



**HAL**  
open science

## Solid Solution/Exsolution

C. Noguera, B. Fritz

► **To cite this version:**

C. Noguera, B. Fritz. Solid Solution/Exsolution. Encyclopedia of Geochemistry, pp.1-8, 2018, 10.1007/978-3-319-39193-9\_350-1 . hal-02505590

**HAL Id: hal-02505590**

**<https://hal.science/hal-02505590v1>**

Submitted on 7 Jul 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Solid-solution/Exsolution.

C. Noguera<sup>1</sup> and B. Fritz<sup>2</sup>

<sup>1</sup>*CNRS-Sorbonne Universités, UPMC Univ. Paris 06, UMR 7588, INSP, F-75005 Paris, France*

<sup>2</sup>*Université de Strasbourg/EOST, CNRS, Laboratoire d'Hydrologie et Géochimie de Strasbourg,  
1 rue Blessig, F-67084 Strasbourg Cedex, France*

(Dated: June 21, 2017)

PACS numbers:

## I. DEFINITION

By analogy with aqueous solution, a solid solution, sometimes called mixed crystal, is defined as an homogeneous solid-state solution of one or more solutes in a solvent. Its composition may vary in a more or less wide range of compositions, between extreme values which correspond to pure solids, known as its end-members. At variance with a mechanical mixture in which the components are mixed but not chemically bonded, mixing in a solid solution occurs at the atomic level, generally by substitution of one type of atoms by another on the same lattice. Many metal alloys, oxides and silicates are substitutional solid solutions, but solid solutions may also be formed by insertion of foreign atoms at interstitial sites in the host crystal (interstitial solid-solutions), or by loss of atoms in non-stoichiometric compounds (omissional solid solutions). The importance of solid solutions comes from the synergistic properties that they may display compared to their end-members and to their ubiquity in the natural environment.

In some cases, an homogeneous SS may become unstable with respect to its components and phase separation, also called demixing or exsolution, may occur. More precisely, exsolution is the processes of separation of an initially homogeneous solution phase (liquid or solid) into two compositionally different immiscible phases. This process may be triggered by pressure, temperature, or composition changes, but mostly by the two former for solid phases which show little volume change upon pressure.

## II. INTRODUCTION

Solid solutions (SSs) are often encountered in chemistry, metallurgy as well as in the Earth Sciences: mineralogy, petrology or geochemistry. In metallurgy, alloying elements are added to metals to improve their strength and their hardness or their resistance to corrosion. In the natural environment, compared to pure minerals, mixed minerals are the generality rather than the exception. Indeed, the formation of SSs is often thermodynamically preferred over the separate formation of their end-members, as can be judged by the frequent incorporation of trace elements in minerals, the ubiquity of complex oxides, silicates or carbonates, and the scarcity of pure

minerals (See Trace Elements, Clay Minerals, Oxide Minerals, Silicate Minerals, Carbonate Minerals). Two main processes lead to the formation of SSs: condensation from a melt or precipitation from a supersaturated aqueous fluid. Understanding SS formation conditions may bring insight into global element cycles, composition of natural waters, diffusion of elements in contaminated soils, and may be useful to try reconstructing past conditions.

In substitutional SSs, the process of mixing relies on the existence of local interactions between substituent (solute) and host atoms. In order that mixing takes place at the atomic level, several conditions have to be fulfilled:

- the crystal structure of the solvent should remain unchanged upon addition of the solute. End-members should thus have the same atomic structure.
- the substituting and host ions should have ionic radii differing by less than  $\approx 15\%$  (Hume Rothery rule) (See Ionic Radii).
- for single substitutions, the substitution has to be isoelectronic (replacing ion of the same valence as host ion). For multiple substitutions, global electric neutrality requires a coupling between charges and molar fractions. For example, substitution of Si by Al in the tetrahedral sites of phyllosilicate minerals requires a correlated charge compensation in the interlayer space or in the octahedral sites.
- the chemical affinity of host and solute atoms should be low, otherwise defined compounds are formed rather than solid solutions.

If these conditions are not fulfilled, SSs are restricted to a composition range of a few percents. Conversely, SSs which exist in a large composition range are usually made from elements which are close to each other in the periodic table.

Depending on the sign and strength of the interatomic interactions, fully disordered SSs, SSs with short range order or defined compounds with long range order may form. In some instances, phase separation may take place, for example leading to exsolution upon cooling. Simple models of mixing account for all these possibilities and allow deriving generic phase diagrams as a function of the thermodynamic conditions (temperature, pressure, composition, contact with an aqueous solution) and discussing out-of-equilibrium processes.

