

Parameters for mineral-aqueous reaction kinetics

(devPhase and devKinMet projects)

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1. Theoretical background

Most mineral-aqueous (mineral-gas) kinetic rate equations can be expressed using a general form (after [Schott et al., 2012]), written here with GEM notation indices as:

$$\frac{dn_k}{dt} = -A_k \sum_r^{n(r)_k} \left\{ \theta_{k,r} \cdot \left(\kappa_{k,r}^o \Lambda_{k,r} e^{\frac{-E_{k,r}}{RT}} \right) \cdot f(\Pi a)_{k,r} \cdot f(\Omega)_{k,r} \right\} = R_p A_k \quad (1.1)$$

where $k \in \Phi$ is the index of (solid) phase;

n_k is the mole amount of k -th phase at time t ;

A_k is the current surface area (or pore volume) of k -th phase in m^2 (or m^3) – time-dependent, may either depend on a built-in model of particle size/area evolution or be externally controlled e.g. from the mass transport code;

R_p is the total net growth (or dissolution) rate (in $\text{mol}/\text{m}^2/\text{s}$);

$n(r)_k$ is the number of «parallel reactions» that affect the amount of k -th phase (1, 2, 3, ...), 1 by default;

r is the index of one of these «reactions» (0 by default), called “xPR” in the program; dissolution, nucleation, and precipitation should be treated as different parallel reactions;

$\theta_{k,r}$ is the effective fraction of k -th phase surface area (or pore volume) that corresponds to the effective area (pore volume) where the r -th «reaction» occurs (1 by default) – time-dependent, externally controlled e.g. from the mass transport code.

$\left(\kappa_{k,r}^o \Lambda_{k,r} e^{\frac{-E_{k,r}}{RT}} \right)$ is the «reaction» rate constant term including temperature correction, where:

$\kappa_{k,r}^o$ is the rate constant at reference temperature in $\text{mol m}^{-2}\text{s}^{-1}$ (or $\text{mol m}^{-3}\text{s}^{-1}$) or other appropriate units;

the sign convention of $\kappa_{k,r}^o$ is: positive sign for dissolution and negative for precipitation; T is temperature in K;

$\Lambda_{k,r}$ is the Arrhenius parameter (1 by default); R is the universal gas constant ($8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$);

$E_{k,r}$ is the activation energy (J mol^{-1}) of r -th «parallel reaction» involving k -th solid phase; the expression

$e^{\frac{-E_{k,r}}{RT}}$ is sometimes represented in a different form: $e^{\frac{-E_{k,r}^*}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right)}$; both forms are connected through a

relation: $\Lambda_{k,r} \cdot e^{\frac{-E_{k,r}}{RT}} = \Lambda_{k,r}^* \cdot e^{\frac{-E_{k,r}^*}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right)}$

So, to use Palandri's terms [Palandri & Kharaka, 2004] within the general equation, we need to input

$$\Lambda_{k,r} = \Lambda_{k,r}^* \cdot e^{\frac{-E_{k,r}^*}{R \cdot 298.15}}$$

where $\Lambda_{k,r}^*$ is the Arrhenius parameter coming from Palandri's report. We assume that $E_{k,r}^* = E_{k,r}$.

$$f(\Pi a)_{k,r} = I^{b_{I,k,r}} \text{pH}^{b_{\text{pH},k,r}} \text{pe}^{b_{\text{pe},k,r}} \text{Eh}^{b_{\text{Eh},k,r}} \left(\prod_j^{n(j)_{k,r}} a_{j,k,r}^{b_{j,k,r}} \right)^{p_{k,r}} \quad (1.2)$$

is the activity product term (sometimes called «reaction catalysis» term), where:

I is the (effective molal) ionic strength, and $b_{I,k,r}$ is the empirical parameter related to I (default 0); $b_{\text{pH},k,r}$ is the empirical parameter related to pH (default 0); $b_{\text{pe},k,r}$ is the parameter related to pe (default 0); $b_{\text{Eh},k,r}$ is the parameter related to Eh, V (default 0);

$p_{k,r}$ is the «reaction order» parameter for the far-from-equilibrium case (default 1);

$n(j)_{k,r}$ is the number of (aqueous or gaseous or surface) species from other reacting phases involved;

$a_{j,k,r}$ is the activity (fugacity) of j -th species ($a_{\text{H}^+} = 10^{-\text{pH}}$, $a_e = 10^{-\text{pe}}$);

$b_{j,k,r}$ is the (reaction stoichiometry coefficient) parameter (default 0).

