MASKE test *basic_Ca(OH)2-CaCO3*

Enrico Masoero

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Abstract The document describes the inputs and outputs of the MASKE test simulation called *basic_Ca(OH)2-CaCO3*. The rationale of the simulation is explained first, followed by a description of the inputs for the chemistry database, the initial configuration, the interaction potentials, and the MASKE input script. The outputs of the simulations show the kinetics of $Ca(OH)_2$ dissolution and $CaCO_3$ precipitation, following also the composition of the solution with respect to the relevant equilibrium constants.

Contents

1   General description

The simulation describes an initial layer of $Ca(OH)_2$ in pure water at equilibrium with atmospheric CO_2. Some strong assumptions are made regarding the solution chemistry, since here we do not simulate the equilibration of the solution and of its pH (for that, see examples where MASKE is coupled with PHREEQC). In particular, the formation of $Ca(CO)_3$ is linked to the reaction of carbonate ions $CO_3{}^{2-}$, and an initial concentration of such ions is given.

This initial concentration is then let to deplete as $Ca(CO)_3$ precipitates; in reality, $CO_3{}^{2-}$ can be replenished both by additional CO_2 dissolving and by other species reacting to form it (carbonic acid and bicarbonate). In the results section below, various initial concentrations of $CO_3{}^{2-}$ are sampled, as well as various ratios of solution volume per unit surface area of $Ca(OH)_2$.

2 Chemistry database: relevant entries

2.1 Molecules data

The following molecules are included in the MASKE simulation. The names of the molecules match the names of the corresponding species in the PHREEQC database *CEMDATA18.1*.

- *Ca(OH)2* – solid Portlandite (calcium hydroxide)
  Being a solid, only its foreground linear sizes are required in MASKE. It is assumed that the molecule is a cube, hence its linear sizes are obtained as cubic root of the molecular volume. This latter volume, is obtained from the molar mass (74.093 g/mol) and the density (2.21 g/cm^3).

- *CaCO3* – solid calcite
  Analogous to the Portlandite above, but with molar mass of 100.0869 g/mol and density of 2.71 g/cm^3.

- *Ca+2* – calcium ions in solution
  Ions in solution require apparent volume ϕ in solution and a and b parameters for Debye-Hückel activity coefficients. Unless otherwise stated, the apparent volume of ion i is computed at infinite dilution (excluding dependence on other ion concentrations) using a Redlich-type equation [1] as in PHREEQC:

$$\phi_{i,inf} = 41.48 \left(a1 \times 0.1 + \frac{a2 \times 100}{(2600 + P_b)} + \frac{a3}{T_K - 228} + \right.$$
$$\left. + \frac{a4 \times 10^4}{(2600 + P_b)(T_K - 228)} - W \times Q_{Born} \right) \quad (1)$$

The terms in the equation are: 5 empirical constants $(a1, a2, a3, a4, W)$, the pressure in bars P_b, the temperature in Kelvin T_K, and the Born's dependence of the dielectric constant of the solvent ε_r as a function of pressure $Q_{Born} = \left(\frac{1}{\varepsilon_r^2} \frac{\partial}{\partial P} \varepsilon_r \right)_T$. For water at room pressure and temperature, $Q_{Born} = 9.76156E - 07$, from Ref. [2]. The 5 empirical constants

for $Ca+2$ can be found in PHREEQC databases. From the *phreeqc.dat* database we have: $a1 = -0.3456$, $a2 = -7.252$, $a3 = 6.149$, $a4 = -2.479$, and $W = 1.239$. These return an apparent volume ϕ in cm^3/mol, then converted per molecule in the MASKE database units (*e.g.* , for $Ca+2$, $\phi = -0.025129603$ nm^3 per molecule).

The Debye-Hückel constants can be read directly from a PHREEQC database; for $Ca+2$, from the CEMDATA18.1 database, these are $a = 0.486$ nm, and $b = 0.15$.

