Kirkwood–Buff Solution Theory: Derivation and Applications

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1 Preamble

The development of rigorous theories of the liquid state and of multi-component liquid mixtures has always been hampered by both the complexity of the statistical mechanics and the complex nature of intermolecular interactions. There are two central themes within chemical thermodynamics. The first deals with internal energy or enthalpy. As an example let us consider the internal energy E of a monatomic solid subject only to pairwise interactions. We can write for E (on a per atom basis):

$$E = (1/2)\sum N(r)E(r) \tag{1.1}$$

where $N(r)$ equals the number of atoms at a distance r from an arbitrarily chosen central atom and $E(r)$ is the pairwise interaction energy at a distance r. The summation is taken over all atoms. This equation needs to be modified to take into account the random structure of a liquid (or gas) composed of molecules of species 1:

$$E(1/2)\rho_1\int_0 4\pi r^2 g_{11}(r)E(r)\mathrm{d}r \tag{1.2}$$

where ρ_1 equals the number density (*i.e.* atoms per unit volume) of 1 and $g_{11}(r)$ is the so-called radial distribution function (rdf), the probability of finding a molecule of species 1 a distance r from the central atom relative to the probability of finding a molecule of species 1 a large distance from the central atom. In mixtures, rdfs between different components can also be defined. For example in a mixture of i and j, there are three rdfs, $g_{ii}(r)$, $g_{jj}(r)$, $g_{ij}(r)$. The rdf can be more rigorously defined than given here and it is also defined for molecules with angular dependence in their intermolecular potentials by suitable angular averaging. The rdf is also in principle measurable by X-ray or neutron diffraction experiments. Figure 1 gives examples of diffraction-derived rdfs for argon and water. The function is zero at very small distances (less than the molecular diameter) and near the distance of closest approach there is a pronounced peak. The area under this first peak relates to the number of nearest neighbours around any given molecule. The much more pronounced peak for argon corresponds to approximately ten nearest neighbours, unlike water which has only four or so. The function oscillates to unity after three or four molecular diameters. The small peaks for argon at roughly two and three molecular diameters correspond to lattice-like packing that occurs in a dense fluid. For water there is a peak at a value less than two diameters which is strong direct evidence for the tetrahedral structure of water. A knowledge of $g_{11}(r)$ is central to our understanding about the 'structure' of the fluid. It is clear that in some sense $g_{11}(r)$ and $E(r)$ must be correlated since a strongly repulsive energy would imply a low value of $g_{11}(r)$ and *vice versa*. In practice, the radial dependence $E(r)$ is chosen either empirically or from quantum mechanical calculations and the variation of $g_{11}(r)$ is estimated using various different 'closure' approximations. Such approaches are referred to as 'integral equations'.

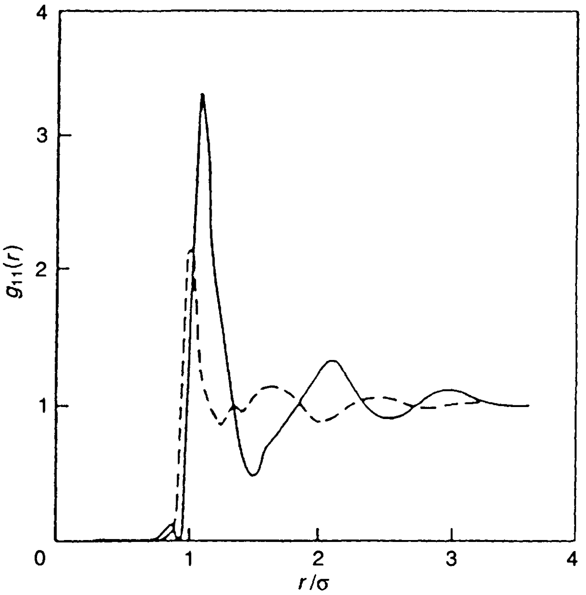


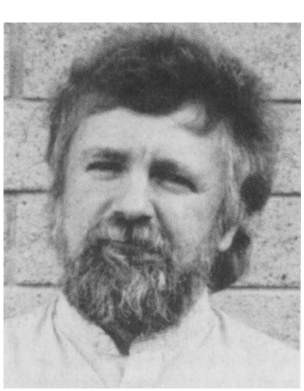
Figure 1 Radial distribution functions of liquid argon (solid line) at $T = 84.3$ K, $P = 71$ kPa, and water (broken line) at $T = 227$ K, $P = 101$ kPa. σ equals 0.34 nm for argon and 0.282 nm for water. (Reproduced with permission from, F. Franks, 'Water', The Royal Society of Chemistry, 1983.)

An example of the other major theme in thermodynamics, the second law, is the equation $\Delta G^\circ = -RT\ln\mathrm{K}$. In this case the equilibrium constant K gives us information about the molecular nature, the 'structure' of the system which is related to the free energy without recourse to knowledge about the interactions occurring in the system. Kirkwood–Buff (KB) theory[1] is analogous to this idea in that it relates the thermodynamic parameters to the structure without recourse to knowledge of the interactions in the system. The 'structure' parameters which occur in this theory are the so-called Kirkwood–Buff integrals:

$$G_{ij} = \int_0^\infty 4\pi r^2[g_{ij}(r) - 1]\mathrm{d}r \tag{1.3}$$

The theory is unable to obtain rdfs, only their integrals. The results of KB theory are relatively straightforward, although the original derivation is somewhat complicated being formulated in terms of matrix algebra. Our aim in this article is to demystify KB theory by mapping out its theoretical background and derivation as well as giving various examples of the utility of the approach.

Dr. Ken Newman was born in London, England and pursued his studies at the University of Durham and Newcastle-upon-Tyne where he received a Ph.D. in Physical Chemistry under the supervision of Professor Arthur Covington. Following periods at the Université de Lausanne, Simon Fraser University, and the Université de Sherbrooke, he is presently Associate Professor of Chemistry at The King's University College (a privately funded Christian University) where he continues his research interests on the relationship between the thermodynamic and structural properties of both electrolyte and non-electrolyte solutions.



2 Theory as derived by Hall

In 1971, Hall[2] rederived much of KB theory using a more intuitive molecular thermodynamic approach As a prelude to the full, more formal derivation, we present with certain modifications, the approach of Hall Let us consider a very dilute solution of a solute S in a mixture of 1 and 2 Let us consider two regions in solution one containing a molecule of S and its sphere of influence It is not necessary to define precisely this sphere of influence except to make sure that it contains all 1 and 2 that has been perturbed by S Such a region of solution is shown schematically in Figure 2a Let the number of molecules of 1 and 2 in this sphere of influence equal N_1'' and N_2'' respectively Let us also consider a region of solution exactly the same size and shape as the first but far from any molecule of S, and thus containing only unperturbed solvent mixture 1 and 2 Let the number of molecules of A and B in this region equal N_1' and N_2' (Figure 2b)

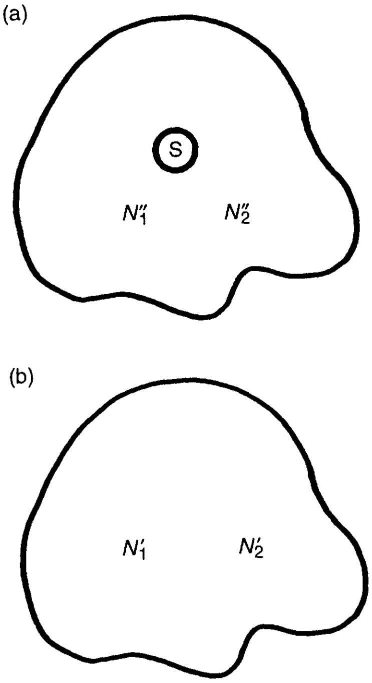


Figure 2 (a) Schematic diagram of a solute S and its region of influence N_1'' and N_2'' are the number of molecules of 1 and 2 in this volume (b) Schematic diagram of volume identical to that in (a) which contains neither a solute molecule nor solute-perturbed solvent molecules N_1' and N_2' are the number of molecules of 1 and 2 in this volume

