

# Supersaturation functions in binary solid solution–aqueous solution systems

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**Abstract**—In this paper, we present a brief review of the thermodynamic equilibrium of binary solid solution–aqueous solution (SS-AS) systems and derive an expression that allows us to evaluate the supersaturation or undersaturation of a given aqueous solution with respect to the whole range of solid compositions: the  $\delta(x)$  function. Such an expression is based on the two conditions that define the SS-AS thermodynamic equilibrium. The derivation of the new supersaturation function,  $\delta(x)$ , was made by considering in detail the compositional relationships between solid and aqueous phases. To represent the new formulation on Lippmann diagrams, we have defined a new thermodynamic concept: the “actual activity.” In addition, we show how our supersaturation function behaves for both ideal and subregular solid solutions. The behaviour and applicability of both the  $\delta(x)$  function and a previous supersaturation function,  $\beta(x)$ , defined by Prieto et al. (1993), is discussed.

## 1. INTRODUCTION

Crystallisation implies in most cases the formation of solids with more or less wide compositional ranges, i.e., solid solutions. On the Earth’s surface, the crystallisation of minerals from multicomponent aqueous solutions is one of the most ubiquitous processes. The study of the relationships between mineral and solution compositions can provide very valuable information about natural environments, contamination of soil and groundwaters, and global element cycles. Several studies have recently examined the thermodynamics of solid solution–aqueous solution (SS-AS) systems (Lippmann, 1980; Glynn and Reardon, 1990; Gamsjäger et al., 2000; Glynn, 2000), as well as the dissolution processes of solid solutions (Thorstenson and Plummer, 1977; Plummer and Busenberg, 1987; Königsberger et al., 1991; Kornicker et al., 1991; Felmy et al., 1993). Although these works constitute a fundamental basis for understanding SS-AS systems, they do not consider in depth an essential parameter: the supersaturation or undersaturation of the system with respect to the whole range of solid compositions. Supersaturation is a determining parameter in partitioning of major, minor, and trace components between solid and aqueous phases (Chernov, 1984) and other precipitation processes that take place far from equilibrium. Obviously, a precise knowledge of the mechanisms that control the distribution coefficient between solid and solution phases requires a rigorous expression for evaluating the supersaturation of an aqueous solution with respect to a solid of variable composition. The first attempt to evaluate supersaturation in SS-AS was made by Prieto et al. (1993), who proposed the so-called  $\beta(x)$  supersaturation function. The  $\beta(x)$  function has been demonstrated to be useful to interpret and predict a number of experimental findings (Prieto et al., 1993; Fernández-González et al., 1999; Pina et al., 2000; Astilleros et al., 2000). However, the derivation of the  $\beta(x)$  function is based on the so-called stoichiometric saturation concept (Thorstenson and Plummer, 1977; Glynn and

Reardon, 1990), which is a limiting equilibrium state that, in principle, can be applied only to congruent dissolution processes in certain SS-AS systems.

In this paper, we present a formulation for calculating supersaturations in binary SS-AS systems, which is directly based on the two conditions of thermodynamic equilibrium for such systems. The derivation of a new supersaturation function,  $\delta(x)$ , was conducted by considering in detail the compositional relationships between solid and aqueous phases. The new formulation is also consistent with the description of thermodynamic equilibrium in SS-AS systems and can be represented on Lippmann diagrams.

## 2. EQUILIBRIUM IN SS-AS SYSTEMS: THE LIPPMANN DESCRIPTION

Any supersaturation calculation requires information about equilibrium conditions. In the general case of an SS-AS system,  $(B,C)A-H_2O$ , these equilibrium conditions are

$$[B^+][A^-] = K_{BA}a_{BA} = K_{BA}X_{BA}\gamma_{BA}, \quad (1)$$

$$[C^+][A^-] = K_{CA}a_{CA} = K_{CA}X_{CA}\gamma_{CA}, \quad (2)$$

where  $[A^-]$ ,  $[B^+]$  and  $[C^+]$  are the activities of  $A^-$ ,  $B^+$  and  $C^+$  ions in the aqueous solution;  $K_{BA}$  and  $K_{CA}$  are the solubility products of the solid solution end-members;  $a_{BA}$  and  $a_{CA}$  are the activities of  $BA$  and  $CA$  in the solid;  $X_{BA}$  and  $X_{CA}$  are the molar fractions of  $BA$  and  $CA$  in the solid; and  $\gamma_{BA}$  and  $\gamma_{CA}$  are the solid phase activity coefficients.

Lippmann (1980) defined the total solubility product variable,  $\Sigma\Pi$ , as

$$\Sigma\Pi = [A^-]([B^+] + [C^+]). \quad (3)$$

At thermodynamic equilibrium, the value of  $\Sigma\Pi$  as a function of the solid solution composition is obtained by adding together Eqn. 1 and 2:

$$\Sigma\Pi_{\text{eq}} = K_{BA}a_{BA} + K_{CA}a_{CA}. \quad (4)$$

This is the expression of Lippmann’s solidus.

