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Estimation of Phase Diagrams and Solubilities for Aqueous Multi-ion Systems

C. L. KUSIK

Arthur D. Little, Inc.
Cambridge, Massachusetts

H. P. MEISSNER

Massachusetts Institute of Technology
Cambridge, Massachusetts

and

E. L. FIELD

Arthur D. Little, Inc.
Cambridge, Massachusetts

Calculation of the phase diagram for saturated aqueous multi-ion solutions of strong electrolytes, based upon use of the thermodynamic solubility products, is illustrated for the four-ion system: Na^+, K^+, Mg^{++}, $SO_4^=$. Solid phases are identified along with the ion concentrations of the associated saturated solutions.

SCOPE

Solubility information for strong electrolytes in aqueous solutions containing several ions is often desired, such as

when producing sodium hydroxide by reacting a sodium carbonate solution with lime, evaporating a natural brine containing various alkali and alkaline earth chlorides and sulfates to precipitate individual salts, calculating the vapor pressure of dissolved hydrochloric acid over a

chloride based pickle liquor, etc. Experience has shown that electrolyte activity coefficients in aqueous solution vary widely not only as a function of ionic strength and temperature, but also with solution composition. Estimation of activity coefficients has proved to be difficult, resulting in limited application of the solubility product concept to determine when a concentrated solution becomes saturated in one or more salts. For complex systems like these, the object here is to describe and illustrate a technique of developing thermodynamic solubility products and suitable isothermal solubility diagrams where only limited solubility data exist.

CONCLUSIONS AND SIGNIFICANCE

Using activity coefficient data readily available in the literature for solutions of single electrolytes, a method is presented for calculating solubility limits of multicomponent solutions from 0° to 200°C or higher and for determining the stable solid phase(s), which may be simple or double salts. Application of the equations developed to the magnesium-potassium-sodium-sulfate system at 35°C shows relatively good agreement between calculated and experimentally determined values.

SOLUTION CHARACTERIZATION

Regardless of the number of ions present, the composition of an electrolyte solution can be characterized in a variety of ways, including the equivalents of each ion present per 1 000 g of water, designated as E_{Na}, E_{Cl}, etc., or the moles of each ion present per 1 000 g of water (the molality), designated as m_{Na}, m_{Cl}, etc. Obviously, for a monovalent ion like sodium, $E_{Na} = m_{Na}$; for a divalent ion like magnesium, $E_{Mg} = 2m_{Mg}$; and for a trivalent ion like aluminum, $E_{Al} = 3m_{Al}$. Composition can also be characterized in terms of W and f, respectively, the moles of water per total equivalent of electrolyte in solution and the so called cationic and anionic equivalent fractions. Thus in a solution containing the ions Na^+, K^+, Mg^{++}, Cl^-, and SO_4^{--}, the sodium cationic equivalent fraction equals $E_{Na}/(E_{Na} + E_K + E_{Mg})$, the chloride anionic equivalent fraction equals $E_{Cl}/(E_{Cl} + E_{SO_4})$, etc. These ion fractions are especially suitable for use with composition diagrams such as the triangle of Figure 1. Obviously W equals $(1 000/18)/$

Fig. 1. Phase diagram for the system H_2O — Na^+ — K^+ — Mg^{++} — $SO_4^=$. Composition (dry basis) of saturated solutions and their equilibrium solid phases at 35°C.

$(E_{Na} + E_K + E_{Mg})$, and to preserve electrolyte neutrality also equals $(1 000/18)/(E_{Cl} + E_{SO_4})$.

If water is removed from a given unsaturated solution, initially containing 1 000 g water, then f its electrolyte composition on a dry basis remains unchanged, providing no electrolyte precipitation or volatilization occurs. Thus, consider a solution initially containing 1 000 g water, with ion equivalents as follows: $E^o{}_{Na}$, $E^o{}_{Mg}$, $E^o{}_{Cl}$, etc. Upon evaporating water, so that the initial 1 000 g present in the solution is reduced to X g, the corresponding ion equivalents become

$$E_{Na} = \frac{1\ 000\ E^o{}_{Na}}{X}$$

$$E_{Mg} = \frac{1\ 000\ E^o{}_{Mg}}{X}, \text{ etc.}$$

SOLUBILITY PRODUCT EXPRESSIONS

At any fixed temperature, the value of the thermodynamic solubility product of a strong electrolyte is numerically the same in all its saturated solutions, regardless of number and concentration of other ions present in these solutions. This generalization applies not only to salts of low solubility like silver chloride for which actual mean ionic activity coefficients are close to unity but also to salts of considerably higher solubility like potassium sulfate for which γ values are very different from unity. Similarly, it applies to hydrated salts and to double salts. The derivations and form of the solubility product (here called the thermodynamic solubility product to emphasize that a true constant is involved) has been discussed in other work (Meissner and Kusik, 1973, 1979), with examples shown in Table 1 for various types of electrolytes.

