

PSI Center for Nuclear Engineering
and Sciences



GEMS Workshop

Metastability and kinetics Quartz (aggregate) dissolution exercise

G. Dan Miron & Georg Kosakowski
dan.miron@psi.ch

EMPA, 5th of June 2025

Chemical equilibrium

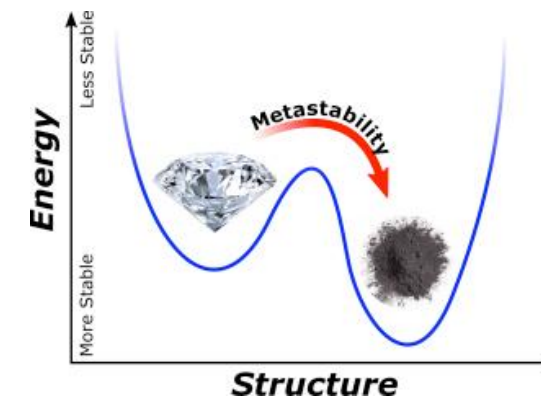
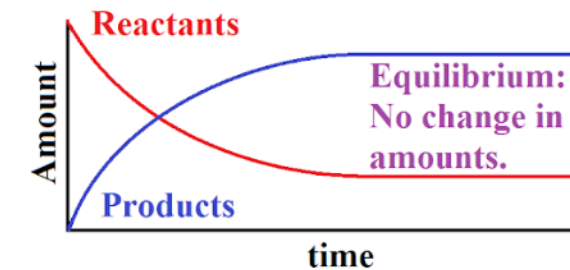
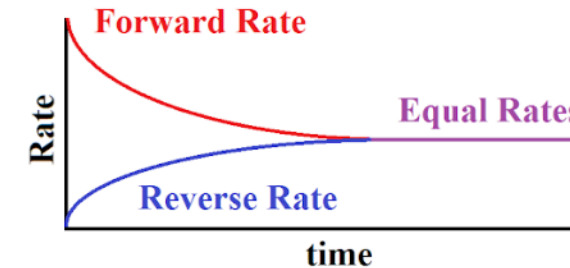
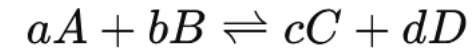


Thermodynamic equilibrium: rate of the forward reaction equals the rate of the reverse reaction, final state of the system (given by the configuration with the minimum Gibbs energy)

Kinetics: deals with the rate at which chemical reactions occur, pathway, speed, and mechanism leading to equilibrium

Metastability: an intermediate state that appears stable but is not the true equilibrium state, energy barriers; very slow transition; stuck when energy barrier too high (strong bonds)

All can be modeled using thermodynamics (with constraints) in GEMS (e.g., dissolution, precipitation)



GEMS Thermodynamic equilibrium (complete equilibrium)

GEMS finds the **amounts of chemical components in phases** with stability indexes Ω in an **equilibrium state** (with minimum Gibbs energy) **defined by T, P, bulk elemental composition, thermodynamic data.**

- all reactions are infinitely fast
- slow reactions over infinite time

In many cases this is not attained at Earth surface conditions.

Time dependent metastability → use the principle of partial equilibria (discretize the path to equilibrium as a sequence of partial equilibrium states)

- Lower metastability constraints allow stepwise simulation of mineral **dissolution** (min. amount imposed)
- Upper metastability constraints allow stepwise simulation of mineral **precipitation** (max. amount allowed)



Metastability constraints in recipe

Saturation Index

$\log_{10}(\Omega) = 0 \rightarrow$ saturated (equilibrium)

$\log_{10}(\Omega) < 0 \rightarrow$ undersaturated

$\log_{10}(\Omega) > 0 \rightarrow$ oversaturated

Upper metastability, precipitation

1. Create

SysEq Recipe 0: 'PortlKin' at 1 bar 25 C, var. 0

Property	Name	Quantity	Units
xa_	Aqua	1	G
xd_	Portlandite	0.05	M
bi_	O	0.0004	M

2. Clone

SysEq Recipe 0: 'PortlKin' at 1 bar 25 C, var. 1

Property	Name	Quantity	Units
xa_	Aqua	1	G
xd_	Portlandite	0.05	M
bi_	O	0.0004	M
dul_	Portlandite	0.01	M