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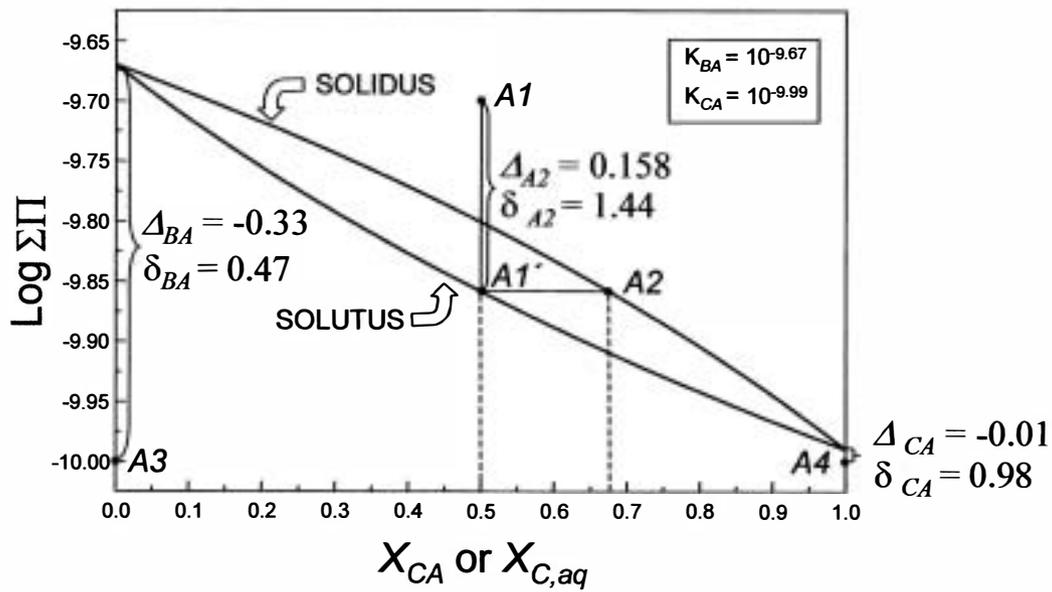


Fig. 1. Lippmann diagram for a hypothetical ideal solid solution–aqueous solution system. The solubility products of the end-members are  $K_{BA} = 10^{-9.67}$  and  $K_{CA} = 10^{-9.99}$ . Horizontal tie lines connecting solutus and solidus curves define equilibrium pairs. Point A1 represents an aqueous solution with composition  $[A^-] = [B^+] = [C^+] = 1 \times 10^{-5}$  mol/L. Point A2 gives the solid solution composition at equilibrium with an aqueous solution A1' with the same activity fraction as A1 but projected on solutus curve. Points A3 and A4 represent the log IAP (ionic activity product) values for components BA and CA in the A1 solution, respectively; i.e.,  $\log [A^-][B^+]$  and  $\log [A^-][C^+]$ . Supersaturation (or undersaturation) of the aqueous solution with respect to both the solid with A2 composition and the end-members of the solid solution is proportional to the vertical distances of points A1, A3, and A4 from the solutus, respectively. For the end-members,  $\delta_{BA} = 10^{\Delta_{BA}}$  and  $\delta_{CA} = 10^{\Delta_{CA}}$ .

In addition, the value of  $\Sigma\Pi$  at equilibrium as a function of the aqueous solution composition is given by

$$\Sigma\Pi_{\text{eq}} = \frac{1}{\frac{X_{B,\text{aq}}}{K_{BA}\gamma_{BA}} + \frac{X_{C,\text{aq}}}{K_{CA}\gamma_{CA}}}, \quad (5)$$

where  $X_{B,\text{aq}}$  and  $X_{C,\text{aq}}$  are the activity fractions in the aqueous phase, defined as

$$X_{B,\text{aq}} = \frac{[B^+]}{[B^+] + [C^+]}, \quad (6)$$

$$X_{C,\text{aq}} = \frac{[C^+]}{[B^+] + [C^+]}. \quad (7)$$

Eqn. 5 is Lippmann's solutus expression, whose derivation is carried out by simple arithmetic combination of Eqn. 1 and 2.

Lippmann's solidus and solutus curves can be plotted on a diagram, similar to phase diagrams used for binary-solid/binary-melt systems. However, in this case, the  $\Sigma\Pi_{\text{eq}}$  value must be plotted on the ordinate against two superimposed scales ( $X_{BA}$  and  $X_{B,\text{aq}}$ ) on the abscissa. Equilibrium compositions pairs are defined by horizontal tie lines connecting solutus and solidus curves. Figure 1 shows the Lippmann diagram for a hypothetical SS-AS system, assuming a thermodynamically ideal solid-solution series.

### 3. SUPERSATURATION IN BINARY SS-AS SYSTEMS: THE $\delta(x)$ FUNCTION

The Lippmann  $\Sigma\Pi$  formulation and Lippmann diagrams can be used not only to define and represent thermodynamic equilibrium states but also to describe the departure from such states, i.e., supersaturation or undersaturation. It is evident that for a given aqueous solution, there is only one solid solution composition to which the system will evolve as the final equilibrium state. A paper by Glynn et al. (1990) is devoted to predicting final thermodynamic states and pathways for initially supersaturated aqueous solutions by assuming that the compositions of both the nuclei and the successive growth layers are controlled by the aqueous solution composition and the equilibrium distribution coefficient. However, sometimes it is necessary to consider not only the composition of the final thermodynamically stable phase but also the composition of the first nuclei (Prieto et al., 1993; Fernández-González et al., 1999; Pina et al., 2000). For this purpose, we need to define a suitable expression that allows us to evaluate the supersaturation or undersaturation states of a solution with respect to the whole range of solid compositions. The usefulness of such an expression is not limited only to nucleation processes. By evaluating the degree of supersaturation, it is possible to determine if a given aqueous solution in contact with a solid phase of general composition  $B_{1-x}C_xA$  is undersaturated, saturated, or supersaturated with respect to such a solid. This simple but important question cannot easily be answered with the present state of SS-AS theory (except for the special case in which the

