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Theoretical considerations of solubility with emphasis on mixed aqueous electrolytes

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Abstract - The theoretical bases for prediction of solubilities are provided by thermodynamics and statistical mechanics. In many cases statistical mechanics yields the chemical potential as an equation including several terms. While one or more terms may be fully determined theoretically, the parameters in other terms must be evaluated empirically at present. Then the solubility is obtained by equating the chemical potential for each species in different phases or by minimizing the total Gibbs energy at constant pressure and temperature. As an example of a recent major advance, the problem of the solubility of salts, including complex minerals, in multicomponent aqueous solutions is discussed in some detail. The status of predictive calculations for 25°C is described and new results for higher temperatures are reported. Brief comments are added concerning theories for other types of solubility systems.

INTRODUCTION

Thermodynamics provides a structure of the quantities required for the calculation of solubilities together with valuable relationships between these quantities and other measurable properties of the substances involved. From statistical mechanics one obtains valuable equations based on molecular models where the form of the equation and some terms may be fully determined from theory while the numerical values of parameters in other terms remain to be determined from experiments on the systems of interest. These procedures, however, allow a few experiments to determine the well-defined parameters from which predictions can be made for wide ranges of composition, temperature, and pressure. After a brief summary of equations and status of knowledge for solids the primary emphasis will be on the properties determining solubilities in mixed aqueous electrolytes. In this area there have been major advances in the last decade; these will be reviewed in some detail. Brief comments will be added about other types of solubility systems at the end.

GENERAL THEORY

The basic theory for a solubility equilibrium is well known. At constant temperature and pressure the equilibrium lies at the minimum of the Gibbs energy, G.

$$G = \sum_i n_i \mu_i \tag{1}$$

Here μ_i is the chemical potential of the i^{th} substance or species of which there are n_i moles. If the species i is present in more than one phase, this requires that μ_i be the same in each phase. For a phase of variable composition, it is convenient to define activities a_i for each species as follows:

$$RT \ln a_i = \mu_i - \mu_i^\circ \tag{2}$$

where μ_i° is the chemical potential in a defined standard state. Both a's and μ's are functions of T and P; μ° is independent of composition but both μ and a are also dependent on composition variables which may be defined as molalities or mole fractions.

For aqueous solutions the composition is ordinarily given by the molalities m_i of all solute species where m_i is the number of moles of i per kilogram of water. Then for a neutral solute the activity is

$$a_i = m_i \gamma_i \tag{3}$$

with γ_i the activity coefficient. In the case of a strong electrolyte, MX, which dissociates into ν_M positive ions, M, and ν_X negative ions, X, of molality m_M and m_X, respectively, the activity becomes

$$a_{MX} = (m_M\gamma_M)^{\nu_M} (m_X\gamma_X)^{\nu_X} \qquad (4)$$

One cannot determine absolute values of γ's for ions. One procedure is to define a mean activity coefficient $\gamma_\pm$, which is unambiguous,

$$\gamma_\pm = (\gamma_M^{\nu_M} \gamma_X^{\nu_X})^{1/\nu} \qquad (5)$$

with $\nu = \nu_M + \nu_X$; then

$$a_{MX} = \gamma_\pm^{\nu} m_M^{\nu_M} m_X^{\nu_X} \qquad (6)$$

Each electrolyte has its own $\gamma_\pm$ and ν; an additional subscript, MX, is implied for each.

It can be shown, however (ref. 1), that one can write equations for γ_M and γ_X where the only ambiguity is a term which cancels for the $\gamma_\pm$ product for any charge type. It is optional whether equations for $\gamma_\pm$ are used or those for γ_M and γ_X. The former are given in (refs. 1 and 2) for the general statistical model described below whereas we will give the separate equations for γ_M and γ_X. In a complex mixture such as seawater including minor components, the number of possible $\gamma_\pm$ is much larger than the number of γ_M and γ_X; hence, the latter system is advantageous.

The conventional standard state for aqueous solutions is taken at infinite dilution where all γ_i become unity. The activity of water is related to the osmotic coefficient, ϕ.

$$\ell n\ a_1 = -\phi(M_1/1000) \sum_i m_i \qquad (7)$$

where M_1 is the molecular mass of water in g and the sum covers all solute species. Water is given the subscript 1 for aqueous solutions. The Gibbs-Duhem equation relates the composition dependence of μ_1 to that of the various solute μ_i and therefore ϕ to the various γ_i or $\gamma_\pm$.

In the case of a hydrated crystal; with ν_0 molecules of water as well as ν_M positive ions, M, and ν_X negative ions, X, the total chemical potential becomes

$$\mu_j/RT = (\nu_M\mu_M^\circ + \nu_X\mu_X^\circ + \mu_0\mu_{H_2O}^\circ)/RT + \nu_M\ \ell n(m_M\gamma_M) + \nu_X\ \ell n(m_X\gamma_X) + \nu_0 \ell n\ a_1 \qquad (8)$$

where the last term is related to the osmotic coefficient through equation (7).

For the calculation of the solubilities of solids in aqueous solutions one requires the μ_i values for the solids and for the species in solution. If the solids have fixed compositions, the μ_i values equal the μ_i° and are functions only of P and T. The relationships between the dependencies of μ_i° on P and T and volumes, entropies (or enthalpies) and heat capacities are well known. The data base for these quantities is well organized (refs. 3-5). While there are inaccuracies and voids at higher temperatures where research is needed, the methods are well established and will not be discussed further here. If the solid has variable composition, then the μ_i depends also on composition variables. This is an important field and a few comments will be made subsequently concerning it.

ACTIVITIES IN MIXED ELECTROLYTES

The recent advances which have made it feasible to predict solubilities of a wide variety of salts in complex mixed electrolytes have concerned the activities or chemical potentials of various species in the liquid. We turn now to that topic.

