

arxim, a library for thermodynamic modeling of fluid - rock systems

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Chemical thermodynamics is involved in many fields of the earth sciences, from magmatic and metamorphic petrology through hydrothermal fluid-rock interactions to subsurface reactive transport processes. Addressing a petrological issue commonly involves the solution of multi-variate problems, where a large number of parameters (system composition, P, T, μ 's, ...) interact with each other. Moreover, petrological problems often involve coupled processes, where the thermodynamic approach is intimately coupled with other physical processes, such as material fluxes, heat flux, etc.

This has triggered, with computers becoming largely accessible, the development of a large number of codes. Such codes are currently available for nearly every situation where a thermodynamic approach may help understanding geological processes. Many are dedicated to water-rock interaction processes at subsurface conditions (e.g. EQ3/6, PHREEQC, CHESS, GEM-Selektor...), while others are devoted to metamorphic petrology (THERIAK, PERPLEX, TWEEQU, THERMOCALC, etc).

The aim of the ARXIM project, rather than adding still another program to the current list, is the development of an open, modular, and extensible library that would comprise the general tools for multiphase equilibrium / reaction calculations. The tools should be susceptible to modification and extension by the user and easily imported from other codes.

Fortran 90 is chosen as language because, while keeping with the relative simplicity of fortran77, it incorporates the essential features for building modular codes, easier to understand, modify, share, and extend.

ARXIM (Αρχιμήδης) was developed as a successor of the Fortran77 code ARCHIMEDE (Cassou, 2000), which was used as a "chemical reactor" of the reactive transport code DIAPHORE (Le Gallo et al, 1998). Further developments of ARCHIMEDE (Nourtier-Mazauric et al., 2003; Corviser, 2006) showed the difficulty of maintenance of complex codes in Fortran 77, and pointed to the need for completely rewriting the code using a modular language.

Although not strictly "object-oriented" (lacking a dedicated class construct and class heritage derivation), Fortran 90 allows the construction of "objects", i.e. computer constructs representing a given physical entity ("phase", "species", ...), by using modules, which "encapsulate" a dedicated data structure and the specific methods acting on this structure and interact with each others by well defined interfaces. It has thus the essential feature, for long term maintenance and cooperative development, that the computer representations of the physical notions of interest can be modified, extended or adjusted to specific needs, without breaking the whole code.

objects for chemical thermodynamics

Essential for an efficient implementation is the construction of a hierarchy of abstract data types and related methods that describe the "objects" involved in chemical thermodynamics, emphasizing their mutual dependencies.

We do not intend to give here a comprehensive account of chemical thermodynamics, but we present some fundamental concepts that underlie the construction of the library.

The main thermodynamic constructs can be organized along the following hierarchy: a chemical *system* is defined in terms of phases, a *phase* is defined in terms of *species* and *mixing models*, and a species is defined in relation to *elements*.

describing the chemical space

element

The chemical element is the most "basic" chemical / stoichiometric entity considered. The first step in the definition of a chemical space is the element list, e.g. (O,H,C), which provides the basis for the stoichiometric definition of higher level entities.

The minimal "element" construct comprises purely atomic properties (name, atomic weight, ...), but, for the element set to be able to generate all substances possibly involved in the system, it may also, depending on the chemical system under consideration, include additional properties, such as valency, oxidation state, etc., as discussed in detail hereafter

substance

A substance is *a combination of elements* (e.g. H₂O, CO₂, O₂, H₂, CH₄, CO) with a definite stoichiometry, which is considered potentially present in the system.

A substance is thus defined by a "formula vector" in the elemental basis, and the substance list of the system consists of all substances present in at least one phase.

The term "compound" (French: "composé") is considered synonymous with "substance".

species

A species is defined here as *a substance in a specific phase*.

For instance, a (O,H,C,Ca) system may comprise CaCO₃(aq), as a species of the aqueous phase, and CaCO₃(cc), as another species present in a calcite phase.

In a dilute aqueous phase, species are divided between a dominant species, the so-called "solvent", and subordinate "solute" species. In solid solutions, species commonly correspond to end-members.

thermodynamic models

In addition to stoichiometric properties, a species s_i has specific thermodynamic properties ($s_i\%H$, $s_i\%S$, $s_i\%V$, ...) at its reference state (e.g. pure phase).

The library will have to implement the thermodynamic models which describe how these properties are computed at the conditions of interest (T , P , V , μ_j , ...), from the species' properties at its reference state (T_{ref} , P_{ref}). Different types of species (e.g. aqueous vs minerals) may follow different thermodynamic models, whose parameters are stored in specific databases.

phase

A phase is defined by an array of species, a thermodynamic model, and a composition.

thermodynamic mixing models

The thermodynamic model of the phase (its "equation of state", EoS) is a set of functions that relate its thermodynamic properties (e.g. molar volume, enthalpy, entropy, chemical potential of each species in the phase, ...) with its composition and other constraints. The role of the mixing model is to describe the energetics of interactions between species within the phase.

Thermodynamic models can be categorized into different "classes".

The most basic class is that of the "pure phase", or "single-species phase": the species list contains a single species, and the molar properties of the phase are those of the species.

For phases of variable composition, a first order distinction is made between "solutions" and "mixtures": following a IUPAC recommendation, the term "solution" is used for phases that follow an asymmetric model, and "mixture" for symmetric models. A typical "solution" is an aqueous solution, where different concentration scales are used for the solvent, water, and the solute. On the other hand, solid solutions and gaseous mixtures are generally modeled as "mixtures" between end-members whose concentrations are measured as mole fractions.

Distinct modules are used in ARXIM to implement the mixing models for "solutions" and for "mixtures".

A distinction is made, when it comes to implementation, between "interaction models" and "association models":

◆ in a pure **interaction model**, the number of species equals the number of independent components that describe the phase composition. Such models do not require any "speciation calculation": energetics involved in the mixing process are accounted for by interaction parameters between the end-members. That is often the case for a "molecular model" of a solid mixture, be it ideal (energy of mixing originates in configurational entropy only) or more complex (regular, etc.). Many models for mineral or gas mixtures belong to this class.

◆ in an **association model**, interactions between species are accounted for through the presence of complex species: a speciation calculation becomes necessary.

phase composition

The composition of a mixture phase can be characterized in terms of end-members components, or, alternatively, in terms of elemental abundances. For mixing models involving order-disorder, site occupancy preferences, etc., additional parameter(s) may be required for a complete description of the phase.

chemical space

The "chemical space" under consideration will be defined by a set of elements, a set of species in that element space, a set of mixing models based on the species set, and a set of phases that rely on species and mixing models.

Example of chemical space:

```
elements
{ O(-2), H(+1), C(4), Ca(+2) }
species
{ H2O, H+, OH-, CO2(aq), HCO3-, CO3-2, Ca+2, CaCO3(aq), Calcite, CO2(g), H2O(g) }
mixing models
{ pure, electrolyte, cubic_EOS }
phases {
  Aqueous
    mixing model= electrolyte
    species= H2O, H+, OH-, CO2(aq), HCO3-, CO3-2, Ca+2, CaCO3(aq) ,
  Calcite
    mixing model= pure
    species= Calcite ,
  Gas
    mixing model= cubic_EOS
    species= CO2(g), H2O(g)
}
```

thermodynamic system and components

system

Once the chemical space has been constructed, it is possible to define the thermodynamic system of interest.

Depending on the type of problem to be solved, the system is defined in different ways. In some cases, the system is defined as a set of phases with given amounts and compositions; in other cases, the system is restricted to one or more phases of the chemical space, and the other phases constitute the environment of the system.

When solving fluid - rock interaction problems, it is often favorable, due to the central role of the fluid phase, to adopt the latter strategy. That is the case in ARXIM modules dedicated to fluid-rock interactions, where "the fluid system" is a given amount of aqueous fluid in a given environment of other phases (minerals, fluids).

component

A component is a chemical formula unit representing one of the minimum number of independent variables required to describe the composition of the system.

By contrast with "substance" or "compound", thermodynamic components do not necessarily have a physical connotation. They do not necessarily correspond to any species' stoichiometry: the "independent components" only have to form a set of linearly independent entities that can generate the whole list of substances comprised in the "chemical space".

The number of independent components will thus equal the dimension of the stoichiometric space generated by the substance list. This dimension is at most the dimension of the element list.

The term "component" (*French*: "*constituant*") is used here in its strict thermodynamic sense.

closed vs. open system

A "closed system" has a fixed composition, it does not exchange matter with its environment. The environment only imposes physical constraints such as pressure, temperature or volume.

An "open system" can exchange matter in response to chemical constraints imposed by its environment. For instance, if the system is defined as an aqueous phase in equilibrium with an environment of other phases, these may fix the values of the chemical potential of a number of components of the system.

Example: if a fluid is at equilibrium with the earth's atmosphere, considered as an "infinitely large volume" that buffers the CO₂ partial pressure, the potential of CO₂ in the fluid is imposed.

compositional constraints vs potential constraints

For a system to be defined, it needs as many independent constraints as its number of independent components. To the distinction between open and closed systems, correspond the two types of constraints that can be involved in the definition of a system at equilibrium: there can be constraints imposed on compositions, and constraints on potentials.

- In a closed system, all constraints are **compositional constraints**: the amounts (e.g. mole numbers) of all components are fixed.
- If at least one constraint is a **potential constraint** (e.g. partial pressure or activity of a species), we have an open system.

This composition / potential duality corresponds largely, in the reality of hydrochemistry, to the two types of data commonly available for a given sample of water. Data are

compositional for some elements: for instance, the total elemental concentration has been measured. For others, the constraint is on the potential of a species: it has been obtained by a potentiometric method (pH, pe), or it corresponds to an observation, such as the equilibrium with a buffering phase (contact with air imposing CO₂ or O₂ partial pressure, presence of excess calcite in a rock for a long time, ...).

Some data, however, may not translate directly to a constraint on potential nor on composition. This is the case of results of titration methods, which correspond to a balance of species abundances (e.g. the carbonate alkalinity, which involves the sum of modalities of carbonate and other species); they do not correspond to a single elemental abundance nor to a single species activity constraint and would deserve special implementation.

type of constraint and component status: "inert" versus "mobile"

There are as many independent components as external chemical constraints on the system. It is thus possible to associate to each component a constraint and to establish a direct correspondence between the constraint's type and the status of the associated component.

Using the terminology developed for the interpretation of metasomatic processes (Khorzhinskii, 1950; Thompson, 1959), we call "**inert**" the components whose amounts are the independent variables, and "**mobile**" those whose chemical potentials are the independent variables.

In other words, compositional constraints are imposed on "inert" components, and potential constraints on "mobile" components.

Mobile components can correspond to species from other phases (minerals, gases) with which the system is in equilibrium, but the concept can be extended to aqueous species. For instance, when a pH measurement is given as a data on an aqueous system, it corresponds to a fixed value of the potential of the H⁺ species: this species is a mobile component.

a hierarchy of dedicated data structures

The consequences for computer implementation is that a systematic hierarchy will be built between the different objects involved in the description of a system: the global "chemical space" is a set of phase models, which consist of species, which are themselves constructed from elements.

The following data structures are implemented:

t_Element

a container for storing a chemical element.

t_Species

implements a species structure: a name, a formula (an array of elements), and a pointer to the species' thermodynamic database.

t_MixModel

implements a symmetric mixing model (mole fraction scale): points to a set of species (*t_Species* structures), and contains parameters of the thermodynamics of interaction between the component species (i.e. activity-composition relationships).

t_SolModel

implements an asymmetric mixing model (molality scale); used for solutions with a

dominant solvent and subordinate solutes, typically an aqueous solution.

t_MixPhase

implements a mixture phase that obeys a symmetric model: contains pointer to a mixing model, and composition data.

t_SolPhase

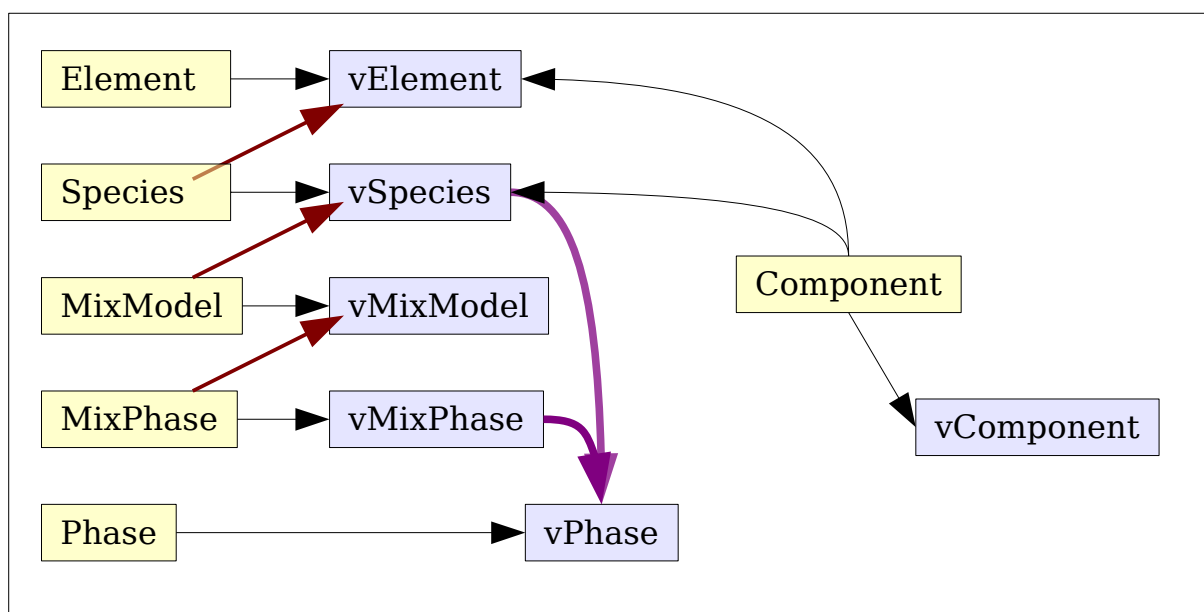
implements a solution phase that obeys an asymmetric model; contains a pointer to a solution model, and composition data.

t_Phase

any phase of the system, of any type (pure, mixture, solution). Comprises mainly a pointer to the species list (if a pure phase) or to the mixture or solution lists, and properties of the phase at (T,P).

implementation of the chemical space

The chemical space is completely described by a data module that contains a set of arrays (vEle, vSpc, vMixModel, vMixPhase, vPhase), respectively of T_Element, T_Species, T_MixModel, T_Mixphase, and T_Phase variables.



This diagram illustrates the hierarchy established between the arrays (where *Element* is a structure of type *t_Element*, *Species* a structure of type *t_Species*, ...). For example, a *Species* points to a set of indexes in the array *vElement*; a *MixModel* comprises a list of end-members indexed in *vSpecies* (similar construction for a *SolModel*); a *MixPhase* follows a mixing model indexed in *vMixModel*, etc.

Once the chemical space has been defined, any system of this space is described as a set of independent components.

t_Component

implements a thermodynamic component.

Comprises mainly

- ▷ a status description (= whether inert or mobile),
- ▷ two pointers, respectively to an element and to a species,
- ▷ depending on the status, either the mole number of the element or the activity of the species.

This is the current implementation (inherited from ARCHIMEDE) built for cases where all chemical elements are independent, and that implies that the number of components equals the number of chemical elements.

In the more general implementation under construction, an inert component, like a mobile one, points more generally to a stoichiometry (possibly defined in terms of elements), instead of having always a single element stoichiometry.

examples

Example of chemical space:

```
elements {O(-2),H(+1),C(4)}
species {H2O,H+,OH-,CO2_aq,HCO3-,CO3-2,CO2_g}
solution models {pure, electrolyte}
phases {
  Aqueous {
    model= electrolyte,
    species= {H2O,H+,OH-,CO2_aq,HCO3-,CO3-2}
  },
  CO2_g {model= pure, species= {CO2_g}}
}
```

Examples of systems in this chemical space:

```
system_1= {
  c1= {H2O, inert, mole=55.5},
  c2= {H+, balance},
  c3= {CO2_aq, inert, mole=1.0}
}
```

```
system_2= {
  c1= {O, H2O, inert, mole=55.5},
  c2= {H, H+, balance},
  c3= {C, CO2_g, mobile, activity=0.03}
}
```

Once the tools have been developed for all basic concepts and tasks (implement a chemical space, describe a system, implement constraints, etc.), they can be used for solving a variety of problems concerning multiphase systems, in equilibrium and in non-equilibrium conditions.

"LMA" versus "GEM"

A vast literature is available on techniques of equilibrium calculation of a multi-component system. General presentations can be found for example in SMITH & MISSEN (1982) or LICHTNER (1996).