It is clear that the difference $N_1'' - N_2'$ relates to the KB integral of 2 around S

$$\rho_2 G_{S2} = \rho_2 \int_0^\infty 4\pi r^2 [g_{S2}(r) - 1] dr = (N_2'' - N_2') \qquad (2\ 1)$$

Let us now consider unit volume of the dilute solution of S with 1 and 2 in osmotic equilibrium with unit volume of the mixture 1 and 2 We may write for the constant temperature Gibbs–Duhem equation for the two solutions

$$0 = d(P + \Pi) - \rho_S d\mu_S - \rho_1 d\mu_1 - \rho_2 d\mu_2 \qquad (2\ 2)$$

$$0 = dP - \rho_1^\circ d\mu_1 - \rho_2^\circ d\mu_2 \qquad (2\ 3)$$

The ρ_1 and ρ_1° refer to the number densities of 1 in the two solutions At this point Hall made the eminently reasonable assumption that the difference $\rho_1 - \rho_1^\circ$ must relate immediately to the term G_{S1}

$$\rho_1 - \rho_1^\circ = \rho_S \rho_1 G_{S1} \qquad (2\ 4)$$

Subtraction of equation (2 3) from (2 2) and substitution of (2 4) readily yields

$$0 = d\Pi - \rho_S d\mu_S - \rho_S \rho_1 G_{S1} d\mu_1 - \rho_S \rho_2 G_{S2} d\mu_2 \qquad (2\ 5)$$

Since we are dealing with very dilute solutions, we may substitute for the limiting expression for osmotic pressure*

$$\Pi = \rho_S k_B T \qquad (2\ 6)$$

which gives

$$d(\mu_S - k_B T \ln \rho_S) = -\rho_1 G_{S1} d\mu_1 - \rho_2 G_{S2} d\mu_2 \qquad (2\ 7)$$

In the limit that n_S goes to zero, the term on the left hand side of equation (2 7) is simply the derivative of the standard chemical potential of S Thus

$$d\mu_S^\circ = \lim_{\rho_S \to 0}[d(\mu_S - k_B T \ln \rho_S)] = \lim_{\rho_S \to 0}(-\rho_1 G_{S1} d\mu_1 - \rho_2 G_{S2} d\mu_2) \qquad (2\ 8)$$

This equation is readily extendable to any number of solvent components simply by adding further terms to the right hand side The equation which is readily obtainable from the full KB theory is applicable to the effect of change of solvent composition on solute chemical potential which experimentally are measured as free energies of transfer, primary medium effect, salting in/out effects It has also been used in conjunction with transition state theory to discuss solvent effects in kinetics We will discuss the use of this equation below

In order to develop equations that could be used for solutions that were not infinitely dilute, Hall introduced the clever idea of considering what would happen if solute S were identical in all of its chemical properties to one of the solvent components, *e g* component β but is in some way distinguishable It is clear that

$$G_{S1} = G_{21} \text{ and } G_{S2} = G_{22} \qquad (2\ 9)$$

We now wish to make the connection between the chemical potentials of S and 2 It can be readily shown that they are related by

$$d\mu_S = d\mu_2 + k_B T \ln(\rho_S/\rho_2) \qquad (2\ 10)$$

Substituting equations (2 9) and (2 10) into (2 7) we obtain

$$k_B T d\ln \rho_2 = (1 + \rho_2 G_{22}) d\mu_2 + \rho_1 G_{21} d\mu_1 \qquad (2\ 11)$$

This equation, which has great utility in interpreting activity coefficients and osmotic pressure measurements, is also obtainable using the rigorous theory Its use will be discussed below

3 Kirkwood–Buff Theory

The full derivation of Kirkwood–Buff theory arises out of Grand Canonical Ensemble statistical thermodynamics[3] and as such is not very accessible to many chemists In this section we wish to present an outline of the derivation as well as some background theory on the ensemble so as to permit the reader to comprehend the original work In order to help the reader, Figure 3 gives a flowchart of the ideas to be presented The original work was given in matrix algebra form for an *n*-component mixture and whilst it is an extremely elegant formulation, it can be very daunting to the neophyte Thus we shall develop the equations explicitly for a binary mixture and simply point out the matrix nature of the equations at suitable points in the development In fact our initial development of Grand Canonical Ensemble statistical mechanics commences with a

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* Throughout this work the theoretical development is performed on a per molecule rather than a per mole basis Thus we use Boltzmann s constant k_B rather than the gas constant R When comparisons are made with experimental data on a per mole basis it is simply necessary to change k_B for R and the resultant equations are automatically transformed into a per mole basis

SECTION	THEORETICAL THEME	REPRESENTATIVE EQUATIONS, FIGURES, *ETC*
3 1	The Grand Canonical Ensemble for a pure liquid	FIGURE 4
3 2	The Grand Canonical Ensemble partition function	$P(j,N) = \frac{\exp(\gamma N)\exp(-\beta E(j))}{\Xi}$ $\Xi = \sum_N\sum_j \exp(\gamma N)\exp[-\beta E(j)]$
3 3	Calculation of average properties	For example $\langle N\rangle = \sum_N\sum_j NP(j,N)$
3 3	Relationship between $\langle N^2\rangle$ and the chemical potential	$\langle N^2\rangle - \langle N\rangle^2 = k_BT(\partial N/\partial\mu)_{V\,T}$
3 4	Generalization of the ideas to include a binary mixture 1 + 2	$\langle N_1N_2\rangle - \langle N_1\rangle\langle N_2\rangle = k_BT(\partial N_1/\partial\mu_2)_{V\,T\,\mu_1}$
3 5	Relation between $g_{12}(r)$ and the term $\langle N_1N_2\rangle$	$\langle N_1N_2\rangle - \langle N_1\rangle\langle N_2\rangle = V\rho_1\rho_2\int 4\pi r^2[g_{12}(r) - 1]\mathrm{d}r$
3 6	Conversion of the term $(\partial N_1/\partial\mu_2)_{T\,V\,\mu_1}$ to $(\partial\mu_2/\partial N_1)_{T\,V\,N_2}$	Equations such as 3 26
3 7	Conversion of equations from constant volume to constant pressure	Equations such as 3 30
3 7	Final manipulation of equations to give useful results	Equations such as 3 36—3 39

Figure 3 Flowchart of various steps in theoretical development of Kirkwood–Buff theory

pure liquid and is only generalized to a binary mixture as a second step

3.1 The Grand Canonical Ensemble

Gibbs developed the ideas of statistical mechanical ensembles so as to forge a formal connection between the thermodynamic properties of a system and its mechanical properties By mechanical properties we mean those properties which are peculiar to the individual atoms and molecules such as velocity, kinetic energy, *etc* An ensemble is a conceptual collection of an extremely large number of systems, each one constructed so as to be a replica at a thermodynamic level of the actual thermodynamic system of interest However, since the numbers of molecules and the possible quantum (or classical) states are extremely large indeed, the various systems will not be identical on the molecular level In order to forge the link between the mechanical and thermodynamic properties two postulates are necessary The first (often called the ergodic hypothesis) simply states that the long-time averages of the mechanical properties equal the ensemble averages The second hypothesis states that, subject to the external constraints on the system, all of the quantum (or classical) states are *a priori* equally probable

The Grand Canonical Ensemble consists of systems all of volume V immersed in a bath at constant temperature T with the walls of each of the systems being permeable to the molecular species The ensemble thus acts as a reservoir of molecules and thus each system is characterized by the thermodynamic variables V, T, and μ (the chemical potential) See Figure 4 Note that the number of molecules N within the systems is not fixed but fluctuates around an average value $\langle N\rangle$ Similarly, the energy of any system is not fixed It is important to note that the word 'fluctuation', which is frequently used in the context of the Grand Canonical Ensemble, has a highly specific meaning It

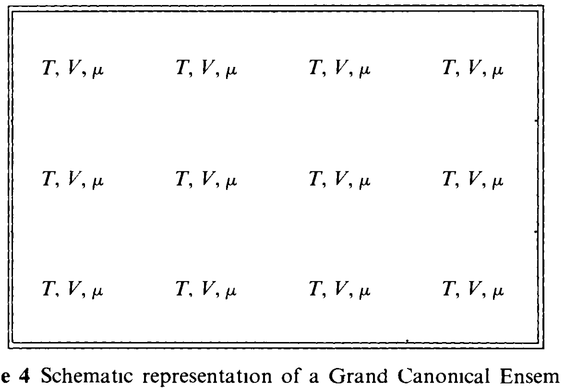

Figure 4 Schematic representation of a Grand Canonical Ensemble Each system is characterized by a fixed volume, chemical potential, and temperature However, the walls between each system are permeable to both energy and matter

has nothing to do with time-dependent changes in a parameter. It simply means that different replicate systems will have different values of the parameter of interest.

