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LAW OF MASS ACTION FOR CO-PRECIPITATION

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RAPPORT CEA-R-6193 - Pierre VITORGE

"Loi d'action de masse de la co-précipitation"

Résumé - $K_{s,B}^{1-x} K_{s,C}^{x} = [A^{zA}]\ [B^{zB}]^{b(1-x)}\ [C^{zC}]^{cx}\ /((1-x)^{b(1-x)}\ x^{cx})$ et $K_{s,C}/K_{sB} = (1-x)^b\ [C^{zC}]^c\ /([B^{zB}]^b\ x^c)$ sont les 2 formules permettant de calculer la solubilité aqueuse contrôlée par la solution solide (idéale) $AB_{b(1\ x)}C_{cx}$, où $K_{s,B}$ et $K_{s,C}$ sont les produits de solubilité (constants, classiques) des pôles purs, AB_b et AC_c, les valeurs de b et c assurent l'électro-neutralité compte tenu des charges (z_i) des ions. Ce rapport donne une démonstration (thermodynamique) calquée sur celle, habituelle, de la loi d'action de masse, afin de confirmer les bases scientifiques de l'utilisation de ces formules en géosciences (piégeage de radionucléides par un co-précipité) et de faciliter l'utilisation des formules en question. En particulier la loi d'action de masse est ici un système de 2 équations (et non une seule) pour un système idéal ou proche de l'idéalité. Conformément à la règle des phases, elles sont suffisantes (avec les bilans de matière) pour calculer toutes les concentrations dans toutes les phases : $[A^{zA}]$, $[B^{zB}]$, $[C^{zC}]$ et y compris x.

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RAPPORT CEA-R-6193 - Pierre VITORGE

"Law of mass action for co-precipitation"

Abstract - $K_{s,B}^{1-x} K_{s,C}^{x} = [A^{zA}]\ [B^{zB}]^{b(1-x)}\ [C^{zC}]^{cx}\ /((1-x)^{b(1-x)}\ x^{cx})$ et $K_{s,C}/K_{sB} = (1-x)^b\ [C^{zC}]^c\ /([B^{zB}]^b\ x^c)$ are the two formula are needed to calculate the aqueous solubility when controlled by the ideal $AB_{b(1\ x)}C_{cx}$ solid solution, where $K_{s,B}$ and $K_{s,C}$ are the -classical constant- solubility products of the AB_b and AC_c end-members, the b and c values are calculated form the (z_i) charges of the ions and from charge balance. This report is essentially written to provide a -thermodynamic- demonstration of the law of mass action in attempts to confirm scientific bases for solubility calculations in geosciences (as typically retention of radio-nuclides by co-precipitation), and to facilitate such calculations. Note that the law of mass action is here a set of 2 equations (not only 1) for the ideal or near ideal systems. Since they are consistent with the phase rule, no extra formula (beside mass balance) is needed to calculate the concentrations of all the species in both phases, namely: $[A^{zA}]$, $[B^{zB}]$, $[C^{zC}]$ and specially x.

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LAW OF MASS ACTION FOR CO-PRECIPITATION

par

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- Septembre 2008 -

Law of Mass Action for co-Precipitation

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Forewords and acknowledgements.

The forewords and acknowledgements are written in French, -this is the only section written in French.

Avant-propos et remerciements.

Ce rapport contient essentiellement une démonstration de la loi d'action de masse pour les solutions solides. Naturellement, nous obtenons des formules connues. Ainsi, pour la solution solide (idéale) $AB_{b(1-x)}C_{cx}$ nous retrouvons le pseudo produit de solubilité variable

$$K_{s,B}^{1-x}K_{s,C}^{x} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b(1-x)}\left[C^{z_C}\right]^{cx}}{(1-x)^{b(1-x)}\,x^{cx}}$$

où $K_{s,B}$ et $K_{s,C}$ sont les produits de solubilité (eux constants et classiques) des pôles purs AB_b et AC_c respectivement, les valeurs de b et c étant imposées par les charges (z_i) des ions, pour assurer l'électro-neutralité. Toutefois, le fait d'avoir rendu une composition variable (x) dans un solide initialement pur (un des pôles purs), rajoute un degré de liberté au système d'une part. D'autre part, la loi du produit de solubilité (pour le pôle pur initial) n'est plus valable. Ainsi, là où on avait une équation, celle du produit de solubilité, il en faut maintenant deux. Celle ci-dessus (du pseudo produit de solubilité variable) en est une ; nous démontrons que l'autre est, par exemple

$$\frac{K_{s,C}}{K_{s,B}} = \frac{(1-x)^{b}\left[C^{z_C}\right]^{c}}{\left[B^{z_B}\right]^{b}x^{c}}$$

le classique coefficient de partage qui, en fait, est la loi d'action de masse appliquée à l'équilibre d'échange des ions qui sont en proportions variables dans $AB_{b(1-x)}C_{cx}$ ($\left[B^{z_B}\right]$ et $\left[C^{z_C}\right]$).

Même si les deux équations sont publiées, il n'est pas vraiment clair dans la littérature ou les manuels de cours de géochimie, qu'il faille deux équations et non une seule, ou du moins que ces deux équations sont simultanément vérifiées. Naturellement, il y a plusieurs variantes dans la littérature, puisque la combinaison d'un système de deux équations, peut donner des systèmes de deux équations équivalents. L'un des plus connus est le système

$$\frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b}}{(1-x)^{b}} = K_{s,B}$$

$$\frac{\left[A^{z_A}\right]\left[C^{z_C}\right]^{c}}{x^{c}} = K_{s,C}$$

On trouve aussi des écritures équivalentes où 1-x et x sont remplacés par les fractions molaires de AB_b et AC_c dans le mélange solide. Même si ceci est parfaitement justifié, le mélange n'est pas une mosaïque des pôles purs; mais bien une répartition au hasard de B et C sur les sites d'échange d'ions : on ne retrouve pas les pôles purs dans la solution solide, cette écriture ne correspond pas à la géométrie, elle représente une moyenne. Quelques auteurs donnent des démonstrations exactes de certaines de ces formules, en s'appuyant sur une interprétation correcte de la loi d'action de masse classique telle qu'elle doit être appliquée à une solution solide ; mais les conditions d'application de la loi d'action de masse, sont assez subtiles dans ce cas là (voir par exemple la discussion de Lippmann, dans le texte en anglais) et la plupart des justifications publiées, sans être nécessairement fausses, restent floues, intuitives et peu convaincantes.

Ceci a d'importantes **implications pratiques**. La co-précipitation peut, en effet, être un moyen de piégeage de radio-nucléides par des minéraux naturels, encore faut-il faire admettre que les équations pour prévoir cette rétention, sont bien établies et non, plus ou moins empiriques. Les agences chargées de la gestion des déchets radioactifs ont ainsi récemment soutenu un travail de compilation des modélisations géochimiques existantes dans ce domaine (évoqué dans le texte en anglais).

Comme elle devait faire le point de ce qui est publié sur cette question pour des minéraux relativement simples (rapport non publique), j'ai proposé à **Marie-Hélène Fauré** de ne pas se contenter de trier des formules utilisées par les géochimistes ; mais d'en chercher aussi les justifications théoriques ou expérimentales. Elle en a ainsi testé un bon nombre sur des systèmes simples, ce qui a permis de se rendre compte que souvent une seule des équations ci-dessus est utilisée, puis une autre plus ou moins empirique, de forme variée suivant les auteurs, est éventuellement rajoutée pour interpréter des résultats expérimentaux. Ces derniers sont malheureusement souvent trop imprécis sur la composition de la solution aqueuse pour pouvoir calculer l'influence des réactions en solution aqueuse, concurrentes à la co-précipitation : les vérifications expérimentales sont alors peu convaincantes quand elles nécessitent l'ajustement de paramètres ad hoc. Le pseudo produit de solubilité variable est, en particulier, souvent un point de départ, puis sont parfois rajoutés des raisonnements (explicitement ou non) approximatifs pour trouver l'équation manquante qui donnera, par exemple, la stoechiométrie dans le solide (la valeur de x). Une approximation mathématiquement simple est de supposer la dissolution stoechiométrique (c'est-à-dire à x constant) ; mais il ne semble pas qu'il existe de justification convaincante de cette hypothèse ou d'autres dans le même esprit. Examinant, en effet, ce type de démarche j'ai proposé que la valeur de x devrait correspondre à un minimum partiel de solubilité ; comme il y a plusieurs espèces chimiques (A, B et C) minimiser la solubilité (en fonction de x uniquement) signifie en fait trouver l'énergie libre de formation de la solution solide, la plus faible ; on se rend alors aisément compte que cela revient à minimiser son pseudo produit de solubilité variable. Effectivement, dérivant (par rapport à x uniquement) le log de son expression, on trouve exactement le log de la loi d'action de masse de l'équilibre d'échange d'ions. C'est l'équation manquante. Cette approche a ensuite été appliquée au système NpO_2^+ / Na^+ / CO_3^{2-} pour lequel il avait été (intuitivement) proposé, sur la base de résultats expérimentaux de solubilité, que la stoichiométrie pourrait varier dans le solide or l'allure des résultats expérimentaux est finalement nettement différente de celle des courbes de solubilité théorique de solutions solides dans le domaine où des traces d'un des cations serait incorporé dans la phase pure de l'autre. Inversement, si les proportions des deux cations sont du même ordre dans le solide, la différence des solubilités aqueuse contrôlée soit par la solution solide soit par une phase pure, est de l'ordre de grandeur de la précision expérimentale [99VIT/BEA, 03VIT/CAP].

Serge Maillard est à l'origine de la généralisation de la démonstration de la loi d'action de masse que nous donnons (pour un équilibre à double degré d'avancement). Il a, en effet, trouvé que la réaction de dissolution de la solution solide ne correspond pas à un équilibre satisfaisant aux conditions d'application de la loi d'action de masse tel qu'on la démontre classiquement dans les manuels de cours (c'est évident puisque la réaction en question n'est pas caractérisée par une constante d'équilibre, mais par un pseudo produit de solubilité variable, encore fallait-il y penser). La démonstration passe, en effet, par une minimisation de de l'enthalpie libre du système, ainsi on annule

$$dG = \sum_i \mu_i dn_i$$

avec

$$dn_i = \nu_i d\xi$$

où ξ est le degré d'avancement et ν_i un coefficient stoechiométrique : quand ce dernier varie, la formule $dn_i = \nu_i d\xi$ n'est évidemment plus valable. Une fois rendus à cette évidence, il suffit alors de généraliser la démonstration de la loi d'action de masse en utilisant

$$dn_i = \left(\frac{\partial n_i}{\partial \xi}\right)_x d\xi + \left(\frac{\partial n_i}{\partial x}\right)_\xi dx$$

On retrouve et démontre ainsi toutes les formules correctes publiées sur le sujet. Cette démonstration est bien plus compliquée que celle de Lippmann , qui est vraiment plus élégante, surtout si on y rajoute la façon qu'a Michard de généraliser cette approche à des ions de charges différentes. Inversement, comme nous re-démontrons directement la loi d'action de masse dans le cas particulier qui nous intéresse, la justification en est explicite et immédiate.

Les équations trouvées peuvent être combinées de différentes manières pour en mettre en évidence le sens physique ou chimique. Comme il s'agit d'équations équivalentes à celles de Lippmann et Michard, au moins dans l'esprit, nous avons, dans le texte en anglais, présenté ces commentaires comme discussion des équations de Lippmann et Michard. Ceci a l'avantage de ne pas faire porter le débat sur la validité des équations (puisqu'elles viennent d'auteurs reconnus) ; mais uniquement leur signification. Dans le même esprit il n'y a pas, à cet endroit, de souci de démonstration mathématique. Celle-ci vient à la fin, ce qui permet de ne pratiquement pas y mêler de commentaire sur la signification physique ou chimique des équations.

Gil Michard m'a fait d'utiles remarques. Je me souviens de celle sur le fait qu'on utilise les produits de solubilité des pôles purs dans les calculs sur leur solution solide (pour rattacher cette dernière à l'état standard) ; mais que les pôles purs ne peuvent, en général, pas être thermodynamiquement stables si la solution solide l'est.

J'ai souvent sollicité **Patrick Lovera** pour qu'il vérifie certains des calculs (présentés ici et bien d'autres). Il m'a, en particulier, fait remarquer que je n'utilise pas (ou plus) les fractions molaires. J'ai d'abord considéré que c'était pour simplifier les calculs et que mes unités de concentration (dans le solide) devaient être équivalentes aux fractions molaires ; en voulant vérifier j'ai finalement vu qu'il n'en est rien et ç'a aussi permis de me rendre compte que les fractions molaires ne sont pas des variables intensives et donc pas des unités de concentration dans le cas où les ions échangés ($\left[B^{z_B}\right]$ et $\left[C^{z_C}\right]$) sont de charges différentes. Les unités de concentration que j'utilise sont, en effet, ramenées à la quantité de matrice (représentée par le nombre de moles de A dans $AB_{b(1-x)}C_{cx}$) et non au nombre total de moles qui change au cours de l'échange de B et C, sauf quand ils sont de même charge (alors b = c). Les unités de concentration que j'utilise, préservent une certaine symétrie entre les rôles de B et C ; c'est vraisemblablement ce qui permet de résoudre ce paradoxe (relevé par Michard dans l'édition de 1989 de son livre) qu'en utilisant les fractions molaires, on peut trouver des équations non équivalentes suivant la façon de faire les calculs. Cela rejoint aussi une remarque de **Dominique You**, sur le fait que les concentrations doivent être des variables intensives, ce qui est assez évident (mais ça ne dispense pas d'y faire attention), en fait nécessaire pour démontrer $G = n\ \mu$. Pour cette raison il y a problème a utiliser des concentrations de surface, ce qui est également évident puisqu'il faut effectivement connaître le lien entre variation de la surface et taille du système ; or ce lien peut prendre des formes très variées.

Dominique You, m'a également donné un éclairage complémentaire des solutions solides, en utilisant l'approche mélange de solides purs, plutôt que solution solide. Les deux approches sont équivalentes. Chacun avec ses avantages et inconvénients. Les solutions solides présentent la difficulté d'isoler un des constituants pour en faire le solvant (ou la matrice) qui représente la taille du système, les solutés n'interviennent pas dans la taille du système. Ca peut être pris en compte comme écart à l'idéalité. L'avantage des solutions solides est qu'on peut plus facilement faire intervenir les ions réellement mis en jeux (ce qui peut être indispensable pour traiter l'écart à l'idéalité), alors que les mélanges ne connaissent que les pôles purs comme espèces chimiques. Je n'ai pas spécialement développé ce genre de discussion.

Comme Michard a montré que les calculs ne sont pas beaucoup plus compliqués quand les ions échangés sont de charges différentes, j'ai surtout traité ce cas. On peut toutefois se demander comment les changements de coordination et stoechiométrie accompagnant alors forcément l'échange d'ions, peuvent être compatibles avec la rigidité de la matrice. La réponse est dans la nature. Les métallurgistes connaissant bien, aussi, ce genre de problème. Dominique You m'en a expliqué un exemple... mais je n'ai pas inclus d'exemple dans ce texte, je m'en suis toutefois inspiré pour traiter les lacunes. En fait, ce n'est pas si simple, car il faut faire intervenir des lacunes, plus précisément une maille élémentaire généralement plus grande que celle de constituants purs et souvent vue de façon différente. On s'efforce alors d'avoir le même réseau pour les deux pôles purs en laissant éventuellement des sites vacants. Cela suppose donc de bien examiner les structures. Il peut y avoir plusieurs descriptions géométriques possibles, particulièrement si on accepte de petites distorsions de structures parfaites. Ces petites distorsions sont physiquement réalistes en raison des lacunes et surtout de l'échange d'ions de types différents. Ceci met en évidence que trouver la (ou les) façon(s) pertinente(s) d'écrire la stoechiométrie de la solution solide, peut-être délicat. Déjà le choix de l'écriture $AB_{b(1-x)}C_{cx}$ n'est pas immédiat.

Les équations permettant de traiter les solutions solides AnO_{2+x} [02VIT/CAP] ont été corrigées par **Thomas Vercouter** ; mais je n'ai pas considéré de lacune dans ces solides. Cette description permet toutefois de se faire une idée qualitative de l'influence de la formation de solutions solides ou de composés stoechiométriques intermédiaires, de montrer comment calculer le potentiel d'oxydo-réduction contrôlé par la solution solide et donc de modéliser des résultats électrochimiques.

Philippe Jean-Baptiste m'a signalé la publication de Sillén dont j'utilise la méthode pour montrer qu'on rajoute un degré de liberté du système.

Pascal Reiler m'a forcé à terminer ce texte.