Two main types of approaches are classically considered (SMITH & MISSEN, 1982):

▷ In the *Free Energy Minimization* approach (**GEM**, when the relevant potential function is the Gibbs free energy), the equilibrium is solved globally, by minimizing, under the constraints of material conservation, the free energy of the system. GEM methods are of common use for systems involving several phases of variable composition (e.g. in metamorphic or igneous petrology, or in flash calculations on fluids); they are less commonly implemented for speciation of an aqueous solution, except for concentrated brines where an ion interaction (Pitzer) model is used.

▷ In a **LMA** (*Law of Mass Action*) approach, the speciation problem is implemented as a system of equations that express, on one hand, the mass conservation constraints and, on the other, the chemical equilibrium among species, commonly written in the mass action form. This approach is dominant among programs for aqueous geochemistry (EQ3, PHREEQ, CHESS, ...).

Phase-equilibrium solvers based on the mass-action approach provide accurate results up to very small solute concentrations, but cannot unambiguously address phase stability, in particular when solid solutions are non-ideal or phase separation appears ([Reed, 1982], [Reed, 1998], [Wolery, 1992] and [Bethke, 1996]). This is common in many rock-forming minerals (e.g., feldspars, micas, amphiboles, pyroxenes).

In contrast, methods using Gibbs free energy minimization are suitable for evaluating phase stability but they were often insufficient to accurately predict very small concentrations of aqueous species ([Karpov and Kazmin, 1972] and [Karpov et al., 1997]) and only recently could the minimizers incorporate non-ideal mixing behavior (e.g., [Shvarov, 1999] and [Kulik, 2006]).

For equilibrium computations of systems involving a complex aqueous phase, ARXIM uses a LMA approach, implementing two sets of equations, described hereafter, one describing material conservation, the other the chemical equilibrium conditions, but the latter are expressed, like in GEM approach, in terms of linear potential constraints, rather than activity products. And, rather than working on solute molalities like many LMA approaches, ARXIM uses extensive variables (mole numbers) as primary variables.

Applications currently developed within ARXIM

LMA:

- ▷ homogeneous equilibrium (speciation) of an aqueous fluid under compositional and potential constraints
- ▷ heterogeneous equilibrium of a multi-phase water-bearing system
- ▷ kinetic evolution of a fluid-rock system - 0D dynamic cell

GEM:

- ▷ equilibrium composition of a system of pure phases, using linear programming

▷ equilibrium composition of a system comprising complex mixtures, by free energy minimization.

The question of speciation is central in aqueous chemistry. The development of a robust speciation solver is thus essential for most simulations of fluid-rock interactions.

Solving a speciation problem is typically the calculation of the homogeneous thermodynamic equilibrium of a mixture phase that follows an asymmetric solution model, giving rise to homogeneous reaction between species. For speciation calculations, the thermodynamic system under consideration is a given amount of aqueous solution (for example, corresponding to 1 kilogram water), in a given environment that controls temperature, pressure, and eventually, through heterogeneous equilibrium with other phases, the chemical potentials of some components.

The solution of a speciation problem involves the implementation of the two types of constraints, on chemical compositions ("material balance" constraints) and on chemical potentials ("mass action" constraints, which are "potential balance" constraints).

In the case of a closed system, given N independent components of known mole numbers $c(1:N)$, and M chemical species with given stoichiometric / thermodynamic properties, we have to determine how the N components are distributed among the M species.

material balance constraints: choice of components

Various approaches are possible for selecting the set of independent components used for the description of composition constraints.

the "basis species" approach ("Morel tableau")

One approach is to use chemical species as components. A set of linearly independent species ("basis species", or "component species", or "primary species") is selected, which will be the "basis" against which the stoichiometry of the other species is described.

This approach seems the most "natural" for an homogeneous closed system; one of its advantage is to use a minimum number of variables to describe both the stoichiometry and the chemical equilibrium of the system. Moreover, it allows a compact formulation of the speciation problem: the mass action relations expressing the "secondary species" as explicit functions of the primary ones can be substituted in the material conservation equations, giving a system with a minimal number of equations, one for each "primary species".

This approach is well suited for equilibrium calculations of an homogeneous system, e.g. purely aqueous, but it can make more complex the solution of "open system speciation" problems.

It is to note that, in this approach, the role of a basis species is twofold: it is both a component involved in the stoichiometric description of the mass balance and a chemical species involved in mass action relations. The denomination of "component species" better emphasizes this duality.

Consequently, a "basis species" is assigned two types of abundances: a true "chemical" abundance relevant to the chemical species itself, and a "total" or "generalized abundance" for the corresponding "component species" (Lichtner, 1996).

Example

For a carbonate-bearing aqueous solution with six chemical species considered

potentially present (H_2O , H^+ , HO^- , CO_2 , HCO_3^- , CO_3^{2-}), we can select $\{\text{H}_2\text{O}, \text{H}^+, \text{CO}_2\}$ as basis and describe HO^- as (1,-1,0), HCO_3^- as (1,-1,1), CO_3^{2-} as (1,-2,1).

The mass balance relation for "total carbonate" will be, in mole numbers:

$$n_{\text{total}}(\text{CO}_2) = n(\text{CO}_2) + n(\text{HCO}_3^-) + n(\text{CO}_3^{2-})$$

the elements as components

The "basis species" set correspond to a particular choice of "independent components", but, as already pointed out, thermodynamic components do not necessarily correspond to any species' stoichiometry; they only have to form a set of linearly independent entities that can generate the whole "chemical space" defined by the species under consideration.

Moreover, it is not necessary to use the same component set in the two sets of constraints, on compositions and on potentials respectively. In the "basis species" case, the two component sets apparently coincide, but the same "species" is actually used as a stoichiometric substance in one set, and as a chemical species in the other.

In ARXIM, we chose the apparently most "basic" option, which is to use as components, for the implementation of material conservation, the chemical elements present in the system.

In the case of an aqueous system, where the component set should be able to describe ionic species, the electron (or the electronic charge) has to be considered as a component, but a peculiarity of this "charge component" is that it is generally assigned a total balance of zero, because we assume that electrolytic solutions are at electrostatic equilibrium.

For example, considering a carbonate-bearing aqueous solution with six chemical species (H_2O , H^+ , HO^- , CO_2 , HCO_3^- , CO_3^{2-}), a "basis" composed of the four components (O,H,C,Chg) describe the species compositions using the following stoichiometric table

	O	H	C	Chg
H2O	1	2	0	0
H+	0	1	0	+1
CO2	2	0	1	0
HO-	1	1	0	-1
HCO3-	3	1	1	-1
CO3-2	3	0	1	-2

We obtain here the "formula table" of the system, where each species is represented by its "formula vector", e.g. the line vector (1,2,0,0) for H_2O .

accounting for redox state

From the stoichiometry of the species listed in the former example, it appears that only one oxidation state has been considered for each element. Actually, an element list such as $\{\text{O}[-2], \text{H}[+1], \text{C}[+4]\}$, would state more explicitly the oxidation state considered for each element in this example.

The oxidation state of an element is directly deduced from the stoichiometry of the species it enters in. The method can be explained with the example of the carbonate system: to account for the presence of species H^+ , H is assigned the oxidation state [+1]; as a result, O is assigned the state [-2], because of the presence of OH^- or H_2O ; finally, element C must be assigned the state (+4), to be consistent with the charge of three species it forms with $\text{O}[-2]$ and $\text{H}[+1]$.

By making the oxidation state an intrinsic property of the "element component", it is possible to have a full description of the system's stoichiometry without resorting to an additional "charge" component. In order that the solution of the speciation problem satisfies the electro-neutrality equation (the global balance of the species' charges is null), the global balance of the elements' valencies must be zero.

If we consider now an aqueous system where reduced and oxidized species (e.g.

CH₄, H₂, O₂) are potentially present, then we have to introduce an additional component, a "redox component" (component called "Ox" in ARXIM), which describes the oxidation state of the different species with respect to the "default oxidation state" of the elements.

The following table is obtained:

	O	H	C	Ox	(Chg)
vVal	-2	1	4	1	-1
H2O	1	2	0	0	0
H+	0	1	0	0	1
CO2	2	0	1	0	0
HO-	1	1	0	0	-1
HCO3-	3	1	1	0	-1
CO3-2	3	0	1	0	-2
O2	2	0	0	4	0
H2	0	2	0	-2	0
CH4	0	4	1	-8	0

Here, the vector line vVal, which contains the default oxidation states, is not a part of the formula table, but rather a property assigned to the respective element components.

The value of the redox component Ox of a species in a system will depend on the choice of the default values of the oxidation states of elements.

equations for material balance constraints

There are as many material balance constraints as inert components.

The formula matrix $\alpha(1:nC,1:nAq)$ of the whole system describes the stoichiometry of all aqueous species in terms of the elements.

The material conservation is expressed by **nC equations** of the form:

$$\Psi_{i \in C} = \sum_{j \in Aq} (\alpha_i^j \cdot n_j) - b_i = 0$$

with

▷ **b(1:nC)** the mole numbers of inert components,

▷ **n(1:nAq)** the mole numbers of aqueous species ($\{Aq\}$ = index set of aqueous species,

▷ **α(1:nC,1:nAq)** the species' formula matrix.

case of aqueous species of fixed potential

When mobile aqueous species (species index set Ax) are present, their contribution to the mole balance of component *i* can be separated from that of the inert aqueous species (species index set Ai).

$$\sum_{j \in Ai} (\alpha_i^j \cdot n_j) + \sum_{j \in Ax} (\alpha_i^j \cdot n_j) - b_i = 0$$

Here, the mobile species abundances can be calculated from their (fixed) activities if their activity coefficients (γ) and the solvent abundance are known:

$$n_i = m_i n_w M_w \Rightarrow n_i = \frac{a_i}{\gamma_i} \cdot n_w \cdot M_w$$

where M_w is the molar weight (kg) of solvent.

In this expression, only n_w , the solvent mole number, is unknown, because the activity coefficients $\gamma(1:S)$, which depend on the solution composition and thermodynamic model, are held constant within the execution of the solver routine and calculated in an external loop.

$$\text{Equ}[i=1:nC] : \sum_{j \in A_i} \alpha_i^j \cdot n_j + n_w \cdot M_w \sum_{j \in A_x} \alpha_i^j \cdot \frac{a_j}{\gamma_j} - \mathbf{b}_i = 0$$

equilibrium constraints in closed systems

In a mixture where the number of species equals the number of independent components (case of "interaction" mixing models, common for minerals, melts, gases), the species abundances are completely determined by the phase composition and the species stoichiometry. But, if the phase follows a model of "association solution", each time an additional species is considered, an additional equation is provided by a chemical equilibrium condition, i.e. an "internal constraint" among the species' chemical potentials.

primary and secondary species

In a "LMA approach", the equilibrium condition of a closed system of {nC components, nAq aqueous species} is implemented as a set of independent mass action relations among the aqueous species.

The number of such independent reactions is nAq - nC. To write these reactions, it is convenient to split the species set into,

nC linearly independent "primary species",

nAq - nC "secondary species" whose formation (or dissociation) reactions are expressed in terms of the "primary species".

ARXIM follows an approach similar to LMA approaches, except that, instead of mass action relations expressed in terms of activity products, equilibrium is written as a set of linear relations between chemical potentials.

There are as many "basis species" as components, 3 in the example system {(H,O,C), (H⁺, H₂O, CO₂, HO⁻, HCO₃⁻, CO₃⁻²)}. The selection of the "primary species", as long as they form a basis for the system, is rather arbitrary. Practically, in aqueous systems, H₂O is always chosen as primary species, for its role as solvent. It is also practical to have H⁺ (or OH⁻ in basic conditions) as component, because of its central role in acid-base reactions. For other elements, the species with the highest dissociation degree (e.g. Na⁺ for Na, Ca⁺² for Ca, PO₄⁻³ for P) can be selected as the default primary species.

The primary species selection is arbitrary, but the program may modify the species set during speciation calculation, in order to have the most dominant species as primary species, which secure the numerical resolution of the problem. Such a systematic basis change is essential when the equilibrium conditions are formulated in terms of concentrations or mole numbers as variables; it is not critical when the formulation, as done in ARXIM, is in terms of their logarithms, which gives linear equilibrium equations.

In the case of open system, the mobile species are selected as primary species. This simplifies the expression of the equilibrium conditions: if a mobile species is not aqueous, its selection as primary species allows the implementation of equilibrium conditions with the same type of equations as those used for homogeneous equilibrium. The remaining inert "primary species" are selected among aqueous species that are independent from each other and from the mobile species.

example

For the system {(H,O,C), (H⁺, H₂O, CO₂, HO⁻, HCO₃⁻, CO₃⁻²)}, if (H₂O, H⁺, CO₂) is selected as "basis", the other species ("secondary species") are defined in relation with this basis by the following stoichiometry matrix v(1:nS-nC, 1:nC), the same as that used for stoichiometry description in the pure "basis species approach":

	H2O	H+	CO2
HO-	1	-1	0
HCO3-	1	-1	1
CO3-2	1	-2	1

stoichiometry of the reactions of formation of secondary species

If the basis species have been appropriately selected, then the matrix made of the primary species column vectors of the formula matrix, $\mathbf{a}(1:nC,iP)$, is non singular. Its inverse, which expresses the elements (1:nC) in terms of the basis species (1:nC), will constitute the "transformation matrix" used to compute the matrix $\mathbf{v}_{As}(1:nAs,1:nC)$ giving the stoichiometry of the aqueous nAs secondary species in terms of the nC primary species.

The same transformation matrix is used to compute the stoichiometry matrix $\mathbf{v}_{Ms}(1:nMs,1:nC)$ of non-aqueous species (species in minerals and gases).

The matrices \mathbf{v}_{As} and \mathbf{v}_{Ms} are also used for computing $\Delta G^{\circ}_{As}(1:nAs)$ and $\Delta G^{\circ}_{Ms}(1:nMs)$, the ΔG° 's of the formation reactions of all secondary species, respectively aqueous and non-aqueous.

equations for chemical potential constraints

If the system is at equilibrium, then $nAs=nS-nC$ independent chemical reactions between the primary and secondary species are at equilibrium.

There are **nAs chemical potential constraints**, one for each secondary species:

$$\Psi_{js \in As} = \mu_{js} - \sum_{jp \in Pr} v_{js}^{jp} \cdot \mu_{jp} = 0$$

where

▷ $\mu(1:nS)$ is the array of the chemical potentials of all species of the system,

▷ $\{Pr\}$ is the primary species set,

▷ $\{As\}$ is the secondary species set,

the matrix $\mathbf{v}(1:nAs,1:nC)$ describes the stoichiometry of the formation reactions of secondary aqueous species from primary species.

example: System $\{(H,O,C), (H^+, H_2O, CO_2, HO^-, HCO_3^-, CO_3^{2-})\}$

Having selected (H_2O, H^+, CO_2) as basis, the equilibrium conditions, $\Delta G=0$, for the formation of the three secondary species yield the following relations:

$$\begin{array}{lcl} \mu(HO^-) & = & \mu(H^+) + \mu(H_2O) \\ \mu(HCO_3^-) & = & -\mu(H^+) + \mu(H_2O) + \mu(CO_2) \\ \mu(CO_3^{2-}) & = & -\mu(H^+) + \mu(H_2O) + \mu(CO_2) \end{array}$$

where $\mu(X)$ is the chemical potential of the species X.

The "reduced potential" μ_j (i.e. potential divided by $R.T$, which makes it dimensionless) is related with the activity of species j , a_j , by the relation

$$\mu_j = \mu_j^0 + \ln a_j$$

where μ_j^0 is the reduced molar Gibbs enthalpy of species j in the reference state, calculated at (T,P) from data retrieved from the thermodynamic database.

The equilibrium conditions can be written as follows:

$$\Psi_{js \in As} = 0 = \ln a_{js} - \sum_{jp \in Pr} v_{js}^{jp} \cdot \ln a_{jp} - \Delta G_{js}^0$$

where $\mathbf{a}(1:nAq)$ contains the activities of all species and ΔG_{js}^0 is the "reduced" free energy change of the dissociation reaction of the secondary aqueous species js :

$$\Delta G_{js}^0 = \sum_{jp \in Pr} v_{js}^{jp} \cdot \mu_{jp}^0 - \mu_{js}^0$$

This formulation is equivalent to the classical "mass action" form, using "ion activity

products" and "equilibrium constants", which is more common in aqueous geochemistry. In mass action form, the equilibrium condition for species js would become:

$$a_{js} = K_{js} \prod_{jp \in Pr} (a_{jp})^{v_{js}^{jp}} \text{ with } K_{js} = \exp(\Delta G_{js}^0)$$

relating potential constraints with material balance constraints

We have thus two sets of linear equations, one in species mole numbers, the other in species potentials. We have to relate the species' potentials with their mole numbers: that is the role of the mixing model to implement these "activity - composition" relationships.

in the case of aqueous solutions

In aqueous solutions, there is a dominant species, the "solvent" H_2O , against which the concentrations of the other species, the "solute" species, are measured. The mixing model is asymmetric: solvent and solutes follow respectively a mole fraction and molality scale and have different forms of activity - composition relations.

