

# Aqueous solution database and modelling using the Pitzer formalism and ChemApp/ChemSheet

GTT Annual Users' Meeting 2018

Risto Pajarre, VTT

# Outline

- Pitzer formalism in brief
- VTT aqueous database work
- Limitations
- Some practical tips related to aqueous modelling:
  - Supersaturation
  - Target calculation with pH

## Pitzer activity model

- Probably the most commonly applied formalism for modelling aqueous solutions of fairly high concentrations
- At dilute limit the model reduces to Davies like (and finally Debye-Hückel) model where the activity coefficient only depends on the ionic charge.
- With sufficient experimentally derived interaction parameters, the properties of solutions up to about 6 M can usually be modelled satisfactorily. Without parameters for the system, the Davies/DH model typically works for a concentration up to about 0.1 M.

## Starting points for VTT work

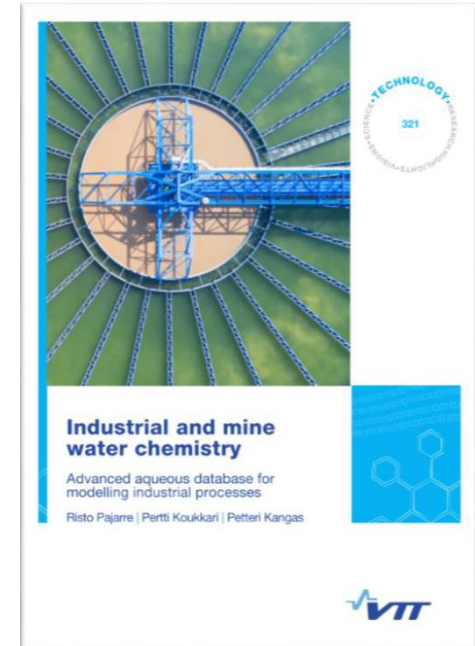
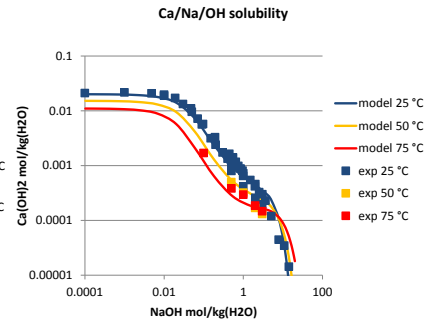
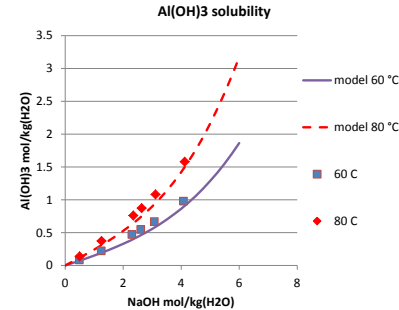
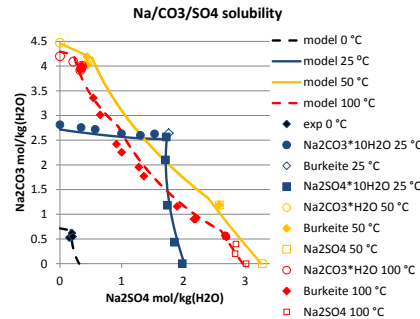
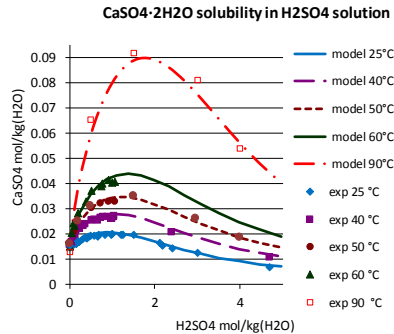
- Needed a model for common alkali and earth alkali carbonates, sulfates, chlorides and hydroxides that works on wide pH range and temperatures up to 100 °C
- Additional cations, ions and solid precipitates added as needed.

## VTT database

- Contains circa 40 elements, 500 aqueous species and 150 solids. Extended as needed from other sources.
- Aqueous solution model implemented using the PIMZ formalism (basic Pitzer model with some extensions available). Pure solid phases + non-ideal mixture description for burkeite and glaserite mixed salts
- Best and most accurate data for system (25 °C – 100 °C)  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{H}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$
- Less evaluated data and/or for limited temperature range  
 $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Si}^{2+}$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{NH}_3$  + some organics

Number of Pitzer interactions parameterized: ~400

Database documented in the report: *Industrial and mine water chemistry - Advanced aqueous database for modelling industrial processes*, Pajarre, R., Koukkari, P. and Kangas, P. (2018)



## VTT database

Known needs for further development:

- Highly concentrated solutions ( $> 6\text{M}$ ).
- Concentrated ( $> 0.1\text{-}0.5\text{M}$ ) solutions of “less common” ions.
- High temperature ( $> 50\text{ }^{\circ}\text{C}$ ) equilibria with most ions, heat capacity and enthalpy calculations with almost all systems when temperature is higher than  $25\text{ }^{\circ}\text{C}$

