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Pitzer, K.S.

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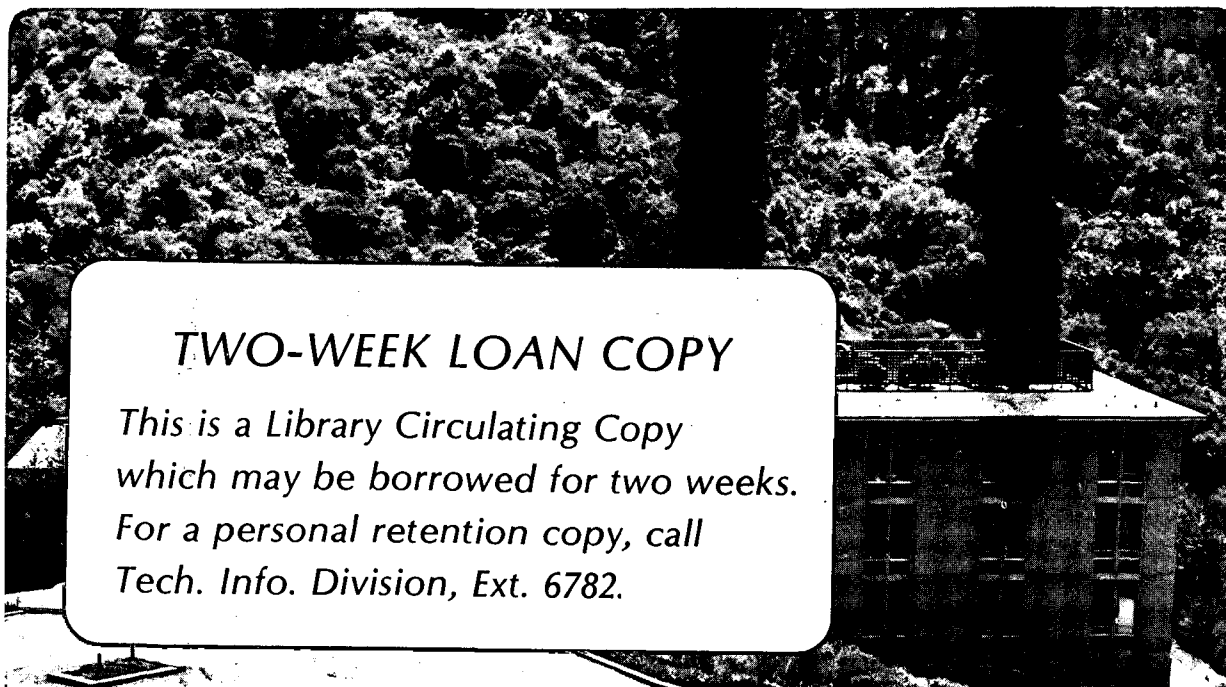
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THERMODYNAMICS OF ELECTROLYTE SOLUTIONS OVER THE ENTIRE MISCIBILITY RANGE

Kenneth S. Pitzer

Department of Chemistry and Lawrence Berkeley Laboratory

University of California

Berkeley, California 94720 USA

Introduction

Two general methods will be described for the treatment of relatively concentrated aqueous electrolytes. One approach is based on a virial expansion in concentration or molality of the solute. Molality is the preferable quantity since it is not temperature dependent. This approach has an excellent theoretical basis. The MacMillan-Mayer (1) solution theory established that a treatment formally similar to that for nonideal gases was valid for solutes in a solvent provided the intermolecular potentials are replaced by potentials of mean force in that solvent. For electrolytes one must recognize the long-range character of coulombic forces which prevents their inclusion in the virial series. But as Mayer (2) and others have shown, one may combine a Debye-Hückel term for electrostatic effects with a virial series for the effects of short range forces. In this case, however, the virial coefficients depend on the ionic strength as well as the temperature and pressure. These theoretical principles were used by the writer (3) to establish the form of an equation for electrolyte properties in which the virial coefficients are evaluated empirically. The effectiveness of the virial equations for mixed electrolytes is well established (4,5). It is not easy to state a maximum concentration since a virial series can be extended indefinitely. But with only third virial coefficients the data on many systems have been represented accurately up to ionic strength of 10 molal.