▷ for the solvent, $a_w = x_w \cdot \lambda_w$, where mole fraction $x_w = \frac{n_w}{n_w + \sum_{i \neq w} n_i}$

▷ for a solute species, $a_j = m_j \cdot \gamma_j$, where molality $m_j = \frac{n_j}{n_w \cdot M_w}$

We have thus $a_{j \neq w} = \gamma_j \cdot \frac{n_j}{n_w \cdot M_w}$

The equilibrium condition between secondary species js and primary species (jp in $\{Pr\}$) comprises two terms, respectively for solvent species (w) and for other primary species,

$$\Psi_{js} = v_{js}^w \cdot \ln a_w + \sum_{jp \in Pr/w} (v_{js}^{jp} \cdot \ln a_{jp}) - \ln a_{js} + \Delta G_{js}^0 = 0$$

or, in terms of mole numbers of aqueous species, $\mathbf{n}(1:nAq)$:

$$\begin{aligned} \Psi_{js} = 0 = & \sum_{jp \in Pr/w} (v_{js}^{jp} \cdot \ln n_{jp}) - \ln n_{js} - \left[\sum_{jp \in Pr/w} v_{js}^{jp} - 1 \right] \cdot \ln(n_w M_w) \\ & + v_{js}^w \cdot \ln a_w + \Delta \ln \gamma_{js} + \Delta G_{js}^0 = 0 \end{aligned}$$

where $\Delta \ln \gamma_{js}$ is the "balance" of activity coefficients in the dissociation reaction of species js :

$$\Delta \ln \gamma_{js} = \sum_{jp \neq w} (v_{js}^{jp} \cdot \ln \gamma_{jp}) - \ln \gamma_{js}$$

implementation

the system of equations, closed system

For the $nAq = nC + nAs$ unknown mole numbers of aqueous species, represented by the array $\mathbf{n}(1:nAq)$, we have a system of $nC + nAs$ equations:

▷ **nC material balance equations:**

$$\Psi_{i \in C} = 0 = \sum_{j \in Aq} \alpha_i^j \cdot \mathbf{n}_j - \mathbf{b}_i$$

▷ **nAs chemical potential balance equations:**

$$\begin{aligned} \Psi_{js \in As} = 0 = & \\ & v_{js}^w \cdot \ln a_w + \sum_{jp \in Pr/w} (v_{js}^{jp} \cdot \ln \mathbf{n}_{jp}) - \ln \mathbf{n}_{js} \\ & - \left[\sum_{jp \in Pr/w} v_{js}^{jp} - 1 \right] \cdot (\ln \mathbf{n}_w + \ln M_w) + \Delta \ln \gamma_{js} + \Delta G_{js}^0 \end{aligned}$$

open system

For an open system comprising **nCi** inert and **nCx** mobile components (pointing respectively to index set $\{Ci\}$ and set $\{Cx\}$, with $nCi + nCx = nC$), the system of equations is modified as follows:

▷ **nCi material balance equations:**

$$\Psi_{i \in Ci} = 0 = \sum_{j \in Aq} \alpha_i^j \cdot \mathbf{n}_j - \mathbf{b}_i$$

▷ **nAq - nCi potential balance equations:**

$$\begin{aligned} \Psi_{js \in As} = 0 = & \\ & v_{js}^w \cdot \ln a_w + \sum_{jp \in Ci/w} (v_{js}^{jp} \cdot \ln \mathbf{n}_{jp}) - \ln \mathbf{n}_{js} \\ & - \left[\sum_{jp \in Ci/w} v_{js}^{jp} - 1 \right] \cdot (\ln \mathbf{n}_w + \ln M_w) + \Delta \ln \gamma_{js} + \Delta G_{js}^0 \\ & + \sum_{jp \in Cx} (v_{js}^{jp} \cdot \ln a_{jp}) \end{aligned}$$

Thus, for an open system, compared to a closed system with the same number of aqueous species, the number of material balance equations decreases by the number of mobile components, whereas the number of secondary aqueous species, and thus of associated internal constraints on chemical potentials, increases by the same number.

For example, if all constraints but on the solvent are potentials of non-aqueous species, the system becomes:

$$\begin{aligned} \Psi_w = 0 = & \sum_{j \in Aq} \alpha_w^j \cdot \mathbf{n}_j - \mathbf{b}_w \\ \Psi_{js \in As} = 0 = & \\ & v_{js}^w \cdot \ln a_w - \ln \mathbf{n}_{js} - (\ln \mathbf{n}_w + \ln M_w) \\ & + \Delta \ln \gamma_{js} + \Delta G_{js}^0 \\ & + \sum_{jp \in Cx} v_{js}^{jp} \cdot \ln a_{jp} \end{aligned}$$

resolution

This system of non-linear equations can be solved for the species' mole numbers, $X(:) = \mathbf{n}(1:nAq)$, or for their logarithms, which are homogeneous to the species affinities, the primary variables in the chemical potential equations.

When solving the system for $X(:) = \ln(\mathbf{n}(1:nAq))$, the equilibrium equations are linear, but the conservation equations become sums of exponential terms, with possibly strong non-linearity.

The solvent activity a_w and the activity coefficients of solutes, γ_j , are functions, generally non-linear, of the composition \mathbf{n} . The system is solved by iteration: an internal loop, where the system is solved for $\text{Ln}(\mathbf{n})$ with fixed values of the solute activity coefficients and the solvent activity, and an external loop that uses the composition \mathbf{n} to update these parameters until convergence is attained between successive estimations of the activities.

The system is solved first on the $\text{Ln}(\mathbf{n})$ array with an arbitrary value of the $v\Delta\text{Ln}\gamma(\text{js})$ (for example zero, corresponding to a highly dilute solution); then the solution $\text{Ln}(\mathbf{n})$ is used to compute a new set of $\Delta\text{Ln}\gamma(\text{js})$ that enters as constant terms in the residual system. The procedure is repeated until convergence on $\Delta\text{Ln}\gamma(\text{js})$. As a matter of fact, the variation of the mole numbers within the non-linear iteration loop is, especially at beginning, several orders of magnitude higher than the variation observed between successive values of the activity coefficients. The "strategy" of keeping constant, within the solver routine, the entities of second order variations, is also applied to the solvent activity, which is updated together with the activity coefficients.

This approach produces, without significant loss in efficiency, a Jacobian matrix whose expression is not specific to the model of activity correction chosen. An important advantage of this approach is to make possible for the user the implementation of a large variety of activity models in the dedicated module, 'outside' the Jacobian.

The Jacobian matrix, when the equilibrium equations are not substituted in the conservation equations, with $X_i = \text{Ln}(n_i)$:

	jw	$jp \neq jw$	js
Eq[Ci]	$[\alpha_i^w e^{X_w}]$	$[\alpha_i^{jp} e^{X_{jp}}]$	$[\alpha_i^{js} e^{X_{js}}]$
Eq[As]	$[1 - \sum_{jp \neq jw} v_{js, jp}]$	$[v_{js}^{jp}]$	I

As the module implementing the non-linear system and its Jacobian are clearly separated from the module in charge of the numerical resolution, the latter can be easily changed in order to test the efficiency of different types of numerical schemes. The scheme currently used is a Newton-Raphson iterative algorithm, with a line-search and backtracking method proposed by Kelley (2003). Other methods, implemented in ARXIM, can also be used in lieu of Kelley's Newton-Armijo method, for example methods described by Walker () and by Press et al. (1992).

alternative approach

Using primary species as components for material balance, and formulating the system in terms of molalities, the equilibrium conditions can be represented in a rather compact form.

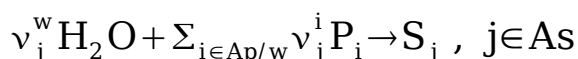
The same set of basis species, necessarily including the solvent H_2O , is used to describe the stoichiometric relations between species and the formation of secondary species.

Working with molalities, there is no equation for the solvent, and material balance equations are written for primary solute species:

$$\Psi_{i \in \text{Ap/w}} = m_i + \sum_{j \in \text{As}} v_j^i m_j - t_i \quad ,$$

where t_i is the "total molality" of primary species i .

Considering the secondary species S forming from basis species $\{\text{H}_2\text{O}, P\}$ by the reaction



the corresponding equilibrium condition is

$$\gamma_j m_j = K_j \prod_i m_i^{\nu_j^i} \prod_i \gamma_i^{\nu_j^i} a_w^{\nu_j^w}, \text{ or, with } K_j^{\text{app}} = \prod_i \gamma_i^{\nu_j^i} a_w^{\nu_j^w},$$

$$m_j = K_j^{\text{app}} \prod_i m_i^{\nu_j^i}$$

where the "apparent" equilibrium constant includes the activity coefficient product and solvent activity, which will be kept constant within the internal solution procedure.

Molalities of secondary species may be substituted directly in the material balance equations, giving a system of reduced size, whose Jacobian is

$$\frac{\partial \Psi_{ip}}{\partial m_{jp}} = \delta_{ip}^{jp} + [\sum_{k \in As} \nu_k^{ip} \nu_k^{jp} m_k] / m_{jp}, \text{ with } m_k = K_k^{\text{app}} \prod_i m_i^{\nu_k^i}$$

A condition for the solver to converge is that the primary species are those that actually dominate in the current system, otherwise the equation system is ill conditioned.

[next: examples of speciation runs]

SPC: examples of speciation runs

The following examples illustrate some speciation calculations possible with ARXIM.

The text of the actual script is given on left side, results are represented on right side with diagrams drawn with ArximDraw (ARXIM's drawing program).

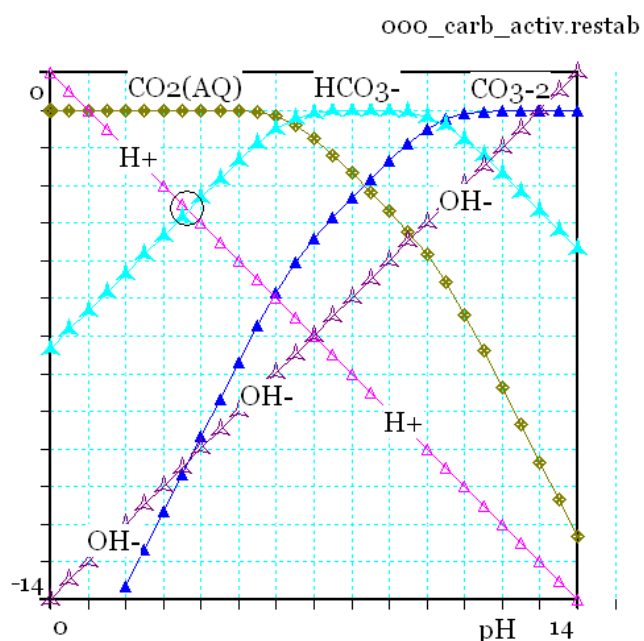
carbonate speciation as a function of pH ("Sillen diagram")

define the system,
total carbonate = 0.1
mole/kgH₂O

```
SYSTEM
  TdgC 25
  C MOLE CO2(AQ) 0.1
  H PK    H+    7.00
END
```

program a path,
changing the constraint on H:

```
PATH CHANGE
  H initial 0.00 final 14.0 delta
  0.5
END
```



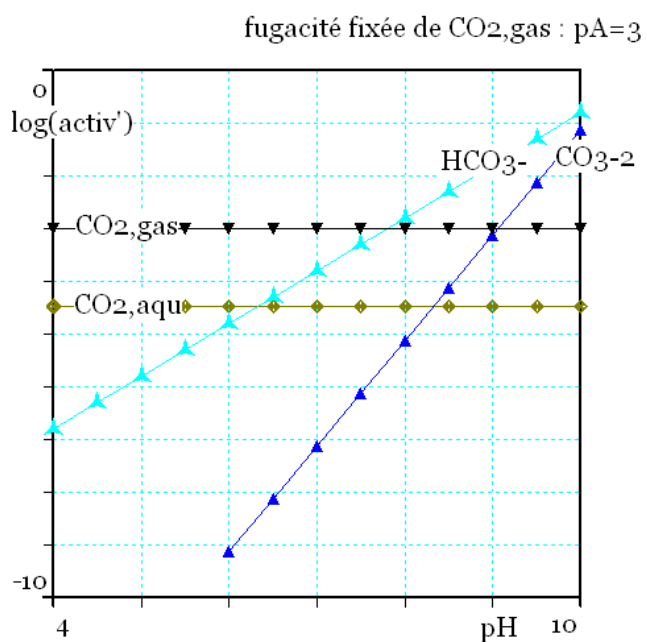
carbonate speciation under fixed CO₂ partial pressure

define the system,

```
SYSTEM
  TdgC 25
  C    PK    CO2(G) 3.0
  H    PK    H+    7.00
END
```

program a path,
changing the constraint on H:

```
PATH CHANGE
  H initial 4.00 final 10.0 delta
  0.5
END
```



EQU: equilibrium composition of a fluid-rock system

Having considered the case of homogeneous equilibrium state of an aqueous fluid under composition / potential constraints, we consider now the equilibrium state of a system that may comprise, in addition to the aqueous phase, non-aqueous phases such as minerals or gases.

Among the non-aqueous phases considered potentially present, we call hereafter "active phases" those at equilibrium and "inactive" the others.

To the equation system describing the homogeneous equilibrium of the aqueous phase, there is, for each active phase:

- ▶ an additional unknown: its mole number, which enters in the material balance equations,
- ▶ an additional chemical potential equation: its equilibrium condition with the aqueous phase.

To compute the composition of the system at equilibrium, ARXIM uses an iterative method that is classical for mineral / fluid equilibrium in the LMA way (e.g. EQ6, Wolery, 1979). The speciation of the aqueous phase plays the central role, as it is called at each iteration for computing the disequilibrium degree between water and other phases considered in the chemical space.

The scheme is as follows, starting with an arbitrary set of active phases:

```
given the amounts of aqueous phase and other active phases
do:
  1. solve for equilibrium state with the current active phase set
  2. if any active phase has a negative mole number:
      make inactive that phase with the most negative mole number
      cycle
  3. if any inactive phase is super-saturated versus aqueous phase:
      3a. activate (add) the most super-saturated
      3b. inactivate (remove) any active phase in conflict
      cycle
exit
```

Similar iterative scheme are used in water-rock interaction codes such as CHESSE (van der Lee, 1998), or GWB (Bethke, 1996), but, at variance with GWB or CHESSE, the non-aqueous active species are not swapped into the set of primary species for equilibrium conditions.

The main difficulty with this scheme lies in step 3b, if the new phase happens to be compositionally dependent of the current active set and the question arises of which active phase should leave the active set. If there is dependency, we can compute the stoichiometry of the formation of the new phase from the currently active phases, and the phase to be removed will be the phase i with the lowest X_i / ν_i , where X_i is the mole number of phase i and ν_i its coefficient in the reaction of formation of the new phase.

equilibrium involving mixtures

When mixture phases (gas mixtures, solid solutions) are considered as potentially entering the active set, their compositions are additional unknowns, but the same scheme can be adapted as follows:

At step 3, when computing the saturation degree of all possible phases, we compute,

for each mixture, the mixture composition that gives the maximum super-saturation with respect to the current aqueous composition. The most super-saturated mixture phase, if any exists, is added, as a pure phase with this composition, to the set of phases considered in 3a. If, on next loop, a mixture enters the active set, its composition is adjusted by iterating step 1 (convergence is reached in 2-3 iterations).

next: examples of equilibrium calculations

examples of equilibrium calculations (EQU)

The following examples illustrate some equilibrium calculation runs with ARXIM.

titration runs under imposed pH

A typical run of numerical titration (Helgeson, 1969) consists in adding aliquots of a substance of given stoichiometry to a fluid of given composition, and to compute the equilibrium composition of the fluid - mineral system obtained at each increment.

The diagrams hereafter show the results, in mole numbers of minerals for 1 kg H₂O, of several titration runs with ARXIM. Each run is a series of ARXIM / EQU calculations, each calculation being made for 1 kg H₂O plus a fixed amount of KAlSi₃O₈, incremented from 10⁻⁶ to 10. mole /kg H₂O.

Here, at variance with more classical titration, each titration run is computed for a fixed value of pH (pH= 4, 5, 6, 9), the charge being balanced by HCl at low pH or by NaOH at high pH.

