

COMMENT: SUPERSATURATION IN BINARY SOLID SOLUTION-AQUEOUS SOLUTION SYSTEMS

(Comment on “Crystallization kinetics in binary solid solution – aqueous solution systems” by Alexander G. Shtukenberg, Yurii O. Punin and Pavel Azimov, American Journal of Science, v. 306, p. 553–574.)

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INTRODUCTION

Shtukenberg and others (2006) present a general model for predicting growth rates in solid solution – aqueous solution (SS–AS) systems. The key parameter for such a model is the supersaturation, which is particularly stressed and discussed throughout the text. The paper starts with a review of the equilibrium thermodynamics in SS-AS systems on the basis of the Lippmann “total solubility product” (Lippmann, 1980; Glynn and Reardon, 1990; Glynn and others, 1990; Glynn, 2000). Then, the authors discuss the so-called “quasi-equilibria”, defined as those states where “the driving force for the ionic fluxes of one or both components between aqueous solution and solid solution can be negligible”. Finally, the approach is completed by considering the misfit strain arising at the interface between the crystal surface and a newly deposited solid-solution layer of different composition. According to Shtukenberg and co-workers, this strain is expected to have a strong effect on the physical-chemistry of crystal growth, and their model promises to predict the growth and dissolution behavior of solid-solution crystals from aqueous solutions.

Whereas the proposed model contains interesting ideas and most of the derived equations are formally correct, some conclusions and, particularly, the underlying terminology are misleading and may result in a wrong interpretation of SS-AS physical-chemistry. There are two main parts to this discussion. The first disputes the concept of “quasi-equilibrium” as defined by Shtukenberg and others (2006) and the second revises the expressions of supersaturation applied to these kinds of systems. In addition, we introduce some remarks on other aspects of the model that are directly or indirectly affected by the concept of quasi-equilibrium and supersaturation of Shtukenberg and co-workers.

The physical-chemistry of SS-AS systems is a complex issue that has generated a number of controversies during the last three decades (Thorstenson and Plummer, 1977; Lafont, 1978; Garrels and Wollast, 1978; Thorstenson and Plummer, 1978; Stoessell, 1992; Glynn and others, 1992; Königsberger and Gamsjäger, 1992; Glynn and Reardon, 1992). At present (Glynn, 2000), most of those controversies can be considered as ended, but many kinetic aspects remain unsolved and it is therefore not unusual that new controversies arise. In our opinion, one of the key factors to progress in the understanding of the growth/dissolution behavior in SS-AS systems is to avoid the use of misleading concepts. This is the approach that we mean to give to the present criticism.

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QUASI-EQUILIBRIA

Starting from the Lippmann model for a binary (B,C)A solid solution (where the cations B^{n+} and C^{n+} and the anions A^{n-} are present in the aqueous solution and react to form solid solution crystals), Shtukenberg and others (2006) arrive at the equations:

$$\Sigma\Pi_{B_{eq}} \equiv \Sigma\Pi_{eq}(y_B) = \frac{K_{BA}f_{BA_s}x_{BA_s}}{y_B} \tag{1}$$

$$\Sigma\Pi_{C_{eq}} \equiv \Sigma\Pi_{eq}(y_C) = \frac{K_{CA}f_{CA_s}x_{CA_s}}{y_C} \tag{2}$$

where K_{BA} and K_{CA} are the solubility products of the pure end-members (BA and CA) of the series, and f_{BA_s} and f_{CA_s} are the activity coefficients of the components BA and CA in a solid solution with a “fixed” (indicated by the subscript *s*) composition $x_{BA_s} = 1 - x_{CA_s}$ (the compositions being expressed as molar fractions, x_{BA} and x_{CA} , of BA and CA). $\Sigma\Pi$ stands for the total ionic activity product, $(a_B + a_C) \times a_A$, as defined by Lippmann. Finally, y_B is the activity fraction, $a_B / (a_B + a_C)$, of the B^{n+} ions in the aqueous solution, with $y_B = 1 - y_C$. These two equations corresponding to equations (19) and (20) in the original paper by Shtukenberg and others (2006), are equivalent to equations (46) and (47) in Glynn and Reardon (1990), and cannot be used independently to describe equilibrium. True equilibrium occurs for a value of y_B for which both equations give the same value of $\Sigma\Pi$, that is:

$$\Sigma\Pi_{eq} = \frac{K_{BA}f_{BA_s}x_{BA_s}}{y_B} = \frac{K_{CA}f_{CA_s}x_{CA_s}}{y_C} \tag{3}$$

This value plots on the Lippmann “solutus” curve (point O in fig. 1) and is the only one in the series that describes a true equilibrium situation. Although Shtukenberg and co-workers admit this, they then extract conclusions about the meaning of each function, $\Sigma\Pi_{eq}(y_B)$ or $\Sigma\Pi_{eq}(y_C)$, in a separate way. As a result, these authors define four compositional regions (see fig. 1) for the aqueous solutions that they interpret as undersaturated or supersaturated with respect to the components BA and/or CA. This idea is, however, misleading and can lead to wrong conclusions. The fundamental problem is that the terms saturation, supersaturation, and undersaturation should be preserved to exclusively refer to the saturation state of an aqueous solution with respect to a given solid phase. Equilibrium or disequilibrium (and this is not just a linguistic question) occurs between two (or more) phases, not between components or between components and phases. Therefore, aqueous solutions are not saturated, supersaturated, or undersaturated with respect to components, but with respect to phases, whatever the nature (pure solids or solid solutions) of these phases is.

