On the Kirkwood–Buff inversion procedure

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A general approach is presented to express the Kirkwood–Buff integrals, the central component of the Kirkwood–Buff theory of solutions, in terms of thermodynamic properties of solution mixtures. A general expression valid for any number of components is provided in terms of matrix cofactors, while explicit expressions are given for three and four component mixtures. The corresponding symmetric ideal solution values are also presented for four and higher component mixtures.

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INTRODUCTION

Kirkwood–Buff (KB) theory is an exact theory of solution mixtures containing any number of components of any kind.¹ The theory relates properties of a solution mixture to the relative intermolecular distributions between the various species present. The KB integrals have provided a physical picture of the local solution composition around each species in both open and closed systems.² While it does not provide information concerning the distance over which the local composition around a molecule differs significantly from the bulk composition, it has proved a solid framework for the interpretation of molecular distributions.^{2–4} Consequently, KB theory has been used to understand a variety of solution behaviors.^{2–5}

The central focus of KB theory is the KB integrals (G_{ij}) between the different species i and j in a solution mixture,¹

$$G_{ij} = G_{ji} = 4\pi \int_0^\infty [g_{ij}^{\mu VT}(r) - 1] r^2 dr, \quad (1)$$

where g_{ij} is the corresponding radial distribution function (RDF) and r is the intermolecular separation. The above RDFs are defined in the grand canonical (μVT) ensemble open to all species. Various combinations of the KB integrals provide expressions for chemical potential derivatives, partial molar volumes ($\bar{V}$), and the isothermal compressibility (κ_T) of a stable solution mixture as a function of composition at constant T and P .³ Alternatively, if the compressibility, partial molar volumes (PMVs), and a set of appropriate chemical potential derivatives are known as a function of composition, then the corresponding experimental KB integrals can be determined.⁶ The latter is known as the KB inversion procedure.

For a general n component system there are $n(n+1)/2$ unique G_{ij} integrals. To determine the integrals from the experimental data using the KB inversion approach requires 1 compressibility, $n-1$ independent PMVs, and therefore $n(n-1)/2$ independent chemical potential derivatives (μ_{ij}) as

a function of composition. The required chemical potential derivatives at constant T and P can be denoted by

$$\mu_{ij} = \beta \left(\frac{\partial \mu_i}{\partial \ln N_j} \right)_{T, P, N_{k \neq j}}. \quad (2)$$

We note that this is a slightly different definition than used previously. Inversion has been achieved for binary systems and expressions for the KB integrals in terms of experimental properties of the solution is available.⁶ A general expression for the KB integrals has appeared somewhat indirectly in the form of matrix cofactors.⁷ However, evaluating the previous matrix cofactors and determinants is rather cumbersome as the matrix elements themselves involve multiple terms. While this is satisfactory for practical applications, general expressions for the KB integrals in terms of the experimental data would certainly be useful. In particular, this will allow the determination of the KB integrals for symmetric ideal (SI) solutions, which is a useful reference state for the analysis of complicated multicomponent systems.² Here, a simpler general approach to the KB inversion process is developed.

THEORY

If we consider the species number densities ($\rho_i = n_i/V$) in the grand canonical ensemble to be functions of temperature (T) and all the chemical potentials (μ), then we can write

$$d \ln \rho_i = \sum_{j=1}^n \left(\frac{\partial \ln \rho_i}{\partial \mu_j} \right)_{T, \mu_{k \neq j}} d\mu_j \quad (3)$$

for any component i at constant T . Here, the summation is over the n components of the solution. We note that all the chemical potentials are independent thermodynamic variables in this open ensemble. The above derivatives can be expressed in terms of KB integrals using the fact that,

$$\left(\frac{\partial \ln \rho_i}{\partial \mu_j} \right)_{T, \mu_{k \neq j}} = \beta (\delta_{ij} + N_{ij}), \quad (4)$$

which is essentially the starting equation for KB theory.² Here, δ_{ij} is the Kronecker delta function, $N_{ij} = \rho_j G_{ij} \neq N_{ji}$, and $\beta = 1/RT$ with R as the gas constant. The physical interpretation of N_{ij} 's is the change in the average number of j

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molecules in a local spherical volume caused by placing an i molecule at the center of the sphere.⁸ From the two above equations, one finds

$$d \ln \rho_i = \beta \sum_{j=1}^n (\delta_{ij} + N_{ij}) d\mu_j, \quad (5)$$

which is valid for changes in the number density of any component in any multicomponent system and any (thermodynamically reasonable) ensemble with T constant.