Such an equilibrium path is implemented by the following script:

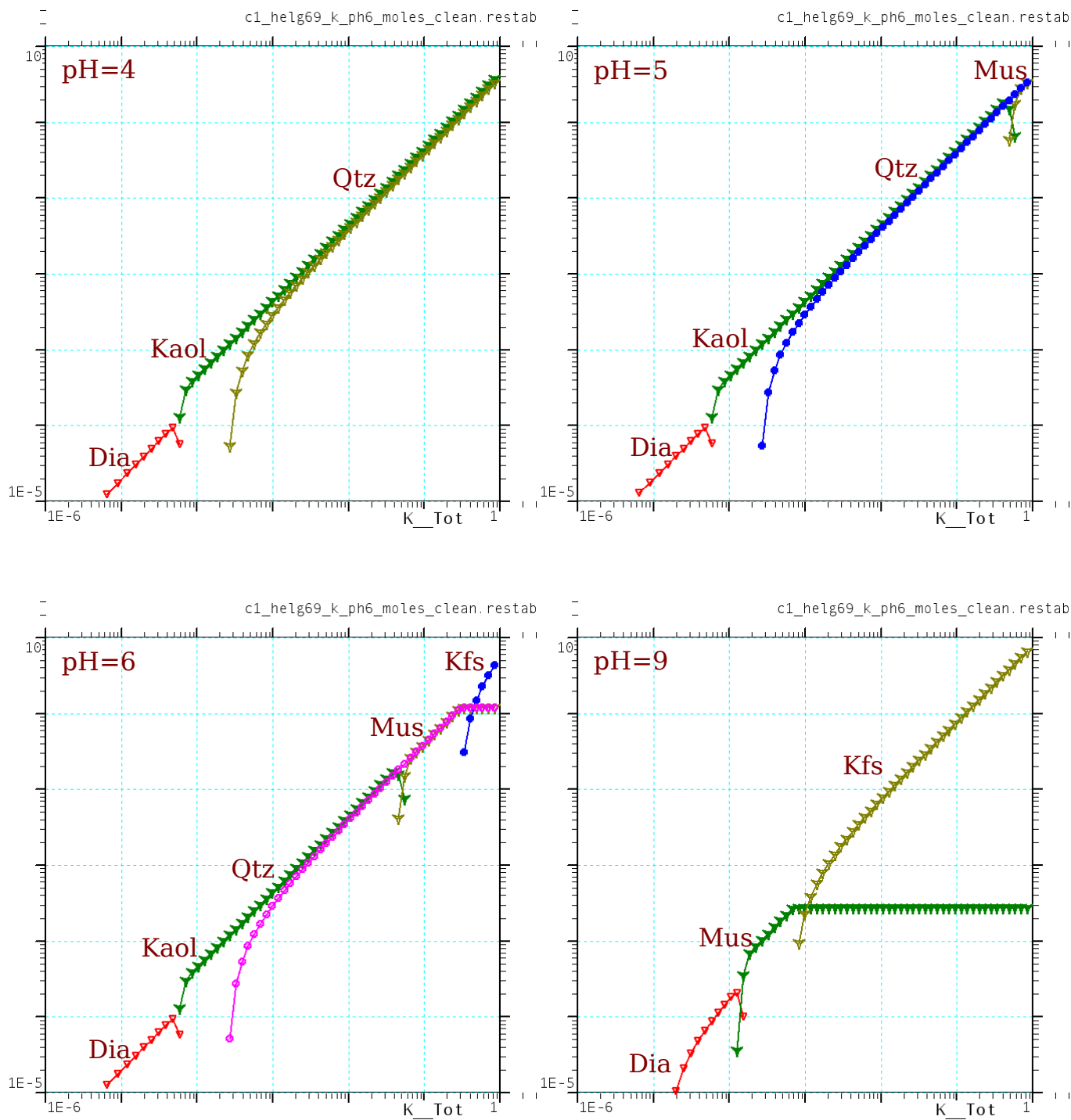
.1. The SYSTEM block lists the constraints on the system:

```
SYSTEM
  TDGC 75
  PBAR 200
  K   MOLE   K+   0.1
  SI  MOLE   SI02(AQ) 0.3
  AL  MOLE   AL+3 0.1
  H   PK     H+   6.00
  CL  BALANCE Cl-
END
```

.2. The PATH block defines the evolution of the constraints along the path:

```
PATH CHANGE
  SI  INITIAL 3.D-6 FINAL 12.00 RATIO 1.2
  AL  INITIAL 1.D-6 FINAL 4.00 RATIO 1.2
  K   INITIAL 1.D-6 FINAL 4.00 RATIO 1.2
END
```


[diagrams, titration runs under imposed pH]



Computation of the equilibrium state of a water-rock system is essential for one of the main objects of the ARXIM project, which is to serve as the "chemical reactor" of a reactive transport code. It is used in this way in COORES (CO₂ Reservoir Environmental Simulator), a code coupling ARXIM with SIMUSCOPP (Trenty, 2003), a code for multiphase transport in porous media. COORES-ARXIM is currently used for simulating scenarios of injection and sequestration processes of green house gases.

A "dynamic" run simulates the temporal evolution of a given volume of porous media as it is flushed by a given flux of fluid of given composition. It is thus a 0D reactive transport model, equivalent to the "continuous stirred tank reactor" (CSTR) model of chemical engineering.

The data at time t are the composition of the box (volume fractions and compositions of fluids and minerals) and the flux rate and composition of the injected fluid.

The main assumptions are that

- material transfer between fluid and minerals occurs only through dissolution - precipitation reactions which are kinetically controlled;
- an instantaneous equilibrium is realized among the aqueous species.

The variables comprise the mole numbers of fluid species in the box, $\mathbf{n}(1:nAq)$, and the mole numbers of mineral species, $\mathbf{n}(1:nM)$.

The system to be solved comprises three sets of equations:

- ▷ material balance of the independent components:

$$\frac{d}{dt} n_{Ci} + (Q_{Ci}^{\text{inj}} + Q_{Ci}^{\text{out}}) + R_{Ci} = 0$$

- ▷ potential constraints among aqueous species (same as in speciation):

$$\ln a_{js} - \sum_{jp \in Pr} \nu_{js}^{jp} \cdot \ln a_{jp} - \Delta G_{js}^0 = 0$$

- ▷ material balance on minerals:

$$\frac{d}{dt} n_m + R_m = 0$$

→ *accumulation term*

The accumulation term is the mole numbers of component $[C_i]$ in the fluid in the box, computed as

$$n_{Ci} = \sum_j \alpha_i^j n_j$$

→ *flux terms*

The flux comprises an explicit input term, Q^{inj} , imposed to the box as a volumetric Darcy flux, and an implicit output term Q^{out} .

Thus, for each component:

$$\blacktriangleright Q_{Ci}^{\text{inj}} = \sum_j \alpha_i^j Q_j^{\text{inj}} = F_{\text{vol}}^{\text{inj}} \times \sum_j \alpha_i^j c_j^{\text{inj}} ,$$

where $c_j^{\text{inj}} = \frac{n_j^{\text{inj}}}{\text{Vol}_F^{\text{inj}}}$ is the imposed concentration in the input fluid.

$$\blacktriangleright Q_{Ci}^{\text{out}} = \sum_j \alpha_i^j Q_j^{\text{out}} = F_{\text{vol}}^{\text{out}} \times \sum_j \alpha_i^j c_j ,$$

where $c_j = \frac{n_j}{\text{Vol}_F}$ is the concentration in the box.

→ reaction term

$$R_{C_i} = - \sum_m \alpha_{i,m} \frac{d}{dt} n_m = - \sum_m \alpha_{i,m} V_m ,$$

where V_m is the rate of precipitation / dissolution of mineral m , modeled as a sum of several reaction mechanisms:

$$V_m = (V_m^{\text{d1}} + V_m^{\text{d2}} + \dots + V_m^{\text{dk}}) + (V_m^{\text{p1}} + V_m^{\text{p2}} + \dots + V_m^{\text{pl}})$$

The following formalism (Lasaga et al, 1994), of common usage in water-rock simulation codes (Palandri & Kharaka, 2004), is used for the rate laws:

► precipitation rate:

$$\text{if } \Omega_m < 1 ; \text{ then } V_m^{\text{d}} = A_m \times k_m(T) \times \prod_j (a_j)^{n_j} \times (1 - \Omega_m^\alpha)^\beta ; \text{ else } V_m^{\text{d}} = 0$$

► dissolution rate:

$$\text{if } \Omega_m > 1 ; \text{ then } V_m^{\text{p}} = A_m \times k_m(T) \times \prod_j (a_j)^{n_j} \times (\Omega_m^\alpha - 1)^\beta ; \text{ else } V_m^{\text{p}} = 0$$

where

$$\triangleright \Omega_m = \exp\left(-\frac{\Delta G_m}{RT}\right)$$

measures the disequilibrium between mineral and the fluid, ΔG_m being the molar free energy change attending the dissolution reaction of the mineral in the current fluid,

► A_m is the reactive surface area of the mineral,

► $k_m(T)$ is its kinetic rate coefficient "far from equilibrium".

It depends on temperature according to an Arrhenius law:

$$k_m(T) = 10^{-pk_{T_{\text{ref}}}} \exp\left(-E_{m, T_{\text{ref}}} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right) / R\right)$$

where $E_{m, T_{\text{ref}}}$ is the activation energy at temperature T_{ref} .

$$\triangleright \prod_j (a_j)^{n_j}$$

represents the influence of the fluid composition on the mineral rate, through the activity of aqueous species j that, depending on the sign of the exponent n_j , act as

catalyst or inhibitor.

Actually, in the current implementation, the different elementary rate laws share the same reactive surface A_m and disequilibrium function and differ only in parameters k_m and in the nature of catalyzing and inhibiting species.

the relationship of surface to volume

Initial reactive surface areas, in terms of grain radius or of specific area, are given in the run's definition, along with initial mineral volume fractions.

It is possible to have several kinetic phases, pointing to the same thermodynamic species but having different textural properties, for example a coarse-grained quartz population and a fine-grained one.

To describe the relationship between the mole numbers of the kinetic phases in the reactive cell and their surface, each kinetic phase is considered as an ensemble of spherical grains of homogeneous radius (e.g. Lichtner, 1988).

In this "floating sphere" model, the reactive surface area for dissolution or precipitation of phase m at time step t is:

$$A_m = A_{m,0} \left(\frac{n_m}{n_{m,0}} \right)^{\frac{2}{3}}, \text{ for precipitation and dissolution (option1)}$$

where $A_{m,0}$ and $n_{m,0}$ are respectively the initial mole number and area of phase m.

This model, adapted to minerals growing or shrinking freely in a high porosity medium, becomes inconsistent at low porosity, when the grains come in contact with each other and part of their reactive surfaces becomes inaccessible.

Thus, optionally, introducing the porosity as a damping factor, the following dependence can be used for precipitation, in order to have the reactive surface tend to zero when porosity vanishes:

$$A_m = A_{m,0} \left(\frac{\phi}{\phi_0} \right)^{\frac{2}{3}} \left(\frac{n_m}{n_{m,0}} \right)^{\frac{2}{3}}, \text{ for dissolution (option 2)}$$

where ϕ and ϕ_0 are the current and initial values of porosity.

For precipitation, instead of having the same relationship as for dissolution, we consider that it takes place not only on minerals of the same type, but on all the surface of the pores, and this results in the following surface / volume relationship:

$$A_m = A_{m,0} \left(\frac{\phi}{\phi_0} \right)^{\frac{2}{3}}, \text{ for precipitation (option2)}$$

implementation: the equation system

There are $nF+nM$ unknowns, which are:

- nF **mole numbers of aqueous species** contained in the cell at time t, $vYf(1:nF)$, or their logarithms, $vXf(1:nF) = \text{LOG}(vYf(1:nF))$
- nM **mole numbers of mineral species** contained in the cell at time t, $vXm(1:nM)$

For a given timestep Δt , the system to be solved comprises $nF+nM$ equations, $\Psi(1:nF+nM)=0$, which can be distributed as three sets of equations, respectively

nC equations for the independent components,
 nF-nC equations for the secondary species,
 nM equations for the minerals

► **nC equations** implementing the mass balance constraints on the nC components:

$$\begin{aligned} \Psi_{iC} = & \left(1 + \frac{U_{\text{Darcy}}}{\Delta x} \cdot \phi_f\right) \cdot \sum_{j=1}^{nAs} (\alpha_{iC,j} \cdot vYf_j) \quad (\text{mole nrs in fluid from aqu'species}) \\ & - vF_{iC}^{t-\Delta t} \quad (\text{mole nr. in fluid at previous step}) \\ & - vF_{iC}^{\text{Inj}} \cdot \frac{U_{\text{Darcy}}}{\Delta x} \cdot \Delta t \quad (\text{mole nr. injected}) \\ & + \sum_{j=1}^{nMk} (\alpha_{iC,nAq+j} \cdot vVm_j) \quad (\text{to/from minerals}) \end{aligned}$$

In these equations, the porosity ϕ_f is not explicit, as it is a function of the minerals' mole numbers vXm .

► **nF-nC equations** describing the equilibrium between all nAq aqueous species, and eventually with a buffer component. Their formulation is equivalent to that used for static speciation calculations.

► **nM rate equations** for the nM mineral species currently "active":

$$\Psi_{nAq+j} = vXm_j - vMolM_j - \Delta t \cdot vVm_j$$

At beginning of a time step, the status of each mineral, is either dissolution, precipitation, or inaction, depending on its saturation state with respect to the fluid composition.

As already mentioned, Vm_j , the rate for precipitation / dissolution of mineral j, is the product of three factors ($VmS \cdot VmAct \cdot VmQsK$), respectively functions of the mineral surface, the activities of species fluid, and the affinity of mineral - fluid reaction. These three factors have not the same degree of dependency on the dynamic evolution of the system. As a result, they are not necessarily updated at the same stage of the numerical scheme. Some of them, like the fluid activity factor, can be handled as explicit parameters, whereas others, especially the affinity factor, are better implicated, in order to allow the solution of large time steps.

numerical method

To solve this system of non-linear equations, the modules for the residual system, for its jacobian, and for the convergence criteria are written according to the generic interface that makes them callable by the Newton-Raphson solvers already mentioned for the speciation issue.

Convergence of the Newton-Raphson algorithm is improved by using as initial values of the minerals mole numbers the values obtained by extrapolation according to their rates at the previous step. Extrapolation is also used for time step adjustment to prevent over-dissolution of a dissolving mineral.

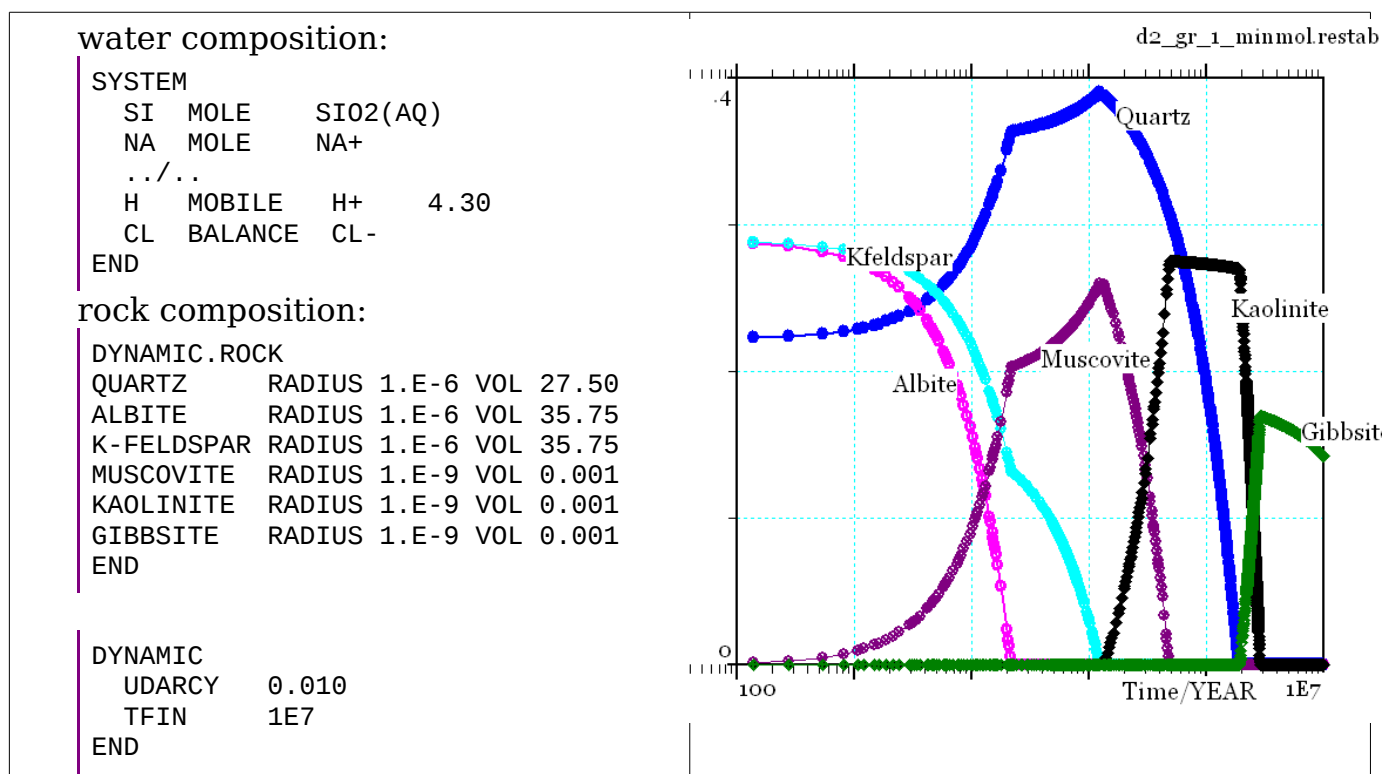
example of reactive cell calculations, ARXIM / DYN

The following examples illustrate some calculations of the evolution of a reactive cell.

