THERMODYNAMICS OF LIQUID MIXTURES

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Abstract – Selected experimental and theoretical aspects of the thermodynamic properties of liquid mixtures are reviewed. Particular reference is made to the contributions presented at the session on Liquid Mixtures at the IUPAC Conference on Chemical Thermodynamics, London, 1982. Recent developments in the techniques for measuring the excess functions of liquid mixtures are outlined. The properties of mixtures of aliphatic hydrocarbons are discussed in terms of various equation-of-state treatments and the principle of congruence. A rudimentary outline of the perturbation theory is given in order to explain the results for mixtures containing simple polar molecules. The properties of more complex organic mixtures are considered in terms of interaction parameters and chemical equilibria resulting from interactions between both like and unlike molecules.

INTRODUCTION

In recent years there has been an upsurge in the number of measurements made on the thermodynamic properties of liquid mixtures. Such measurements include the molar excess Gibbs free energy G_m^E, the molar excess volume V_m^E, the molar excess enthalpy H_m^E, the molar excess heat capacity $C_{p,m}^E$, and the compressibility of liquid mixtures. The major reason for this increased activity is the ready availability of commercial apparatus. In parallel there has been a rapid increase in the number of theoretical treatments, the majority being based on an equation-of-state approach which differ by variations in the equation, the combining rules, and the mixture recipes. Also fashionable are theories, based on interaction parameters, which seek to relate the properties of one mixture to those of closely related mixtures, or mixtures formed from constituent groups. Hydrogen-bonded systems have, in general, been interpreted by various chemical equilibria treatments, the form of the theory and the magnitude of the parameters often depending on the types of measurements considered and the concentration range over which the measurements are made. Selected theoretical treatments will be discussed and compared.

EXPERIMENTAL TECHNIQUES AND METHODS OF ANALYSIS

Excess Gibbs free energy. The molar excess Gibbs free energy, G_m^E, cannot be measured directly. The majority of G_m^E values are derived from isothermal vapour-liquid equilibria measurements made with either recirculating stills or with the static vapour-pressure technique. Both have their advocates and advantages and disadvantages can be claimed for both methods. The two major problems with recirculating stills are the difficulty in establishing a steady state that differs insignificantly from true equilibrium and the difficulty in the accurate analysis of the vapour-phase composition. Techniques for measuring isothermal vapour-liquid equilibria have recently been reviewed by Marsh (Ref. 1) and Malanowski (Ref. 2). Armitage and Osborne (Ref. 3) describe an interesting computer controlled static vapour-pressure apparatus from which they obtain excess Gibbs free energy results for the ternary mixture benzene + cyclohexane + hexafluorobenzene. With their apparatus they were able to rapidly measure the vapour pressure of 63 three-component mixtures. Wagner and Lichtenthaler (Refs. 4,5) describe an apparatus for measuring the composition dependence of the total vapour pressure of binary and multicomponent mixtures up to 250 kPa and 350 K in a continuous way over the whole composition range. The temperature is only measured to 0.02 K and the pressure to 0.02 kPa. The major source of error however is in the determination of the mole fraction because the components have to be metered in from a precision burette. The apparatus appears to give reasonable results, it can be used over a wide temperature range, and results can be obtained rapidly. Naumann (Refs. 6,7) describes a dynamic still in which the steady state is obtained within a few minutes. The pressure can be measured to 0.01 kPa and the temperature to 0.01 K. The apparatus has been used to make measurements on binary and ternary mixtures. The method is particularly useful if one of the chemical components decompose. For such systems the static method is useless.

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The methods used to analyse and test the reliability of the results from both static and dynamic measurements are a continuous source of contention. Recently Plank et al. (Ref. 8) have described some common pitfalls encountered in the reduction of total-pressure vapour-liquid equilibria data using the Barker method. In the Barker method, G_m^E is assumed to have some functional form, usually

$$G_m^E/RTx(1-x) = \sum_{i=0}^{n} A_i(2x-1),\qquad (1)$$

and the coefficients are adjusted using a least-squares method until the total pressure residual is at a minimum. Plank et al. conclude that the Barker method gives a poor fit and wrong limiting activity coefficients when used for mixtures such as alcohols with non-polar solvents if the standard fitting equations are used. Diaz Pena et al. (Ref. 9) have analysed their static vapour-pressure measurements for the system methanol + various heptanones using the Padé approximate for G_m^E

$$G_m^E/RTx(1-x) = \sum_{i=0}^{n} A_i(2x-1)/[1 + \sum_{j=1}^{m} B_j(2x-1)],\qquad (2)$$

suggested by Marsh (Ref. 10). This equation should overcome some of the problems associated with the Barker method. However care must be taken in using equation (2) because spurious results can be obtained and the denominator can go to zero at finite x with certain combinations of B_j. The argument usually advanced in favour of the dynamic technique is that the results can be tested for consistency since the measurement of p, x, and y at constant temperature is an over determination and the three quantities can be related by the Gibbs-Duhem equation. However, since most consistency tests are based on the integrated form of the Gibbs-Duhem equation, no knowledge of the total pressure is required and hence the test can only be regarded as a consistency test in a very restricted sense. Van Ness et al. (Refs. 11,12) have suggested that the only valid test is to calculate the excess Gibbs free energy from three alternative methods, each making use of only two of the variables and the Gibbs-Duhem equation. The third variable can then be predicted and compared with the experimental value. Van Ness et al. concluded that, for the majority of dynamic vapour-pressure measurements considered, the vapour-phase composition was the major source of error and that more accurate values of G_m^E would be obtained if only the p and x data were used. For mixtures where the two components have similar densities and refractive index, the analysis of the composition can present a problem. For such mixtures the differential refractometer described by Nieto de Castro et al. (Ref. 13), which can measure changes in refractive index to 10^{-7}, could be a useful analytical tool.