In these solubility product ·expressions, the mean ionic activity coefficients in the various two-ion and multi-ion solutions involved are calculated by the earlier published methods (Meissner and Tester, 1972; Meissner et al., 1972; Kusik and Meissner, 1978). It will be noted that each solubility product is always expressed here per gram equivalent of electrolyte. This basis is chosen because it simplifies the graphical presentation of solubility data on triangular and on a Janecke type of diagrams.

It is obvious that the expression $(K_{sp})_{thermo}$ is really the electrolyte activity in saturated solution (Meissner
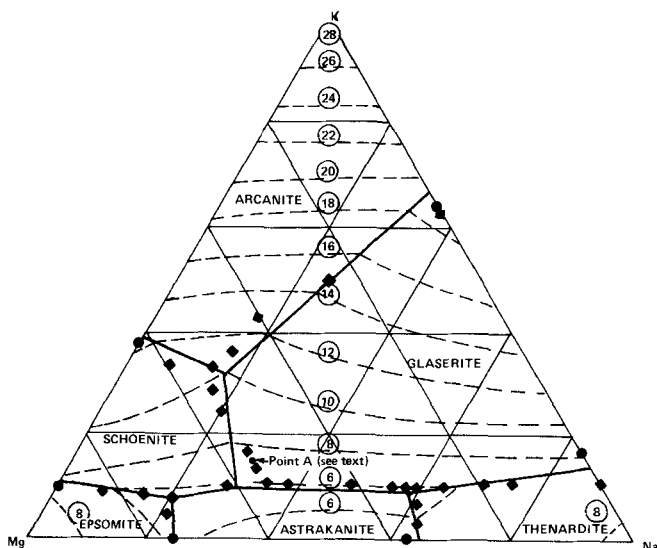
TABLE 1. EXAMPLES OF SOLUBILITY PRODUCT FORMULAS ON AN EQUIVALENT BASIS*

Electrolyte Type	Example	Algebraic form of electrolyte activity a_e or thermodynamic solubility product $(K_{sp})_{thermo}$
1:1	KBr	$m_K m_{Br} \gamma_{KBr}$
1:2	0.5(Na₂SO₄·10H₂O)	$m_{Na}^{0.5} m_{SO_4}^{1.5} \gamma_{Na_2SO_4}^{5} a_w$
2:1	0.5(FeCl₂·4H₂O)	$m_{Fe}^{0.5} m_{Cl}^{1.5} \gamma_{FeCl_2}^{2} a_w$
2:2	0.5(MgSO₄·6H₂O)	$m_{Mg}^{0.5} m_{SO_4}^{0.5} \gamma_{MgSO_4}^{3} a_w$
3:2	0.167(Al₂(SO₄)₃·6H₂O)	$m_{Al}^{0.33} m_{SO_4}^{0.5} \gamma_{Al_2(SO_4)_3}^{0.83} a_w$
Double salt	0.25(Na₂Mg(SO₄)₂·4H₂O)	$m_{Na}^{0.5} m_{Mg}^{0.25} m_{SO_4}^{0.5} \gamma_{Na_2SO_4}^{0.75} \gamma_{MgSO_4}^{0.5} a_\omega$

* All formulas are expressed on a basis of 1 g equivalent of anions or cations.

and Kusik, 1979). If the solution under study at a specified temperature is less than saturated, then the electrolyte activity a_e is numerically smaller than $(K_{sp})_{thermo}$, while if the solution is supersaturated, then a_e is greater than $(K_{sp})_{thermo}$. A solution is saturated with any given electrolyte at a specified temperature only when a_e and $(K_{sp})_{thermo}$ are numerically equal.