Two further sets of equations can be derived from the above equation. If we take derivatives with respect to $\ln N_k$ while keeping T , P , and all other $N_{j \neq k}$ constant, we find that

$$\delta_{ik} - \rho_k \bar{V}_k = \sum_{j=1}^n (\delta_{ij} + N_{ij}) \mu_{jk} \quad (6)$$

for any i species. We note that by taking derivatives with P constant we have avoided the usual transformation from constant volume to constant pressure which, in the traditional derivation of KB theory, becomes tedious as the number of components increases. Alternatively, if one starts from Eq. (5) and then takes derivatives with respect to pressure with all N_j and T constant, one can show that for any component i

$$RT\kappa_T = \sum_{j=1}^n (\delta_{ij} + N_{ij}) \bar{V}_j, \quad (7)$$

where κ_T is the isothermal compressibility.

These equations can be used to relate the KB integrals to properties of the solution. It is easier, albeit less general, if we chose a particular species to continue. We chose $i=1$ and $k \neq 1$, and then write Eqs. (6) and (7) in an $n \times n$ matrix form so that

$$\begin{bmatrix} \mu_{12} & \mu_{22} & \mu_{32} & \cdots & \mu_{n2} \\ \mu_{13} & \mu_{23} & & & \mu_{n3} \\ \mu_{14} & & \mu_{34} & & \mu_{n4} \\ \vdots & & & \ddots & \vdots \\ \bar{V}_1 & \bar{V}_2 & \bar{V}_3 & \cdots & \bar{V}_n \end{bmatrix} \begin{bmatrix} 1 + N_{11} \\ N_{12} \\ N_{13} \\ \vdots \\ N_{1n} \end{bmatrix} = \begin{bmatrix} -\phi_2 \\ -\phi_3 \\ \vdots \\ -\phi_n \\ RT\kappa_T \end{bmatrix}, \quad (8)$$

where $\phi_i = \rho_i \bar{V}_i$ is the volume fraction. Hence, we have a set of simultaneous equations that can be solved quite easily for the required KB integrals to give,

$$\begin{bmatrix} 1 + N_{11} \\ N_{12} \\ N_{13} \\ \vdots \\ N_{1n} \end{bmatrix} = M_n^{-1} \begin{bmatrix} -\phi_2 \\ -\phi_3 \\ \vdots \\ -\phi_n \\ RT\kappa_T \end{bmatrix}, \quad (9)$$

where M_n is the matrix from Eq. (8). The general solution for the above set of equations can be expressed as

$$\delta_{1i} + N_{1i} = \frac{1}{|M_n|} \left[M^{n,1} RT\kappa_T - \sum_{j=1}^{n-1} M^{j,i} \phi_{j+1} \right], \quad (10)$$

where the $M^{\alpha,\beta}$ are cofactors of the original M_n matrix.

Before leaving this section we also note that the same matrix (M_n) can be used to represent a different set of equations. The Gibbs–Duhem relationships at constant T and P , and the usual relationship between the PMVs, can be written using the above matrix,

$$M_n \begin{bmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \\ \vdots \\ \rho_n \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix}. \quad (11)$$

Solutions to the above set of equations provide alternative expressions for the determinant of M_n . Therefore,

$$\rho_i = \frac{M^{n,i}}{|M_n|}. \quad (12)$$

Consequently, a combination of Eqs. (10) and (12) provide our final expression,

$$\delta_{1i} + N_{1i} = \rho_i RT\kappa_T - \frac{\rho_i}{M^{n,i}} \sum_{j=1}^{n-1} M^{j,i} \phi_{j+1}, \quad (13)$$

which applies to a solution containing any number of components. Expressions involving N_{22} , N_{23} , etc., can be obtained via simple index changes after the cofactors have been evaluated. We note that only cofactors (and no determinants) appear in the above expression, and that each element of the M_n matrix involves only a single thermodynamic variable.