After reading the “quasi-equilibrium” section in the paper by Shtukenberg and others (2006), one can misinterpret that all aqueous compositions in region II are supersaturated with respect to the pure end-member CA and that all aqueous solutions in region IV are supersaturated with respect to pure BA. This is, however, completely wrong. In fact, both regions enclose zones that are below the “solutus” curve (the striped area) and, as Glynn and Reardon (1990) state, “aqueous solutions that plot below the solutus curve are undersaturated with respect to any solid phase, including the end-member solids, whereas solutions plotting above the solutus are supersaturated with respect to a series of solid-solutions”. There is no kind of (pseudo, temporary or metastable) equilibrium involved in the hyperbolas defined by equations (1) and (2), except the “true equilibrium” determined by the intersection between them. Possible metastable equilibrium scenarios are represented by the so-called “pure end-member saturation states”. These states correspond to the compositions of aque-

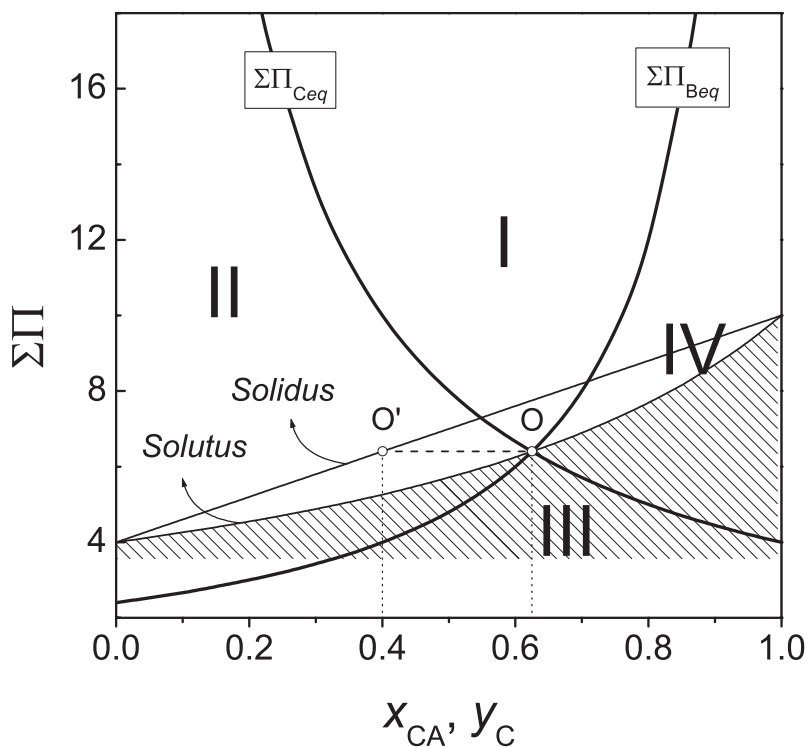


Fig. 1. Lippmann's diagram for a hypothetical SS-SA system. In order to reproduce the example of Shtukenberg and others (2006) an ideal solid solution with $K_{BA} = 4$ and $K_{CA} = 10$ has been considered. The solidus and solutus relationships are represented, respectively, against two superimposed scales, x_{CA} and y_C , on the abscissa. The bold solid lines, $\Sigma\Pi_{Ceq}$ and $\Sigma\Pi_{Beq}$, have been calculated from eqs 1 and 2 for $x_{CA,s} = 0.4$ and are represented against y_C on the abscissa. The intersection point "O" on the solutus is at equilibrium with a solid solution of composition $x_{CA} = 0.4$. The meaning of regions I, II, III, and IV is discussed in the text.

ous solutions that are at saturation with respect to the pure end-members and are given by the expressions (Glynn and others, 1990):

$$\Sigma\Pi_{BA} = \frac{K_{BA}}{y_B} \quad (4)$$

$$\Sigma\Pi_{CA} = \frac{K_{CA}}{y_C} \quad (5)$$

These equations define the families of $(y_B, \Sigma\Pi_{BA})$ and $(y_C, \Sigma\Pi_{CA})$ conditions for which a solution containing A^{n-} , B^{n+} , and C^{n+} ions can be at metastable equilibrium with respect to pure BA or pure CA solid phases. Differently to equations (1) and (2), equations (4) and (5) are independent as they correspond to two different compositions ($x_{BA} = 0$ and $x_{BA} = 1$) of the solid solution. Moreover, the pure end-member saturation curves defined by equations (4) and (5) plot above the solutus curve for all aqueous activity fractions, concurring with the solutus (true equilibrium) only for $y_B = 1$ or $y_C = 1$, respectively (see fig. 2).