3.2 The Grand Canonical Ensemble Partition Function

As mentioned above, for any system in the ensemble neither the total number of molecules N nor the total energy E is fixed. They fluctuate. As molecules pass in and out of any of the systems both N and the quantum state of the system j change. In this section we wish to explore the consequences of these fluctuating properties; in particular we wish to consider the expression for the probability that a given system is in a certain state, *i.e.* the probability $P(N,j)$ that the system contains exactly N molecules and is in the quantum state represented by the index j. By expanding out $\ln[P(N,j)]$ as a Taylor expansion in both N and the energy E and considering two members of the ensemble which are widely separated and hence independent, it can be shown that:[4]

$$P(N,j) = \exp(K)\exp[-\beta E(j)]\exp(\gamma N) \tag{3.1}$$

where K, β, and γ are as yet undetermined constants. It turns out that $\beta = 1/k_BT$ and $\gamma = \mu/k_BT$ where μ is the chemical potential. We require that the probability is correctly normalized, *i.e.* the sum of the probabilities for all values of N and j equals unity. Thus we obtain from equation (3.1):

$$\sum_j\sum_N P(N,j) = 1 = \exp(K)\sum_j\sum_N \exp[-\beta E(j)]\exp(\gamma N) \tag{3.2}$$

and hence:

$$\exp(-K) = \sum_j\sum_N \exp[-\beta E(j)]\exp(\gamma N) \equiv \Xi \tag{3.3}$$

where Ξ is referred to as the Grand Canonical Ensemble partition function. Ξ is a function of both T and μ and is evidently a thermodynamic state function. The probability of a system being in the state (j,N) is thus:

$$P(j,N) = \frac{\exp[-\beta E(j)]\exp(\gamma N)}{\Xi} \tag{3.4}$$

3.3 Calculation of Average Properties

The average value of any set of replicate values is simply the value observed multiplied by the probability of occurrence and then summed over all of the set. Thus for N we may write:

$$\langle N\rangle = \sum_j\sum_N NP(j,N) = \frac{\sum\sum N\exp[-\beta E(j)]\exp(\gamma N)}{\Xi} \tag{3.5}$$

It is interesting to compare equation (3.3) and (3.5). If we differentiate equation (3.3) with respect to γ we obtain the dividend of equation (3.5). (Several other important manipulations of the Grand Canonical Ensemble follow from this selfsame property of differentiation of exponentials.) Thus we can write:

$$\langle N\rangle = \frac{1}{\Xi}\left\{\frac{\partial\Xi}{\partial\gamma}\right\}_{V,\beta} = \left\{\frac{\partial\ln\Xi}{\partial\gamma}\right\}_{V,\beta} \tag{3.6}$$

The distribution of N around the mean value $\langle N\rangle$ is very narrow (see below for further details) and may be approximated by a Gaussian distribution whose variance σ_N^2 is given by:

$$\sigma_N^2 = (1/T)\sum[(N-\langle N\rangle)^2] = \langle N^2\rangle - \langle N\rangle^2 \tag{3.7}$$

where T is the total number of terms in the sum. As we shall see next, σ_N^2 is very closely related to $(\partial\langle N\rangle/\partial\mu)_{T,V}$. It is also related closely to the radial distribution function; once we have extended the treatment to multicomponent systems we will have all of the keys of the puzzle necessary to connect μ to $g(r)$, the basis of Kirkwood–Buff theory. The ensemble average $\langle N^2\rangle$ can be written:

$$\langle N^2\rangle = \sum\sum N^2P(j,N) = \frac{\sum\sum N^2\exp[-\beta E(j)]\exp(\gamma N)}{\Xi} \tag{3.8}$$

If we recast equation (3.5) in the form:

$$\Xi\langle N\rangle = \sum\sum N\exp[-\beta E(j)]\exp(\gamma N) \tag{3.5a}$$

we readily obtain by differentiation with respect to γ (at constant T and V):

$$\langle N\rangle\partial\Xi/\partial\gamma + \Xi\partial\langle N\rangle/\partial\gamma = \sum\sum N^2\exp[-\beta E(j)]\exp(\gamma N) \tag{3.9}$$

If we now substitute equations (3.6) and (3.8) into equation (3.9), we obtain (having removed the ensemble average $\langle\ \rangle$ from around the N in the $\partial N/\partial\gamma$ term):

$$\langle N^2\rangle - \langle N\rangle^2 = (\partial N/\partial\gamma)_{T,V} = (k_BT)(\partial N/\partial\mu)_{T,V} \tag{3.10}$$

Finally, we can transform this equation through constant temperature thermodynamic equation $d\mu = (V/N)dp$, to give:

$$\frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle^2} = -\frac{k_BT}{V^2}\left(\frac{\partial V}{\partial p}\right)_{N,T} = \frac{\kappa k_BT}{V} \tag{3.11}$$

where κ is the isothermal compressibility$[= (+1/N)(\partial N/\partial p)_{T,V} = (-1/V)(\partial V/\partial p)_{T,N}]$. This equation is one of the celebrated equations of the Grand Canonical Ensemble. As an example of the use of this equation for liquid water at 298.15 K, if we choose the volume to equal the molar volume, then from the experimental values of κ (4.53×10^{-10} Pa^{-1}), we find $\sigma_N = 1.93 \times 10^{11}$. This is the width of the distribution of values of N whose average value is obviously 6.022×10^{23}. The fluctuations in N, and hence in concentration, are only one part in 3×10^{12}.

3.4 Generalization to a Binary Mixture

If we refer back to Section 3.1, we see that the changes necessary to accomodate a binary mixture 1 + 2 in place of a pure component in the setting up of the ensemble are insignificant. We require simply that the walls of each system are permeable to both components. The natural variables are in this case the temperature T, the volume V, and the two chemical potentials μ_1 and μ_2. The equation for the partition function thus becomes:

$$\Xi = \sum_j\sum_N \exp[-\beta E(j)]\exp(\gamma_1N_1)\exp(\gamma_2N_2) \tag{3.12}$$

Probability expressions occur in an analogous manner. However, crucial to the development of Kirkwood–Buff theory are terms of the form $\langle N_1N_2\rangle - \langle N_1\rangle\langle N_2\rangle$, corresponding to covariance terms in statistics which measure the correlation of fluctuations between 1 and 2. As an example, if 1 and 2 were to have an affinity for each other, then we would expect to see any positive fluctuation in N_1 to be occurring simultaneously with a positive fluctuation in N_2; this would be manifest as a positive co-variance. Here we begin to see some form of chemically useful information emerging from the theory. Thus, following the idea suggested above, we obtain relatively straightforwardly:

$$\langle N_1N_2\rangle - \langle N_1\rangle\langle N_2\rangle = k_BT(\partial N_1/\partial\mu_2)_{T,V,\mu_1} = k_BT(\partial N_2/\partial\mu_1)_{T,V,\mu_2} \tag{3.13}$$

The corresponding terms for $\langle N_1^2\rangle$ and $\langle N_2^2\rangle$ are identical with those of equation 3.10.