Complete equilibrium (saturation):

pH = 12.47; IS = 0.05 m;

m_t(Ca) = 0.0204 m;

n(Portlandite) = 0.0296

$\Omega(\text{Portlandite}) = 1$

$\log_{10}(\Omega) \text{ SI/Fa(Portlandite)} = 0 \text{ } (-9.2\text{e-}7)$

Partial equilibrium (oversaturation):

pH = 12.72; IS = 0.097 m;

m_t(Ca) = 0.04 m;

n(Portlandite) = 0.01

$\Omega(\text{Portlandite}) = 4.66$

$\log_{10}(\Omega) \text{ SI/Fa(Portlandite)} = 0.67$

A 'dul_ = f(time)' would account for the precipitation rate

Metastability constraints in recipe



Saturation Index

$\log_{10}(\Omega) = 0 \rightarrow$ saturated (equilibrium)

$\log_{10}(\Omega) < 0 \rightarrow$ undersaturated

$\log_{10}(\Omega) > 0 \rightarrow$ oversaturated

Lower metastability, dissolution

3. Clone

SysEq Recipe 1: 'PortlKin' at 1 bar 25 C, var. 0

Property	Name	Quantity	Units
xa_	Aqua	1	G
xd_	Portlandite	0.02	M
bi_	O	0.0004	M

4. Clone

SysEq Recipe 1: 'PortlKin' at 1 bar 25 C, var. 1

Property	Name	Quantity	Units
xa_	Aqua	1	G
xd_	Portlandite	0.02	M
bi_	O	0.0004	M
dll_	Portlandite	0.01	M

A 'dll_ = f(time)' would account for the dissolution rate

Homework: Check out and test the "Kinetics" test project

(look at Process simulators and Phase definitions for calcite, portlandite)

Complete equilibrium (undersaturation):

pH = 12.46; IS = 0.05 m;

m_t(Ca) = 0.02 m;

n(Portlandite) = 0.0

$\Omega(\text{Portlandite}) = 0.958$

$\log_{10}(\Omega) \text{ SI/Fa Fa(Portlandite)} = -0.018$

Partial equilibrium (undersaturation):

pH = 12.2; IS = 0.027 m;

m_t(Ca) = 0.01 m;

n(Portlandite) = 0.01

$\Omega(\text{Portlandite}) = 0.183$

$\log_{10}(\Omega) \text{ SI/Fa Fa(Portlandite)} = -0.738$

Kinetic rate law

General equation (Lasaga, 1998), t (time s)

$$\underset{\substack{\text{net rate} \\ (\text{mol s}^{-1})}}{r} = \pm \underset{\substack{\text{rate constant} \\ (\text{mol m}^{-2} \text{s}^{-1})}}{k} \underset{\substack{\text{reactive surface} \\ \text{area (m}^2\text{)}}}{S} \left| 1 - \underset{\substack{\text{saturation ratio}}}{\Omega} \right| \overset{\substack{\text{possible fitting} \\ \text{parameters}}}{\eta}$$

$$dul_{-t+\Delta t} = dul_{-t} + r_t \Delta t \text{ if } \log_{10} \Omega > 0$$

$$dll_{-t+\Delta t} = dll_{-t} - r_t \Delta t \text{ if } \log_{10} \Omega < 0$$

Kinetic rate law

The rate constant can be written as a function of T, activity (e.g., pH), ionic strength, partial pressure of a gas, etc.

Can be defined as a summation of different mechanisms.