- *OH-* – hydroxyl ions in solution
  Same logics as for $CA+2$ above. Empirical parameters for ϕ are: $a1 = -9.66$, $a2 = 28.5$, $a3 = 80$, $a4 = -22.9$, and $W = 1.89$. Resulting apparent volume $\phi = 0.001030404$ nm^3 per molecule. Debye-Hückel constants from the CEMDATA18.1 database: $a = 1.065$ nm, and $b = 0.064$.

- *CO3-2* – carbonate ions in solution
  Same logics as for $CA+2$ above. Empirical parameters for ϕ are: $a1 = 5.95$, $a2 = 0$, $a3 = 0$, $a4 = -5.67$, and $W = 6.85$. Resulting apparent volume $\phi = 0.019702472$ nm^3 per molecule. Debye-Hückel constants from the CEMDATA18.1 database: $a = 0.54$ nm, and $b = 0.064$.

2.2   Rate expressions

This section gives an overview of the rate equations used in MASKE for solid-liquid transitions (dissolution or precipitation). Consider the generic reaction:

$$A + B \rightleftharpoons C + D \tag{2}$$

MASKE implements TST to express the net rate of reactions, with correction for the activity of the solid based on the excess enthalpy of individual particles, coming from their interaction energy. MASKE assumes a meso-scale parametrisation of the interaction potential, such that the change in interaction energy upon dissolving strss-free a kink particle is $\Delta U_{kink,0} = \gamma \Omega$, where γ is the solid-solution interfacial energy and Ω is the particle surface. The rate

expressions in MASKE are:

$$\mathscr{R}^{diss}_{net} = \kappa \frac{k_B T}{h} \frac{c^{\ddagger}}{\gamma^{\ddagger}} \exp\left(-\frac{\Delta G^{\ddagger}_{diss}}{k_B T}\right) \left\{ Q_{reac} \exp\left[\frac{-\Delta U_{diss}(r) - \gamma \Delta \Omega_{diss}}{k_B T}\right] - \frac{Q_{prod}}{K_{eq,diss}} \right\} \cdot$$
$$\cdot V_{m,i}^{\frac{\alpha-3}{3}} \cdot V_{m,i} \tag{3}$$

$$\mathscr{R}^{prec}_{net} = \kappa \frac{k_B T}{h} \frac{c^{\ddagger}}{\gamma^{\ddagger}} \exp\left(-\frac{\Delta G^{\ddagger}_{prec}}{k_B T}\right) \left\{ Q_{reac} - \frac{Q_{prod}}{K_{eq,prec}} \exp\left[\frac{-\Delta U_{diss}(r) - \gamma \Delta \Omega_{diss}}{k_B T}\right] \right\} \cdot$$
$$\cdot V_{m,i}^{\frac{\alpha-3}{3}} \cdot \Delta V \tag{4}$$

The units of $\mathscr{R}$ are events per unit time, which MASKE samples over the relevant domains (for dissolution, all the existing particles; for precipitation, a discretised set of cells covering all the possible positions in the domain). In the equation, κ is the probability that the activated complex vibrates towards the products (as customary, MASKE takes $\kappa = 1$), k_B is the Boltzmann constant, T the temperature in Kelvin, h the Planck constant. $\gamma^{\ddagger}$ is the activity coefficient of the activated complex: in principle it could be computed with the Davies equation [3] from the ionic strength of the system, knowing the charge of the complex (or from the Setschenow equation [4] with constant = 0.1 for neutral complexes - see PHREEQC manuals); however, for now MASKE only accepts a constant value of $\gamma^{\ddagger}$, typically chosen as 1. $c^{\ddagger}$ is the concentration of the activated complex in standard state; it must be the same as the one used to obtain the activation energy $\Delta G^{\ddagger}$ (or, more specifically, the entropy part of it, as $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \cdot \Delta S^{\ddagger}$; a change in $c^{\ddagger}$ to any other $c^{\ddagger}_{new}$ would require a correction of entropy to $\Delta S^{\ddagger}_{new} = \Delta S^{\ddagger} + k_B \ln\left(\frac{c^{\ddagger}}{c^*_{new}}\right)$). In the dissolution reaction, $V_{m,i}$ is the tributary volume of particle i, $viz.$ the volume of the region of space in which a particle would equilibrate to the position of particle i; as this is hard to compute, MASKE approximates it with the molecular volume. For a precipitation reaction, ΔV is the volume used to discretise the simulation domain to sample precipitation everywhere. α transforms the dimensions of $c^{\ddagger}$ from a generic dimension α (2 if per unit surface, 3 if per unit volume), to per unit volume.