While the majority of values of G_m^E are obtained from vapour-liquid equilibria data, it is also possible to obtain values from the freezing temperatures of binary mixtures. Ott and Goates (Ref. 14) propose a semi-empirical equation

$$T = T_0[1 + \sum_{j=1}^{n} a_j(x-r)^j].\qquad (3)$$

which is useful for describing the melting temperature-composition curve for binary mixtures. The coefficients a_j are fit to the results by least squares and r is the value (usually 0 or 1) of x at $T = T_0$, which is usually 0 or 1. However in the case of compound formation, r becomes the mole fraction of the compound. The inclusion of various skewing parameters enables the equation to describe the most complex of phase diagrams. A useful extension would be to subtract the ideal term calculated from the enthalpy of fusion and its variation with temperature, and hence obtain the activity coefficients and the Gibbs free energy. This method would give values of G_m^E at the freezing temperature, so to obtain values at other temperatures the excess enthalpies and the heat capacity change on mixing over a temperature range would be required. With present commercial apparatus such measurements can be made readily.

Excess enthalpy. In recent years the majority of reliable excess enthalpy measurements have been made with either the step-wise isothermal dilution calorimeter or the flow calorimeter. The isothermal dilution calorimeter is capable of a higher precision, approaching 0.1% for endothermic mixtures and 0.25% for exothermic mixtures (Ref. 15). The commercial flow calorimeters based on the design of either Monk and Wadso (Ref. 16) or Picker (Ref. 17) give rapid results with a precision typically of 1% or slightly better. It is difficult to improve the precision of the flow calorimeters without a radical redesign of the flow system. Letcher (Ref. 18) and Inglese et al. (Ref. 19) use flow calorimeters while Atik, Ewing, and McGlashan (Ref. 20) and Miller and Williamson (Ref. 21) use dilution calorimeters.

Excess volumes. The majority of reliable excess volume measurements are now made with either continuous dilution dilatometers (Ref. 22) or with commercially available digital densimeters (Ref. 23). The latter method is based on the determination of the frequency of vibration of a small tube filled with the liquid. It is necessary to take great care to ensure that evaporation losses which occur during the preparation and the transfer of the solution are kept to a minimum because the composition of the mixture has to be known to a much higher precision when compared with direct mixing methods. The effect of dissolved air on the density of both the mixture and the pure components needs to be considered; for example, the density difference between an air saturated and a degassed sample of tetrachloromethane is about 10^{-4} g cm^{-3}. Zheng et al. (Ref. 24) compare results for binary mixtures of n-hexane isomers determined with a normal single-shot mixing dilatometer with those obtained with a dilution dilatometer and a vibrating-tube densimeter. In the majority of cases the values of $V_m^E(x = 0.5)$ obtained by the single-shot dilatometer are more negative by about 0.03 cm^3 mol^{-1} compared with those obtained with a dilution dilatometer or the digital densimeter (which agree). This difference, which is approximately 10 times the expected experimental error, could not be explained.

Other measurements. Since the introduction of the heat-capacity attachment to the Picker flow calorimeter, the number of publications of the heat-capacity change on mixing has increased rapidly. Measurements made with this apparatus are reported by Rodriguez and Patterson (Ref. 25), Inglese et al. (Ref. 19), and Zegers and Somsen (Ref. 26). Precise measurements with this apparatus on mixtures of cyclohexane with n-hexane agree with the values derived from the temperature dependence of the enthalpy of mixing, but there exists a discrepancy for mixtures of benzene + tetrachloromethane (Ref. 27). A few direct measurements have been made on the isothermal compressibility, the number being insignificant when compared with the number of measurements of the isentropic compressibility determined from the ultrasonic speed (Ref. 28). At present these results are much more difficult to interpret in comparison with the traditional excess functions. Viswanath and Rao (Ref. 29) report the enthalpy of vaporization of mixtures of p-xylene + 1,1,2,2-tetrachloroethane and find they agree, within experimental error, with that calculated from the enthalpy of vaporization of the pure compounds and the extrapolated values of the excess enthalpy.

In February 1981 McGlashan (Ref. 30) suggested that the potential of flow-calorimetric methods for the measurement of H_m^E and $C_{p,m}^E$ had not been realized fully. Within two years this method has now become the preferred method for the majority of measurements. Christensen et al. (Ref. 31) have described a simple but versatile flow calorimeter capable of operating to 40 MPa and 350 K. Thus we have now reached the situation where any research group, using commercially available equipment, can produce a publication containing acceptable values of H_m^E, V_m^E, and $C_{p,m}^E$ within a few weeks. The temptation to saturate the literature with stranger and stranger pairs of mixtures could become epidemic and in the longer term will do this subject no good. The most useful determinations are those of all the excess functions over a wide temperature range on mixtures carefully selected so that they are representative of a particular type of interaction. There is little point in making measurements if there is little or no likelihood that they will contribute to our understanding of the subject.

THEORIES OF LIQUID MIXTURES

At present there are four fundamentally different approaches used to explain and predict the properties of liquid mixtures. The first of these is often termed the equation-of-state approach but one can include in this category various corresponding states theories.