Equations

For nonideal gases the virial series, an expansion in increasing powers of the concentration, is a valuable expression and the successive coefficients are related by statistical mechanics to the potentials of interaction of molecules pairwise, threefold, etc. The McMillan-Mayer (ref. 6) formulation of solution properties allows the same expansion, but now the solute interactions are given by the potentials of mean force in the solvent. Also the relationships apply strictly to conditions of osmotic equilibrium with pure solvent, but for semi-empirical applications the same form of equation may be used with coefficients determined from macroscopic measurements at constant pressure. These equations apply to neutral molecules or solute species, but Mayer (ref. 7) showed that the statistical equation for an ionic system could also be transformed to a virial expansion. For the ionic system, however, there is an additional term, which is found to be exactly the Debye-Hückel limiting law, and all of the virial coefficients now become dependent on the ionic strength.

The virial expansion is in terms of concentrations of solute species, but at moderate concentrations the molalities are nearly proportional to concentrations. Concentration is an inconvenient measure of composition since it depends on pressure and temperature. Thus, it seemed a good, practical procedure to recast the virial expansion into a series in molalities with the result for the excess Gibbs energy (ref. 8);

$$G^{EX}/n_wRT = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk} + \cdots \qquad (9)$$

Various working equations are derived by derivatives of equation (9); these are now commonly called the Pitzer equations. The first term on the right includes the Debye-Hückel limiting law while n_w is the number of kg of solvent, $\lambda_{ij}(I)$ is the second virial coefficient (or ion-interaction parameter) with the dependence shown on the ionic strength, I.

$$I = (1/2) \sum_i m_i z_i^2 \qquad (10)$$

Here z_i is the number of charges on the i^{th} particle. In equation (9) the third virial coefficient μ_{ijk} also depends in principle on I, but in most cases this can be ignored. An exception was found recently (ref. 9) where the ionic strength dependence of μ was significant. The virial series continued, of course, to fourth and higher order terms but these are only rarely needed. Also μ_{ijk} can ordinarily be ignored when all three interacting particles have the same sign of charge. This is reasonable since the virial coefficients arise from short-range interparticle forces and the electrical repulsion keeps like-charged particles away from one another most of the time. Note that this μ_{ijk} is not the chemical potential. The λ and μ depend on temperature and pressure but on composition only through the ionic strength.

While the Mayer theory introduced just the Debye-Hückel limiting law as the additional term, it is found that there is a redundancy between extended Debye-Hückel terms and the ionic strength dependence of the second virial coefficients. The latter can be simplified by making f(I) a simple extended form, specifically

$$f(I) = -(4IA_\phi/b)\ \ell n(1 + bI^{1/2}) \qquad (11)$$

where b is a constant selected to be 1.2 $kg^{1/2} \cdot mol^{-1/2}$ independent of temperature, pressure, or solute type for the full range of applicability of this type of equation. A_ϕ is the Debye-Hückel parameter given by

$$A_\phi = (1/3)(2\pi N_0 d_w/1000)^{1/2} (e^2/\varepsilon kT)^{3/2} \qquad (12)$$

with ε the relative permittivity and d_w the density of the solvent. The factor $4\pi\varepsilon_0$ precedes ε for SI units.

The requirement of electrical neutrality precludes the evaluation of λ_{ij} or μ_{ijk} for individual ions; rather one evaluates terms for neutral combinations as follows:

$$B_{ca} = \lambda_{ca} + |z_a/2z_c|\lambda_{cc} + |z_c/2z_a|\lambda_{aa} \qquad (13)$$

$$C_{ca} = (3/2)(\mu_{cca}/|z_c| + \mu_{caa}|z_a|) \qquad (14)$$

$$\Phi_{cc'} = \lambda_{cc'} - (z_{c'}/2z_c)\lambda_{cc} - (z_c/2z_{c'})\lambda_{c'c'} \qquad (15)$$

$$\psi_{cc'a} = 6\mu_{cc'a} - (3z_{c'}/z_c)\mu_{cca} - (3z_c/z_{c'})\mu_{c'c'a} \qquad (16)$$

Here c,c',...are cations and a,a',...are anions. B'_{ca} and Φ'_{ca} are the ionic strength derivatives of B and Φ. Other terms in $\Phi_{aa'}$ and $\psi_{caa'}$ arise from permutation of the indices.

The appropriate derivatives of equation (9) with respect to n_w and m_i yield the osmotic and activity coefficients:

$$(\phi-1) = (2/\sum_i m_i)[-A_\phi I^{3/2}/(1 + bI^{1/2}) + \sum_c \sum_a m_c m_a (B^\phi_{ca} + Z\, C_{ca})$$

$$+ \sum_{c>c'} \sum_{c'} m_c m_{c'} (\Phi^\phi_{cc'} + \sum_a m_a \psi_{cc'a}) + \sum_{a>a'} \sum_{a'} m_a m_{a'} (\Phi^\phi_{aa'} + \sum_c m_c \psi_{caa'}) \qquad (17)$$

$$\ell n\, \gamma_M = z_M^2 F + \sum_a m_a (2B_{Ma} + Z\, C_{Ma}) + \sum_c m_c (2\Phi_{Mc} + \sum_a m_a \psi_{Mca})$$

$$+ \sum_{a>a'} \sum_{a'} m_a m_{a'}\, \psi_{Maa'} + |z_M| \sum_c \sum_a m_c m_a\, C_{ca} \qquad (18a)$$

$$\ell n\, \gamma_X = z_X^2 F + \sum_c m_c (2B_{cX} + Z\, C_{cX}) + \sum_a m_a (2\Phi_{Xa} + \sum_c m_c \psi_{cXa})$$

$$+ \sum_{c>c'} \sum_{c'} m_c m_{c'}\, \psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a\, C_{ca} \qquad (18b)$$