$f(\Omega)_{k,r}$ in eq (1.1) is the affinity term for r -th reaction involving this k -th solid phase, which can take several different forms, all using the current k -th phase stability (saturation) index Ω_k computed in GEM IPM (see GEMS3K paper Kulik et al. 2013, eq B-10). The different forms of affinity term used in «parallel reaction» contributions reflect different growth or dissolution mechanisms; these forms are selected using the $\text{OCPR}(k, r)$ integer flag, with values indicated below in brackets, e.g. (0) – default term.

$$(0) (u_{k,r} + 1 - \Omega_k^{q_{k,r}})^{m_{k,r}}$$

$$(1) (\Omega_k^{q_{k,r}} - 1 - u_{k,r})^{m_{k,r}}$$

In «classic» transitional states theory (0) and (1) forms, $q_{k,r}$ and $m_{k,r}$ are the reaction order parameters (default values = 1 and 0, respectively). The $u_{k,r}$ is the empirical parameter augmenting the constant in the affinity term (default value is 0, may be equal to 1 or ...).

$$(2) e^{-u_{k,r}/\Omega_k} \text{ [Schott et al. 2012 Fig. 1e] where } u_{k,r} \text{ is the empirical parameter (default value 0).}$$

$$(3) 1 - e^{-(q_{k,r} \ln \Omega_k)^{u_{k,r}}} \text{ [Hellmann \& Tisserand, 2006 eq (9)] , where } q_{k,r} \text{ and } u_{k,r} \text{ are the reaction order parameters (default values = 1).}$$

$$(4) u_{k,r} (\Omega_k - 1) \cdot \ln \Omega_k \text{ [Teng et al., 2000, eq (13)] where } u_{k,r} \text{ is the empirical parameter (default 1).}$$

$$(5) \Omega_k^{m_{k,r}} \text{ [Teng et al., 2000, Fig. 6] where } m_{k,r} \text{ is the empirical parameter (default 0).}$$

$$(6) (\Omega_k - \Omega_{k,\text{eff}})^{m_{k,r}} \text{ [Fritz et al. 2009 eq (6)] for nucleation and growth, where } \Omega_{k,\text{eff}} \text{ is the «effective» saturation index (an input empirical parameter related to the mineral), and } m_{k,r} \text{ is the empirical parameter (default 0).}$$

$$(7) \text{ Prieto nucleation term ...}$$

Nucleation kinetics

To account for nucleation: input Ω_{eff} , the “efficient” saturation index. For precipitation reactions involving seed crystal: disabled function; without seed crystal: precipitation only occurs when $\Omega > \Omega_{\text{eff}}$
<This is not clear yet how this nucleation equation is related to seeded growth/dissolution (a-f)>.

We can hardcode the things as follow: if nucleation is accounted for (i.e. no seed crystal), with this equation:

if $\Omega_k \geq \Omega_{eff}$, use selected classical precipitation equation (i.e. a-e);

if $1 < \Omega_k < \Omega_{eff}$, selected classical precipitation equation is disabled;

if $\Omega_k < 1$, selected dissolution equation is enabled.

Idea: we can do everything like this, simply putting $\Omega_{eff} = 1$ when nucleation is not accounted for.

In eq. (1.1), $dn/dt/A$ is taken in mol/m²/s, as default units. The linear growth velocity (or radial velocity for large enough spherical particles) will then be in m/s units. It is related to molar growth rate as

$$V_k = 3 \cdot 10^9 \frac{M_k}{\rho_k} R_p \quad (1.3)$$

where V_k is the net average linear growth (or dissolution) velocity in nm/s, $R_p = \frac{1}{A_k} \frac{dn_k}{dt}$ is the net growth (or dissolution) rate, M_k is the molar mass of the phase in g/mol, ρ_k is the mineral density in g/m³. Because $M_k/\rho_k = 10^{-6} V_{M,k}$ where $V_{M,k}$ is the mineral molar volume in cm³/mol, this equation also can be written as $V_k = 3 \cdot 10^3 V_{M,k} R_p$.

Equations and parameters for the surface area correction upon growth or dissolution

For homogeneous-size particles:

$$A_{S,k} = \Psi_k \cdot A_{S,k,0} \left(\frac{n_k}{n_{k,0}} \right)^{\frac{1}{3}} \quad (1.4)$$

where $A_{S,k}$ is the current surface area of k-th phase in m², $A_{S,k,0}$ is the initial surface area, Ψ_k is the shape factor (default value=1 for spherical particles), n_k is the current mineral mole amount, $n_{k,0}$ is the initial mole amount. The power coefficient is negative for precipitation (as shown in eq 1.4) and positive for dissolution, in which case the specific surface area increases when n_k decreases.

