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A DERIVATION OF THE CROSS-SQUARE RULE IN TERMS OF A COMPOSITE DESCRIPTION OF MIXED SALT SOLUTIONS

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ABSTRACT

The cross square rule for mixed salt solutions is derived using the formalism described by Guggenheim [Trans. Faraday Soc., 62 (1966) 3446] by reference to the thermodynamic properties of six composite salts formed by four reciprocal salt pairs. Contributions to excess molar Gibbs functions of these salt solutions are described in terms of pairwise interaction parameters. Conditions are enumerated under which the cross square rule is and is not obeyed.

INTRODUCTION

Within the context of the thermodynamic properties of aqueous salt solutions, a most interesting pattern centres around the cross square rule (CSR) [1,2]. Originally discovered with respect to the enthalpies of mixing [3,4], CSR was later shown to apply to Gibbs functions [5] and volumes [6] of salt solutions. Several authors have discussed the CSR using different models for mixed aqueous salt solutions. The most widely quoted explanation is offered by Reilly and Wood [7] who based their explanation on the formalism suggested by Friedman [8]. Reilly and Wood commented [7] on the stoichiometries of the salts forming the aqueous solution and on the conditions demanded if the CSR is to be obeyed. These conditions refer to the symmetry of the charges forming the four salts (see below). Another explanation of the CSR was given by Guggenheim [9] with reference to the Gibbs functions for a square formed by 1 : 1 salts. Lilley made comments [10] on the extension of the same argument to volumes and enthalpies of mixing for 1 : 1 salts. In the following section we extend the procedures described by Guggenheim [9] to salts having more complicated stoichiometries. The treatment describes mixed salt solutions as composite salts along the lines discussed previously [11].

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ANALYSIS

Composite salt

A given salt solution is prepared by mixing two solutions containing the salts (1) $\nu_m^{(1)}\mathrm{M}^{z(m)}\nu_x^{(1)}\mathrm{X}^{z(x)}$ and (2) $\nu_n^{(2)}\mathrm{N}^{z(n)}\nu_x^{(2)}\mathrm{X}^{z(x)}$. Thus salt-1 and salt-2 have common anions $\mathrm{X}^{z(x)}$ although one mole of salt-1 contains $\nu_x^{(1)}$ moles of $\mathrm{X}^{z(x)}$ and one mole of salt-2 contains $\nu_x^{(2)}$ moles of $\mathrm{X}^{z(x)}$ ions, $z(x)$ being the charge number. The molalities of the individual salt solutions are m_1^0 and m_2^0. The mixed salt solution contains 1 kg of water prepared by mixing solutions of salt-1 and salt-2 containing y kg and $(1-y)$ kg of water respectively. In these terms the final solution contains the composite salt $y \cdot \nu_M^{(1)}\mathrm{M}^{z(m)}\ (1-y) \cdot \nu_n^{(2)}\mathrm{N}^{z(n)}\ [y \cdot \nu_x^{(1)} + (1-y) \cdot \nu_x^{(2)}]\mathrm{X}^{z(x)}$, having molality $m = y \cdot m_1^0 + (1-y) \cdot m_2^0$. This solution in 1 kg of water contains $y \cdot \nu_m^{(1)} \cdot m_1^0$ moles of $\mathrm{M}^{z(m)}$, $(1-y) \cdot \nu_n^{(2)} \cdot m_2^0$ moles of $\mathrm{N}^{z(n)}$ and $\{y \cdot \nu_x^{(1)} \cdot m_1^0 + (1-y) \cdot \nu_x^{(2)} \cdot m_2^0\}$ moles of $\mathrm{X}^{z(x)}$ ions.

Ionic strength

Ionic strengths of aqueous solutions containing salt-1 and salt-2 are given in the following equations

$$I(1) = (1/2) \cdot \left[\nu_m^{(1)} \cdot m_1^0 \cdot z_m^2 + \nu_x^{(1)} \cdot m_1^0 \cdot z_x^2\right] \tag{1}$$

$$I(2) = (1/2) \cdot \left[\nu_n^{(2)} \cdot m_2^0 \cdot z_n^2 + \nu_x^{(2)} \cdot m_2^0 \cdot z_x^2\right] \tag{2}$$

Similarly the ionic strength of the composite salt solution, $I(1{,}2)$ is given by

$$I(1{,}2) = (1/2) \cdot \left[y \cdot \nu_m^{(1)} \cdot m_1^0 \cdot z_m^2 + y \cdot \nu_x^{(1)} \cdot m_1^0 \cdot z_x^2 + (1-y) \cdot \nu_n^{(2)} \cdot m_2^0 \cdot z_n^2 + (1-y) \cdot \nu_x^{(1)} \cdot m_1^0 \cdot z_x^2\right] \tag{3}$$

Then

$$I(1{,}2) = y \cdot I(1) + (1-y) \cdot I(2) \tag{4}$$

A condition which applies throughout the remainder of this paper requires that the ionic strengths of all salt solutions considered here are set at some predetermined ionic strength I^0. Consequently the molalities of salt-1 and salt-2 in their separate solutions are determined by this condition. Moreover the ionic strength of the solution containing the composite salt is fixed, i.e. $I(1) = I(2) = I(1{,}2) = I^0$. (In the event that salt-1 and salt-2 are 1 : 1 salts, then $m_1^0 = m_2^0 = m$.) Therefore the ionic strength is constant for all fractions y where $0 < y < 1.0$.