For dissolution

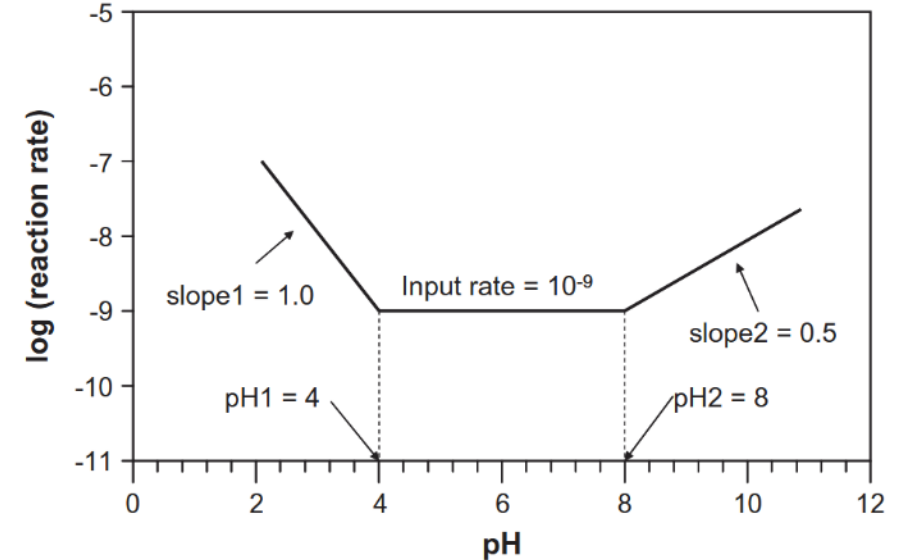
$$dll_{-t+\Delta t} = dll_{-t} - r_t \Delta t$$

$$r_t^{nu} = k^{nu} S |1 - \Omega^\ominus|^\eta$$

$$r_t^H = k^H S |1 - \Omega^\ominus|^\eta$$

$$r_t^{OH} = k^{OH} S |1 - \Omega^\ominus|^\eta$$

$$dll_{-t+\Delta t} = dll_{-t} - (r_t^{nu} + r_t^H + r_t^{OH}) \Delta t$$



$$k = k_{25}^{nu} \exp \left[\frac{-E_a^{nu}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] +$$

$$k_{25}^H \exp \left[\frac{-E_a^H}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H^{n_H} +$$

$$k_{25}^{OH} \exp \left[\frac{-E_a^{OH}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_{OH}^{n_{OH}}$$

parameters from experiments

2. Aggregate (quartz) dissolution (kinetics)

We define a kinetic rate law function in our jupyter notebook and we couple it with xgems to simulate a dissolution reaction, and sample the aqueous and solid changes

1st we need a GEMS chemical system from GEM-Selektor – we export it to be used in xgems, then we continue in the Jupyter Lab

Defining the initial system in GEM-Selektor (PC2 project)

NAGRA NTB 23-03

Tab. A-3: GEMS recipes of CPW systems at degradation Stage I

Property	Compos or species name	Units	Stage-I-mt/sh (oxic)	Recipe variants: Porosity after hydration	Stage-I-mt/sh (reducing)	Recipe variants: Porosity after hydration
xa_	Aqua (H ₂ O)	g	254.047 371.2	~ 11 % ~ 20 %	254.047 371.2 533.6	~ 11 % ~ 20 % ~ 30 %
xa_	CEM-I-52.5R	g	400		400	400
xa_	CaCO ₃	g	180		180	180
xa_	O ₂ ***	mol	-		-0.0017	-0.017
xa_	SiO ₂	g	1,603		1,603	1,603