The quantity F includes the Debye-Hückel term and other terms as follows:

$$F = -A_\phi [I^{1/2}/(1 + bI^{1/2}) + (2/b)\, \ell n(1 + bI^{1/2})] + \sum_c \sum_a m_c m_a B'_{ca}$$

$$+ \sum_{c>c'} \sum_{c'} m_c m_{c'}\, \Phi'_{cc'} + \sum_{a>a'} \sum_{a'} m_a m_{a'}\, \Phi'_{aa'} \qquad (19)$$

Also

$$Z = \sum_i m_i |z_i| \qquad (20)$$

$$B^\phi_{ca} = B_{ca} + I\, B'_{ca} \qquad (21)$$

$$\Phi^\phi_{cc'} = \Phi_{cc'} + I\, \Phi'_{cc'} \qquad (22)$$

Sums over i include all solute species; uncharged species do not contribute to I or Z. For equations (17) and (18), C_{ij} and ψ_{ijk} were assumed to be independent of ionic strength; if these quantities are I dependent, there are additional terms.

The ionic strength dependency was first studied for the osmotic coefficient and the best simple expression was found to be (ref. 8):

$$B^\phi_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} \exp(-\alpha I^{1/2}) \qquad (23)$$

where $\beta^{(0)}_{MX}$ and $\beta^{(1)}_{MX}$ are constants at a given P and T and are characteristic of the interaction of the ions M and X. A transformation related to equation (9) then yields

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}\, g(\alpha I^{1/2}) \qquad (24)$$

$$B'_{MX} = \beta^{(1)}_{MX}\, g'(\alpha I^{1/2})/I \qquad (25)$$

$$g(x) = 2[1-(1 + x)\, \exp(-x)]/x^2 \qquad (26)$$

$$g'(x) = -2[1-(1 + x + x^2/2)\, \exp(-x)]/x^2 \qquad (27)$$

For a wide variety of 1-1, 2-1, and 3-1 electrolytes equations (23-27) fit experimental data very well with $\alpha = 2.0\ \mathrm{kg}^{1/2} \cdot \mathrm{mol}^{-1/2}$ (refs. 8,10). However, other values of α can be used without undue complication (ref. 11).

In the case of 2-2 electrolytes there is an electrostatic ion pairing at quite low concentration which must be represented. Many investigators assume an additional species, the MX ion pair, with its own chemical potential, etc. This treatment involves an iterative solution for the amount of ion pair present. Actually, better agreement with experiment is obtained (ref. 12) by a modification of equations (23 to 25) by the addition of a third term of the same form as the second.

$$B^\phi_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} \exp(-\alpha_1 I^{1/2}) + \beta^{(2)}_{MX} \exp(-\alpha_2 I^{1/2}) \qquad (28)$$

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}\, g(\alpha_1 I^{\frac{1}{2}}) + \beta^{(2)}_{MX}\, g(\alpha_2 I^{\frac{1}{2}}) \tag{29}$$

$$B'_{MX} = [\beta^{(1)}_{MX}\, g'(\alpha_1 I^{\frac{1}{2}}) + \beta^{(2)}_{MX}\, g'(\alpha_2 I^{\frac{1}{2}})]/I \tag{30}$$

The coefficient of the additional term $\beta^{(2)}_{MX}$ is large and negative. It can be shown that the initial effect of this term at low concentration is the same as that of the ion association reaction with $\beta^{(2)}_{MX} = -K/2$ where K is the association constant. For aqueous 2-2 electrolytes at 298 K the optimized value of α_2 is 12 $kg^{\frac{1}{2}}\cdot mol^{-\frac{1}{2}}$ and for these cases $\alpha_1 = 1.4$ $kg^{\frac{1}{2}}\cdot mol^{-\frac{1}{2}}$. These values of 1.4 and 12 for α_1 and α_2 can be held independent of P and T for many applications. However, there are theoretical reasons for taking α_2 to be proportional to the Debye-Hückel parameter A_{ϕ}. These matters are discussed in detail in ref. 13.

The terms in Φ and ψ for mixing different ions of the same sign appear only for mixed electrolytes. They are expected to be small because like-charged ions repel one another and therefore will seldom be close enough to have significant short-range interaction. Also, from equations (15) and (16) one notes that these terms are differences between small quantities and, therefore, are even smaller in magnitude. Nevertheless, these small terms are needed in many cases to yield quantitative agreement with experiment at moderate or high molality.

In principle a Φ depends on ionic strength since the λ's have that dependence. Also for unsymmetrical mixing such as Na^+ with Mg^{+2}, there is a large ionic-strength dependence of Φ which arises from long-range forces and is given by theory (refs. 14 and 15). Thus one writes

$$\Phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) \tag{31}$$

$$\Phi'_{ij} = {}^{E}\theta'_{ij}(I) \tag{32}$$

$$\Phi^{\phi}_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) + I\,{}^{E}\theta'_{ij}(I) \tag{33}$$

where ${}^{E}\theta$ and ${}^{E}\theta'$ are the terms arising for unsymmetrical mixing from purely electrical forces for which the theoretical formula involves the ionic charges and the solvent properties ε, d_w, etc. The remaining term θ_{ij} arising from short-range forces is taken as a constant for any particular c,c' or a,a' at a given T and P.

The quantity θ_{ij} in equations (31) and (33) is independent of ionic strength and is tabulated for various pairs of ions of the same sign. Even when the ions have the same charge there may be an ionic-strength dependence which would add ionic-strength dependent terms to equations (31) - (33), but this effect is very small and is usually neglected. Recent calculations of heats of mixing (ref. 9), however, find this effect to be significant in some cases. With future measurements of activity and osmotic coefficients at higher precision, there will be need to recognize the ionic-strength dependence of the Φ's for symmetrical mixing, but for the present this can usually be ignored.