### III. MIXING PROPERTIES OF SUBSTITUTIONAL SOLID SOLUTIONS

The thermodynamic state (molar volume  $V$ , entropy  $S$ , enthalpy  $H$ , Gibbs free energy  $G$ ) of a SS of the  $A_{1-x}B_xC$  type is conveniently characterized with respect to the thermodynamic functions of its pure end-members AC and BC (McGlashan 1979) (See Geochemical Thermodynamics). When no chemical interaction takes place at the atomic level, which is the case of a *mechanical mixture*, these quantities are obtained by simple linear interpolation between those of the end members, weighted by their respective mole fractions  $X_{AC} = 1 - x$  and  $X_{BC} = x$ . For example, the molar volume of a mechanical mixture is equal to  $V_{MM} = X_{AC}V_{AC} + X_{BC}V_{BC}$ , which is the expression of the Vegard's rule, and its Gibbs free energy is equal to  $G_{MM} = X_{AC}G_{AC} + X_{BC}G_{BC}$ .

When mixing takes place, the linear relationship between the SS thermodynamic functions and those of its end-members no longer holds. Mixing quantities ( $\Delta V_M$ ,  $\Delta S_M$ ,  $\Delta H_M$ ,  $\Delta G_M$ ) are then defined by difference between  $V$ ,  $S$ ,  $H$ , and  $G$  and those of the mechanical mixture, e.g.  $\Delta G_M = G - X_{AC}G_{AC} - X_{BC}G_{BC}$ .

A first contribution to  $\Delta G_M$ , of entropic origin, arises due to the disorder induced by the substitution. In the case of full randomness, it reads ( $R$  the gas constant):

$$\Delta S_M^{id} = -R(X_{AC} \ln X_{AC} + X_{BC} \ln X_{BC}) \quad (1)$$

$\Delta S_M^{id}$  is a positive quantity, which lowers  $\Delta G_M = \Delta H_M - T\Delta S_M$  ( $T$  the temperature) and thus stabilizes the SS with respect to the mechanical mixture in the whole compositional range. When  $\Delta G_M$  has no other contribution than  $\Delta S_M^{id}$ , the SS is said to be *ideal* (hence the superscript *id*).

However, very few SSs are ideal, as shown by numerous results of advanced calorimetric and diffraction methods (Geiger 2001; Navrotsky 2014) (See Calorimetry). This stems from so-called *excess* mixing terms, including entropy as well as enthalpy contributions. The excess mixing entropy includes the vibrational entropy and a contribution due to the decrease in the number of accessible configurations with respect to perfect randomness when short range order exists (Benisek and Dachs 2012). The excess mixing enthalpy involves elastic and chemical terms. The elastic one, always positive, results from the lattice distortions associated to mixing which increases the internal energy of both end-members. The chemical term is associated to effective interactions between substituent and host atoms. They are both accounted for in the following polynomial expansion of  $\Delta H_M$  proposed by Guggenheim (Guggenheim 1937) for *non-ideal* SSs:

$$\begin{aligned} \Delta H_M = & X_{AC}X_{BC}A_0 \\ & + X_{AC}X_{BC}(X_{AC} - X_{BC})[A_1 + A_2(X_{AC} - X_{BC}) + \dots] \end{aligned} \quad (2)$$

The first term relies on the number and strength of each type of nearest-neighbor bond. Its constant  $A_0$  depends

on the energy difference between chemical bonds connecting identical or distinct species  $A_0 \propto 2W_{A-B} - W_{A-A} + W_{B-B}$ . Usually, the largest contribution comes from nearest neighbors but longer range interactions are also included in this term. Multi-body interactions (triplet, quadruplet, etc) are accounted for in the higher order terms  $A_1, A_2$ , and so on.  $\Delta H_M$  varies with temperature but usually more weakly than  $\Delta S_M^{id}$ .

Aside from experimental methods to determine mixing properties, the huge development of numerical simulations in the last decades has allowed calculations of alloy thermodynamic properties such as short-range order in SSs and composition-temperature phase diagrams. A methodology, known as the cluster expansion method (Kikuchi 1951; Ducastelle 1991; Vinograd 2010), consists in parametrizing the energy of an alloy under the form:

$$E = \sum_i g_i J_i (\prod_j p_j) \quad (3)$$

in which the index  $i$  scans all existing pairs (in which case,  $j$  takes two values), triplets ( $j$  takes three values), etc, of degeneracy  $g_i$  associated to occupation numbers  $p_j = \pm 1$  in the configuration upon consideration. The coefficients  $J_i$  of the cluster expansion are determined by fitting them to the energy of a relatively small number of configurations obtained through first-principles computations (See Density Functional Theory). The convergence of the expansion is usually rapid. Only a few terms representing pairs and small triplets are necessary to obtain good accuracy on thermodynamic properties.