Equation-of-state treatments

There are many theories based on this approach such as those termed the van der Waals, the Prigogine, the Flory, and the Redlich-Kwong theories. Some variations use analytical equations of state while other use equations of state derived from either real substances or from computer simulations. One form of the theory uses the generalized van der Waals equation

$$p = p_H - a/f(V,T), \qquad (4)$$

where p_H is the pressure of a hard-particle fluid and a is a constant representing the attractive forces. Different attractive terms have been proposed: for example the Redlich-Kwong equation has an attractive term of the form $a/V(V+b)$ or $a/[T^{1/2}V(V+b)]$ (Ref. 32) while the Flory (Ref. 33) and van der Waals theories (Ref. 34) use a/V^2 for the attractive term. Various approximations to p_H have been used, one is the Percus-Yevick compressibility equation (Ref. 34)

$$p_H = RT(V^2 + vV + v^2)/(V - v)^3, \qquad (5)$$

where v is the volume of hard spheres occupying a total volume V. The Redlich-Kwong equation

uses the original van der Waals term for the effective volume of the particles,

$$p_H = RT/(V - 4v).$$ (6)

The Flory approach uses a hard sphere term based on a solid lattice model

$$p_H = RT/[1 - (v/V)^{1/3}],$$ (7)

and hence one cannot integrate the equation to the vapour phase to obtain analytically the entropy of mixing. As a result the various theories based on this equation have to assume some functional form, usually the Flory-Huggins expression, for the entropy of mixing. Various other equations have been proposed but computer simulations indicate that the general features of all the equations are similar in the normal fluid density range.

The parameters a and v for the pure fluid can be determined by fitting the equation to properties of the pure fluid such as the liquid volume, the isothermal compressibility, the expansivity, the vapour-pressure curve, the enthalpy of vaporization, or the gas-liquid critical constants. As a general rule, since no simple analytical equation yet proposed gives a good fit to the properties of the pure components over a wide temperature range, it is best to determine the parameters from properties determined close to the temperature of interest. The pure-component properties usually used are the molar volume, the isothermal compressibility and the thermal expansivity. Any general equation of state can be extended to mixtures in a variety of ways. One way is to use the van der Waals one-fluid approximations (vdW1),

$$a_x = x_1^2 a_1 + 2x_1 x_2 a_{12} + x_2^2 a_2,$$ (8)

$$v_x = x_1^2 v_1 + 2x_1 x_2 v_{12} + x_2^2 v_2.$$ (9)

Flory uses an alternative approximation which assumes core-volume additivity

$$v_x = x_1 v_1 + x_2 v_2,$$ (10)

and for a_x he uses a complex surface-fraction averaging. A variety of other theories have been proposed which use different approximations for extending the equations to the mixture. For example, the recent theory of Brandani and Prausnitz (Ref. 35) uses the van der Waals two-fluid approximation and the local-composition concept. It is claimed that these approximations account for order in complex mixtures containing polar compounds.

The parameters a_{12} and v_{12} for the unlike interactions in the mixtures are generally given by an extension of the Lorentz-Berthelot combining rules:

$$a_{12} = \xi v_{12} (a_1 a_2/v_1 v_2)^{1/2},$$ (11)

$$v_{12}^{1/3} = \eta (v_1^{1/3} + v_2^{1/3})/2.$$ (12)

The Redlich-Kwong treatment uses the approximation

$$v_{12} = (v_1 + v_2)/2.$$ (13)

It is known from measurements of the second virial coefficients for mixtures of the noble gases that these rules are inadequate. The parameter ξ is either set to unity or is adjusted so that one of H^E or G^E is correctly predicted. Usually η is put equal to unity but sometimes it is simultaneously adjusted so that V^E is also correctly predicted. In the Flory theory, the adjustable parameter X_{12} is directly related to ξ. The need for a combining rule for a_x is unavoidable in any equation of state formulation and the form can be justified in varying degrees from molecular dynamics studies. However the expression for v_x can be avoided by, for example, using a generalized equation for mixtures such as that proposed by Gibbons (Ref. 36) for hard convex particles,

$$p_H = RT[1/(V-v) + ABL/(V-v)^2 + B^2 CL^2/3(V-v)^3],$$ (14)

where L is the Avogadro constant and A, B, and C are constants related to the average radius, surface area, and volume which can be determined from various formulae depending on the shape. For a mixture, the attractive parameter is defined in terms of the average radius rather than the hard core volumes. For spherical particles this equation reduces to the Snider and Herrington equation (Ref. 37). The excess functions at negligible pressure can be calculated from the following general expressions:

$$H^E = x_1 a_1/V_1 + x_2 a_2/V_2 - a_x/V_x,$$ (15)

$$G^E = H^E + \phi_x - x_1\phi_1 - x_2\phi_2,\tag{16}$$

$$V^E = V_x - x_1V_1 - x_2V_2,\tag{17}$$

where

$$\phi_j = - \int_0^{V_j} (p_H - RT/V)dV - RT\ln V_j.\tag{18}$$

V_x, the molar volume of the mixture, is obtained by solving the equation of state at negligible pressure. From the above it is clear that the Flory theory does not account for the shape of molecules, except in a very superficial sense by the inclusion of the parameter c which generally increases from unity with increasing molecular size and flexibility. Other theories have accounted for shape by the inclusion of shape parameters which can be related to the Pitzer accentric factor ω (Ref. 38). Table 1 gives results for a selection of organic mixtures calculated from the Percus-Yevick compressibility equation using the van der Waals one-fluid (vdWl) approximation. Similar results are obtained with other equations and the van der Waals two-fluid approximation.