Parameters for 298.15 K

The $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, C_{MX} (and $\beta^{(2)}_{MX}$ if pertinent) are evaluated from osmotic or activity coefficient data for pure electrolytes. This information is available for a large number of solutes at 298.15 K (25°C) (refs. 1,10,12). If the measurements do not extend above ionic strength 2 $mol\cdot kg^{-1}$, the third virial parameter C_{MX} should be omitted. For cases of very high solubility, such as $CaCl_2$, one must either restrict the range of m (to $m \lesssim 5$, $I \lesssim 15$ for $CaCl_2$) or add higher virial coefficients to the series (refs. 16 and 17). Unless there is real interest in the range of very high concentration, the former procedure is preferable.

The remaining parameters θ_{ij} (for Φ_{ij}) and ψ_{ijk} can be evaluated from activity or osmotic coefficient data for common-ion mixtures. Thus, for $\theta_{Na,K}$ and $\psi_{Na,K,Cl}$ interaction one may measure the osmotic coefficient in NaCl-KCl solutions. The θ_{ij} parameter is independent of the ion of opposite charge. Thus, all data for Na^+-K^+ mixing are considered together (NaCl - KCl, $NaNO_3$ - KNO_3, Na_2SO_4 - K_2SO_4, etc.) to determine a single value of $\theta_{Na,K}$ and values of the various $\psi_{Na,K,Cl}$, ψ_{Na,K,NO_3}, etc. The solubility of a solid salt in a common-ion mixture depends on a ψ value, and the best values of ψ for many cases come from solubility data (refs. 18 and 19).

There are extensive tables of parameters for 298 K which have been tested for solubility calculations; values of $\mu°/RT$ for solids and for ions in their standard states are also included. Since these are in conveniently available sources (refs. 18 and 19), they will not be listed in full here. Tables 1-4 contain the values at 298 K for certain cases (refs. 20-24) where there are data over a wide range of temperature.

TABLE 1. Values of $\beta_{MX}^{(0)}$ for various temperatures

	25°	50°	100°	150°	200°	250°	300°C
			1:1 Electrolytes				
HCl[a]	0.1775	0.1690	0.1509	0.2117	0.5235		
LiCl[b]	0.1485	0.1446	0.1369	0.1291	0.1214	0.1137	
NaCl[c]	0.0754	0.0892	0.1002	0.1000	0.0938	0.0848	0.0768
NaI[a]	0.1195	0.1353	0.1559	0.1757	0.1790		
NaOH[d]	0.0864	0.0943	0.0827	0.0640	0.0543	0.0520	0.0476
KCl[b]	0.0481	0.0593	0.0695	0.0718	0.0707	0.0674	
CsF[a]	0.1306	0.1294	0.1197	0.1061	0.0689		
CsCl[b]	0.0335	0.0467	0.0576	0.0609	0.0624	0.0630	
CsI[a]	0.0244	0.0415	0.0567	0.0625	0.0348		
			1:2 or 2:1 Electrolytes				
Li_2SO_4	0.1308	0.1398	0.1445	0.1356	0.1157	0.0868[e]	
Na_2SO_4	0.0181	0.0629	0.1029	0.1227	0.1338	0.0929[e]	
K_2SO_4	0.0000	0.0277	0.0682	0.1124	0.1743	0.2596[e]	
Cs_2SO_4	0.0804	0.0936	0.1273	0.1381	0.1497	0.1656[e]	
$MgCl_2$	0.3509	0.3442	0.3242	0.3094	0.3191[f]		
$CaCl_2$	0.3053	0.3067	0.3024	0.2922	0.2547[f]		
$SrCl_2$	0.2834	0.2956	0.2993	0.2975	0.3070[f]		

[a] Saluja et al., ref. 20.
[b] Holmes and Mesmer, ref. 21.
[c] Pitzer et al., ref. 22.
[d] Pabalan and Pitzer, ref. 23.
[e] Holmes and Mesmer, ref. 11.
[f] Phutela et al., ref. 24.

TABLE 2. Values of $\beta_{MX}^{(1)}$ for various temperatures; see Table 1 for references

	25°	50°	100°	150°	200°	250°	300°C
			1:1 Electrolytes				
HCl	0.2945	0.2978	0.3030	0.3070	0.3102		
LiCl	0.3070	0.3229	0.3547	0.3865	0.4183	0.4501	
NaCl	0.2770	0.2967	0.3326	0.3726	0.4175	0.4667	0.5192
NaI	0.3439	0.3630	0.3935	0.4168	0.4352		
NaOH	0.2530	0.3022	0.3985	0.5036	0.5886	0.6078	0.5132
KCl	0.2187	0.2494	0.3042	0.3592	0.4149	0.4705	
CsF	0.2570	0.2708	0.2928	0.3096	0.3228		
CsCl	0.0429	0.0854	0.1665	0.2438	0.3186	0.3916	
CsI	0.0262	0.1064	0.2346	0.3324	0.4096		
			1:2 or 2:1 Electrolytes				
Li_2SO_4	1.2913	1.3212	1.3679	1.6383	2.4707	4.5383	
Na_2SO_4	1.0559	1.1708	1.3421	1.5710	2.0773	3.6887	
K_2SO_4	1.1023	1.2578	1.4637	1.6415	1.8578	2.1511	
Cs_2SO_4	1.3660	1.4783	1.5140	2.1072	3.0920	5.8923	
$MgCl_2$	1.651	1.735	1.989	2.294	2.503		
$CaCl_2$	1.708	1.806	2.049	2.351	2.706		
$SrCl_2$	1.626	1.702	1.910	2.233	2.701		

Parameters for high temperatures

Parameters for other temperatures can be obtained by either of two methods or by a least-squares optimization of the results of both methods. One approach involves the same type of measurements as were made at 25°C to obtain osmotic or activity coefficients. Freezing point measurements often yield especially precise osmotic coefficients for 0°C. Vapor pressure measurements have been used to temperatures of 350°C (refs. 25-27), and once vapor pressures are established for reference substances, isopiestic measurements are effective (refs. 11 and 21). These sources of osmotic coefficients at high temperatures are excellent for concentrated solutions but often lack precision for dilute solutions.