composition of the aqueous solution plots below the solutus curve, when it is undersaturated with respect to any solid phase, including the pure endmembers (Glynn and Reardon, 1990). From Lippmann diagrams, it is clear that for SS-AS systems, saturation cannot be expressed by a unique value but is a function of the composition of both the solid and the aqueous phases. To illustrate this concept and the other concepts needed to define the supersaturation in SS-AS systems, we use an example throughout so that the equations can be plotted for a specific aqueous solution.

Let us consider an aqueous solution with composition  $[A^-] = [B^+] = [C^+] = 1 \times 10^{-5}$  mol/L (although other ions can be present in the aqueous solution, only the three ions above concern our system. The presence of other anions can provide charge balance for the  $B^+$  and  $C^+$  cations in our example). The  $\log \Sigma II$  value,  $-9.70$  for this solution, calculated using Eqn. 3, is plotted on the Lippmann diagram as point A1 (see Fig. 1). Because this composition is projected above the solutus curve, the solution is supersaturated with respect to a series of solid solutions (Glynn and Reardon, 1990). To determine the supersaturation of this aqueous solution relative to a solid with molar fraction given by the point A2 ( $X_{CA} = 0.6763$ ) on the solidus, we can use the expression

$$\delta_{A2} = \frac{[A^-]([B^+] + [C^+])}{K_{BA}a_{BA,A2} + K_{CA}a_{CA,A2}} \quad (8)$$

However, this equation can be applied only to determine the supersaturation of an aqueous solution whose composition is projected directly above (or below) the point on the solutus that defines the equilibrium with the solid composition in question (i.e., point A1'). This is the case in Figure 1 (therefore, for the special case of an aqueous solution projected exactly on the solutus curve, the supersaturation with respect to such a solid will be equal to 1). It cannot be used to determine the supersaturation of this solution relative to any general composition.

However, it is trivial to define the supersaturation of any aqueous solution relative to the end-members of the solid solution. Relative to BA, the supersaturation is given by

$$\delta_{BA} = \frac{[A^-][B^+]}{K_{BA}}, \quad (9)$$

and relative to CA,

$$\delta_{CA} = \frac{[A^-][C^+]}{K_{CA}}. \quad (10)$$

Points A3 and A4 in Figure 1 represent the log IAP (ionic activity product) values for components BA and CA in the A1 solution (i.e.,  $\log [A^-][B^+]$  and  $\log [A^-][C^+]$ ). The supersaturation values  $\delta_{BA}$  and  $\delta_{CA}$  for the solution A1 (calculated using Eqn. 9 and 10) relative to the end-members BA and CA, respectively, are also shown in Figure 1. Supersaturation (or undersaturation in this case) is proportional to the vertical distance,  $\Delta$ , between points A3 (and A4) and the values of  $\log K_{BA}$  (and  $\log K_{CA}$ ), respectively ( $\Delta_{BA} = \log \text{IAP}_{BA} - \log K_{BA} = \log [\text{IAP}_{BA}/K_{BA}]$ ). Because  $\text{IAP}_{BA} = [A^-][B^+]$ , then  $\delta_{BA} = 10^{\Delta_{BA}}$ ; similarly for  $\delta_{CA}$ ).

The calculation of supersaturation of the aqueous solution for pure solids AB and AC has been made considering only the

activity of the components of the aqueous solution that are relevant for them. So, because the solid AB is at equilibrium with an aqueous solution with  $X_{C, \text{aq}} = 0$ , the activity of ion  $C^+$  present in the aqueous solution is irrelevant for such a calculation. This argument can be also applied to any other composition of the solid solution.

In other words, if we want to calculate the supersaturation of a given aqueous solution with respect to a specific solid solution composition, the first step is to define the activity fraction in the aqueous solution that is in equilibrium with this solid solution composition. If the aqueous solution considered projects directly above (or below) the point on the solutus that defines the equilibrium, we can directly apply Eqn. 8. This is the condition in the case shown in Figure 1, in which the supersaturation of A1 can be determined relative to solid A2 because A1 has the same activity fraction as the solution (A1') at equilibrium with A2. For other solid solution compositions, we must recalculate the composition of the aqueous solution and express it in terms of the activity fraction that is at equilibrium with such solids. Expressed in this way, the recalculated composition of the aqueous solution directly projects above (or below) the point that defines the equilibrium, and we can then proceed to calculate the supersaturation. This leads to the definition of "actual activity" as that part of the activity of the ions necessary to calculate the supersaturation of the aqueous solution with respect to the solid considered. The value of actual activity is constrained by the activity fraction of the aqueous solution at equilibrium with such a solid.