The cluster expansion method gives a rationale for the Guggenheim expansion. However, the latter is a mean field approximation in which the probability of finding an AB pair is replaced by the (uncorrelated) product of site probabilities  $X_{AC}$  or  $X_{BC}$ . Going beyond such an approximation, for example by using Monte Carlo approaches, based on the cluster expansion Hamiltonian, Eq. 3, is necessary to account for fluctuations of probabilities around their mean values and for possible ordered phases (van de Walle and Asta 2002).

When only the first term in the Guggenheim expansion is important, i.e. when the strength of the interactions is independent on composition, the SS is said to be *regular* and  $\Delta G_M$  is symmetric with respect to  $x = 0.5$ . Depending on the sign and the value of  $A_0$ ,  $\Delta G_M$  displays a single minimum ( $A_0/RT < 2$ ) or two minima ( $A_0/RT > 2$ ), as shown in Figure 1.

SSs which require two terms in the polynomial expansion of  $\Delta H_M$  (so-called two-parameter Margules model) are called *sub-regular* SSs. The  $A_1$  term accounts for a linear dependence of the interactions on composition. It yields an asymmetry of  $\Delta G_M$  with respect to  $x = 0.5$ . In the infinite dilution limits,  $A_0 + A_1$  and  $A_0 - A_1$  represent the solubilities of B in pure AC and A in pure BC, respectively (See Solubility).

The chemical potentials  $\mu_i$  of the end-members ( $i = AC$  or  $BC$ ) in the SS are derived from the knowledge of the

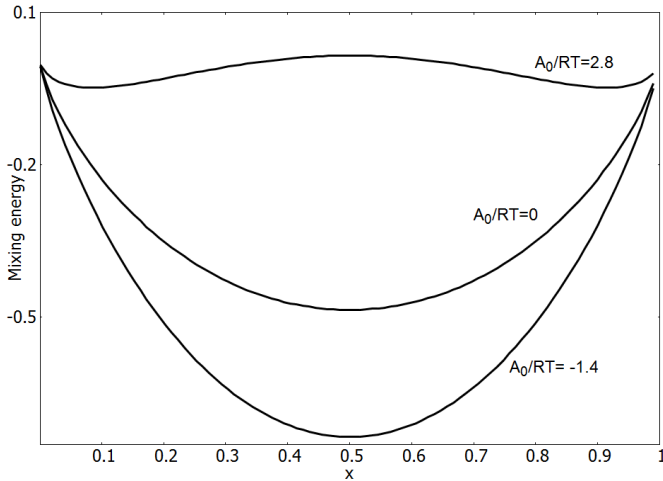


FIG. 1: Composition dependence of the mixing Gibbs free energy of a regular SS for three values of  $A_0/RT = -1.4, 0$  and  $+2.8$ .

molar Gibbs free energy  $G = \sum_i \mu_i X_i$ , as:

$$\mu_i = G + (1 - X_i) \left( \frac{\partial G}{\partial X_i} \right)_{P,T} \quad (4)$$

and this allows determining their activities  $a_i$  (See Activity and Activity Coefficients) through the relationship  $\mu_i = G_i + RT \ln a_i$ . For a given composition of the SS,  $a_{AC}$  and  $a_{BC}$  can be graphically read at the intersections of the tangent to the  $G$  curve at  $x = 0$  and  $x = 1$ , respectively (Figure 2, left panel). The activity coefficients  $\gamma_i = a_i/X_i$  of the end-members in the SS are equal to 1 in ideal SSs, and their deviation from 1 evidences the existence of excess terms of mixing in the Gibbs free energy. Following Redlich-Kister, they read (Glynn 1991):

$$\begin{aligned} RT \ln \gamma_{AC} &= X_{BC}^2 (A_0 + A_1(3X_{AC} - X_{BC}) + \dots) \\ RT \ln \gamma_{BC} &= X_{AC}^2 (A_0 - A_1(3X_{BC} - X_{AC}) + \dots) \end{aligned} \quad (5)$$

These concepts may be generalized to the case of multiple substitutions. For example, when the two substitutions occur on different sites and are uncoupled, the solid solution, of generic chemical formula  $A_{(1-x)(1-y)}B_{x(1-y)}C_{y(1-x)}D_{xy}$  has four end-members (A, B, C, D), associated to molar fractions  $X_A = (1-x)(1-y)$ ,  $X_B = x(1-y)$ ,  $X_C = y(1-x)$ , and  $X_D = xy$ . The molar fractions are linked not only by the usual relationship  $X_A + X_B + X_C + X_D = 1$ , but also by the cross-product equality  $X_A X_D = X_B X_C$ , which results from the fact that there are only two independent composition parameters ( $x$  and  $y$ ). Such solid solutions are referred to as *reciprocal* solid solutions. Contrary to the case of a single substitution, they are non-ideal with end-member activity coefficients different from 1 (Ganguly 2001), even when the mixing in each site is ideal, i.e. when  $\Delta G_M$

only involves the ideal mixing entropy term:

$$\Delta S_M^{id} = -R(x \ln x + (1-x) \ln(1-x) + y \ln y + (1-y) \ln(1-y)) \quad (6)$$