[99VIT/BEA] P.Vitorge, C.Beaucaire, M.-H. Fauré, S.Maillard, H.Capdevila. *Solubilities of actinides in complex solutions. What are the solubility controlling phases in complex media?* Workshop on Solubility of actinides in relation with nuclear waste matrices. Mol (Belgium) 19-20/05/1999

02VIT/CAP] P.Vitorge, H.Capdevila, S.Maillard, M.-H. Fauré, T.Vercouter *Thermodynamic Stabilities of* $MO_{2+x}(s)$ *(M = U, Np, Pu and Am), Pourbaix diagrams.* J. Nuclear Sc. Techno., Supplement 3, p713-716(2002).

[03VIT/CAP] P.Vitorge, H.Capdevila, *Thermodynamic data for modelling Actinide speciation in environmental waters.* Radiochim. Acta., 91, 11, p.623–631 (2003).

Contents

1 Introduction.

Coprecipitation is often understood as the incorporation of elements at trace concentrations into -initially pure- solid compounds. It is rather believed to be observed, when the trace element is a chemical analogue of an element at macro-concentration of the -initially pure- solid compound. It has typically been used to identify radioactive isotopes [1898CUR/CUR]. Co-precipitation can result in lowering solubility as compared to the solubility, when controlled by pure compounds. For this reason it is also important for Geochemistry, waste management and (de)pollution studies.

The solid resulting from co-precipitation is a new homogeneous solid phase called Solid Solution or Mixture, where the original pure compound now contains variable concentrations of the co-precipitated impurities. These two terms (Solid Solution or Mixture) reflect two different approaches for the thermodynamic descriptions: these two approaches use slightly different ways for describing the same system. Mixtures are built from pure solid compounds (namely end-members or equivalently pure components) in various proportions -none of them specially at trace concentration-, while for solid solutions one of the pure compounds is identified as the matrix, in which various elements are soluble. The later description is actually also used for aqueous solutions, it is more convenient for handling chemical equilibria written with the actual chemical species -including ions- and this is needed to identify ideal systems.

Aqueous solubilities can be calculated by using classical chemical thermodynamics for the solid and ideal aqueous phases. These equations are also well known, and typically implemented in geochemical computer codes for the case of ideal solid solutions (see typically Ref.[PHREEQC]). Extension to diluted (ionic strength less than typically 0.1 $mol.L^{-1}$) real aqueous solutions can be performed by using activity coefficients as calculated with the Davies' equation, or other empirical formula. For this, the stoichiometries and thermodynamic stabilities -*i.e.* $^{\cdot}\Delta_rG$ values or equivalently equilibrium constants- are needed for all the chemical species at each temperature and pressure. Mass balance equations are also needed. They are written for concentrations, while equilibrium constants are for activities. The later are equivalent to concentrations for ideal systems, which is the case for chemical species diluted at very low concentrations in solutions or solid matrix. This is relevant for coprecipitation of trace elements. However, such theoretical description is still valid for any concentration, providing the system is ideal, unless further approximations are introduced for neglecting trace concentrations in typically mass balance equations. For this reason we will essentially describe ideal systems, giving only a few indications on the way to use it as the starting point for real (non-ideal) systems. On the other hand, it is interesting to start with trace concentrations for understanding how solid solutions can be formed, and to get qualitative pictures. We will start with such simple cases for pointing out more general features. Thermochemical equations are widely used for calculating aqueous speciation, including aqueous solubilities as controlled by pure compounds, while it is often a bit confusing for aqueous solubilities controlled by solid solutions, despite the basic thermodynamic equations for solid mixtures are well known for a long time (see typically Textbook [52GUG]). As an example of this complexity for modelling coprecipitation, one can cite a recent compilation published by the AEN-TDB, where many equations used by geo-chemists are reviewed.

The simplest solid solutions are certainly pure compounds with several isotopes: there is no problem to qualitatively imagine the (isotopic) equilibrium for such compounds, when equilibrated with aqueous solutions. One of the isotopes can further be replaced with a chemical analogue. We first examine isotopic exchange equilibria in an aim to point out qualitative features, when using the law of mass action for solubility equilibria -namely the solubility product equation-. This is supported by a few equations given without rigorous demonstration. Finally demonstrations are given for general cases, including exchanges of ions with different charges inside the solid phase. Before these mathematical demonstrations we point out that vacancies can allow exchanges of ions with different charges still accommodating electro-neutrality.

We take the example of the simple $AB_b(s)$ solid made with Ions A^{z_A} and B^{z_B} of charges z_A and z_B. For electro-neutrality z_A and z_B are of opposite signs, and

$$b=-\frac{z_A}{z_B}. \qquad (1)$$

$$K_{s,B}=\left[A^{z_A}\right]\left[B^{z_B}\right]^b \qquad (2)$$

is the solubility product of $AB_b(s)$, where [i] is the concentration of Species i. [i] is the usual notation for molar concentrations (mole per litre of solution), while molal concentrations (mole per kg of water -water, not solution) should be used as thermodynamic unit; furthermore, activity should be used instead of concentrations. This will be done only when demonstrations will be given (Section 4.). Going from activities to molalities and then to molarities is classically done by introducing molar activity coefficients (γ), then molar to molal correction factors (ϱ). These corrections are included in equilibrium constants (here $K_{s,B}$) -they must be small corrections (less than an order of magnitude)- which finally does not change the formula (here Eq.2): the equilibrium "constant" (here $K_{s,B}$) -which actually is not a constant: it is a function of the pressure (P) and the temperature (T)- slightly depends on the medium, essentially ionic strength (for γ) and density (for ϱ). $K_{s,B}$, the solubility product is the constant of Equilibrium

$$AB_b(s) \rightleftarrows A^{z_A} + b\ B^{z_B} \qquad (3)$$

Since A^{z_A} can form a solid compound with B^{z_B}, it might very well also form soluble complexes with B^{z_B} : $\left[A^{z_A}\right]$ is not necessarily the total aqueous concentration of A^{z_A}. For this reason, we focus only on the law of mass action (for the solid): not on the mass balance equations in the aqueous solution. Calculating the exact aqueous speciation is now easily done with popular computer codes, it is usually well done in the literature, and well understood. Classical approximations can also be useful. Typically, when an excess of B^{z_B} is used, $AB_n^{z_A-n\,z_B}$ is the major chemical species of A, and $\left[AB_n^{z_A-n\,z_B}\right]$ is approximately its total concentration. In that case the relevant equilibrium and equation are

$$AB_b(s) \rightleftarrows AB_n^{z_A-n\,z_B} + (b\text{-}n)\ B^{z_B} \qquad (4)$$

$$K_{sn,B} = \left[A^{z_A}\right]\left[AB_n^{z_A-n\,z_B}\right]^{b\text{-}n} \qquad (5)$$

This points out that we have written actual aqueous species by using the corresponding stoichiometric coefficients (as typically n in $AB_n^{z_A - n\,z_B}$), while in the solid phase the stoichiometric coefficient (here b for $AB_b(s)$) is only for electro-neutrality: b does not give any (direct) indication on coordination chemistry. This illustrates that both phases are not treated in the same way; while we will see that the solid solution approach attempt to treat the solid phase as any solution.

2 The law of mass action for an isotopic equilibrium.

We first examine a simple example: $^{\#}B$, a radioactive isotope, is added to the above $AB_b(s)$ / A^{z_A} / B^{z_B} system, where B is also one isotope. In equilibrium conditions the isotopic ratio of $^{\#}B$ to B is identical for any of their chemical species. $^{\#}B$ is here considered as a new chemical species with virtually the same properties as B: the equilibrium constants with $^{\#}B$ are virtually the same as those with B. Namely, the solid is now $A(B_{1-x}{}^{\#}B_x)_b$ or equivalently $AB_{b(1-x)}{}^{\#}B_{bx}$, where

$$r = \frac{\left[\overline{^{\#}B^{z_B}}\right]}{\left[\overline{B^{z_B}}\right]} = \frac{x}{1-x} \tag{6}$$

is the isotopic ratio in the solid. The species in the solid are over-lined. The isotopic ratio is the same in the aqueous solution:

$$\frac{\left[^{\#}B^{z_B}\right]}{\left[B^{z_B}\right]} = \frac{\left[\overline{^{\#}B^{z_B}}\right]}{\left[\overline{B^{z_B}}\right]} = r. \tag{7}$$

From Equation 7

$$\frac{\left[\overline{B^{z_B}}\right]\left[^{\#}B^{z_B}\right]}{\left[B^{z_B}\right]\left[\overline{^{\#}B^{z_B}}\right]} = 1 \tag{8}$$

which can be interpreted as the constant of the

$$B^{z_B} + \overline{^{\#}B^{z_B}} \rightleftarrows \overline{B^{z_B}} + {}^{\#}B^{z_B} \tag{9}$$

exchange equilibrium, where we are using $\left[\overline{B^{z_B}}\right]$ and $\left[\overline{^{\#}B^{z_B}}\right]$, the concentrations (of B^{z_B} and $^{\#}B^{z_B}$) inside the ($AB_{b(1-x)}{}^{\#}B_{bx}$) solid. For this reason, it is more convenient to write:

$$AB_{b(1-x)}{}^{\#}B_{bx} = \overline{A^{z_A}} + b(1-x)\ \overline{B^{z_B}} + b\,x\ \overline{^{\#}B^{z_B}}. \tag{10}$$

The

$$\chi_A = \frac{1}{1+b} \; , \; \chi_B = b\frac{1-x}{1+b} \text{ and } \chi_{\#B} = \frac{b\,x}{1+b} \qquad (11)$$

mole fractions are usual concentrations, but we will use the concentrations obtained by multiplying the mole fractions by the (1+b) constant term:

$$\left[\overline{A^{z_A}}\right] = 1,\; \left[\overline{B^{z_B}}\right] = \frac{\chi_B}{\chi_A} = b(1\text{-}x) \text{ and } \left[\overline{{}^{\#}B^{z_B}}\right] = \frac{\chi_{\#B}}{\chi_A} = b\,x \qquad (12_{\#B})$$

These definitions of the concentrations are relative to $\overline{A^{z_A}}$, which concentration is constant, consistently with the $AB_{b(1\text{-}x)}{}^{\#}B_{bx}$ notation: $\overline{A^{z_A}}$ is considered as the amount of solid matrix, namely the solvent, in which $\overline{B^{z_B}}$ and $\overline{{}^{\#}B^{z_B}}$ are dissolved and can be exchanged. Definition of concentrations are part of the definition of the reference state [91STO]: the standard state is the matrix, here represented by $\overline{A^{z_A}}$ at constant concentration, in the same way as the standard state for aqueous solutions is pure liquid water, where molal concentrations, the concentrations used for thermo-chemistry are relative to water -not solution contrary to molal concentrations-. For this reason, we will see later that these definitions of the concentrations in the solid allow generalisations.

When ${}^{\#}B^{z_B}$ is at trace concentration the system is still quite simple: the concentration of ${}^{\#}B^{z_B}$ is lower than the solubility limit of the $A{}^{\#}B_b(s)$ pure compound. $\left[\overline{{}^{\#}B^{z_B}}\right]$ can be neglected as compared to $\left[\overline{B^{z_B}}\right]$: x << (1-x) or equivalently r << 1, and the solid phase now contains a few traces of ${}^{\#}B^{z_B}$, nevertheless the solubility product law is approximately valid:

$$K_{s,B} \approx \left[A^{z_A}\right]\left[B^{z_B}\right]^b \qquad 2$$

from which the concentration of ${}^{\#}B^{z_B}$ can be estimated from Eq.2 and 7 using the above x << 1 approximation:

$$\left[A^{z_A}\right]\left[{}^{\#}B^{z_B}\right]^b \approx K_{s,B}\, r^b = K_{s,B} \frac{x^b}{(1-x)^b} \approx K_{s,B}\, x^b \qquad (13)$$

Note that since x ≈ r << 1, $\left[A^{z_A}\right]\left[{}^{\#}B^{z_B}\right]^b << K_{s,B} = K_{s,{}^{\#}B}$, which consistently means that we are well below the solubility of $A{}^{\#}B_b(s)$. Eq.13 can be rearranged as $K_{s,B} \approx \dfrac{\left[A^{z_A}\right]\left[{}^{\#}B^{z_B}\right]^b}{\left[\overline{{}^{\#}B^{z_B}}\right]^b}$ which can be divided by $\left[\overline{A^{z_A}}\right] \approx 1$ to interpret

$$K_{s,{}^{\#}B} \approx K_{s,B} \approx \frac{\left[A^{z_A}\right]\left[{}^{\#}B^{z_B}\right]^b}{\left[\overline{A^{z_A}}\right]\left[\overline{{}^{\#}B^{z_B}}\right]^b} = \frac{\left[A^{z_A}\right]\left[{}^{\#}B^{z_B}\right]^b}{x^b} = K_{A\text{-}{}^{\#}B} \qquad (14)$$

as $K_{A\text{-}^{\#}B}$, the constant of Equilibrium

$$\overline{A^{z_A}} + b\ \overline{{}^{\#}B^{z_B}} \rightleftarrows A^{z_A} + b\ {}^{\#}B^{z_B}. \tag{15}$$

$K_{s,B}$, the solubility product of the pure AB_b(s) compound appears to be an estimate of $K_{A\text{-}^{\#}B}$, the partition equilibrium constant of $A^{\#}B_b$ between the solid and aqueous phases. However, it was obtained only for trace concentrations ($x << 1$). It is not a demonstration, it only points out that the isotopic partition equilibrium of ${}^{\#}B^{z_B}$ also gives the above partition equilibrium, and the corresponding law of mass action, when using the concentrations inside the solid phase.

Lippmann demonstrated equations similar to Eq.14. For this, he correctly deduced Eq.14 as the law of mass action for Equilibrium 15 assuming that the solid phase is an ideal solid solution. This is always the case for isotopic exchanges: the standard chemical potentials are independent of the isotopic ratio. Similarly the law of mass action is readily obtained for the following equilibrium

$$\overline{A^{z_A}} + b\ \overline{B^{z_B}} \rightleftarrows A^{z_A} + b\ B^{z_B} \tag{16}$$

namely

$$K_{A\text{-}B} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^b}{\left[\overline{A^{z_A}}\right]\left[\overline{B^{z_B}}\right]^b} \approx \frac{K_{s,b}}{\left[\overline{A^{z_A}}\right]_{x=0}\left[\overline{B^{z_B}}\right]^b_{x=0}} \approx \frac{K_{s,b}}{1 \times 1^b} = K_{s,b} \tag{17}$$

where now only macro-concentrations are used, however this is again valid only for ${}^{\#}B^{z_B}$ at trace concentrations. Again $K_{s,B}$ is also an estimate of $K_{A\text{-}B}$, the constant of a partition equilibrium.

3 Using the law of mass action for co-precipitation.

3.1 Introduction.

For the above (Eq.9) isotopic exchange (Section 2) we have used the following descriptions that will be generalized to other ionic exchange reactions:

- We have written -and used- $\left[\overline{B^{z_B}}\right]$ and $\left[\overline{{}^{\#}B^{z_B}}\right]$, the concentrations (of B^{z_B} and ${}^{\#}B^{z_B}$) inside the ($AB_{b(1-x)}{}^{\#}B_{bx}$) solid.
- Consistently, we have written $AB_{b(1-x)}{}^{\#}B_{bx} = \overline{A^{z_A}} + b(1-x)\ \overline{B^{z_B}} + b\,x\ \overline{{}^{\#}B^{z_B}}$ (Eq.10).
- b, the stoichiometric coefficient (inside AB_b(s)) is determined by electro-neutrality (Eq.1),
- while we have written actual aqueous species by using the corresponding stoichiometric coefficients (as typically n in $AB_n^{z_A - n\,z_B}$),
- we have written the law of mass action (Eq.14 and 17) for partition equilibria between the solid and aqueous phases (Equilibria 15 and 16).

Such approach can be generalized now considering C^{z_B} instead of ${}^{\#}B^{z_B}$, where C is a chemical analogue of B; for this reason they have the same charge (z_B). Namely, the example of ${}^{\#}B^{z_B}$ / B^{z_B} isotopic exchange can be generalized to C^{z_B} / B^{z_B}. This has typically been done by Lippmann [77LIP]. Furthermore, the equations are not much complicated when B and C have different charges, as typically shown by Michard [02MIC]. In this part we recall these equations using our own notations and concentration units, because usual mole fractions are not always intensive variables (see below Eq.22). We do not attempt to give demonstrations, we rather focus on classical published equations and their meaning as already outlined by Lippmann for many of them. Demonstrations will be given later (Section 4.). We are still using aqueous molar concentration units, including medium effects in the equilibrium constants for the same reasons as already explained above (Section 1.).