PHASE DIAGRAM

The techniques used here are generally applicable to any multi-ion systems. The following example is for a solution containing the four ions: Na^+, K^+, Mg^{++}, and $SO_4^=$. Such a system, with three cations and one anion, can readily be represented on a triangular diagram (Meissner, 1971). Thus, any solution of the three salts sodium sulfate, potassium sulfate, and magnesium sulfate can be represented by a point on the triangle of Figure 1. Consider a solution at 35˚C made by adding X g of water to the following 1 g equivalent of salt mix: 0.15 g equivalent of potassium sulfate, 0.3 g equivalent of sodium sulfate, and 0.55 g equivalent of magnesium sulfate. As a result, E_{Na} is $(0.3)(1\,000)/X$; E_{Mg} is $(0.55)(1\,000)/X$, E_K is $(0.15)(1\,000)/X$. The potassium cation equivalent fraction f_K is then $0.15/(0.15 + 0.3 + 0.55)$ or 0.15, while the cation equivalent fractions for Na^+ and Mg^{++} similarly are 0.30 and 0.55. This mixture is located as point A on Figure 1. The value of f_{SO_4} in this solution is obviously unity.

The possible solid phases which might precipitate from this solution at 35°C, depending upon its composition, are known to be thenardite, astrakanite, epsomite, schoenite, arcanite, and glaserite, with the chemical compositions listed in Table 2. The numerical values of $(K_{sp})_{thermo}$ shown in Table 2 are averages calculated from the various experimental data points of D'Ans (1933) and Bayliss (1947) by the methods already referred to. These data points, plotted on Figure 1, are all for solutions at 35°C saturated with two of the various solid salts mentioned above. Also plotted on Figure 1 as solid lines are the phase boundaries calculated as described below from the averaged values of $(K_{sp})_{thermo}$. Lines of constant water content (W) are also presented. The method of locating these lines is now discussed.

CALCULATION OF BOUNDARY LINES

For any point on this diagram, two calculations are made:

1. Determining the moles of water (W) per equivalent of total salt in the saturated solution.
2. Determining the solid phase (or phases) with which the solution is saturated at this point.

Both calculations are made here for the arbitrarily chosen point A on Figure 1. An initial and relatively large trial value of X is first assumed, and the values of a_e for each of the six possible salts which might precipitate are calculated to verify that in no case is the corresponding value of $(K_{sp})_{thermo}$ exceeded. The solution at point A, containing X moles of water, is therefore shown to be less than saturated. (Obviously, calculation of these a_e values involves determining the ionic strength, a_w and the γ

TABLE 2. VALUES USED FOR THERMODYNAMIC SOLUBILITY PRODUCT
For Na-K-Mg-SO₄ System at 35°C

Species	Chemical formula*	Algebraic form for both a_e and $(K_{sp})_{thermo}$	K_{sp} activity of electrolyte at saturation
Epsomite	0.5 MgSO₄·7H₂O	$m_{Mg}^{0.5} m_{SO_4}^{0.5} \gamma_{MgSO_4}^{3.5} a_w$	0.109
Thenardite	0.5 Na₂SO₄	$m_{Na}^{0.5} m_{SO_4}^{1.5} \gamma_{NaSO_4}$	0.605
Arcanite	0.5 K₂SO₄	$m_K^{0.5} m_{SO_4}^{1.5} \gamma_{K_2SO_4}$	0.558
Schoenite	0.25[K₂Mg(SO₄)₂·6H₂O]	$m_K^{0.5} m_{Mg}^{0.25} m_{SO_4}^{0.5} \gamma_{K_2SO_4}^{0.75} \gamma_{MgSO_4}^{0.5} a_w^{1.5}$	0.104
Astrakanite	0.25[Na₂Mg(SO₄)₂·4H₂O]	$m_{Na}^{0.5} m_{Mg}^{0.25} m_{SO_4}^{0.5} \gamma_{Na_2SO_4}^{0.75} \gamma_{MgSO_4}^{0.5} a_w$	0.203
Glaserite	0.25[K₃Na(SO₄)₂]	$m_K^{0.75} m_{Na}^{0.25} m_{SO_4}^{0.5} \gamma_{K_2SO_4}^{9/8} \gamma_{Na_2SO_4}^{3/8}$	0.149

* Based on 1 g equivalent of anions or cations. Note that $(K_{sp})_{thermo}$ and a_e are numerically equal only for saturated solutions.