#### IV. TEMPERATURE-COMPOSITION PHASE DIAGRAM

Igneous rocks are formed when a magma or a lava cools and solidifies. Metamorphic rocks, for their part, result from the transformation of existing rocks when they are subject to heat and/or pressure. SSs are often encountered in these cases. The phases in presence, once thermodynamic equilibrium has been reached, can be read on a temperature-composition  $T - x$  phase diagram, directly derived from the canonical ensemble expression of  $G$  discussed previously (See Phase Equilibria).

##### A. Thermodynamic equilibrium

When the mixing Gibbs energy is negative and displays a single minimum as a function of composition, as in the case of ideal or weakly non-ideal SSs, an homogeneous mixing is energetically favorable over a mechanical mixture and a SS exists in the whole composition range.

When  $\Delta G_M$  displays two minima, as in the case of strongly non-ideal mixing, there exists a composition range  $x_1 < x < x_2$ , called the *miscibility gap*, in which an homogeneous SS is unstable with respect to the co-existence of two immiscible SSs  $\alpha$  and  $\beta$  of compositions  $x_1$  and  $x_2$ . Phase separation thus takes place. For such a process to be thermodynamically stable, the chemical potentials of the end-members  $\mu_i$  ( $i = AC$  or  $BC$ ) have to be equal in the two phases:  $\mu_i^\alpha = \mu_i^\beta$ . This requirement graphically defines the compositions  $x_1$  and  $x_2$  of the  $\alpha$  and  $\beta$  SSs as the abscissa of the points of common tangent to the  $G$  curve (Figure 2, left panel). The locus of these points when temperature varies is called the *solvus* (Figure 2, right panel). For a given average composition  $x$  of the solid phase, the proportions  $Q_\alpha$  and  $Q_\beta$  of the  $\alpha$  and  $\beta$  phases are given by the ratios  $MM_2/M_1M_2$  and  $MM_1/M_1M_2$  of the tangent segments represented in Figure 2, respectively (lever rule). When  $T$  increases at fixed pressure, the miscibility gap generally becomes narrower, because the negative contribution to  $G$  coming from the ideal entropy term increases (in absolute value) much more rapidly than the positive enthalpic contribution. Beyond a critical temperature  $T_M$ , called the *upper consolute temperature*, the region of phase coexistence vanishes and the components of the mixture are soluble in all proportions.

The generic phase diagram displayed in Figure 2 is highly simplistic, since only two ordered phases are considered (the end-members). The phase diagrams of metallic alloys, for example, often involve several ordered phases, several regions of miscibility gaps between them