Switch off ` `:

gibbsite, kaolinite

hematite, goethite,

ettringite-AlFe, ettringite-FeAl, SO₄_CO₃_AFt

monosulph-AlFe, monosulph-FeAl, SO₄_OH_AFm,

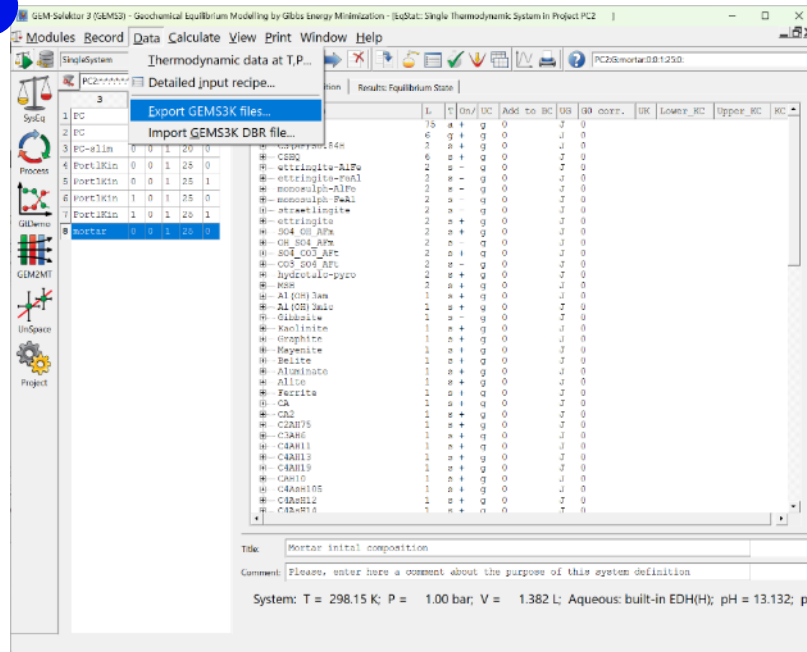
The image displays two overlapping windows from the GEM-Selektor software. The background window, titled 'SysEq: Please, enter a new record key:', shows fields for 'PC2' (Name of the modeling project), 'G' (Thermodynamic potential to minimize), 'mortar' (Name of the chemical system definition), and various numerical inputs for CSD variant, volume, pressure, temperature, and constraints. The foreground window, titled 'Input Recipe of Single Thermodynamic System: PC2:Gmortar:0:0:1:25:0:', shows a 'Recipe Input' table with columns for Property, Name, Quantity, and Units. The table lists six entries: 1. xa_ Aqua (371.2 g), 2. xa_ PC (400 g), 3. xa_ CaCO3 (180 g), 4. xa_ O2 (0.01 M), 5. xa_ SiO2 (26.679 M), and 6. dll_ Qtz (26.679 M). A 'Selection' panel on the left lists various chemical components like FeOOHmic, Gt, Py, Tro, Melanterite, K2SO4, Na2O, Syngenite, K2O, hydrotalcite, and Mgs. A 'Conflict Warning' dialog box is also visible, indicating that mole amounts of some Independent Components (IC) are missing in the calculated bulk composition vector and offering actions like 'EXCLUDE ALL', 'RETAIN ALL', or 'CHECK/Ok'.