For systems approaching pure fused salts, however, the virial expansion method is unsatisfactory. In this domain one can consider equations that are successful for miscible nonelectrolytes. A nonrandom distribution of ions with those of opposite charge close to one another presumably applies from the fused salt throughout the range of high concentration. Only in dilute aqueous solutions does the ion distribution approach randomness, and this can be expressed by a Debye-Hückel term. Various short range forces dominate the behavior of very concentrated electrolytes; hence, one expects the equations developed for nonelectrolytes to be appropriate. This has been demonstrated (6) for the few systems which are miscible to the pure fused salt.

Virial Expansion

The basic equation on the virial basis is postulated for the excess Gibbs energy from which other functions can be obtained from appropriate derivatives.

$$G^{\text{ex}}/n_w RT = f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k. \quad (1)$$

Here G^{ex}/n_w is the excess Gibbs energy per kilogram of solvent and m_i , m_j , etc., are the molalities of the various ions or neutral solutes present. The long-range electrostatic forces lead to the Debye-Hückel term $f(I)$ where I is the ionic strength. Short-range interparticle-potential effects are taken into account by the virial coefficients λ_{ij} for binary interactions, μ_{ijk} for ternary, etc. As noted above, electrostatic effects lead to an ionic strength dependence of λ for ionic interactions. For μ this is neglected; also μ is omitted if all ions are of the same sign. While fourth virial coefficients could be added, they do not appear to be needed for most applications. Indeed the third virial coefficients are so small that they can often be omitted at moderate concentration (I up to about 2).

The derivative equations for osmotic and activity coefficients, which are presented below, were applied to the experimental data for wide variety of pure aqueous electrolytes at 25°C by Pitzer and Mayorga (7) and to mixtures by Pitzer and Kim (4). Later work (8-12) considered special groups of solutes and cases where an association equilibrium was present (H_3PO_4 and H_2SO_4). While there was no attempt in these papers to include all solutes for which experimental data exist, nearly 300 pure electrolytes and 70 mixed systems were considered and the resulting parameters

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reported. This represents the most extensive survey of aqueous electrolyte thermodynamics, although it was not as thorough in some respects as the earlier evaluation of Robinson and Stokes (13) or recent work at the U. S. National Bureau of Standards (14).

In addition to the activity and osmotic coefficients at room temperature, the first temperature derivatives and the related enthalpy of dilution data were considered for over 100 electrolytes (12,15). The data for electrolytes at higher temperatures become progressively more sparse. Quite a few solutes have been measured up to about 50°C (and down to 0°C). Also, over this range, the equations using just first temperature derivatives have some validity for rough estimates in other cases. But the effects of the second derivative (or the heat capacity) on activity coefficients at higher temperatures is very substantial.

Sodium chloride has been studied much more thoroughly at high temperature than any other electrolyte. The osmotic coefficient measurements of Liu and Lindsay (16) and various types of measurements of Franck and associates (17) and of Federov and associates (18) are particularly noteworthy. A preliminary effort to represent many of the data on sodium chloride by virial coefficient equations has been published (19). A revision and extension has progressed to the point of an equation for the volumetric properties to 300°C and 1 kbar (20). The derivatives of this equation yield the effects of pressure on other thermodynamic properties. A comprehensive treatment of these thermodynamic properties which will yield a full equation of state is nearing completion.

Over the wide range of temperature to 300°C and concentration to 10 M, sodium chloride remains a fully ionized electrolyte; the principal change is the increase in the Debye-Hückel (21) parameter which lowers both activity and osmotic coefficients.

Holmes, *et al.* (22) have investigated to about 200°C several systems including $KCl-NaCl-H_2O$ and $CaCl_2-NaCl-H_2O$.