<More to add here on SSA and PSD corrections>

Aqueous - Solid Solution systems

The distribution of a trace element Tr between the aqueous solution and the condensed (crystalline solid(solution)) relative to the host component Hc is usually described by the fractionation coefficient $\Delta_{Tr,Hc}$, which is the ratio of two distribution ratios R_d :

$$\Delta_{Tr,Hc} = \frac{R_d(Tr)}{R_d(Hc)} \quad (1.5)$$

The distribution ratio is defined as the ratio of component concentration in the solid to that in the aqueous phase. Taking mole fraction x for the solid and total dissolved molality $[]$ for the aqueous part, equation (1.5) can be rewritten as follows:

$$\Delta_{Tr,Hc} = \left(\frac{x_{Tr}}{[Tr]} \right) / \left(\frac{x_{Hc}}{[Hc]} \right) \quad \text{or} \quad \Delta_{Tr,Hc} = \frac{x_{Tr}}{x_{Hc}} \cdot \frac{[Hc]}{[Tr]} \quad (1.6)$$

From the known fractionation coefficient $\Delta_{Tr,Hc}$ and the mole fraction x_{Hc} of Hc end member (usually unity or close to a constant if there are 2 or more host (major) end members), the mole fraction of Tr end member can be estimated as e.g.

$$x_{Tr} = \Delta_{Tr,Hc} x_{Hc} \frac{[Tr]}{[Hc]} \quad (1.7).$$

2. Tr uptake kinetics

2.1 SEMO

The Surface (Growth) Entrapment MOdel was originally proposed by Watson and Liang (1995) and later improved by Watson (2004) to account for the surface depletion of some elements and the depth variability of the diffusivity in calcite. The main assumption of SEMO is: “*a growing crystal takes the composition of its surface, unless diffusivity in a thin near-surface region is effective during growth.*” In general, the equilibrium fractionation coefficient of a trace element adsorbed on the mineral surface (i.e. $\Delta_{Tr,Hc,ads}$) will be different than its fractionation coefficient in solid solution in equilibrium with the same medium (e.g. aqueous electrolyte phase) (i.e. $\Delta_{Tr,Hc,eq}$). If the mineral growth is faster than the diffusion of the trace element within the few-nanometer-thick layer beneath the mineral surface, the bulk solid will partly “inherit” the trace element concentration on the surface determined by the adsorption partial equilibrium. If the diffusion flux is faster than the mineral growth rate, the trace element content of the solid will approach that of a solid solution in equilibrium with the aqueous phase.

In other words, the progressing precipitation tends to ‘entrap’ the composition of surface, whereas the diffusivity drives the sub-surface layer to take a composition closer to that in a (hypothetical) equilibrium between aqueous electrolyte (or melt) and solid solution. Since the mineral continues to grow, the uptake of trace elements in ‘older’ layers is, in principle, metastable. This irreversible process of enrichment or depletion with trace element relative to the expected aqueous-solid or melt-solid equilibrium concentration is called “surface entrapment”.

The general reactive-transport equation of the SEMO model is:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial h} \left[D \frac{\partial C}{\partial h} \right] + \left[V - \frac{\ln(F)}{l} D \exp\left(\frac{h}{l}\right) \right] \frac{\partial C}{\partial h} - \frac{\ln(F)}{l} C \exp\left(\frac{h}{l}\right) \frac{\partial D}{\partial h} - D \frac{\ln(F)}{l^2} \exp\left(\frac{h}{l}\right) C \quad (2.1)$$

$$\text{with } D(h) = D_l \left\{ \left(\frac{D_s}{D_l} \right)^{\exp\left(\frac{h}{ml}\right)} \right\} \quad (2.2)$$

where C is the relative Tr concentration (normalized to this in the bulk mineral, calculated considering an equilibrium between the medium and the solid solution), t is the time, h is the mineral depth (from 0 at the surface, to negative values toward the bulk), D_l is the lattice diffusion coefficient, D_s is the sub-surface diffusivity, V is the linear growth rate (**units?**), F is the relative surface enrichment factor ($= \Delta_{Tr,Hc,ads} / \Delta_{Tr,Hc,eq}$), l is the half-thickness of the surface enriched layer, and m is the multiplier linking l to the maximal thickness of the diffusivity region. Equations (2.1) and (2.2) can be solved by a reactive-transport code that calculates the relative trace-element concentration profile as a function of the depth of the mineral at a given time point. Some parameters of SEMO are not measurable and must be fitted by inverse modeling (e.g. D_s , l , m).