TABLE 1. Comparison between calculated and experimental values at x = 0.5 for selected mixtures. The value of ξ has been obtained by adjusting G_m^E to fit the experimental results

		Expt.			P-Y(vdWl)	
System	T/K	$H_m^E/J\ mol^{-1}$	$V_m^E/cm^3\ mol^{-1}$	ξ	$H_m^E/J\ mol^{-1}$	$V_m^E/cm^3\ mol^{-1}$
$C_6H_6 + CCl_4$	298	116	0.00	0.992	130	0.16
$C_6H_6 + c-C_6H_{12}$	298	799	0.65	0.970	514	0.64
$c-C_6H_{12} + CCl_4$	298	166	0.17	0.993	115	0.13
$C_6F_6 + c-C_6H_{12}$	313	1534	2.57	0.919	1325	2.83
$CCl_4 + c-C_5H_{10}$	298	79	-0.04	0.997	42	-0.03
$C_2H_4Cl_2 + C_6H_6$	293	60	0.25	0.996	65	0.00
$C_6F_6 + C_6H_6$	313	-435	0.80	1.011	-76	-0.93
$n-C_6H_{14} + c-C_6H_{12}$	293	216	0.10	0.998	110	-0.37
$n-C_6H_{14} + n-C_{16}H_{34}$	298	112	-0.54	0.942	-81	-3.1

TABLE 2. Comparison between calculated and experimental values at x = 0.5 for cycloalkane + cycloalkane mixtures at 298 K. The value of ξ has been obtained by adjusting G_m^E to fit the experimental results.

	$G_m^E/J\ mol^{-1}$				$V_m^E/cm^3\ mol^{-1}$			
System	Expt.	Fr	SH	Fl	Expt.	Fr	SH	Fl
$c-C_5H_{10} + c-C_6H_{12}$	-4	31	23	25	0.04	-0.09	0.00	0.00
$c-C_7H_{14} + c-C_8H_{16}$	5	8	2	2	-0.03	-0.09	-0.03	-0.03
$c-C_5H_{10} + c-C_8H_{16}$	-2	87	22	29	-0.28	-1.0	-0.31	-0.29

The predictions for mixtures of approximately spherical molecules of similar size are surprisingly good, especially for the excess volumes. The exception is benzene + hexafluorobenzene. For mixtures of cyclic + n-alkanes and for mixtures of n-alkanes the theory is clearly unsatisfactory. In order to test the theories for spherical molecules differing considerably in size we made a series of measurements on mixtures of cycloalkanes (Ref. 39). Some selected comparisons are given in Table 2.

As the size difference increases (eg $c-C_5H_{10} + c-C_8H_{16}$), the predictions of the theories using the van der Waals one-fluid approximation becomes poor. This is further confirmed by calculations on mixtures of the large globular organic molecules (octamethylcyclotetrasiloxane and tetrakis-(2-ethylbutoxy)-silane) with typical small organic molecules (Ref. 40.41). For mixtures of spherical molecules differing considerably in size, G_m^E is reasonably well predicted from H_m^E but the calculated excess volume depends very much on which theory one uses. Surprisingly the Flory theory in general gives the best predictions, but they are still poor.

TABLE 3. Comparison between calculated and experimental values at x = 0.5 for octamethylcyclotetrasiloxane (OMCTS) and tetrakis-(2-ethylbutoxy)-silane (TKEBS) with small globular molecules. The value of ξ has been obtained by adjusting either G_m^E or H_m^E to fit the experimental results.

| System | H_m^E or G_m^E/J mol^{-1} | | | | V_m^E/cm^3 mol^{-1} | | | |
	Expt.	Fr	SH	Fl	Expt.	Fr	SH	Fl
c-C_5H_{10} + OMCTS*	212	125	480	299	−0.05	−6.4	0.02	0.47
C_6H_6 + OMCTS*	793	671	1038	780	−0.01	−6.9	−0.58	−0.83
c-C_6H_{12} + TKEBS	−494	455	−596	−447	−0.25	−19.1	1.31	0.34
CCl_4 + TKEBS	−633	112	−1059	−855	−0.24	−21.1	1.14	0.15

* values of H_m^E.