In Eqs. 3 and 4, the activation energies for dissolution and precipitation are linked via the equilibrium constant:

$$\Delta G^{\ddagger}_{diss} - \Delta G^{\ddagger}_{prec} = \Delta G_{r,diss} = -k_B T \ln(K_{eq,diss}) \tag{5}$$
$$\Delta G^{\ddagger}_{prec} - \Delta G^{\ddagger}_{diss} = \Delta G_{r,prec} = -k_B T \ln(K_{eq,prec}) \tag{6}$$

where ΔG_r is the reaction free energy change in standard state (NB: all these values depend on the choice of standard state, as already discussed above).

From Eqs. 5 and 6 one can easily derive the relationship between equilibrium constants of the dissolution and precipitation reactions: $K_{eq,diss} = K_{eq,prec}^{-1}$. The equations also provide a way to obtain $\Delta G_{diss}^{\ddagger}$ when $\Delta G_{diss}^{\ddagger}$ and K_{eq} are known, and similarly for $\Delta G_{prec}^{\ddagger}$.

The activity products of the reactants and of the products are Q_{reac} and Q_{prod}, and the equilibrium constant for the reaction is $K_{eq} = \frac{Q_{prod,eq}}{Q_{reac,eq}}$. The stoichiometry of a reaction, in MASKE, is given as a vector of change of number of molecules of various species in the solution (called "background") and change of number of molecules of various species from the solid (the "foreground"). MASKE considers as reactants to compute Q_{reac} all the terms that have negative values in the vectors of stoichiometric coefficients, and as products in Q_{prod} all the terms with positive values. The activity of solid particles is taken as 1, and then explicitly corrected by a change in excess enthalpy upon dissolution $\Delta H_{ex,diss} = \Delta U_{diss} + \gamma \Delta \Omega_{diss}$. Here, ΔU_{diss} is the change in interaction energy between particles following dissolution, and $\Delta \Omega_{diss}$ is the change in surface area caused by particle dissolution ($= -\Omega$ for the cases of full particle dissolution or nucleation used here, but conceptually extensible to cases of partial dissolution or growth). In general, the $\Delta \Omega_{diss}$ reflects a particular choice of the interaction energy change from removing an unstressed kink particle $\Delta U_{kink,0} = \gamma \Omega$, hence MASKE in its current version can only be used if the interaction potentials respect said constraint on $\Delta U_{kink,0}$.

2.3   Input data for the rate expressions

Two reactions are considered in this example, one for calcium hydroxide dissolution and the other one for calcite precipitation:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2\, OH^- \tag{7}$$

$$Ca^{2+} + CO_3{}^{2-} \rightarrow CaCO_3 \tag{8}$$
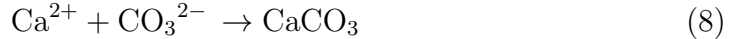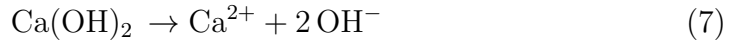
In this example, $\gamma^{\ddagger} = 1$ for both reactions.