To obtain the actual activities, it is necessary to recalculate the ionic activities of the aqueous solution and express them in terms of each activity fraction, taking into account that the initial concentration of both substituting cations cannot be exceeded. To determine the supersaturation of a given aqueous solution with respect to a general solid composition  $X_{CA}$ , we first determine the activity fraction  $X_{C, \text{aq}}^{\text{eq}}$  of an aqueous solution that is in equilibrium with this solid. If  $X_{C, \text{aq}}^{\text{sol}}$  is the activity fraction of the given aqueous solution (0.5 in our example), we must define two different cases:

1.  $X_{C, \text{aq}}^{\text{sol}} \leq X_{C, \text{aq}}^{\text{eq}}$ . For this range of activity fractions, the ratio of  $[C^+]$  to  $[B^+]$  in  $X_{C, \text{aq}}^{\text{sol}}$  is equal to or higher than in  $X_{C, \text{aq}}^{\text{sol}}$ . As a consequence, because the initial concentration of substituting cations cannot be exceeded,  $[C^+]$  remains as a constant, and  $[B^+]$  must be recalculated using the expression for activity fractions (Eqn. 7). This leads to the definition of actual activity:

$$[C^+]_{\text{actual}} = [C^+], \quad (11)$$

and

$$[B^+]_{\text{actual}} = \frac{[C^+](1 - X_{C, \text{aq}}^{\text{eq}})}{X_{C, \text{aq}}^{\text{eq}}}. \quad (12)$$

2.  $X_{C, \text{aq}}^{\text{sol}} \geq X_{C, \text{aq}}^{\text{eq}}$ . Similar to the previous case, for this range of activity fractions, the ratio of  $[C^+]$  to  $[B^+]$  in  $X_{C, \text{aq}}^{\text{sol}}$  is equal to or lower than in  $X_{C, \text{aq}}^{\text{sol}}$ . As a consequence,  $[B^+]$  remains as a constant, and  $[C^+]$  must be recalculated using the expression for activity fractions (Eqn. 6). Therefore,

$$[B^+]_{\text{actual}} = [B^+], \quad (13)$$

and

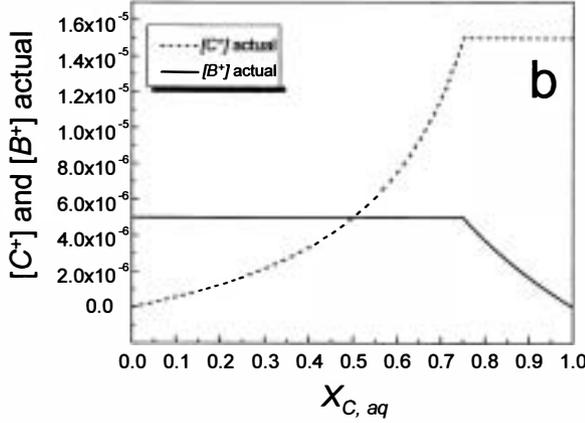
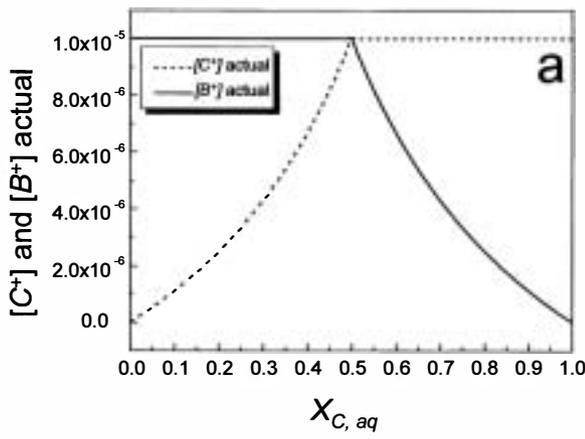


Fig. 2. Variation of the actual activities,  $[B^+]_{\text{actual}}$  and  $[C^+]_{\text{actual}}$ , as a function of  $X_{C, \text{aq}}$  for (a) an aqueous solution with composition  $[A^-] = [B^+] = [C^+] = 1 \times 10^{-5}$  mol/L and (b) an aqueous solution with composition  $[A^-] = 1 \times 10^{-5}$  mol/L,  $[B^+] = 5 \times 10^{-6}$  mol/L, and  $[C^+] = 1.5 \times 10^{-5}$  mol/L.

$$[C^+]_{\text{actual}} = \frac{[B^+](1 - X_{B, \text{aq}}^{\text{eq}})}{X_{B, \text{aq}}^{\text{eq}}} \quad (14)$$

It is easy to see that in the limiting case of the end-member solids  $AC$  and  $AB$ , the  $[B^+]_{\text{actual}}$  and  $[C^+]_{\text{actual}}$  are zero, respectively, as they must be.

Figure 2 shows the variation of  $[B^+]_{\text{actual}}$  and  $[C^+]_{\text{actual}}$  as a function of the activity fraction  $X_{C, \text{aq}}$  of the fluid for two different aqueous solutions.

Although Eqn. 11 to 14 are applicable in the general case, Figure 2a is plotted for the specific value of fluid composition A1, where  $[B^+] = [C^+]$ . To illustrate the use of these equations further, we could consider a case in which the fluid composition is  $[A^-] = 1 \times 10^{-5}$  mol/L,  $[B^+] = 5 \times 10^{-6}$  mol/L, and  $[C^+] = 1.5 \times 10^{-5}$  mol/L. In this case,  $X_{C, \text{aq}}^{\text{sol}} = 0.75$ , and Figure 2b shows the variation of  $[B^+]_{\text{actual}}$  and  $[C^+]_{\text{actual}}$  as a function of the activity fraction  $X_{C, \text{aq}}$  of the fluid.