The other general method involves calorimetric measurements of heats of dilution and of mixing and heat capacities. This information gives the temperature derivatives of the various parameters and the expressions can then be integrated from 298 K to the temperature of interest. As a test, the parameters for Na_2SO_4 were determined by use of heat capacity data up to 473 K together with heats of dilution and other data at 298 K (ref. 28). Comparison with high-temperature osmotic-coefficient data was reasonably satisfactory, but a better set of parameters was derived from fitting to the combined set of all data.

There are now an extensive array of data for the most important aqueous solutes extending upward in temperature. Where the second temperature derivatives are given by accurate heat capacity measurements, extrapolation of the parent parameters should be valid to considerably higher temperatures. Tables 1-4 summarize these results and the pertinent references. Thus, one can now calculate the chemical potential of water (ref. 29) and of various solute species for a variety of mixed electrolytes of great complexity over a wide range of temperature.

TABLE 3. Values of C_{MX} at various temperatures; see Table 1 for references

	25°	50°	100°	150°	200°	250°	300°C
			1:1 Electrolytes				
HCl	4.00×10^{-4}	1.12×10^{-3}	2.26×10^{-3}	3.14×10^{-3}	3.83×10^{-3}		
LiCl	1.86×10^{-3}	1.29×10^{-3}	3.75×10^{-4}	-3.51×10^{-4}	-9.48×10^{-4}	1.46×10^{-3}	
NaCl	0.70×10^{-3}	-0.40×10^{-3}	-1.65×10^{-3}	-2.24×10^{-3}	-2.42×10^{-3}	-2.32×10^{-3}	-1.95×10^{-3}
NaI	9.00×10^{-4}	-6.18×10^{-5}	-1.60×10^{-3}	-2.77×10^{-3}	-3.70×10^{-3}		
NaOH	2.05×10^{-3}	9.54×10^{-4}	6.15×10^{-5}	-1.82×10^{-4}	-4.38×10^{-4}	-7.19×10^{-4}	-6.71×10^{-4}
KCl	-3.94×10^{-4}	-1.00×10^{-3}	-1.56×10^{-3}	-1.72×10^{-3}	-1.72×10^{-3}	-1.58×10^{-3}	
CsF	-2.15×10^{-3}				-2.15×10^{-3}		
CsCl	-1.31×10^{-4}	-7.05×10^{-4}	-1.14×10^{-3}	-1.25×10^{-3}	-1.28×10^{-3}	-1.20×10^{-3}	
CsI	-1.82×10^{-3}				1.82×10^{-3}		
			1:2 or 2:1 Electrolytes				
Li_2SO_4	-8.94×10^{-4}	-2.75×10^{-3}	-5.06×10^{-3}	-5.43×10^{-3}	-4.24×10^{-3}	-1.75×10^{-3}	
Na_2SO_4	2.02×10^{-3}	-1.07×10^{-3}	-4.05×10^{-3}	-6.01×10^{-3}	-6.32×10^{-3}	-3.03×10^{-3}	
K_2SO_4	6.65×10^{-3}	6.17×10^{-3}	2.87×10^{-3}	-2.62×10^{-3}	-9.60×10^{-3}	-1.76×10^{-2}	
Cs_2SO_4	-9.66×10^{-4}	-1.37×10^{-3}	-2.02×10^{-3}	-2.52×10^{-3}	-2.91×10^{-3}	-3.23×10^{-3}	
$MgCl_2$	2.301×10^{-3}	9.558×10^{-4}	-1.193×10^{-3}	-2.834×10^{-3}	-4.128×10^{-4}		
$CaCl_2$	7.61×10^{-4}	-3.353×10^{-4}	-2.088×10^{-3}	-3.426×10^{-3}	-4.481×10^{-3}		
$SrCl_2$	-3.15×10^{-4}				-3.15×10^{-4}		

TABLE 4. Pitzer parameters for $MgSO_4$(aq) at various temperatures[a]

Parameter	25°	50°	100°	150°	200°
$\beta^{(0)}$	0.2150	0.2275	0.2491	0.2862	0.3795
$\beta^{(1)}$	3.3636	3.6130	4.0980	4.8046	5.9123
$10^{-2} \times \beta^{(2)}$	-0.3274	-0.4021	-0.7237	-0.13910	-2.5558
$10^{3} \times C$	6.993	4.939	0.727	-3.688	-11.783

[a] Phutela and Pitzer, ref. 13.

Pressure effects

The effect of pressure on the chemical potential is given by the molar or partial molar volume and can be determined from density data. For moderate pressures, these effects are usually small but can be significant. Thus, the pressure dependency of the various parameters for solution properties are of interest and have been determined for a number of solutes. As an example, the changes in the parameters from saturation pressure to 1 kbar (100 MPa) for NaCl(aq) are given in Table 5 (ref. 22). Equivalent information for other solutes is given in references 20, 23, 24.