The text of the actual script is given on left side, results are represented on right side with diagrams drawn with ArximDraw (ARXIM's drawing program).

granitic rock flushed by rain water

A simplified granitic assemblage (quartz - albite - K-feldspar) is flushed, at a given Darcy velocity, by a slightly acidic pure water. Potential secondary minerals (kaolinite, muscovite, gibbsite) are given as initially present in the cell at small amounts and fine radius.



global approach to equilibrium computation

LMA methods (formulations based on Law of Mass Action) are well adapted to simulations of water-rock interactions, where the speciation of the aqueous phase plays the central role, and they are actually dominant among hydrochemistry codes, but it appears essential, for a library devoted to multiphase equilibrium computations, to implement also tools for Global (or Gibbs) Energy Minimization (GEM) methods.

Free energy minimization is by far the preferred strategy for solving multiphase equilibrium in material science and chemical engineering, and a large array of numerical schemes have been proposed, such as SOLGASMIX (Eriksson, 1974) and its relatives (e.g. CHEMSAGE, Eriksson and Hack, 1990), or the CALPHAD methods (Saunders and Miodownik AP, 1998).

For petrology also, using GEM rather than LMA methods appears necessary in many situations:

- ▷ systems with many potential mixture phases, commonly encountered in metamorphic and magmatic petrology,
- ▷ systems that are not always saturated with respect to the aqueous phase; for example, evaporation processes, such as dessication in the vicinity of CO₂ injection wells and salt scaling.

For metamorphic petrology, a number of GEM programs are available [THERIAK (de Capitani & Brown, 1987), PERPLEX (Connolly 1990, 2005), FLASK-SG (Takeno, 2001)], which take into account mixture phases (fluid phases, solid solutions) that follow complex non-ideal EoS.

linear programming

Given a multi-component space and a set of possible phases (minerals and fluids), the objective is to find the stable phase assemblage for a given bulk composition and T,P conditions.

When all phases are of fixed compositions ("pure phases"), the problem becomes a classical problem of linear programming (White et al, 1958; De Capitani & Brown, 1987).

In this case, we have simply to transform the petrological question into a form that fits with standard implementations of linear programming. A systematic implementation of the basic stoichiometric and thermodynamic manipulations on species and phases, such as built in ARXIM, largely simplifies this interfacing task.

The system is defined by:

- ▷ a list of (1:nC) components, which defines the chemical space of interest;
- ▷ the bulk composition of the system, given by the vector $b(1:nC)$ of mole numbers of the components,
- ▷ the T,P conditions;
- ▷ a set of phases (1:nF) potentially present, having fixed compositions and known Gibbs energy of formation, $g(1:nF)$, at the given (T,P) condition.

The stable phase assemblage is the set of phases ($nF \leq nC$) that, for the given bulk composition, minimizes the Gibbs energy of the system.

The problem is thus to solve for n the following linear programming problem:

- ▷ minimize the "objective function"

$$\mathbf{G} = \sum_{j=1}^{nF} \mathbf{n}_j \cdot \mathbf{g}_j(T, P)$$

▷ under nC equality constraints

$$\sum_{j=1}^{nF} \alpha_j^i \cdot \mathbf{n}_j = \mathbf{b}_i \quad (i=1..nC) ,$$

▷ and

$$\mathbf{n}_j \geq 0 \quad (j=1..nF)$$

\mathbf{g}_j is the molar Gibbs free energy of formation of the phase j at (T,P), and \mathbf{n}_j its mole number, which will be either positive (phase j is present) or zero (phase j is absent).

\mathbf{b}_i is the mole number of component i , i.e. a given positive number.

The stoichiometry table $\alpha(1:nC, 1:nF)$ describes the compositions of the different phases (1:nF) in terms of the components (1:nC).

To solve this problem using the simplex algorithm according to its implementation in most codes (e.g. Press et al, 1992), the following tableau is built:

$$\begin{bmatrix} 0 & \mathbf{g}_1 & \dots \mathbf{g}_j \dots & \mathbf{g}_{nF} \\ \mathbf{b}_1 & -\alpha_1^1 & \dots & -\alpha_{nF}^1 \\ \mathbf{b}_i & \dots & -\alpha_j^i & \dots \\ \mathbf{b}_{nC} & -\alpha_1^{nC} & \dots & -\alpha_{nF}^{nC} \end{bmatrix}$$

linear programming with mixtures

When the system comprises mixtures (e.g. solid solutions), whose molar free energies g_i are non-linear functions of their compositions, linear programming can still be used, by discretization of each mixture to a series of phases of fixed composition. That is viable in applications, for example in metamorphic petrology (Connolly, 2005), where each type of mixture potentially present involves a small number of independent composition variables (e.g. Mg-Fe exchange, Tschermak substitution, Na-K exchange). The number of phases may become large, but still within the capabilities of standard linear programming codes.

non-linear optimization

Among the numerous GEM algorithms proposed, the THERIAK method (De Capitani & Brown, 1987) is among the most simple to implement using simple numerical tools. A characteristic of this method is that it adjusts concurrently the composition of the stable assemblage and the compositions of the mixtures that belong to the assemblage.

The THERIAK method combines linear programming and non-linear minimization along the following scheme:

▷ 1. linear minimization: find the assemblage of pure (i.e. invariant) phases that minimizes G ;

▷ 2. basis change: compute the free energies of all invariant phases (including the mixtures' end-members) with respect to the stable assemblage found at step 1; this results in a new set of free energy values, which are 0 for the stable phases, and >0

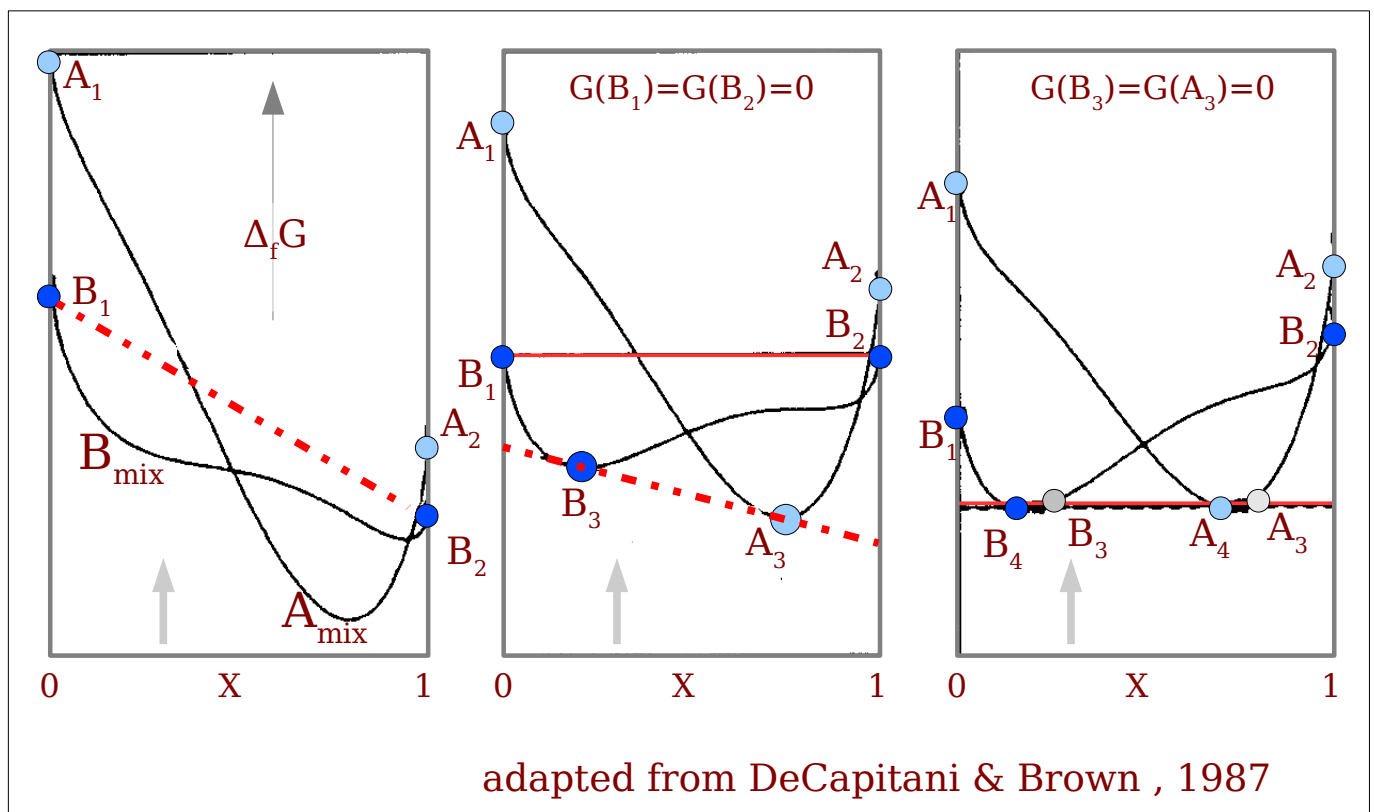
for the others;

▷ 3. non-linear minimization: for each mixture of the chemical space, compute the composition x_{\min} that has the lowest free energy of formation from the current stable assemblage, $g_{\min}=G(x_{\min})$

▷ 4a. if any mixture has a negative g_{\min} , which means the current assemblage is unstable with respect to that mixture, then add that mixture, as a phase of invariant composition x_{\min} , to the set of invariant phases, go to step 1;

▷ 4b. if $g_{\min}>0$ for all mixtures, then exit, the current phase assemblage is stable.

The method is illustrated graphically here (adapted from DeCapitani & Brown, 1987) for the case of a binary system of given bulk composition (arrow on diagram). The system comprises 4 species (A1,B1,A2,B2) that can mutually mix to form two distinct mixtures, called A (A1-A2) and B (B1-B2).



.i/ First, if we consider only the pure phase (A1,B1,A2,B2), the stable assemblage is {B1,B2}

.ii/ Then, the free energies of formation of all end-members are computed with assemblage {B1,B2} as basis (i.e. $G(B1)=G(B2)=0$), and the compositions that minimize the formation energies of the mixtures are computed; it appears that the mixtures A_{mix} and B_{mix} , at compositions A3 and B3 respectively, have negative free energies, which means that a more stable assemblage, for the bulk composition, is {B_{mix} of composition B3, A_{mix} of composition A3}

.iii/ the free energies of formation of the end members are updated, with this new assemblage {B3,A3} as reference ($G(B_{\text{mix}},B3)=G(A_{\text{mix}},A3)=0$), and the compositions that minimize the formation energies of the mixtures are computed again, in this new framework; as the free energies of the mixtures at these compositions are still slightly negative, another loop is executed, with the assemblage {B4,A4} as reference.

This algorithm closely associates the search for the stable assemblage and the adjustment of the mixtures' compositions, in contrast with many other methods of free energy minimization in multi-mixture systems, which compute an equilibrium composition for a given set of phases, and develop a separate procedure to check the supersaturation of other phases.

case of ideal mixtures

With ideal mixtures, the minimization (step 3) has an analytical solution, which can be derived as follows, on the example of a simple one-site mixing model:

$$\text{minimize } G^{\text{ideal}} = \sum x_i g_i^0 + \sum x_i \ln(x_i) \quad \text{s.t.} \quad \sum x_i = 1$$

$$\text{the Lagrangian is } \Lambda(\vec{x}, \lambda) = \sum x_i g_i^0 + \sum x_i \ln(x_i) + \lambda(1 - \sum x_i)$$

The function is convex and has one minimum, found as the stationary point of the Lagrangian:

$$\frac{\partial \Lambda}{\partial x_i} = g_i^0 + 1 + \ln(x_i) - \lambda = 0 \quad ; \quad \frac{\partial \Lambda}{\partial \lambda} = 1 - \sum x_i = 0$$

$$\rightarrow \text{for two components } \mathbf{i, j}, \quad \ln \frac{x_i}{x_j} = -(g_i^0 - g_j^0) \quad \rightarrow \quad x_i = \frac{\exp(-g_i^0)}{\sum_k \exp(-g_k^0)}$$

case of non-ideal mixtures

To take account of deviation from ideality, an "excess energy of mixing" is added to G^{ideal} . The different mixing models implemented in ARXIM are described in the chapter on physical models. A form commonly used to describe the excess interaction is a Margules polynomial development of the form

$$G^{\text{XS}} = \sum W_{i_1 \dots i_p} x_{i_1} \dots x_{i_p} \quad .$$

The compositions minimizing $G^{\text{ideal}} + G^{\text{XS}}$ of each candidate mixture phase can be found numerically, using publicly available optimization tools, but DeCapitani & Brown (1987) describe in detail a specific algorithm, which takes as input the expressions of the chemical potentials of the end-members as functions of their mole fractions in the mixture. This method has been implemented in ARXIM, and its results have been validated against results obtained with programs for constrained optimization such as SQPlab (Gilbert, 2006) or ALGENCAN (Andreani et al, 2007).

examples of GEM equilibrium calculations

Codes dedicated to metamorphic petrology are firstly used (THERMOCALC, TWEEQU) for the estimation of the (T,P) conditions of crystallization of a given mineral assemblage. More recently, the utilization of (T,P) pseudo-sections, constructed using GEM code such as THERIAK or PERPLEX, has become very popular.

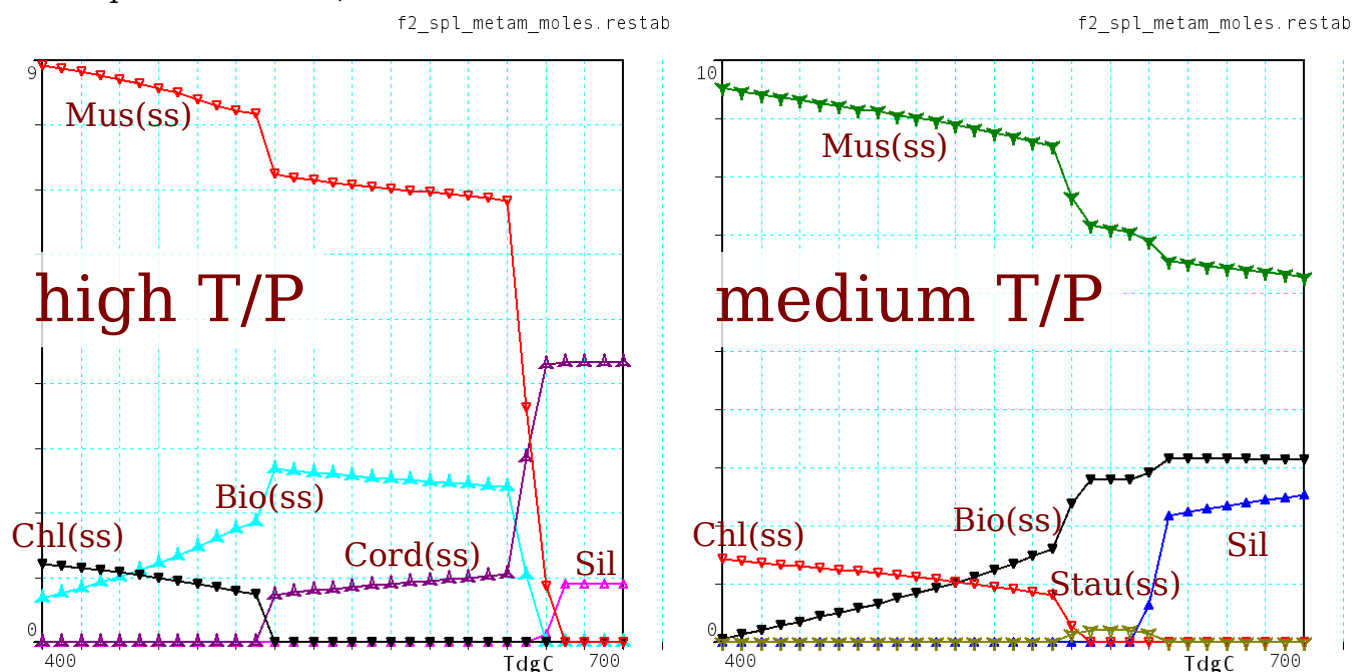
ARXIM does not currently integrate the routines for mapping T,P domains, which would be used for the construction of pseudo-sections, but it can be used more simply to analyze a phase assemblage evolution along a given T,P path.