3.5 Relationship between $\langle N_i N_j \rangle$ and $g_{ij}(r)$

The relationship between the composition fluctuation terms such as $\langle N_1 N_2 \rangle$ and the radial distribution function $g_{12}(r)$ have been dealt with at various levels of rigour in different texts [5] In this review we will present a somewhat informal argument in order to limit the scope of this article somewhat Let us choose at random a molecule of species 1 in a mixture of 1 + 2 and consider the local (number) density of molecules of species 2 at a distance $r \rho_{12}(r)$ In a shell of thickness δr the total number of molecules will be $4\pi r^2 \rho_{12}(r)\delta r$ The number N_{12} of molecules of species 2 within a large volume V defined by the large distance R ($R \to \infty$) from the reference molecule [$V = 4/3)\pi R^3$] is

$$N_{12} = \int_0^R 4\pi r^2 \rho_{12}(r) \mathrm{d}r \tag{3 17}$$

The number of molecules of species 1 in this region equals $V\rho_1$, and thus the product of molecules of species 1 and 2 within this region equals $\langle N_1 N_2 \rangle$

$$V\rho_1 \int_0^R 4\pi r^2 \rho_{12}(r) \mathrm{d}r = \langle N_1 N_2 \rangle \tag{3 18}$$

The corresponding values of $\langle N_1 \rangle$ and $\langle N_2 \rangle$ are then given by

$$\langle N_1 \rangle = V\rho_1, \qquad \langle N_2 \rangle = V\rho_2 \tag{3 19}$$

and noting that $\rho_{12}(r)$ relates to the radial distribution function $g_{12}(r)$

$$g_{12}(r) = \rho_{12}(r)/\rho_2 \tag{3 20}$$

we obtain from equations 3 18, 3 19, and 3 20

$$\langle N_1 N_2 \rangle - \langle N_1 \rangle\langle N_2 \rangle = V\rho_1\rho_2 \int_0^R 4\pi r^2 [g_{12}(r) - 1] \mathrm{d}r = V\rho_1\rho_2 G_{12} \tag{3 21}$$

Since at large values of R, $\rho_{12}(r)$ should tend to ρ_2 (*i e* there is no correlation between 1 and 2, and $g_{12}(r)$ tends to unity) then the upper limit of equation 3 35 can be set to infinity The last equality comes from equation 1 3 where G_{12} is the Kirkwood–Buff integral We now notice that $\langle N_1 N_2 \rangle - \langle N_1 \rangle\langle N_2 \rangle$ increases with V

If we return to the above derivation, as applied to the term $\langle N_1^2 \rangle$, we need to note one important difference When applied to molecules of species 2 around 1, equation 3 17 represents the number of molecules of species 2 in the volume If 1 and 2 are identical, then we must add one molecule so as to include the central molecule Thus we write

$$N_{11} = 1 + \int_0^R 4\pi r^2 \rho_{11}(r) \mathrm{d}r \tag{3 22}$$

Repeating the above treatment for species 1 around species 1 yields

$$\langle N_1^2 \rangle - \langle N_1 \rangle^2 = V\rho_1^2 \int_0^R 4\pi r^2 [g_{11}(r) - 1] \mathrm{d}r + V\rho_1 = V\rho_1^2 G_{11} + V\rho_1 \tag{3 23}$$

3.6 The Problems of Equations 3.14, 3.15, and 3.16

These celebrated equations of Grand Canonical Ensemble statistical mechanics link the conventional thermodynamic properties to the ensemble fluctuations However, they are somewhat problematical since virtually all thermodynamic measurements involve measuring a chemical potential as a function of composition, and not by fixing the second chemical potential as is required in these equations Thus our problem at this stage is simply to recast the equations to give terms of the form $(\partial N_2/\partial\mu_1)_{T\,V\,N_1}$ and not $(\partial N_2/\partial\mu_1)_{T\,V\,\mu_2}$ Using the rules of partial differentiation we may write for example

$$(\partial\mu_1/\partial N_2)_{T\,V\,\mu_2} = (\partial\mu_1/\partial N_2)_{T\,V\,N_1} + (\partial\mu_1/\partial N_1)_{T\,V\,N_2}(\partial N_1/\partial N_2)_{T\,V\,\mu_2} \tag{3 24}$$

The permuter rule of partial differentiation then gives

$$(\partial N_1/\partial N_2)_{T\,V\,\mu_2} = -(\partial N_1/\partial\mu_2)_{T\,V\,N_2}(\partial\mu_2)/\partial N_2)_{T\,V\,N} \tag{3 25}$$

Combining equations 3 24 and 3 25 and rearranging we obtain (at constant T and V)

$$\begin{aligned}\left(\frac{\partial N_2}{\partial\mu_1}\right)_{\mu_2\,T\,V} &= \frac{(\partial\mu_2/\partial N_1)_{N_2}}{(\partial\mu_1/\partial N_2)^2_{N_1} - (\partial\mu_1/\partial N_1)_{N_2}(\partial\mu_2/\partial N_2)_{N_1}} \\ &= \langle N_1 N_2 \rangle - \langle N_1 \rangle\langle N_2 \rangle \end{aligned} \tag{3 26}$$

where we have noted the definition of chemical potential implies that $(\partial\mu_2)/\partial N_1)_{N_2}$ equals $(\partial\mu_1)/\partial N_2)_{N_1}$ Similar expressions are easily obtainable for $(\partial N_1/\partial\mu_1)_{\mu_2}$ and $(\partial N_2/\partial\mu_2)_{\mu_1}$ If we refer to the original work of Kirkwood and Buff written for an *n*-component mixture, we find equation 3 26 written in determinant form [their equation 8]

$$\left(\frac{1}{k_\mathrm{B}T}\right)\left(\frac{\partial N_\alpha}{\partial\mu_\beta}\right)_{\mu_\alpha} = \langle N_\alpha N_\beta \rangle - \langle N_\alpha \rangle\langle N_\beta \rangle = |A|_{\alpha\beta}/|A| \tag{3 27}$$

where A is the determinant whose factors are

$$A_{\alpha\beta} = (\partial\mu_\alpha/\partial N_\beta)_{N_\alpha} \tag{3 28}$$

The determinant $|A|_{\alpha\beta}$ is obtained by removing row α and column β from $|A|$

In summary then, for a binary mixture 1 + 2, there are three equations which relate the fluctuations to the conventional chemical potentials (equations such as 3 26), and three equations which relate the fluctuations to the integrals of the radial distribution functions (equations such as 3 21 and 3 23)

We now wish to solve equation 3 26 and the other two corresponding equations explicitly for the terms such as $(\partial\mu_1/\partial N_2)_{N_1}$ and we readily obtain equations such as

$$\frac{1}{k_\mathrm{B}T}\left(\frac{\partial\mu_1}{\partial N_2}\right)_{N_1\,T\,V} = \frac{\rho_1\rho_2 G_{12}}{\rho_1^2\rho_2^2 G_{12}^2 - \rho_1(1 + \rho_1 G_{11})\rho_2(1 + \rho_2 G_{22})} \tag{3 29}$$

which are the determinantal equations given by Kirkwood–Buff (their equation 9) At this point in the development we should note that the only problem with equations such as 3 29 is that they hold at constant volume, and the final step is to recast them into constant pressure form and to put them into useful form

3.7 Algebraic Manipulation to Obtain Useful Equations

It is perhaps useful at this stage to consider what we can expect from our equations They have all been derived at constant temperature and so the theory as cast can only refer to free energies and not to entropies (the temperature derivative of free energy) nor to enthalpies We have in equations such as 3 29 three independent expressions and thus would hope to be able to obtain equations for three useful parameters The Gibbs–Duhem expression tells us that for a binary mixture we have only one independent chemical potential and one independent partial molar volume A third parameter could be osmotic pressure (treating one of the two components as solute the other as solvent) However, osmotic pressures can be converted into chemical potentials with the aid of a partial molar volume and the solution compressibility Thus the three 'naturally occurring' thermodynamic parameters can be considered to be either the set *chemical potential partial molar volume*, *compressibility* or the set *chemical potential*, *partial molar volume*, *osmotic pressure* For either of the two sets the resulting equations arise as different combinations of the terms G_{12}, G_{11}, and G_{22} In order to convert equation 3 29 from a constant volume to a constant pressure expression, we may write using the rules of partial differentiation

$$\left(\frac{\partial\mu_1}{\partial N_2}\right)_{V\,T\,N_1} = \left(\frac{\partial\mu_1}{\partial N_2}\right)_{p\,T\,N_1} + \left(\frac{\partial\mu_1}{\partial p}\right)_{T\,N_1\,N_2}\left(\frac{\partial p}{\partial N_2}\right)_{T\,V\,N_1} \quad (3.30)$$