For $Ca(OH)_2$ dissolution, $\Delta G_{diss}^{\ddagger}$ is obtained from the rate constant value $k_{diss} = 0.66\ \mu\text{mol m}^{-2}\ \text{s}^{-1}$ from Bullard [5]. Since:

$$k_{diss} = \kappa \frac{k_B T}{h} \frac{c^{\ddagger}}{\gamma^{\ddagger}} \exp\left(-\frac{\Delta G_{diss}^{\ddagger}}{k_B T} \right) \tag{9}$$

we obtain:

$$\Delta G_{diss}^{\ddagger} = -RT \ln\left(k_{diss} \frac{h}{\kappa k_B T} \frac{\gamma^{\ddagger}}{c^{\ddagger}} \right) \tag{10}$$

where k_B has been replaced by R in the prefactor to obtain a result in units of per-mole. This leads to $\Delta G^{\ddagger}_{diss} = 74.009$ kJ/mol, having considered k_{diss} in units of μmol m^{-2} s^{-1}, and therefore $c^{\ddagger}$ in μmol m^{-2}. Therefore, $c^{\ddagger} = 0.6022$ nm^{-2} and $dim = 2$ are given as inputs in $ChemDB.dat$ alongside $\Delta G^{\ddagger}$. This latter input is converted from kJ/mol to the *nano* units used in the simulation, via a multiplying factor of 1.66, giving $\Delta G^{\ddagger}_{diss} = 122.85$ ag nm^2 ns^{-2}.

For CaCO$_3$ precipitation, $\Delta G^{\ddagger}_{prec}$ is obtained starting from the dissolution rate constant in neutral conditions $k_{diss} = 10^{-5.81} = 1.54882$ μmol m^{-2} s^{-1}, in Palandri and Kharaka [6]. From the equation above, we obtain:

$$\Delta G^{\ddagger}_{diss} = -RT \ln \left(k_{diss} \frac{h}{\kappa k_B T} \frac{\gamma^{\ddagger}}{c^{\ddagger}} \right) = 71.9369 \text{ kJ/mol} \tag{11}$$

with $c^{\ddagger}$ in μmol m^{-2}, as for Ca(OH)$_2$ dissolution before. Using the equilibrium constant $K_{eq,diss} = 3.31157 \cdot 10^{-9}$ from the CEMDATA18.1 database in PHREEQC, and using Eq. 5, we obtain $\Delta G^{\ddagger}_{prec} = 23.532$ kJ/mol (still for $c^{\ddagger}$ in μmol m^{-2}). This is converted to *nano* units in MASKE by multiplying times 1.66, hence $\Delta G^{\ddagger}_{prec} = 39.064$ ag nm^2 ns^{-2} is input.

The equilibrium constant for Ca(OH)$_2$ dissolution is $K_{eq_{diss}} = 6.30866 \cdot 10^{-6}$, from the CEMDATA18.1 database in PHREEQC. For CaCO$_3$ precipitation, we started from $K_{eq_{diss}} = 3.31157E \cdot 10^{-9}$ (CEMDATA18.1 database in PHREEQC) and inverted it to obtain $K_{eq_{p}rec} = K^{-1}_{eq_{d}iss} = 3.02E \cdot 10^8$.

The water-solid interfacial energy for Ca(OH)$_2$ is taken to be $\gamma = 68.4$ mJ/nm^2, from experiments in Ca(OH)$_2$ solutions in distilled water by Estrela et al. [7]. For CaCO$_3$, we chose $\gamma = 120$ mJ/nm^2 suggested for homogeneous nucleation of calcite in water, by Fernandez-Martinez et al. [8] (they indicated a range of 83-170 mJ/nm^2 for homogeneous nucleation, from other literature, and obtained 36 mJ/nm^2 for heterogeneous nucleation on quartz).

3 The input_CaCO3_1p.dat file, for nucleation mesh dependence

This input file is for a preliminary simulation addressing the precipitation of CaCO$_3$ alone on a pre-existing surface of CaCO$_3$. The purpose is to test various mesh sizes for the precipitation part of the problem, aiming for an appropriate balance between precision and simulation time.