3.2 Lippmann's remarks.

After a brief history of solubility products, Lippmann indicated that they very well account for solubilities of pure compounds providing a few complications are taken into account: "*electrolytic dissociation, notably in solutions containing additional dissolved ions*" and "*ionic activities*". He then pointed out a few general features of solid solutions interesting for their thermodynamic descriptions, even though he finally treated only simple specific cases:

- "*the* [solubility] *product is constant under certain conditions. The most important of these are [...] "chemical purity" of the solid phase. [...] binary compounds are indeed chemically pure, because [...] their stoichiometry is determined by electroneutrality.*" This to insist that solubility products are only valid for constant compositions of the solid phases, because to derive it "*from the principle of thermodynamics [...] chemical purity [...] postulate is indispensable in formulating the law of mass action*". Indeed, the law of mass action is demonstrated by minimising Gibbs energy, hence by differentiating it assuming constant stoichiometric coefficients. This will be explained below (Section 4.3.): the derivative of variable stoichiometric coefficients -as typically b(1-x) and bx in $AB_{b(1-x)}{}^{\#}B_{bx}$- introduces new terms. Furthermore, the activity of the (pure) solid phase is constant: "*In the derivation of the constancy of the solubility product starting from the law of mass action, a fixed composition of the solid is required [...] In the same way, the procedure followed in derivations based on thermochemical potentials [...] is realistic only if the solid composition is invariant.*"
- The previous remarks and other ones point out that the solubility product has no reason to be valid for "*minerals [...] in which [...ions] may replace each others in varying degrees.*" or any "*mixed crystals (or solid solutions) [...] described by continuously variable stoichiometric coefficients. [...] The pertinent equilibria are appropriately described in terms of Nernst's distribution (or partition) coefficients*". Indeed, we wrote partition equilibria (Eq.9, 15 and 16) and their equilibrium constants (Eq.8, 14 and 17 respectively).
- There are "*additional degrees of freedom resulting from variable composition of the solid*". One new variable is introduced in a two component solid solution -the continuously variable ratio of the two components in the solid, typically x in $AB_{b(1-x)}{}^{\#}B_{bx}$- and this will need an additional equation: namely instead of one solubility product for a pure compound, two equations are now needed. Since equivalent sets of equations can be derived by combining a set of two equations, there are different equivalent ways to present the results.
- "*crystalline minerals contain non fractional multiples of their chemical formulae in the unit cell [...] because a set of atomic sites [(equipoints)...] is either completely filled or completely vacant [...] Fractional occupation [...is] equivalent to variable composition*". Actually, vacancies can explain how ions with different charges can

be exchanges in solid solutions without important structural changes and still keeping electro-neutrality: a (big enough) pertinent elementary cell needs to be identified.

- "*Each chemical species is bonded by the crystal in its own characteristic manner distinguished by [...] a preferred coordination number.*" As pointed out above, the stoichiometry in the solid is given by the electro-neutrality, while from a chemical point of view, it is well known that characteristic coordination geometries are expected for each type of ion. For example a cation is surrounded by several anionic ligands, which can be shared by two cations: this explains how electro-neutrality stoichiometry can accommodate usual coordination numbers. This again can be possible (without much structural changes) for big elementary cells with vacancies.
- Solid solutions are supposed to be built from "*End-members*". This often results in using mole fractions of the end-members as concentration unit, typically $x_{\mathrm{CaCO_3}}$ in a mixture with $\mathrm{CO_3^{2-}}$ as common anion, and where $\mathrm{Ca^{2+}}$ can (continuously) be exchanged with other di-cations. However, in simple cases it is also -or it is proportional to- the concentration of the exchanged ion, in our example $x_{\mathrm{CaCO_3}}$ (= $x_{\mathrm{Ca^{2+}}}$ = $\left[\overline{\mathrm{Ca^{2+}}}\right]/2$) is rather used in the mixture approach, while $\left[\overline{\mathrm{Ca^{2+}}}\right]$ is rather used in the solid solution approach, where the system is described with the actual chemical species -as in aqueous solutions- rather than with (neutral) compounds. Note that solution chemists do not use end-members to describe aqueous solutions.
- "*mixed crystals*" of the $\mathrm{CaCO_3}$ and $\mathrm{MnCO_3}$ "*end member[s]*" are "*represented by a series of solid solutions [...] characterised by their common anion [...] Any composition may be characterised either by the mole fraction* $x_{\mathrm{CaCO_3}}$ *of the calcite end member or by [...]* $x_{\mathrm{MnCO_3}}$ "= 1- $x_{\mathrm{CaCO_3}}$. "*Under equilibrium conditions ...* $\left[\mathrm{Ca^{2+}}\right]\left[\mathrm{CO_3^{2-}}\right]$ *... must be smaller than the solubility product* $K_{calcite}$ *[...] The activity of* $CaCO_3$ *in the solid solution may now be defined in such a way that [...]* $\left[\mathrm{Ca^{2+}}\right]\left[\mathrm{CO_3^{2-}}\right]$ = $K_{calcite}\ y_{\mathrm{CaCO_3}}\ x_{\mathrm{CaCO_3}}$ ". This writes

$$\left[\mathrm{Ca^{2+}}\right]\left[\mathrm{CO_3^{2-}}\right] = \mathrm{K_{s,calcite}}\ \left[\overline{\mathrm{Ca^{2+}}}\right]\left[\overline{\mathrm{CO_3^{2-}}}\right] = \mathrm{K_{s,calcite}}\ (1\text{-}x) \qquad (18)$$

with our concentrations units, where constant concentration factors are included in the equilibrium constant, as well as activity coefficients as usual in solution chemistry. "*Similarly* $\left[\mathrm{Mn^{2+}}\right]\left[\mathrm{CO_3^{2-}}\right]$ = $\mathrm{K_{rhodochrosite}}\ y_{\mathrm{MnCO_3}}\ x_{\mathrm{MnCO_3}}$ " and

$$\left[\mathrm{Mn^{2+}}\right]\left[\mathrm{CO_3^{2-}}\right] = \mathrm{K_{s,rhodochrosite}}\ \left[\overline{\mathrm{Mn^{2+}}}\right]\left[\overline{\mathrm{CO_3^{2-}}}\right] = \mathrm{K_{s,rhodochrosite}}\ x. \qquad (19)$$

Eq.18 and 19 are Eq.14 and 17 respectively.

Lippmann gave (correct) indications and remarks to write the law of mass action for any solid solution, but he actually gave examples essentially for mixtures made from two end-members with similar structures, where $z_C = z_B$. However, the formula are not much complicated, when $z_C \neq z_B$, a case we start to examine in the next section.

3.3 Published equations.

In his text book, Michard gave equations for the

$$(1\text{-}x)AB_b + x\ AC_c = AB_{b(1-x)}C_{cx} = \overline{A^{z_A}} + b(1\text{-}x)\ \overline{B^{z_B}} + c\ x\ \overline{C^{z_C}} \tag{20}$$

solid [02MIC], where now the B^{z_B} and C^{z_C} exchanged cations are of different charges. This can be considered as a generalization of Lippmann's approach -to the cases where z_C is not necessarily equal to z_B-. Instead of Isotope ${}^{\#}B^{z_B}$ we are now generalizing Eq.10 with the C^{z_B} analogue ion or any C^{z_C}. Similarly to Eq.1

$$c = -\frac{z_A}{z_C}. \tag{21}$$

Michard used mole fractions for concentration units:

$$\chi_A = \frac{1}{1+b+(c\text{-}b)x}, \quad \chi_B = \frac{b(1-x)}{1+b+(c\text{-}b)x} \quad \text{and} \quad \chi_C = \frac{c\,x}{1+b+(c\text{-}b)x} \tag{22}$$

They cannot be considered as actual -intensive- concentration units, since the total amount of solid depends on the advancement of the ion exchange reaction, when $b \neq c$, or equivalently $z_B \neq z_C$ (Eq.1 and 21, note that z_B and z_C are of same sign for electro-neutrality): the total amount of solid is not constant, it is proportional to (1+b+(c-b)x) as reflected in the value of the mole fractions (Eq.22). This actually points out it is not straightforward to decide which stoichiometry should best be used to describe solid solutions. Such problem is well known -and correctly handled- for aqueous solutions: molar concentrations (mole per litre of solution) are commonly used for aqueous solutions, while molal concentrations (mole per kg of water: water, not solution) are used for thermodynamic theoretical calculations as already noted in Section 1. In aqueous solutions, the major component (water including liquid bulk water and all the water molecules hydrating the solutes) gives the size of the system, in which solutes are added. The corresponding "solvent" of the solid solution is not exactly the major solid component (= end-member): it is rather the matrix, the pure component, where all the ionic exchange sites are imagined vacant, or equivalently homo-ionic (depending on the reference state) *i.e.* all the sites are occupied by the same ion.

However, we do not here consider vacancies (this will be outlined in Section 3.6.), because the description of the stoichiometry would become quite complicated: in a first step, we consider exchanges of ions with different charges, which is interesting to avoid simplifications introduced by isotopic exchanges and exchanges of homo-ions (ions with the same charge). Typically, by considering hetero-ion exchanges Michard pointed out there is a problem: depending on the way he performed the calculations, he found different non-equivalent equations [89MIC]. The problem might have been in using mole fractions. For this reason we rather use our concentration units. Lippmann's approach is to write the

$$\overline{A^{z_A}} + b\ \overline{B^{z_B}} \rightleftarrows A^{z_A} + b\ B^{z_B} \tag{23}$$

$$\overline{A^{z_A}} + c\ \overline{C^{z_C}} \rightleftarrows A^{z_A} + c\ C^{z_C} \tag{24}$$

partition equilibria between $AB_{b(1-x)}C_{cx}$ and the aqueous phase (similar to Eq.15 and 16). As for Eq.14 and 17, $K_{A\text{-}B}$ and $K_{A\text{-}C}$ are the constants of their equilibrium, and the values of these constants are obtained in the limiting cases where x = 0 or 1 respectively, which gives the solubility products of the pure (end-member) compounds:

$$K_{A\text{-}B} = \frac{[A^{z_A}][B^{z_B}]^b}{[\overline{A^{z_A}}][\overline{B^{z_B}}]^b} = \frac{[A^{z_A}][B^{z_B}]^b}{(1-x)^b} = K_{s,B} \tag{25}$$

$$K_{A\text{-}C} = \frac{[A^{z_A}][C^{z_C}]^c}{[\overline{A^{z_A}}][\overline{C^{z_C}}]^c} = \frac{[A^{z_A}][C^{z_C}]^c}{x^c} = K_{s,C} \tag{26}$$

where we have used Eq.12 as definitions of the concentrations inside the solid phase. Combining Eq.25 and 26 give other equivalent equations corresponding to other chemical equilibria: we give below the corresponding -actually classical- equations.

3.4 Remarks on published approaches.

3.4.1 Concentration units

We already pointed out that the

$$\chi_A = \frac{1}{1+b+(c-b)x}, \quad \chi_B = \frac{b(1-x)}{1+b+(c-b)x} \text{ and } \chi_C = \frac{cx}{1+b+(c-b)x} \tag{22}$$

mole fractions are not -intensive- concentration units, since the total amount of solid depends on the advancement of the ion exchange reaction, when b ≠ c, or equivalently $z_B \neq z_C$ (Eq.1 and 21): the total amount of solid is not constant, it is proportional to (1+b+(c-b)x). We use the

$$[\overline{A^{z_A}}] = 1,\ [\overline{B^{z_B}}] = \frac{\chi_B}{\chi_A} = b(1-x) \text{ and } [\overline{C^{z_C}}] = \frac{\chi_C}{\chi_A} = c\,x \tag{12}$$

concentration units. With these definitions $\overline{A^{z_A}}$ can represent the matrix, for this reason its concentration is constant, here taken equal to 1, in the same way -and with the same chemical meaning- as the activity of water is chosen to be 1 for solution chemistry at given P and T.

Other definitions are possible, and are typically needed when A^{z_A} can also be continuously exchanged in the solid phase: in that case A^{z_A} geometrical sites can typically be chosen for the matrix. Such definition can also be used when A^{z_A} vacancies need to be considered: in that case the matrix is indeed represented by all the sites that could be occupied by A^{z_A}.

3.4.2 Number of equations needed

We wrote two law of mass action equations (Eq.25 and 26) for equilibria of the $AB_{b(1-x)}C_{cx}$ solid phase with aqueous solutions. Two -and only two- such equations are indeed needed. This can be qualitatively understood using the Sillén's approach [67SIL]:

- Imagine an aqueous solution equilibrated with the AB_b(s) pure compound, the solution is described with mass balance and law of mass action equations, including $K_{s,B}$, the solubility product of AB_b(s) (Eq.2)
- Now allow the solid be a solid solution. This allows variations of the chemical composition of the solid, typically x. A new variable (x) is added: an extra equation is now needed.

Finally, two -and only two- law of mass action equations are indeed needed to describe the equilibration of aqueous solutions with the $AB_{b(1-x)}C_{cx}$ solid phase, where x can continuously vary. This result is now familiar when using computer solubility codes, where it is needed to indicate the exact number of mass balance and law of mass action equations: this is equivalent to the above Sillén's approach. This of course gives Gibbs' phase rule [1876GIB]. However, a direct demonstration of this result will also be given: while the dissolution of the AB_b(s) pure compound is a normal reaction with one advancement variable, the dissolution of $AB_{b(1-x)}C_{cx}$ appears to be a "reaction" with two advancement variables.

3.5 A dissolution reaction with two advancement variables

3.5.1 Advancement variables

ξ, the advancement variable of the reaction corresponding to Equilibrium

$$AB_b(s) \rightleftarrows A^{z_A} + b\ B^{z_B} \qquad (3)$$

is defined such as

$$d[i] = \nu_{i,AB_b}\, d\xi \qquad (27)$$

where ν_{i,AB_b} is the stoichiometric coefficient of Species i (in Equilibrium 3): $\nu_{A^{z_A},AB_b}$ = 1 and $\nu_{B^{z_B},AB_b}$ = b, namely

$$d\left[A^{z_A}\right] = \nu_{A^{z_A},AB_b}\ d\xi = d\xi \qquad (28)$$

$$d\left[B^{z_B}\right] = \nu_{B^{z_B},AB_b}\ d\xi = b\ d\xi \qquad (29)$$

Now, generalizing Equilibrium 3, the equilibrium corresponding to the dissolution of $AB_{b(1-x)}C_{cx}$ is often written

$$\overline{A^{z_A}} + b(1\text{-}x)\ \overline{B^{z_B}} + c\,x\ \overline{C^{z_C}} \rightleftarrows A^{z_A} + b(1\text{-}x)\ B^{z_B} + c\,x\ C^{z_C} \qquad (30)$$

where

$$\mathrm{AB_{b(1\text{-}x)}C_{cx}} = \overline{\mathrm{A}^{z_A}} + \mathrm{b(1\text{-}x)}\ \overline{\mathrm{B}^{z_B}} + \mathrm{c\,x}\ \overline{\mathrm{C}^{z_C}}, \tag{20}$$

a notation already used for isotopic exchanges (Eq.10). Eq.28 still stands, which means that ξ can still be interpreted as the advancement variable for the dissolution (Eq.30) of the matrix -as represented by $\overline{\mathrm{A}^{z_A}}$- while Eq.29 is no more valid because B^{z_B} can now be exchanged with C^{z_C}. The

$$\mathrm{b}\ \mathrm{B}^{z_B} + \mathrm{c}\ \overline{\mathrm{C}^{z_C}} \rightleftarrows \mathrm{b}\ \overline{\mathrm{B}^{z_B}} + \mathrm{c}\ \mathrm{C}^{z_C} \tag{31}$$

corresponding ion exchange equilibrium -similar to isotopic exchange (Eq.9)- is obtained by typically varying $\left[\mathrm{C}^{z_C}\right]$ at constant $\left[\mathrm{A}^{z_A}\right]$ -or equivalently constant ξ (Eq.28)- in the (Eq.30) solubility equilibrium. For this reason the (Eq.31) ion exchange equilibrium is actually already included in the (Eq.30) solubility equilibrium, which appears to have two advancement variables: one (ξ) for the dissolution of the matrix (at constant x) and the other one for the ion exchange (at constant $\left[\overline{\mathrm{A}^{z_A}}\right]$). For the (Eq.30) solubility equilibrium Eq.28 is still valid: $\mathrm{d}\left[\mathrm{A}^{z_A}\right] = \nu_{\mathrm{A}^{z_A},x}\mathrm{d}\xi$ = dξ (since $\nu_{\mathrm{A}^{z_A},x} = 1$), while Eq.29 is no more valid, because $\mathrm{d}\left[\mathrm{B}^{z_B}\right]$ now corresponds to two independent variations: $\mathrm{d}\left[\mathrm{B}^{z_B}\right] = \left(\frac{\partial\left[\mathrm{B}^{z_B}\right]}{\partial\left[\mathrm{A}^{z_A}\right]}\right)_x \mathrm{d}\left[\mathrm{A}^{z_A}\right] + \left(\frac{\partial\left[\mathrm{B}^{z_B}\right]}{\partial x}\right)_{\left[\mathrm{A}^{z_A}\right]}\mathrm{d}x = \nu_{\mathrm{B}^{z_B},x}\mathrm{d}\xi + \frac{\mathrm{d}\nu_{\mathrm{B}^{z_B},x}}{dx}\mathrm{d}x = \nu_{\mathrm{B}^{z_B},x}\mathrm{d}\xi + \mathrm{d}\nu_{\mathrm{B}^{z_B},x} = \nu_{\mathrm{B}^{z_B},x}\,\mathrm{d}\xi - \mathrm{b}\,\mathrm{d}x$, where $\nu_{i,x}$ is the stoichiometric coefficient of Species i in Equilibrium 30, and where we used $\nu_{\mathrm{B}^{z_B},x}$ = b(1-x) from which $\frac{\mathrm{d}\nu_{\mathrm{B}^{z_B},x}}{dx}$ = -b. Similarly the other d[i] terms can be calculated for i = $\nu_{\mathrm{A}^{z_A},x}$ (= 1) and $\nu_{\mathrm{C}^{z_C},x}$ (= c x). Furthermore, as expected