In the example illustrated here, the stable phase assemblage is computed for a fixed bulk composition, along two series of T,P conditions:

along a high T/P gradient: from 400°C / 1200 bar to 700°C / 3200 bars

along a medium T/P gradient: from 400°C / 3500 bar to 700°C / 6500 bars

The diagrams illustrate the variations in mole numbers of the minerals (quartz and feldspars not shown).



The bulk composition is that of a pelitic rock from the Ryôké belt (Japan), projected on the FMCNKASH system (FeO-MgO-CaO-Na₂O-K₂O-Al₂O₃-SiO₂-H₂O):

```
SYSTEM.GEM
TdgC 600.
Pbar 2300.
H2O 20.0
SiO2 127.
Al2O3 18.3
CaO 1.41
Na2O 2.67
K2O 4.66
FeO 4.80
MgO 3.80
END
```

The following mixing models have been taken in consideration here:

BIOTITE(PHLOGOPITE, ANNITE, EASTONITE, OBIOTITE) HP, 2005
CORDIERITE_SS(CORDIERITE, FE-CORDIERITE, HYDR.CORDIERITE) Avchenko, 2006
OPX(ENSTATITE, FERROSILITE, MG-TSCHER.PYX) Avchenko, 2006
TALC_SS(TALC, FE-TALC, TSCHERMAK-TALC) Avchenko, 2006
CHLORITE(CHLORITE-AF, CLINOCHLORE, AMESITE, DAPHNITE) HP, 2005
MUSCOVITE_SS(MUSCOVITE, PARAGONITE, CELADONITE, FE-CELADONITE) HP, 2005
GARNET(ALMANDINE, PYROPE) ideal
STAUROLITE(MG-STAUROLITE, FE-STAUROLITE) ideal (4))
CHLORITOID(MG-CHLORITOID, FE-CHLORITOID) ideal
FELDSPAR_SS(ALBITE-LOW, MICROCLINE, ANORTHITE) Fuhrman & Lindsley(1988)

physical models implemented in arxim

Analyzing the thermodynamics of a chemical system boils down to the evaluation of gradients of chemical potentials of components. We have thus to evaluate changes of free energy attending all possible reactions among the different species of the chemical space. We describe here the methods used for the computation of the free energy of a species in a phase.

The molar free energy, or chemical potential, of a species j in a phase p at given (T,P) can be written as

$$\mu_j(T, P) = \mu_j^0(T, P) + RT \ln a_j(T, P, \vec{x}_p) \quad (1)$$

where μ_j^0 is the chemical potential of the species j at its reference state (e.g. pure phase for a mineral) at (T,P) and a_j is the activity of the species in the phase p of composition \mathbf{x}_p .

The first term is computed from the equation of state (EoS) of the species at (T,P), the second depends on the EoS and composition of the phase.

We will thus consider successively:

- how to obtain the chemical potential μ_j^0 of a species in its reference state at the (T,P) condition of interest,
- how to compute the activity a_j of a species in a phase, as a function of phase composition \mathbf{x}_p .

thermodynamic data for reactions

The free energy is written in (1) for an individual species, but, rather than with absolute values, we are actually concerned with relative changes of free energy, ΔG 's, for all possible reactions between species of the chemical space.

For a reaction \mathbf{R} described by a vector \mathbf{v}^R of stoichiometric coefficients, i.e. for a reaction

$$\sum_j v_j^R S_j = 0 \quad ,$$

the change in chemical potential is obtained by:

$$\sum_j v_j^R \mu_j(T, P) = \sum_j v_j^R \mu_j^0(T, P) + RT \ln \left(\prod_j (a_j)^{v_j^R} \right)$$

or

$$\Delta G_R(T, P) = \Delta G_R^0(T, P) + RT \ln \left(\prod_j (a_j)^{v_j^R} \right) \quad ,$$

where $\Delta G_R^0(T, P) = \sum_j v_j^R \mu_j^0(T, P)$

Hence, the database can be reduced to a set of ΔG° 's, or so-called $\log K$'s ($\log K = -\Delta G^\circ / RT \ln 10$) , of all possible independent reactions R among species of the chemical space.

two types of thermodynamic databases: logK and HSV

Programs currently available for thermodynamics of geo-systems are often connected with a specific type of database, which restrict their application to a specific domain (e.g. hydro-geochemistry, metamorphism, ...). One of the objectives of ARXIM is to develop tools with the

largest range of applications. Fundamental to this respect is the ability to interface the ARXIM tools with various formats of thermodynamic databases.

Programs for modeling water-rock interaction at sub-surface conditions often rely on databases that contain the $\log K$'s of reactions among aqueous species and pure substances (minerals and gases), for a given discrete series of T,P conditions.

On the other hand, programs for metamorphic petrology (e.g. TWEEQU [Berman, 1988], THERMOCALC [Holland & Powell(1998)], THERIAK-DOMINO [DeCapitani & Brown, 1987]), ... need a more complete dataset, in order to allow the calculations of molar thermodynamic properties at any consistent (T,P) condition, on the basis of dedicated equations of state (EoS) for each pure phase (mineral or fluid) of interest. Such databases are referred here as '*HSV databases*', for they allow the separate computation of molar enthalpy H, entropy S and volume V.

To use such data in aqueous geochemistry, we need the same type of approach for species dissolved in aqueous solutions: the Helgeson -Kirkham -Flowers (HKF) equation of state, and its related databases, plays a central role, making a bridge between metamorphic petrology and aqueous geochemistry

The $\log K$ approach has the advantage of simplicity, but it presents some limitations: it yields only Gibbs free energy data, relevant for equilibrium analysis at some T,P points, whereas the HSV approach makes possible, within a divariant T,P domain, the calculation of G and of other important functions such as the enthalpy, entropy and volume changes of a reaction.

ARXIM can work directly with $\log K$ databases, but it includes also tools for computing the $\log K$'s of reactions directly from equations of states of the species involved.

Tools are currently available for calculations on two main types of species:

- pure phases (minerals and gases),
- aqueous species, according to the HKF (Helgeson -Kirkham -Flowers) equation of state.

calculation of thermodynamic properties of minerals from HSV data

A HSV table will typically contain, for each species, molar thermodynamic properties of the pure species at some standard conditions (e.g. $T^\circ = 298.15 \text{ K}$ / $P^\circ = 1 \text{ bar}$): enthalpy of formation ΔH_f° , entropy S° , volume V° , heat capacity C_p° , and parameters

For minerals, the reference state is the pure phase at the T,P conditions of interest.

Calculation of a thermodynamic state function Ξ (such as G, H, S, V,...) at (T,P), from data "from the table", for the pure phase at some standard conditions (e.g. $T^\circ = 298.15 \text{ K}$ / $P^\circ = 1 \text{ bar}$), can be based on a two step integration:

$$\Xi_{T,P} = \Xi_{T^\circ, P^\circ} + \int_{T^\circ, P^\circ}^{T,P} \left(\frac{\partial \Xi}{\partial T} \right)_P dT + \int_{T,P^\circ}^{T,P} \left(\frac{\partial \Xi}{\partial P} \right)_T dP$$

The following fundamental relations are used for this integration:

- ◆ for entropy S: $\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_p}{T}$ and $\left(\frac{\partial S}{\partial P} \right)_T = -\left(\frac{\partial V}{\partial T} \right)_P$
- ◆ for enthalpy H: $\left(\frac{\partial H}{\partial T} \right)_P = C_p$ and $\left(\frac{\partial H}{\partial P} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P$
- ◆ for volume V: $\left(\frac{\partial V}{\partial T} \right)_P = \alpha \cdot V_{298}^0$ and $\left(\frac{\partial V}{\partial P} \right)_T = -\beta \cdot V_{298}^0$

for Gibbs free energy G , $\left(\frac{\partial G}{\partial T}\right)_P = -S$ and $\left(\frac{\partial G}{\partial P}\right)_T = V$

The thermodynamic databases used in ARXIM contain, on a molar basis, all data necessary to implement such calculations:

- standard enthalpy of formation from the elements $\Delta_f H_{Tref, Pref}$,
- standard entropy $S_{Tref, Pref}$,
- heat capacity C_p as a function T , e.g. Maier-Kelly expression,
- volume $V_{Tref, Pref}$, and the compressibility factors α and β , or a polynomial expression $V(T, P)$.

Practically, concerning minerals, ARXIM uses currently two types of 'HSV' databases:

◆ either "SupCrt-compatible", such as used by the program SupCrt92 (Johnson et al, 1992); data on minerals are found in the same file (e.g. slop98.dat) that contain the HKF parameters for aqueous species;

◆ or a "Berman-compatible" format, such as used by TWEEQU or by THERIAK, which are programs for equilibrium calculations of metamorphic assemblages. THERIAK databases include, in addition to the Berman data set, data for the THERMOCALC program by Holland & Powell (1998) formatted à la Berman.

The main differences between the two data sets, SUPCRT vs THERIAK, are:

- ▷ different forms of polynomial fits for the temperature dependence the heat capacities,
- ▷ the absence of T,P dependence of molar volumes of minerals in SupCrt92;
- ▷ more importantly, Gibbs free energy can be either derived from (H_{ref}, S_{ref}) or from (G_{ref}, S_{ref}) . SupCrt92 uses $\Delta_f G^\circ(Tref, Pref)$ to compute Gibbs free energy at (P,T), whereas calculation à la Berman-Theriak uses $\Delta_f H^\circ(Tref, Pref)$. In the latter case, $\Delta_f G^\circ(Pref, Tref)$ is tabulated, but not used.

Benson-Helgeson Versus Berman-Brown Convention

As already mentioned concerning databases, a given database is designed, primarily, for the calculation of thermodynamic functions according to a given specific convention.

Whereas SupCrt

Taking as an example the computation of the Gibbs free energy of a mineral of formula $A(n)B(m)$,

- one convention, referred to as "Benson-Helgeson convention" (Anderson & Crerar, 1993), is to consider the "apparent ΔG of formation from the elements" of the compound as the difference between G of compound at (P,T) and the G 's of the elements A and B at (P_{ref}, T_{ref}) :

$$\Delta_{app} G_{AnBm, BenHel}(P, T) = G_{AnBm}^0(P, T) - [n \cdot G_A^0(P_r, T_r) + m \cdot G_B^0(P_r, T_r)]$$

- another convention, referred to as "Berman-Brown convention" (Anderson & Crerar, 1993), is to consider the apparent ΔG as the difference between G at (P,T) and the enthalpies of the elements A and B at (P_{ref}, T_{ref}) :

$$\Delta_{app} G_{AnBm, BerBro}(P, T) = G_{AnBm}^0(P, T) - [n \cdot H_A^0(P_r, T_r) + m \cdot H_B^0(P_r, T_r)]$$

- comparing the two expressions, and writing $G^\circ = H^\circ - T_{ref} \cdot S^\circ$ at (P_{ref}, T_{ref}) for the

elements, the following relation is obtained between the apparent G's of compounds calculated according to the two conventions:

$$\begin{aligned} \Delta_{app} G_{AnBm, BenHel}(P, T) \\ = G_{AnBm}^0(P, T) - [n.H_A^0(P_r, T_r) + m.H_B^0(P_r, T_r)] + T_r \cdot [n.S_A^0(P_r, T_r) + m.S_B^0(P_r, T_r)] \\ = \Delta_{app} G_{AnBm, BerBro}(P, T) + T_r \cdot [n.S_A^0(P_r, T_r) + m.S_B^0(P_r, T_r)] \end{aligned}$$

or

$$\begin{aligned} \Delta_{app} G_{A_1(v_1) \dots A_n(v_n), BenHel}(P, T) \\ = \Delta_{app} G_{A_1(v_1) \dots A_n(v_n), BerBro}(P, T) + T_r \cdot \sum_{i=1}^n v_i \cdot S_{A_i}^0(P_r, T_r) \end{aligned}$$

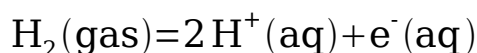
The values of the entropy of the elements at (P_{ref}, T_{ref}) are found in the element database. Values tabulated in the file *elements.dtb* of the distribution are those reported by Robie & Hemingway (USGS report), and are consistent mostly with the CODATA compilation. They have been found to yield consistent values between databases for supcrt92 and databases from Berman or Holland-Powell.

the entropy of the electronic charge

The electron (i.e. the "element" that accounts for the charge on aqueous species) is assigned an entropy, equal to that of hydrogen, which is itself half the entropy of $H_2(gas)$ at (T_{ref}, P_{ref}) .

This stems from the convention that, at all temperatures, the hydrogen ion H^+ has zero entropy, as well as zero values of Gibbs energy of formation and heat capacity.

Then, we must also have a zero variation of entropy for the reaction of formation of H^+ , which is written



$$2.S^0(H^+(aq), T) + 2.S^0(e^-, T) = S^0(H_2(gas), T)$$

$$\text{with } S^0(H^+(aq), T) = 0 \quad , \quad S^0(e^-, T) = \frac{1}{2} S^0(H_2(gas), T)$$

Then, using the CODATA values, $S^0(e^-, 298.15K) = 65.340 \text{ J/K/mol}$

calculation from G,S vs. calculation from H,S

The "Benson-Helgeson convention", which is that used in SupCrt, is used for calculations with SupCrt-compatible databases. For such databases, **G at (T,P) is computed from G, S at (T_{ref}, P_{ref})**.

On the contrary, the "Berman-Brown convention" is used with "Berman-compatible" databases. $G(P_{ref}, T_{ref})$ is sometimes tabulated in such files (e.g. files used with TWEEQU), but it is not used: **G at (P,T) is computed from H, S at (T_{ref}, P_{ref})**. Then, the term M%S0Ele is added to M%G to obtain a value compatible with M%G calculated from SupCrt-compatible databases.

In ARXIM, the two different methods are taken into account in modules specific to each type of database.

example, equation of state according to Berman (1988)

For a given mineral, the Berman (1988) database gives:

> molar enthalpy of formation at $(T_{\text{ref}}, P_{\text{ref}})$,

> molar entropy at $(T_{\text{ref}}, P_{\text{ref}})$,

> molar heat capacity at P_{ref} , as a polynomial function of temperature:

$$C_p = K_1 + K_2 T + K_3/T^2 + K_4/T^{1/2} + K_5 T^2 + K_6/T + K_7 T^{1/2} + K_8/T^3 + K_9 T^3$$

> molar volume V° at $(T_{\text{ref}}, P_{\text{ref}})$ and parameters v_1 to v_4 describing its dependence on T and P :

$$V = V^0 [1 + v_1 (T - T_{\text{ref}}) + v_2 (T - T_{\text{ref}})^2 + v_3 (P - P_{\text{ref}}) + v_4 (P - P_{\text{ref}})^2]$$

thermodynamic properties of a pure gas

For gases, the conventional reference state is the pure gas at (T, P°) , where T is the temperature of interest and P° is a fixed pressure (standard pressure $P=1\text{bar}$, or $P=1\text{ atm} = 1.013\text{ bar}$).

The conventional reference for a gas is not the same as that used for species in mineral or aqueous phases; to be consistent with other species, the reference potential of a gas can be brought from (T, P°) to (T, P) , giving a new reference potential μ^* defined by the relation:

$$\mu^*(T, P) = \mu^0(T, P^0) + \int_{P^0}^P v(T, P) dP$$

where the volume function is computed according to the relevant EoS.

thermodynamic properties of aqueous species at reference state

The standard state properties of solute aqueous species are calculated according to the HKF model (Helgeson-Kirkham-Flowers: Helgeson et al., 1981; Tanger & Helgeson, 1988), which, to a large degree, can be considered (Anderson, 2005) as an "equation of state" for aqueous solutions.