Gibbs function

We express the excess Gibbs function for a salt solution in 1 kg of water, $G^{\mathrm{E}}(\mathrm{aq};T;p)$ in terms of electrical and cosphere [12] contributions, $G^{\mathrm{E}}(\mathrm{elect})$

and $G^{\mathrm{E}}(\mathrm{cosph})$ respectively. Thus $G^{\mathrm{E}}(\mathrm{elect})$ describes the contribution arising from charge–charge interactions. $G^{\mathrm{E}}(\mathrm{elect})$ can be estimated using the Debye–Hückel Limiting Law, DHLL for both simple and mixed salt solutions. A "DHLL solution" is analogous to the "standard electrolyte" defined [9] by Guggenheim. Moreover $G^{\mathrm{E}}(\mathrm{aq;DHLL};T;p)$ $\{=G^{\mathrm{E}}(\mathrm{elect})\}$ for salt solutions is constant [13] at constant ionic strength. We assume that in real salt solutions the contribution $G^{\mathrm{E}}(\mathrm{cosph})$ to $G^{\mathrm{E}}(\mathrm{aq};T;p)$ is determined by pairwise cosphere–cosphere interactions; i.e. cation–cation, anion–anion and cation–anion. Here we extend the procedures used by Savage and Wood [13] for apolar solutes to the description of cosphere interactions between ions [14]. Thus for salt-1 in an aqueous salt solution of molality m_1^0, the cosphere interaction contribution to the excess Gibbs function at ionic strength I^0, $G^{\mathrm{E}}(\mathrm{cosph};1;I^0)$ is given by

$$G^{\mathrm{E}}(\mathrm{cosph};1;I^0) = g_{mm}\cdot\left\{\nu_m^{(1)}\cdot m_1^0\right\}^2 + 2\cdot g_{mx}\cdot\left\{\nu_m^{(1)}\cdot m_1^0\cdot\nu_x^{(1)}\cdot m_1^0\right\} + g_{xx}\cdot\left\{\nu_x^{(1)}\cdot m_1^0\right\}^2 \quad (5)$$

Here g_{mm} is the pairwise Gibbs function interaction parameter describing interactions between cospheres of $\mathrm{M}^{z(m)}$ and $\mathrm{M}^{z(m)}$ ions in aqueous solution. Similarly g_{mx} describes interactions between cospheres associated with $\mathrm{M}^{z(m)}$ and $\mathrm{X}^{z(x)}$ ions. For an aqueous solution of salt-2, $G^{\mathrm{E}}(\mathrm{cosph};2;I^0)$ is given by

$$G^{\mathrm{E}}(\mathrm{cosph};2;I^0) = g_{nn}\cdot\left\{\nu_n^{(2)}\cdot m_2^0\right\}^2 + 2\cdot g_{nx}\cdot\left\{\nu_n^{(2)}\cdot m_2^0\cdot\nu_x^{(2)}\cdot m_2^0\right\} + g_{xx}\cdot\left\{\nu_x^{(2)}\cdot m_2^0\right\}^2 \quad (6)$$

As noted above, m_1^0 and m_2^0 are defined by the stoichiometries and charge numbers, and by the condition of constant ionic strength, I^0.

Composite salt

Following the procedures which produced eqns. (4) and (5), $G^{\mathrm{E}}(\mathrm{cosph};1,2;I^0)$ for the composite salt-1,2 is given in Table 1. The equation takes account of the fact that each ion interacts with each and every other ion in solution. For clarity we set out these equations in a form resembling the lower left hand part of a matrix. The terms in the equation are regrouped in Table 2 which incorporates eqns. (5) and (6). A curve generated by a plot of $G^{\mathrm{E}}(\mathrm{cosph};1,2;I^0)$ against y (at constant I^0) is parabolic having intercepts $G^{\mathrm{E}}(\mathrm{cosph};1;I^0)$ at $y=0$ and $G^{\mathrm{E}}(\mathrm{cosph};2;I^0)$ at $y=1$. One approach at this stage defines double excess functions based on the equation in Table 2, e.g. $\Delta G^{\mathrm{E}}(\mathrm{cosph};1,2;I^0) = y\cdot(1-y)\cdot m_1^0\cdot m_2^0\cdot\{g_{mn}$

TABLE 1

$G^{\mathrm{E}}(\text{cosph};1,2;I^{0})$ for composite salt-1,2

$$\text{Salt} = y\cdot\nu_m^{(1)}\cdot \mathrm{M}^{z(m)}\,(1-y)\cdot\nu_n^{(2)}\mathrm{N}^{z(n)}\,\{y\cdot\nu_x^{(1)}+(1-y)\cdot\nu_x^{(2)}\}\mathrm{X}^{z(x)}$$

$$\begin{aligned}
&G^{\mathrm{E}}(\text{cosph};1,2;I^{0}) = \\
&\quad g_{mm}\cdot\{\nu_m^{(1)}\cdot m_1^0\cdot y\}^2 \\
&\quad +2\cdot g_{mn}\cdot\{\nu_m^{(1)}\cdot m_1^0\cdot \mathrm{y}\cdot\nu_n^{(2)}\cdot m_2^0\cdot(1-y)\}+g_{nn}\cdot\{(1-y)\cdot m_2^0\cdot\nu_n^{(2)}\}^2 \\
&\quad +2\cdot g_{mx}\cdot\{\nu_m^{(1)}\cdot m_1^0\cdot y\}\cdot\{\nu_x^{(1)}\cdot m_1^0\cdot y+(1-y)\cdot\nu_x^{(2)}\cdot m_2^0\} \\
&\qquad +2\cdot g_{nx}\cdot\{\nu_n^{(2)}\cdot m_2^0\cdot(1-y)\}\cdot\{y\cdot\nu_x^{(1)}\cdot m_1^0+(1-y)\cdot\nu_x^{(2)}\cdot m_2^0\} \\
&\qquad\quad + g_{xx}\cdot\{\nu_x^{(1)}\cdot m_1^0\cdot y+\nu_x^{(2)}\cdot m_2^0\cdot(1-y)\}^2
\end{aligned}$$