Actually, equations (4) and (5) represent two different limiting cases (for $x_{BA} = 0$ and for $x_{BA} = 1$) of stoichiometric saturation of an aqueous solution with respect to a solid $B_xC_{1-x}A$ ($x = x_{BA}$). For a solid solution with a "fixed" composition, $x_{BA,s} = 1 - x_{CA,s}$,

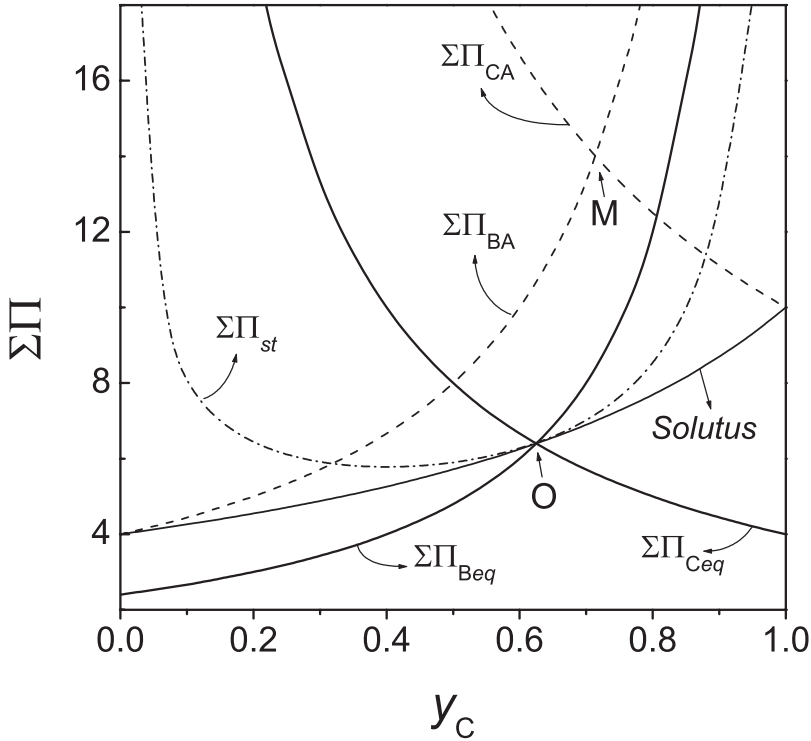


Fig. 2. Pure end-member saturation curves ($\Sigma\Pi_{CA}$ and $\Sigma\Pi_{BA}$, eqs 4 and 5, dashed lines) and stoichiometric saturation ($\Sigma\Pi_{st}$) curve calculated for $x_{CA_s} = 0.4$ using eq 6 (dot-dash line). The solutus relationship and the $\Sigma\Pi_{Ceq}$ and $\Sigma\Pi_{Beq}$ curves for $x_{CA_s} = 0.4$ (eqs 1 and 2) have also been represented. Note the single scale y_C on the abscissa. At point “O” the stoichiometric-saturation curve concurs with the solutus and with the intersection of the curves $\Sigma\Pi_{Ceq}$ and $\Sigma\Pi_{Beq}$. Point M corresponds to an aqueous solution that is at equilibrium with a mechanical mixture of the two end-members.

the stoichiometric-saturation curve describes a series of metastable equilibrium scenarios, given by the expression (Glynn and others, 1990):

$$\Sigma\Pi_{st} = \frac{K_{st}}{y_B^{x_{BA_s}} y_C^{x_{CA_s}}} \tag{6}$$

in which K_{st} is the so-called stoichiometric solubility product (Thortenson and Plummer, 1977), given by:

$$K_{st} = (K_{BA/BAs} x_{BA_s})^{x_{BA_s}} (K_{CA/CA_s} x_{CA_s})^{x_{CA_s}} \tag{7}$$

Equation (6) does not describe a true equilibrium situation, which would require simultaneous satisfaction of the Lippmann solidus and solutus relationships. In fact, the stoichiometric saturation concept is related to the experimental evidence that solid solutions tend to dissolve congruently until an initial metastable equilibrium is reached. However, an aqueous solution can largely remain metastable at stoichiometric saturation with respect to a given solid solution. This occurs because to reach true equilibrium, a solid solution that is at stoichiometric saturation should undergo a dissolution-recrystallization process, whose kinetics can be very sluggish.