$$\left(\nu_{i,x}\right)' = \nu_{i,\mathrm{B\text{-}C}}, \tag{32}$$

where $\left(\nu_{i,x}\right)' = \frac{\mathrm{d}\nu_{i,x}}{dx}$, and where $\nu_{i,\mathrm{B\text{-}C}}$ is the stoichiometric coefficient of Species i in Equilibrium 31:

$$-\ \mathrm{d}\left[\overline{\mathrm{A}^{z_A}}\right] = \mathrm{d}\left[\mathrm{A}^{z_A}\right] = \mathrm{d}\xi = \nu_{\mathrm{A}^{z_A},x}\mathrm{d}\xi + \nu_{\mathrm{A}^{z_A},\mathrm{B\text{-}C}}\mathrm{d}x \tag{33}$$

$$-\ \mathrm{d}\left[\overline{\mathrm{B}^{z_B}}\right] = \mathrm{d}\left[\mathrm{B}^{z_B}\right] = \mathrm{b(1\text{-}x)d}\xi\text{-}\ \mathrm{b\ dx} = \nu_{\mathrm{B}^{z_B},x}\mathrm{d}\xi + \nu_{\mathrm{B}^{z_B},\mathrm{B\text{-}C}}\mathrm{d}x \tag{34}$$

$$-\ \mathrm{d}\left[\overline{\mathrm{C}^{z_C}}\right] = \mathrm{d}\left[\mathrm{C}^{z_C}\right] = \mathrm{c\ x\ d}\xi\text{+ c dx} = \nu_{\mathrm{C}^{z_C},x}\mathrm{d}\xi + \nu_{\mathrm{C}^{z_C},\mathrm{B\text{-}C}}\mathrm{d}x \tag{35}$$

for the reaction corresponding to Equilibrium 30. The two advancements variables are ξ and x, corresponding to the stoichiometric coefficients $\nu_{i,x}$ and $\left(\nu_{i,x}\right)'$ respectively, of Equilibrium30 with fixed x or $\left[\mathrm{A}^{z_A}\right]$ (= ξ) respectively: this confirms that Equilibrium 30 corresponds to a two advancement variable reaction including Equilibrium 31.

This is unusual and actually misleading: Lippmann strongly insisted that the usual form of the law of mass action should not be written for equilibria "*where the stoichiometric coefficients are not whole numbers*". This is indeed the case of Equilibrium 30, where some of the stoichiometric coefficients can continuously vary with x:

$$\nu_{A^{z_A},x} = -\ \nu_{\overline{A^{z_A}},x} = 1 \tag{36}$$

$$\nu_{B^{z_B},x} = -\ \nu_{\overline{B^{z_B}},x} = b(1-x) \tag{37}$$

$$\nu_{C^{z_C},x} = -\ \nu_{\overline{C^{z_C}},x} = c\,x \tag{38}$$

Note that the stoichiometric coefficients appear to be also the concentrations in the solid phase:

$$\nu_{A^{z_A},x} = -\ \nu_{\overline{A^{z_A}},x} = 1 = \left[\overline{A^{z_A}}\right] \tag{36}$$

$$\nu_{B^{z_B},x} = -\ \nu_{\overline{B^{z_B}},x} = b(1-x) = \left[\overline{B^{z_B}}\right] \tag{37}$$

$$\nu_{C^{z_C},x} = -\ \nu_{\overline{C^{z_C}},x} = c\,x = \left[\overline{C^{z_C}}\right] \tag{38}$$

A reaction with two advancement variables, stoichiometric coefficients that are also concentrations (in the solid phase): all this is well known, but easily misleading. Indeed it is well known that the law of mass action is not valid for Equilibrium 30, namely

$$Q_x = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b(1\text{-}x)}\left[C^{z_C}\right]^{cx}}{\left[\overline{A^{z_A}}\right]\left[\overline{B^{z_B}}\right]^{b(1\text{-}x)}\left[\overline{C^{z_C}}\right]^{cx}} \tag{39}$$

is not constant.

3.5.2 The non-constant solubility quotient of the solid solution.

The value of Q_x can be obtained as follows. $AB_{b(1-x)}C_x$ is considered as an ideal mixture of its end-members:

$$AB_{b(1\text{-}x)}C_x = (1\text{-}x)AB_b + x\ AC_c \tag{40}$$

For this reason the two law of mass action equations write

$$\frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^b}{\left[\overline{A^{z_A}}\right]\left[\overline{B^{z_B}}\right]^b} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^b}{(1-x)^b} = K_{s,B} \tag{25}$$

$$\frac{\left[A^{z_A}\right]\left[C^{z_C}\right]^c}{\left[\overline{A^{z_A}}\right]\left[\overline{C^{z_C}}\right]^c} = \frac{\left[A^{z_A}\right]\left[C^{z_C}\right]^c}{x^c} = K_{s,C} \tag{26}$$

The linear Eq.40 suggests to consider (1-x)log $K_{s,B}$ + x log $K_{s,C}$, or equivalently

$$K_{s,B}^{1\text{-}x} K_{s,C}^{x} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b(1\text{-}x)}\left[C^{z_C}\right]^{cx}}{\left[\overline{A^{z_A}}\right]\left[\overline{B^{z_B}}\right]^{b(1\text{-}x)}\left[\overline{C^{z_C}}\right]^{cx}} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b(1\text{-}x)}\left[C^{z_C}\right]^{cx}}{(1\text{-}x)^{b(1\text{-}x)}\, x^{cx}} = Q_x \qquad (41)$$

which confirms that Q_x is not constant. Note that this equation is often considered alone, while two equations are needed. The second equation can typically be Eq.25, 26 or

$$\frac{K_{s,C}}{K_{s,B}} = \frac{\left[\overline{B^{z_B}}\right]^{b}\left[C^{z_C}\right]^{c}}{\left[B^{z_B}\right]^{b}\left[\overline{C^{z_C}}\right]^{c}} = \frac{(1-x)^{b}\left[C^{z_C}\right]^{c}}{\left[B^{z_B}\right]^{b} x^{c}} = K_{C\text{-}B} \qquad (42)$$

the constant of Equilibrium 31: the law of mass action is the set of Eq.s 25 and 26, or equivalently the set of Eq.s 41 and 42, or any equivalent set of two equations, while one of the Eq.s 41 or 42 is sometime considered alone in the literature. Similarly, starting from any pair of the above law of mass action equations the other equations can be obtained by linear combinations of the log of their equilibrium constants. Such linear combinations can correspond to thermodynamics cycles. However, the coefficients of the linear combination should be constant, which is not the case, when Q_x is involved: as already pointed out introducing Q_x is indeed misleading despite it is here correct as will be demonstrated below (Section 4.).

3.5.3 Ionic exchange as derivative of dissolution and conversely

3.5.3.1 Ionic exchange as derivative of dissolution.

Each stoichiometric coefficient $(\nu_{i,B\text{-}C})$ of the C^{z_C} / B^{z_B} ion exchange Equilibrium (Eq.30) is obtained from the corresponding one $(\nu_{i,x})$ in the solubility equilibrium (Eq.31):

$$\nu_{i,B\text{-}C} = \frac{d\,\nu_{i,x}}{dx} = \left(\nu_{i,x}\right)' \qquad (32)$$

where f' is for df/dx; which we summarize

$$\text{Equilibrium 30} = (\text{Equilibrium 31})' \qquad (43)$$

Consistently, $K_{s,C}$ / $K_{s,C}$ = $K_{C\text{-}B}$ is the constant of Equilibrium 30 (Eq.69) and $K_{s,B}^{(1-x)}$ $K_{s,C}^{x}$ = Q_x the quotient for Equilibrium 31 (Eq.41): it appears that:

$$\frac{d\ln(Q_x)}{dx} = \ln\frac{K_{s,C}}{K_{s,B}} = \ln K_{C\text{-}B} \qquad (44)$$

namely

$$(\ln(\text{Eq.41}))' = \ln(\text{Eq.69}) \qquad (45)$$

Ionic exchange (31) is included in the solubility equilibrium (30). Furthermore (Eq.43), Equilibrium 31 can be consider as the "derivative" of Equilibrium 30, and this is even the case for their equilibrium constants (45).

3.5.3.2 Matrix as integral of ionic exchange.

Conversely, many ionic exchanges are well known and interpreted with the law of mass action (Eq.69) for Equilibrium 30. The equilibrium constant of the ionic exchange can very well be interpreted as the ratio of the solubility products of the end-members (Eq.69) of the ion exchanger matrix. By integrating (Eq.43) the solubility equilibrium of the ion exchanger matrix (Equilibrium 31) is obtained. They are several possible matrix, each corresponding to a different integrating constant (Eq.45), which provides the equilibrium quotient (Eq.41) of the resulting equilibrium (Equilibrium 30). Thus one obtains the two solubility products needed to describe the system.

3.5.3.3 Surface or liquid ion exchangers

As pointed out in the previous sections, integrating an ion exchange reaction (Eq.43) gives the dissolution reaction of its matrix from the aqueous solution. This can be generalized to those ion exchanges, where the matrix can be prepared by precipitation from aqueous solutions, as typically minerals and their surface; but in the later case, supplementary pieces of information are needed to know the amount of surface created for a given quantity of reactants, namely the volume / surface ratio -hence transforming surface "concentrations" into intensive variables. For solid mineral ion exchangers, it is indeed well known that the dissolution reaction of the matrix can control the concentrations of some aqueous soluble species, and these aqueous species should be taken into account when interpreting experimental ion exchange data.

3.5.4 Using mass action law equations.

3.5.4.1 The equilibrium stoichiometry

There are sometimes discussions in the literature on how to obtain the (variable) stoichiometry of a solid solution equilibrated with an aqueous solution of known composition. For this, "stoichiometric dissolution" or other approaches are typically proposed. This is surprising: no supplementary hypothesis seems needed, since thermodynamics gives the concentrations of all the species in all the phases for ideal systems, from mass balance and equilibrium constants. Note that no new equilibrium constant is needed for solid solutions: only the solubility products of the pure components are needed. Typically, x, the stoichiometry in the solid can be calculated from the concentrations of two of the aqueous species by using one of the following equations:

$$K_{s,B} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^b}{(1-x)^b} \tag{25}$$

$$K_{s,C} = \frac{\left[A^{z_A}\right]\left[C^{z_C}\right]^c}{x^c} \tag{26}$$

$$K_{C\text{-}B} = \frac{(1-x)^b \left[C^{z_C}\right]^c}{\left[B^{z_B}\right]^b x^c} \tag{42}$$

3.5.4.2 The saturation indexes of the end-members

Rearranging Eq.25 and 26 as

$$(1\text{-}x)^b = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^b}{K_{s,B}} \tag{25}$$

$$x^c = \frac{\left[A^{z_A}\right]\left[C^{z_C}\right]^c}{K_{s,C}} \tag{26}$$

it appears that the left members of the above equations are the saturation indexes of the end-members: their values are $(1\text{-}x)^b$ and x^c. Consistently, they are smaller than 1, since $0 \leq x \leq 1$, and the values of 0 and 1 correspond to the end-members.

3.5.4.3 Slope analysis of solubility curves

The law of mass action is classically used to interpret experimental data, extracting equilibrium constants and stoichiometric coefficients from them. For Equilibrium 3 this can be done as follows. Eq.2 is rearranged

$$\lg K_{s,B} = \lg\left[A^{z_A}\right] + b \lg\left[B^{z_B}\right] \tag{2}$$

similarly, Eq.5 can be rearranged:

$$\lg K_{s,n,B} = \lg\left[A^{z_A}\right] + (b\text{-}n) \lg\left[AB_n^{z_A - n\,z_B}\right] \tag{5}$$

the log-log plot of the solubility of B is a straight line of slope (b-n), and the intercept gives the equilibrium constant, when $AB_n^{z_A - n\,z_B}$ is the major aqueous species of B. When the solid is known this provides the stoichiometries of aqueous species. Conversely this can provide the stoichiometry of the solid phase. In this later case:

$$b = -\frac{d \lg\left[A^{z_A}\right]}{d \lg\left[B^{z_B}\right]} \tag{46}$$

(Eq.2). Similarly, for solid solutions the stoichiometry is obtained by deriving Eq.25 at constant $\left[C^{z_C}\right]$, a constraint given by deriving Eq.26:

$$\left(\frac{\partial \lg\left[B^{z_B}\right]}{\partial \lg\left[A^{z_A}\right]}\right)_{\left[C^{z_C}\right]} = \frac{-1}{c(1-x)}+\frac{1}{c}-\frac{1}{b} \tag{47}$$

this result is similar to Eq.46 only when b = c. In that case -c(1-x) = -b(1-x) is both the stoichiometric coefficient of B and the slope of its solubility curve. Conversely, when this (b = c) simplification does not stand, the simple stoichiometric meaning of the slope does not stand any more. This, actually because when dissolving the solid at constant $\left[C^{z_C}\right]$, the x value change in the remaining solid solution when $z_B \neq z_C$ (this is equivalent to b ≠ c), namely in this case "stoichiometric dissolution" at constant $\left[C^{z_C}\right]$ is not possible for electro-neutrality reason. Similarly

$$\left(\frac{\partial \lg\left[C^{z_C}\right]}{\partial \lg\left[A^{z_A}\right]}\right)_{\left[B^{z_B}\right]} = \frac{-1}{b\,x}+\frac{1}{b}-\frac{1}{c} \tag{48}$$

lead to similar conclusions.

3.5.4.4 Slope analysis for ion exchange equilibria

Equation

$$K_{B\text{-}C} = \frac{K_{s,C}}{K_{s,B}} = \frac{\left[\overline{B^{z_B}}\right]^b\left[C^{z_C}\right]^c}{\left[B^{z_B}\right]^b\left[\overline{C^{z_C}}\right]^c} = \frac{(1-x)^b\left[C^{z_C}\right]^c}{\left[B^{z_B}\right]^b x^c} \tag{69}$$

is classically used to interpret the corresponding

$$b\ B^{z_B} + c\ \overline{C^{z_C}} \rightleftarrows b\ \overline{B^{z_B}} + c\ C^{z_C} \tag{31}$$

ion exchange equilibrium. Typically, the ion exchange matrix can initially be prepared in homo-ionic form, here saturated with the ion B^{z_B}. Now, if the ion exchanger is a natural mineral this saturation preparation can as well be used to characterise the natural ions initially present in the ion exchanger. For this, one can typically use repeated lixiviations with concentrated aqueous solutions of B^{z_B}. It can easily be shown that $\log\left[C^{z_C}\right]$ varies linearly with the number of lixiviations by aqueous solutions of same concentrations of B^{z_B} in well chosen range of chemical conditions, and this gives the equilibrium constant of the corresponding ion exchange [83VIT page 91]. This saturation experiment can also give the ion exchange capacity providing the affinity of B^{z_B} is high enough. This exchange capacity is needed to determine relevant concentrations in the ion exchanger. Now when this is done, Eq.69 is classically rearranged as

$$c \log K_{d,C} = b \log K_{d,B} - \log K_{B\text{-}C} \tag{49}$$

where

$$K_{d,Y} = \frac{[\overline{Y}]}{[Y]} \qquad (50)$$

is measured form the aqueous concentrations and mass balance equations. Eq.49 can then be used for slope analysis, which provides the c/b ratio of stoichiometric coefficients, here it is also the ratio of the charges of the exchanged ions.