TABLE 2

$G^{\mathrm{E}}(\text{cosph};1,2;I^{0})$, $G^{\mathrm{E}}(\text{cosph};1;I^{0})$ and $G^{\mathrm{E}}(\text{cosph};2;I^{0})$

$$\begin{aligned}
&G^{\mathrm{E}}(\text{cosph};1,2;I^{0}) = \\
&\quad (y\cdot m_1^0)^2\cdot G^{\mathrm{E}}(\text{cosph};1;I^{0}) \\
&\quad + y\cdot m_1^0\cdot(1-y)\cdot m_2^0\cdot\{2\cdot g_{mn}\cdot\nu_m^{(1)}\cdot\nu_n^{(2)}+2\cdot g_{mx}\cdot\nu_m^{(1)}\cdot\nu_x^{(2)}+g_{nx}\cdot\nu_n^{(2)}\nu_x^{(1)}\} \\
&\quad +(1-y)^2\cdot(m_2^0)^2\cdot G^{\mathrm{E}}(\text{cosph};2;I^{0})
\end{aligned}$$

$\cdot\,\nu_m^{(1)}\cdot\nu_n^{(2)}+g_{mx}\cdot\nu_m^{(1)}\cdot\nu^{(2)}+g_{nx}\cdot\nu_n^{(2)}\cdot\nu_x^{(1)}$. In practice, another approach is adopted which forms the starting point for the CSR. In effect a solution of salt-1 in y kg of water is mixed with a solution of salt-2 in $(1-y)$ kg of water. Bearing in mind that $G^{\mathrm{E}}(\text{elect})$ is unchanged at constant I^0, then we assume that no interactions occur between cospheres associated with ions of salt-1 and cospheres associated with ions of salt-2. The equation in Table 3 is written in a form which emphasises this point. The corresponding contribution to $G^{\mathrm{E}}(\text{aq})$ namely $G^{\mathrm{E}}(\text{cosph};1,2;I^0;\text{id})$ is ideal. The case commonly considered is composite salts where $y = 0.5$. The equation for $G^{\mathrm{E}}(\text{cosph};1,2;I^0;\text{id})$, Table 3, can be compared with the equation given in Table 4 for $G^{\mathrm{E}}(\text{cosph};1,2;I^0)$ for a real solution at $y = 0.5$. The difference between these two Gibbs functions defines a mixing property, $\Delta_{\text{mix}}G^{\mathrm{E}}(\text{aq};1,2;I^0)$

$$\begin{aligned}
\Delta_{\text{mix}}G^{\mathrm{E}}(\text{aq};1,2;I^0) &= G\,(\text{cosph};1,2;I^0) - G^{\mathrm{E}}(\text{cosph};1,2;I^0;\text{id}) \\
&= G^{\mathrm{E}}(\text{aq};1,2;I^0) - G^{\mathrm{E}}(\text{aq};1,2;I^0;\text{id}) \qquad (7)
\end{aligned}$$

The second condition in eqn. (7) emerges because $G(\text{elect};I^0)$ is constant.

TABLE 3

Functions of mixing; ideal

$$\begin{aligned}
&G^{\mathrm{E}}(\text{cosph};1,2;I^{0};\text{id}) = \\
&\quad g_{mm}\cdot\{\nu_m^{(1)}\cdot m_1^0\}^2/2 \\
&\quad +2\cdot g_{mx}\cdot\{\nu_m^{(1)}\cdot m_1^0\}\cdot\{\nu_x^{(1)}\cdot m_1^0\}/2+g_{xx}\cdot\{\nu_x^{(1)}\cdot m_1^0\}^2/2 \\
&\quad\ + g_{nn}\cdot\{\nu_n^{(2)}\cdot m_2^0)^2/2 \\
&\quad +2\cdot g_{nx}\cdot\{\nu_n^{(2)}\cdot m_2^0\}\cdot\{\nu_x^{(2)}\cdot m_2^0)/2\ + g_{xx}\cdot\{\nu_x^{(2)}\cdot m_2^0\}^2/2
\end{aligned}$$