RESULTS

Four component systems

As an example of the current approach we will generate expressions for the KB integrals in a four component system. To do this, we only require expressions for N_{11} and N_{12} as N_{22} , N_{33} , N_{13} , and N_{14} , etc., expressions can be obtained from N_{11} and N_{12} expressions via appropriate index changes. Expressions for N_{11} and N_{12} require eight cofactors of the 4×4 M_4 matrix. After some minor rearrangement the required cofactors are given by

$$\begin{aligned} M^{1,1} &= (\mu_{33}\mu_{44} - \mu_{43}\mu_{34})\bar{V}_2 + (\mu_{43}\mu_{24} - \mu_{23}\mu_{44})\bar{V}_3 \\ &\quad + (\mu_{23}\mu_{34} - \mu_{24}\mu_{33})\bar{V}_4, \\ M^{2,1} &= (\mu_{42}\mu_{34} - \mu_{32}\mu_{44})\bar{V}_2 + (\mu_{22}\mu_{44} - \mu_{42}\mu_{24})\bar{V}_3 \\ &\quad + (\mu_{32}\mu_{24} - \mu_{34}\mu_{22})\bar{V}_4, \\ M^{3,1} &= (\mu_{32}\mu_{43} - \mu_{42}\mu_{33})\bar{V}_2 + (\mu_{42}\mu_{23} - \mu_{43}\mu_{22})\bar{V}_3 \\ &\quad + (\mu_{22}\mu_{33} - \mu_{32}\mu_{23})\bar{V}_4, \\ M^{4,1} &= -\mu_{22}(\mu_{33}\mu_{44} - \mu_{43}\mu_{34}) - \mu_{32}(\mu_{43}\mu_{24} - \mu_{23}\mu_{44}) \\ &\quad - \mu_{42}(\mu_{23}\mu_{34} - \mu_{24}\mu_{33}), \\ M^{1,2} &= (\mu_{43}\mu_{34} - \mu_{33}\mu_{44})\bar{V}_1 + (\mu_{13}\mu_{44} - \mu_{43}\mu_{14})\bar{V}_3 \\ &\quad + (\mu_{14}\mu_{33} - \mu_{13}\mu_{34})\bar{V}_4, \end{aligned}$$

$$\begin{aligned}
M^{2,2} &= (\mu_{32}\mu_{44} - \mu_{42}\mu_{34})\bar{V}_1 + (\mu_{42}\mu_{14} - \mu_{12}\mu_{44})\bar{V}_3 \\
&\quad + (\mu_{12}\mu_{34} - \mu_{32}\mu_{14})\bar{V}_4, \\
M^{3,2} &= (\mu_{42}\mu_{33} - \mu_{32}\mu_{43})\bar{V}_1 + (\mu_{12}\mu_{43} - \mu_{42}\mu_{13})\bar{V}_3 \\
&\quad + (\mu_{32}\mu_{13} - \mu_{12}\mu_{33})\bar{V}_4, \\
M^{4,2} &= \mu_{12}(\mu_{33}\mu_{44} - \mu_{43}\mu_{34}) + \mu_{32}(\mu_{43}\mu_{14} - \mu_{13}\mu_{44}) \\
&\quad + \mu_{42}(\mu_{13}\mu_{34} - \mu_{14}\mu_{33}), \quad (14)
\end{aligned}$$

which provide

$$\begin{aligned}
1 + N_{11} &= \rho_1 RT \kappa_T - \frac{\rho_1}{M^{4,1}} [M^{1,1}\phi_2 + M^{2,1}\phi_3 + M^{3,1}\phi_4], \\
N_{12} &= \rho_2 RT \kappa_T - \frac{\rho_2}{M^{4,2}} [M^{1,2}\phi_2 + M^{2,2}\phi_3 + M^{3,2}\phi_4]. \quad (15)
\end{aligned}$$