3.5.5 Comparison with pure compounds.

Both $AB_b(s)$ and $AC_c(s)$ pure compounds can be simultaneously stable, when no solid solution is formed. As already pointed out (Section 3.4.2.) adding a new solid phase -and the corresponding solubility product (Eq.2 for $AB_b(s)$ and $AC_c(s)$)- decreases by one the number of degrees of freedom of the system: Ratio

$$\frac{[C^{z_C}]^c_{s,B,C}}{[B^{z_B}]^b_{s,B,C}} = \frac{K_{s,C}}{K_{s,B}} \qquad (51)$$

is constant, where subscript s,B,C is to stress that both $AB_b(s)$ and $AC_c(s)$ pure compounds are formed. The ratio of two equilibrium constant is the constant of a new equilibrium (their difference): $\frac{K_{s,C}}{K_{s,B}}$ (Eq.51) is the constant for Equilibrium

$$AC_c(s) + b\ \ B^{z_B} \rightleftarrows AB_b(s) + c\ \ C^{z_C} \qquad (52)$$

Using Eq.51

$$\frac{[C^{z_C}]^c_{s,B,C}}{[B^{z_B}]^b_{s,B,C}} = \frac{K_{s,C}}{K_{s,B}} = K_{C\text{-}B} = \frac{[\overline{B^{z_B}}]^b[C^{z_C}]^c}{[B^{z_B}]^b[\overline{C^{z_C}}]^c} = \frac{(1-x)^b[C^{z_C}]^c}{[B^{z_B}]^b x^c} \qquad (69)$$

It can be rearranged as

$$\frac{[\overline{B^{z_B}}]^b}{[\overline{C^{z_C}}]^c} = \frac{(1-x)^b}{x^c} = \frac{[B^{z_B}]^b}{[C^{z_C}]^c}\frac{K_{s,C}}{K_{s,B}} = \frac{[B^{z_B}]^b[C^{z_C}]^c_{s,B,C}}{[C^{z_C}]^c[B^{z_B}]^b_{s,B,C}} = \left(\frac{[B^{z_B}]}{[B^{z_B}]_{s,B,C}}\right)^b\left(\frac{[C^{z_C}]_{s,B,C}}{[C^{z_C}]}\right)^c : \qquad (69)$$

the $([\overline{B^{z_B}}]^b/[\overline{C^{z_C}}]^c$ and $[B^{z_B}]^b/[C^{z_C}]^c)$ ratios of exchanged ions are usually not the same in the solid and aqueous phases:

- This ratio in the solid phase can be obtained from that in the aqueous solution in equilibrium conditions and conversely.
- The so called "stoichiometric dissolution" does not specially correspond to equilibrium conditions.

- The constants of Equilibria 31
  ($b\ B^{z_B} + c\ \overline{C^{z_C}} \rightleftarrows b\ \overline{B^{z_B}} + c\ C^{z_C}$) and 52
  $b\ B^{z_B} + (AC_c(s) \rightleftarrows AB_b(s) + c\ C^{z_C}$) have the same value, consequently it is tempting to write that the difference between these two (31 and 52) equilibria is an equilibrium with an equilibrium constant of 1; but this interpretation is not correct because the result of this mathematical difference is not an equilibrium, since the solid phases involved in both equilibria cannot be simultaneously stable, namely the achievement of equilibrium conditions would typically result in the dissolution of the incorporation of impurities by the end-members transforming them in the solid solution. The common aqueous ions (B^{z_B} or C^{z_C}) have not the same concentrations when equilibrated with these different solid phases. Furthermore, using our notations inside the solid phases Equilibrium 52 writes exactly the same way as Equilibrium 31 assuming $\overline{A^{z_A}}$ can be simplified, despite it is in the two different ($AC_c(s)$ and $AB_b(s)$) end-members, this assumption is correct for end-members that can form an ideal solid solutions in any proportion ($0 \le x \le 1$): Notations $\overline{A^{z_A}}$, $\overline{B^{z_B}}$ and $\overline{C^{z_C}}$ are relevant in the whole range of chemical compositions for the solid solution including the end-members. Consequently the constants of Equilibria 31 and 52 have the same value. However, this is a bit misleading.

Conversely, $\dfrac{\left[B^{z_B}\right]^b\left[C^{z_C}\right]^c_{s,B,C}}{\left[C^{z_C}\right]^c\left[B^{z_B}\right]^b_{s,B,C}} = 1 = \dfrac{(1-x)^b}{x^c}$ provides a value of x, typically when b = c this value of x is 0.5, corresponding to a mixture where none of the two end-members is at trace concentration. This x value -hence when the solid solution is stable- corresponds to the value of the $\left[B^{z_B}\right]^b/\left[C^{z_C}\right]^c$ ratio identical to that when the two pure compounds are simultaneously stable. However, the concentrations are not identical in both situations -ideal solution or two pure components- as typically shown by the saturation indexes. Namely, introducing the $[i]_{s,C,B}$ notations in Eq.25 and 26

$$(1-x)^b = \frac{\left[A^{z_A}\right]}{\left[A^{z_A}\right]_{s,C,B}}\left(\frac{\left[B^{z_B}\right]}{\left[B^{z_B}\right]_{s,C,B}}\right)^b \tag{25}$$

$$x^c = \frac{\left[A^{z_A}\right]}{\left[A^{z_A}\right]_{s,C,B}}\left(\frac{\left[C^{z_C}\right]}{\left[C^{z_C}\right]_{s,C,B}}\right)^c \tag{26}$$

for a given aqueous concentration of A^{z_A} the concentrations of B^{z_B} and C^{z_C} are divided by the same factor $(1-x)^b = x^c$. Thess decreases again illustrate that

- The -single solid phase- mixture is less soluble -more stable- than the two end-members. This is the well known: pure compounds "should not be stable", only mixtures are stable. However, this is true only for ideal mixtures. Most of the mixtures cannot be ideal for straightforward geometrical reasons. Nevertheless according to the entropy principle "pure" compounds always include impurities.
- The decrease in solubility is not very important because x is neither close to zero, neither close to 1 when $(1-x)^b = x^c$.
- Conversely, the decrease in solubility is important only when x is close to zero or

one corresponding to a solid solution virtually identical to end-member $AB_b(s)$ or $AC_c(s)$ respectively, and there is a dramatic decrease in the solubility of C (by x^c) or B (by $(1-x)^b$) respectively in the solid solution as compared to the solubility controlled by the $AC_c(s)$ or $AB_b(s)$ pure compound respectively. This is possible only for high enough concentrations of A.

- Now looking for conditions where the solubilities of both B and C are decreased, it is natural to restrict ourself to conditions where the same value is imposed for the saturation indexes of both pure compounds, namely $(1-x)^b = x^c$, which is actually where we started from in this section. For this reason it can also be considered as the maximum decrease of solubility for the solid solution as compared to the two pure components. This can as well be deduced from Eq.41.

Indeed, in this part we introduced the $[i]_{s,C,B}$ notations in the definition of several equilibrium constants. This can as well be done for

$$Q_x = \frac{[A^{z_A}][B^{z_B}]^{b(1-x)}[C^{z_C}]^{cx}}{[\overline{A^{z_A}}][\overline{B^{z_B}}]^{b(1-x)}[\overline{C^{z_C}}]^{cx}} = \frac{[A^{z_A}][B^{z_B}]^{b(1-x)}[C^{z_C}]^{cx}}{(1\text{-}x)^{b(1\text{-}x)}\,x^{cx}} = K_{s,B}^{(1-x)}K_{s,C}^{x} = [A^{z_A}]_{s,B,C}[B^{z_B}]_{s,B,C}^{b(1\text{-}x)}[C^{z_C}]_{s,B,C}^{cx} \qquad (41)$$

which can be rearranged as

$$(1\text{-}x)^{b(1\text{-}x)}x^{cx} = [\overline{A^{z_A}}][\overline{B^{z_B}}]^{b(1\text{-}x)}[\overline{C^{z_C}}]^{cx} = \frac{[A^{z_A}][B^{z_B}]^{b(1\text{-}x)}[C^{z_C}]^{cx}}{[A^{z_A}]_{s,B,C}[B^{z_B}]_{s,B,C}^{b(1\text{-}x)}[C^{z_C}]_{s,B,C}^{cx}} \qquad (41)$$

3.5.6 Summary of equations

$$\overline{A^{z_A}} + b\ \overline{B^{z_B}} \rightleftarrows A^{z_A} + b\ B^{z_B} \qquad (23)$$

$$K_{s,B} = [A^{z_A}]_{s,C,B}[B^{z_B}]_{s,C,B}^{b} = \frac{[A^{z_A}][B^{z_B}]^{b}}{[\overline{A^{z_A}}][\overline{B^{z_B}}]^{b}} = \frac{[A^{z_A}][B^{z_B}]^{b}}{(1-x)^{b}} \qquad (25)$$

$$\overline{A^{z_A}} + c\ \overline{C^{z_C}} \rightleftarrows A^{z_A} + c\ C^{z_C} \qquad (24)$$

$$K_{s,C} = [A^{z_A}]_{s,C,B}[C^{z_C}]_{s,C,B}^{c} = \frac{[A^{z_A}][C^{z_C}]^{c}}{[\overline{A^{z_A}}][\overline{C^{z_C}}]^{c}} = \frac{[A^{z_A}][C^{z_C}]^{c}}{x^{c}} \qquad (26)$$

$$b\ B^{z_B} + c\ \overline{C^{z_C}} \rightleftarrows b\ \overline{B^{z_B}} + c\ C^{z_C} \qquad (31)$$

$$\frac{K_{s,C}}{K_{s,B}} = \frac{[C^{z_C}]_{s,B,C}^{c}}{[B^{z_B}]_{s,B,C}^{b}} = \frac{[\overline{B^{z_B}}]^{b}[C^{z_C}]^{c}}{[B^{z_B}]^{b}[\overline{C^{z_C}}]^{c}} = \frac{(1-x)^{b}[C^{z_C}]^{c}}{[B^{z_B}]^{b}x^{c}} \qquad (69)$$

$$\overline{A^{z_A}} + b(1\text{-}x)\ \overline{B^{z_B}} + c\,x\ \overline{C^{z_C}} \rightleftarrows A^{z_A} + b(1\text{-}x)\ B^{z_B} + c\,x\ C^{z_C} \qquad (30)$$

$$K_{s,B}^{(1-x)}K_{s,C}^{x} = \left[A^{z_A}\right]_{s,B,C}\left[B^{z_B}\right]_{s,B,C}^{b(1-x)}\left[C^{z_C}\right]_{s,B,C}^{cx} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b(1-x)}\left[C^{z_C}\right]^{cx}}{\left[\overline{A^{z_A}}\right]\left[\overline{B^{z_B}}\right]^{b(1-x)}\left[\overline{C^{z_C}}\right]^{cx}} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b(1-x)}\left[C^{z_C}\right]^{cx}}{(1\text{-}x)^{b(1-x)}\,x^{cx}} = Q_x \tag{41}$$

3.5.7 Approximations for trace concentrations

When C is at trace concentrations:

$$K_{s,B} = \left[A^{z_A}\right]_{s,C,B}\left[B^{z_B}\right]_{s,C,B}^{b} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b}}{\left[\overline{A^{z_A}}\right]\left[\overline{B^{z_B}}\right]^{b}} \approx \left[A^{z_A}\right]\left[B^{z_B}\right]^{b} \quad \text{for } x<<1 \tag{25}$$

$$K_{s,C} = \left[A^{z_A}\right]_{s,C,B}\left[C^{z_C}\right]_{s,C,B}^{c} = \frac{\left[A^{z_A}\right]\left[C^{z_C}\right]^{c}}{\left[\overline{A^{z_A}}\right]\left[\overline{C^{z_C}}\right]^{c}} = \frac{\left[A^{z_A}\right]\left[C^{z_C}\right]^{c}}{x^{c}} \tag{26}$$

$$\frac{K_{s,C}}{K_{s,B}} = \frac{\left[C^{z_C}\right]_{s,B,C}^{c}}{\left[B^{z_B}\right]_{s,B,C}^{b}} = \frac{\left[\overline{B^{z_B}}\right]^{b}\left[C^{z_C}\right]^{c}}{\left[B^{z_B}\right]^{b}\left[\overline{C^{z_C}}\right]^{c}} \approx \frac{\left[C^{z_C}\right]^{c}}{\left[B^{z_B}\right]^{b}x^{c}} \quad \text{for } x<<1 \tag{69}$$

$$K_{s,B}K_{s,C}^{x} \approx \left[A^{z_A}\right]_{s,B,C}\left[B^{z_B}\right]_{s,B,C}^{b}\left[C^{z_C}\right]_{s,B,C}^{cx} \approx \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b}\left[C^{z_C}\right]^{cx}}{\left[\overline{A^{z_A}}\right]\left[\overline{B^{z_B}}\right]^{b}\left[\overline{C^{z_C}}\right]^{cx}} \approx \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b}\left[C^{z_C}\right]^{cx}}{x^{cx}} \approx Q_x \text{ for } x<<1 \tag{41}$$

$$\frac{K_{s,C}}{K_{s,B}} = \frac{\left[C^{z_C}\right]_{s,B,C}^{c}}{\left[B^{z_B}\right]_{s,B,C}^{b}} = \frac{\left[\overline{B^{z_B}}\right]^{b}\left[C^{z_C}\right]^{c}}{\left[B^{z_B}\right]^{b}\left[\overline{C^{z_C}}\right]^{c}} = \frac{(1-x)^{b}\left[C^{z_C}\right]^{c}}{\left[B^{z_B}\right]^{b}x^{c}} \quad \text{for } x<<1 \tag{69}$$

It essentially appears that the partition equilibria equation is not changed for $AC_c(s)$ (Eq.26), while the solubility product equation (Eq.25) is now virtually valid for $AB_b(s)$. This can be checked experimentally as follows. C is introduced (at trace concentrations) in an aqueous solution used to precipitate $AB_b(s)$. The solubility product law is checked by classical slope analysis (Section 3.5.4.3.). When the uptake of C (by $AB_b(s)$) is important, the remaining C aqueous concentration also gives precisely the amount of C in the solid, namely x, which finally allows to check Eq.s 26 and 69: log-log plot gives c, the stoichiometric coefficient and the equilibrium constant. Note that this involves free -not total- aqueous concentrations, which need to be deduced from independent studies in homogeneous aqueous solutions or from published complexing constants (see typically Eq.4).

C can also be introduced in an aqueous solution already equilibrated with $AB_b(s)$. A rapid uptake of C by the $AB_b(s)$ surface is expected, while further penetration of C into the $AB_b(s)$ bulk is much slower. The amount of C that has penetrated inside the solid can still be known, but it is difficult to deduce x, its concentration, because it must be divided by the total surface or the total volume (of $AB_b(s)$ contaminated by C), which are not easily known. However, the surface or the volume factor cancels out when considering several analogue trace elements (typically including a radioactive isotope of B) for checking they actually have similar behaviours by observing ratios of their concentrations. This also allows to use surface concentrations, despite they are not intensive variables.