2.2 SRKM

The Surface Reaction Kinetics Model (*DePaolo (2011)*) is based on the concept of dynamic precipitation-dissolution close to equilibrium. The mineral-aqueous equilibrium is considered as a dynamic process, in which precipitation and dissolution rates are equal and compensate each other. In aqueous medium, any mineral is affected simultaneously by a “gross forward precipitation rate” R_f (related to a kinetic rate constant k_f), and a “gross backward dissolution rate” R_b (related to a kinetic constant k_b). The net precipitation rate R_p is the difference between R_f and R_b . In equilibrium, R_b is exactly balanced by R_f so that $R_p=0$. Using relations between forward rates and kinetic rate constants, and considering that the amount of Tr is negligible compared to the amount of Hc , one can obtain the model equation:

$$\Delta_{Tr,Hc} = \frac{\alpha_f}{1 + \frac{R_b}{R_b + R_p} \left(\frac{\alpha_f}{\alpha_{eq}} - 1 \right)} \quad (2.3)$$

where R_b and R_p are rates related to the Hc , α_f is the fractionation coefficient due to the gross forward precipitation rate (maximum fractionation coefficient), and α_{eq} is the fractionation coefficient at equilibrium. Note that if $R_p=0$, $\Delta_{Tr,Hc}=\alpha_{eq}$; if R_p is high, $\Delta_{Tr,Hc}$ tends toward α_f . There is a growth rate dependency that is qualitatively similar to that produced in the SEMO.

2.3 ADDM

This model was originally proposed by Barrow (*1983*) to describe sorption and desorption of phosphate by soils. It was later improved in Barrow and Bowden (*1987*). In the present context, the main assumption of ADDM is that the adsorption or desorption of Tr creates a diffusion gradient for sorbed Tr to/from the mineral interior. This model does not account for precipitation or dissolution of the host mineral. The ADDM consists of two parts: adsorption and in-diffusion. At present, the adsorption model part is no longer of interest because several well-developed surface complexation models are available.

The increase of the surface activity triggers a diffusion gradient. This is the main difference between ADDM and SEMO, which assumes that surface material is at equilibrium at zero mineral growth rate and thus excludes any macroscopic mass transfer under such conditions. According to Crank (1964), the amount of material transferred to the interior of the mineral (mol/m^2) as function of time and considering a semi-infinite medium is given as:

$$n(t) = 2C_{Tr,s} \sqrt{D_k f t / \pi} \quad (2.4)$$

where $C_{Tr,s}$ is concentration of the considered Tr at the surface of the mineral assumed to be constant (at constant composition of aqueous solution) in mol/m^2 , D_k is a coefficient (time^{-1}) (a diffusion coefficient divided by the square of the adsorbed layer thickness), t is the time, and $f = 1/(1-\theta)$ is close to 1 in trace concentration region. In reality, the surface concentration is not necessarily constant, thus, eq (2.4) needs to be integrated over sufficiently small time steps.

The ADDM model allows explaining the frequently observed hysteresis between adsorption and desorption steps. A hysteresis means that the previously sorbed Tr amount is not fully desorbed after a certain ageing time. For instance, it was observed and successfully modeled that the longer the ageing time the more pronounced the hysteresis for phosphates on soils (Barrow (1983)) and for Zn on goethite (Barrow et al. (1989)). Strauss et al. (1997) observed that the higher the specific surface area of goethite the higher the sorption of phosphate, as well as its hysteresis. This kind of retention is explained using ADDM by the diffusion process of adsorbed Tr migration into the bulk mineral.

2.4. Unified uptake kinetics model (Thien, Kulik, Curti 2013)

The common outcome from both SEMO and SRKM is that the fractionation coefficient $\Delta_{Tr,Hc}$ varies between two limits, $\Delta_{Tr,Hc,eq}$ and $\Delta_{Tr,Hc,ads} = F \cdot \Delta_{Tr,Hc,eq}$. This suggests that SRKM might be considered as an integrated form of SEMO (which is a reactive transport model), and raises the question whether the two uptake models could be merged into a generalized one, ideally having the physics of SEMO and the simplicity of the SRKM. In both concepts, high precipitation rates constrain the composition of the newly-grown incremental layer, with Tr content greater than expected from Aq-SS equilibrium if Tr is incompatible with the host mineral structure ($F > 1$), and less than that, if Tr is compatible ($F < 1$). In both models, this enrichment or depletion can be counterbalanced by a release of entrapped Tr back to aqueous solution. This release is assigned to a dissolution phenomenon in SRKM and to an out- or in-diffusion phenomenon in SEMO, although it must not necessarily be regarded as a “true” diffusion phenomenon. In this regard, the hypothesis was that D_s in SEMO is equivalent to R_b in SRKM. Hence, to consider in SEMO the quantity V_b (in nm/s), it can be regarded as a 1-D analogue of the surface diffusivity:

$$V_b = \frac{D_s}{ml} \quad (2.5)$$

Considering that the same phenomenon triggers D_s and R_b , we further assume:

$$\frac{R_b}{R_p} = \frac{V_b}{V_k} \quad (2.6)$$

By combining eq (1.7) with eqs (1.9 and 1.10), one obtains:

$$\Delta_{Tr,Hc} = \frac{F \cdot \Delta_{Tr,Hc,eq}}{1 + \frac{\left(\frac{D_s}{ml}\right)}{\left(\frac{D_s}{ml}\right) + V_k} (F-1)} = \frac{F \cdot \Delta_{Tr,Hc,eq}}{1 + \frac{D_s (F-1)}{D_s + V_k ml}} = \Delta_{Tr,Hc,eq} \frac{D_s + V_k ml}{D_s + \frac{V_k ml}{F}} \quad (2.7)$$

where V_k is taken in nm/s. This equation has a mathematical form similar to eq (2.3), yielding also a very similar curve shape (Thien et al., 2013). A limitation of this unified model is that the lattice diffusion (present in SEMO and, as in-diffusion parameter, in the ADDM) is not accounted for, although, at very long reaction time, the effect of lattice diffusion may be significant. Further improvement of the merged model should account for the in-diffusion phenomenon.

At every time step of length Δt , the correction of upper and lower metastability constraints for the host Hc and trace Tr end members is done using the previous amount $n^{(x)}$ of the respective end member and an increment, which is calculated according to kinetic rates, mole fraction of and the corrected (eq 2.7) Tr fractionation coefficient:

$$\bar{n}_{HcEM,t+\Delta t}^{(x)} = n_{HcEM,t}^{(x)} + A_k R_p \Delta t \cdot x_{t,Hc} \quad (2.8);$$

$$\bar{n}_{TrEM,t+\Delta t}^{(x)} = n_{TrEM,t}^{(x)} + A_k R_p \Delta t \cdot x_{Tr,t} \quad \text{where} \quad x_{Tr,t} = \Delta_{TrHc} \frac{[Tr]}{[Hc]} \quad (2.9)$$

<Extend here about the account for several Hc and Tr end members in the SS phase>

Example: For modelling trace element uptake in calcite, eq (2.7) can be combined with the empirical calcite precipitation rate law, for example from (Wolthers et al., 2012):

$$V_{Cal} = I^{-0.004} pH^{-10.71} \cdot \left(\frac{a_{Ca^{2+}}}{a_{CO_3^{2-}}} \right)^{-0.35} \cdot (\Omega^{0.5} - 1)^2 \quad (2.10)$$

where V_{Cal} is an average one-dimensional growth velocity (m/s). Assuming spherical particles of uniform size, it can be converted (Thien et al., 2013) into the net precipitation rate R_p (mol/m²/s):

$$R_p = \frac{V_{Cal} \rho_{Cal}}{3M_{Cal}} = \frac{10^6}{3} \frac{V_{Cal}}{V_{m,Cal}} = 9025.1 \cdot V_{Cal} \quad (2.11)$$

where M_{Cal} is the molar mass of the host mineral (g/mol), ρ_{Cal} is the host mineral density (g/m³), and $V_{m,Cal}$ is the molar volume in cm³/mol, $V_{m,cal} = 36.934$ cm³/mol). For seawater (diluted and undiluted), Wolthers et al. (2012) give a slightly different rate law to account for the inhibition effects of Mg²⁺ and other ions:

$$V_{Cal,SW} = I^{0.36} pH^{-10.99} \cdot \left(\frac{a_{Ca^{2+}}}{a_{CO_3^{2-}}} \right)^{-0.71} \cdot (\Omega^{0.5} - 2)^2 \quad (2.12)$$

The coefficient 9025.1 in eq (2.11) can be put on place of the «reaction» rate constant term

$\left(\kappa_{k,r}^o \Lambda_{k,r} e^{\frac{-E_{k,r}}{RT}} \right)$ in eq (1.1). This makes the rate law (Wolthers et al. 2012) compatible with the “standard”

TST kinetic rate law equation, presented in general form in our implementation.