This is sufficient to calculate the required KB integrals and/or relate them directly to combinations of the solution properties. The expression for N_{11} can be simplified by noting that

$$\begin{aligned}
M^{1,1}\phi_2 + M^{2,1}\phi_3 + M^{3,1}\phi_4 \\
= (\mu_{33}\mu_{44} - \mu_{43}\mu_{34})\bar{V}_2\phi_2 + (\mu_{22}\mu_{44} - \mu_{42}\mu_{24})\bar{V}_3\phi_3 \\
+ (\mu_{22}\mu_{33} - \mu_{32}\mu_{23})\bar{V}_4\phi_4 + 2(\mu_{23}\mu_{43} - \mu_{24}\mu_{33})\bar{V}_4\phi_2 \\
+ 2(\mu_{42}\mu_{34} - \mu_{32}\mu_{44})\bar{V}_2\phi_3 + 2(\mu_{42}\mu_{23} - \mu_{43}\mu_{22})\bar{V}_3\phi_4, \quad (16)
\end{aligned}$$

where we have used the fact that $N_i\mu_{ij} = N_j\mu_{ji}$ during the process. We attempted to simplify the corresponding expression appearing in the equation for N_{12} but without success.

To develop expressions for the KB integrals in SI solutions, we note that under these conditions $\mu_{ij} = \delta_{ij} - x_j$ for all components. The results in Eqs. (14) and (15) then reduce to

$$\begin{aligned}
1 + N_{11}^{\text{SI}} &= \rho_1 RT \kappa_T + (\rho_1 + \rho_2)\bar{V}_2\phi_2 + (\rho_1 + \rho_3)\bar{V}_3\phi_3 \\
&\quad + (\rho_1 + \rho_4)\bar{V}_4\phi_4 + 2\phi_2\phi_3 + 2\phi_2\phi_4 + 2\phi_3\phi_4, \\
N_{12}^{\text{SI}} &= \rho_2 RT \kappa_T + \rho_2 [\bar{V}_1(\phi_1 - 1) + \bar{V}_2(\phi_2 - 1) + \bar{V}_3\phi_3 \\
&\quad + \bar{V}_4\phi_4]. \quad (17)
\end{aligned}$$

In the above equations, all the PMVs refer to the pure liquid values at the same T and P and,

$$\kappa_T = \sum_{i=1}^n \phi_i \kappa_{T,i}, \quad \rho = \sum_{i=1}^n \rho_i, \quad V = \sum_{i=1}^n N_i \bar{V}_i, \quad (18)$$

where $\kappa_{T,i}$ is the isothermal compressibility of pure i at the same T and P .

Three component systems

The corresponding expressions for three component systems can be obtained from Eq. (15) by noting that $\mu_{i4} \rightarrow \delta_{i4}$ and $\phi_4 \rightarrow 0$ as $\rho_4 \rightarrow 0$. This is facilitated by our choice of $i = 1$ and $k \neq 1$ in Eqs. (6) and (7). Therefore, the expressions for the KB integrals can be written as

$$\begin{aligned}
1 + N_{11} &= \rho_1 RT \kappa_T + \rho_1 \frac{\rho_2 \mu_{33} \bar{V}_2^2 + \rho_3 \mu_{22} \bar{V}_3^2 - 2\rho_3 \mu_{32} \bar{V}_2 \bar{V}_3}{\mu_{22}\mu_{33} - \mu_{32}\mu_{23}}, \\
N_{12} &= \rho_2 RT \kappa_T + \rho_2 \frac{(\mu_{13} \bar{V}_3 - \mu_{33} \bar{V}_1)\phi_2 + (\mu_{32} \bar{V}_1 - \mu_{12} \bar{V}_3)\phi_3}{\mu_{32}\mu_{13} - \mu_{12}\mu_{33}}. \quad (19)
\end{aligned}$$

The other KB integrals can then be obtained after a suitable change in indices.