This simulation is run on a single processor, with a single subcommunicator (*Antonello*) which runs LAMMPS. The random number generator for the subcommunicator is initiated with the seed specified in the input file.

Three particle types are used: type 1 for real particles with fixed position, type 2 for real particles that can move, and type 3 for trial particles sampled by the nucleation fix. All these particle types represent $CaCO_3$ molecules.

LAMMPS is initiated with units *nano*, atom style *sphere*, and activating the atom *map* for the nucleation fix (which uses the fix *deposit* in LAMMPS).

A place-holder simulation box is created in the input file, assigning periodic boundaries in the X and Y directions, and fixed boundaries in the Z direction. The initial configuration is then imported from a previous dump file: this is shown in Fig. 1. The red particles in the figure are of type 1, forming a fixed layer. The blue particles are type 2, representing some already formed layers with FCC order. The diameters and interaction potentials in this initial configuration must be consistent with the same quantities that will be employed in the MASKE simulation.
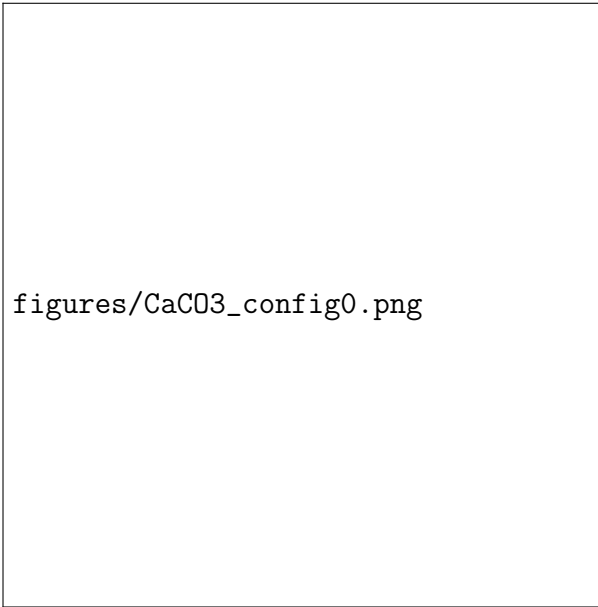

figures/CaCO3_config0.png

Fig. 1: Initial configuration for $CaCO_3$ precipitation.

The particles diameter D is set to match the molar volume $V_M = 36.93243542$ cm^3/mol of $CaCO_3$:

$$\frac{\pi}{6}D^3 = \frac{V_M}{N_A} \tag{12}$$

where N_A is the Avogadro number. This leads to $D = 0.489278566$ nm.

The equilibrium distance r_0 between particles must be such that the porosity of the lattice (for the FCC lattice to be used here, $1 - \eta = 0.26$, with

$\eta = 0.74$ the solid fraction) is compensated by the overlap between particles. This translates to:

$$r_0^3 = \eta D^3 \quad \rightarrow \quad r_0 = D\sqrt[3]{\eta} = 0.442554503 \text{ nm} \tag{13}$$

The interaction potential is loaded from a table. It consists of a pairwise harmonic (linear spring) potential, with cutoff in tension. The governing equations are:

$$U(r) = \frac{1}{2}K(r - r_0)^2 - \varepsilon_0 \qquad\qquad \text{for } r \leq r_0$$

$$U(r) = \min\left[\frac{1}{2}K(r - r_0)^2 - \varepsilon_0, \ 0\right] \qquad\qquad \text{for } r > r_0 \tag{14}$$