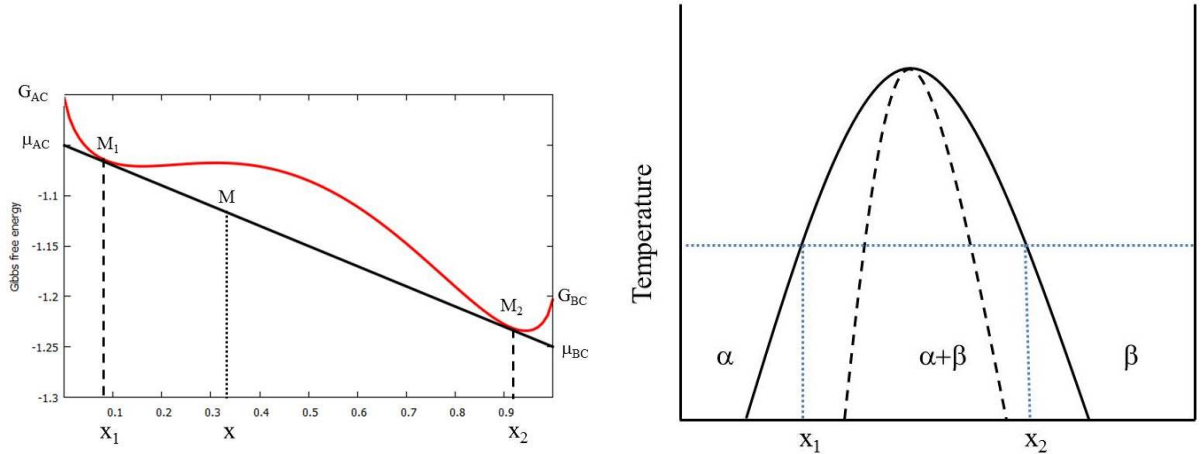


FIG. 2: Left panel: Composition dependence of the Gibbs free energy of a strongly non-ideal regular SS at fixed temperature  $T$  ( $A_0/RT = +2.8$ ). The plain straight line is the common tangent to  $\Delta G_M$ , marking the limits of the miscibility gap  $x_1 < x < x_2$ . Right panel: Typical phase diagram of a strongly non-ideal SS. The region of the miscibility gap is delineated by the solvus (plain line). The spinodal line is represented by a dashed line.

and SS phases with various compositions. Mixed carbonate minerals may also display more complex phase diagrams, the most famous example being the calcite-magnesite system with the ordered dolomite phase at 50% composition. Several numerical codes allow calculation of the phase diagrams of binary systems, e.g. the ATAT code (and the OpenCalphad code (Fries 2013).

### B. Exsolution process

When a SS which is homogeneous in the temperature range  $T > T_M$  enters the region of a miscibility gap, phase separation, also called demixing or exsolution, occurs. Exsolution begins at the atomic scale but as it continues, the exsolved phase usually forms irregular patterns (lamellae, films or patches), depending on the region of the miscibility gap in which it takes place. A special curve, called *spinodal* (Figure 2 right panel), which connects the inflection points of  $G$  inside the miscibility gap (condition  $\partial^2 G/\partial x^2 = 0$ ), separates the latter in two regions in which the early composition fluctuations leading to exsolution are either periodic or exponentially decaying in space.

Most minerals exsolve upon appropriate conditions of temperature, pressure and composition, e.g. feldspars, pyroxenes, amphiboles, micas, oxides, carbonates, sulfides (e.g. Schumacher 2007). For example, the important group of feldspars, to which belong the most abundant phases of igneous rocks, can be described in the ternary solid-solution system : albite  $\text{NaAlSi}_3\text{O}_8$ , microcline  $\text{KAlSi}_3\text{O}_8$  and anorthite  $\text{CaAl}_2\text{Si}_2\text{O}_8$ . Albite-microcline SSs, called alkali feldspars, which are formed at high temperature, easily exsolve at low temperature, each end-member being only able to substitute a small amount of the other alkali ion. At variance, plagioclases

which are also formed at high temperature, do not exsolve. All intermediate compositions are known between their end-members albite and anorthite. These feldspar SSs play an important role as components of granitic rocks and major contributors to hydrothermal alteration or weathering processes at lower temperature.

The process of exsolution of a SS may be used in solvus geothermobarometry (See Geothermometry and Geobarometry), due to the sensitivity of the exsolved phase composition to temperature and pressure. Data on geothermometers are derived from both laboratory studies on artificial mineral assemblages, where minerals are grown at known temperatures and pressures and the chemical equilibrium measured directly, and from calibration using natural systems. They also require a theoretical thermodynamic understanding of the components and phases involved. The measurements and interpretation are not straightforward and may lead to noticeable uncertainties, because it is difficult to assess if a system has truly reached thermodynamic equilibrium. Moreover, the synthesized minerals are difficult to characterize due to their often poor crystallinity and their submicrometer sizes.

### V. SOLID SOLUTIONS FORMED BY PRECIPITATION FROM A SUPERSATURATED AQUEOUS FLUID

Another important class of SS formation processes concerns the precipitation from a supersaturated aqueous solution (AS) (See Aqueous Solutions). At variance with results obtained in the canonical ensemble (fixed  $P$ ,  $T$  and composition), the mean composition of a SS in equilibrium with a multi-component aqueous medium is not a priori fixed but depends on the composition of the AS,

which may change if external conditions do so (Glynn and Reardon 1990; Prieto, 2009). In natural solutions, a large number of chemical elements are usually present which may participate to the formation of secondary minerals, either as major constituents or as trace elements in solid solutions. Clay minerals which are very commonly produced in geochemical systems (weathering sequences, hydrothermal alterations, diagenetic transformations) are striking examples of SS phases formed in the presence of an AS. They display a large composition variability, by substitution in their skeleton (tetrahedral and octahedral sites) and/or cation exchange in their interlayer space (See Fluid-Rock Interactions, Hydrothermal Alteration, Weathering: Chemical). Clays as well as other SSs share the major property of being able to adapt their composition to the evolution of the fluid composition as a function of time.