The importance of the virial-coefficient equations is especially great for mixed electrolytes. Of the needed virial coefficients for a complex mixture such as sea water, most are determined by the pure electrolyte measurements and all the others of any significance are determined from data on simple mixtures such as $NaCl-KCl$, $NaCl-MgCl_2$, $NaCl-Na_2SO_4$, etc., which have been measured. The effect of the terms obtained from mixtures is very small in any case and these terms can be ignored for all but the most abundant species.

A very severe test of these virial-coefficient equations for the sea-water-related $Na-K-Mg-Ca-Cl-SO_4-H_2O$ system has been made by Harvie and Weare (5) who calculated the solubility relationships for all solids which can arise from this complex system. There are 13 invariant points with four solids present and the predicted solution composition in all 13 cases agrees with the experimental values of Braitsch (23) substantially within the estimated error of measurement. In particular, Harvie and Weare found that fourth virial coefficients were not required even in the most concentrated solutions.

There are also many less severe tests (4) of predictions for mixed electrolytes which illustrate the accuracy to be expected in various cases. Thus it is well-established that the virial coefficient equations for electrolytes yield reliable predictions of mixed-electrolyte properties provided the coefficients measurable for the pure electrolyte components are known. The predictions are more accurate if the additional coefficients measurable from simple mixtures are also known but their effect is usually very small.

The working equations for osmotic and activity coefficients, derived from equation (1) are given as equations (2) and (3), respectively. The various secondary relationships are defined in several additional equations stated and briefly described thereafter. Additional details and derivations of equations for the entropy, the heat capacity, and other related functions can be found in various published papers (3,4,7-15,19-21).

$$\begin{aligned}
(\phi-1) = & \frac{2}{\left(\sum_i m_i\right)} - \frac{A_\phi I^{3/2}}{1+bI^{1/2}} + \sum_c \sum_a m_c m_a (B_{ca}^\phi + ZC_{ca}) + \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} \times \\
& (\Theta_{cc'}^\phi + \sum_a m_a \psi_{cc'a}) + \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} (\Theta_{aa'}^\phi + \sum_c m_c \psi_{aa'c}) \quad (2)
\end{aligned}$$

Although one wishes activity coefficients for neutral combinations of ions, it is convenient to use equations for single-ion activity coefficients which can then be combined appropriately.

$$\begin{aligned}
\ln \gamma_M = & z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c (2\Theta_{Mc} + \sum_a m_a \psi_{Mca}) \\
& + \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} \psi_{aa'M} + |z_M| \sum_c \sum_a m_c m_a C_{ca} \quad (3a)
\end{aligned}$$

$$\begin{aligned}
\ln \gamma_X = & z_X^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}) + \sum_a m_a (2\Theta_{Xa} + \sum_c m_c \psi_{Xac}) \\
& + \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} \psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca}. \quad (3b)
\end{aligned}$$

Here m_c is the molality of cation c with charge z_c and correspondingly for anion a . Sums over c or a cover all cations or anions, respectively. B 's and Θ 's are measurable combinations of λ 's whereas C 's and ψ 's are combinations of the μ 's in equation (1). Note that the Θ 's and ψ 's are zero and these terms disappear for pure electrolytes.

The electrostatic function f must contain the Debye-Huckel limiting law with the parameter

$$A_\phi = (1/3)(2\pi N_o d_w/1000)^{1/2} (e^2/DkT)^{3/2}$$

but it proves empirically advantageous to take an extended form. Among alternatives, the form found best was

$$f(I) = -4A_\phi I b^{-1} \ln(1+bI^{1/2}) \quad (4)$$

with $b = 1.2$ chosen for all electrolytes in water. Bradley and Pitzer (21) give values of A_ϕ to 350°C and 1 kbar. The appropriate derivative gives the term in equation (2) for ϕ . For the activity coefficient it is convenient to define

$$\begin{aligned}
F = & -A_\phi [I^{1/2}/(1+bI^{1/2}) + (2/b)\ln(1+bI^{1/2})] + \sum_b \sum_a m_c m_a B'_{ca} \\
& + \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} \Theta'_{cc'} + \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} \Theta'_{aa'} \quad (5)
\end{aligned}$$

which includes both the Debye-Hückel term with A_ϕ and certain derivatives of the second virial terms.