TABLE 4

$\Delta_{\text{mix}}G^{\text{E}}(1{,}2;I^0)$

From eqn. (7) and Tables 1 and 3

$$\begin{aligned}
\Delta_{\text{mix}}G^{\text{E}}(\text{aq};1{,}2;I^0) = \\
& g_{mm}\cdot[-(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0)^2] \\
& +2\cdot g_{mn}\cdot[(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0\cdot \nu_n^{(2)}\cdot m_2^0)]+g_{nn}\cdot[-(1/4)\cdot(\nu_n^{(2)}\cdot m_2^0)^2] \\
& +2\cdot g_{mx}\cdot[(1/4)\cdot(-\nu_m^{(1)}\cdot m_1^0\cdot \nu_x^{(1)}\cdot m_1^0+\nu_m^{(1)}\cdot m_1^0\cdot \nu_x^{(2)}\cdot m_2^0)] \\
& +2\cdot g_{nx}\cdot[(1/4)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_x^{(1)}\cdot m_1^0)-(1/4)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_x^{(2)}\cdot m_2^0)] \\
& \qquad +g_{xx}\cdot[-(1/4)\cdot\{\nu_x^{(1)}\cdot m_1^0\}^2 \\
& \qquad\qquad +(1/2)\cdot\{\nu_x^{(1)}\cdot m_1^0\cdot \nu_x^{(2)}\cdot m_2^0\}-(1/4)\cdot\{\nu_x^{(2)}\cdot m_2^0\}^2]
\end{aligned}$$

Reciprocal salt pairs

The significance of the equation in Table 4 emerges from a consideration of the systems defined in Fig. 1. Four simple salts, salt-1, salt-2, salt-3 and salt-4, are described at the corners of a square leading to the specification of six composite salts, i.e. salt-1,2, salt-2,3, salt-3,4, salt-1,4, salt-2,4 and salt-1,3. The four reciprocal salt pairs at the vertices are formed from four ions $M^{z(m)}$, $N^{z(n)}$, $U^{z(n)}$, and $X^{z(x)}$. The analysis outlined in the previous sections refers to the composite salt-1,2 formed from salt-1 and salt-2. Equations similar to those in Table 4 are obtained from salt-2,3, salt-3,4 and salt-1,4 (Tables 5–7). The sum of the mixing functions for the four composite salts identified by the square is given in Table 8.

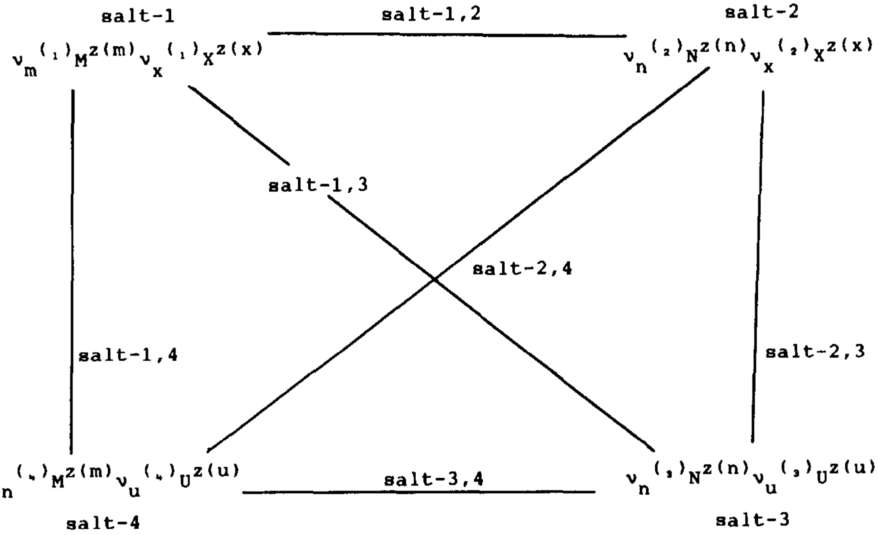

Fig. 1. Reciprocal salt pairs.

TABLE 5

Composite salt-2,3

$$\begin{aligned}
&\Delta_{\mathrm{mix}}G^{\mathrm{E}}(\mathrm{aq};2,3;I^{0}) = \\
&\quad g_{nn}\cdot[-(1/4)\cdot(\nu_n^{(2)}\cdot m_2^0)^2-(1/4)\cdot(\nu_n^{(3)}\cdot m_3^0)^2 \\
&\qquad +(1/2)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_n^{(3)}\cdot m_3^0)] \\
&\quad +2\cdot g_{nx}\cdot[-(1/4)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_x^{(2)}\cdot m_2^0)+(1/4)\cdot(\nu_n^{(3)}\cdot m_3^0\cdot \nu_x^{(2)}\cdot m_2^0) \\
&\qquad + g_{xx}\cdot\{-(1/4)\cdot(\nu_x^{(2)}\cdot m_2^0)^2] \\
&\quad +2\cdot g_{nu}\cdot[(1/4)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_u^{(3)}\cdot m_3^0)-(1/4)\cdot(\nu_n^{(3)}\cdot m_3^0\cdot \nu_u^{(3)}\cdot m_3^0)] \\
&\quad +2\cdot g_{ux}\cdot[(1/4)\cdot(\nu_x^{(2)}\cdot m_2^0\cdot \nu_u^{(3)}\cdot m_3^0)] \\
&\qquad + g_{uu}\cdot[-(1/4)\cdot(\nu_u^{(3)}\cdot m_3^0)^2]
\end{aligned}$$