TABLE 5. Pressure dependence of the parameters related to the chemical potential of H_2O and NaCl(aq). The entries are the value at 1 kbar less that at saturation pressure[a]

	25°	50°	100°	150°	200°	250°	300°C
(μ_1°/RT)	0.7132	0.6643	0.5921	0.5410	0.5031	0.4727	0.4453
(μ_2°/RT)	0.745	0.718	0.587	0.387	0.126	-0.225	-0.764
A_ϕ	-0.0171	-0.0195	-0.0276	-0.0420	-0.0684	-0.1197	-0.2339
$\beta^{(0)}$	0.0102	0.0050	0.0022	0.0030	0.0031	-0.0025	-0.0226
10^3C	-0.64	-0.24	-0.03	-0.02	0.13	0.56	1.45

[a] The pressure dependence of $\beta^{(1)}$ is zero; values from ref. 22.

SOLUBILITIES IN AQUEOUS ELECTROLYTES

The solubility of a solid in a mixed aqueous electrolyte can be calculated by minimizing the Gibbs energy or by setting the chemical potential of the solid equal to that for the same material in solution, equation (8). Both methods are iterative; an initial solution composition is assumed and then improved in successive approximations until the criteria are satisfied within acceptable limits of precision. There are various mathematical methods for this calculation (refs. 18,30); they will not be discussed in detail here.

Calculations for 298.15 K

Harvie and Weare (ref. 18) demonstrated the effectiveness of these methods by a remarkable series of calculations of solubilities of all possible salts related to the seawater system Na-K-Mg-Cl-SO_4-H_2O. A fixed point in this system involves four solids and there are 13 such fixed points, all of which have measured carefully (ref. 31). Table 6 compares the predicted and observed compositions of the solutions at each of these fixed points (the unstated molality of Cl^- is determined from electrical neutrality). The agreement is remarkably good throughout and is probably within experimental error. Harvie and Weare (ref. 18) present in addition a number of solubility calculations for other systems; one is for $CaSO_4$ solubility in NaCl - Na_2SO_4 solutions. Figure 1 shows two of these comparisons which indicate excellent agreement for the present solution equations and poor agreement for earlier methods (refs. 32-34).

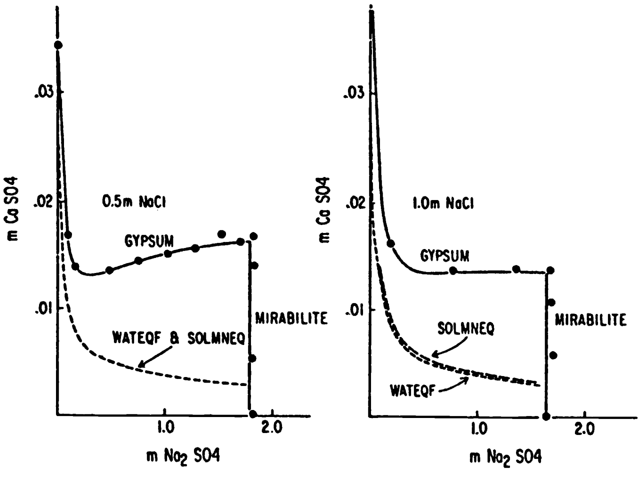

Fig. 1. Calculated mineral solubilities (solid curves) in the Ca-Na-Cl-SO_4-H_2O reciprocal system compared to the experimental points (at 25°C). The dashed curves show the calculated values from previous models.

TABLE 6. Invarient points for the system Na-K-Mg-Cl-SO_4-H_2O. Calculated values from ref. 18 above; experimental values below and in parentheses from ref. 31

m_{Na}	m_K	m_{Mg}	m_{SO_4}	Solid Phases
2.62 (2.69)	1.63 (1.58)	2.08 (1.97)	.84 (.78)	Halite + Sylvite + Glaserite + Schoenite
2.52 (2.41)	1.59 (1.51)	2.16 (2.19)	.84 (.78)	Halite + Leonite + Sylvite + Schoenite
1.16 (1.31)	1.01 (1.10)	3.40 (3.17)	.86 (.79)	Halite + Sylvite + Leonite + Kainite
.48 (.49)	.57 (.64)	4.21 (4.05)	.32 (.29)	Halite + Sylvite + Carnallite + Kainite
.30 (.26)	.22 (.20)	4.75 (4.81)	.40 (.35)	Halite + Kieserite + Carnallite + Kainite
5.20 (5.32)	1.04 (.90)	.95 (.89)	1.31 (1.24)	Halite + Thenardite + Glaserite + Bloedite
3.08 (3.21)	1.31 (1.30)	2.00 (1.85)	1.14 (1.06)	Halite + Glaserite + Gloedite + Schoenite
2.49 (2.96)	1.18 (1.22)	2.40 (2.01)	1.11 (1.05)	Halite + Bloedite + Schoenite + Leonite
1.43 (1.25)	.85 (.72)	3.31 (3.46)	1.14 (1.10)	Halite + Epsomite + Bloedite + Leonite
1.16 (1.18)	.85 (.75)	3.51 (3.54)	1.03 (1.04)	Halite + Epsomite + Leonite + Kainite
.76 (.66)	.50 (.68)	3.95 (4.01)	.81 (.79)	Halite + Kainite + Hexahydrite + Epsomite
.40 (.33)	.23 (.32)	4.57 (4.63)	.59 (.45)	Halite + Kainite + Hexahydrite + Kieserite
.09 (.07)	.02 (.02)	5.74 (5.83)	.06 (.05)	Halite + Bischofite + Kieserite + Carnallite

Harvie et al (ref. 19) have considered the even more complex system Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O with comparable success. In this extended system, however, it is necessary to consider the dissociation equilibria of water and carbonic acid in addition to the solubility of the various solids.

