

SOLID SOLUTIONS(Mixtures)

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[Abstract]

The aim of this paper is essentially to propose a common starting point for handling so-called solid solutions, co-precipitation processes or mixtures. This starting point is Thermodynamics of ideal Mixtures -non-ideality is outlined in Appendix-. The thermodynamic formulae are first recalled –and demonstrated in Appendix- for simple three component Mixtures. This gives well known formulae. Based on them, several features of solid solutions are discussed, as typically the chemical meaning of the choice for stoichiometric coefficients, dramatic decrease of aqueous solubility for co-precipitation of elements at trace concentrations, and conversely little influence on aqueous solubilities, when the components of the mixture are at macro concentrations. The stoichiometry of ideal solid mixtures equilibrated is deduced from the composition of the equilibrated aqueous solution. Stoichiometric coefficients inside the mixture also appeared to be the saturation indexes of the pure components –*i.e.* end-members-; which suggests graphical representations. No new thermodynamic parameters are needed: the solubility product of the pure components –or equivalently their Gibb's energy of formation- are enough, which simply make the equations consistent with standard state. The dissolution reaction of a three component mixture was handled as a two advancement variables reaction, one of these reaction is ionic exchange inside the mixture. In that respect any ionic exchange equilibrium –in solid, surface or liquid phases- can be interpreted as deriving from the dissolution reaction of the ion exchanger matrix;; this give a theoretical to Standard State for sorption, at least when described as Ionic Exchange.



[Introduction]

Co-precipitation can considerably decrease aqueous concentrations of radionuclides, specially when their concentrations are less than the solubility as controlled by simple classical stoichiometric solid compounds –namely pure components also called end-members-. This can delay the migration of radioactivity from eventual underground waste disposals. Words Solid Solutions, Mixtures and Co-Precipitation are used for solid compounds of variable stoichiometries: they can be considered as mixed compounds (**mixtures**), or as one compound diluted in the other one (**solid solutions**), specially when the solute is at trace concentrations (**co-precipitation**); which actually corresponds to important chemical conditions, since 100 % purity cannot reasonably be achieved –and would correspond to infinite Entropy-. Intuitively impurities can exchange with analogue macro-components, namely **ions are exchanged**, when they are of same charge and analogous ionic radii; such elements at trace concentrations can accommodate the solid matrix -it is often at the origin of low temperature **ideal solid solutions-** to a certain limit; conversely, these limits are usually reached at macro-concentrations, when the exchanged ion cannot fit the matrix any more. Co-precipitation cannot be considered as mechanical trapping of trace elements, since their saturation indexes in equilibrium conditions are always much less than one for pure components. Co-Precipitation and Solid Solution intuitively refer to non-symmetric situations. However, this is not specially needed for demonstrating the thermodynamic equations needed to describe mixtures [52GUG]: we will rather start by describing aqueous solubilities of mixtures, the symmetric situation. For describing solid solutions several partial or empirical approaches are proposed, and widely used, despite Thermodynamics of mixtures is well known, and even implemented in computer codes [PHREEQC, GEM-Selektor]. Karpov *et al.* discussed general mathematical equations for mixtures and their implementations in computer codes (see [97KAR/CHU] and reference therein) and Kulik *et al.* discussed empirical approaches and published examples [00KUL]. Direct demonstrations and interesting discussions were also given by Michard [83DEN/MIC, 86MIC, 89MIC and 02MIC]. However, apparent "paradoxes" still stand, reflecting poor qualitative understanding for some aspects of aqueous solubility as controlled by mixtures, despite Theory is well established:

- The stoichiometry inside the solid solution can very well change in the course of its dissolution, despite stoichiometric dissolution is sometimes assumed as a first approximation. This is often a correct approximation for trace concentrations, and we will see that the stoichiometry of ideal mixtures can be calculated from aqueous speciation. Aqueous speciation is not discussed in this paper [PHREEQC].
- Since experimental solid solutions are not necessarily ideal mixtures, empirical equations or kinetics are often added to thermodynamics descriptions, without clearly evidencing this is really needed. This is surprising since we will recall that solid solutions can induce dramatic changes in solubilities only for trace concentrations, where solid solutions are often ideal.
- For introducing Ideal Mixtures in Thermochemical Data Bases, the only needed thermodynamic parameters are the solubility products of their pure components, which actually are not new parameters. Consequently, one might be surprised that Thermodynamics indicate solid solutions should always form (see [KUL] and we will confirm this), since mixtures are more stable than unmixed pure components (End-Members) for Entropy reasons. However, this is only for ideal mixtures: the paradox only means that most mixtures are not ideal for macro-concentrations at low temperatures (see above).
- Different non-equivalent equations can be obtained depending on the way the stoichiometric coefficients –of the solid solution- are written, when ions of different charges are exchanged inside



the solid solution. Again these situations usually do not correspond to ideal solid solutions [89MIC]. Nevertheless, we will see that thermodynamic cycles can produce non-intuitive exchange equilibria in solid mixtures.