The second virial coefficients, B_{MX} , are functions of ionic strength. Again an empirical choice was made among theoretically plausible forms for B_{MX} and the following was chosen with $\beta^{(0)}$ and $\beta^{(1)}$ parameters fitted to the data for each solute.

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha I^{1/2}} \quad (6a)$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha I^{1/2}) \quad (6b)$$

$$B_{MX}' = \beta_{MX}^{(1)} g'(\alpha I^{1/2})/I, \quad (6c)$$

here the functions g and g' are given by

$$g(x) = 2[1 - (1+x)e^{-x}]/x^2 \quad (7a)$$

$$g'(x) = -2[1 - (1+x+1/2 x^2)e^{-x}]/x^2 \quad (7b)$$

with $x = \alpha I^{1/2}$. In equations (6) the form given is for 1-1 and 1-2 electrolytes for which the value $\alpha = 2$ was chosen empirically. For higher valence types, such as 2-2 electrolytes, where there is a tendency toward ion-pairing, an additional term is added and equations (6) become

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha_1 I^{1/2}} + \beta_{MX}^{(2)} e^{-\alpha_2 I^{1/2}} \quad (8a)$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} g(\alpha_2 I^{1/2}) \quad (8b)$$

$$B'_{MX} = \beta_{MX}^{(1)} g'(\alpha_1 I^{1/2})/I + \beta_{MX}^{(2)} g'(\alpha_2 I^{1/2})/I. \quad (8c)$$

In this case the values of $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$ are assigned.

The parameters, C_{MX} , are related to the tabulated parameters of Pitzer and Mayorga (7), C_{MX}^ϕ , as follows,

$$C_{MX} = C_{MX}^\phi / 2 |z_M z_X|^{1/2} \quad (9)$$

also the quantity Z is defined to be

$$Z = \sum_i m_i |z_i| = 2 \sum_c m_c z_c. \quad (10)$$

The mixed electrolyte terms in Θ and Ψ account for differences among interactions between ions of like sign. The defining equations for the second virial coefficients, Θ_{ij} , are given by equations (11),

$$\Theta_{ij} = S_{\Theta_{ij}} + E_{\Theta_{ij}}(I) + I E'_{\Theta_{ij}}(I) \quad (11a)$$

$$\Theta_{ij} = S_{\Theta_{ij}} + E_{\Theta_{ij}}(I) \quad (11b)$$

$$\Theta'_{ij} = E'_{\Theta_{ij}}(I) \quad (11c)$$

$S_{\Theta_{ij}}$, a single parameter for each pair of anions or each pair of cations, is the only adjustable parameter in equations (11).

The terms $E_{\Theta_{ij}}(I)$ and $E'_{\Theta_{ij}}(I)$ account for the electrostatic effects of unsymmetrical mixing. Equations for calculating these terms were derived by Pitzer (24); this effect was discovered by Friedman (25). The important features of $E_{\Theta_{ij}}(I)$ and $E'_{\Theta_{ij}}(I)$ are that they depend only on the charges of the ions i and j and the total ionic strength. They do not constitute additional parameterization. $E_{\Theta_{ij}}(I)$ and $E'_{\Theta_{ij}}(I)$ are zero when the ions i and j are of the same charge. Although these terms can be neglected in some cases of 2-1 mixing (with adjustment in S_Θ), it is safest to include them for all systems where the unsymmetrical mixing is significant.

It would burden this paper excessively to list the parameters for all known electrolytes, even at room temperature. As examples giving the pattern of magnitudes as well as values for widely appearing salts, the values for the Na-K-Mg-Ca-Cl-SO₄-H₂O system are listed in Tables 1 and 2. Most of these are taken from Pitzer and Mayorga (7) or Pitzer and Kim (4) but a few were revised in later work. It is apparent that the pure-electrolyte parameters in Table 1 are much larger than those for mixing of ions of the same sign in Table 2. Also the second virial coefficients are much larger than the third virial coefficients in Table 1.