The last term of the above equation can be rewritten as

$$\left(\frac{\partial p}{\partial N_2}\right)_{T\,V\,N_1} = \frac{(\partial V/\partial N_2)_{T\,p\,N_1}}{(\partial V/\partial p)_{T\,N_1\,N_2}} = \frac{v_2}{\kappa V} \quad (3.31)$$

Equation 3.30 thus becomes [Kirkwood and Buff's equation 11)

$$\left(\frac{\partial\mu_1}{\partial N_2}\right)_{V\,T\,N_1} = \left(\frac{\partial\mu_1}{\partial N_2}\right)_{p\,T\,N_1} + \frac{v_1 v_2}{\kappa V} \quad (3.32)$$

There are of course two other very similar equations to 3.32. Final generation of the useful equations requires use of the Gibbs–Duhem equation

$$N_1(\partial\mu_1/\partial N_1)_{p\,N_2} + N_2(\partial\mu_2/\partial N_1)_{p\,N_2} = 0 \quad (3.33)$$

It is readily shown by combining equations 3.23 and 3.33 and using the relationship $V = N_1V_1 + N_2V_2$

$$N_1^2(\partial\mu_1/\partial N_1)_{T\,V\,N_2} + N_1N_2(\partial\mu_1/\partial N_2)_{T\,V\,N_2} + N_2^2(\partial\mu_2/\partial N_2)_{T\,V\,N}$$
$$+ N_1N_2(\partial\mu_2/\partial N_1)_{T\,V\,N_1} = V/\kappa \quad (3.34)$$

This then gives us the required expression for the isothermal compressibility in conjunction with equations of the form of 3.29. Similarly, we can obtain from equations 3.23 and 3.33

$$N_1\left(\frac{\partial\mu_1}{\partial N_2}\right)_{V\,T\,N_1} + N_2\left(\frac{\partial\mu_2}{\partial N_2}\right)_{V\,T\,N} = \frac{v_2}{\kappa} \quad (3.35)$$

This equation, in conjunction with 3.34 gives the final expression for the partial molar volume with expressions such as 3.29. Finally, with expressions for both compressibility and partial molar volume, we can obtain an expression for $(\partial\mu_1/\partial N_2)_{T\,p\,N_1}$ from equation 3.32 and such as 3.29. The osmotic pressure expression is obtained by conventional thermodynamic manipulation of the other quantities and is not derived explicitly here. To summarize, the equations of Kirkwood–Buff theory as applied to a binary mixture

$$\kappa k_B T = \frac{1 + \rho_1G_{11} + \rho_2G_{22} + \rho_1\rho_2(G_{11}G_{22} - G_{12}^2)}{\rho_1 + \rho_2 + \rho_1\rho_2(G_{11} + G_{22} - 2G_{12})} \quad (3.36)$$

$$\bar{v}_1 = \frac{1 + \rho_2(G_{22} - G_{12})}{\rho_1 + \rho_2 + \rho_1\rho_2(G_{11} + G_{22} - 2G_{12})} \quad (3.37)$$

$$\frac{1}{k_BT}\left(\frac{\partial\pi}{\partial\rho_2}\right)_{T\,\mu_1} = \frac{1}{1 + \rho_2G_{22}} \quad (3.38)$$

$$\frac{1}{k_BT}\left(\frac{\partial\mu_2}{\partial\rho_2}\right)_{T\,P} = \frac{1}{\rho_2} + \frac{G_{12} - G_{22}}{1 + \rho_2(G_{22} - G_{12})} \quad (3.39)$$

3.8 Electrolyte Solutions

One of the important constraints with the theory of electrolyte solutions is that of electroneutrality. As well as requiring the well-known condition that in any given volume of solution, the total charge on the cations plus the anions must equal zero, it requires some other important conditions. First, in terms of Debye–Huckel ideas, the charge on any given ion plus that of its ion atmosphere must equal zero. Thus for the cation M^+ in a 1:1 electrolyte MX in solvent 1 we may write [6–8]

$$1 + \rho_MG_{MM} - \rho_XG_{MX} = 0 \quad (3.40)$$

with a similar equation for the anion X^- which implies that $G_{MM} = G_{XX}$. In addition, the solvent around the ions is correlated such that the total solvent correlated around a central ion is due to the solvent around the ion plus the solvent correlated with both the cations and anions that are around the central ion. Hall[6] has treated this problem by arguing that the solvent correlations are much shorter range than the ion–ion interactions. Thus he defines, in dilute solution, a slightly different KB integral

$$G^*_{M1} = 4\pi r^2\int_0^R[g_{M1}(r) - 1]\mathrm{d}r \quad (3.41)$$

where R is chosen to be sufficiently large to include all ion–solvent interactions but sufficiently small to exclude ion–ion interactions. Thus we write for G_{M1}

$$G_{M1} = G^*_{M1} + \rho_MG_{MM}G^*_{M1} + \rho_XG_{MX}G^*_{X1} \quad (3.42)$$

with a similar equation for anion–solvent interactions. If these equations are combined with equation 3.40, we can show that G_{M1} equals G_{X1} which is the normal way of expressing this other electroneutrality condition. Many of the salt properties of interest refer to infinite dilution and it is of interest to consider the behaviour of the various KB parameters in this domain by using the Poisson–Boltzmann radial distribution which occurs in Debye–Huckel theory for the ion–ion parameters. It has been shown[9] that for a 1:1 electrolyte such as NaCl, G_{MM} is given by

$$G_{MM} = -0.5/\rho_M + A/[4\rho_M^{0.5}(1 + Ba\rho_M^{0.5})^2] - V_e \quad (3.43)$$

where A and B are the conventional Debye–Huckel parameters with a the distance of closest approach and V_e the excluded volume of the ions. We note in passing that the limiting behaviour would arise if a more rigorous treatment were to be used in place of the Debye–Huckel approach. We may note that G_{MM} tends to infinity as the salt concentration tends to zero, but that ρ_MG_{MM} equals -0.5 in the same limit. Note also that ρ_XG_{MX} equals $+0.5$. In order to apply Kirkwood–Buff theory to a 1:1 electrolyte, we simply replace the solute–solute term with G_{MM} and the solute–solvent term with G_{M1}. As we shall see below, this procedure, whilst not proved rigorously, guarantees that the derived equations have the correct form, *i.e.* they exhibit ion additivity where required, give the correct limiting form, and the correct Debye–Huckel limiting behaviour. For higher charge type electrolytes, related expressions are obtained.[8] More rigorous methods of treating electrolyte solutions are available but are generally formulated in terms of matrix algebra.[10]

4 Comparison with Experiment

4.1 Introduction

Equations 3.36—3.39 are the central results of Kirkwood–Buff theory with equation 2.11 being the corresponding equation from Hall's derivation.[6] It is very straightforward to obtain equation 3.39 from equation 2.11 by application of the Gibbs–Duhem relationship

$$\rho_1\mathrm{d}\mu_1 + \rho_2\mathrm{d}\mu_2 = 0 \quad (4.1)$$

We note that in the limit of pure 1, equation 3.36 yields

$$\kappa k_BT = 1/\rho_1 + G_{11} \quad (4.2)$$

which is the celebrated equation of Grand Canonical Ensemble which also arises directly from equations 3.11 and 3.23. We note in passing that for typical liquids, the compressibilities are very small and G_{11} is very close to minus the molar volume $(1/\rho_1)$. For a dilute gas, the value of G_{11} is simply twice the second virial coefficient.[11] Figure 5 shows the calculated values of G_{11} for a van der Waals fluid with parameters corresponding to carbon dioxide as a function of density for three temperatures. At the critical point, the compressibility and hence also G_{11} are infinite which is the origin of the maximum for the $T/T_c = 1.5$ graph. It is only at temperatures sufficiently high above the critical temperature that we see a monatonic variation with density.