It has been possible to test the various approximations and mixture rules used in the theories by the application of computer simulations to hypothetical mixtures of hard spheres and spheres with Lennard-Jones potentials. Recent progress in this aspect of the subject has been reviewed by Rowlinson (Ref. 42). Such simulations have allowed the testing of statistical mechanical theories in a rigid manner without being inhibited by the often unknown restraints imposed by real liquids and liquid mixtures. These simulations indicate that the various mixture approximations hold only over a rather narrow range of volume ratios; thus it is surprising that the Flory theory does so well for real mixtures containing molecules of considerably different size. Moreover, it is clear that treatments based on the properties of hard spheres cannot be extended to non-spherical molecules in a simple way. For example Smith and Nezbeda (Ref. 43) show that an equivalent spherical particle requires a very soft potential if it is to exhibit the same properties of a hard spherocylinder having a length to breadth ratio of about 3 to 1. In view of the above it is not surprising that Letcher finds the Flory theory satisfactory for mixtures of hexane and cycloalkanes but that the discrepancy between the calculated and experimental values for both H_m^E and V_m^E increases as one goes from n-hexane to n-hexadecane. He also finds that the Flory parameter X_{12} increases as the n-alkane chain increases. Trejo Rodriguez and Patterson (Refs. 25) propose an extended corresponding- states treatment which uses an equation of state for n-alkanes which changes in a systematic way with an increase in the carbon number. They are able to account for the majority of the thermodynamic properties of n-alkane mixtures. An important conclusion is that, by using an adequate equation, the Flory parameter X_{12} could be put equal to zero. Their treatment is satisfactory for mixtures of n-alkane because the effects of elongation are incorporated as a smooth function in their extended equation of state. However the treatment cannot be extended to mixtures of n-alkanes with spherical molecules. Inglese et al. (Ref. 19) report measurements of H_m^E, V_m^E, and $C_{p,m}^E$ for the approximately spherical molecules fluorobenzene and 1,4-difluorobenzene with a series of n-alkane while Wagner and Lichtenthaler (Ref. 4) report G_m^E results for mixtures of cyclohexane with branched and straight-chain hydrocarbons. It is argued that deviations from the Flory predictions can be explained by a correlation of molecular order in liquids with long chain molecules. I would contend that the Flory theory does not account adequately for both the change in shape and size as the n-alkane increases so any conclusions based on deviations from that theory have little theoretical significance. One would expect deviations from any theory to be systematic if one changes one component in a systematic way and Anderson and Swinton (Ref. 44) have confirmed this with measurements on the excess volumes for mixtures of seventeen isomeric octanes with tetrachloromethane and cyclohexane. They find a correlation between the equimolar V_m^E and the molar volume of the pure octane, obtaining three straight lines corresponding to mixtures containing the 6 pentanes, the 7 hexanes, and the 3 heptanes. The simple equation-of-state treatments predict a similar correlation but the order of V_m^E is reversed. Such a result is not surprising as these theories make no pretence at accounting for the properties of non-spherical molecules. Zheng et al. (Ref. 24) could find no definite correlation in the excess volumes of a variety of hexane isomers except that V_m^E becomes more negative as the number of methyl groups increase. However that conclusion, taken to the extreme, led to the absurd prediction that mixtures of cyclohexane with itself would have the largest positive excess volume.

The principle of congruence, initially proposed to explain the properties of binary mixtures of n-alkanes, has been used by Miller and Williamson (Ref. 21) to explain the enthalpies of multicomponent n-alkane mixtures. They compare the results for three and four component mixtures containing n-pentane, n-hexane, n-octane, and n-octadecane with those for n-hexane + n-hexadecane. The initial ´components´ are pseudo-binary mixtures where the compositions are chosen to have a mole-fraction average carbon number of 6 and 16. Previously Lim and Williamson (Ref. 45) found the extended principle of congruence held for the excess volumes of similar

mixtures. McLure et al. (Ref. 46) have measured a number of properties of mixtures of dimethysiloxane oligomers with tetramethylsilane (which can be regarded as the first member of the series). A number of the properties can be accounted for by the principle of congruence while the shape and magnitude of some other properties can be explained by a corresponding-states approach.

A major advantage of the general van der Waals approach is that the calculations are relatively simple and the theory can be readily extended to high pressures where the theory (in its various forms) can predict the majority of phase behaviour found experimentally (Ref. 47,48). The major weakness of the general van der Waals approach is that the majority of mixture recipes are known to be a good approximation only for spherical particles where the ratios of both the distance and potential parameters are not far from unity. Further, the form of the general van der Waals equation makes it difficult to make systematic improvements to the theory. A basic assumption of these theories is that the force fields between the components are similar so one cannot readily extend these theories to mixtures which include polar molecules. Gubbins and co-workers (Ref. 49) have shown that the mixing rules used for simple non-polar mixtures will be unsuitable for mixtures containing polar compounds, hence these theories will not be able to predict the correct composition dependence of the excess functions and in particular cannot predict azeotrope compositions.

Before considering the perturbation treatment, it is relevant to consider the possibility of chiral discrimination in mixtures of optically active isomers.

Chiral discrimination
Most theories of solutions will predict that mixtures of two pure enantiomers A+ and A- will have zero excess functions. However, it is clear that the equilibrium properties of such mixtures will be affected by chiral discrimination because a chiral molecule will interact differently with a neighbourhood molecule of chirally different conformation compared with one of identical conformation. In an attempt to determine if chiral discrimination does exist Atik et al. (Ref 50) measured the excess volumes of mixtures of optical isomers of limonene, fenchone, and α-methylbenzylamine. They found excess volume of between -0.001 and -0.002 cm^3 mol^{-1}. These values are indeed small but they were approximately ten times the estimated experimental error. They have now obtained results for the molar excess enthalpies for the above mixtures and find $H_m^E(x=0.5)$ of -4.51 J mol^{-1} for fenchone and $+7.34$ J mol^{-1} for α-methylbenzylamine at 303.11 K. These values are small but significant. They cannot be explained by the observed impurity levels. Lepori et al. (Ref. 51) have measured excess volumes for six pairs of chiral molecules, using a digital densitometer, and find small but significant effects. An interesting curiosity would be an optically active component where the chiral discrimination is so large that phase separation occurs.

Perturbation treatments
If one starts with a mixture of molecules that interact according to a simple molecular potential u_{ref}, one can calculate, either by molecular dynamics or statistical mechanics, the complete thermodynamic information on that system. It is then possible to calculate the equivalent information for a more complex intermolecular potential u by performing a perturbation expansion, usually as a Taylor expansion in either $(u - u_{ref})$ or $[exp(-u/kT) - exp(-u_{ref}/kT]$. This approach was used by Barker and Henderson (Ref. 52) for pure liquids and liquid mixtures with moderate success. Improvements to the equation of state of the reference mixture and the inclusion of second-order terms has lead to steady improvements in the predictions for simple mixtures.