The corresponding expressions for ternary SI solutions are provided by the limiting expressions obtained from Eq. (17) or directly from Eq. (19),

$$\begin{aligned}
1 + N_{11}^{\text{SI}} &= \rho_1 RT \kappa_T + (\rho_1 + \rho_2)\bar{V}_2\phi_2 + (\rho_1 + \rho_3)\bar{V}_3\phi_3 + 2\phi_2\phi_3, \\
N_{12}^{\text{SI}} &= \rho_2 RT \kappa_T + \rho_2 [\bar{V}_2(\phi_2 - 1) + \bar{V}_1(\phi_1 - 1) + \bar{V}_3\phi_3], \quad (20)
\end{aligned}$$

which are in agreement with previous results.⁹

Two component systems

As a further check of the above expressions one can take the additional limit of $\rho_3 \rightarrow 0$ to obtain the results for a binary system. Consequently, one finds,

$$\begin{aligned}
1 + N_{11} &= \rho_1 RT \kappa_T + \rho_1 \frac{\phi_2 \bar{V}_2}{\mu_{22}} = \rho_1 RT \kappa_T + \frac{\phi_2^2}{\mu_{11}}, \\
N_{12} &= \rho_2 RT \kappa_T + \rho_2 \frac{\phi_2 \bar{V}_1}{\mu_{12}} = \rho_2 RT \kappa_T - \frac{\phi_1 \phi_2}{\mu_{22}}, \quad (21)
\end{aligned}$$

which are in agreement with previous results.² The expressions for SI binary solutions are then,

$$\begin{aligned}
1 + N_{11}^{\text{SI}} &= \rho_1 RT \kappa_T + \rho \phi_2 \bar{V}_2, \\
N_{12}^{\text{SI}} &= \rho_2 RT \kappa_T - \rho \phi_2 \bar{V}_1, \quad (22)
\end{aligned}$$

which again are in agreement with previous results.²

Implications from the stability requirements for solutions

Not all solutions are miscible over the full range of compositions. The relationship between KB theory and the conditions for solution stability has been investigated previously.^{2,10} However, as explicit expressions for N_{ij} in three and four component solutions have not appeared before, the relationships between the corresponding N_{ij} 's and thermodynamic properties of the solution remain relatively unknown. Furthermore, in practice, the inversion procedure is sensitive to the fitted thermodynamic data,¹¹ especially at the extremes of the composition ranges. It is therefore desirable to further understand these relationships in order to ensure that thermodynamically consistent N_{ij} values are obtained.

The stability requirements for a general n component solution mixture have been discussed by Prigogine and Defay.¹² They can be summarized as

$$\begin{aligned}\mu_{ii} &\geq 0, \\ \mu_{ij} &< 0\end{aligned}\quad (23)$$

for all i and j components where $i \neq j$. Alternatively, stability requires the α, α minors of the following determinant to be positive or zero,¹²

$$\begin{vmatrix} \mu_{11} & \mu_{21} & \mu_{31} & \cdots & \mu_{n1} \\ \mu_{12} & \mu_{22} & & & \mu_{n2} \\ \mu_{13} & & \mu_{33} & & \mu_{n3} \\ \vdots & & & \ddots & \vdots \\ \mu_{1n} & \mu_{2n} & \mu_{3n} & \cdots & \mu_{nn} \end{vmatrix}. \quad (24)$$

The 1,1 minor of the above determinant also appears as a minor of our M_n matrix. The stability condition applied to the 1,1 minor for quaternary systems provides

$$\begin{aligned}\mu_{22}(\mu_{33}\mu_{44} - \mu_{43}\mu_{34}) - \mu_{32}(\mu_{23}\mu_{44} - \mu_{43}\mu_{24}) \\ + \mu_{42}(\mu_{23}\mu_{34} - \mu_{33}\mu_{24}) \geq 0.\end{aligned}\quad (25)$$

Analysis of the terms in the above expression using the requirements in Eq. (23) indicates that one must also have

$$\mu_{33}\mu_{44} - \mu_{43}\mu_{34} \geq 0 \quad (26)$$

for the condition in Eq. (25) to be valid. As there is nothing unique about components 3 and 4, this must also be true for all $\mu_{ii}\mu_{jj} - \mu_{ij}\mu_{ji}$ combinations.