Substituting  $[B^+]_{\text{actual}}$  (Eqn. 12) and  $[C^+]_{\text{actual}}$  (Eqn. 11) into the definition of the  $\Sigma\Pi$  variable (Eqn. 3) gives for  $X_{C, \text{aq}}^{\text{sol}} \leq X_{C, \text{aq}}^{\text{eq}}$  the expression

$$\Sigma\Pi_{C, \text{aq}}^{\text{sol}} = [A^-] \left( [C^+] + \left( \frac{[C^+] - X_{C, \text{aq}}^{\text{sol}} [C^+]}{X_{C, \text{aq}}^{\text{eq}}} \right) \right) = \frac{[A^-][C^+]}{X_{C, \text{aq}}^{\text{eq}}} \quad (15)$$

Substituting  $[B^+]_{\text{actual}}$  (Eqn. 13) and  $[C^+]_{\text{actual}}$  (Eqn. 14) into the definition of the  $\Sigma\Pi$  variable (Eqn. 3) gives for  $X_{C, \text{aq}}^{\text{sol}} \geq X_{C, \text{aq}}^{\text{eq}}$  the expression

$$\Sigma\Pi_{C, \text{aq}}^{\text{sol}} = [A^-] \left( [B^+] + \left( \frac{[B^+] - X_{C, \text{aq}}^{\text{sol}} [B^+]}{X_{C, \text{aq}}^{\text{eq}}} \right) \right) = \frac{[A^-][B^+]}{X_{C, \text{aq}}^{\text{eq}}} \quad (16)$$

The curve defined by Eqn. 15 and 16 can be plotted on a Lippmann diagram. It represents the variation of the total solubility product of the aqueous solution as a function of the aqueous activity fractions (Fig. 3). As was mentioned before, the supersaturation or undersaturation of a given aqueous solution with respect to a particular solid solution composition is proportional to the vertical distance from  $\Sigma_{X_{B, \text{aq}}^{\text{sol}}}$  and  $\Sigma_{X_{C, \text{aq}}^{\text{sol}}}$  to the solutus. Figure 3 shows an example of the supersaturation of the A1 aqueous solution with respect to a solid of composition  $B_{0.25}C_{0.75}A$ .

Eqn. 15 and 16 are expressed in terms of the aqueous solution composition. However, to simplify the supersaturation equations, it is convenient to rewrite them as functions of the solid composition. For this purpose, we can use the relations between solidus and solutus curves. The activity fractions of the free  $B^+$  and  $C^+$  ions in the solutus curve are related to  $X_{BA}$  and  $X_{CA}$  in the solidus by means of

$$X_{BA} = \frac{X_{BA}\gamma_{BA}K_{BA}}{([B^+] + [C^+])[A^-]} = \frac{X_{BA}\gamma_{BA}K_{BA}}{K_{BA}a_{BA} + K_{CA}a_{CA}} \quad (17)$$

$$X_{CA} = \frac{X_{CA}\gamma_{CA}K_{CA}}{([B^+] + [C^+])[A^-]} = \frac{X_{CA}\gamma_{CA}K_{CA}}{K_{BA}a_{BA} + K_{CA}a_{CA}} \quad (18)$$

Using Eqn. 17 and 18, we can express the curves of Eqn. 15 and 16 in terms of the solid-phase mole fraction. The resulting expression for  $X_{C, \text{aq}}^{\text{sol}} \leq X_{C, \text{aq}}^{\text{eq}}$  is

$$\Sigma\Pi_{C, \text{aq}} = \frac{[A^-][C^+]}{X_{CA}\gamma_{CA}K_{CA}/K_{BA}a_{BA} + K_{CA}a_{CA}} \quad (19)$$

and for  $X_{C, \text{aq}}^{\text{sol}} \geq X_{C, \text{aq}}^{\text{eq}}$ ,

$$\Sigma\Pi_{B, \text{aq}} = \frac{[A^-][B^+]}{X_{BA}\gamma_{BA}K_{BA}/(K_{BA}a_{BA} + K_{CA}a_{CA})} \quad (20)$$

Figure 4 shows the relationship between the curves defined by Eqn. 15 and 16 and Eqn. 19 and 20. As can be seen, supersaturation of the aqueous solution with respect to any composition of the solid solution is now proportional to the vertical distance from the dotted line to the solidus curve. The supersaturation with respect to a certain solid solution can therefore be obtained by dividing Eqn. 19 or 20 by the corresponding solidus value. The supersaturation functions will be given for  $X_{C, \text{aq}}^{\text{sol}} \leq X_{C, \text{aq}}^{\text{eq}}$  by