where $K = \frac{E\pi\frac{D^2}{4}}{r_0}$ is the spring stiffness, with $E = 69.9$ GPa the Young modulus of calcite. ε_0 is the bond energy in stress-free conditions; here it is parametrised imposing that the change in interfacial energy from detaching a kink particle is null, translating into $6\varepsilon_0 = \gamma\Omega$, where γ is the interfacial energy with water, and $\Omega = \pi D^2$ is the surface area of the particle. The resulting interaction potential is shown in Fig. 2.
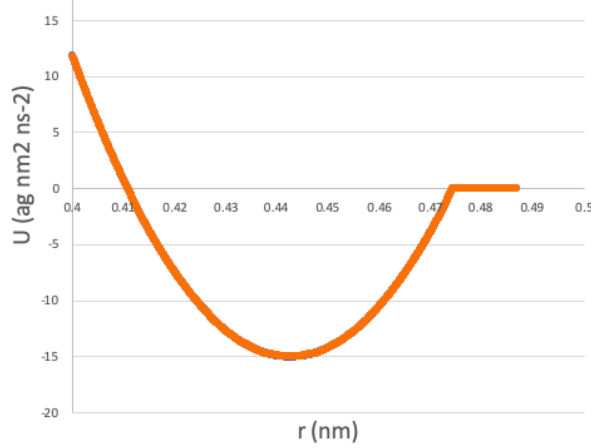

Fig. 2: Initial configuration for CaCO$_3$ precipitation.

A neighbour list is created in LAMMPS, with a skin of $r_0/10$ beyond the interaction cutoff.

Boltzmann constant k_B and Planck constant h are provided in *nano* units.

The bottom layer, made of particles of type 1, is fixed *via* the *setforce* fix.

The composition of the initial solution is set via the *sol$_s$tart* command. The solution is uniform, as currently MASKE does not allow concentration gradients within the simulation domain. 4 molecules are to be considered in

the simulation: H_2O, $Ca+2$, $CO3-2$, and $OH-$; their initial concentrations are specified here in mol/L. The temperature us set to 298 K, and the Debye-Hückel constants of the solvent ($A = 0.51$ and $B = 3.29$ nm^{-}1 for water here) are given. The initial volume of voids in the domain is set to $voidV = 0$, and an additional reservoir of volume $dV = 1e30$ nm is attached to the simulation box, assuming it is equally interfaced with all sides of the simulation box (*iso*, standing for isotropic). The initial volume of voids in dV is also set to 0. A unit conversion factor, *unitC*, is then provided, which is the ratio between MASKE's volume units and litres: here, 1 nm^3 / 1 L = 10^{-24}.

For the *nucleation* fix, a cubic lattice is stored for sampling the box. The lattice is defined within a region, spanning the whole box in X and Y directions, and only the part of the box in Z direction (excluding a top and bottom layer of r_0 thickness each). The reason for excluding the top and bottom parts of the box is to avoid the "lost atoms" if trail particles move outside the fixed box boundary in Z direction. The number of lattice sites is fixed in the three directions: n_x, n_y, and n_z; the larger these n's are, the finer the sampling lattice will be, leading to a more precise solution, but also to a more computationally expensive simulation. In this exercise, we will be exploring a range of n values, to appreciate the mesh-sensitivity of the results. The formula to compute the volume of a lattice site, ΔV, is stored, associating it to the just-stored lattice name, *latnuc*; Storing ΔV as a LAMMPS formula, instead of giving a fixed value, allows for more flexibility in case the lattice dimensions should change during the simulation (*e.g.* upon deforming the domain).

The nucleation fix uses by default the *maske* style for energy minimization. The parameters for this minimizer are stored as well. Here we use a minimisation displacement of $d_max = r_0/2,000$, and allow for a maximum of 2,000 steps in any direction.

The nucleation fix is then invoked, specifying the region, lattice, and minimizer to be considered. The trial type, 3, and the real type, 2 (for the actually nucleated particles) are provided, along with the particle style *sphere* and the diameter D. The mechanism from *ChemDB.dat* is also indicated here, specifying that the solution information used to compute the activities assumes uniform concentrations in the box, and the changes in solution caused by a nucleation event would create a uniform changes of solution composition both in the box and in the additional volume dV attached to the simulation box.