## Limitations of the Pitzer model

- Maximum concentrations allowed typically of the order of 6 M
- It is not theoretically completely clear how is this applied for multicomponent systems. In practical cases, model for the individual salts at their relevant concentrations + the mixed cation/anion parameters seems to lead to reasonably working mixture model.
- The non-specific part of the interaction energy is generally not a good initial guess for other than univalent salts (or at least salts charged higher than 1:2). It almost certainly gives excessively low activity coefficients in even moderately concentrated salt solutions for ions that are trivalent (or higher)

(model assumption:  $\ln\gamma_i = z_i^2 F(I)$ )

- For unknown systems, values of “similar” known salts are recommended
- Ongoing project at VTT to predict Pitzer parameters based on the physical properties of relevant ions
- Limitations on temperature dependency from the formalism used by ChemApp



# Some often encountered features of aqueous modelling

- Supersaturation
- Setting pH

# Supersaturation

Commonly used quantity to give quantitative definition for supersaturation is the saturation index (SI), defined in terms of ionic activity product (IAP) and solubility product constant  $K_{sp}$

$$SI = \lg \frac{IAP}{K_{sp}} = \lg \frac{a(\text{Ca}^{+2aq}) \cdot a(\text{CO}_3^{-2aq})}{K_{sp}(\text{CaCO}_3)}$$

For salt  $\text{CaCO}_3$

$$SI = \lg \frac{a(\text{Ca}^{+2aq}) \cdot a(\text{CO}_3^{-2aq})}{K_{sp}(\text{CaCO}_3)}$$

# Supersaturation

There is a generic method for handling non-equilibrium states in equilibrium calculations (such as in ChemApp) called Constrained Free Energy (CFE) method (\*) that has been extensively developed at VTT.

A more limited, but usefull, functionality is supported by the ChemApp (ChemSheet) target calculation option where we can set the (relative) activity of the supersaturated (or undersaturated) phase, so that

$$SI = \lg \frac{a(\text{Ca}(+2aq)) \cdot a(\text{CO}_3(-2aq))}{K_{sp}(\text{CaCO}_3)} = \lg[a(\text{CaCO}_3)]$$

(limitation here that the feed amount of CaCO<sub>3</sub> can not be fixed)

(\*) R. Pajarre, P. Koukkari, P. Kangas, Constrained and extended free energy minimisation for modelling of processes and materials, Chem. Eng. Sci. 146 (2016) 244–258. <http://dx.doi.org/10.1016/j.ces.2016.02.033>  
P. Koukkari, R. Pajarre, Calculation of constrained equilibria by Gibbs energy minimization, Calphad Comput. Coupling Phase Diagrams Thermochem. 30 (2006). <http://dx.doi.org/10.1016/j.calphad.2005.11.007>  
R. Pajarre, Modelling of chemical processes and materials by free energy minimisation. Additional constraints and work terms, Aalto University, 2016. <http://www.vtt.fi/inf/pdf/science/2016/S141.pdf>

## Calculation of pH

pH obtained from activity of hydrogen ion in the model

$$\text{pH} = -\lg(a(\text{H}^{+}\text{aq}))$$

Often a calculation at some specific pH is desired (acid or base feed is varied to achieve the result)

Two options:

1. direct iteration with adjusting the acid/base feed. As the pH is a strongly non-linear phenomena, not all the iteration methods work very well. Bisection method is robust and easy to implement, but it can require fairly many equilibrium calculations (= it may be slow)

## Calculation of pH

2. The “target calculation” option of ChemApp/ChemSheet allows setting the activity of  $H(+aq)$  ( $= 10^{-pH}$ ) directly when  $H(+aq)$  input is varied.
  - ChemApp allows negative target feed amounts for  $H(+aq)$  or alternatively the activity of  $OH(-aq)$  may be specified for basic solutions.

As any physical input to system should be charge neutral, the suitable amount of balancing anion/cation should be added on the next step

## Calculation of pH (direct target iteration)

- Strong acid (example: HCl):
  - Target calculation with a fixed H(+aq) activity => H(+aq) feed amount solved
  - Equal amount of Cl(-aq) added to system feed
- Weak acid (example: HCOOH)
  - Target calculation with a fixed H(+aq) activity => H(+aq) feed amount solved
  - Equal amount of HCOO (-aq) added to system feed as well as an additional amount of HCOOH corresponding to distribution in the system (or Henderson-Hasselbach - equation)

$$\frac{\Delta n(\text{HCOOH}(\text{aq}))}{\Delta n(\text{HCOO}(-\text{aq}))} = \frac{n(\text{HCOOH}(\text{aq}))}{n(\text{COO}(-\text{aq}))}$$



[www.vttresearch.com](http://www.vttresearch.com)  
#vttpeople / @VTTFinland