TABLE 6

Composite salt-3,4

$$\begin{aligned}
&\Delta_{\mathrm{mix}}G^{\mathrm{E}}(\mathrm{aq};3,4;I^{0}) = \\
&\quad g_{nn}\cdot[-(1/4)\cdot(\nu_n^{(3)}\cdot m_3^0)^2] \\
&\quad +2\cdot g_{nu}\cdot[-(1/4)\cdot(\nu_n^{(3)}\cdot m_3^0\cdot \nu_u^{(3)}\cdot m_3^0)+(1/4)\cdot(\nu_u^{(4)}\cdot m_4^0\cdot \nu_m^{(3)}\cdot m_3^0)] \\
&\quad + g_{uu}\cdot[-(1/4)\cdot(\nu_u^{(3)}\cdot m_3^0)^2+(1/2)\cdot(\nu_u^{(3)}\cdot m_3^0\cdot \nu_u^{(4)}\cdot m_4^0) \\
&\qquad -(1/4)\cdot(\nu_u^{(4)}\cdot m_4^0)^2] \\
&\quad +2\cdot g_{nm}\cdot[(1/4)\cdot(\nu_n^{(3)}\cdot m_3^0\cdot \nu_m^{(4)}\cdot m_4^0) \\
&\quad +2\cdot g_{mu}\cdot[(1/4)\cdot(\nu_u^{(3)}\cdot m_3^0\cdot \nu_m^{(4)}\cdot m_4^0)-(1/4)\cdot(\nu_u^{(4)}\cdot m_4^0\cdot \nu_m^{(4)}\cdot m_4^0)] \\
&\qquad + g_{mm}\cdot[-(1/4)\cdot(\nu_m^{(4)}\cdot m_4^0)]^2
\end{aligned}$$

TABLE 7

Composite salt-1,4

$$\begin{aligned}
&\Delta_{\mathrm{mix}}G^{\mathrm{E}}(\mathrm{aq};1,4;I^{0}) = \\
&\quad g_{mm}\cdot[-(1/4)\cdot(\nu_m^{(4)}\cdot m_4^0)^2+(1/2)\cdot(\nu_m^{(4)}\cdot m_4^0\cdot \nu_m^{(1)}\cdot m_1^0) \\
&\qquad -(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0)^2] \\
&\quad +2\cdot g_{mu}\cdot[-(1/4)\cdot(\nu_m^{(4)}\cdot m_4^0\cdot \nu_u^{(4)}\cdot m_4^0)+(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0\cdot \nu_u^{(4)}\cdot m_4^0)] \\
&\qquad + g_{uu}\cdot[-(1/4)\cdot(\nu_m^{(4)}\cdot m_4^0)^2] \\
&\quad +2\cdot g_{mx}\cdot[(1/4)\cdot(\nu_m^{(4)}\cdot m_4^0\cdot \nu_x^{(1)}\cdot m_1^0)-(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0\cdot \nu_x^{(1)}\cdot m_1^0)] \\
&\qquad +2\cdot g_{ux}\cdot[(1/4)\cdot(\nu_u^{(4)}\cdot m_4^0\cdot \nu_x^{(1)}\cdot m_1^0)] \\
&\qquad + g_{xx}\cdot[-(1/4)\cdot(\nu_x^{(1)}\cdot m_1^0)^2]
\end{aligned}$$

Two composite salts, salt-1,3 and salt-2,4, are formed by mixtures across the diagonal of the square. As before we assume that these composite salt solutions are prepared using separate solutions each containing 0.5 kg of water. The procedures described above are used in the definitions of the mixing functions, $\Delta_{\mathrm{mix}}G^{\mathrm{E}}(\mathrm{aq};2,4;I^{0})$ and $\Delta_{\mathrm{mix}}G^{\mathrm{E}}(\mathrm{aq};1,3;I^{0})$ (Tables 9 and 10).

In a key step we obtain the cross term Σ(cross) as shown in Table 11. The final step involves calculating the difference, Σ(square) minus Σ(cross), as shown in Table 12. If the CSR is valid this difference should be zero.