Solution A Contains: 0.15 equivalent K_2SO_4, 0.3 equivalent Na_2SO_4, 0.55 equivalent $MgSO_4$, and 128 grams water

Salt	$(K_{sp})_{thermo}$	a_e	$a_e/(K_{sp})_{thermo}$
		For solution A	
Epsomite	0.109	0.076	0.70
Thenardite	0.605	0.008	0.01
Arcanite	0.558	0.40	0.72
Schoenite	0.104	0.99	0.95
Astrakanite	0.203	0.15	0.74
Glaserite	0.149	0.149	1.0

values for each possible salt, using the techniques of the above-mentioned references.)

Increments of water are now successively removed from solution and the foregoing calculation repeated after each increment. New values of m, γ, a_w, and a_e are calculated after each increment, for each possible salt, as listed in Table 2. Eventually, a point is reached when the ratio $a_e/(K_{sp})_{thermo}$ is unity for one of these salts, indicating saturation, while remaining less than unity for all the other salts. For example, the first salt for which this ratio reaches unity for solution A is glaserite, when X equals 128, as shown in Table 3 which compares well with 125 g as interpolated from the experimental data of Bavliss (1947). Thus, the moles of water per equivalent of salt (W) for this solution is $(128/18)/(0.15 + 0.30 + 0.55) = 7.1$, and the saturating salt (only one in this case) is glaserite.

By the method just outlined, these calculations can be repeated for each of an arbitrary number of points scattered over the diagram. At each point, the identity of the saturating phase can be established. Occasionally, it will be found that, for an arbitrarily chosen point on the diagram, the ratio $a_e/(K_{sp})_{thermo}$ simultaneously becomes equal to unity for two or even three salts, indicating that the solution is saturated with these two or three salts simultaneously. Boundaries separating the stability fields for the various salts can thus be mapped as illustrated by the solid lines in Figure 1.

DISCUSSION

As shown by the agreement between the experimental points and the calculated lines, reasonable success has been attained in calculating the solubility diagram of Figure 1 from the solubility products for the six possible solids which might precipitate in different parts of this diagram. Boundaries separating a given salt solubility field are seen to have a large range in concentrations. For example, the glaserite-arcanite boundary ranges from 10 to 19 moles of water/equivalent of electrolyte. In making these calculations, errors in estimating water activities or ion activity coefficients in multicomponent solutions are generally within 10% with occasional values showing larger deviations (Meissner and Tester, 1972; Kusik and Meissner, 1973). Errors of this magnitude can significantly affect calculated values of $(K_{sp})_{thermo}$ especially for double salts which are in equilibrium only with mixed (multicomponent) solutions. It is sometimes found that a very small percentage change in the magnitude of $(K_{sp})_{thermo}$ can bring about a significant shift in the location of the boundary lines such as in Figure 1. Nevertheless, it is significant that single values of $(K_{sp})_{thermo}$ for each of these salts exist, from which a

phase diagram of the type shown in Figure 1 can be mapped.

Overall, we have found that calculations on water content can often be made with an accuracy of about 10 to 20%. Larger errors can be expected if the activity coefficients of electrolytes under consideration do not follow the generalized correlations developed (Meissner and Tester, 1972), or if solid solutions are known to exist.

NOTATION

a_e = activity of dissolved electrolyte which has an algebraic form identical to $(K_{sp})_{thermo}$ but which has a value that varies with solution concentration and composition

a_w = activity of water, mainly p/p^o, where p is the water vapor pressure over the solution and p^o is the water vapor pressure over pure water at the same temperature

E = ion gram equivalents present in solution for 1 000 g water, ion involved is identified by subscript

f = cationic or anionic equivalent fractions; in a system of Na^+, K^+, Mg^{++}, $SO_4^=$, NO_3^-, f_{Na} is $E_{Na}/(E_{Na} + E_K + E_{Mg})$, while f_{SO4} is $E_{SO4}/(E_{NO3} + E_{SO4})$

$(K_{sp})_{thermo}$ = thermodynamic solubility product at a given temperature with examples shown in Table 1

m = molality, gram moles (of the ion indicated by subscript) per 1 000 g water

W = moles water per total equivalents of cations or anions in a saturated solution

X = grams water in the system under consideration

γ = mean activity coefficient of the ion pair, indicated by subscript, in the solution under consideration

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