3.6 Toward real solid solutions.

3.6.1 Vacancies

Up to now, we considered ideal solid solutions of stoichiometry $AB_{b(1-x)}C_{cx}$ without paying much attention to their microscopic structures, since their thermodynamics descriptions only require the solubility products of their ($AB_b(s)$ and $AC_c(s)$) end-members, and their stoichiometries -these stoichiometries are given by electro-neutrality-. Ideal (or near ideal) solid solution means that substituting B by C does not much modify the matrix, the chemical potentials of the other atoms and finally the chemical potentials of B and C; hence their geometric environments are virtually the same in the solid solution and in the end-members. This is clearly possible when C is an isotope of B, or at least a chemical analogue, namely an ion with same charge and similar size and coordination chemistry. Conversely, this might appear impossible when B and C are ions of different charges. Nevertheless, exchanges in minerals are known for ions with different charges. This is typically the case for clays. In clays, a few Si^{4+} tetra-cations are substituted with Al^{3+} tri-cations in matrix layers, charge compensation is obtained by exchanging cations in inter-layers. It is still debated whether the inter-layer cations are fixed on specific anionic sites of the matrix layer surface, or less ordered. Other ion exchanger minerals can be described with typically O^{2-} matrix, where only some of the cationic sites are occupied. We here give one generic example based on such idea. We imagine a matrix, where the minimum cell contains n_A atoms A. For simplicity, we assume that all the matrix sites that can be occupied by A are indeed occupied by A. Conversely, some of the sites that could be occupied by B or C could be vacant. For electro-neutrality, the stoichiometry of the unit cell is still given by b and c, it is now

$$\begin{aligned} n_A\, AB_{b(1-x)}C_{cx} &= A_{n_A}B_{n_A b(1-x)}C_{n_A cx} \\ &= n_A \overline{A^{z_A}} + n_A\, b(1-x)\ \overline{B^{z_B}} + n_A\, c\, x\, \overline{C^{z_C}} + (n_{-A} - n_A(b+(c-b)x))\ \overline{v} \end{aligned} \tag{53}$$

where $\overline{v}$ are vacancies in the solid, $n_v = n_{-A} - n_A(b+(c-b)x)$ the number of vacancies and n_{-A} the total number of sites for A counter-ions. $A_{n_A}B_{n_A b(1-x)}C_{n_A cx}$ is rather a mean stoichiometry: A and B -hence vacancies- are placed at random in the sites of A counter-ions. This disorder allows continuous variations of x. Conversely, when virtually all the $A_{n_A}B_{n_A b(1-x)}C_{n_A cx}$ cells are exactly the same, it rather appears as a new stoichiometric compound for each x value, and in this case there are only a limited number of possibilities for the x values, because n_A is a fixed finite integer. The concentrations in the solid are chosen as follows

$$\left[\overline{A^{z_A}}\right] = 1 \tag{36}$$

$$\left[\overline{B^{z_B}}\right] = b(1-x) \tag{37}$$

$$\left[\overline{A^{z_A}}\right] = 1 \tag{36}$$

$$\left[\overline{C^{z_B}}\right] = c\,x \tag{38}$$

$$\left[\overline{v}\right] = a\text{-}b+(b\text{-}c)x \tag{54}$$

where

$$a = \frac{n_{-A}}{n_A} \tag{55}$$

Note that when a = b or a = c there is no vacancies in $AB_b(s)$ or $AC_c(s)$ respectively: when B and C are of different charge a =b =c is not possible, and there are necessarily vacancies in the solid solution and at least in one of the end-members. The end-members are

$$n_A\,AB_b(s) = A_{n_A}B_{n_A b}(s) = n_A\overline{A^{z_A}} + n_A\,b\;\overline{B^{z_B}} + n_A(a\text{-}b)\;\overline{v} \tag{56}$$

$$n_A\,AC_c(s) = A_{n_A}C_{n_A c}(s) = n_A\overline{A^{z_A}} + n_A\,c\;\overline{C^{z_C}} + n_A(a\text{-}c)\;\overline{v} \tag{57}$$

The stoichiometric coefficients are integers, specially (n_{-A} - n_A b) = n_A(a-b) and (n_{-A} - n_A c) = n_A(a-c). Previous equations (their numbers are italicized) are changed as follows

$$\overline{A^{z_A}} + b\;\overline{B^{z_B}} + (a\text{-}b)\;\overline{v} \;\rightleftarrows\; A^{z_A} + b\;B^{z_B} \qquad (\mathit{23}) \tag{58}$$

$$K_{s,B}\,(a\text{-}b)^{a\text{-}b} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^b}{(1-x)^b\,(a\text{-}b+(b\text{-}c)x)^{a\text{-}b}} \qquad (\mathit{25}) \tag{59}$$

$$\overline{A^{z_A}} + c\;\overline{C^{z_C}} + (a\text{-}c)\;\overline{v} \;\rightleftarrows\; A^{z_A} + c\;C^{z_C} \qquad (\mathit{24}) \tag{60}$$

$$K_{s,C}\,(a\text{-}c)^{a\text{-}c} = \frac{\left[A^{z_A}\right]\left[C^{z_C}\right]^c}{x^c\,(a\text{-}b+(b\text{-}c)x)^{a\text{-}c}} \qquad (\mathit{26}) \tag{61}$$

$$b\;B^{z_B} + c\;\overline{C^{z_C}} + (b\text{-}c)\;\overline{v} \;\rightleftarrows\; b\;\overline{B^{z_B}} + c\;C^{z_C} \qquad (\mathit{31}) \tag{62}$$

$$\frac{K_{s,C}\,(a\text{-}b)^{a\text{-}b}}{K_{s,B}\,(a\text{-}c)^{a\text{-}c}} = \frac{(1-x)^b\left[C^{z_C}\right]^c}{\left[B^{z_B}\right]^b x^c}\,(a\text{-}b+(b\text{-}c)x)^{c\text{-}b} \qquad (\mathit{69}) \tag{63}$$

$$\begin{aligned} &\overline{A^{z_A}} + b(1\text{-}x)\;\overline{B^{z_B}} + c\,x\;\overline{C^{z_C}} + (a\text{-}b+(b\text{-}c)x)\;\overline{v} \\ &\qquad\qquad \rightleftarrows\; A^{z_A} + b(1\text{-}x)\;B^{z_B} + c\,x\;C^{z_C} \qquad (\mathit{30}) \end{aligned} \tag{64}$$

$$\left(K_{s,B}\,(a\text{-}b)^{a\text{-}b}\right)^{(1-x)}\left(K_{s,C}\,(a\text{-}c)^{a\text{-}c}\right)^{x} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b(1\text{-}x)}\left[C^{z_C}\right]^{cx}}{(1\text{-}x)^{b(1\text{-}x)}\,x^{cx}\,(a\text{-}b+(b\text{-}c)x)^{a\text{-}b+(b\text{-}c)x}} \qquad (\mathit{41}) \tag{65}$$

For qualitative discussion, let us simplify to the case, where there are no vacancy in

AB_b(s), while there are still vacancies in AC_c(s): in this case a = b (Eq.56), Eq.59 is now identical to Eq.25, while Eq.61 is simplified into $K_{s,C}\,(b\text{-}c)^{2(b\text{-}c)} = \frac{\left[A^{z_A}\right]\left[C^{z_C}\right]^c}{x^b}$; which is still different from $K_{s,C} = \frac{\left[A^{z_A}\right]\left[C^{z_C}\right]^c}{x^c}$ (Eq.26): the exponent of x is changed from b to c. Similarly, Eq.63 simplifies into $\frac{K_{s,C}}{K_{s,B}} = \left(\frac{1\text{-}x}{x}\right)^b \frac{\left[C^{z_C}\right]^c}{\left[B^{z_B}\right]^b}$, which is different from $\frac{K_{s,C}}{K_{s,B}} = \frac{(1-x)^b\left[C^{z_C}\right]^c}{x^c\left[B^{z_B}\right]^b}$ (Eq.69). This illustrates that introducing vacancies really changed the law of mass action equation, and the corresponding slope analysis as typically based on Eq.49. However, this needs confirmations: to our knowledge such equations does not seem to have been published. As already pointed out, the exponent stoichiometric coefficients are classically determined experimentally by slope analysis of log-log plot for relevant experimental partition or solubility measurements. Nevertheless, several other physical and chemical phenomena can also change such slopes:

- Complexation in the aqueous phase, this can be qualitatively taken into account by writing the chemical equilibria with the major species (see typically Eq.4 and 5) or quantitatively by aqueous equilibrium calculations, namely by calculating the concentrations of the free aqueous species from the chemical composition of the aqueous solution. This is classical and there is no need to include these complications in the present paper. Note that this results in different stoichiometries for the ions in the aqueous and solid phases.
- Chemical reactions with the water HO^- or H^+ ions.
- Non-ideality, which explains that most of the solid solutions are not formed, while as already pointed out, the saturation indexes of the end-members are always less than 1 if an ideal solid solution can form. Pure compounds would not exists, only solid solutions. This is actually the entropy principle, which explains there are always default and impurities in real solids.

Furthermore, when a = c Eq.63 simplify into $\frac{K_{s,C}}{K_{s,B}}(c\text{-}b)^{2(c\text{-}b)} = \left(\frac{1\text{-}x}{x}\right)^c \frac{\left[C^{z_C}\right]^c}{\left[B^{z_B}\right]^b}$, which is different from $\frac{K_{s,C}}{K_{s,B}} = \frac{(1-x)^b}{x^c}\frac{\left[C^{z_C}\right]^c}{\left[B^{z_B}\right]^b}$ (Eq.69): again the exponent of x is changed, it is no more controlled by electro-neutrality. The same remark can be deduced from Eq.41 and 65.

Excepted in these particular cases (a = b or c) and in cases closed to them (a ≈ b or c, *i.e.* only very few vacancies in one of the end-members as compared to the number of occupied B or C sites), vacancies do not seem to induce major changes: in the above equations equilibrium constants are multiplied by constant ($(a\text{-}b)^{a\text{-}b}$ or $(a\text{-}c)^{a\text{-}c}$) terms and by a term originated in the concentration of vacancies, which now does not vary much. The concentration of vacancies is $\left[\bar{v}\right]$ = a-b+(b-c)x (Eq.54): it linearly varies between a-b and a-c, since $0 \le x \le 1$. Instead of $\lg\left[\bar{v}\right]$ we use its mean value <lg v> = [lg(a-b) + lg(a-c)]/2 with the corresponding uncertainty $\delta_{\lg v}$ = |lg(a-b) - lg(a-c)|/2. With this approximation,

- Eq.59 is Eq.25, where Equilibrium Constant $K_{s,B}$, is no more exactly constant: lg $K_{s,B}$ is changed to [lg $K_{s,B}$ +(lg(a-b)+<lg v>± $\delta_{\lg v}$)(a-b)].

- Eq.61 is Eq.26 where $K_{s,C}$ is changed to [lg $K_{s,C}$ +(lg(a-c)+<lg v>± $\delta_{\lg v}$)(a-c)]

and similarly for Eq.63 and 65.

Finally, except for very specific cases, it does not seem that introducing vacancies qualitatively changes the equations. This *a posteriori* justify not to have taken them into account at the beginning of this paper. Nevertheless, introducing vacancies pointed out the importance of correctly describing the structure of the solid solution -and this is not straightforward- to obtain the correct stoichiometric coefficients. Indeed, stoichiometric coefficients correspond to the actual number of exchanged ions, they are also linked to electro-neutrality and reasonable coordination chemistry. All these properties where merged in the simplified stoichiometric description we used before taking into account vacancies.

3.6.2 Non-ideal solid solutions.

Adding a solute (or exchanging it) in an ideal system do not modify the rest of the system. This is a usual starting point to treat a real system considered as an ideal system with small modifications. Conversely, when such an ideal system cannot be identified -trying various unit cell of different stoichimetries and geometries-, there is no special reason to use the law of mass action.

3.6.3 Distortion of the matrix and identification of the geometry.

Adding new ions in vacant sites of the matrix, or exchanging ions of different sizes more or less modifies the geometry of the matrix. As a result, the same geometry can be considered as deriving from different ideal geometries, and it is not straightforward to identify the most relevant basic cell -and corresponding stoichiometries- to describe solid systems.

3.7 Comparing aqueous and solid solutions

3.7.1 Introduction

The description of our $AB_{b(1-x)}C_{cx}$ solid solutions did not specially seem to use that the matrix of this solution is solid: one can wonder to which extend this approach can be generalized. On the other hand, stoichiometries are given by the electro-neutrality, which is not specially the case for aqueous solutions. It seems we essentially had to define the stoichiometry of the reaction to write the corresponding law of mass action equations. This seems to be possible in any type of solutions: bulk solids, surfaces, liquid. In this part we consider such comparisons. For this we essentially compare our solid solution with aqueous solutions, outlining a few usual chemical concepts as typically solvation, complexation, coordination chemistry... that actually all more or less deal with the stoichiometric description of the system.

3.7.2 Solvation and complexation

In aqueous solutions, water molecules are usually not written in chemical reactions and the corresponding equilibria, because the activity of water is constant (= 1): it must not be written in the law of mass action. They are a few specific exception when writing H_2O in an equilibrium is needed for mass balance or when considering ionic strength corrections: in that case the activity of water is no more 1 (the activity of the solvent is 1; but the solvent is no more pure water), it can be measured by typically measuring its partial pressure equilibrated with the aqueous solution. We do not consider these specific cases.

Notation B^{z_B} is for $B^{z_B}(aq)$, where (aq) is often omitted (as we did here for simplicity) despite one or even two hydration layers of the B^{z_B} central ion can usually very well be identified. One can typically admit that the number of water molecules more or less fixed by B^{z_B} is negligible and this does not change the size of the system -determined by the total number of water, while intuitively one would rather consider only bulk water- neither the mean activity of water. Actually, when this approximation does not stand any more, this is classically taken into account by activity coefficients, since the activity of water can be calculated from the mean activity coefficient. Again we do not consider here such small corrections.

In our solid solution, the equivalent of water -the solvent- is the matrix. In our description it is represented by $\overline{A^{z_A}}$. Note that for the B^{z_B}/C^{z_C} ion exchange equilibrium (Eq.31) we indeed did not write $\overline{A^{z_A}}$ because it cancels out, despite the matrix is implicitly here. As a consequence -for mass balance- we neither wrote A^{z_A}. Conversely, for all the other equilibria we had to write $\overline{A^{z_A}}$: this because they actually correspond to reactions of dissolution of the matrix, namely $\overline{A^{z_A}}$ is dissolved. This is a difference with aqueous solutions.

This is a bit misleading: when $\overline{A^{z_A}}$ is in the solid phase it is the solvent for $\overline{B^{z_B}}$, while in aqueous solution A^{z_A} can very well be a ligand for B^{z_B} to form a complex (Eq.4). Coordinations are usually different between aqueous and solid phases, nevertheless they are the same in some special cases as typically aqueous limiting complexes and well chosen solid compounds, and this is experimentally used. For this reason, it is tempting to write $\overline{AB_n^{z_A-n\,z_B}}$ instead of $\overline{B^{z_B}}$, where n is the number of A ligands in the solid. This can very well be done for Equilibrium 31, hence writing $\overline{AB_n^{z_A-n\,z_B}}$ and $\overline{AC_p^{z_A-p\,z_C}}$ instead of $\overline{B^{z_B}}$ and $\overline{C^{z_C}}$ respectively, where mass balance is obtained by adding $(n-p)\overline{A^{z_A}}$. This does not introduce any new term in the corresponding equilibrium constant since $\left[\overline{A^{z_A}}\right]$ = 1. It is clear that such procedure is possible only for equilibria that do not correspond to any dissolution / precipitation of the matrix. In this later case stoichiometric coefficients are controlled by electro-neutrality as for pure compounds.

3.7.3 Coordination chemistry

$\overline{B^{z_B}}$ and $\overline{C^{z_C}}$ are coordinated to $\overline{A^{z_A}}$ in the solid, but this is not reflected in the stoichiometry, because $\overline{A^{z_A}}$ also stands for the matrix, as explained in the previous section. Furthermore, in our relatively simple solid solution $\overline{A^{z_A}}$ is necessarily the only -or at least the major- ligand of $\overline{B^{z_B}}$ and $\overline{C^{z_C}}$. Nevertheless, several coordinations are possible, corresponding to different sites for $\overline{B^{z_B}}$ or $\overline{C^{z_C}}$: see the next section.

3.7.4 Several types of sites for the same ion

Several types of sites can exist for $\overline{B^{z_B}}$ or $\overline{C^{z_C}}$: typically $\overline{{}^1B^{z_B}}$ and $\overline{{}^2B^{z_B}}$ for $\overline{B^{z_B}}$, where it is not needed to indicate the corresponding coordination chemistry, namely the number of $\overline{A^{z_A}}$ ligand, despite this number is certainly different for each site, because

$\overline{A^{z_A}}$ also stands for the matrix (see Sections 3.7.2. and 3.7.3.). Equilibrium between these two sites simply writes $\overline{{}^1B^{z_B}} \rightleftarrows \overline{{}^2B^{z_B}}$. The corresponding equilibrium constant is K = $\left[\overline{{}^1B^{z_B}}\right]/\left[\overline{{}^2B^{z_B}}\right]$. This ratio is constant. For this reason it does not seem specially needed to writes equilibrium constants with two sites: $\left[\overline{B^{z_B}}\right] = \left[\overline{{}^1B^{z_B}}\right] + \left[\overline{{}^2B^{z_B}}\right]$ can be used, in the same way as in aqueous solution $[{}^{\dagger}CO_2]$ is usually written for $[CO_2(aq)] + [H_2CO_3(aq)]$.

4 Law of mass action for solid solutions, a demonstration.

4.1 Introduction.

We have seen that the law of mass action has correctly been used in the literature, and demonstrated by typically Lippmann, who also already gave most of the comments needed to understand the chemical meaning of such a thermodynamic description. One important point is that for a two end-members mixtures the law of mass action is a set of two equations. Consequently, combining such equations give equivalent sets of equations: the law of mass action does not have a unique form. As usual, the scientific basis of these equations are often forgotten. Furthermore, the non-constant solubility product equation became quite popular despite, as pointed out, it is a quite unusual, a bit misleading equations with two advancement variables, non-constant stoichiometric coefficients, stoichiometric coefficients that are also concentrations... we choose to start directly from this equation to give a demonstration of law of mass action. Before this we briefly recall the most simple correct demonstrations already published by Lippmann and Michard. However we will use our own notations and concentrations units, specially because mole fraction are intensive variable only in particular cases: in several cases they are not concentration units. It is first important to obtain a correct description for the stoichiometry of the solid solution. This is not given by thermodynamics. This specially provides what is the matrix, whether all its anionic and cationic sites are occupied, if not vacancies should be taken into account. We already showed that above. Nevertheless, for simplicity, we here only consider the simple $AB_{b(1-x)}C_x$ solid solution.