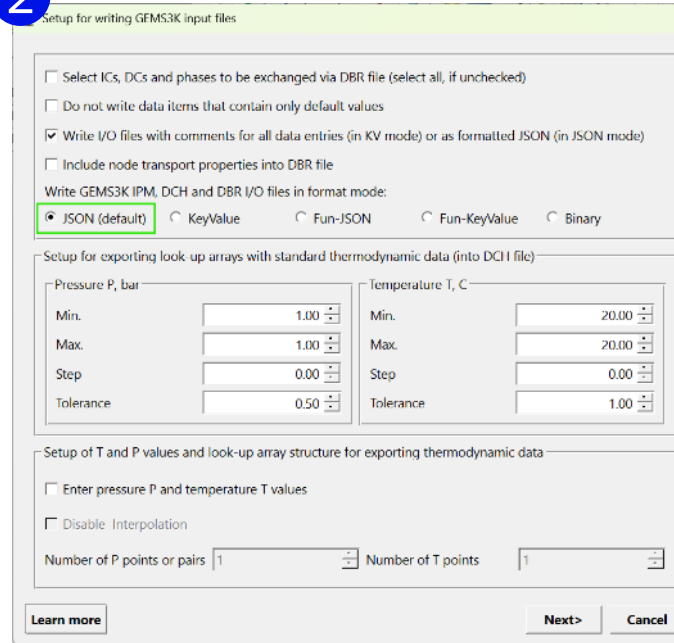
Export GEMS3K files

In gemsworkshop folder create subfolders dissolution and inside gems_files

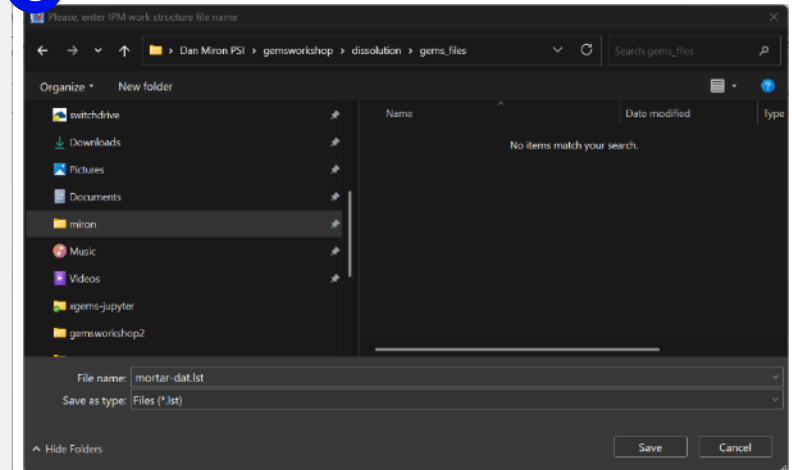
1



2



3



For dissolution example create a new notebook aggregate_dissolution inside the leaching folder.

We use the following parameters for the rate law (neutral and basic)

Table 6

Selected parameters for the dissolution rate model: regression curve model. Kinetic constants (k) are expressed in $\text{mol m}^{-2} \text{s}^{-1}$ and the activation energy (E_a) in kJ mol^{-1} .

Mineral	Type of surface normalisation	k_{25}^{nu}	E_a^{nu}	k_{25}^{H+}	E_a^{H+}	n^{H+}	k_{25}^{OH-}	E_a^{OH-}	n^{OH-}
Albite	BET	5.1×10^{-20}	57	8.5×10^{-11}	58	0.34	1.4×10^{-10}	56	0.32
Biotite	BET	2.3×10^{-12}	49	1.1×10^{-09}	49	0.67	9.1×10^{-08}	49	0.79
Celestite	BET	2.2×10^{-08}	34	1.4×10^{-06}	33	0.10			
Chlorite	0.2% BET ^a	6.4×10^{-17}	16	8.2×10^{-09}	17	0.28	6.9×10^{-09}	16	0.34
C-S-H	BET	1.6×10^{-18}	23	5.9×10^{-08}	23	0.28			
Cristobalite	BET	6.4×10^{-14}	69				1.9×10^{-10}	69	0.34
Dolomite	BET	1.1×10^{-08}	31	2.8×10^{-04}	46	0.61			
Gibbsite	BET						3.1×10^{-06}	48	1.0
Illite	ESA	3.3×10^{-17}	35	9.8×10^{-12}	36	0.52	3.1×10^{-12}	48	0.38
Kaolinite	BET	1.1×10^{-14}	38	7.5×10^{-12}	43	0.51	2.5×10^{-11}	46	0.58
Microcline	BET	1.0×10^{-14}	31	1.7×10^{-11}	31	0.27	1.4×10^{-10}	31	0.35
Portlandite	BET	2.2×10^{-08}	75	8.0×10^{-04}	75	0.60			
Quartz	BET	6.4×10^{-14}	77				1.9×10^{-10}	80	0.34
Siderite	BET	2.1×10^{-09}	56	5.9×10^{-06}	56	0.60			
Montmorillonite	ESA	9.3×10^{-15}	63	5.3×10^{-11}	54	0.69	2.9×10^{-12}	61	0.34

Thank you for your attention!

Questions?