### A. Thermodynamic equilibrium

As a general statement, a solid of fixed composition is in equilibrium with an AS when their chemical potentials are equal. The chemical potential of the relevant ions in the AS is equal to  $\mu_{ions} = RT \ln(IAP)$ , with  $IAP$  the ion activity product, and the chemical potential of the solid phase is equal to its Gibbs energy per mole, which defines its solubility product  $K$ :  $\mu_{solid} = RT \ln K$  (See Solubility). Equilibrium is thus reached when  $K = IAP$ , or equivalently, when the saturation state of the AS with respect to the solid  $I = IAP/K = 1$ .

The generalization of this condition to a binary SS  $A_{1-x}B_xC$  in equilibrium with an AS involves two conditions, one for each end-member  $i$  ( $i = AC$  or  $BC$ ), stating that their chemical potentials are equal to the chemical potential of their corresponding ions in the AS. Using the expression  $\mu_i = G_i + RT \ln X_i \gamma_i$  and introducing the solubility products  $K_i$  of the end-members and the saturation states  $I_i$  of the AS with respect to them, the conditions for thermodynamic equilibrium read:

$$\begin{aligned} I_{AC} &= (1 - x_0) \gamma_{AC}(x_0) \\ I_{BC} &= x_0 \gamma_{BC}(x_0) \end{aligned} \quad (7)$$

Numerical codes, like KINDIS (Madé et al. 1994) or PHREEQC (Parkhurst and Appello 2013,) allow the determination of the SS characteristics in equilibrium with an aqueous solution.

Eq. 7 shows that, while a BC compound would not form as a pure phase in a highly under-saturated AS ( $I_{BC} \ll 1$ ), B ions may easily be incorporated as trace elements in the substitutional sites of an AC compound, if the AS is nearly saturated with respect to the latter ( $I_{AC} \simeq 1$ ). This illustrates why most mineral phases produced in natural systems are not pure end-members. Conversely, quasi pure phases are strong indicators of the composition of the fluids that produced them and may be an indicator of paleo-conditions.

### B. Stoichiometric saturation state

Thermodynamic equilibrium conditions (Eq. 7) are equivalent to saying that the stoichiometric saturation state  $I(x)$  of the AS with respect to the SS of composition  $x$  is simultaneously equal to 1 and maximum with respect to  $x$ . This can be proved by considering the stoichiometric solubility product  $K(x)$  of the SS, equal to:

$$K(x) = K_{AC}^{1-x} K_{BC}^x \exp\left(\frac{\Delta G_M}{RT}\right) \quad (8)$$

and writing  $I(x) = IAP/K(x)$ , i.e.:

$$I(x) = \left[ \frac{I_{AC}}{(1-x)\gamma_{AC}(x)} \right]^{1-x} \left[ \frac{I_{BC}}{x\gamma_{BC}(x)} \right]^x \quad (9)$$

When only the condition that  $I(x)$  is maximum with respect to  $x$  is fulfilled, one speaks of the *stoichiometric saturation state*. It amounts to considering the SS with respect to which the AS is the most supersaturated (Prieto 2009). Its composition  $x_{st}$  obeys the implicit equation:

$$\frac{I_{AC}}{(1-x_{st})\gamma_{AC}(x_{st})} = \frac{I_{BC}}{x_{st}\gamma_{BC}(x_{st})} \quad (10)$$

It obviously only depends on the composition of the AS through the quantity  $W = I_{BC}/I_{AC} = [B]K_{AC}/[A]K_{BC}$ , proportional to the ratio of activities of the exchangeable ions. Eq. 10 has no analytic solution. However, it can be solved numerically quite easily for regular and sub-regular SSs (Noguera et al. 2016). It has a single root whenever  $\Delta G_M$  displays a single minimum and three roots if  $\Delta G_M$  has two minima. The number of solutions of Eq. 10 thus only depends on the values of the coefficients  $A_0$  and  $A_1$  in the Guggenheim expansion of  $\Delta H_M$ .

When Eq. 10 has three roots, two correspond to a minimum of  $I(x)$  and one to a maximum. Of the two minima, the one which is relevant is associated to the lowest Gibbs free energy of the system (lowest value of  $-\ln I(x)$ ). Because the  $I(x)$  curves associated to the three roots cross each other, a discontinuity in  $x_{st}$  between two values  $x_1$  and  $x_2$ , characterized by the same Gibbs free energy, takes place for some specific value of  $W$ , as shown in Figure 3. The discontinuity  $x_2 - x_1$  marks the existence of a miscibility gap, which increases as the SS becomes more and more non-ideal. In this representation,  $W$  combines the information on the AS composition and on the solubility products of the end-members, in a more compact way than the (equivalent) classical Roozeboom plot (Mullin 1993) which displays  $x_{st}$  as a function of  $[B]/([A] + [B])$  but requires one curve for each  $K_{BC}/K_{AC}$  ratio.