Miscible Electrolytes

There are two systems for which the vapor pressure and thereby the activity of water has been measured over the full range of composition from fused salt to dilute solution in water (26-28). In each of these systems (Ag, Tl) NO₃-H₂O and (Li, K) NO₃-H₂O the salt is a simple mixture of approximately equal molal proportions. These results are shown on Figure 1 which also includes similar data for several systems of large but limited solubility. The composition variable is the mole fraction on an ionized basis, i.e., $x_1 = n_1 / (n_1 + \nu n_2)$ where n_1 and n_2 are moles of water and salt, respectively, and ν is the number of ions in the salt. On this basis Raoult's law applies in the very dilute range, with the Debye-Hückel correction applicable as the concentration increases.

The similarity of the curves on Figure 1 to those for nonelectrolyte solutions is striking. The dashed line representing $a_1 = x_1$ can be called "ideal-solution behavior" for these systems, as it is for nonelectrolytes, but it is realized that a statistical model yielding that result would be more complex for the ionic case. Also the Debye-Hückel effect is a departure from this ideal behavior. Nevertheless, it seemed worthwhile to explore the use for these systems of the simple equations for nonelectrolytes. One of the simplest and most successful had its origin in the work of van Laar (29) and has been widely used since. Prausnitz (30) discusses this and related equations as well as the contributions of Margules, Hildebrand, Scatchard, Guggenheim, and others to this topic. For the activity of either component, referenced to the pure liquid, one has

$$\ln a_1 = \ln x_1 + w_1 z_1^2, \quad \ln a_2 = \ln x_2 + w_2 z_2^2 \quad (12)$$

$$w_2 = w_1 (b_2/b_1), \quad z_1 = n_1 / [n_1 + \nu n_2 (b_2/b_1)], \quad z_2 = \nu n_2 / [n_1 (b_1/b_2) + \nu n_2].$$

Note first that if (b_1/b_2) is unity, z_1 and z_2 reduce to the mole fractions x_1 and x_2 and one has even simpler equations. The non-ideality parameter w (sometimes

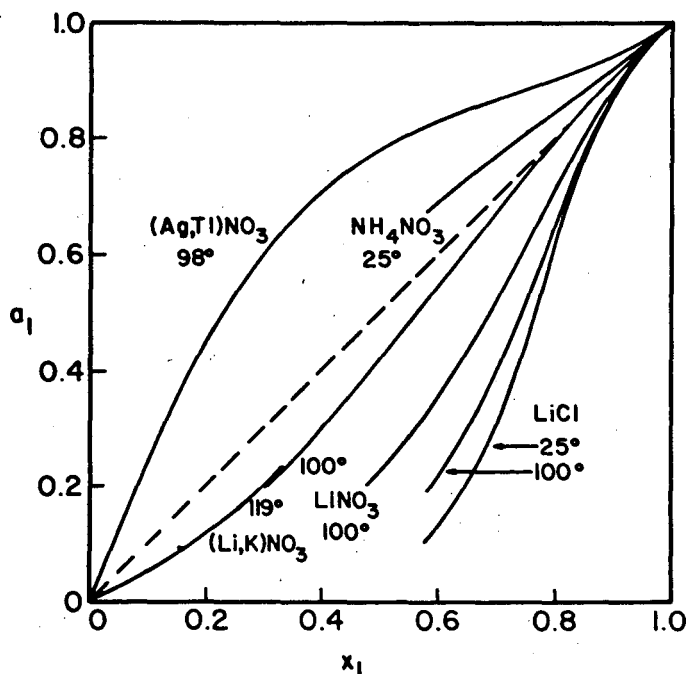


Figure 1. Activity of water for water-salt solutions over a very wide range of composition.

written w/RT) arises from the difference between the intermolecular attraction of unlike species as compared to the mean of the intermolecular attraction for pairs of like species. The second parameter in equation (12), (b_1/b_2) , is sometimes ascribed to the ratio of the volumes of the molecules or to the ratio of molal volumes in the liquid, although in some systems, especially metallic solutions, equation (12) is still quite satisfactory but (b_1/b_2) departs greatly from the ratio of molal or atomic volumes. For fused salt-water mixtures it seems best to regard (b_1/b_2) as a freely adjustable parameter and subsequently to compare the values with ratios of molal volumes.