We now examine the expressions provided in Eq. (12). The same combination of derivatives found in the expression for the $M^{n,1}$ cofactor is provided by the 1,1 minor of the determinant in Eq. (24), which must be positive or zero. Consequently, the sign of $M^{n,1}$ is given by $(-)^{n+1}$. Equation (12) indicates that $|M_n|$ must have the same sign as $M^{n,1}$. Therefore, all the $M^{n,i}$ cofactors must have the same sign as $M^{n,1}$. Analysis of the cofactors $M^{i,1}$ ($i \neq n$) using the conditions in Eq. (23) indicates that all these cofactors are positive for a four component mixture [Eq. (14)] as long as all the corresponding PMVs are positive (by far the most common situation). Hence, we can conclude that in the vast majority of cases all the terms in the right hand side of Eq. (13) must be positive or zero when $i=1$. This is in accord with the fact that the KB integrals can also be written in terms of particle number fluctuations in the grand canonical ensemble,²

$$\delta_{ij} + N_{ij} = \frac{\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle}{\langle N_i \rangle}, \quad (27)$$

which must be positive for $i=j$. The same is true for all the possible N_{ii} expressions. The above conclusion can be readily established for ternary and binary mixtures by inspection of Eqs. (19) and (21) using the conditions provided in Eq. (23).

Application of the stability requirements to the expression for N_{12} is more complicated. If we ignore the compressibility term, which is usually small away from a critical point, then the sign of N_{12} is determined by the expression in the brackets of Eq. (15). As an example we will consider the

three component case provided in Eq. (19). The denominator must be positive. Hence, a negative value of N_{12} will be observed when

$$(\mu_{13}\bar{V}_3 - \mu_{33}\bar{V}_1)\phi_2 + \mu_{32}\bar{V}_1\phi_3 < \mu_{12}\bar{V}_3\phi_3, \quad (28)$$

which can be rewritten as

$$\mu_{31}\phi_2\phi_3 - \mu_{33}\phi_1\phi_2 + \mu_{32}\phi_1\phi_3 < \rho_2\mu_{21}\bar{V}_3\phi_3. \quad (29)$$

The above relationship is only guaranteed when $\rho_3 \rightarrow 0$, i.e., a binary mixture of 1 and 2.

Limiting expressions in three component systems

Here we investigate the limiting expressions obtained for G_{11} and G_{12} when ρ_1 and ρ_2 tend toward zero, respectively. We will focus on three component systems for simplicity. To obtain these expressions we require the Gibbs–Duhem relations,

$$\begin{aligned}\rho_1\mu_{11} + \rho_2\mu_{21} + \rho_3\mu_{31} &= 0, & \mu_{11} + \mu_{12} + \mu_{13} &= 0, \\ \rho_1\mu_{12} + \rho_2\mu_{22} + \rho_3\mu_{32} &= 0, & \mu_{21} + \mu_{22} + \mu_{23} &= 0, \\ \rho_1\mu_{13} + \rho_2\mu_{23} + \rho_3\mu_{33} &= 0, & \mu_{31} + \mu_{32} + \mu_{33} &= 0.\end{aligned}\quad (30)$$

The limiting expression for G_{11} as $\rho_1 \rightarrow 0$ is difficult to obtain directly from Eq. (19) due to the singularity appearing in the left hand side of the equation. The limit can be obtained more easily from Eq. (19) by rewriting several of the terms using the Gibbs–Duhem relationships. One finds that

$$\begin{aligned}\rho_2\mu_{33}\bar{V}_2^2 + \rho_3\mu_{22}\bar{V}_3^2 - 2\rho_3\mu_{32}\bar{V}_2\bar{V}_3 \\ = \frac{\mu_{22}(1-\phi_1)^2 + \rho_1\mu_{11}\phi_2\bar{V}_2 + 2\rho_1\mu_{12}(1-\phi_1)\bar{V}_2}{\rho_3},\end{aligned}\quad (31)$$

$$\frac{\mu_{22}\mu_{33} - \mu_{32}\mu_{23}}{\rho_1} = \frac{\mu_{22}\mu_{11} - \mu_{12}\mu_{21}}{\rho_3}.$$

In this form it is relatively easy to take the appropriate limit. Therefore, as $\rho_1 \rightarrow 0$, one obtains

$$G_{11}^\infty = RT\kappa_T - 2\bar{V}_1^\infty + \bar{V}_2 \frac{\phi_2 + 2\mu_{12}^\infty}{\mu_{22}}, \quad (32)$$

which can be used to obtain limiting expressions for any G_{ii} as $\rho_i \rightarrow 0$.