In the last few years Gubbins and co-workers (Refs. 53,54) have extended the perturbation theory to include mixtures containing multipolar non-spherical molecules, the perturbation potential in such molecules resulting from both long-range attractive multipolar forces (dipole, quadrupole, and octopole), and a small anisotropic overlap potential which result when the molecules differ in shape from spherical. Initially they studied the effects of the perturbations on a simple system consisting of a mixture of Lennard-Jones molecules whose parameters were chosen to simulate the mixture argon + krypton (Ref. 53). For the unperturbed mixture both G_m^E and H_m^E were small and positive while both V_m^E and S_m^E were negative. As the magnitude of the various perturbing potentials increased all the excess functions became more positive. At some intermediate strengths S^E became S-shaped. A significant result was that, for a given value of the reduced multipole moment, all the excess functions became more positive in the order going from dipole to quadrupole to octopole moment, independent of whether the multipole was placed on the argon or krypton molecule. Also a small change in shape of either molecule caused the excess functions to become more positive. Over the range of parameters considered there was no indication of phase separation.

Subsequently Gubbins and coworkers have modified the theory to include induction and dispersion forces and they were able to predict reasonable vapour-liquid equilibrium curves, excess volumes, and phase diagrams for mixtures containing polar (HCl, HBr), quadrupolar (CO_2, C_2H_2, C_2H_4, C_2H_6), and octopolar (CH_4, CF_4) molecules. They have also compared the thermodynamic excess functions for mixtures involving HBr, HCl, and Xe with the theory. For these mixtures they used the Lennard-Jones (12,6) model for the reference potential and the
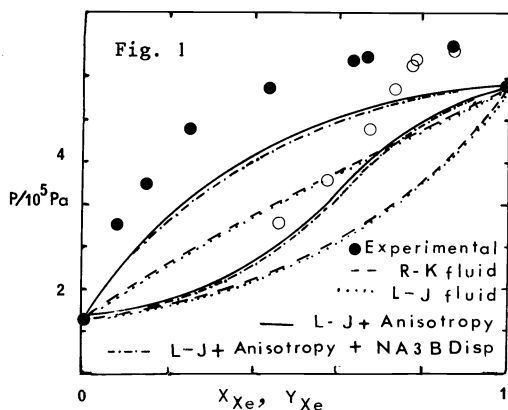
Fig. 1. Binary phase diagram for Xe + HCl using the Lorentz-Berthelot combining rule for the reference mixture without adjustment.
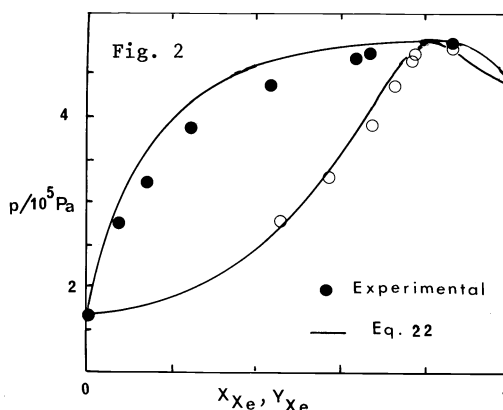
Fig. 2. The binary phase diagram for Xe + HCl using alternative combining rule for the reference mixture (eq. 22).

potential included contributions from electrostatic (multipolar), dispersion, shape, and electrostatic induction effects. For the linear molecules HCl and HBr the theory included such terms as the dipole-dipole, dipole-quadrupole, quadrupole-dipole, and quadrupole-quadrupole potentials. The dispersion term also included a polarizability and a higher polarizability tensor resulting from the dipole moment induced by a field gradient or the quadrupole induced by the field. The induction term results when the dipole of one molecule induces a dipole on a second molecule which in term reacts back with the original dipole (or some other multipole). The perturbation was made about a reference fluid using the Padé approximation for the Helmholtz free energy A suggested by Stell:

$$A = A^{(12,6)} + A_1 + A_2[1/(1 - A_3/A_2)].\tag{19}$$

This approximation has been found to converge even for the strongest of dipoles and quadrupoles observed in nature. The expression for A_1 includes contributions from induction and three-body dispersion forces while the expressions for A_2 and A_3 involve summations over various state variables, intermolecular parameters, and complex integrals. The reference fluid used is usually the Lennard-Jones (12-6) fluid since accurate computer simulation results exist for this system. The properties of the reference fluid have normally been extended to mixtures by the usual van der Waals one-fluid approximations. It must be stressed that these mixing rules apply only to the reference-fluid contribution to the Helmholtz free energy. For the other terms the composition dependence is given exactly by the theory. The remaining interaction parameters required were given by the Lorentz-Berthelot combining rules without any adjustable parameters:

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2},\tag{20}$$

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2.\tag{21}$$

In Figure 1 the predictions of this theory are compared with the results for Xe + HCl (Ref. 49). Included are the values calculated by neglecting the non-additive three body forces, and also anisotropic forces. Also given are the results from the Redlich-Kwong equation. No adjustable parameter has been used in the Lorentz-Berthelot combining rule. They also considered an alternative combining rule for the dispersion energies suggested by Kohler (Ref. 55):

$$\varepsilon_{12}\sigma_{12}^6 = 2\ \varepsilon_{11}\sigma_{11}^6\varepsilon_{22}\sigma_{22}^6\alpha_1\alpha_2/(\varepsilon_{11}\sigma_{11}^6\alpha_1^2 + \varepsilon_{22}\sigma_{22}^6\alpha_1^2).\tag{22}$$

When the only change was to replace $\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2}$ with equation (22) the results shown in Figure 2 were obtained.