TABLE 8

The square

$$
\begin{aligned}
&\Sigma(\text{square}) = \Delta_{\text{mix}}G^{\text{E}}(\text{aq};1,2;I^0) + \Delta_{\text{mix}}G^{\text{E}}(\text{aq};2,3;I^0)\\
&\qquad + \Delta_{\text{mix}}G^{\text{E}}(\text{aq};3,4;I^0) + \Delta_{\text{mix}}G^{\text{E}}(\text{aq};4,1;I^0) =\\
&g_{mm}[(1/2)\cdot(\nu_m^{(4)}\cdot m_4^0\cdot \nu_m^{(1)}\cdot m_1^0) - (1/2)\cdot(\nu_m^{(1)}\cdot m_1^0)^2\\
&\qquad - (1/2)\cdot(\nu_m^{(4)}\cdot m_4^0)^2]\\
&+2\cdot g_{mx}\cdot[(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0\cdot \nu_x^{(2)}\cdot m_2^0) + (1/4)\cdot(\nu_m^{(4)}\cdot m_4^0\cdot \nu_x^{(1)}\cdot m_1^0)\\
&\qquad - (1/2)\cdot(\nu_m^{(1)}\cdot m_1^0\cdot \nu_x^{(1)}\cdot m_1^0)]\\
&+ g_{xx}\cdot[(1/2)\cdot(\nu_x^{(1)}\cdot m_1^0\cdot \nu_x^{(2)}\cdot m_2^0) - (1/2)\cdot(\nu_m^{(1)}\cdot m_1^0)^2\\
&\qquad - (1/2)\cdot(\nu_x^{(2)}\cdot m_2^0)^2]\\
&+2\cdot g_{mn}\cdot[(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0\cdot \nu_n^{(2)}\cdot m_2^0) + (1/4)\cdot(\nu_n^{(3)}\cdot m_3^0\cdot \nu_m^{(4)}\cdot m_4^0)]\\
&+2\cdot g_{nx}\cdot[(1/4)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_x^{(1)}\cdot m_1^0) + (1/4)\cdot(\nu_n^{(3)}\cdot m_3^0\cdot \nu_x^{(2)}\cdot m_2^0)\\
&\qquad - (1/2)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_x^{(2)}\cdot m_2^0)]\\
&+ g_{nn}\cdot[(1/2)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_n^{(3)}\cdot m_3^0) - (1/2)\cdot(\nu_n^{(2)}\cdot m_2^0)^2\\
&\qquad - (1/2)\cdot(\nu_n^{(3)}\cdot m_3^0)^2]\\
&+2\cdot g_{mu}\cdot[(1/4)\cdot(\nu_u^{(3)}\cdot m_3^0\cdot \nu_m^{(4)}\cdot m_4^0) + (1/4)\cdot(\nu_m^{(1)}\cdot m_1^0\cdot \nu_u^{(4)}\cdot m_4^0)\\
&\qquad - (1/2)\cdot(\nu_u^{(4)}\cdot m_4^0\cdot \nu_m^{(4)}\cdot m_4^0)]\\
&+2\cdot g_{xu}\cdot[(1/4)\cdot(\nu_x^{(2)}\cdot m_2^0\cdot \nu_u^{(3)}\cdot m_3^0) + (1/4)\cdot(\nu_u^{(4)}\cdot m_4^0\cdot \nu_x^{(1)}\cdot m_1^0)]\\
&+2\cdot g_{nu}\cdot[(1/4)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_u^{(3)}\cdot m_3^0) + (1/4)\cdot(\nu_u^{(4)}\cdot m_4^0\cdot \nu_n^{(3)}\cdot m_3^0)\\
&\qquad - (1/2)\cdot(\nu_n^{(3)}\cdot m_3^0\cdot \nu_u^{(3)}\cdot m_3^0)]\\
&+ g_{uu}\cdot[(1/2)\cdot(\nu_u^{(3)}\cdot m_3^0\cdot \nu_u^{(4)}\cdot m_4^0) - (1/2)\cdot(\nu_u^{(3)}\cdot m_3^0)^2\\
&\qquad - (1/2)\cdot(\nu_u^{(4)}\cdot m_4^0)^2]
\end{aligned}
$$

TABLE 9

Composite salt-1,3

$$
\begin{aligned}
&\Delta_{\text{mix}}G^{\text{E}}(\text{aq};1,3;I^0) =\\
&\qquad g_{mm}[(-(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0)^2]\\
&\quad +2\cdot g_{mx}\cdot[-(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0\cdot \nu_x^{(1)}\cdot m_1^0)] + g_{xx}\cdot[-(1/4)\cdot(\nu_x^{(1)}\cdot m_1^0)^2]\\
&\quad +2\cdot g_{mn}\cdot[(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0\cdot \nu_n^{(3)}\cdot m_3^0)]\\
&\qquad +2\cdot g_{xn}\cdot[(1/4)\cdot(\nu_x^{(1)}\cdot m_1^0\cdot \nu_n^{(3)}\cdot m_3^0)] + g_{nn}\cdot[-(1/4)\cdot(\nu_n^{(3)}\cdot m_3^0)^2]\\
&\quad +2\cdot g_{mu}\cdot[(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0\cdot \nu_u^{(3)}\cdot m_3^0]\\
&\quad +2\cdot g_{xu}\cdot[(1/4)\cdot(\nu_x^{(1)}\cdot m_1^0\cdot \nu_u^{(3)}\cdot m_3^0)]\\
&\quad +2\cdot g_{nu}\cdot[-(1/4)\cdot(\nu_n^{(3)}\cdot m_3^0\cdot \nu_u^{(3)}\cdot m_3^0)] + g_{uu}\cdot[-(1/4)\cdot(\nu_u^{(3)}\cdot m_3^0)^2]
\end{aligned}
$$

TABLE 10

Composite salt-2,4

$$
\begin{aligned}
&\Delta_{\text{mix}}G^{\text{E}}(\text{aq};2,4;I^0) =\\
&\qquad \gamma_{nn}\cdot[(-1/4)\cdot(\nu_n^{(2)}\cdot m_2^0)^2]\\
&+2\cdot g_{nx}\cdot[-(1/4)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_x^{(2)}\cdot m_2^0)] + g_{xx}\cdot[(-1/4)\cdot(\nu_x^{(2)}\cdot m_2^0)^2]\\
&+2\cdot g_{nm}\cdot[(1/4)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_m^{(4)}\cdot m_4^0)]\\
&\qquad\qquad +2\cdot g_{mx}\cdot[(1/4)\cdot(\nu_m^{(4)}\cdot m_4^0\cdot \nu_x^{(2)}\cdot m_2^0)]\\
&\qquad\qquad\quad + g_{mm}\cdot[-(1/4)\cdot(\nu_m^{(4)}\cdot m_4^0)^2]\\
&+2\cdot g_{nu}\cdot[(1/4)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_u^{(4)}\cdot m_4^0)]\\
&\qquad\qquad +2\cdot g_{mu}\cdot[-(1/4)\cdot(\nu_m^{(4)}\cdot m_4^0\cdot \nu_u^{(4)}\cdot m_4^0)]\\
&\qquad\qquad\quad +2\cdot g_{xu}\cdot[(1/4)\cdot(\nu_x^{(2)}\cdot m_2^0\cdot \nu_u^{(4)}\cdot m_4^0)]\\
&\qquad\qquad\qquad + g_{uu}\cdot[-(1/4)\cdot(\nu_u^{(4)}\cdot m_4^0)^2]
\end{aligned}
$$