We were also puzzled by the using of Mass Action Law like equations for equilibria with variable stoichiometric coefficients, while Mass Action Law is usually demonstrated by using mathematical derivation with constant stoichiometric coefficients, indeed we shall see a term is missing originated from deriving stoichiometric coefficients, as already outlined on examples [02VIT/CAP, 03VIT/CAP].

Objectives

For clarifying these problems are only paradoxes that can be resolved with the well known thermodynamic description of mixtures, it seems enough to **recall thermodynamic equations describing mixtures, and their associated chemical concepts and features; this is the aim of the present paper**. In the present paper, we shall take a simple example: a system with 3 chemical species, the minimum number of species needed to form a solid solution. We give a direct simple demonstration in Appendix, where most of the equations and chemical reactions are numbered, and the same numbers are used in the main text. We then recall Working Formulae and finally discuss them. It will appear that the dissolution of this simple solid solution is actually a two advancement variable reaction, namely Stoichiometric Dissolution and Ionic Exchange. Intuitively the last reaction should involve ions of same charge and similar radii, or at least ions whose exchange fit the matrix. Conversely any ionic exchange equilibrium can be considered as part of the description of a Mixture, which can link it to usual Standard State through the solubility products of the pure components, providing the description of the ionic exchange reaction is consistent with Thermodynamics, specially it must include a reference state. It will appear that stoichiometric coefficients are also saturation indexes.

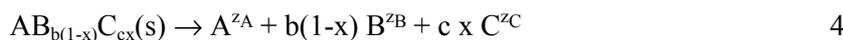
Results and discussion

Solid solution $AB_{b(1-x)}C_{cx}(s)$, includes three ions, A^{z_A} , B^{z_B} and C^{z_C} , of charges z_A , z_B and z_C respectively. $0 \leq x \leq 1$, and for electroneutrality

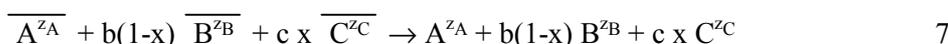
$$b = \frac{-z_A}{z_B} \quad 1$$

$$c = \frac{-z_A}{z_C} \quad 2$$

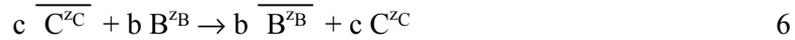
These notations for the stoichiometric coefficients (1, $b(1-x)$ and cx) encompass all the possible three components solid solutions. Other choices are possible for the stoichiometric coefficients, our choice will simplify equations and clarify their meaning, specially concerning ionic exchanges (see below). The dissolution reaction is usually written



but we rather writes



where $\overline{A^{zA}}$ is ion A^{zA} in the solid solution. z_A is the charge of ion A^{zA} , similar notations are used for B and C which are generic elements (not Carbone and Boron respectively) Further reactions in the aqueous phase can be modelled independently by using mass balance and mass action laws, for this reason and for simplicity, we do not consider them. Since we choose 1 for the stoichiometric coefficient of A^{zA} , Dissolution Reaction 7 also includes Ionic Exchange Equilibrium



The set of two equations

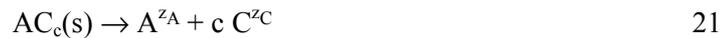
$$\begin{cases} K_{s0}^{1-x} K_{s1}^x = \frac{m_A m_B^{b(1-x)} m_C^{cx}}{(1-x)^{b(1-x)} x^{cx}} \\ \frac{K_{s1}}{K_{s0}} = \frac{m_C^c (1-x)^b}{m_B^b x^c} \end{cases} \quad 52$$

is easily demonstrated for ideal solid solutions, where m_A is the aqueous concentration of ion A^{zA} , and similar notations are used for B and C. **Both equations are well known**; but usually cited separately in literature, hence **it is not well recognized that they must be solved simultaneously**.