With equation (22) as the combining rule for the reference substance the formation of an azeotrope is accurately predicted without the use of adjustment parameters. One is tempted to suggest that this agreement is fortuitous and it remains to be seen if similar agreement is found with other mixtures. The majority of the measurements that have been used to test this theory have been made by Staveley and colleagues. Lobo and Staveley (Ref. 56) now report measurements of the excess functions for mixtures of hydrogen chloride + nitrous oxide, chosen

as a model for mixtures of the type dipolar molecules + quadrupolar molecules. This mixture exhibits a positive azeotrope but the excess functions are in general much smaller than for the mixtures HCl + N_2O and N_2O + Xe. This is the trend expected from the perturbation theory. Calado and Street (Ref. 57) report results for the mixture krypton + ethane over a wide temperature and pressure range and compare the results with various equation-of-state treatments and the perturbation theory. They find excellent agreement with the calculations of the perturbation theory without the need to correct the Lorentz-Berthelot mixing rules. The perturbation theory however cannot yet explain the rather unusual results for the mixture xenon + ethane (Ref. 58); all the excess functions are negative. This type of behaviour is usually observed when there is some form of specific interaction between the molecules or association between two hydrogen bonded compounds. The argument that the negative excess functions result from an interaction between the highly polarizable xenon and the quadrupole on the ethane is not plausible since the excess functions for xenon + hexafluoroethane (Ref. 59) are all positive and hexafluoroethane has a higher quadrupole moment than ethane.

Interaction parameter theories
At present the equation-of-state or perturbation treatments have not reached the stage where they can be used to predict the properties of complex polar organic mixtures. Further the above treatments attempt to predict the properties of mixtures from the properties of the pure components. In general such a prediction is not possible because of inadequate combining rules so one is forced to use one or more of the excess functions to predict the others. The interaction parameter approach is fundamentally different in that one attempts to predict the properties of more complex organic mixtures by the use of empirical parameters associated with interactions between atoms or functional groups on a molecule which are transferable between molecules. The interaction parameter approach forms the basis of various predictive treatments including the Barker, Wilson, UNIQUAC, ASOG, and UNIFAC methods which have been used with some success in the correlation of vapour-liquid equilibria for complex multicomponent organic mixtures. Some of these approaches do make use of equations of state, with the volume and interactions terms being split into group contributions. Kehiaian et al. (Ref. 60) have recently made detailed calculations of the interaction terms in a Barker-type quasi-chemical theory of group surface interactions. They have now extended the application of the theory to mixtures of mono- and diamines by measuring the excess enthalpies of a series of amines with n-alkanes (Ref. 61). They find that, for the diamines, the interchange coefficient depends strongly on the number of CH_2 groups between the two amine groups (termed the proximity effect). They compare the proximity effects with those observed previously for other functional groups. For many mixtures of reasonably complex organic molecules the interaction approach gives reasonable predictions for G_m^E. Some examples of the use of the UNIFAC group contribution method are given by Naumann (Ref. 6) for mixtures of toluene with various aldehydes and ketones.

However the group method is generally less successful in predicting H_m^E, (the treatments tell us nothing about V_m^E and for some of the more sophisticated treatments, the excess volume is required to reduce the results to constant volume conditions). For certain mixtures, such as methanol with various heptanones as reported by Diaz Pena et al. (Ref. 9) this approach is clearly wrong, giving very poor predictions of the activity coefficients of the alcohol at infinite dilution. For mixtures containing H-bonded substances such as acids, alcohols, and amines interactions are strong and indeed often specific to a particular pair of groups within the molecule.

Association theory
In general these mixtures have been treated in terms of an ideal association theory which assumes that the entire deviation from ideal behaviour is attributable to equilibria between the various associates. While this treatment is sometimes considered satisfactory for very strong associates where the equilibrium constant is about 1 and the enthalpy of formation of the complex is greater than 10 kJ mol^{-1}, for mixtures where the association is not as strong it is necessary to consider the effects of both the size of the various associates formed and the contribution from physical interaction terms.

In general for mixtures of polar and nonpolar molecules or polar + polar molecules we need to account for the following interactions:

    (a)   normal van der Waals interactions
    (b)   specific dipole interactions
    (c)   dilution of dipoles (considerable concentration dependence)
    (d)   hydrogen bonding   (considerable concentration dependence)

Our present state of knowledge of molecular interactions does not allow use to make exact statistical mechanical calculations on such mixtures and hence they are generally treated in terms of chemical equilibria. When amines, alcohols, and carboxylic acids, which exist in a

highly associated form in the pure state, are mixed with inert solvents there is a breakdown in the extent of association which continues until there is no association at infinite dilution of the self-associated component. Since the association results from directional hydrogen bonds and the breakage of these bonds is an endothermic process, most mixtures of these liquids with inert solvents show large positive deviations from ideal behaviour. However there are many non-polar solvents that are not inert and it is necessary to postulate specific dipole interactions between the highly polar H-atom and highly polarizable portions of the solvent molecule. Since these interactions are exothermic, the positive deviations from ideality are reduced as some of the energy required to break the hydrogen bonds is supplied by the interaction with the solvent. In carboxylic acids the major species is the cyclic dimer. Amines are only weakly associated and in the pure state only 50 per cent of the molecules are associated. Alcohols are intermediate in behaviour, forming linear and cyclic chains. Many models have been proposed for alcohol association. For example, Diaz Pena et al. (Ref. 9) use a physical interaction term along with a continuous association model to explain the G_m^E values for methanol + heptanone mixtures. Often the models proposed depend on the type of measurements considered and the composition range studied. Frequently measurements are not made at sufficiently low alcohol compositions where the major effects of the association process are observed.