Figure 2 displays the pure end-member saturation curves (eqs 4 and 5) as well as the curves corresponding to equations (1), (2), and (6) for a fixed composition of the

solid solution $x_{CA} = 1 - x_{BA} = 0.4$. In order to reproduce the example of Shtukenberg and others (2006), an ideal solid solution with $K_{BA} = 4$ and $K_{CA} = 10$ has been considered. As can be observed, the stoichiometric saturation curve plots above the solutus curve for all aqueous activity fractions except for $y_C = 1 - y_B = 0.625$. For this value, the stoichiometric saturation curve concurs with both the solutus and the intersection of equations (1) and (2). This intersection point corresponds to $\Sigma\Pi = 6.4$ and represents a true equilibrium situation.

The fact that the stoichiometric saturation curves (including those corresponding to the pure end-members) plot above the solutus curve is not surprising. In all metastable-equilibrium states the aqueous solution is supersaturated with respect to the stable phase, which is inevitably less soluble than the metastable one. To use a simple and well-known example, an aqueous solution saturated with respect to aragonite is supersaturated with respect to calcite, the stable CaCO_3 phase at ambient conditions. Thus, in order to reach equilibrium, the metastable phase must undergo a dissolution-recrystallization process in which the stable and less soluble phase is formed. Obviously, the situations described by using (separately) equations (1) and (2) do not represent any kind of metastable-equilibrium state and should not be defined as a “quasi-equilibrium” state because they do not involve phases. Moreover, the subscript “*eq*” should be kept for the total solubility product as defined by Lippmann’s solidus and solutus expressions.

In their treatment, Shtukenberg and others (2006) define “the solid solution as a mixture of two components (BA and CA) and find the conditions for the *equilibrium of each component* separately with respect to a series of aqueous solutions”. This statement leads to further confusion, since, in that context, a “mixture” of the components can be misinterpreted as a mechanical mixture of the pure end-members. However, a mechanical mixture of the pure end-members is a mixture of two phases. Then, a hypothetical situation in which an aqueous solution is simultaneously at equilibrium with two phases could be defined. In the case of the pure end-members, such a simultaneous equilibrium situation is located at the intersection of the saturation curves for pure BA and CA (point M in fig. 2). It is worth noting that whereas point M represents a metastable-equilibrium state between an aqueous solution and two pure solid phases, point O represents true equilibrium between an aqueous solution and a single solid phase, which is a definite member of the solid solution.

Equations (1) and (2) are not independent, but form a system whose solution defines the true equilibrium state for a fixed, $x_{BA^s} = 1 - x_{CA^s}$ solid composition. However, the independent meaning of these two equations can still be considered within the framework of the SS-AS thermodynamics. As Shtukenberg and co-workers state, these equations simply define the conditions “when the chemical potential difference between solid and aqueous solution for one of the components is equal to zero”, that is:

$$\mu_{BA}^{SS} - \mu_B^{aq} - \mu_A^{aq} = 0 \quad (8)$$

$$\mu_{CA}^{SS} - \mu_C^{aq} - \mu_A^{aq} = 0 \quad (9)$$

where μ_{BA}^{SS} and μ_{CA}^{SS} are the chemical potentials of the BA and CA components in the solid solution, whereas μ_B^{aq} , μ_C^{aq} , and μ_A^{aq} are the respective chemical potentials of the A^{n-} , B^{n+} , and C^{n+} ions in the aqueous solution. Therefore, equations (1) and (2) can be used to explore the fluxes of the components BA and CA between aqueous and solid phases. As a matter of example, figure 3 shows a set of $\Sigma\Pi_{Ceq}$ curves calculated for different fixed values x_{CA^s} . The solutus position is also shown. The circle (point P) plotted below the solute represents an initial aqueous solution for which $\Sigma\Pi = 5$ and $y_C = 0.8$. As can be observed, this aqueous solution exactly plots on the $\Sigma\Pi_{Ceq}$ curve