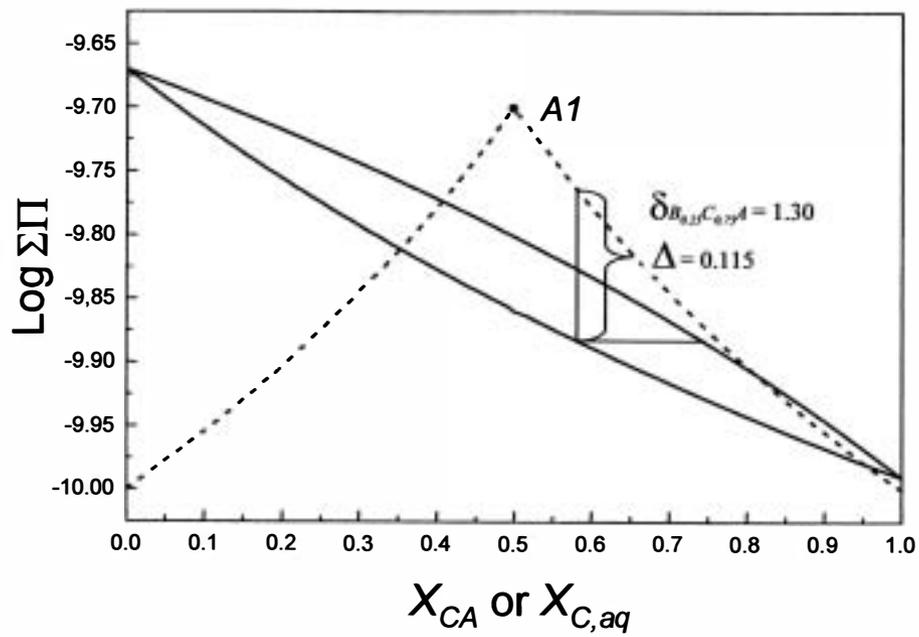


Fig. 3. Composition of the A1 solution expressed as a function of the whole range of activity fractions of the aqueous solution. The supersaturation with respect to a solid with composition  $X_{CA} = 0.75$  is proportional to the vertical line:  $\delta_{B_{0.25}C_{0.75}A} = 10^{\Delta}$ ;  $\Delta = 0.115$ .

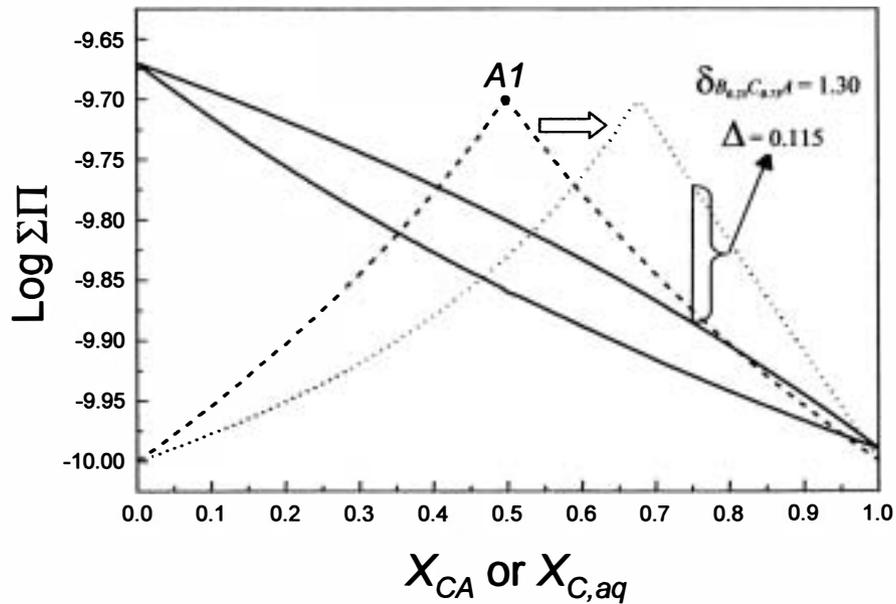


Fig. 4. Composition of the A1 solution expressed as a function of the activity fractions of the aqueous solution (dashed line) and the molar fraction of the solid solution (dotted line). As in Figure 3, the vertical line is proportional to the supersaturation with respect to the solid, with  $X_{CA} = 0.75$ .

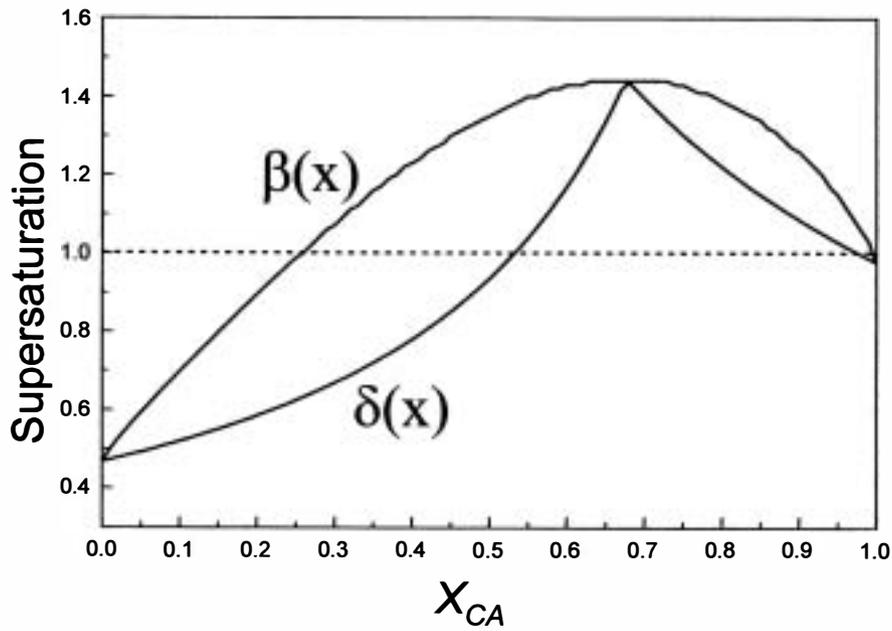


Fig. 5. Supersaturation functions  $\delta(x)$  and  $\beta(x)$  for an aqueous solution with composition  $[A^-] = [B^+] = [C^+] = 1 \times 10^{-5}$  mol/L. The dotted line represents saturation. The maximum supersaturation is reached for a solid with a molar fraction  $X_{CA} = 0.68$ . Supersaturations given by both functions are the same only for the end-members and a solid with  $X_{CA} = 0.68$ .