$$K_{s0} = m_A m_B^b \quad 24$$

$$K_{s1} = m_A m_C^c \quad 24a$$

are the solubility products of the end-members corresponding to Equilibria



where $AB_b(s)$ and $AC_c(s)$ are the end-members corresponding to $x = 0$ and 1 respectively, while when the solid solution is stable $0 < x < 1$, which means no end-member can be stable (when the solid solution is stable). Since aqueous concentrations are often easily measured, it is useful rearranging the above equations for extracting x , the **stoichiometric coefficient in the solid phase**:

$$1 - x = \frac{m_A^{1/b} m_B}{K_{s0}^{1/b}} \quad 59$$

$$x = \frac{m_A^{1/c} m_C}{K_{s1}^{1/c}} \quad 68$$

$K_{s0} b^b$ and $K_{s1} c^c$ can now be interpreted as the constants of ionic exchange Equilibria



and



respectively. However, such ionic exchanges are of little chemical interest, since they involve ions of opposite charges: such mathematical results probably do not correspond to ideal solid solutions. Introducing Notations $m_{A,0/1}$, $m_{B,0/1}$ and $m_{C,0/1}$ for the concentrations of A^{zA} , B^{zB} and C^{zC} respectively, when both end-members control the aqueous solubility (in that case not any solid solution is formed), the above equations for solid solutions write

$$\begin{cases} \frac{m_A}{m_{A,0/1}} \left(\frac{m_B}{m_{B,0/1}} \right)^{b(1-x)} \left(\frac{m_C}{m_{C,0/1}} \right)^{cx} = x^{cx} (1-x)^{b(1-x)} \\ \left(\frac{m_C}{m_{C,0/1}} \right)^c \left(\frac{m_{B,0/1}}{m_B} \right)^b = \frac{x^c}{(1-x)^b} \end{cases} \quad 74$$

$$\text{where } m_{A,0/1} = K_{s0} m_{B,0/1}^{-b} = K_{s1} m_{C,0/1}^{-c} \quad 73$$

For slope analysis of Solubility



$$\left(\frac{\partial \lg(m_B)}{\partial \lg(m_A)}\right)_{m_C} = \frac{-1}{c(1-x)} + \frac{1}{c} - \frac{1}{b} \quad 76$$

$$\left(\frac{\partial \lg(m_C)}{\partial \lg(m_A)}\right)_{m_B} = \frac{-1}{bx} + \frac{1}{b} - \frac{1}{c} \quad 76a$$

it appears that when $b = c$ (*i.e.* when $z_B = z_C$) these slopes are obtained from stoichiometric coefficients of the non-stoichiometric dissolution reaction (Eq.4), in the same way as for stoichiometric compounds (*i.e.* generalising slope analysis of End-members).

A general formula for three component solid solutions is $A_{v_A}B_{v_B}C_{v_C}(s)$; but the same solid solutions can as well be noted $AB_{v_B/v_A}C_{v_C/v_A}(s)$ for any constant value of v_A , and the stoichiometric coefficients are also constrained by electroneutrality (Eq.1 and 2): for these reasons $AB_{b(1-x)}C_{cx}(s)$ notation encompass all possible three component solid solutions. x is the proportion of the end-members in the solid solution

$$AB_{b(1-x)}C_{cx}(s) = x AB_b(s) + (1-x) AC_c(s) \quad 3$$

and **exchanging ions B^{z_B} and C^{z_C}** (Eq.6) appears to be a "natural" way to vary the stoichiometry **within the solid solution**. When A, B and C are molecules *-i.e.* not necessarily elements, but groups of elements- several choices are possible for dividing any real solid solution in such three groups of elements. Chemists "natural" **choices of A, B, C and x** should typically ensure that "natural" End-Members $AB_b(s)$ and $AC_c(s)$, are of same structure, and Exchanged Ions B^{z_B} and C^{z_C} , of same charge ($z_B = z_C$, hence $b = c$ (Eq.1 and 2)) and similar ionic radii for having more chances of eventually evidencing any ideal solid solution. These choices of A, B, C and x -not provided by Thermodynamics- are important for chemical interpretations; which explains paradoxes as outlined in Introduction. At least one ionic exchange equilibrium is intrinsically associated with any Mixture: typically Equilibrium 7 -with variable x - includes ionic Exchange Equilibrium 6, and it is better choosing notations consistent with realistic chemical ionic exchanges. Conversely, linear combinations of these two equilibria provide other equilibria as typically