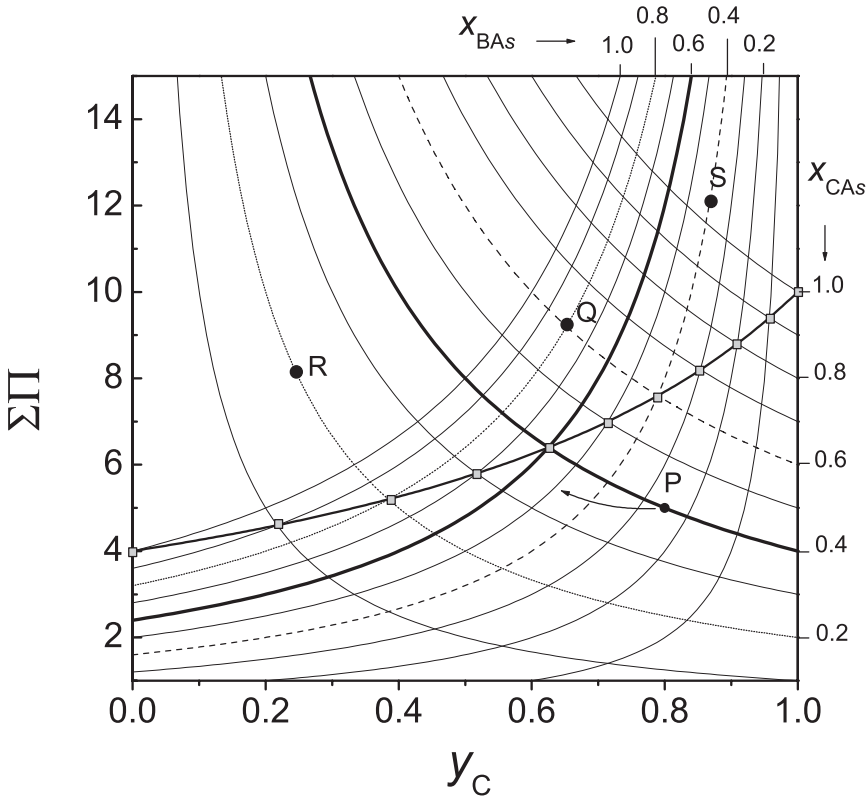


Fig. 3. $\Sigma\Pi_{Ceq}$ curves (eq 1) calculated for different fixed values x_{CA} s. The counterparts ($\Sigma\Pi_{Beq}$) and the solutus position are also shown. Note that the intersections between counterparts determine the solutus curve. Point P below the solute represents an initial aqueous solution and the arrow indicates a hypothetical reaction pathway. As can be observed, this aqueous solution exactly plots on the $\Sigma\Pi_{Ceq}$ curve corresponding to $x_{CA} = 0.4$ and below its $\Sigma\Pi_{Beq}$ ($x_{BA} = 0.6$) counterpart. The meanings of the points Q, R, and S are discussed in the text.

corresponding to $x_{CA} = 0.4$ and below its $\Sigma\Pi_{Beq}$ ($x_{BA} = 0.6$) counterpart. In contact with this aqueous solution, a solid solution of composition $x_{CA} = 0.4$ will tend to release BA into the aqueous phase, whereas the net flux of CA between both phases will tend to be nil. Although such a “lixiviation” scenario is unrealistic (congruent stoichiometric dissolution is the most likely process), one can imagine a hypothetical process in which the bulk solid-solution composition changes in a gradual way. During such a process the proportion of the substituting ions in both phases will change, with the aqueous solution becoming richer in B^{n+} and the solid solution becoming richer in CA. As a consequence, the compositional trajectory followed by the aqueous solution plots below the newly relevant $\Sigma\Pi_{Ceq}$ curves and the process will continue by releasing both components from the solid solution; that is, net dissolution will occur. In the presence of a sufficient amount of solid solution, the process would continue until a final equilibrium endpoint (whose location on the solutus will depend on the specific initial amounts of solid and fluid) is reached.

The previous hypothetical course illustrates that, when used separately, equations (1) and (2) do not represent an equilibrium scenario comparable to stoichiometric or pure end-member saturation. The real meaning of the regions I, II, III, and IV defined by Shtukenberg and others (2006) can be understood by considering the reaction

trajectories that are thermodynamically possible. In any case, the “location” of the aqueous solution with respect to the solutus is the relevant factor in order to decide whether the solid phase (whatever its subsequent compositional evolution is) will tend to develop net growth or dissolution.

Region I deserves a special mention. A solid solution with the fixed composition x_{CA_s} (0.4 in fig. 1), when maintained in contact with an aqueous solution plotting in this region, will tend to undergo a net growth process. During this process the total amount of both BA and CA in the solid phase will increase. This does not mean that the solid solution will grow without undergoing compositional changes. In practice, the actual reaction paths will depend on many (structural, thermodynamic, kinetic, *et cetera*) factors (Prieto and others, 1997). However, the thermodynamically relevant argument is that a net increase in the amount of solid solution with this composition will lead to a decrease of the free energy of the SS-AS system. This is so because the chemical potential difference $\mu_{iA}^{SS} - \mu_i^{aq} - \mu_A^{aq}$ is smaller than zero for both ($i = C$ or B) components. Net growth (increment of the total amount of solid) can also occur in contact with any aqueous solution that plots above the solutus in regions II and IV. However, in this last case the solid will tend to get richer in one of the components and poorer in the other one. Such compositional evolution can only occur by a dissolution-recrystallization process. Therefore, only those aqueous solutions plotting in region I are strictly supersaturated with respect to a solid solution with the fixed composition x_{CA_s} (0.4 in fig. 1).