Before we discuss in detail the use of Kirkwood–Buff theory to interpret the thermodynamic properties of mixtures, it is worth noting that the expression for the osmotic pressure (equation

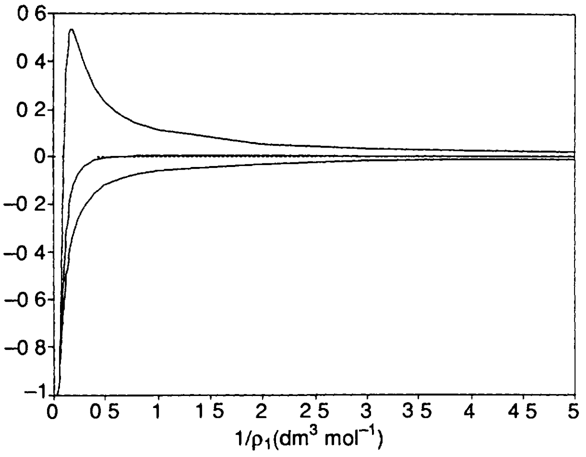

Figure 5 Variation of G_{11} with density for van der Waals' fluid corresponding to CO_2 Top curve $T/T_c = 1\ 5$, middle curve $T/T_c = 3$, bottom curve $T/T_c = 10$

3 38) involves only solute–solute interactions The theoretical ideas concerning the use of osmotic equilibrium conditions to remove solvent interactions were developed by McMillan and Mayer[12] and has led to the phrase 'McMillan–Mayer standard state' whereby the solution of interest is in osmotic equilibrium with pure solvent Their theory is in many senses a precursor to KB theory and it is probably fair to say that it has found more acceptance than KB theory in that it concentrates attention on solute–solute interactions The beauty of KB theory is that through equations such as 2 11, one can work either in the McMillan–Mayer standard state (where $d\mu_1 = 0$) or for normal (otherwise known as Lewis and Randall) standard states where μ_1 and μ_2 are connected by the Gibbs–Duhem expression thus allowing the effect of solute–solvent interactions to be included in a rigorous fashion in any treatment of solutions

4.2 Binary Solvent Mixtures

Ben-Naim[13] was the first to consider the use of equations (3 36—3 39) to obtain the values of G_{ij} (i,j = 1,2) in the binary mixture $H_2O + EtOH$ (1 + 2) Although the problem is in essence simple (we have three equations and three unknowns), there are many practical difficulties involved which relate to the requirements of highly precise data, the need to curve fit data and then differentiate them so as to obtain partial molar volumes, *etc* and then to combine the differentiated data so as to obtain the KB integrals The reader is referred to the original paper for specific details (*cf* the work of Donkersloot[14] which also includes an analysis of the $H_2O + EtOH$ system) An interesting attempt at forging a connection between the other major theme in solution theory, that of 'integral equation' approaches (see Preamble above) involves the use of the 'Percus–Yevick' closure approximation to estimate KB parameters for various model liquids [15] Donkersloot[14] has explored the connection of thermodynamically obtained KB parameters with the information obtainable from X-ray and neutron diffraction data It turns out (see also ref 7) that the KB parameters arise very naturally in expressions for the diffraction experiment in the limit of zero scattering angle Thus either the thermodynamic data can be used to calibrate the diffraction experimental data or else the diffraction data can be used to estimate thermodynamic information In a homogenous liquid, light scattering occurs due to composition fluctuations, the same fluctuations manifest in KB theory To date most light scattering data have been interpreted in terms of association equilibria, but recently efforts have been made to interpret light scattering results through KB theory [16]

Work in the area of binary solvent mixtures discussed above has been somewhat hampered by a lack of intepretation of the values of the various KB parameters In particular, there is criticism that the r^2 weighting in the KB integral (equation 1 3) implies that it can be dominated by molecules beyond the first shell of neighbours [14] If this is the case then a simple 'chemical' interpretation is likely to prove to be daunting This problem will be discussed further in the section on molar volumes of electrolyte solutions It seems likely that a value of G_{11} in a binary mixture considerably more positive than minus the molar volume of pure component 1 is evidence of strong self-association (see *e g* refs 13 and 14) Similar arguments could apply to G_{12} where (as we will see below) in the limit of pure 2, G_{12} is close to minus the molar volume of 1 What is needed are analyses of systems that are well understood Examples could be hard spheres of different sizes, very weakly interacting systems, and mixtures of single H-bond donors and acceptors where conventional analysis using classical thermodynamics and association equilibria already give unequivocal results

4.3 Free Energies of Transfer

The variation of the thermodynamic properties of a solute in dilute solution as the solvent composition is varied is of major importance throughout chemistry, impinging as it does on solvent effects on solubility, kinetics, equilibria, pH, *etc* Much of the work in this area has involved the idea of preferential solvation where, for example, the composition of solvent close to the solute in a binary solvent mixture 1 + 2 will be different from the bulk solvent composition Thus for example, if solvent component 1 is found preferentially close to the solute then we expect that the solute chemical potential will be lower in 1 than in 2 Preferential solvation can in principle be estimated spectroscopically and here is apparently a method for obtaining thermodynamic information for single ions (an idea not in accord with classical ideas about thermodynamics) Earlier work[17] used the ideas of successive equilibria of discrete solvates but the rigorous development of such ideas did require extra-thermodynamic assumptions

In order to use KB theory for this problem, we need to explore the consequences of the electroneutrality conditions discussed above (Section 3 9) on the equations of interest If we start with equation 2 11 for a ternary mixture of S + 1 + 2

$$k_B T \mathrm{d}\ln\rho_S = (1 + \rho_S G_{SS})\mathrm{d}\mu_S + \rho_1 G_{S1}\mathrm{d}\mu_1 + \rho_2 G_{S2}\mathrm{d}\mu_2 \quad (4\ 5)$$

and simply substitute the expression G_{M1} (and G_{M2}) in equation 3 42 for G_{S1} (and G_{S2}), and G_{MM} in equation 3 43 for G_{SS}, we obtain

$$kT\mathrm{d}\ln\rho_S = 0\ 5\ \mathrm{d}\mu_S + 0\ 5(G^*_{M1} + G^*_{X1})\,\mathrm{d}\mu_1 + 0\ 5(G^*_{M2} + G^*_{X2})\mathrm{d}\mu_2$$
$$+ \text{ terms in } \rho_S^{0\ 5} \text{ and higher} \quad (4\ 6)$$

This equation has the required form for extrapolation to infinite dilution for a 1 1 electrolyte

$$\begin{aligned}\operatorname*{Lim}_{\rho_S \to 0} \mathrm{d}(\mu_S - 2kT\ln\rho_S) &= \mathrm{d}\mu_S^\circ \\ &= -\ \rho_1(G^*_{M1} + G^*_{X1})\mathrm{d}\mu_1 - \rho_2(G^*_{M2} + G^*_{X2})\mathrm{d}\mu_2\end{aligned} \quad (4\ 7)$$

Equation 4 7 exhibits the required ion additivity relationship from which Hall[6] defined a single ion medium effect

$$\mathrm{d}\mu_M^\circ = \rho_1 G^*_{M1}\mathrm{d}\mu_1 - \rho_2 G^*_{M2}\mathrm{d}\mu_2 \quad (4\ 8)$$