Results of ARXIM calculations have been checked for accuracy against results of similar calculations with SUPCRT92 (Johnson et al., 1992), a Fortran 77 program specific for the HKF model.

The HKF model depends on the calculation of the physical properties of H_2O (density and dielectric constant and their derivatives against T and P): in HKF / SUPCRT92, they are computed according to the equation of state of H_2O of Haar et al. (1984), also implemented in ARXIM.

mixing models, mixtures and solutions

Following a IUPAC recommendation, we call "solution" a phase of variable composition where a species, called the solvent, plays a specific role (e.g. it is dominant on the other species, the solute species). The term "mixture" is used for phases where the end-members are all treated in the same way: this is the case for gaseous mixtures and so-called "solid solutions".

To describe the composition of a mixture, a symmetric concentration scale is used, generally the mole fraction scale.

$$x_i = \frac{n_i}{\sum_{j \in \phi} n_j}$$

where the n_j are the mole numbers of end-members in the mixture ϕ .

For a solution, an asymmetric scale is used. The preferred concentration scale for solute species in thermodynamics of aqueous solution is the molality:

$$m_j = \frac{n_j}{M_w n_w}$$

where n_j is the mole number of the solute, n_w that of the solvent, M_w its molecular weight (in kg).

note on conversions between molality and mole fraction

$$x_{j \neq w} = \frac{n_j}{n_w + \sum_{k \neq w} n_k} = \frac{m_j}{\frac{n_w}{M_w} + \sum_{k \neq w} m_k}$$

$$\text{thus } \ln(m_j) = \ln(x_j) + \ln\left(\frac{1}{M_w} + \sum_{k \neq w} m_k\right),$$

$$\text{and } \ln(x_w) = -\ln\left(1 + M_w \sum_{k \neq w} m_k\right)$$

$$\text{And also, } x_j = x_w \frac{n_j}{n_w} = x_w \frac{m_j}{1/M_w} \rightarrow \ln(m_j) = \ln(x_j) - \ln(M_w x_w)$$

activity models

The activity of a species, $a_j = \exp((\mu_j - \mu_j^\circ)/RT)$, measures how the potential of a species changes when it is brought from its reference state to its current state in the system.

In other words, the activity model describes how the activity of a species in a given phase depends on the composition of the phase.

activity coefficient :

The activity - composition dependency is described in terms of deviation from some defined ideal behavior, such as, for gases, *the perfect gas*. This deviation is represented by an activity coefficient, whose definition will depend on the conventions used for the different types of species, especially the concentration scale.

for a mineral species:

the reference state is the pure mineral at (T, P) , and the concentration scale is the mole fraction x_j .

$$\mu_j(T, P) = \mu_j^0(T, P) + RT \ln x_j + RT \ln \lambda_j(T, P, \vec{x}),$$

where λ_j is the activity coefficient (mole fraction based).

for a gas species:

the reference state is the pure ideal gas at (T, P^0) , and the concentration scale is the mole fraction x_j .

$$\mu_j(T, P) = \mu_j^0(T, P^0) + RT \ln x_j \frac{P}{P^0} + RT \ln \phi_j(T, P, \vec{x}) ,$$

where ϕ_j is the fugacity coefficient.

for an aqueous solute species:

the reference state is the ideal (i.e. "at infinite dilution") at one molar concentration, at (T, P) , and the concentration scale is the molality.

$$\mu_j(T, P) = \mu_j^0(T, P) + RT \ln m_j + RT \ln \gamma_j(T, P, \vec{x}) ,$$

where γ_j is the activity coefficient (molality based).

activity models for aqueous species

An aqueous solution containing dissolved charged species is a typical example of "solution". Specific routines for speciation and activity corrections are implemented for the aqueous solutions.

Aqueous solutions being electrolytes, the activity - composition relation is strongly controlled by electrostatic interactions. An essential parameter in that respect is the ionic strength of the electrolyte, which is defined as

$$I = \frac{1}{2} \sum_j m_j z_j^2$$

where the summation extends on all charged solute species of molality m_j and charge z_j . For instance, the ionic strength of a fully dissociated 1:1 electrolyte equals molality.

The activity models currently implemented in ARXIM are based either on adaptations of the Debye-Hückel equation, or on the Pitzer's equations.

In ARXIM, the model used in a run is selected by an argument (DH1, DAV_1, PITZER, ...) to the keyword MODEL of the block SOLVENT.

model: ideal

An ideal solution is commonly defined by the condition

$$\text{activity} = \text{concentration} \quad (a_j = c_j)$$

Applied to the dual concentration scale used for aqueous solution, we would have:

♦ for a solute species j , $\gamma_j = 1$

$$a_j = c_j = m_j = \frac{n_j}{M_w n_w} ,$$

where M_w is the molecular weight (in kg) of solvent species w ,

♦ for the solvent, $\lambda_w = 1$

$$a_w = c_w = x_w = \frac{n_w}{n_w + \sum_{j \neq w} n_j} = \frac{1}{M_w + \sum_{j \neq w} m_j}$$

However, the different concentration scales used for solvent and solutes lead to inconsistencies. Actually, the statement "activity = concentration" is valid for an ideal gas, where concentration is mole fraction for all components, it is valid also, to some extent, for other symmetric ideal mixtures, but, when applied to the asymmetric solution model used for electrolytes, it leads to inconsistencies.

Instead of "ideal", the limiting model, corresponding to vanishing interactions between species, is better the "infinitely dilute" condition, where the activity of a solute is its molality, and the solvent activity is 1, which is also the solvent mole fraction in infinitely dilute solutions.

In Arxim, when the aqueous solution model selection is IDEAL, activity is molality for solute species and 1 for the solvent.

the Debye-Hückel equation

Debye & Hückel (1923) derived the following equation for the activity coefficient of a charged solute species:

$$\log_{10} \gamma_j = - \frac{A_{DH} z_j^2 \sqrt{I}}{1 + a_j^0 B_{DH} \sqrt{I}}$$

where

a_j^0 is the "ion size parameter" (more precisely, a "distance of closest approach"), specific to the ionic species considered

A_{DH} and B_{DH} are functions of the solvent properties and temperature,

$$A_{DH} = (2\pi N_a \rho)^{1/2} e^3 (4\pi \epsilon_0 \epsilon \cdot k T)^{-3/2} / \ln 10$$

$$B_{DH} = (8\pi N_a \rho)^{1/2} \cdot e \cdot (4\pi \epsilon_0 \epsilon \cdot k T)^{-1/2}$$

or

$$A_{DH} = 1.824 \cdot 10^6 \rho^{1/2} (\epsilon T)^{-3/2}$$

$$B_{DH} = 50.2915 \rho^{1/2} (\epsilon T)^{-1/2}$$

where ρ and ϵ respectively are the density and dielectric constant of pure water at (T,P). These are obtained from the equation of state of water. ARXIM implements the Haar et al. (1984) equation, which is also necessary for the HKF model.

The validity of the equation is known to be limited to very low values of the ionic strength ($I < 0.005$?). It is generally not used under this simple form, but with an additional term, function of ionic strength.

model: Davies

This model (Davies, 1962), widely used in subsurface hydrochemistry codes, is a purely empirical adaptation of the Debye-Hückel model; it is supposed to be valid for ionic strength up to around 0.1-0.5 mole/kg (?).

♦ for charged solute species,

$$\log_{10} \gamma_j = -A_{DH} z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$$

Notice the simplified denominator : No size parameter here, the charge is the only species-specific parameter.

Notice also that some texts mention a coefficient of 0.3 instead of 0.2 ...

♦ for neutral solute species, this relation would give unit activity, but, as an option, ARXIM can use an simple empirical correction to take account of the salting-out effect:

$$\log_{10} \gamma_j = 0.064 \cdot I$$

♦ for the solvent, this model is commonly used with water activity set to 1 or to its mole fraction.

However, for thermodynamical consistency, the activity can be computed according to an expression derived by Wolery (1992):

$$\log_{10} a_w = M_w \cdot \left[\frac{2}{3} A_{DH} I^{3/2} \sigma(\sqrt{I}) - 0.4 A_{DH} I^2 - \frac{1}{\ln 10} \cdot \sum_{j \neq w} m_j \right]$$

$$\text{where } \sigma(x) = \frac{3}{x^3} \left[1 + x - \frac{1}{1+x} - 2 \ln(1+x) \right]$$

model: B-dot à la Helgeson (1969)

The B-dot equation implemented in ARXIM is that proposed by Helgeson (1969). It is also an extension of the Debye-Hückel equation, obtained by adding a "B-dot" empirical correction term to the classical DH equation for charged species.

♦ for charged species,

$$\log_{10} \gamma_j = -\frac{A_{DH} z_i^2 \sqrt{I}}{1 + a_i^0 B_{DH} \sqrt{I}} + \dot{B} I$$

The B-dot parameter is a function of temperature and of the nature of the dominant electrolyte.

The B-dot values tabulated in Helgeson (1969) for NaCl, for temperature from 25°C to 300°C and for $m(\text{NaCl}) = 0$ to 3, are fitted as follows in ARXIM:

$$\dot{B}(T_K) = -0.616616 + 6.90440 \cdot 10^{-3} T - 2.73898 \cdot 10^{-5} T^2 + 4.87313 \cdot 10^{-8} T^3 - 3.26030 \cdot 10^{-11} T^4$$

♦ for neutral solute species,

the B-dot equation, as B-dot is positive, would fit a "salting out effect", but it is commonly not used for such species.

ARXIM gives the option to use, following the usage in EQ3NR (Wolery, 1992; also used in Xu et al,), the activity coefficient of CO₂ in a NaCl solution of the same ionic strength, according to an expression proposed by Drummond (1981):

$$\ln \gamma_j = (-1.0312 + 0.0012806 T_K + 255.9/T_K) \cdot I - (0.4445 - 0.001606 \cdot T_K) \frac{I}{1+I}$$

♦ for the solvent,

the activity is computed according to an expression derived by Wolery (1992):

$$\log_{10} a_w = M_w \left[\frac{2}{3} \cdot A_{DH} \cdot I^{3/2} \sigma(4 \cdot B_{DH} \sqrt{I}) - \dot{B} \cdot I^2 - \frac{1}{\ln 10} \cdot \sum_{j \neq w} m_j \right]$$

where $\sigma(x) = \frac{3}{x^3} \left[1 + x - \frac{1}{1+x} - 2 \ln(1+x) \right]$

model: HKF (Helgeson et al, 1981)

♦ for charged species, [p 1478]

$$\log_{10} \gamma_j = -\frac{A_{DH} z_i^2 \sqrt{I}}{1 + a^0 B_{DH} \sqrt{I}} + \Gamma_y + (\omega_j^{\text{abs}} b_{\text{NaCl}} + b_{\text{Na+Cl-}} - 0.19(|z_j| - 1)) I ,$$

where

: a^0 is the "ion size parameter" (a minimum distance of charge separation),

: $= 3.72$ Angstroms for NaCl-dominant electrolyte (Tab.2, p.1298)

: $\Gamma_y = -\log(x_w) = \log(1 + M_w \sum m_j)$

: $b_{\text{Na+Cl-}}$ is the short range interaction parameter for NaCl,

$= (T,P)$ -dependent [Tab.30, p 1477], $-9.77 \cdot 10^{-2}$ at (25°C / 1 bar)

: b_{NaCl} is the solvation parameter for NaCl

$= (T,P)$ -dependent [Tab.29, p. 1477], $2.47 \cdot 10^{-3}$ at (25°C / 1 bar)

: ω_j^{abs} is the absolute Born coefficient of species j (eq. 130, p.300)

$$\omega_j^{\text{abs}} = \frac{\eta z_j^2}{r_{e,j}}$$

Databases dedicated to the HKF model (e.g. used with SUPCRT92) contain data for ω , the conventional Born coefficient, which is related with ω^{abs} by:

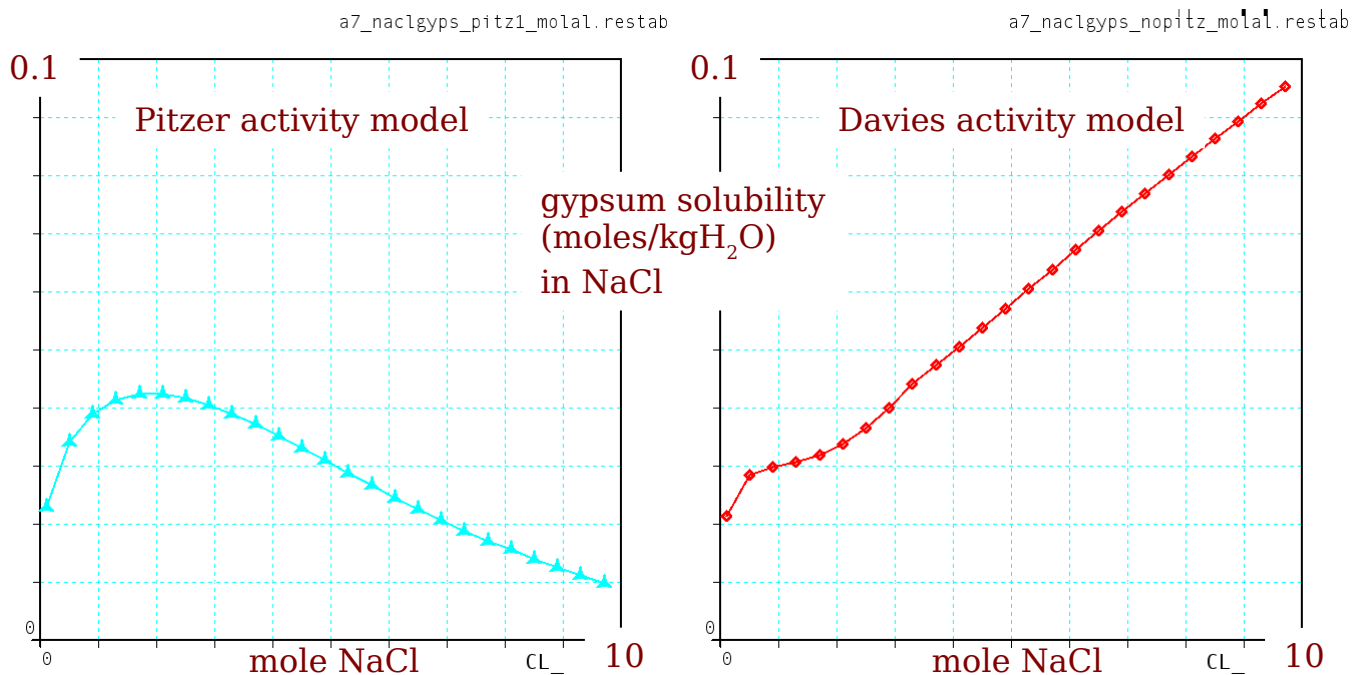
$$\omega_j = \omega_j^{\text{abs}} - z_j \omega_{\text{H}^+}^{\text{abs}} \quad [\text{equ.135, p.1300}], \text{ with } \omega_{\text{H}^+}^{\text{abs}} = 0.5387$$

model: Pitzer

Descriptions of the Pitzer's method are found in many textbooks and papers (e.g. Pitzer, 1973, 1991; Anderson & Crerar, 1982).

Pitzer's model is an "interaction model": interactions between species are modeled by a set of specific interaction coefficients between a limited number of charged species (e.g. Na^+ , Cl^- , ...). This is in contrast with the "association models" such as

the HKF model, where interaction between Na^+ and Cl^- is taken into account by the activity of a complex neutral species NaCl .



Comparison of gypsum / anhydrite solubility in NaCl at (25°C, 1bar), computed with a Pitzer activity model (left) and with the Davies activity model.

mixing models for gas mixtures

Note: Activity vs Fugacity

For a species of a gas mixture, the activity can be defined as the ratio of its fugacity in the mixture at (T,P) over the fugacity of the corresponding pure phase at the same (T,P).

The chemical potential of a species j in a gas mixture at T,P is

$$\mu_j(T, P) = \mu_j^0(T, P^0) + RT \ln(\chi_j P) + RT \ln \phi_j(T, P, \vec{\chi})$$

For gaseous mixtures, some classical cubic equation of states (Redlich & Kwong, Peng & Robinson, Kerrick & Jacobs) are implemented. No generic cubic model is currently available in ARXIM, but, the code being open source, other cubic equations can be programmed by the user, based on the existing ones.

mixing models for mineral phases

For mineral mixtures, generic models are currently implemented for two types of mixing models generally encountered in petrology: molecular mixing and site-mixing models (Ganguly, 2008). Excess mixing, when necessary, is modeled by a Margules polynomial expression.

The block structure of the input format, and the modular structure of the code will allow the implementation of other types of models.