$$\delta_{X_{CA}} = \left[ \frac{[A^-][C^+]}{X_{CA}\gamma_{CA}K_{CA}/(K_{BA}a_{BA} + K_{CA}a_{CA}) / K_{BA}a_{BA} + K_{CA}a_{CA}} \right] = \frac{[A^-][C^+]}{X_{CA}\gamma_{CA}K_{CA}}, \quad (21)$$

and for  $X_{C, \text{aq}}^{\text{sol}} \geq X_{C, \text{aq}}^{\text{eq}}$  by

$$\delta_{X_{BA}} = \left[ \frac{[A^-][B^+]}{X_{BA}\gamma_{BA}K_{BA}/(K_{BA}a_{BA} + K_{CA}a_{CA}) / K_{BA}a_{BA} + K_{CA}a_{CA}} \right] = \frac{[A^-][B^+]}{X_{BA}\gamma_{BA}K_{BA}}, \quad (22)$$

Figure 5 shows the  $\delta(x)$  supersaturation function (given by Eqn. 21 and 22) calculated for our A1 example aqueous solution. If we introduce now the saturation conditions into Eqn. 21 and 22 (i.e.,  $\delta_{X_{BA}} = \delta_{X_{CA}} = 1$ ), Eqn. 1 and 2 are then again obtained. Therefore, Eqn. 21 and 22 evaluate supersaturation in SS-AS from the two thermodynamic equilibrium conditions. It demonstrates the consistency of our derivation.

To make clearer the development of our supersaturation function, we have chosen an ideal solid solution. In such a system, the solid phase activity coefficients  $\gamma_{BA}$  and  $\gamma_{CA}$  are 1, and the calculation of the  $\delta(x)$  function is straightforward. The extension of our formulation to other systems (e.g., regular or subregular solid solutions with a miscibility gap) is, however, not difficult.

Figure 6a shows the Lippmann diagram for the (Sr, Ca)CO<sub>3,orthorhombic</sub>-H<sub>2</sub>O system at 25°C and 1 bar. The solid solution is subregular with the dimensionless Redlich-Kister coefficients  $a_0 = 3.43$  and  $a_1 = -1.82$  (Plummer and Busenberg, 1987). The effect of non ideality of the solid solutions results in a “eutectic” point on the solutus curve (left side of the

diagram). The intersections of horizontal lines through the “eutectic” point with the solidus curve determine the miscibility gap of the solid solution. Such a miscibility gap can be found for compositions  $0.0058 < X_{\text{SrCO}_3} < 0.875$  (Plummer and Busenberg, 1987). Figure 6b shows, as an example, the  $\delta(x)$  corresponding to an aqueous solution of composition  $[\text{Sr}^{2+}] = 0.05$  mmol/L,  $[\text{Ca}^{2+}] = 0.2$  mmol/L, and  $[\text{CO}_3^{2-}] = 0.1$  mmol/L. As can be observed, the maximum supersaturation ( $\delta = 10.1$ ) is reached for a solid with molar fraction  $X_{\text{SrCO}_3} = 0.931$ . This is a direct consequence of the shape and relative positions of the solutus curves on the Lippmann diagram (see Fig. 6a). In addition, the extension of the solid solution is limited, and therefore, such a maximum is located near the end-member position. It is also worth noting that for the compositional ranges for which there are miscibility gaps, SS-AS thermodynamic equilibria cannot be defined. Therefore, for such composition ranges, supersaturation cannot be calculated, and the range of the gap in the supersaturation function is the same as the miscibility gap.

#### 4. COMPARISON BETWEEN THE $\delta(x)$ AND THE $\beta(x)$ FUNCTIONS

The  $\delta(x)$  function derived in the previous section is not the first attempt to evaluate the supersaturation of an aqueous solution with respect to a range of solid solutions in SS-AS systems. An alternative formulation for calculating supersaturations in SS-AS systems was given by Prieto et al. (1993):

$$\beta(x) = \frac{[B^+]^{1-n}[C^+][A^-]}{(K_{BA}X_{BA}\gamma_{BA})^{1-n}(K_{CA}X_{CA}\gamma_{CA})^n} \quad (23)$$

This expression is obtained by assuming that the equilibrium condition is given by