According to the previous arguments, the character of a given aqueous solution which is strictly supersaturated with respect to a fixed solid-solution composition can be decided after inspection of both the point ($y_C, \Sigma\Pi$) representing the aqueous solution and the “region I” corresponding to that specific solid solution. In figure 3 several examples are used to illustrate this statement. For instance, the aqueous solution “Q” plots on the left limit (see the dashed curves) of region I corresponding to $x_{CA} = 0.6$ ($x_{BA} = 0.4$) and on the right limit (dotted lines in fig. 3) of region I corresponding to $x_{CA} = 0.2$ ($x_{BA} = 0.8$). Therefore, the aqueous solution represented by point Q is strictly supersaturated with respect to all solid-solution compositions in the range $0.2 \leq x_{CA} \leq 0.6$. A similar inspection shows that the aqueous solution “R” is strictly supersaturated with respect to all compositions in the range $0 \leq x_{CA} \leq 0.2$. Finally, the aqueous solution “S” is supersaturated with respect to all compositions in the range $0.6 \leq x_{CA} \leq 1$.

The range of solid-solution compositions for which a given aqueous solution is strictly supersaturated can be calculated analytically by separately solving the equations:

$$\Sigma\Pi_{aq} = \frac{K_{BA}f_{BA}x_{BA}}{y_{Baq}} \quad (10)$$

$$\Sigma\Pi_{aq} = \frac{K_{CA}f_{CA}x_{CA}}{y_{Caq}} \quad (11)$$

These equations are analogous to (1) and (2) but now we are dealing with a particular aqueous solution, that is, with “fixed” values (indicated by the subscript *aq*) of both the aqueous activity fraction ($y_{Baq} = 1 - y_{Caq}$) and the total activity product ($\Sigma\Pi_{aq}$). The two extremes of the range can be obtained by solving equation (10) for variable x_{BA} and equation (11) for x_{CA} . It is worth noting that both, f_{BA} and f_{CA} , are functions of the corresponding variable.

SUPERSATURATION

In their paper, Shtukenberg and co-workers refer to supersaturation in two different sections using two different and, somehow, contradictory approaches. In the

section “CRYSTAL GROWTH: THERMODYNAMIC APPROACH” these authors state that “the deviation from the equilibrium depends on crystal composition as well as on the aqueous solution composition”. Then, provided that the composition of the growing crystal is unknown *a priori*, Shtukenberg and co-workers propose a parameter to measure the supersaturation, given by:

$$\xi = \ln\left(\frac{\Sigma\Pi}{\Sigma\Pi_{eq}}\right) \tag{12}$$

where $\Sigma\Pi$ is the total activity product of the current solution (point 1 in fig. 4) and $\Sigma\Pi_{eq}$ is the total (equilibrium) solubility product corresponding to an aqueous solution with the same aqueous activity fraction (y_C) as the current solution. This last value plots on the Lippmann solutus curve on the same vertical line as the current solution (point 3 in fig. 4). In reality, eq 12 defines the supersaturation of the aqueous solution with respect to the specific member, x^{eq} , of the solid solution (point 2 in fig. 4) that is at equilibrium with the aqueous solution defined by the point ($y_C, \Sigma\Pi_{eq}$) on the solutus. However, aqueous solutions that plot above the solutus curve are supersaturated with respect to a series of solid solutions (Glynn and Reardon, 1990) and all the members of this series are susceptible to precipitate. This means that, in dealing with a SS-AS system, the saturation state of a particular aqueous solution cannot be expressed by a single value. To make predictions, we should know the range of solid-solution compositions for which such a specific aqueous solution is supersaturated (or undersaturated) and what is the magnitude of the supersaturation (or undersaturation) with respect to each possible solid composition. The best way to solve this problem is to express the supersaturation in functional form, that is, as a function of the solid

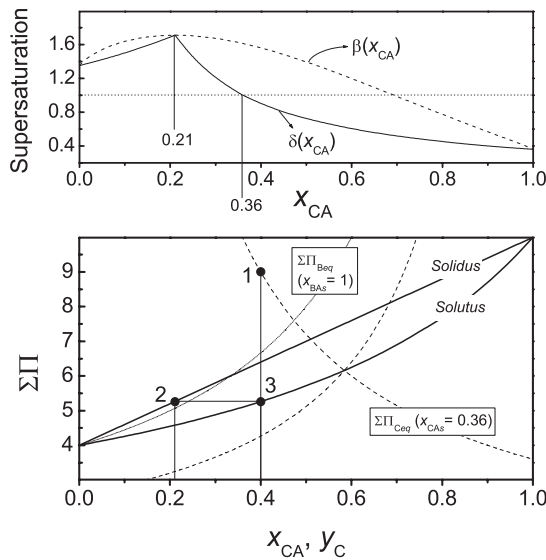


Fig. 4. Correlation between supersaturation models. The current solution (point 1) corresponds to $y_C = 0.4$ and $\Sigma\Pi = 9$. On the solutus, point 3 represents an aqueous solution with the same aqueous activity fraction ($y_C = 0.4$) as the current solution. This last aqueous solution is at equilibrium ($\Sigma\Pi_{eq} = 5.26$) with a solid solution of composition $x^{eq} = 0.21$ (point 2 on the solidus). In the upper graph both the stoichiometric-supersaturation function and the δ -functions are represented. Note the three common points ($\delta(0) = \beta(0)$, $\delta(1) = \beta(1)$, and $\delta(x^{eq}) = \beta(x^{eq}) = \beta_{max}$) and the range of solid-solution compositions, $0 \leq x_{CA} \leq 0.36$, for which the aqueous solution is “strictly” supersaturated ($\delta > 1$). The dashed curves in the lower graph delineate “region I” corresponding to $x_{CA} = 0.36$.