Specific models not amenable to these generic models can be added to the code, by writing a routine that takes as input the mole fractions of the independent

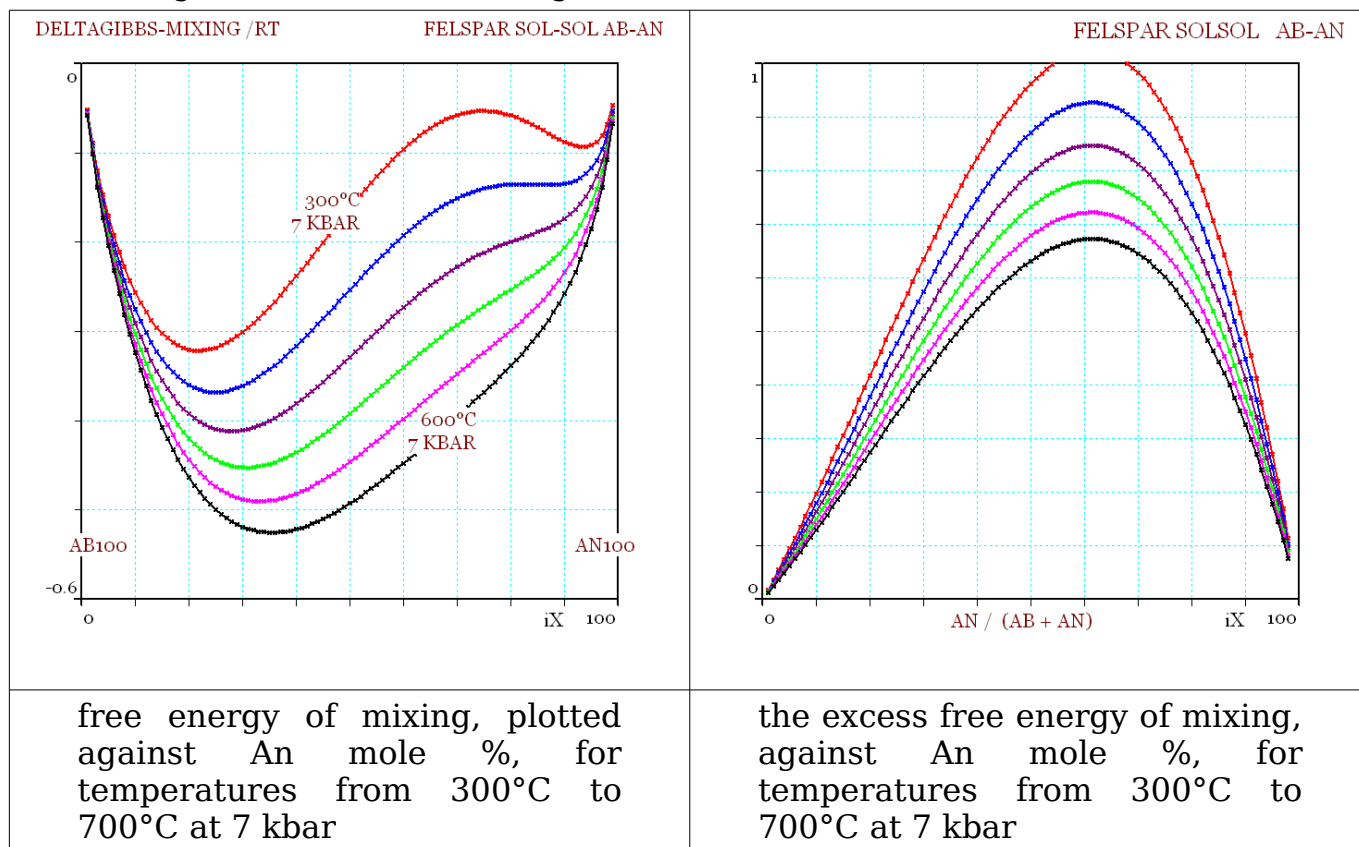
components of the mixture and gives their activities in the mixture. This routine will be used to compute both the Gibbs free energy of mixing at a given composition and the descent direction for minimization. An expression of the mixing free energy is not needed, but the activity expressions implemented should be thermodynamically consistent: that can be checked, for example, by the results of cross differentiation, which should give:

$$\frac{\partial \ln(a_i)}{\partial n_j} = \frac{\partial \ln(a_j)}{\partial n_i} ; \forall i \neq j$$

tests of the implementation of mixing models

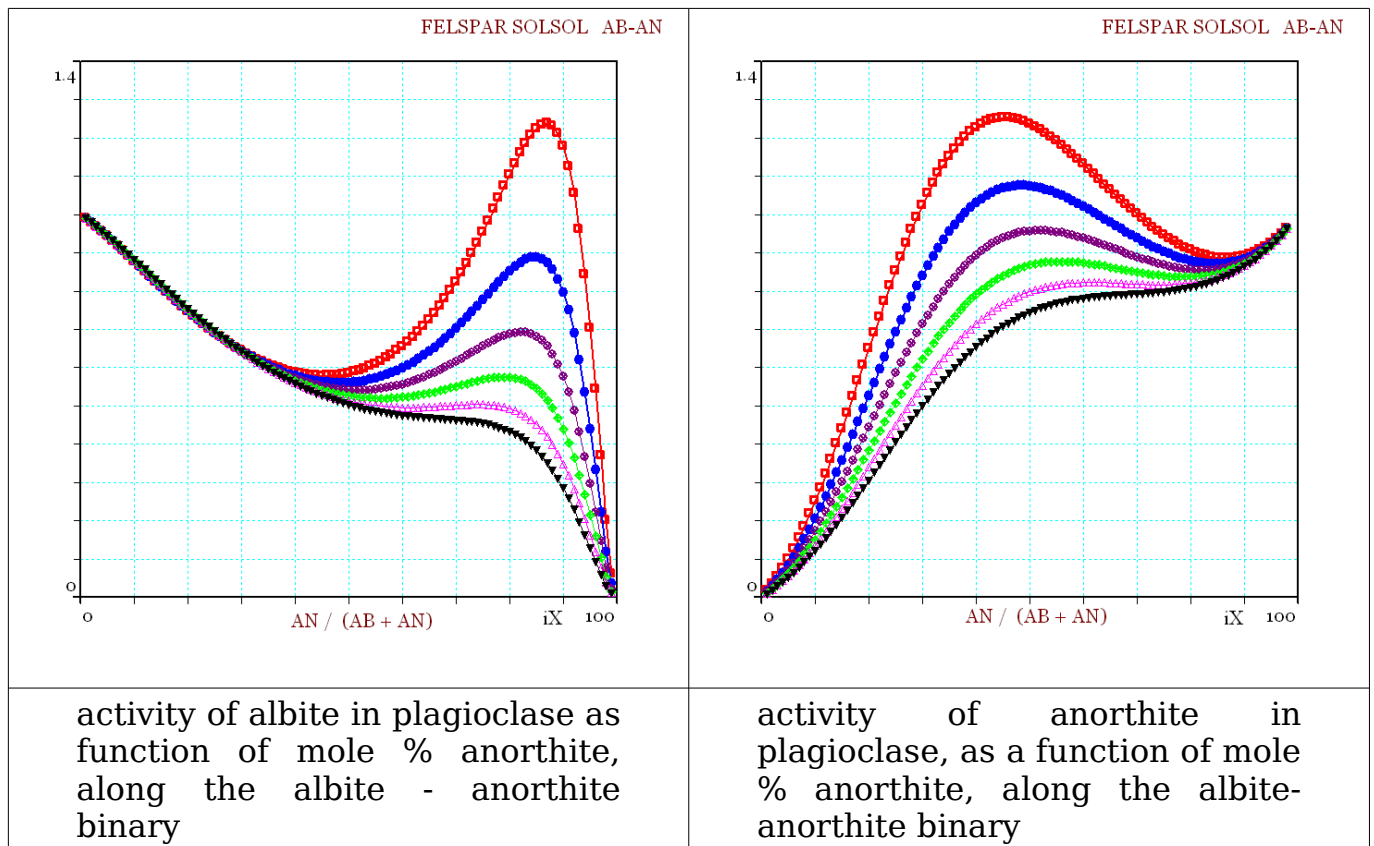
The validity of the implementation of a given mixture model can be tested using utility routines that computes the free energy variations upon mixing (ideal mixing, excess mixing) and the activities of two end-members of the mixture, when their relative proportions are incrementally changed.

For example, for the plagioclase mixing model of Fuhrman & Lindsley (1988), the following X-G and X-Activities diagrams are obtained:

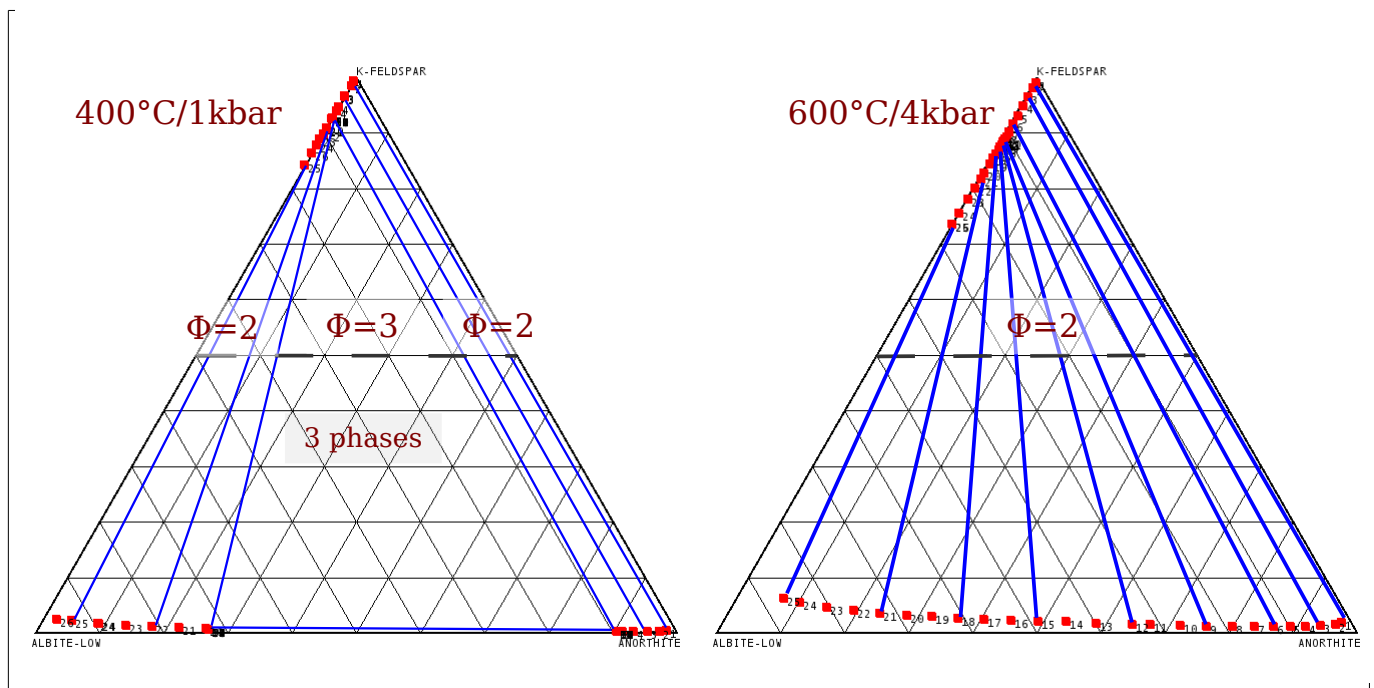


This plot of G_{Mixing} versus $An/(Ab+An)$, calculated at various temperatures and at $P=7$ kbar, shows how the width of the miscibility gap (as defined by the "common tangent" construction) progressively decreases as temperature increases.

The change of convexity in the G-X curves above originates in the excess mixing term, calculated according to the Margules parameters implemented in the mixture model. The diagram on right illustrates the asymmetric shape of the mixing term, and its progressive decrease with increasing T , which results in evolution toward continuous miscibility of the solid solution.



The implementation of a mixing model can also be tested by running equilibrium calculations along a composition path, using the free energy minimization module GEM. An example is given below for the feldspar mixing model of Fuhrman & Lindsley (1988), where the compositions of coexisting alkali-feldspar and plagioclase are shown for a system composition changing from $\text{Ab}_{49}\text{Or}_{50}\text{An}_1$ to $\text{Ab}_1\text{Or}_{50}\text{An}_{49}$.



kinetic database

The kinetic database contains the parameters for the methods that compute the rates of precipitation / dissolution of kinetic phases (minerals) as a function of fluid composition, saturation state with respect to fluid (quantified by Q/K), and temperature.

The specific rate (mole /time /surface) of phase iM is calculated as the product of two factors, $R_{Act}(iM)$. $R_{QsK}(iM)$, where

▷ R_{QsK} is an "affinity factor", which is a function of the saturation state of the phase against the fluid.

▷ R_{Act} is an "activity factor", a function of the chemical characteristics of the fluid (the nature and activities of "inhibitors" and "activators"),

R_{QsK} is computed as $(1 - (Q/K)^\alpha)^\beta$, where α and β are parameters with default value 1.

R_{Act} is computed as the sum of up to N terms, each being the product of a temperature-dependent factor, $k(T)$, by the activity of an aqueous species raised to a given power.

The following extract from database kinetic_usgs.dtb illustrates the format used to input the parameters:

```
ALBITE USGS2004-1068
& DISSOL 1 1 QsK
& DISSOL 10.6 65 H+ 0.457
& DISSOL 15.6 71 H+ -0.572
& DISSOL 12.56 69.8 H2O 0
& PRECIP 1 1 QsK
& PRECIP 10.6 65 H+ 0.457
& PRECIP 15.6 71 H+ -0.572
& PRECIP 12.56 69.8 H2O 0
```

The keywords DISSOL/ PRECIP signals whether the subsequent parameters are for dissolution or precipitation factor.

Then the line should contain two numbers, followed by either the keyword QSK, or the name of an aqueous species.

If the word is QSK, then the numbers are the parameters α and β of the *affinity factor*:

$$R_{QsK} = \left(1 - \left(\frac{Q}{K}\right)^\alpha\right)^\beta, \text{ or } R_{QsK} = (1 - e^{-\alpha \Delta G/RT})^\beta$$

If it is a species name, the numbers are the parameters of the "*activity factor*": successively the colog of coefficient K at 25°C and the activation energy (in kJoules) used for computing K at another temperature T (in Kelvin).

In the example given here, the "activity factor" would be computed as follows, as a sum of three terms,

$$\begin{aligned} R_{Act} = & 10^{-10.6} \cdot e^{65000(\frac{1}{298} - \frac{1}{T})/R} a_{H+}^{0.457} \\ & + 10^{-15.6} \cdot e^{71000(\frac{1}{298} - \frac{1}{T})/R} \\ & + 10^{-12.56} \cdot e^{69800(\frac{1}{298} - \frac{1}{T})/R} a_{H+}^{-0.572} \end{aligned}$$

In this example, the rate appears as a combination of three mechanisms, one that dominates in low-pH fluid, one at neutral condition, one at high-pH (exponent to H^+ activity being negative).

More complex mechanisms, involving up to three species, can be taken into account, as illustrated by the example of pyrite (Palandri and Kharaka, 2004):

```
PYRITE USGS2004-1068
& DISSOL 7.52 56.9 H+ -0.5 FE+3 0.5
& DISSOL 4.55 56.9 H2O 0 O2(AQ) 0.5
```

$$R_{\text{Act}} = 10^{-7.52} \cdot e^{56900(\frac{1}{298} - \frac{1}{T})/R} a_{H^+}^{0.5} a_{Fe+3}^{0.5} \\ + 10^{-4.55} \cdot e^{56900(\frac{1}{298} - \frac{1}{T})/R} a_{H_2O} a_{O_2(aq)}^{0.5}$$

Values currently tabulated in kinetic_usgs.dtb are essentially retrieved from a compilation by Palandri and Kharaka (2004). Experimental data on precipitation kinetics are scarce, most data in this compilation come from dissolution experiments, and parameters for precipitation kinetics are taken identical to dissolution parameters.

The database format, however, allows implementation of distinct laws for precipitation and dissolution, as illustrated by the following example, which reproduces parameters used by Soler & Lasaga (1998):

```
GIBBSITE
& DISSOL 7 9 QSK
& DISSOL 10.28 60 H+ 0.29
& DISSOL 11.73 60 H2O 0
& DISSOL 9.94 60 H+ -0.3
& PRECIP 1.1 0 QSK
& PRECIP 10.67 60 H+ 0.29
& PRECIP 12.12 60 H2O 0
& PRECIP 10.32 60 H+ -0.3
```

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