4.2 A quick way to write the law of mass action for solid solutions.

We use Notation

$$(1\text{-}x)AB_b + x\ AC_c = AB_{b(1\text{-}x)}C_{cx} = \overline{A^{z_A}} + b(1\text{-}x)\ \overline{B^{z_B}} + c\ x\ \overline{C^{z_C}} \qquad (20)$$

which means we know -usually from structural observation- that the $AB_{b(1-x)}C_x$ stoichiometry corresponds to a unique structure for $0 \le x \le 1$, specially the $AB_b(s)$ and $AC_c(s)$ end-member must be in this structure with eventually vacancies that should then be explicitly written (Eq.53). The law of mass action for Equilibria

$$AB_b(s) = \overline{A^{z_A}} + b\ \overline{B^{z_B}} \rightleftarrows A^{z_A} + b\ B^{z_B} \qquad (66)$$

$$AC_c(s) = \overline{A^{z_A}} + c\ \overline{C^{z_C}} \rightleftarrows A^{z_A} + c\ C^{z_C} \qquad (67)$$

writes

$$K_{A\text{-}B} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^b}{\left[\overline{A^{z_A}}\right]\left[\overline{B^{z_B}}\right]^b} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^b}{(1-x)^b} = K_{s,B} \tag{25}$$

$$K_{A\text{-}C} = \frac{\left[A^{z_A}\right]\left[C^{z_C}\right]^c}{\left[\overline{A^{z_A}}\right]\left[\overline{C^{z_C}}\right]^c} = \frac{\left[A^{z_A}\right]\left[C^{z_C}\right]^c}{x^c} = K_{s,C} \tag{26}$$

where equilibrium constants $K_{A\text{-}B}$ and $K_{A\text{-}C}$ appear to be the $K_{s,B}$ and $K_{s,C}$ solubility products of the end-members for the limiting cases x = 0 and 1 respectively. From Eq.25 and 26 the two classical equations

$$K_{s,B}^{1\text{-}x} K_{s,C}^{x} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b(1\text{-}x)}\left[C^{z_C}\right]^{cx}}{\left[\overline{A^{z_A}}\right]\left[\overline{B^{z_B}}\right]^{b(1\text{-}x)}\left[\overline{C^{z_C}}\right]^{cx}} = \frac{\left[A^{z_A}\right]\left[B^{z_B}\right]^{b(1\text{-}x)}\left[C^{z_C}\right]^{cx}}{(1\text{-}x)^{b(1\text{-}x)}\, x^{cx}} \tag{41}$$

$$\frac{K_{s,C}}{K_{s,B}} = \frac{\left[\overline{B^{z_B}}\right]^b\left[C^{z_C}\right]^c}{\left[B^{z_B}\right]^b\left[\overline{C^{z_C}}\right]^c} = \frac{(1-x)^b\left[C^{z_C}\right]^c}{\left[B^{z_B}\right]^b x^c} \tag{42}$$

are deduced. They correspond to Equilibria

$$\overline{A^{z_A}} + b(1\text{-}x)\ \overline{B^{z_B}} + c\,x\ \overline{C^{z_C}} \rightleftarrows A^{z_A} + b(1\text{-}x)\ B^{z_B} + c\,x\ C^{z_C} \tag{30}$$

$$b\ B^{z_B} + c\ \overline{C^{z_C}} \rightleftarrows b\ \overline{B^{z_B}} + c\ C^{z_C} \tag{31}$$

In this part, we will demonstrate the law of mass action for Equilibrium 30. For this we will first demonstrate the usual form of law of mass action for pure solids, namely solubility products.

4.3 Law of mass action for pure compounds.

The thermodynamic demonstration of the law of mass action is obtained by minimising the Gibbs Energy of the system at constant P ant T ($(dG)_{P,T} = 0$):

$$0 = \mu_{A^{z_A}} dn_{A^{z_A}} + \mu_{B^{z_B}} dn_{B^{z_B}} + \mu_{AB_B(s)} dn_{AB_B(s)} \tag{68}$$

for the A^{z_A} / B^{z_B} / AB_b(s) system, where μ_i is the chemical potential of species i, and n_i its number of moles. For Equilibrium

$$AB_b(s) \rightleftarrows A^{z_A} + b\ B^{z_B}, \tag{3}$$

$$dn_{A^{z_A}} = d\xi \tag{28}$$

$$dn_{B^{z_B}} = b\ d\xi \tag{29}$$

$$dn_{A^{z_A}} = d\xi \tag{28}$$

$$dn_{AB_b(s)} = -d\xi \tag{69}$$

Reporting Eq.28, 29 and 69 into Eq.68

$$0 = \mu_{A^{z_A}} + b\ \mu_{B^{z_B}} - \mu_{AB_b(s)} \tag{70}$$

the definition of a_i, the absolute activity of species i, is

$$\mu_i = \mu_i^o + R\ T\ \ln a_i \tag{71}$$

with the supplementary definitions in the reference state a_i =1 hence $\mu_i = \mu_i^o$. μ_i^o is another notation for $\Delta_f G_i^o$, the molar Gibbs energy of formation of species i. For ideal systems $a_i = m_i/m_i^o$, where m_i is the molal concentration of species i, and $1 = m_i^o$ is the value of m_i in the reference state when i is an aqueous species. m_i^o is often omitted. Similar definitions stand for species in each phase. However, the chemical potential and activity of the solid are constant:

$$\mu_{AB_B(s)} = \mu^o_{AB_B(s)} \tag{72}$$

Reporting Eq.71 and 72 into Eq.70

$$0 = \Delta_r G^o_{s,b} + R\,T \ln K^o_{s,B} \tag{73}$$

where

$$\Delta_r G^o_{s,b} = \mu^o_{A^{z_A}} + b\ \mu^o_{B^{z_B}} - \mu^o_{AB_B(s)} \tag{74}$$

$$K^o_{s,B} = a_{A^{z_A}}\ a^b_{B^{z_B}} \tag{75}$$

which is the solubility product law. It is Eq.(2) taking into account non-ideality, namely

$$K^o_{s,B} = K_{s,B}\ \gamma_{A^{z_A}}\ \gamma^b_{B^{z_B}}\ \varrho^{1+b} \tag{76}$$

where $\gamma_{Y^{z_Y}}$, the activity coefficient of Y^{z_Y} is defined as

$$a_{Y^{z_Y}} = \frac{m_{Y^{z_Y}}}{m^o_{Y^{z_Y}}}\gamma_{Y^{z_Y}} \tag{77}$$

and ϱ = V/m is the factor for the conversion of molar to molal concentrations: V is the volume (dm^3) of solution containing m kg of water. Medium effects are thus included in

$K_{s,B}$. Classically, constant high concentration of a strong electrolyte is used to obtain a constant aqueous medium, where the values of ϱ and γ_i are virtually constants. In that case a new ideal aqueous solution is obtained, which indicates that $K_{s,B}$ has similar thermodynamics meaning as $K^o_{s,B}$: the only difference is the reference state.

4.4 Law of mass action for solid solutions.

4.4.1 A demonstration

We use the same type of demonstration as for the solubility product of the $AB_b(s)$ pure compound (Section 4.3.). The main difference is at the beginning when calculating dn_i, (Eq.28, 29 and 69): for this reason we give more details on these equations, while the following ones are only mathematical consequences. Note that

$$\nu_{i,B\text{-}C} = \frac{d\,\nu_{i,x}}{dx} \qquad (32)$$

where $\nu_{i,x}$ is the stoichiometric coefficient of Species i in Equilibrium

$$\overline{A^{z_A}} + b(1\text{-}x)\ \overline{B^{z_B}} + c\,x\ \overline{C^{z_C}} \rightleftarrows A^{z_A} + b(1\text{-}x)\ B^{z_B} + c\,x\ C^{z_C}, \qquad (30)$$

and $\nu_{i,B\text{-}C}$ is the stoichiometric coefficient of Species i in Equilibrium

$$b\ B^{z_B} + c\ \overline{C^{z_C}} \rightleftarrows b\ \overline{B^{z_B}} + c\ C^{z_C} \qquad (31)$$

Typically, $dn_{B^{z_B},0} = \nu_{B^{z_B},0}\,d\xi = b\,d\xi$ for Equilibrium 3 is only the first term of $dn_{B^{z_B}}$ when x varies as typically in Equilibrium 30: for Equilibrium 30 this first term is indeed $\left(\partial n_{B^{z_B},x}\right)_x = \left(\frac{\partial n_{B^{z_B},x}}{\partial \xi}\right)_x d\xi = \nu_{B^{z_B},x}\,d\xi = b(1\text{-}x)\,d\xi$. Similarly $dn_{A^{z_A},0} = \nu_{A^{z_A},0}\,d\xi = d\xi$ and $\left(\partial n_{A^{z_A},x}\right)_x = \nu_{A^{z_A},x}\,d\xi = d\xi$: it appears that ξ is an advancement variable for both equilibria, and in both cases it corresponds to $n_{A^{z_A}}$. Consequently, the second term of $dn_{B^{z_B},x}$ can be obtained as $\left(\partial n_{B^{z_B},x}\right)_\xi = \left(\partial n_{B^{z_B},x}\right)_{n_{A^{z_A}}} = d\,\nu_{B^{z_B},x} = -b\,dx$. Note that (Eq.32) $d\,\nu_{B^{z_B},x} = \nu_{B^{z_B},B\text{-}C}\,dx$. Such calculation is performed for each species: we here reproduce the equations already given for pure compounds, we italicize them, and we add the new equations modified for taking into account variable stoichiometry in the solid.

$$AB_b(s) \rightleftarrows A^{z_A} + b\ B^{z_B} \tag{3}$$

$$\overline{A^{z_A}} + b(1\text{-}x)\ \overline{B^{z_B}} + c\,x\ \overline{C^{z_C}} \rightleftarrows A^{z_A} + b(1\text{-}x)\ B^{z_B} + c\,x\ C^{z_C} \tag{30}$$

$$dn_{A^{z_A},0} = d\xi \tag{28}$$

$$-dn_{\overline{A^{z_A}},x} = dn_{A^{z_A},x} = \left(\frac{\partial n_{A^{z_A},x}}{\partial \xi}\right)_x d\xi + \left(\frac{\partial n_{A^{z_A},x}}{\partial x}\right)_\xi dx = \nu_{A^{z_A},x} d\xi + \nu_{A^{z_A},B\text{-}C} dx \tag{33}$$
$$= d\xi$$

$$dn_{B^{z_B},0} = b\ d\xi \tag{29}$$

$$-dn_{\overline{B^{z_B}},x} = dn_{B^{z_B},x} = \left(\frac{\partial n_{B^{z_B},x}}{\partial \xi}\right)_x d\xi + \left(\frac{\partial n_{B^{z_B},x}}{\partial x}\right)_\xi dx = \nu_{B^{z_B},x} d\xi + \nu_{B^{z_B},B\text{-}C} dx \tag{34}$$
$$= b(1\text{-}x)d\xi - b\ dx$$

Similarly

$$-dn_{\overline{C^{z_C}},x} = dn_{C^{z_C},x} = \left(\frac{\partial n_{C^{z_C},x}}{\partial \xi}\right)_x d\xi + \left(\frac{\partial n_{C^{z_C},x}}{\partial x}\right)_\xi dx = \nu_{C^{z_C},x} d\xi + \nu_{C^{z_C},B\text{-}C} dx \tag{78}$$
$$= c\ x\ d\xi + c\ dx$$

Eq.(69) is now included in Eq.33, 34 and 78. Equation

$$0 = \mu_{A^{z_A}} dn_{A^{z_A}} + \mu_{B^{z_B}} dn_{B^{z_B}} + \mu_{AB_B(s)} dn_{AB_B(s)} \tag{68}$$

now writes

$$0 = \mu_{A^{z_A}} dn_{A^{z_A}} + \mu_{B^{z_B}} dn_{B^{z_B}} + \mu_{C^{z_C}} dn_{C^{z_C}} - \left(\mu_{\overline{A^{z_A}}} dn_{\overline{A^{z_A}}} + \mu_{\overline{B^{z_B}}} dn_{\overline{B^{z_B}}} + \mu_{\overline{C^{z_C}}} dn_{\overline{C^{z_C}}}\right) \tag{79}$$

Substituting Eq.33, 34 and 78 into Eq.79, and using Notation

$$\delta_Y = \mu_{Y^{z_Y}} - \mu_{\overline{Y^{z_Y}}}, \tag{80}$$

$$\begin{aligned} 0 &= \delta_{A^{z_A}}\left(\nu_{A^{z_A},x} d\xi + d\,\nu_{A^{z_A},x}\right) + \delta_{B^{z_B}}\left(\nu_{B^{z_B},x} d\xi + d\,\nu_{B^{z_B},x}\right) + \delta_{C^{z_C}}\left(\nu_{C^{z_C},x} d\xi + d\,\nu_{C^{z_C},x}\right) \\ &= \sum_{i=A,B,C}\left(\nu_{i,x}\,\delta_i\right) d\xi + \sum_{i=A,B,C}\left(\nu_{i,B\text{-}C}\,\delta_i\right) dx \\ &= \left(\delta_{A^{z_A}} + b(1\text{-}x)\,\delta_{B^{z_B}} + c\,x\,\delta_{C^{z_C}}\right) d\xi + \left(\text{-}b\,\delta_{B^{z_B}} + c\,\delta_{C^{z_C}}\right) dx \end{aligned} \tag{81}$$

Since ξ and x are two independent variables Eq.81 is actually a set of two equations,

$$\left\{\begin{matrix} 0 = \delta_{A^{z_A}} + b(1\text{-}x)\,\delta_{B^{z_B}} + c\,x\,\delta_{C^{z_C}} \\ 0 = \text{-}b\,\delta_{B^{z_B}} + c\,\delta_{C^{z_C}} \end{matrix}\right) \tag{82}$$

consistently the first one corresponds to the law of mass action for Equilibrium 30 (of stoichiometric coefficients $\nu_{i,x}$) and the second one for Equilibrium 31 (of stoichiometric coefficients $\nu_{i,B\text{-}C}$). Indeed, the law of mass action is classically obtained as follows. Reporting Equation

$$\mu_i = \mu_i^o + R\,T\ln a_i \qquad (71)$$

into Eq.82

$$\begin{cases} 0 = \Delta_r G_x^o + R\,T\ln K_x^o \\ 0 = \Delta_r G_{B\text{-}C}^o + R\,T\ln K_{B\text{-}C}^o \end{cases} \qquad (83)$$

Is obtained, where

$$\Delta_r G_x^o = \delta^o_{A^{z_A}} + b(1\text{-}x)\,\delta^o_{B^{z_B}} + c\,x\,\delta^o_{C^{z_C}} \qquad (84)$$

$$\Delta_r G_{B\text{-}C}^o = \text{-}b\,\delta^o_{B^{z_B}} + c\,\delta^o_{C^{z_C}} \qquad (85)$$

$$K_x^o = \frac{a_{A^{z_A}}\,a^{b(1\text{-}x)}_{B^{z_B}}\,a^{cx}_{C^{z_C}}}{a_{\overline{A^{z_A}}}\,a^{b(1\text{-}x)}_{\overline{B^{z_B}}}\,a^{cx}_{\overline{C^{z_C}}}} \qquad (86)$$

$$K_{B\text{-}C}^o = \frac{a^{\text{-}b}_{B^{z_B}}\,a^{c}_{C^{z_C}}}{a^{\text{-}b}_{\overline{B^{z_B}}}\,a^{c}_{\overline{C^{z_C}}}} \qquad (87)$$

Eq.86 and 87 are the law of mass action for Equilibria 30 and 31 respectively. Note that $K_x^{B\text{-}C}$ is constant (Eq.85), while K_x^o is not, since it depends on x (Eq.86).