Again, the limiting expression for G_{12} cannot be obtained directly from Eq. (19). However, the numerator and denominator in Eq. (19) can be rewritten using the Gibbs–Duhem equations. We find that as $\rho_2 \rightarrow 0$,

$$\begin{aligned}\frac{(\mu_{13}\bar{V}_3 - \mu_{33}\bar{V}_1)\phi_2 + (\mu_{32}\bar{V}_1 - \mu_{12}\bar{V}_3)\phi_3}{\rho_2} \\ = \frac{-\mu_{33}\bar{V}_2^\infty + \bar{V}_3(\mu_{23}^\infty + \phi_3)}{\rho_1},\end{aligned}\quad (33)$$

$$\frac{\mu_{32}\mu_{13} - \mu_{12}\mu_{33}}{\rho_2} = \frac{\mu_{33}}{\rho_1},$$

and therefore,

$$G_{12}^{\infty} = RT\kappa_T - \overline{V}_2^{\infty} + \frac{\overline{V}_3(\mu_{23}^{\infty} + \phi_3)}{\mu_{33}}. \quad (34)$$

Again, similar limiting expressions for other ternary G_{ij} 's can be obtained by simple index changes. Equation (34) agrees with the result of Shulgin and Ruckenstein but takes a much simpler form.¹³

General expression for the KB integrals in SI solutions

The KB integrals in SI solutions are provided by Eqs. (17), (20), and (22) for four, three, and two component systems, respectively. Further analysis of these expressions allows one to develop a general expression for the KB integrals in SI solutions,

$$G_{ij}^{\text{SI}} = RT\kappa_T - \overline{V}_i - \overline{V}_j + \sum_{k=1}^n \rho_k \overline{V}_k^2, \quad (35)$$

which is valid for any i and j combination in solutions with $n=1$ to 4 components. Therefore, it is logical to assume that it applies to any n component mixture.

DISCUSSION

The approach presented here differs from that of Matteoli and Lepori in several important aspects.⁷ First, the matrix to be inverted (M_n) is far simpler in form than that used by Matteoli and Lepori and, hence, the resulting expressions are also simpler. In particular, the cofactors appearing in the final expression [Eq. (13)] are dimensionally smaller than the matrix of Matteoli and Lepori, and the corresponding matrix elements of M_n involve only a single thermodynamic variable. Second, by making specific choices for i and k in Eqs. (6) and (7) one further simplifies the resulting expressions, although one loses generality. Fortunately, this is not a serious problem as expressions for the other KB integrals can be obtained with corresponding changes in the indices.

The KB integrals have been expressed in terms of chemical potential derivatives defined by Eq. (2). In principle, one could have used activity coefficient derivatives. For symmetric solutions the corresponding derivatives are related by

$$\mu_{ij} = \left(\frac{\partial \ln f_i}{\partial \ln N_j} \right)_{T,P,N_{k \neq j}} + \delta_{ij} - x_j, \quad (36)$$

where f is the mole fraction activity coefficient. The above expression can be easily substituted into our previous equations. However, there are many systems where the symmetric solution convention is less common, biological systems and

salt solutions, for example, and the corresponding relationships between derivatives of the chemical potentials and derivatives of the activity coefficients are significantly more complicated and also system dependent. Hence, we have focused on the more general quantity, i.e., the chemical potential derivatives.

CONCLUSIONS

A general expression is provided for the KB integrals in terms of thermodynamically measurable properties of solution mixtures. Explicit expressions for the KB integrals are presented for three and four component systems together with the corresponding symmetric ideal results. Clearly, as the number of components increases to three or four the experimental data required to perform the full inversion procedure become more elusive. Matteoli and Lepori indicated quite clearly that for most solutions, well away from any critical point, the KB integrals are relatively insensitive to the compressibility and PMV values.¹¹ Hence, the symmetric ideal values for the pure solutions can be used in many cases. This leaves the chemical potential derivatives. These can be obtained from experiment^{7,14} or via a variety of other approaches.¹⁵ In either case, the expressions provided here allow for a complete description of three and four component systems in terms of the KB integrals.

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