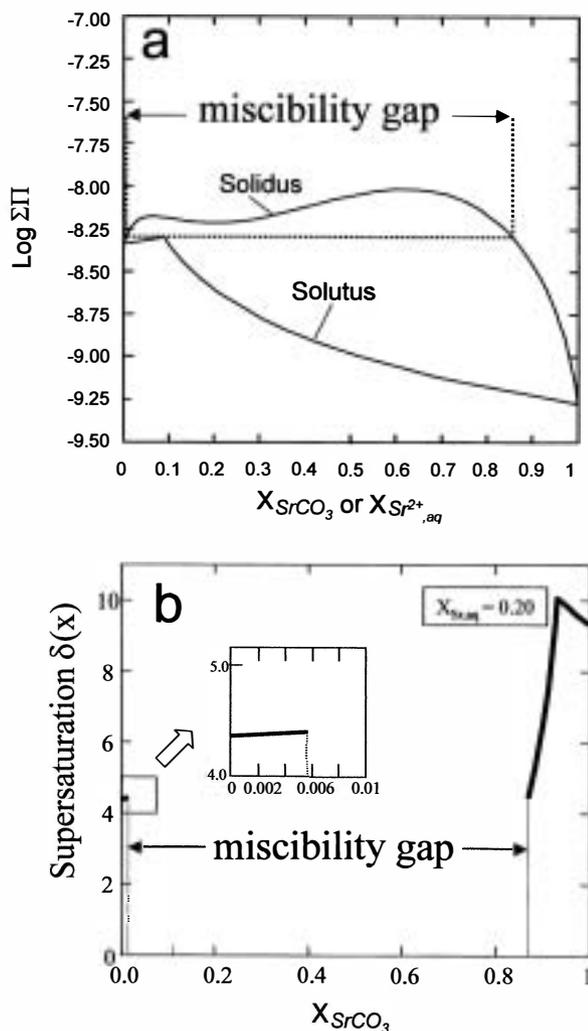
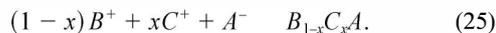


Fig. 6. (a) Lippmann phase diagrams for the  $(\text{Ca}, \text{Sr})\text{CO}_3$ , orthorhombic- $\text{H}_2\text{O}$ . (b) Supersaturation function  $\delta(x)$  for a hypothetical aqueous solution of composition  $[\text{Sr}^{2+}] = 0.05$  mmol/L,  $[\text{Ca}^{2+}] = 0.2$  mmol/L, and  $[\text{CO}_3^{2-}] = 0.01$  mmol/L with respect to the whole range of solid solutions compositions. Supersaturation function cannot be drawn for the solid compositions in the miscibility gaps, i.e., for those solid solution–aqueous solution pairs for which thermodynamic equilibrium is not defined.

$$\Delta\mu = (1 - X)\mu[B^+] + X\mu[C^+] + X\mu[A^-] - [(1 - X)\mu BA + X\mu CA] = 0. \quad (24)$$

However, the free energy change  $\Delta\mu$  defined by such an expression does not correspond to both thermodynamic equilibrium conditions defined by Eqn. 1 and 2 but to a reaction whereby the transfer of ions between the aqueous and solid phases (and vice versa) occurs with a ratio  $B^+/C^+/A^-$  equal to that of the solid:



In such a case, the stoichiometry of the solid phase does not change during the growth or dissolution process (the distribution coefficient is 1). Eqn. 24 therefore describes any state of

stoichiometric saturation, and Eqn. 23 is therefore an evaluation of the “stoichiometric supersaturation.” Stoichiometric saturation is “a limiting equilibrium state, hypothesized by assuming that a solid-solution may behave as a single-component solid of invariant composition” (Thortenson and Plummer, 1977; Glynn and Reardon, 1990). Although such a concept has been successfully applied to the congruent dissolution processes (the transfer of ions between the solid and aqueous phases occurs according to Eqn. 25) that take place in certain SS-AS systems (Plummer and Busenberg, 1987), such a concept cannot generally be applied for interpreting precipitation processes (Lafon, 1978; Glynn et al., 1990, 1992).

In Figure 5, the  $\delta(x)$  and  $\beta(x)$  functions for the A1 aqueous solution are compared. As can be observed, only the supersaturation values obtained for the end-members and the maximum supersaturation are the same for  $\delta(x)$  and  $\beta(x)$  functions. The reason for this concordance is easy to explain for the end-members. In such a case, the activity of  $B^+$  (or  $C^+$ ) in the aqueous and solid phase is 0, and therefore, Eqn. 24 and 25 become equivalent. On the other hand, for solid A2, Eqn. 23 is equivalent to Eqn. 8. As Glynn and Reardon (1990) explained, a point plotted on the solutus curve represents not only the composition of an aqueous solution at thermodynamic equilibrium with respect to a solid phase but also one of the possible aqueous compositions that satisfy the condition of stoichiometric saturation with respect to such a solid. Therefore, the two supersaturation functions must show a coincident maximum. It is important to note that even though the calculation of the most supersaturated solid solution composition is very important, the understanding of many crystallisation and nucleation phenomena in SS-AS systems requires the evaluation of the supersaturation distribution as a function of the composition. Moreover, there is experimental evidence that demonstrates that frequently, both solid solution compositions and their evolution during crystallisation are not determined by maximum supersaturation values (Prieto et al., 1993; Fernández-González et al., 1999; Pina et al., 2000; Astilleros et al., 2000). Because the  $\delta(x)$  function is based on rigorous equilibrium conditions (Eqn. 1 and 2), it provides a precise description of the departure from equilibrium of a given aqueous solution with respect to all the possible compositions of the corresponding solid solution.

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