TABLE 11

The cross

$$\begin{aligned}
&\Sigma(\text{cross}) = \Delta_{\text{mix}}G^{\text{E}}(\text{aq};1,3;I^0) + \Delta_{\text{mix}}G^{\text{E}}(\text{aq};2,4;I^0) = \\
&\quad g_{mn}\cdot[-(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0)^2 - (1/4)\cdot(\nu_m^{(4)}\cdot m_4^0)^2] \\
&+2\cdot g_{mx}\cdot[-(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0\cdot \nu_x^{(1)}\cdot m_1^0) + (1/4)\cdot(\nu_m^{(4)}\cdot m_4^0\cdot \nu_x^{(2)}\cdot m_2^0)] \\
&\quad + g_{xx}\cdot[-(1/4)\cdot(\nu_x^{(1)}\cdot m_1^0)^2 - (1/4)\cdot(\nu_x^{(2)}\cdot m_2^0)^2] \\
&+2\cdot g_{mn}\cdot[(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0\cdot \nu_n^{(3)}\cdot m_3^0) + (1/4)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_m^{(4)}\cdot m_4^0)] \\
&+2\cdot g_{xn}\cdot[(1/4)\cdot(\nu_x^{(1)}\cdot m_1^0\cdot \nu_n^{(3)}\cdot m_3^0) - (1/4)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_x^{(2)}\cdot m_2^0)] \\
&\quad + g_{nn}\cdot[-(1/4)\cdot(\nu_n^{(3)}\cdot m_3^0)^2 - (1/4)\cdot(\nu_n^{(2)}\cdot m_2^0)^2] \\
&+2\cdot g_{mu}\cdot[(1/4)\cdot(\nu_m^{(1)}\cdot m_1^0\cdot \nu_u^{(3)}\cdot m_3^0) - (1/4)\cdot(\nu_n^{(4)}\cdot m_4^0\cdot \nu_u^{(4)}\cdot m_4^0)] \\
&+2\cdot g_{xu}\cdot[(1/4)\cdot(\nu_x^{(1)}\cdot m_1^0\cdot \nu_u^{(3)}\cdot m_3^0) + (1/4)\cdot(\nu_x^{(2)}\cdot m_2^0\cdot \nu_u^{(4)}\cdot m_4^0)] \\
&+2\cdot g_{nu}\cdot[-(1/4)\cdot(\nu_n^{(3)}\cdot m_3^0\cdot \nu_u^{(3)}\cdot m_3^0) + (1/4)\cdot(\nu_n^{(2)}\cdot m_2^0\cdot \nu_u^{(4)}\cdot m_4^0)] \\
&\quad + g_{uu}\cdot[-(1/4)\cdot(\nu_u^{(3)}\cdot m_3^0)^2 - (1/4)\cdot(\nu_u^{(4)}\cdot m_4^0)^2]
\end{aligned}$$

TABLE 12

Difference

$$\begin{aligned}
&\Sigma(\text{square}) - \Sigma(\text{cross}) = \\
&\quad g_{mm}[-(1/4)\cdot\{(\nu_m^{(1)}\cdot m_1^0)^2 - (\nu_m^{(4)}\cdot m_4^0)^2\}] \\
&+2\cdot g_{mx}\cdot[(1/4)\cdot\{\nu_m^{(1)}\cdot m_1^0\cdot \nu_x^{(2)}\cdot m_2^0) + (\nu_m^{(4)}\cdot m_4^0\cdot \nu_x^{(1)}\cdot m_1^0) \\
&\qquad -(\nu_m^{(1)}\cdot m_1^0\cdot \nu_x^{(1)}\cdot m_1^0) - (\nu_m^{(4)}\cdot m_4^0\cdot \nu_x^{(2)}\cdot m_2^0)\}] \\
&\qquad\qquad + g_{xx}\cdot[-(1/4)\cdot\{\nu_x^{(1)}\cdot m_1^0 - \nu_x^{(2)}\cdot m_2^0\}^2] \\
&+2\cdot g_{mn}\cdot[(1/4)\cdot\{(\nu_m^{(1)}\cdot m_1^0\cdot \nu_n^{(2)}\cdot m_2^0) + (\nu_n^{(3)}\cdot m_3^0\cdot \nu_m^{(4)}\cdot m_4^0] \\
&\qquad\qquad -(\nu_m^{(1)}\cdot m_1^0\cdot \nu_n^{(3)}\cdot m_3^0) - (\nu_n^{(2)}\cdot m_2^0\cdot \nu_m^{(4)}\cdot m_4^0)\}] \\
&\quad +2\cdot g_{nx}\cdot[(1/4)\cdot\{\nu_n^{(2)}\cdot m_2^0\cdot \nu_x^{(1)}\cdot m_1^0) + (\nu_n^{(3)}\cdot m_3^0\cdot \nu_x^{(2)}\cdot m_2^0) \\
&\qquad -(\nu_x^{(1)}\cdot m_1^0\cdot \nu_n^{(3)}\cdot m_3^0) - (\nu_n^{(2)}\cdot m_2^0\cdot \nu_x^{(2)}\cdot m_2^0)\}] \\
&\qquad\quad + g_{nn}\cdot[(-1/4)\cdot\{\nu_n^{(3)}\cdot m_3^0 - \nu_n^{(2)}\cdot m_2^0\}^2] \\
&+2\cdot g_{mu}\cdot[(1/4)\cdot\{\nu_u^{(3)}\cdot m_3^0\cdot \nu_m^{(4)}\cdot m_4^0) + (\nu_m^{(1)}\cdot m_1^0\cdot \nu_u^{(4)}\cdot m_4^0) \\
&\qquad\qquad -(\nu_m^{(1)}\cdot m_1^0\cdot \nu_u^{(3)}\cdot m_3^0) - (\nu_m^{(4)}\cdot m_4^0\cdot \nu_u^{(4)}\cdot m_4^0)\}] \\
&\quad +2\cdot g_{xu}\cdot[(1/4)\cdot\{(\nu_x^{(2)}\cdot m_2^0\cdot \nu_u^{(3)}\cdot m_3^0) + (\nu_u^{(4)}\cdot m_4^0\cdot \nu_x^{(1)}\cdot m_1^0) \\
&\qquad -(\nu_x^{(1)}\cdot m_1^0\cdot \nu_u^{(3)}\cdot m_3^0) - (\nu_x^{(2)}\cdot m_2^0\cdot \nu_u^{(4)}\cdot m_4^0)\}] \\
&\quad +2\cdot g_{nu}\cdot[(1/4)\cdot\{(\nu_n^{(2)}\cdot m_2^0\cdot \nu_u^{(3)}\cdot m_3^0) + (\nu_u^{(4)}\cdot m_4^0\cdot \nu_n^{(3)}\cdot m_3^0) \\
&\qquad\quad -(\nu_n^{(3)}\cdot m_3^0\cdot \nu_u^{(3)}\cdot m_3^0) - (\nu_n^{(2)}\cdot m_2^0\cdot \nu_u^{(4)}\cdot m_4^0)\}] \\
&\qquad + g_{uu}\cdot[-(1/4)\cdot\{(\nu_u^{(3)}\cdot m_3^0) - (\nu_u^{(4)}\cdot m_4^0)\}^2]
\end{aligned}$$