2.5. Uptake in seed-overgrowth SS phases (kinetics of linked phases)

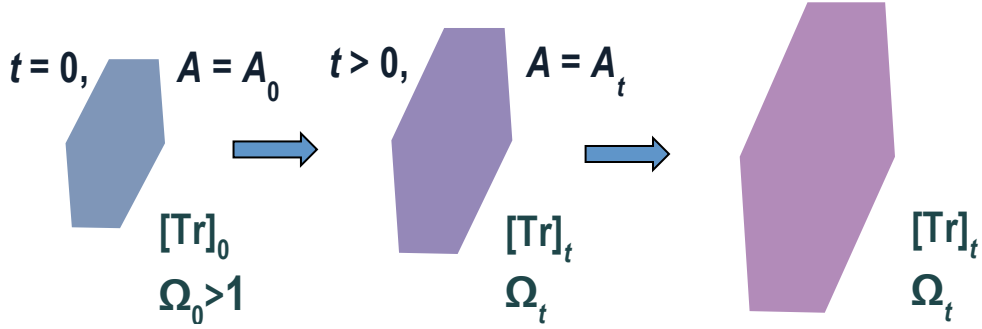
The setup of Aq-SS uptake kinetics upon host-mineral growth, described in Section 2.4, has a shortcoming that the composition of the overgrowth is “mixed” with that of the initial SS phase (e.g. seed crystals). This setup (Fig. 2.1,A) cannot describe various cases of (epitaxial) growth on surfaces of non-isostructural minerals. Therefore, it is desirable to have an option to link the specific surface or kinetic rates of one phase to the volume or surface of another, “seed” or “substrate” phase, which may even be inert, or may have its own kinetics. This can be achieved with a *phase linkage*, in which the surface area or the volume of one “overgrowth” phase k is determined by the surface area of another (“substrate”) phase s (Fig. 2.1,B).

If the linkage occurs via the surface area, the relationships between the surface area A_k and the specific surface area $A_{S,k}$ (m²/g) become different from the usual ones as e.g. for the “substrate” phase. In the latter case, the following relation holds:

$$A_k = A_{S,k} M_k n_k \quad (2.13)$$

where M_k is the molar mass (g/mol) and n_k is the amount (mol) of the phase. However, in case B (Fig.2.1), this relationship holds for the “seed” phase only:

A: Single SS



B: 'Seed'+SS

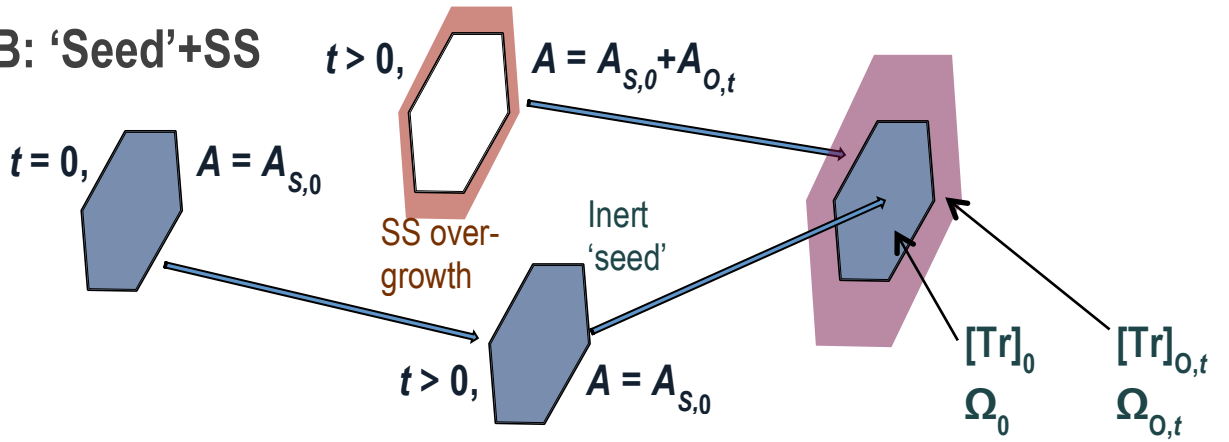


Fig. 2.1. Schematic representation of two cases of Aq-SS uptake: A – single solid solution (SS) phase; B – SS “overgrowth” phase on the surface of “seed” phase (in this case, the overgrowth composition can be controlled/followed independently of the “seed” phase).

$$A_s = A_{S,s} M_s n_s \quad (2.14a)$$

For the “overgrowth” phase, $A_k = A_{S,k} (M_k n_k + M_s n_s)$. Combining this with (2.14a), we get:

$$A_k = A_{S,k} \left(M_k n_k + \frac{A_s}{A_{S,s}} \right) \quad (2.14b)$$

In this case, eq (1.4) also needs to take into account the amount of seed phase:

$$A_{S,k} = \Psi_k \cdot A_{S,k,0} \left(\frac{M_k n_k + M_s n_s}{M_{k,0} n_{k,0} + M_s n_s} \right)^{-\frac{1}{3}} \quad (2.15)$$