The last part of the input file concerns the definition of desired output to place in the configuration files (dump files) and in the thermodynamic quantities files (thermo). A few variables are defined first, to track relevant quantities in LAMMPS: total number of particles N, total interaction energy U,

total pressure P, and particles of type 2, *viz.* non-fixed $CaCO_3$ molecules (a LAMMPS dynamic group must be used to track an increasing number of type 2 particles during the simulation). The interaction energy per atom $PEall$ is computed: it will be added to the configuration file for visualisation in OVITO if needed. The *thermo* style to be produced by LAMMPS is defined: it will be printed after every 1,000 steps in LAMMPS. The subsequent *thermo* command refers then to the thermodynamic output of MASKE (hence it does not start with *lammps all*). This is printed every so many, user-decided, steps in MASKE, each consisting in a realisation of a KMC step (here, a particle insertion). Here, the thermo is plotted every 1 KMC step and a set of relevant concentrations and LAMMPS variables are indicated for this thermo. The MASKE dump file (also not preceded by *lammps all*, hence not a LAMMPS dump) is then specified. Here, the dump file is printed every 1 KMC step and is of type custom, allowing to select the LAMMPS quantities to dump.

Finally, the KMC loop is run until 40 seconds, *i.e.* $4 \cdot 10^{10}$ ns, of simulated time.

4   Mesh and β dependence of results

Three levels of saturation were studies in detail here: low ($\beta =$), intermediate $\beta = 2,608$, and high ($\beta = ...$) saturation index. Even lower β eventually lead to the system's inability to nucleate a new layer after the first one is filled, because of the use of net rates which removes the dissolution rate from the straight precipitation rate. In principle, the code could be used with straight rates as well.

, the linear size of the nucleation lattice cell is set to r_0/c, where r_0 is the equilibrium distance between particles, and c is a number defining the mesh fineness. The results in Fig. **??** correspond to At low β, that the correct mechanism of layered growth is captured as long as of mechanism is already lost when $c < 1$, whereas

5   The input.dat file

For the simulation on 1 processor, two types of real particles are defined (types 1 and 2 for $Ca(OH)_2$ and $CaCO_3$ respectively) and two types of trial particles corresponding to the same phases (types 3 and 4).

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A Obtaining $\Delta S^{\ddagger}$ from rate temperature dependence of rate constants - Ca(OH)$_2$ dissolution

The activation energy $\Delta G^{\ddagger}$ for Ca(OH)$_2$ dissolution is calculated from the temperature-dependence of the rate constants k in [9]. From the slope Fig. 3, the cited paper computed the apparent activation energy $E_a = 29.7 \pm 2.9$ kJ/mol, giving $\Delta H^{\ddagger} = E_a - RT = 27.22$ kJ/mol [10]. The intercept at $1/T \to 0$

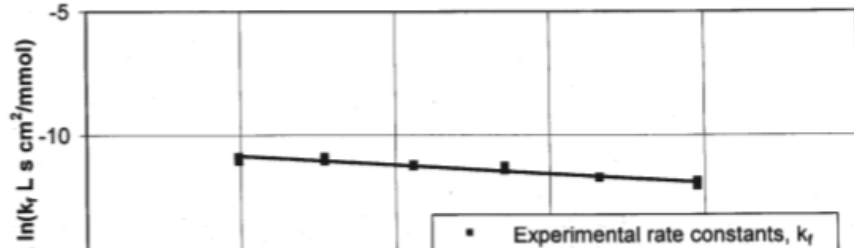Fig. 3: Temperature dependence of the rate constant of Ca(OH)$_2$ dissolution [9].