Equations 4 7 and 4 8 have been used either in conjunction with spectroscopic data (NMR)[18] or as a simple thermodynamic analysis [19] When combined with the Gibbs–Duhem expression (4 1) equation 4 8 becomes

$$\Delta G_t^\circ \equiv \int_0^{x_1}\mathrm{d}\mu_M^\circ = \int_0^{x_1}(G^*_{M1} - G^*_{M2})\rho_1\mathrm{d}\mu_1 \quad (4\ 9)$$

where ΔG_t° is the free energy of transfer of ion M^+ from pure 2 to solvent mixture of mole fraction x_1 The solvent chemical potential μ_1 can be expanded out to give

$$\mathrm{d}\mu_1 = RT\mathrm{d}\ln a_1 = RT\mathrm{d}\ln x_1 + RT\ln\gamma_1 \quad (4\ 10)$$

where a_1, x_1, and γ_1 are respectively the activity, mole fraction, and mole fraction activity coefficient of 1 in the pure solvent mixture Providing that we have solvent mixture density data from which we can obtain an analytical expression for the mole fraction dependence of ρ_1 by curve fitting and an analytical expression for γ_1, then the only unknown on the right-hand side of equation 4 9 is $G^*_{\mathrm{M}2} - G^*_{\mathrm{M}1}$ Two possibilities have been explored First, we can try to estimate $G^*_{\mathrm{M}2} - G^*_{\mathrm{M}1}$ from spectroscopic data for the cation so as to allow integration of equation 4 9 We can do similarly for the anion and then addition of these two free energies of transfer would allow comparison with thermodynamically derived data [18] The other option is not to separate the cation and anion terms in equation 4 7 but to develop a corresponding equation in differential form with respect to x_1, and numerically to differentiate the experimental thermodynamic data so as to extract the term $(G^*_{\mathrm{M}2} - G^*_{\mathrm{M}1} + G^*_{\mathrm{X}2} - G^*_{\mathrm{X}1})$ directly [19]

4.4 Partial Molar volumes

The limiting partial molar volumes of a non-electrolyte solute at zero concentration is readily obtained from equation 3 37 (noting a change of nomenclature to a mixture of solute S in solvent 1)

$$\lim_{\rho_\mathrm{S} \to 0}(\bar{v}_\mathrm{S}) = 1/n_1 + G_{11} - G_{\mathrm{S}1} \qquad (4\ 11)$$

Note that the first two terms on the right-hand side of this equation equal $\kappa k_\mathrm{B}T$ If we refer to equation 2 8 and use the explicit pressure derivative we immediately obtain

$$\bar{v}^\circ_\mathrm{S} = \lim_{\rho_\mathrm{S} \to 0}(-G_{\mathrm{S}1}) \qquad (4\ 12)$$

The reason for the difference between equations 4 11 and 4 12 is in the pressure derivative of the $\ln\rho_\mathrm{S}$ term in equation 2 8, which simply equals minus the compressibility Virtually all experimental measurements of volumes refer to equation 4 11 As mentioned above, the compressibilities of liquids are small far from the critical point, and the difference between the two equations is then small

Using the approach outlined above for free energies, it has been shown[19] that the corresponding equation for the partial molar volume of an ion M^+ in solvent 1 is given by

$$\lim_{\rho_\mathrm{M} \to 0}(\bar{v}_\mathrm{M}) = -G^*_{\mathrm{M}1} + \kappa k_\mathrm{B}T \qquad (4\ 13)$$

which provides an unambiguous definition of single ion molar volumes Ion–solvent radial distribution functions have been obtained for a variety of ions in water by X-ray and neutron diffraction The results are generally interpreted in terms of a given number of water molecules N in a primary solvation shell If the total radius of ion plus solvation shell equals r and the total contribution of solvent beyond the first shell is negligible then it is clear that [8]

$$G^*_{\mathrm{M}1} = N/\rho_1 - (4\pi/3)r^3 \qquad (4\ 14)$$

Using experimental values for the molar volumes of ions in water and knowing N, it is possible to calculate r for the above assumption It is found that for most cations, the value of R is close to 1 Å larger than the position of the first maximum in the radial distribution function (as it should be), which is strong evidence that (at least for ion–solvent interactions) long-range contributions to the KB parameters are negligible [8]

From equation 2 8 it is also apparent that the partial molar volume of the salt MX in a binary solvent mixture 1 + 2 equals

$$\lim_{\rho_\mathrm{M} \to 0}(\bar{v}_\mathrm{MX}) = -G^*_{\mathrm{M}1}\rho_1\bar{v}_1 - G^*_{\mathrm{M}2}\rho_2\bar{v}_2 - G^*_{\mathrm{M}1}\rho_1 v_1 - G^*_{\mathrm{M}2}\rho_2\bar{v}_2 + 2\kappa k_\mathrm{B}T \qquad (4\ 15)$$

Providing partial molar volume data are available for the pure solvent mixture (or can be calculated from density data) as are compressibilities, then, in conjunction with free energy of transfer data (see Section 4 3 above), it is possible to extract $(G^*_{\mathrm{M}1} + G^*_{\mathrm{X}1})$ and $(G^*_{\mathrm{M}2} + G^*_{\mathrm{X}2})$ separately Figure 6 shows such a separation for the salt NaCl in $\mathrm{H_2O}$ + MeOH [19]

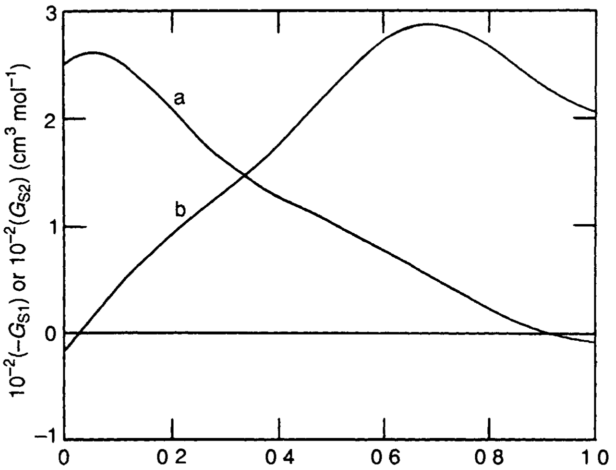

Figure 6 Variation of $G^*_{\mathrm{M}1} + G^*_{\mathrm{X}1} = G_{\mathrm{S}1}$ (curve a) and $G^*_{\mathrm{M}2} + G^*_{\mathrm{X}2} = G_{\mathrm{S}2}$ (curve b, *note change of sign*) with mole fraction for solutions of NaCl (MX) at infinite dilution in methanol (1) + water (2) mixtures

The effect of change of solvent composition on the rate of a chemical reaction has frequently been discussed in terms of free energies of transfer of reactants and transition state from one solvent mixture to another

$$\begin{tikzcd}
\mathrm{A} \arrow[d, "\Delta G^\circ_\mathrm{t}"] & + & \mathrm{B} \arrow[d, "\Delta G^\circ_\mathrm{t}"] \arrow[r, "\text{in solvent 1}"] & \mathrm{C}^\ddagger \arrow[d, "\Delta G^\circ_\mathrm{t}"] \\
\mathrm{A} & + & \mathrm{B} \arrow[r, "\text{in solvent 1 + 2}"] & \mathrm{C}^\ddagger
\end{tikzcd} \qquad (4\ 16)$$

The free energy of activation in solvent mixture 1 + 2 $[\Delta G^\ddagger_\mathrm{t}(1 + 2)]$ is thus given by

$$\Delta G^\ddagger(1 + 2) - \Delta G^\ddagger(1) = \Delta G^\circ_\mathrm{t}(\mathrm{C}^\ddagger) - \Delta G^\circ_\mathrm{t}(\mathrm{A}) - \Delta G^\circ_\mathrm{t}(\mathrm{B}) \qquad (4\ 17)$$

with a similar equation for volumes From a temperature-dependent kinetic study one can obtain the free energies of activation ($\Delta G^\ddagger$) and from a pressure dependence study the corresponding volumes of activation can be obtained Using an analysis similar to the one above, it is possible to estimate the Kirkwood–Buff parameters $(G_{\mathrm{C}1} - G_{\mathrm{A}1} - G_{\mathrm{B}1})$ and $(G_{\mathrm{C}2} - G_{\mathrm{A}2} - G_{\mathrm{B}2})$ The use of these ideas to obtain important insight into the nature of the transition state and its solvation has recently been explored by Blandamer and co-workers [20] We note in passing that if the free energies of transfer of reactants could be measured directly, by *e g* solubilities or electrode measurements, then the KB parameters corresponding to the transition state could be obtained directly