Clearly, at the beginning of co-precipitation, the amount of the overgrowth phase is very small, hence one

can set $A_{S,k,0} = A_{S,s}$ and $n_{k,0} = 0$, then eq (2.15) can be simplified to $A_{S,k} \approx \Psi_k \cdot A_{S,s} \left(\frac{M_k n_k}{M_s n_s} + 1 \right)^{-\frac{1}{3}}$.

3. Data structure for kinetic rate law parameters transfer in TKinMet class implementation

As follows from the above theoretical background:

For k-th phase (Phase definition), the following flags should be used:

`kin_t[2]` Type of mineral-aqueous/gas reaction kinetic rate model (KinProCode)

Code	Comment	
N	not defined	
M	Kinetics of generic dissolution/precipitation (no uptake, ionex, adsorption)	
U	Kinetics of uptake/entrapment (of minor/trace element) into solid solution	
X	Kinetics of ion exchange (clays, C-S-H, zeolites, ...)	
A	Kinetics of adsorption (on MWI), redox	
P	Kinetics of nucleation and precipitation	

`kin_t[3]` Code of the particular form of kinetic model (KinModCode)

Code	Comment	
N	not defined	
T	Generic TST dissolution/precipitation model following (Shott ea 2012)	
P	Dissolution/precipitation model of the form (Palandri 2004)	
W	Carbonate growth model following (Wolthers 2012)	
U	Mineral nucleation and growth model with nuclei/particle size distr. (TBD)	

`kin_t[4]` Type of the uptake kinetics model (KinSorpCode)

Code	Comment	
N	not defined	
E	Unified entrapment model (Thien,Kulik,Curti 2012)	
M	DePaolo (2011) uptake kinetics model	
G	Growth (surface) entrapment model (Watson 2004)	
F	Fast ion exchange kinetics (e.g. montmorillonite, CSH)	
L	Slow ion exchange kinetics (e.g. illite, zeolites)	
I	Adsorption inhibition	
P	Solid solution nucleation model (Prieto 2013)	

`kin_t[5]` Type of metastability links of this phase to other phases (KinLinkCode)

Code	Comment	
N	not defined	
S	link to (fraction of) solid substrate surface	
P	link to (fraction of) solid substrate (pore) volume	
M	link to (fraction of) solid substrate mass	

`kin_t[6]` Type of particle/pore size distribution and SSA correction (KinSizedCode)

Code	Comment	
N	not defined	
U	Uniform particle/pore size distribution	
B	Binodal particle/pore size distribution	
F	Empirical distribution function	

kin_t[7] Reserved code of kinetic rate model (KinResCode)

Code	Comment	
N	not defined	
A	surface-scaled rate model (k in mol/m ² /s)	
V	pore-volume-scaled model (k in mol/m ³ /s)	

Dimensions of arrays of kinetic rate parameters

nPRk $n(r)_k$ number of ‘parallel reactions’ that affect amount constraints for k -th phase (1, 2, 3, ...), 2 by default (one for dissolution, one for precipitation);

nSkr $n(j)_{k,r}$ total number of (aqueous or gaseous or surface) species from other reacting phases involved (assuming that in each ‘parallel reaction’, the same list of external reacting species is used);

nrpC number of parameter (coefficients) involved in “parallel reaction” terms; 0 or 14;

napC number of parameter (coefficients) per species involved in ‘activity product’ terms (0 or 1 ($b_{j,k,r}$));

numpC number of the uptake model parameter coefficients (per end member) 0 or 8

Kinetic rate parameters arrays:

feSAr $\theta_{k,r}$ effective fractions of surface area of solid related to different parallel reactions [nPRk], default: 1

Ascp up to nAscC A_S shape/size growth/dissolution correction parameters [nAscC]

Index	Comment	
0	Ψ shape factor (dimensionless)	
1 Testino parameter (TBD)	
2		

ocPRk[iPR][0] operation codes for kinetic parallel reaction affinity terms [nPRk][2]