which appear to be other exchange equilibria; but they cannot have the same meaning as the "natural" exchange of Ions B^{z_B} and C^{z_C} (Eq.6), at least because z_B and z_C are of same sign, while z_A is not. This again stresses the importance of the meaning of the notations -namely here choosing $v_A = 1$, while v_B and v_C vary with x -, and of the chemical interpretations of equations, namely when $AB_b(s)$ and $AC_c(s)$ are "natural" End-Members -as defined just above for Ionic Exchange Equilibrium 6-, it does not seem possible to simply and simultaneously define equivalent "natural" End-Members for Equilibria 54 or 60. A set of **two equations should be solved together** (Eq.52). To our knowledge, this is not always recognized, despite each formula is already well known separately (see typically [02MIC] where direct demonstrations are proposed). Eq.52 are the thermodynamic description of the ideal solid solution (for non-ideality, see Appendix). In the first equation 52 term $m_A m_B^{b(1-x)} m_C^{cx}$ looks like a solubility product for Equilibrium 7; however, it is not constant; while the second equation 52 is Mass Action Law for the ionic exchange equilibrium (Eq.6). **The stoichiometric coefficients in the solid solution can be calculated** from the aqueous speciation: Eq.59 or equivalently Eq.68 obtained by combining Eq.52, despite it is seldom recognized that x can be calculated for ideal solid solutions. **Coefficients $(1-x)^b$ and x^c , appear to be saturation indexes for End-members $AB_b(s)$ and $AC_c(s)$ respectively** (Eq.59 and 68). This suggests plots -rather log-log plot- of the saturation indexes as a function of the concentration of the non-exchanged ion, namely



A^zA . $0 \leq x \leq 1$ correspond to $0 < x < 1$ when the solid solution is not degenerated into one of its end-members. In that case, **the saturation indexes of the end-members are always less than 1 when assuming ideal solid solutions**. This also means that no end-member is stable. When x is close to zero, the saturation indexes of AB_b and AC_c are close to 1 and very small respectively (Eq.59 and 68): **trace concentrations** of C^zC are co-precipitated in End-member AB_b . Conversely, when x is close to 1, trace concentrations of B^zB are co-precipitated in End-member AC_c . In these cases of trace concentrations, it often makes sense to assume that the solid solution is ideal, while this should be quite exceptional at low temperature in the other cases, where none of the saturation indexes is very small, which then, anyhow, means that Solid Solutions should not dramatically decrease Solubility. Eq.74 again indicates that dramatic changes are expected for ratios $m_B/m_{B,0/1}$ and $m_C/m_{C,0/1}$, only when x is close to 0 or 1. Ionic Exchange Equilibrium 6 can be obtained by mathematical deriving:

$$v_{i,6} = \frac{dv_i}{dx} \quad 8$$

where v_i and $v_{i,6}$ are the stoichiometric coefficients of Reactions 7 and 6 respectively. This is actually the way we introduced Ionic Exchange Equilibrium 6 included in Dissolution Reaction 7. This suggests Notation

$$\text{Reaction 6} = \frac{d(\text{Reaction 7})}{dx} \quad 9$$

For this reason we obtained several pairs of equations, where the second one – corresponding to Ionic Exchange Equilibrium 6- can be obtained by deriving the first one – corresponding to Dissolution Reaction 7-. Conversely **any ionic exchanged equilibrium can be considered as deriving from a mixture**: Ionic Exchange Equations are integrated for obtaining the equations for the matrix, from which the ionic exchange is assumed to derive. The equilibrium constant of the ionic exchange is interpreted as a ratio of equilibrium constants for the pure components (second Eq.52), a second constant is needed for characterising both pure components, it is provided by the integration constant. Equilibrium constants for the pure component are equivalent to Gibbs energies of reactions, and finally to Gibb's Energies of formation by using auxiliary data. This outlines the link with the usual Standard State. Many ionic exchange equilibria have been evidenced in typically liquid, solid or surface phases. Integrating them make a link to their matrix, and finally to Standard State. However when the "matrix" is actually a surface, it is not clear whether surface solubility products can be measured. It is also required to define an ideal matrix, before eventually adding non-ideality (see Appendix), for surfaces this is usually not a problem for Ionic Exchange Theories, when the interface phase is neutral –it is implicitly assumed to include the electric double layers- while it is less clear for Surface Complexation Formulae.

Appendix and References can be asked to the first author, and will be in a separate report, the full version will be referenced at URL <http://www-ist.cea.fr>.