4.4.2 Number of thermodynamics constants.

We have introduced three thermodynamics constants: $\delta^o_{A^{z_A}}$, $\delta^o_{B^{z_B}}$ and $\delta^o_{C^{z_C}}$; but we will see that two are enough. $\Delta_r G_{B\text{-}C}^o$ already depends on only two of these constants (Eq.85); but $\Delta_r G_x^o$ indeed depends on the three $\delta^o_{A^{z_A}}$, $\delta^o_{B^{z_B}}$ and $\delta^o_{C^{z_C}}$ constants (Eq.84); to demonstrate that $\Delta_r G_x^o$ depends only on two constants Eq.84 is rearranged as follows:

$$\begin{aligned} &\text{- } R\,T\ln K_x^o \\ =\ & \Delta_r G_x^o = \delta^o_{A^{z_A}} + b(1\text{-}x)\,\delta^o_{B^{z_B}} + c\,x\,\delta^o_{C^{z_C}} \\ =\ & (1\text{-}x)\left(\delta^o_{A^{z_A}} + b\,\delta^o_{B^{z_B}}\right) + x\left(\delta^o_{A^{z_A}} + c\,\delta^o_{C^{z_C}}\right) \\ =\ & (1\text{-}x)\,\Delta_r G_{A\text{-}B}^o + x\,\Delta_r G_{A\text{-}C}^o \\ =\ & \text{-}R\,T\,\ln\left(\left(K_{A\text{-}B}^o\right)^{1\text{-}x}\left(K_{A\text{-}C}^o\right)^x\right) \end{aligned} \qquad (84)$$

Where

$$\text{- } R\,T\ln K_{A,B}^o = \Delta_r G_{A\text{-}B}^o = \delta^o_{A^{z_A}} + b\,\delta^o_{B^{z_B}} \qquad (88)$$

$$\text{- } R\,T\ln K_{A,C}^o = \Delta_r G_{A\text{-}C}^o = \delta^o_{A^{z_A}} + c\,\delta^o_{C^{z_C}} \qquad (89)$$

This calculation actually demonstrates that the K^o_x function of x writes

$$K^o_x = (K^o_{A\text{-}B})^{1-x}(K^o_{A\text{-}C})^x \qquad (84)$$

and that K^o_x -or equivalently $\Delta_r G^o_x$- depends on only two constants: $K^o_{A\text{-}B}$ and $K^o_{A\text{-}C}$; despite we had initially introduced three constants: $\delta^o_{A^{z_A}}$, $\delta^o_{B^{z_B}}$ and $\delta^o_{C^{z_C}}$. Of course, $K^o_{B\text{-}C}$ depends also of the same parameters. To demonstrate this, the same type of rearrangement can be made for Eq.85:

$$\begin{aligned} &- R\,T\,\ln K^o_{B\text{-}C} \\ &= \Delta_r G^o_{B\text{-}C} = -b\,\delta^o_{B^{z_B}} + c\,\delta^o_{C^{z_C}} \\ &= \left(\delta^o_{A^{z_A}} + c\,\delta^o_{C^{z_C}}\right) - \left(\delta^o_{A^{z_A}} + b\,\delta^o_{B^{z_B}}\right) \\ &= \Delta_r G^o_{A\text{-}C} - \Delta_r G^o_{A\text{-}B} \\ &= -R\,T\,\ln \frac{K^o_{A\text{-}C}}{K^o_{A\text{-}B}} \end{aligned} \qquad (85)$$

namely

$$K^o_{B\text{-}C} = \frac{K^o_{A\text{-}C}}{K^o_{A\text{-}B}} \qquad (85)$$

4.4.3 Partition equilibria.

Reporting Eq.86 and 87 into $K^o_x = (K^o_{A\text{-}B})^{1-x}(K^o_{A\text{-}C})^x$ (Eq.84) and $K^o_{B\text{-}C} = \dfrac{K^o_{A\text{-}C}}{K^o_{A\text{-}B}}$ (Eq.85):

$$K^o_{A,B} = \frac{a_{A^{z_A}}\, a^b_{B^{z_B}}}{a_{\overline{A^{z_A}}}\, a^b_{\overline{B^{z_B}}}} \qquad (90)$$

$$K^o_{A,C} = \frac{a_{A^{z_A}}\, a^c_{C^{z_C}}}{a_{\overline{A^{z_A}}}\, a^c_{\overline{C^{z_C}}}}. \qquad (91)$$

$K^o_{A\text{-}B}$ and $K^o_{A\text{-}C}$ appear to be the constants for the partition equilibria

$$\overline{A^{z_A}} + b\ \overline{B^{z_B}} \rightleftarrows A^{z_A} + b\ B^{z_B} \qquad (66)$$

$$\overline{A^{z_A}} + c\ \overline{C^{z_C}} \rightleftarrows A^{z_A} + c\ C^{z_C} \qquad (67)$$

Eq.90 and 91 are the law of mass action for Equilibria 66 and 67, and this can be demonstrated exactly in the same way as Eq.85 for Equilibrium 31.

Note that $K^o_{B\text{-}C} = \frac{K^o_{A\text{-}C}}{K^o_{A\text{-}B}}$ (Eq.85) merely reflects that Equilibrium

$$b\ B^{z_B} + c\ \overline{C^{z_C}} \rightleftarrows b\ \overline{B^{z_B}} + c\ C^{z_C} \qquad (31)$$

can be obtained by the Equilibirum 31 = Equilibirum 67 - Equilibirum 66 thermodynamic cycle from Equilibria 66 and 67. Now, the same type of mathematical calculation for $K^o_x = (K^o_{A\text{-}B})^{1\text{-}x}(K^o_{A\text{-}C})^x$ (Eq.84) would give Equilibirum 30 = (1-x)Equilibirum 66 + x Equilibirum 67, which is not a thermodynamic cycle since 1-x and x are not constant, they actually represent concentrations. This explains why K^o_x is not constant: it does not correspond to a classical chemical equilibrium or reaction.

Note that we started from Equilibria 66 and 67 characterized K^o_x and $K^o_{B\text{-}C}$. Conversely, following a Lippmann type approach one can start from $K^o_{A\text{-}B}$ and $K^o_{A\text{-}C}$ to obtain $K^o_x = (K^o_{A\text{-}B})^{1\text{-}x}(K^o_{A\text{-}C})^x$ (Eq.84) and $K^o_{B\text{-}C} = \frac{K^o_{A\text{-}C}}{K^o_{A\text{-}B}}$ (Eq.85); namely, $K^o_{A\text{-}B}$ and $K^o_{A\text{-}C}$ have actually be obtained as

$$K^o_{A\text{-}B} = \frac{K^o_x}{(K^o_{B\text{-}C})^x} \qquad (92)$$

$$K^o_{A\text{-}C} = K^o_x (K^o_{B\text{-}C})^{1\text{-}x} \qquad (93)$$

4.4.4 Standard state.

The standard state of aqueous solutions is the pure solvent. A similar definition would not be convenient for solid solutions, since it would correspond to the "pure matrix", which is a concept far from any real solid. Anyhow, we have not the choice of standard state for solids, it is already defined through the standard solubility products. Namely, when the solid solution has the composition of an end-member the solid solution description must be consistent with the standard state as reflected in the solubility product. In such limiting conditions, there has two ways to describe the solid solution, one way is the solubility product, typically for End-member AB_b

$$K^o_{s,B} = a_{A^{z_A}, AB_b}\ a^b_{B^{z_B}, AB_b} \qquad (75)$$

where subscript AB_b is to stress that the aqueous solution is saturated with AB_b. The second way is to use Eq.86 where x = 0 which appears to be Eq.90:

$$K^o_{A,B} = \frac{a_{A^{z_A}, AB_b}\, a^b_{B^{z_B}, AB_b}}{a_{\overline{A^{z_A}}, AB_b}\, a^b_{\overline{B^{z_B}}, AB_b}} \qquad (90)$$

from which

$$K^{o}_{A,B} \;=\; \frac{K^{o}_{s,B}}{a_{\overline{A^{z_A}},AB_b}\, a^{b}_{\overline{B^{z_B}},AB_b}} \qquad (90)$$

Similarly for x = 1

$$K^{o}_{A,C} \;=\; \frac{K^{o}_{s,C}}{a_{\overline{A^{z_A}},AC_c}\, a^{c}_{\overline{C^{z_C}},AC_c}} \qquad (91)$$

It is now needed to define the values of $a_{\overline{i,Aj_q}}$ the activities in the solid solution when it corresponds to one of the pure compounds. As in liquid solutions, this is defined with the concentration units. This because the standard state is an ideal solution where concentrations can be used as activities. The concentration units we have used up to now are

$$\left[\overline{A^{z_A}}\right] = 1,\ \left[\overline{B^{z_B}}\right] = b(1\text{-}x) \text{ and } \left[\overline{C^{z_C}}\right] = c\,x \qquad (12)$$

namely for x = 0, $a_{\overline{A^{z_A}},AB_b} = 1$, $a_{\overline{B^{z_B}},AB_b} = b$, $a_{\overline{C^{z_C}},AB_b} = 0$, while for x = 1, $a_{\overline{A^{z_A}},AC_c} = 1$, $a_{\overline{B^{z_B}},AC_c} = 0$, $a_{\overline{C^{z_C}},AC_c} = c$. Using these definitions:

$$K^{o}_{A,B} \;=\; \frac{K^{o}_{s,B}}{b^{b}} \qquad (90)$$

$$K^{o}_{A,C} \;=\; \frac{K^{o}_{s,C}}{c^{c}} \qquad (91)$$

4.4.5 Activity coefficients.

γ_i, the activity coefficient is classically defined as

$$a_i = \frac{m_i}{m_i^{o}}\gamma_i \qquad (77)$$

for aqueous species i, where m_i is its molal concentration, and 1 = m_i^{o} is the value of m_i in the reference state. m_i^{o} is often omitted. The reference state is an ideal solution, where $a_i = m_i/m_i^{o}$, or equivalently $\gamma_i = 1$. Similarly in the solid solution

$$a_{\bar{i}} \;=\; a_{\overline{Y}} = \frac{[\overline{Y}]}{[\overline{Y}]^{o}}\gamma_{\overline{Y}} \qquad (94)$$

where

$$\left[\overline{A^{z_A}}\right] = 1,\ \left[\overline{B^{z_B}}\right] = b(1\text{-}x) \text{ and } \left[\overline{C^{z_C}}\right] = c\,x \qquad (12)$$

Using these concentration units:

$$K^{o}_{s,B} = b^{b} K^{o}_{A,B} = K_{s,B,m} \quad K^{exc}_{s,B} \qquad (90)$$

$$K^{o}_{s,C} = c^{c} K^{o}_{A,C} = K_{s,C,m} \quad K^{exc}_{s,C} \qquad (91)$$

where

$$K_{s,B,m} = \frac{m_{A^{z_A}} m^{b}_{B^{z_B}}}{b(1\text{-}x)^{b}} \qquad (90)$$

$$K_{s,C,m} = \frac{m_{A^{z_A}} m^{c}_{C^{z_C}}}{c\,x^{c}} \qquad (91)$$

are the molal solubility products, and

$$K^{exc}_{s,B} = \frac{\gamma_{A^{z_A}} \gamma^{b}_{B^{z_B}}}{\gamma_{\overline{A^{z_A}}} \gamma^{b}_{\overline{B^{z_B}}}} \qquad (95)$$

$$K^{exc}_{s,C} = \frac{\gamma_{A^{z_A}} \gamma^{c}_{C^{z_C}}}{\gamma_{\overline{A^{z_A}}} \gamma^{c}_{\overline{C^{z_C}}}} \qquad (96)$$

When species i is an aqueous species, γ_i is a molal activity coefficient, while in the solid the activity coefficient is related to the concentration units we have defined, which are not mole fractions when b ≠ c. Note that we have written $\gamma_{\overline{A^{z_A}}}$, the activity coefficient of the matrix. It can vary, in the same way as the activity of water varies in concentrated aqueous solutions. $\gamma_{\overline{A^{z_A}}}$, can typically be interpreted as corresponding to the distortion of the matrix, however it is equivalent to the mean activity coefficients of the solutes in the same way as in aqueous solutions.

References

[1876GIB] J. W. Gibbs. On the equilibrium of heterogeneous substances (1876). vol. 1, Thermodynamics of The collected works of J. W. Gibbs. Yale University Press (1957)

[1898CUR/CUR] P. Curie, Mme. P. Curie and G. Bémont. *Sur une nouvelle substance fortement radio-active, contenue dans la pechblende.* Comptes rendus de l'Académie des Sciences, Paris, 1898, 127, 1215-1217. http://www.academie-sciences.fr/membres/in_memoriam/Curie/Curie_pdf/Curie_1898lm.pdf , http://www.academie-sciences.fr/membres/in_memoriam/Curie/Curie_pubd1.htm

[52GUG] Guggennheim E. A. *Mixtures (The theory of the equilibrium properties of some simple classes of mixtures solutions and alloys).* Oxford 1952

[67SIL] Sillén, L. G., *The Ocean as a Chemical System*. Science 156, 1189–1197 (1967) DOI: 10.1126/science.156.3779.1189.

[77LIP] Lippmann F., The Solubility Products of Complex Minerals, Mixed Crystals, and

Three-Layer Clay Minerals. N. Jb. Mineral. Abh., (1977) 130,243-263.

[80LIP] Lippmann F. Phase diagrams depicting aqueous solubility of binary carbonate systems. N. Jb. Mineral. Abh., (1980) 139, 1-25.

[83DEN/MIC] Denis J., Michard G., *Dissolution d'une solution solide : étude théorique et expérimentale.* Bull. Minéral (1983) 106, 306-309

[83VIT] Vitorge P., Complexation de lanthanides et d'actinides trivalents par le tripyridyl-triazine. Applications en extraction liquide-liquide. Thèse Université Paris 6 (France) (1983). - SUDOC n° 089013247 - CEA-R-5270.

[86MIC] Michard G., *Dissolution d'une solution solide : compléments et corrections.* Bull. Minéral (1986) 109, 239-251

[89MIC] édition initiale (1989) de [02MIC]

[89RIG] Riglet. Ch., Chimie du neptunium et autres actinides en milieu carbonate. Thèse n°1989PA066423 - SUDOC n° 043928862, Université Paris 6 (France) 17/3/1989. CEA-R-5535 (1990).

[90GLY/REA] Glynn P.D. and Reardon E.J. (1990) Solid Solution aqueous-solution equilibria: thermodynamic theory and representation. Amer. J. Sci. 290, 164-201.

[91STO] Stokes R. *Thermodynamics of Solutions* 28p., page1 in Pitzer K. ed. *Activity coefficients in electrolyte solutions* 2nd edition CRC press (1991) 542p.)

[92GRE/FUG] I.Grenthe, J.Fuger, R.Konings, R.Lemire, A.Muller, C.Nguyen-Trung, H. Wanner. Chemical Thermodynamics. 1 Chemical Thermodynamics of Uranium. ed. by H. Wanner and I. Forest. Paris OCDE AEN, Elsevier (1992), téléchargement gratuit à partir du site de l'OCDE/AEN/TDB http://www.nea.fr/html/dbtdb/pubs/uranium.pdf

[95OFF/CAP] S.Offerlé, H.Capdevila, P.Vitorge. *Np(VI)/Np(V) en milieu carbonate concentré*. CEA-N-2785

[97KAR/CHU] Karpov I., Chudnenko K., Kulil D. *Modeling chemical mass transfer in geochemical processes: thermodynamic relations, conditions of equilibria, and numerical algorithms.* Am. J. Sci 297 (1997) 767-806

[00KUL/KER] Kulil D., Kersten M., Heiser U., Neumann T. *Application of Gibbs Energy Minimization to Model Early-Diagenetic Solid-Solution Aqueous-Solution Equilibria Involving Authigenic Rhodochrosites in Anoxic Baltic Sea Sediments.* Aqua. Geochem. 6 (2000) 147-199.

[00BOT] Michael E. Böttcher. Editorial Honoring Friedrich Lippmann. Aquatic Geochemistry. 6, 2 (2000) pp. 115-117

[00GAM/KON] Heinz Gamsjäger, Erich Königsberger, Wolfgang Preis. Lippmann Diagrams: Theory and Application to Carbonate Systems. Aquatic Geochemistry. 6, 2 (2000) pp.119-132.

[00PRI/FER] M. Prieto, A. Fernández-González, U. Becker and A. Putnis. Computing Lippmann Diagrams from Direct Calculation of Mixing Properties of Solid Solutions: Application to the Barite-Celestite System. Aquatic Geochemistry, 6, 2, (2000) pp.133–146.

[01LEM/FUG] Lemire R., Fuger J., Nitsche H., Potter P., Rand M., Rydberg J., Spahiu K., Sullivan J., Ullman W., Vitorge P, Wanner H.. *Chemical Thermodynamics of Neptunium* *and Plutonium*. Edited by OCDE Nuclear Energy Agency, Data Bank Issy-les-Moulineaux (France). Amsterdam: Elsevier Science Publishers B.V., 2001, 836p.

[02MIC] Michard, G. *Chimie des eaux naturelles : principes de géochimie des eaux*. Paris Publisud (2002) 461 p ISBN 2-86600-890-1 (br.),

[GEM-Selektor] GEM-Selektor version 2-PSI http://les.web.psi.ch/Software/GEMS-PSI/

[02VIT/CAP] P.Vitorge, H.Capdevila, S.Maillard, M.-H. Fauré, T.Vercouter *Thermodynamic Stabilities of* MO_{2+x}*(s) (M = U, Np, Pu and Am), Pourbaix diagrams.* J. Nuclear Sc. Techno. Supplement 3. p713-716(2002).

[03VIT/CAP] P.Vitorge, H.Capdevila *Thermodynamic data for modelling Actinide speciation in environmental waters.* Radiochim. Acta 91, 623–631 (2003).

[PHREEQC] http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/