### C. Out-of-equilibrium processes

The stoichiometric saturation state does not fully characterize thermodynamic equilibrium, but its characteris-

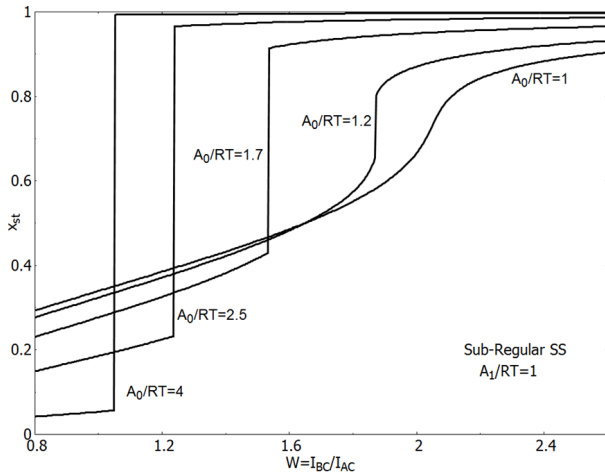


FIG. 3: Representation of the relationship between a sub-regular SS composition  $x_{st}$  and  $W = ([B]K_{AC})/([A]K_{BC})$ , which characterizes the AS composition, for  $A_1/RT = 1$  and various values of the Guggenheim parameters  $A_0/RT$ . When  $A_0/RT \gtrsim 1.15$ , the  $x_{st}$  curve displays a discontinuity.

tics are useful to approach nucleation and growth processes (See Crystal Growth). Within the classical nucleation theory, assuming that the SS surface energy  $\sigma$  and molar volume  $v$  are weakly dependent on composition, the change in Gibbs free energy in the formation of a SS nucleus of composition  $x$  and containing  $n$  formula units reads ( $k_B$  the Boltzmann constant and  $X$  a shape factor)(Markov 1995; Noguera et al. 2016):

$$\Delta G(n, x) = -nk_B T \ln I(x) + n^{2/3} v^{2/3} X \sigma \quad (11)$$

When  $I(x) > 1$ ,  $\Delta G(n, x)$  displays a maximum as a function of  $n$ , which defines the nucleus size and the barrier  $\Delta G_m(x)$  to overcome for its nucleation:

$$\Delta G_m(x) = \frac{4X^3 \sigma^3 v^2}{27(k_B T \ln I(x))^2} \quad (12)$$

The composition  $x^*$  of the critical nuclei is then determined by the condition that the nucleation barrier is minimum with respect to  $x$ , leading to a maximum of the nucleation frequency. Since, according to Eq. 12, this amounts to finding the maximum of  $\ln I(x)$ , the composition of the critical nuclei is equal to  $x_{st}$ . A similar reasoning can be applied to the composition of the incremental growth layers, when growth is limited by surface reactions.

Since the composition of an AS may vary with time, either because external conditions change (temperature or seasonal cycles) or in a closed system due to the precipitation process itself,  $x_{st}$  is also due to depend on time. Time variations of the particle composition thus usually occurs, which leads either to a change in the average composition (if solid state diffusion is efficient) or to composition inhomogeneities inside the particles (composition

profiles) when solid state diffusion does not occur. Considering the typical evolution of  $x_{st}$  as a function of the AS composition  $W$  as shown in Figure 3, the composition profiles are smooth in ideal or weakly non-ideal SSs, while they display a discontinuity for strongly non-ideal SSs. Except under very specific conditions,  $W$  does not remain fixed at the critical value of the discontinuity during the precipitation process, so that demixing is much less likely than in processes at constant  $T$ ,  $P$  and  $x$  conditions. Numerical codes like KINDIS (Madé et al. 1994) or NANOKIN (Noguera et al. 2010) account for the kinetics of precipitation of SSs under various approximations.

The specificity of SS dissolution kinetics has not been considered in details so far. In dissolution processes, SSs are generally assumed to be defined compounds with a fixed composition inherited from their formation conditions. This assumption overlooks the existence of a distribution of compositions inside the particle population, and the existence of composition profiles inside each particle. Moreover, when equilibrium is approached, the activity ratio of the ions released in the AS is likely closer to that in the solid phase than to the one required in the AS for thermodynamic equilibrium. The way equilibrium can be reached thus remains an open question.

## VI. SUMMARY

Solid solutions are ubiquitous in the natural environment, due to the existence of multi-component fluids (aqueous solutions or melts) from which they form. Their major property is their ability to continuously adapt their composition as the fluid composition evolves in time. Their phase diagrams may involve homogeneous phases in part or in the whole concentration range, and regions of phase separation. Incorporation of trace elements is often thermodynamically easy, which explains the scarcity of pure minerals, particularly those formed at low temperature and pressure. While the description of their mixing properties and their equilibrium properties has greatly improved in the last decades, both experimentally and theoretically, much remains to be done to account for the kinetics of their formation and dissolution.

