], or of the recent extension to mixtures[22] of the mean-spherical approximation to the point dipole in a hard sphere[23–25]. These include molecules with not-too-elliptical shapes (propane, for example, but not n-octane), molecules with weak and fairly central dipoles (hydrogen chloride or sulphur dioxide, but not water nor phenol) and molecules with quadrupoles (carbon dioxide and acetylene). To be able to include a substantial number of important molecules within one type of treatment is a worthwhile increase in our understanding of the physics of liquid mixtures.

When we get beyond the range of perturbation theory, we reach quickly the position where almost every molecule must be treated as an individual, and unifying ideas become increasingly hard to find. Everyone will have different ideas of which substances are worth detailed study by experiment, simulation and theory. My list would include:

(1) The n-alkanes above methane. The regularity of structure is reflected in one obvious regularity of thermodynamic properties, which has attracted much research effort, and which has led to the enunciation of certain principles[26–29] stemming from the principle of congruence. These are of interest in their own right, because the n-alkanes are an important series, and for the link they provide with theories of polymer solutions. However, recent progress has been slow, mainly because of the fundamental impossibility of separating the internal and external motions of such molecules.

(2) Aqueous systems. Water is so important a liquid that, whatever the difficulties, we must eventually understand fully the static and dynamic aspects of its structure, and those of its mixtures with polar organic molecules[30].

(3) A few other special cases will certainly prove sufficiently intriguing to warrant detailed study. In the past, we have seen this with the properties of iodine solutions; at the moment, there is the problem of the complex between aromatic fluorocarbons and aromatic hydrocarbons. There will certainly be

others. However, my list would exclude a mass attack, by experiment and theory, of mixtures of all possible polar organic liquids.

## SYSTEMS AT HIGH PRESSURES: CRITICAL PHENOMENA

The behaviour of liquid mixtures discussed so far has been, implicitly, that of systems at or near to atmospheric pressure. When a single component is heated in equilibrium with its vapour the pressure rises to that of the gas–liquid critical point, which is generally between 30 and 70 bars. If a binary mixture of simple and similar liquids is heated the same thing happens, although the critical pressures are now usually higher, often above 100 bars. If, however, the molecules differ greatly in energy or size, so that $(\varepsilon_{11} - \varepsilon_{22})$ or $(\sigma_{11}^3 - \sigma_{22}^3)$ is large, or if the real or apparent value of $\xi_{12}$ differs greatly from unity, then the phenomena are more complicated. As well as the single gas–liquid critical line in $(p, T, x)$ space of the simple systems, we can have a liquid critical line rising from the UCST, or the gas–liquid critical line can break into two unconnected parts, or the liquid–liquid line can intrude into the gas–liquid region. There may be up to three critical points, each in equilibrium with a third fluid phase, and three separate critical lines. These complexities were first uncovered by the van der Waals school some seventy to eighty years ago. More recent work[16, 17, 31], much of it by Schneider[32], has completed the unravelling of the complexities. It is dangerous to use the word 'completed' of any scientific field but, in a review, I may perhaps be allowed the guess that there is little if anything fundamentally new now to be discovered about the topology of critical and azeotropic lines in binary systems. (I exclude those containing liquid crystals.)

The qualitative interpretation of these complexities has proved to be surprisingly simple. Even the van der Waals equation, with suitable choices of three $a$ and three $b$ parameters, leads to almost all the kinds of immiscibility, critical and azeotropic lines found in practice, as is shown in the 'map' of Scott and van Konynenberg[16]. By replacing the $(V - b)$ of the van der Waals equation by a more accurate representation of the 'accessible volume', these calculations can be made even more realistic[33]. By substituting the experimental behaviour of a real fluid (or a good empirical representation of it) for the van der Waals equation, the calculations can be made with sufficient accuracy, at least for the less complicated systems, to yield values of $\xi_{12}$ that compare well with those obtained at lower pressures[9].

This degree of interpretation is very satisfactory, but it touches only on the gross or topological features of such critical lines. If we ask for a more detailed description of exactly how the thermodynamic functions behave at and near a critical point, then the situation is less satisfactory. The singularities of these functions at a critical point in a system of one component are now well described by the so-called scaling functions of Widom, Griffiths, Schofield and others[34–36]. These are essentially empirical relations, for although a certain degree of molecular justification is now emerging, this falls a long way short of a derivation from the principles of statistical mechanics. The extension of scaling to mixtures has been made by Griffiths and Wheeler[37, 38]. Their results do not admit of an easy summary, but they are worth the closest attention of experimentalists in this field since they lead to a

set of quite precise statements about the singularities at critical points, and in particular at those where there is azeotropy, or where the critical line has an extremum in pressure or temperature. Many of these statements have still to be confirmed or denied by experiment.

If we ask further for a statistical theory of the singularities at binary critical points, then we receive very little in the way of an answer. Progress here is closely linked, through what has been called[39-41] 'renormalization', to progress in one-component systems[34], and that is very slow. One of the more tractable models[42], which has both a one-component and a two-component version, has the same formal symmetry as the Ising problem. Recent work with this model[43] has established that the various integral equations for the correlation functions commonly used in treating one-component liquids behave quite differently when they are extended to mixtures. The simplest, the Percuss–Yevick equation, can be extended to mixtures in a straightforward way[43,44] but, when applied to the penetrable sphere model[42], it is closely similar to a mean-field or van der Waals treatment. The critical point is purely classical and so without real interest. If it is taken to second order (the PY2 approximation), then it cannot be extended to mixtures without ambiguity, but, however it is extended, it almost certainly leads to a non-classical point. The other widely used equation, the hypernetted chain (HNC), cannot be extended to mixtures without ambiguity, even at the first order[43], but, again, however it is extended, it appears to lead to a non-classical critical point.

We have, therefore, the interesting situation that some of these simple integral equations are rich enough to yield singularities similar to those observed in real systems, but, if they do, they cannot be used for mixtures in an entirely self-consistent way. Clearly, this is a problem which needs further work, but it is encouraging that realistic singularities can emerge even from comparatively tractable integral equations.

I have tried, in this review, to cover many parts of the field implied by my title, but there are obviously others which I have omitted. In trying to cover some of the current ideas, I am conscious that I have not paid sufficient attention to many current experiments. I apologise to those whose work I have ignored, and thank those who have allowed me to refer to their unpublished work.

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