is $\ln(k) \approx 0$, with k in mmol L^{-1} s^{-1} cm^{-2}. The experiment was run in 0.75 litres of solution, leading to $k = 4.5165 \cdot 10^{17}$ in units of events s^{-1} cm^{-2}. The equality below is then used to compute $\Delta S^{\ddagger}$:

$$\left. \frac{\Delta S^{\ddagger}}{R} \right|_{\frac{1}{T} \to 0} = \ln \left(\frac{k}{c^{\ddagger}} \frac{h\gamma^{\ddagger}}{\kappa k_B T} \right) \tag{15}$$

with $c^{\ddagger}$ in units of cm^{-2}, to be consistent with k. The gas constant is $R = 0.0083145$ kJ/mol/K, $\frac{k_B T}{h} = 6.2028 \cdot 10^{12}$ in s^{-1}, and we assume $\kappa = 1$. The result is $\Delta S^{\ddagger} = 0.093080684$ KJ/mol/K with $c^{\ddagger}$ in units of cm^{-2}. Therefore $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} = 27.22 - 27.738 = -0.518$ at $T = 298$ K, for $c^{\ddagger}$ in units of cm^{-2}. This value is provided in *chemDB.dat*, converted in the simulation units (here, ag, nm, ns).

B Rate constant of CaCO$_3$ dissolution from reworking rate expression in Sjöberg [11]

Another way to obatin $\Delta G^{\ddagger}_{prec}$ for CaCO$_3$ is to start from a dissolution rate constant reconstructed from data in Sjöberg [11]. Obtaining $\Delta G^{\ddagger}_{diss}$ from Sjöberg's results requires some approximations. TST in MASKE assumes integer rate exponents in the activity products, whereas Sjöberg showed that calcite disso-

lution follows a fractional rate law with exponents $\frac{1}{2}$:

$$\frac{d\text{Ca}^{2+}}{dt} = 12.8 \cdot 10^{-6} A \left(C - [\text{Ca}^{2+}]^{\frac{1}{2}}[\text{CO}_3{}^{2-}]^{\frac{1}{2}} \right) \qquad (16)$$

in moles cm^{-3} s^{-1}. $C = 24.6 \cdot 10^{-8}$ mole cm^{-3} is an empirical constant representing the product of the square roots of the concentrations at equilibrium (square brackets indicate concentrations). Sjöberg's experiment was run on 700 cm^3 of solution, thus knowing that each molecule of produced Ca^{2+} implies one molecule of dissolved CaCO_3, we can rewrite:

$$\frac{d\text{CaCO}_3}{dt} = 0.00896 \, A \, C \left(1 - \frac{[\text{Ca}^{2+}]^{\frac{1}{2}}[\text{CO}_3{}^{2-}]^{\frac{1}{2}}}{C} \right) \approx 2.20506 \cdot 10^{-9} \, A \left(1 - \beta^{\frac{1}{2}} \right)$$
$$(17)$$

in moles s^{-1}. In the expression we approximated the saturation index $\beta = \frac{a_{\text{Ca}} a_{\text{CO}_3}}{K_{eq}}$, where a indicates activities, with the ratio of concentrations $\frac{[\text{Ca}^{2+}][\text{CO}_3{}^{2-}]}{C^2}$.

Expanding Eq. 17 in Taylor series around $\beta = 1$ and truncating to the linear term yields:

$$\frac{d\text{CaCO}_3}{dt} \approx \frac{2.20506 \cdot 10^{-9}}{2} \, A \, (1 - \beta) = k_{diss} A \, (1 - \beta) \, , \qquad (18)$$

Therefore, $k_{diss} = 1.10253 \cdot 10^{-9}$ mol cm^{-2} s^{-1}, or $k_{diss} = 11.02$ μmol m^{-2} s^{-1}, which is approximately ten times larger than k_{diss} from Palandri and Kharaka [6] used in this test example. This larger k_{diss} would lead to $\Delta G_{diss}^{\ddagger} = 111.28$ kJ/mol and then $\Delta G_{prec}^{\ddagger} = 62.9$ kJ/mol, which are not very far from the values obtained with the lower rate constant, and used in the simulation.