Code	Comment	
0	Classic TST term $(u_{k,r} + 1 - \Omega_k^{q_{k,r}})^{m_{k,r}}$	
1	Inverse TST term $(\Omega_k^{q_{k,r}} - 1 - u_{k,r})^{m_{k,r}}$	
2	Schott term $e^{-m_{k,r}/\Omega_k}$	
3	Hellmann term $1 - e^{-(q_{k,r} \ln \Omega_k)^{m_{k,r}}}$	
4	Teng term $m_{k,r}(\Omega_k - 1) \cdot \ln \Omega_k$	
5	Teng nucleation term $\Omega_k^{m_{k,r}}$	
6	Fritz nucleation term $(\Omega_k - \Omega_{k,eff})^{m_{k,r}}$	
7	Prieto nucleation term ...	
8	Testino nucleation term ...	

ocPRk[iPR][1] index of surface patch (crystal particle face) default 0, max 3 (check!)

rpCon table of kinetic rate constants for “parallel reaction” regions [nPRk][nrpC]

Parameter coefficients for each parallel reaction:

Index	Comment	Default
0	Standard-temperature net rate constant $\kappa_{k,r}^+$ or $\kappa_{k,r}^-$ (mol/m ² /s)*	0
1	Standard-temperature gross rate constant $K_{k,r}^+$ or $K_{k,r}^-$ (mol/m ² /s)**	0
2	Arrhenius factor $\Lambda_{k,r}$	1
3	Activation energy $E_{k,r}$ (J mol ⁻¹),	0
4	$b_{I,k,r}$: empirical power parameter related to ionic strength I	0
5	$b_{pH,k,r}$: empirical power parameter related to pH	0
6	$b_{pe,k,r}$: empirical power parameter related to pe	0
7	$b_{Eh,k,r}$: empirical power parameter related to Eh, V	0
8	$p_{k,r}$: «reaction order» power parameter for the activity product term (in far-from-equilibrium case)	1
9	$q_{k,r}$: empirical power parameter in the affinity term	1
10	$m_{k,r}$: empirical power parameter for the affinity term	0
11	$u_{k,r}$: power parameter or constant in the affinity term	0 or 1
12	$\Omega_{k,eff}$: «effective» saturation index for nucleation affinity term	1
13	$q_{n,k,r}$: Reserved parameter for nucleation	0

If the net rate constant is 0 and gross rate constant is not 0 then the gross rate constant will be used, and vice versa. If both are not 0 then the net rate constant will be used. If the net rate constant is positive and phase stability index $\lg \Omega_k < -0.001$ (dissolution) then this net rate constant will be used, but if $\lg \Omega_k > 0.001$ (precipitation) then this “parallel reaction” term will be skipped. If the net rate constant is negative and phase stability index $\lg \Omega_k > 0.001$ (precipitation) then the absolute value of this rate constant will be used, but if $\lg \Omega_k < -0.001$ (dissolution) then this “parallel reaction” term will be skipped.

apCon array of parameters per species in “activity product” terms [nPRk] [nSk_r][nap_tC]

[0] $b_{j,k,r}$: (reaction stoichiometry coefficient) parameter (default 0, disables the j-th species contribution to the activity product).

1DCr common list of record keys (from the project system) of DComp, ReacDC records of species involved in the activity product terms [nSk_r] (in MULTI, converted to a composite vector of indexes of dependent components xSk_r involved in parallel reactions activity product terms)

Uptake kinetics models

umpCon Array of uptake model parameters [nDC][numpC]

Index	Comment	Default
0	F_{Tr} in SEMO (or in SRKM $\Delta_{Tr,Hc,sorp} = \alpha_f$) Surface enrichment/depletion factor	1
1	$\Delta_{Tr,Hc,eq} = \alpha_{eq}$: Tr fractionation coefficient in solid solution in equilibrium with the medium	1
2	D_s (or in SRKM, backward gross rate R_b) Tr surface diffusivity nm ² /s	0
3	D_l (or in ADDM, in-diffusion coefficient D_k) lattice diffusion coefficient	0
4	l : half-thickness of the surface enriched/depleted layer (nm)	0
5	m : multiplier linking l to the maximal thickness of the diffusivity region	1
6		

3. Examples of Phase definition setup with kinetic rates

Example 1: Calcite dissolution

Experiments from Alkattan et al. 1998. pH 1 and 3, T = 25, 50 and 80 ° C. Initial seed crystal : 0.02 mol, $6 \cdot 10^{-5}$ mol/m²/s (this last value was fitted because it is not given in the paper).

Kinetic equation and parameters from Palandri et Kharaka 2004

Example 2: Quartz precipitation

Experiments from Ganor et Walter 2004. T = 1 80 ° C. Initial seed crystal: 0.1g, 0.053 mol/m²/s.

Simple precipitation law: $R_p = k (1 - \Omega)$. k had been fitted by the author.

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