Calculations for high temperatures

There are several published calculations related to the solubility of NaCl in H_2O to 300°C (ref. 22), of NaCl and KCl in aqueous mixtures to 200°C (ref. 35) and of NaCl and Na_2SO_4 in aqueous mixtures to 350°C and of NaCl and $MgCl_2$ in aqueous mixtures to 200°C (ref. 36). These calculations were made by the simple method of calculating activity coefficients for the known composition of the saturated solution both (1) from solution parameters and (2) from the thermodynamics of the solid and the standard-state properties of the solute. The comparison of the two values tests the solution equations and indicates whether a calculation of the solubility would have yielded agreement. This calculation requires no iteration, but it is not a true solubility calculation. The agreement was good throughout the range of expected accuracy of the solution model and indicated for NaCl - Na_2SO_4 that the sodium sulfate parameters could be extrapolated from 200 to 300°C with useful results but that there were substantial departures at 350°C.

An especially demanding case at high temperature is that of a 2-2 electrolyte where there is increasing electrostatic ion-pairing as the temperature rises. Figure 2 compares the calculated and experimental solubilities of $MgSO_4 \cdot 7H_2O$, $MgSO_4 \cdot 6H_2O$, and $MgSO_4 \cdot H_2O$ in their respective ranges of stability up to 200°C. The chemical potential of each solid was adjusted slightly to fit the solubility at the lowest temperature. But the heat capacity and either the entropy or enthalpy (whichever is more accurately known, refs. 4,5,37) were determined from measurements on the solid and were independent of the solubility. Thus the temperature dependence was predicted in each case. The agreement gives strong confirmation of the equation for the chemical potentials of the solution (ref. 13).

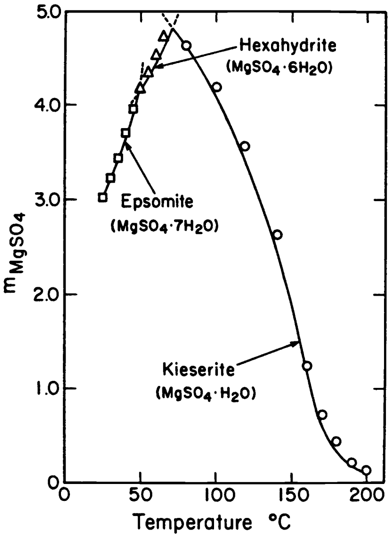

Fig. 2. Calculated solubilities of $MgSO_4$ compared with experimental values for various hydrated solids as a function of temperature.

OTHER TYPES OF SOLUBILITY SYSTEMS

One can consider as a solubility any equilibrium of a component between two or more phases. The pertinent theory is just that of the activity or the chemical potential of each species in each phase.

Gases

For solubilities in low-pressure gases one can assume the ideal gas law or, at somewhat higher pressures, add the effect of the second virial coefficients. But at high gas densities and with strong interactions, higher order terms become significant.

An interesting case is the solubility of solid NaCl in high-pressure steam (ref. 38). In this case the NaCl is almost all in the ion-pair form in the gas, but virial coefficients involving several water molecules interacting with one NaCl must be included. The primary effect is attractive; hence, one may think of this virial series as a set of successive hydration equilibria:

$$NaCl(H_2O)_{j-1} + H_2O = NaCl(H_2O)_j \qquad (34)$$

Strictly, there are repulsive effects which also enter the exact equations for the virial coefficients. Once the virial coefficients and their temperature derivatives have been determined, the solubility of NaCl in steam can be calculated over a wide range of conditions.

Nonionic liquids

There is a very extensive literature concerning the chemical potential or activity of each component in a liquid mixture of neutral molecules. If a wide composition range is to be covered, mole fractions are the appropriate measures of composition. The ideal solution equation can be derived from a simple model which is valid, however, in a very limited range of real systems. But the ideal mixing terms usually arise as the leading terms in more complex theories. Wohl (ref. 39) has discussed purely thermodynamic expansions in increasing powers of mole fraction. There are also many theories derived statistically from various potential models. Prausnitz (ref. 40) and Rowlinson (ref. 41) present excellent reviews of these theories.

Solid solutions

A very important area is that of solid solutions. Most intermetallic systems have solids of variable composition as do many silicates and other minerals. There is an extensive and rapidly advancing body of theory for the chemical potentials of the components of such solids. The details depend on the particular crystal structure in each case, the assumed pattern of substitution at particular lattice sites, and the types and locations of vacancies. But in any case, one considers the configurational entropy related to random rearrangements at each type of site and the energy for each nearest neighbor interaction. Possible refinements include more distant energy interactions and the effect on the entropy of nonrandomness of distributions. An excellent example of this type of analysis is that of Chang and Neumann (ref. 42) for the intermetallic phases with the B2(CsCl) structure. They calculate the activities and enthalpies of about 30 systems with excellent agreement with experimental data. A typical example is AuCd at 700 K over the range 43 to 56 mole%Cd; the model involved two empirically adjusted parameters. The activity of cadmium was measured by the solubility of the vapor in the solid (ref. 43), although electrochemical cell measurements were also reported (ref. 44) and gave higher precision.

A different type of nonstoichiometric system is that of CeO_{2-x} in which x ranges from 0 to 0.33 and data extend from 900 to 1800 K. The measured quantity is the solubility of oxygen in the solid (ref. 45). Below 950 K the solid solution system shows a miscibility gap near x = 0.1 which is reproduced by the model (ref. 46). The model also yields calculated oxygen pressures in good agreement with experiment over the entire range of x and T. In this case the model is essentially the same as is widely used for nonelectrolyte liquid solutions (ref. 39); it can be regarded as a model for the mixing of oxygen atoms and vacancies on a single set of sites and would be applicable without regard to the particular lattice structure. In fact, however, the cerium is present as +3 or +4 ions and their respective locations must be related to the vacancies.

Many silicates and other minerals are nonstoichiometric and there are model calculations of chemical potentials for these systems (ref. 47). The equations used in many of these cases is either the simple regular solution (van Laar) equation or an extension of the Wohl type (ref. 39).