DISCUSSION

It is somewhat surprising that systems as complicated as salt solutions can obey the CSR. It is also surprising that a treatment based on pairwise interactions between ions should emerge with the required patterns. Thus by inspection the somewhat complicated equations in Table 7 identify various important characteristics of the CSR. We summarise the conclusions as follows: (1) at constant temperature, pressure and ionic strength, the CSR only applies to groups of four salts having similar stoichiometries, e.g. 1 : 1, 2 : 2, and 2 : 1 for salt-1, salt-2, salt-3 and salt-4. (2) The CSR does not apply for example to a square formed by salts KCl, K_2SO_4, Na_2SO_4 and NaCl.

Deviations from the CSR depend on the stoichiometries and pairwise interaction parameters. Inspection reveals a combination of signs and magnitudes of these latter parameters which might conspire to highlight in some systems and to minimise in other systems deviations for CSR. (3) The CSR is a direct consequence of differing solvation characteristics of the ions comprising the four salts. These properties play their part in determining the magnitude and signs of cosphere–cosphere interaction parameters. (4) The CSR applies to solutions which are sufficiently dilute that triplet and higher order cosphere interactions can be ignored. In fact these interactions would otherwise produce deviations from the parabolic dependence of $G^{E}(\mathrm{aq}; I^{0})$ on salt fraction y for each composite salt solution.

The foregoing analysis concentrated on the Gibbs function. Clearly the formalism is the same for derived variables such as enthalpies and volumes. In these terms the procedures outlined [9] by Guggenheim form a sound basis for description of systems containing salts having stoichiometries other than simple 1 : 1. Nevertheless the obvious challenge is to say something about the individual pairwise interaction parameters, e.g. g_{mm}, g_{mx} and g_{xx}. We are in the process [12] of tackling this formidable task.

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REFERENCES

1 H.S. Harned and R.A. Robinson, Multicomponent Electrolyte Solutions, Pergamon, London, 1968.
2 F.J. Millero, in E.D. Goldberg (ed.), The Sea, Vol. 5, Marine Chemistry, Wiley, New York, 1974, Chap. 1.
3 T.F. Young, Y.C. Wu and A.A. Krawetz, Discuss. Faraday Soc., 24 (1957) 37.
4 C.C. Briggs, R. Charlton and T.H. Lilley, J. Chem. Thermodyn., 5 (1973) 445; and references therein.
5 A.K. Covington, T.H. Lilley and R.A. Robinson, J. Phys. Chem., 72 (1968) 2759; and references therein.
6 F.J. Millero and S. Sotologo, J. Chem. Eng. Data, 31 (1986) 470.
7 P.J. Reilly and R.H. Wood, J. Phys. Chem., 73 (1969) 4292.
8 H.L. Friedman, Ionic Solution Theory, Interscience, New York, 1962.
9 E.A. Guggenheim, Trans. Faraday Soc., 62 (1966) 3446.
10 T.H. Lilley, Trans. Faraday Soc., 64 (1968) 2947.
11 M.J. Blandamer, J. Burgess and A.W. Hakin, Thermochim. Acta, 125 (1988) 347.
12 M.J. Blandamer, J. Burgess, S. Cottrell and A.W. Hakin, J. Chem. Soc. Faraday Trans. 1, 83 (1987) 3039.