The following model of alcohol association has been proposed by Stokes (Ref. 62) after a detailed analysis of a series of precise measurements on the thermodynamic and dielectric properties of ethanol and butanol mixtures with non-polar solvents over a wide temperature and concentration range.

(1) Open chains of any length are formed: there is an enthalpy of formation for the dimer and another enthalpy of formation, which is independent of the chain length, for subsequent additions to the dimer.

(2) The following equilibrium constants were assumed: K_2 for the dimer formation $A + A = A_2$, K_3 for the trimer formation $A + A_2 = A_3$, and k for all the subsequent polymers $A_i + A = A_{i+1}$, where $i > 2$. To explain the spectroscopic and dielectric properties it was necessary to assume cyclic i-mers in equilibrium with the open chains, with the smallest cyclic group the pentamer. For the equilibrium A_i(open) = A_i(cyclic) the cyclization constant was $K_{cy} = \theta/i$

(3) The infrared results were assumed to determine the proportion of free hydroxyl groups.

(4) The physical-interaction term was given by a Hildebrand-Scatchard term with a single temperature independent adjustable parameter.

The initial model gave excellent results for mixtures of ethanol with cycloalkanes and n-alkanes but was inadequate for mixtures with aromatic components. The model was extended to these mixtures by assuming that the association model in an aromatic solvent would differ from the model in the aliphatic solvents by the inclusion of a solvation equilibrium between a terminal hydroxyl group and the aromatic solvent. The solvation equilibrium constant Q was determined from the difference in the activity coefficients of the alcohol at infinite dilution in the two solvents and the enthalpy of solvation h_s was determined from the temperature dependence of Q. From the parameters determined from the cyclohexane + ethanol system and the values of Q and h_s, the activity coefficients and excess enthalpies for mixtures of ethanol + p-xylene over a wide temperature and composition range were well predicted.

Complex mixtures
A number of complex mixtures have been studied. Ratkovics et al. (Ref. 65) have considered the effect on thermodynamics and transport properties that result from a shift in the keto-enol equilibrium in methylethylketone due to interactions with the aromatic ring. They also consider effects on the association in amines which result from stabilization of the enol form due to various interactions (Ref. 66). Karvo (Ref. 67) finds that H_m^E for mixtures of both p-xylene and mesitylene with sulfolane are positive while Kokkonen et al. (Ref. 68) find that V_m^E for m-xylene + dimethylsulphoxide is negative. Kasprzycka-Guttman and Chreptowicz (Ref. 69) have related the excess enthalpies and the excess Gibbs free energy for mixtures of propanol with various pyridine bases to the number and positions of the methyl groups on the base. Trejo and Murrieta (Ref. 70) have measured the solubility of CO_2 and CH_4 in complex solvents. The main purpose of the work was to determine to possibility of enhanced solubility of acid gases in either pure or mixed solvents in order to sweeten natural gases. Other results of possible industrial significance are the measurements by Ott et al. (Ref. 71) of the excess enthalpy and the phase diagrams of mixtures of various diols with water. The incongruently melting hydrate of 2,5-dimethyl-2,5-hexanediol, which melts at 318 K, could be used as a thermal energy storage material for home heaters. Takagi and Kimura (Ref. 72) have measured the excess enthalpies and excess volumes of mixtures involving water, dimethylsulphoxide, benzene, and methyl-

methylthiomethylsulphoxide. Domanska and Pietrzyk (Ref. 73) propose an equation for solubility and they compare the predictions with solubility measurements on six substituted benzoic acids in benzene.

Multi-component mixtures

Armitage and Osborne (Ref. 3) have developed various techniques for obtaining excess Gibbs free energies from static vapour-pressure measurements and excess volumes from density measurements on ternary mixtures while Naumann (Ref. 6) compare the predictions of the UNIFAC group contribution method for ternary systems of aldehydes, ketones and toluene with their measurements. Mastowska (Ref. 74) has measured acid-base equilibrium of thiocarbamide derivatives in ethanol + water mixtures. Nissema et al. (Ref. 75) have measured excess volumes in binary and ternary mixtures prepared from dimethylsulfoxide, cyclohexane, and m-xylene. They propose that the difference between predicted and experimental results are due to ternary effects. Mickeleit and Lacmann (Ref. 76) have developed a theory for ternary mixtures based on the lattice model of Barker. Christensen and Hanks (Ref. 31) propose a method for calculating multicomponent vapour-liquid equilibria data from binary excess enthalpy measurements. Initially they calculate binary vapour-liquid equilibria data from various equations for G_m^E which contain terms (for example $A_1 e^{-A/RT}$) which, after carrying out the differentiation $H_m^E = - T^2 \partial(G_m^E/T)/\partial T$ no constants are lost. H_m^E is then fitted to a complex equation which contains all the constants for the G_m^E equation. Thus S_m^E is completely determined by the equation proposed for G_m^E. Rätzsch and Kehlen (Ref. 77) address themselves to the important problem of dealing with many, often unknown, components in a mixture. They ascribe separate distribution to distinct classes of compounds (paraffinic, aromatic, naphthenic) and develop a version of thermodynamics based on continuous distributions which they term continuous thermodynamics. In their contribution they derive the phase rule appropriate to such a system.

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