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REFERENCES

1. K. S. Pitzer, Theory: Ion Interaction Approach, Chapter 7 in Activity Coefficients in Electrolyte Solutions, R. M. Pytkowicz, Ed., CRC Press, Boca Raton, FL 1979.
2. K. S. Pitzer and J. J. Kim, J. Phys. Chem. 96, 5701-5707 (1974).
3. D. R. Stull and H. Prophet, Natl. Stand. Ref. Data Ser. (U. S. Natl. Bur. Stand.) NSRDS-NBS 37 (1971).
4. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, The NBS Tables of Chemical Thermodynamic Properties, J. Phys. Chem. Ref. Data, 11, Suppl. 2 (1982).
5. R. A. Robie, B. S. Hemingway, and J. R. Fischer, Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar Pressure and at High Temperature, USGS Bulletin 1452 (1978).
6. W. G. McMillan and J. E. Mayer, J. Chem. Phys. 13, 276-305 (1945).
7. J. E. Mayer, J. Chem. Phys. 18, 1426-2436 (1959).
8. K. S. Pitzer, J. Phys. Chem. 77, 268-277 (1973).
9. R. C. Phutela and K. S. Pitzer, J. Solution Chem. 15, 649-662 (1986).
10. K. S. Pitzer and G. Mayorga, J. Phys. Chem. 77, 2300-2308 (1973).
11. H. F. Holmes and R. E. Mesmer, J. Solution Chem. 15, 495-518 (1986).
12. K. S. Pitzer and G. Mayorga, J. Solution Chem. 3, 539-546 (1974).
13. R. C. Phutela and K. S. Pitzer, J. Phys. Chem. 90, 895-901 (1986).
14. K. S. Pitzer, J. Solution Chem. 4, 249-265 (1975).
15. K. S. Pitzer, J. Phys. Chem. 87, 2360-2368 (1983).
16. R. C. Phutela and K. S. Pitzer, J. Solution Chem. 12, 201-207 (1983).
17. J. Ananthaswamy and G. Atkinson, J. Chem. Engr. Data, 30, 120-128 (1985).
18. C. E. Harvie and J. H. Weare, Geochim. Cosmochim. Acta, 44, 981-997 (1980).
19. C. E. Harvie, N. Moller, and J. H. Weare, Geochim. Cosmochim. Acta, 48, 723-751 (1984).
20. P. P. S. Saluja, K. S. Pitzer, and R. C. Phutela, Can. J. Chem. 64, 1328-1335 (1986).
21. R. F. Holmes and R. E. Mesmer, J. Phys. Chem. 87, 1242-1255 (1983).
22. K. S. Pitzer, J. C. Peiper, and R. H. Busey, J. Phys. Chem. Ref. Data, 13, 1-102 (1984).
23. R. T. Pabalan and K. S. Pitzer, Geochim. Cosmochim. Acta, submitted.
24. R. C. Phutela, K. S. Pitzer, and P. P. S. Saluja, J. Chem. Engr. Data, in press.
25. C. Liu and W. T. Lindsay, Jr., J. Phys. Chem. 74, 341-356 (1970).
26. C. Liu and W. T. Lindsay, Jr., J. Solution Chem. 1, 45-69 (1972).
27. S. A. Wood, D. A. Crerar, S. L. Brantley, and M. Borcsik, Am. J. Sci. 284, 668-705 (1984).
28. P. S. Z. Rogers and K. S. Pitzer, J. Phys. Chem. 85, 2886-2895 (1981).
29. L. Haar, J. S. Gallagher, and G. S. Kell, NBS-NRC Steam Tables, Hemisphere, Washington (1984).

30. P. E. Gill and W. Murray, Numerical Methods for Constrained Optimization, Academic Press, 1974.
31. O. Braitsch, Salt Deposits: Their Origin and Composition, Springer-Verlag, 1971.
32. J. Block and D. B. Waters, Jr., J. Chem. Engr. Data, 13, 336-344 (1968).
33. A. H. Truesdell and B. F. Jones, J. Res. U. S. Geol. Surv. 2, 233-248 (1974).
34. Y. K. Kharaka and I. Barnes, SOLMNEQ: Solution-Mineral Equilibrium Computations. U. S. Geol. Surv., Menlo Park, CA, 1973.
35. M. C. P. de Lima and K. S. Pitzer, J. Solution Chem. 12, 171-185 (1983).
36. M. C. P. de Lima and K. S. Pitzer, J. Solution Chem. 12, 187-199 (1983).
37. H. C. Ko and G. E. Daut, U. S. Bureau of Mines, R.I. 8409, 1979.
38. K. S. Pitzer and R. T. Pabalan, Geochim. Cosmochim. Acta, 50, in press.
39. K. Wohl, Trans. Am. Inst. Chem. Engrs. 42, 215-249 (1946); Chem. Engr. Progress, 49, 218-219 (1953).
40. J. M. Prausnitz, R. N. Lichtenthaler, and E. G. de Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ, 1986.
41. J. S. Rowlinson and F. L. Swinton, Liquids and Liquid Mixtures, 3rd ed., Butterworths, London, 1982.
42. Y. A. Chang and J. P. Neumann, Prog. Solid State Chem. 14, 221-302 (1982).
43. L. J. Bartha and W. A. Alexander, Can. J. Chem. 43, 2319-2327 (1965).
44. K. L. Komarek, E. Reiffenstein, and G. Stummerer, Monatsch Chem. 104, 1570-1585 (1973).
45. J. Campserveaux and P. Gerdanian, J. Solid State Chem. 23, 73-92 (1978).
46. T. B. Lindemer, CALPHAD, 10, 129-136 (1986).
47. J. Grover, Chemical Mixing in Multicomponent Solutions, Chapter 5 of Thermodynamics in Geology, D. G. Fraser, ed., D. Reidel, Dordrecht-Holland, 1977.