Equation (12) was fitted to the two systems remaining liquid over the full range of composition with the results $w_1 = 1.02$, $(b_1/b_2) = 0.50$ for $(Ag, Tl)NO_3-H_2O$ and $w_1 = -0.89$, $(b_1/b_2) = 1.2$ for $(Li, K)NO_3-H_2O$. Water is component 1 and the salt component 2. Even more perfect agreement in the dilute aqueous region is obtained by adding a Debye-Hückel term to equation (12); these results have been reported in detail (6).

These properties shown in Figure 1 demonstrate the similarity of the effects of short-range forces on the properties of nonelectrolytes and concentrated electrolytes. One finds both positive and negative deviations from ideality. Previous discussion of these systems has focused on the hydration of the positive ion as the dominant effect, but we see in Figure 1 that the shift from nitrate to chloride is comparably important. Just as for nonelectrolytes, one must consider all intermolecular forces in electrolytes.

With experimental data for the activity of water, one can, of course, integrate the Gibbs-Duhem equation to obtain the activity of the salt, over the same range in composition, without the use of any model or semi-empirical equation. But equation (12) appears to fit so well that its use is very convenient and yields a_2 based on the pure fused-salt reference state.

If the fused salt does not exist at the temperature of interest, one normally uses the infinitely dilute solute standard state. In that case it is essential to use the extended equation including the Debye-Hückel term (6) to obtain the salt activity.

Conclusions

It is shown that the properties of fully ionized aqueous electrolyte systems can be represented by relatively simple equations over wide ranges of composition. There are only a few systems for which data are available over the full range to fused salt. A simple equation commonly used for nonelectrolytes fits the measured vapor pressure of water reasonably well and further refinements are clearly possible. Over the somewhat more limited composition range up to saturation of typical salts such as $NaCl$, the equations representing thermodynamic properties with a Debye-Hückel term plus second and third virial coefficients are very successful and these coefficients are known for nearly 300 electrolytes at room temperature. These same equations effectively predict the properties of mixed electrolytes. A stringent test is offered by the calculation of all of the solubility relationships of the system $Na-K-Mg-Ca-Cl-SO_4-H_2O$ and the calculated results of Harvie and Weare show excellent agreement with experiment. The more limited data for similar solutions at higher temperatures, up to about $300^\circ C$ at least, are satisfactorily represented by the virial-coefficient equations.

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Table 1. Parameters for virial coefficient equations at 25°C

M	X	$\beta_{MX}^{(0)}$	$\beta_{MX}^{(1)}$	$\beta_{MX}^{(2)}$	C_{MX}^{ϕ}
Na	Cl	.07650	.2264	--	.00127
Na	SO ₄	.01958	1.1130	--	.0057
K	Cl	.04835	.2122	--	-.00084
K	SO ₄	.04995	.7793	--	0
Mg	Cl	.35235	1.6815	--	.00519
Mg	SO ₄	.22100	3.3430	-37.23	.025
Ca	Cl	.31590	1.6140	--	-.00034
Ca	SO ₄	.20000	3.1973	-54.24	0

Table 2. Parameters for mixed electrolytes with the virial coefficient equations (at 25°C)

i	j	k	$S_{\theta_{ij}}$	ψ_{ijk}
Na	K	Cl	-.012	-.0018
		SO ₄		-.010
Na	Mg	Cl	.07	-.012
		SO ₄		-.010
Na	Ca	Cl	.07	-.014
		SO ₄		-.067
K	Mg	Cl	.0	-.022
		SO ₄		-.048
K	Ca	Cl	.032	-.025
		SO ₄		-
Mg	Ca	Cl	.010	0
		SO ₄		.020
Cl	SO ₄	Na	.03	0
		K		-.005
		Mg		-.020
		Ca		-.027

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