## VII. CROSS-REFERENCES

- Activity and Activity Coefficients
- Aqueous Solutions
- Calorimetry
- Carbonate minerals
- Clay Minerals
- Crystal Growth
- Density Functional Theory
- Fluid-Rock Interactions
- Geochemical Thermodynamics
- Geothermometry and Geobarometry

- Hydrothermal Alteration
- Ionic Radii
- Oxide Minerals
- Phase Equilibria
- Silicate Minerals
- Solubility
- Trace Elements
- Weathering: Chemical

### VIII. REFERENCES

- Benisek A, Dachs E (2012) A relationship to estimate the excess entropy of mixing; Application in silicate solid solutions and binary alloys. *J of Alloys and Compounds* 527:127-131
- Ducastelle F (1991) *Order and Phase Stability in Alloys*. Elsevier, New York
- Fries SG (2013) <http://www.openalphad.com/>
- Ganguly J (2001) Thermodynamic modelling of solid solutions. In: Geiger C (ed) *Solid Solutions in Silicate and Oxide systems*, EMU notes in Mineralogy, Eötvös University Press, Budapest, 3:37-70
- Geiger C (2001) Thermodynamic mixing properties of binary oxide and silicate solid solutions determined by measurements: the role of strain. In: Geiger C (ed) *Solid Solutions in Silicate and Oxide systems*, EMU notes in Mineralogy, Eötvös University Press, Budapest, 3:71-100
- Glynn PD (1991) MBSSAS: A code for the computation of the Margules parameters and equilibrium relations in binary solid-solution aqueous solution systems. *Computers and Geosciences* 17:907-966
- Glynn PD, Reardon EJ (1990) Solid-solution aqueous-solution equilibria: Thermodynamic theory and representation. *Am. J. Sci.* 290:164-201
- Guggenheim EA (1937) Theoretical basis of Raoult's Law. *Trans Faraday Soc.* 33:151-159
- Kikuchi R (1951) A theory of cooperative phenomena. *Phys. Rev.* 81:988-1003
- Madé B, Clément A, Fritz B (1994) Modelling mineral solution interactions: the thermodynamic and kinetic code KINDISP. *Comput. Geosci.* 20:1347-1363.
- Markov IV (1995) *Crystal growth for Beginners: fundamentals of nucleation, crystal growth and epitaxy*. World Scientific, Singapore, New Jersey, London, Hong Kong
- McGlashan, M.L. (1979) *Chemical Thermodynamics*. London: Academic Press
- Mullin JW (1993) *Crystallization*. Butterworth-Heinemann
- Navrotsky A (2014) Progress and New Directions in Calorimetry: A 2014 Perspective. *J. Am. Ceram. Soc.* 97:3349-3359
- Noguera C, Fritz B, Clément A (2010) Simulation of the nucleation and growth of binary solid solutions in aqueous solutions. *Chem. Geol.* 269:89-99.
- Noguera C, Fritz B, Clément A (2016) Kinetics of precipitation of non-ideal solid-solutions in a liquid environment. *Chem. Geol.* 431:20-35
- Parkhurst DL, Appello CAJ (2013) Description of input and examples for PHREEQC version 3-A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497pp.
- Prieto M (2009) Thermodynamics of Solid Solution-Aqueous Solution. In: *Thermodynamics and Kinetics of Water-Rock Interaction*. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America and Geochemical Society (Eds), 70:47-85
- Schumacher JC (2007) Metamorphic Amphiboles: composition and coexistence. In: *Amphiboles: Crystal Chemistry, Occurrence, and Health Issues*. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America and Geochemical Society (Eds) 67:359-416
- van de Walle A, Asta M (2002) Self-driven lattice-model Monte Carlo simulations of alloy thermodynamic properties and phase diagrams. *Modelling Simul. Mater. Sci. Eng.* 10:521-538
- van de Walle A (2017) *The Alloy-Theoretic Automated Toolkit (ATAT): A User Guide*. <http://www.brown.edu/Departments/Engineering/Labs/avdw/atat/>
- Vinograd VL, Winkler B (2010) An efficient cluster expansion method for binary solid solutions: application to the halite-silvite, NaCl-KCl, system. In: *Theoretical and Computational Methods in Mineral Physics: Geophysical Applications*, Wentzcovitch R and Stixrude L (eds) Reviews in Mineralogy and Geochemistry, The Mineralogical Society of America, 71:413-436