4.5 Salt Activity Coefficients

As was mentioned above, the Poisson–Boltzmann radial distribution which arises in Debye–Huckel theory is a useful starting point for the application of Kirkwood–Buff theory to electrolytes [9] If equation 3 43 is substituted into equation 3 39 as discussed above, we obtain after some simplification

$$\frac{1}{k_\mathrm{B}T}\left(\frac{\partial\mu_\mathrm{MX}}{\partial\rho_\mathrm{MX}}\right)_{T\,P} = \frac{2}{\rho_\mathrm{M}} + \frac{4(G_{\mathrm{M}1} - G'_\mathrm{MM} + V_\mathrm{e})}{1 + 2\rho_\mathrm{M}(G'_\mathrm{MM} - V_\mathrm{e} - G_{\mathrm{M}1})} \qquad (4\ 18)$$

where

$$G'_{\mathrm{MM}} = A/[4\rho_{\mathrm{M}}^{0\ 5}(1 + Ba\rho_{\mathrm{M}}^{0\ 5})^2 \qquad (4\ 19)$$

If we convert equation 4 18 to activity coefficients we immediately obtain

$$\left(\frac{\partial \ln \gamma_{\pm}}{\partial \rho_{\mathrm{MX}}}\right)_{T\,P} = \frac{2(C - G'_{\mathrm{MM}})}{1 + 2\rho_{\mathrm{M}}(G'_{\mathrm{MM}} - C)} \qquad (4\ 20)$$

with $C = G_{\mathrm{M1}} + V_{\mathrm{e}}$ In the interests of simplicity we have not substituted the corresponding equation for G_{M1} but treat C as a fitting parameter Figure 7 shows the best fit for activity coefficients of KCl up to saturation with two unknowns, a, the distance of closest approach and C [9] The value of A, the Debye-Huckel slope, is fixed at its normal value

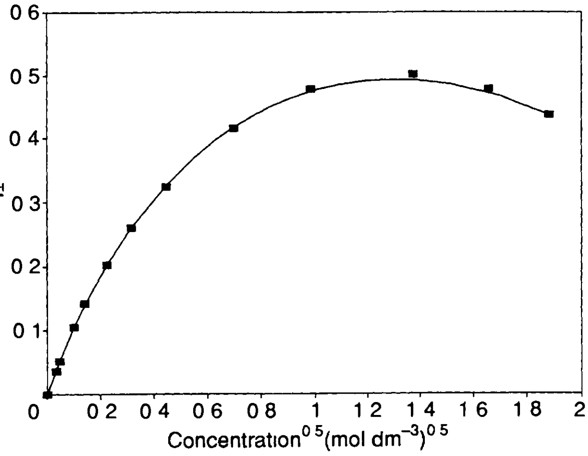

Figure 7 Observed (□) molar standard-state mean ionic activity coefficients for KCl in water and best fit to equation (4 20) with a = 2 95 Å and C = 2 95 cm^3 mol^{-1} (——)

4.6 Separation of KB Parameters for Electrolyte Solutions

As with binary solvent mixtures (Section 4 2 above), all that is required to separate the three KB parameters for electrolyte solutions is three sets of thermodynamic data, most likely molar standard-state activity coefficients, density data so as to obtain partial molar volume, and compressibilities We may note from equation 3 43 that for a 1 1 electrolyte, the term for G_{MM} always contains the term $- 0\ 5/\rho_{\mathrm{M}}$ and that once the expression has been inserted into equation 3 39 this term disappears from the expression for activity coefficients (equation 4 18) If we thus curve fit molar standard-state activity coefficients we obtain $(C - G'_{\mathrm{MM}})$ which equals $G_{\mathrm{M1}} - G_{\mathrm{MM}} + 0\ 5/\rho_{\mathrm{M}}$ This term may be expressed in terms of a power series We may rewrite equation for partial molar volumes (3 37)

$$\bar{v}_{\mathrm{M}} = \frac{1 + \rho_1(G_{11} - G_{\mathrm{MM}})}{\rho_{\mathrm{M}} + \rho_1 + \rho_{\mathrm{M}}\rho_1[G_{\mathrm{MM}} - G_{11} + 2(G_{11} - G_{\mathrm{M1}})]} \qquad (4\ 19)$$

We thus substitute from the activity coefficient the expression for $G_{\mathrm{M1}} - G_{11}$ into equation 4 19 which allows us to obtain $(G_{11} - G_{\mathrm{MM}})$ It is then straightforward but somewhat tedious to substitute $(G_{\mathrm{M1}} - G_{11})$ and $(G_{\mathrm{M1}} - G_{\mathrm{MM}})$ into the compressibility equation 3 36 to obtain an expression for G_{M1}, and thence G_{MM} and G_{11} (See ref 8 for details) In Figure 8 we show unpublished data for the separation of the three KB parameters for aqueous NaCl up to saturation

5 Postlude

In this pedagogic review of the development and applications of KB theory, no attempt has been made to be all encompassing with the literature Rather we give a somewhat biased and personal view of some of the more interesting and hopefully fruitful avenues for the understanding of liquid mixtures There is one theoretical area that we have not touched upon, namely that of direct correlation functions These functions, closely related as they are to radial distribution functions, are of central importance in a whole variety of liquid state and solution theories The only reason for not dealing with them in the meat of the text here is in the interests of brevity Direct correlation functions were introduced by Ornstein and Zernike in 1914 [21] They argued that for a pure liquid, the total correlation $[g(r) - 1]$ of molecule 1 on molecule 2 should be equal to a direct correlation $c(r)$ of molecule 1 on molecule 2 plus an indirect correlation of molecule 1 on all of the other molecules which were themselves correlated with 2 This problem can be treated in terms of a convolution integral [22]

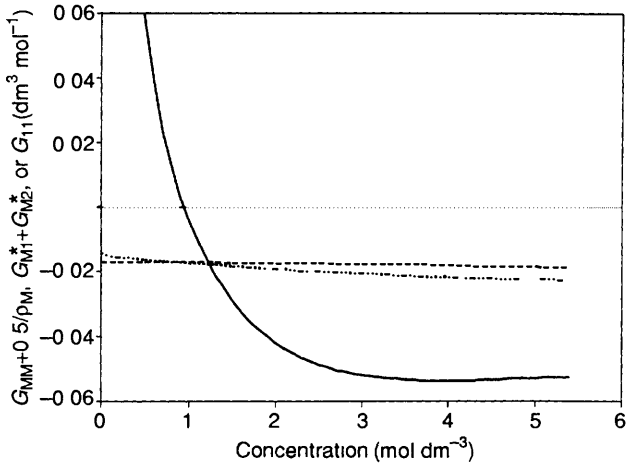

Figure 8 Variation of the Kirkwood–Buff Parameters for NaCl in water as a function of concentration $G_{\mathrm{MM}} + 0\ 5/\rho_{\mathrm{M}}$ (——), G_{11} (------), $G^*_{\mathrm{M1}} + G^*_{\mathrm{X1}}$ (– – – – – –)

$$g(r) - 1 = c(r) + \rho c(r)^*[g(r) - 1] \qquad (5\ 1)$$

where * implies a convolution integral Such functions can be manipulated by Fourier Transform techniques and it can be shown that

$$G_{11} = C_{11} + \rho C_{11} G_{11} \qquad (5\ 2)$$

where $$C_{11} = \int 4\pi r^2 c(r) \mathrm{d}r \qquad (5\ 3)$$

The application of Kirkwood–Buff-type theories which use the integrals C_{ij} may be found in some of the other articles in the multi-author reference 8

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