composition. This is not straightforward and at least two different expressions can be found in the literature. The first one is the so-called stoichiometric supersaturation function (Prieto and others, 1993) which is based on the stoichiometric saturation concept, and is given by:

$$\beta(x_{CA}) = \frac{a_B^{x_{BA}} a_C^{x_{CA}} a_A}{K_M(x_{CA})} \quad (13)$$

This function provides a description of the departure from stoichiometric saturation of a given aqueous solution with respect to all the possible compositions of the solid solution. Obviously, since stoichiometric saturation is not a true-equilibrium state, stoichiometric supersaturation does not represent the strict thermodynamic supersaturation. Actually, the function $\beta(x_{CA})$ represents the deviation with respect to the series of metastable-equilibrium states defined by the corresponding stoichiometric solubility products (eq 7). This function has a maximum β_{\max} that represents the solid composition for which the aqueous solution is most supersaturated. For a given composition of the aqueous solution, this maximum coincides with the single value, ξ , proposed by Shtukenberg and co-workers, and occurs for the same solid composition, that is, for $x_{CA} = x^{eq}$. Figure 4 illustrates this concept. The current solution (point 1) corresponds to $y_C = 0.4$ and $\Sigma\Pi = 9$. On the solutus, point 3 represents an aqueous solution with the same aqueous activity fraction ($y_C = 0.4$) as the current solution. This last aqueous solution is at equilibrium ($\Sigma\Pi_{eq} = 5.26$) with a solid solution of composition $x^{eq} = 0.21$ (point 2 on the solidus).

Equation (13) provides a description of the departure from stoichiometric saturation that is suitable to account for congruent dissolution processes, but does not represent the strict thermodynamic supersaturation, which in fact needs two equations to be described (Astilleros and others, 2003a). However, the function $\beta(x_{CA})$ has three particular values that represent a precise thermodynamic supersaturation: $\beta(0)$, $\beta(1)$, and β_{\max} . Thus, the value of x_{CA} corresponding to β_{\max} represents the solid-solution composition for which the aqueous solution is (in the strict sense) most supersaturated. This becomes clearer by comparing the curve $\beta(x_{CA})$ with those obtained using the functions:

$$\delta_{BA}(x_{BA}) = \frac{a_B a_A}{f_{BA} x_{BA} K_{BA}} \quad (14)$$

$$\delta_{CA}(x_{CA}) = \frac{a_C a_A}{f_{CA} x_{CA} K_{CA}} \quad (15)$$

According to Astilleros and others (2003a), for a given composition of the aqueous solution, equation (14) defines the supersaturation for all the solid compositions with $x_{CA} \leq x^{eq}$, whereas equation (15) defines the supersaturation for all the solid compositions with $x^{eq} \leq x_{CA}$. As can be observed, $\beta(x_{CA})$ and the δ -functions have three points in common, $\delta(0) = \beta(0)$, $\delta(1) = \beta(1)$, and $\delta(x^{eq}) = \beta(x^{eq}) = \beta_{\max} = \xi$.

It is worth noting that the partitioning of the substituting ions involved in the maximum exactly equals the equilibrium partitioning (Andara and others, 2005). In a first approximation, one could think that the composition of the solid solution that is most likely to nucleate from a given aqueous solution is x^{eq} , that is, the one for which $\beta(x_{CA}) = \beta_{\max}$. However, there is ample evidence that demonstrates that nuclei compositions are frequently not determined by maximum supersaturation values (Prieto and others, 1997). As Pina and Putnis (2002) have already pointed out, in many cases “more soluble” solid-solution compositions are kinetically favored and tend to nucleate even though the aqueous solution is less supersaturated for these composi-

tions than for less soluble members. As a result, the initial nuclei tend to be enriched in the less soluble end-member, differing in this way from the composition expected from equilibrium partitioning considerations. For this reason, delineating the range of solid compositions that are susceptible to nucleation becomes crucial.

The δ -functions have the advantage of defining the range of solid-solution compositions for which a given aqueous solution is “strictly” supersaturated. This range is delineated by the solid-solution compositions for which δ_{BA} or δ_{CA} are equal to unity. In the particular example shown in figure 4, the aqueous solution (point 1) plots on the left limit (see the dashed curves in the lower graph) of the “region I” corresponding to $x_{CA} = 0.36$, and is supersaturated with respect to the BA end-member (see the dotted $\Sigma\Pi_{Beq}$ curve in the same graph). This means that the aqueous solution is “strictly” supersaturated with respect to all the solid-solution compositions in the range $0 \leq x_{CA} \leq 0.36$, which correlates with the fact that $\delta(0.36) = 1$ (see upper graph in fig. 4).

Whereas in a first approach Shtukenberg and others (2006) define *a priori* the saturation state of a given aqueous solution using equation (12), they then state (see the “supersaturation” section in the referred paper) that the supersaturation cannot be determined *a priori* from the composition of the aqueous solution. However, an aqueous solution can exist with or without the presence of interacting solids. Therefore, its saturation state needs to be defined independently in order to define the solid phases whose crystallization is thermodynamically possible. This idea is applicable to any aqueous solution, not only to those cases in which the crystallization of a solid solution can be involved. For instance, in the case of an aqueous solution containing calcium and carbonate ions, the saturation state with respect to aragonite, calcite, and vaterite can be defined. The same holds for an aqueous solution containing calcium, cadmium, and carbonate. The only difference is that, in this second case, the involved solid phases are aragonite, vaterite, calcite, otavite and any intermediate member of the otavite-calcite solid solution series. Therefore, one should calculate the saturation state for the complete otavite-calcite series, which can be done using functions (14) and (15). This calculation does not assume *a priori* the phase that will crystallize, but allows determining whether a specific phase can crystallize (or dissolve) from (or in contact with) a particular aqueous solution.

A completely different problem is the prediction of the solid-solution composition that effectively nucleates from a given aqueous solution, as well as the prediction of the growth rate and compositional evolution of a “previously-existing” solid-solution crystal. These are complex kinetic problems that require the use of kinetic parameters. In their approach, Shtukenberg and others (2006) do not consider the nucleation problem, but only the interaction of a previously-existing crystal substrate with the aqueous solution. The nucleation behavior in SS-AS systems has been treated by Pina and Putnis (2002), who have elaborated a model that fits reasonably well with experimental data and is based (among other parameters) on the supersaturation functions described before. In relation to crystal growth, the problem is more complicated and the kinetic model proposed by Shtukenberg and co-workers necessarily contains significant simplifications. Such simplifications can be welcome when they help to understand particular aspects of a complicated process in a qualitative way. What is critical is to avoid any possible confusion between the thermodynamic properties of a given system and the particular features of a given scenario. Unfortunately, that is the situation that one finds in the section entitled “CHEMICAL INTERACTION WITH THE SUBSTRATE”, where Shtukenberg and co-workers take up again the idea of equilibrium between a phase and a component and propose coupled dissolution-precipitation (replacement) reactions that would be occurring under conditions (below the solutus) in which only dissolution can take place.

Another important aspect that should be carefully handled is precision in describing the scenario for which a particular kinetic model has been derived. For instance, in their crystal growth model, Shtukenberg and co-workers implicitly assume that the activities (and the activity fractions) of the reacting ions in the aqueous solution remain constant during crystallization. However, this cannot be the case during crystallization in SS-AS systems, where the substituting ions are not incorporated in the solid in the same stoichiometric proportion as in the aqueous solution. As a result, the compositions of both the aqueous solution and the solids formed tend to vary with the extent of reaction (Glynn and others, 1990), the reaction pathway depending on the specific amounts of solid and fluid. Actually, the model proposed by Shtukenberg and others could only be applicable to a system where the ratio between the precipitated-solid and the aqueous solution is extremely small or when the aqueous phase is continuously renewed.

THERMODYNAMICS AND KINETICS

Equilibrium thermodynamics deals with bulk properties that do not depend on specific scenarios such as the “misfit strain” arising at the interface between a substrate and a newly deposited layer of different composition. The paper by Shtukenberg and co-workers, however, treats this aspect in a misleading way. These authors include elastic energies (arising from a particular interface) in the formulation of the chemical potentials. However, chemical potentials are bulk thermodynamic properties that cannot be related to interfaces. In fact, elastic stress is also present in the vicinity of the surface of pure solids. However, this stress is not included in the formulation of the chemical potential, but in an artificial parameter, the interfacial tension, which includes all the excess energy accumulated in the vicinity of the solution-crystal interface (Wu and Nancollas, 1999).

The misfit strain is an interfacial feature (when the solid solution grows the successive layers relax towards their bulk dimensions) that should be included in the kinetic formulations of crystal growth, whatever the scenario that one considers (layer growth, two-dimensional nucleation, epitaxial overgrowth, heterogeneous nucleation). However, including this effect in the bulk thermodynamic properties leads to paradoxes of which the most striking is the proposal of a different phase diagram for each substrate composition. Perhaps the well-intentioned effort of incorporating kinetic aspects into the modeling of the growth of solid solutions from aqueous solutions is still premature. The experimental evidence of the existence of a complex kinetic behavior during the growth of successive solid-solution monolayers (Astilleros and others, 2003b) increases continuously. Therefore, developing a kinetic model for crystal growth of solid solutions will require a considerable experimentation. This will provide *in situ* nanoscale observations that will help to achieve a much better understanding of the real behavior occurring in these systems.

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