Getting started with Simulis® Thermodynamics

Use Case 11: Management of electrolytic systems with the reactive models editor

Software & Services In Process Simulation

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ProSim

Introduction

This document presents the management of electrolytic thermodynamic models and the configuration tool of these reactive models

- Some definitions
- Use within Simulis Thermodynamics and visualization of parameters
- Presentation of the reactive models editor

Some definitions

- Electrolyte:
  - molecular or atomic species (gaseous, liquid or solid) which has some solubility in a solvent and react with it to form one or more ionic species (charged)

    E. g.: CO_2 (g), NaCl (s)

- Electrolyte equilibrium:
  - Thermodynamic equilibrium involving species that are all in the solvent phase

    E. g.: CO_2 (aq) + H_2O (aq) <==> H^+ (aq) + HCO_3^- (aq)

Some definitions

- Apparent species:
  - molecule or atomic species defined by the user

    E. g.: H_2O, CO_2, NaCl

- True species:
  - all species existing in the mixture, additional species with respect to the apparent species being created through electrolyte reactions (including apparent species)

    E. g.: H_2O, CO_2, NaCl, HCl, NaOH, $NaHCO_3$, Na_2CO_3, Na_2CO_3,H_2O, Na_2CO_3,$7H_2O$, Na_2CO_3,$10H_2O$, H^+, OH^-, CO_3^{2-}, HCO_3^-, Na^+, Cl^-

Some definitions

- **Global presentation of multiphase electrolyte systems**
  - Systems with:
    - → Water: H_2O
    - → Salts: NaCl, KCl, Na_2SO_4 …
    - → Gas: CO_2, NH_3, CH_4 …

    } Apparent species

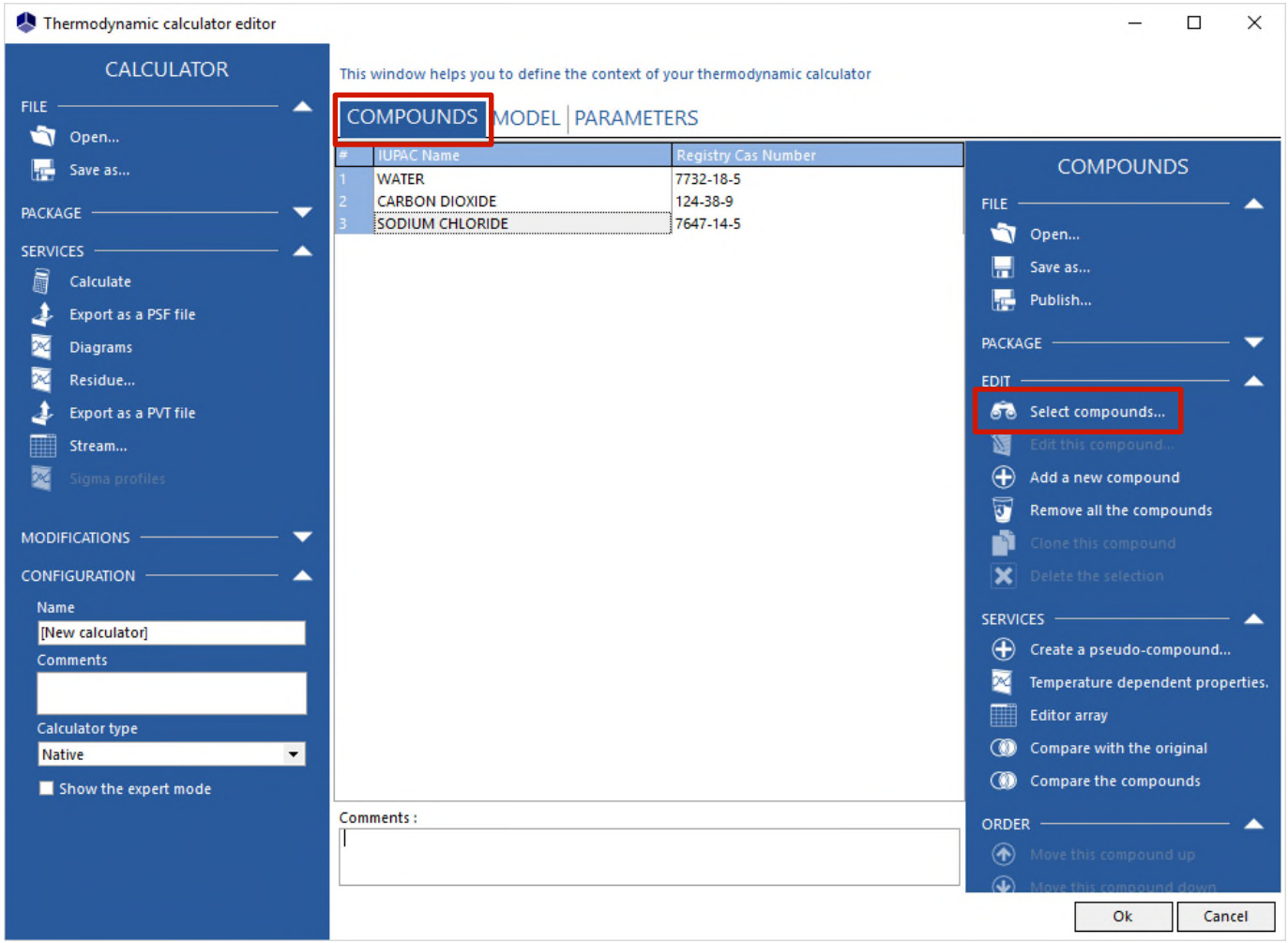
  - Dissociation reactions:
    - → Autoprotolysis of water: $H_2O \rightleftharpoons H^+ + HO^-$
    - → Salts: $NaCl \rightleftharpoons Na^+ + Cl^-$
    - → Gases: $CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$…

  } True species

  - Electrolyte solutions: strongly non ideal solutions (particles with electrically charged, electrostatic interactions)
  - Use of specific thermodynamics to describe aqueous phase
  - Liquid-solid, vapor-liquid, vapor-liquid-solid Equilibria

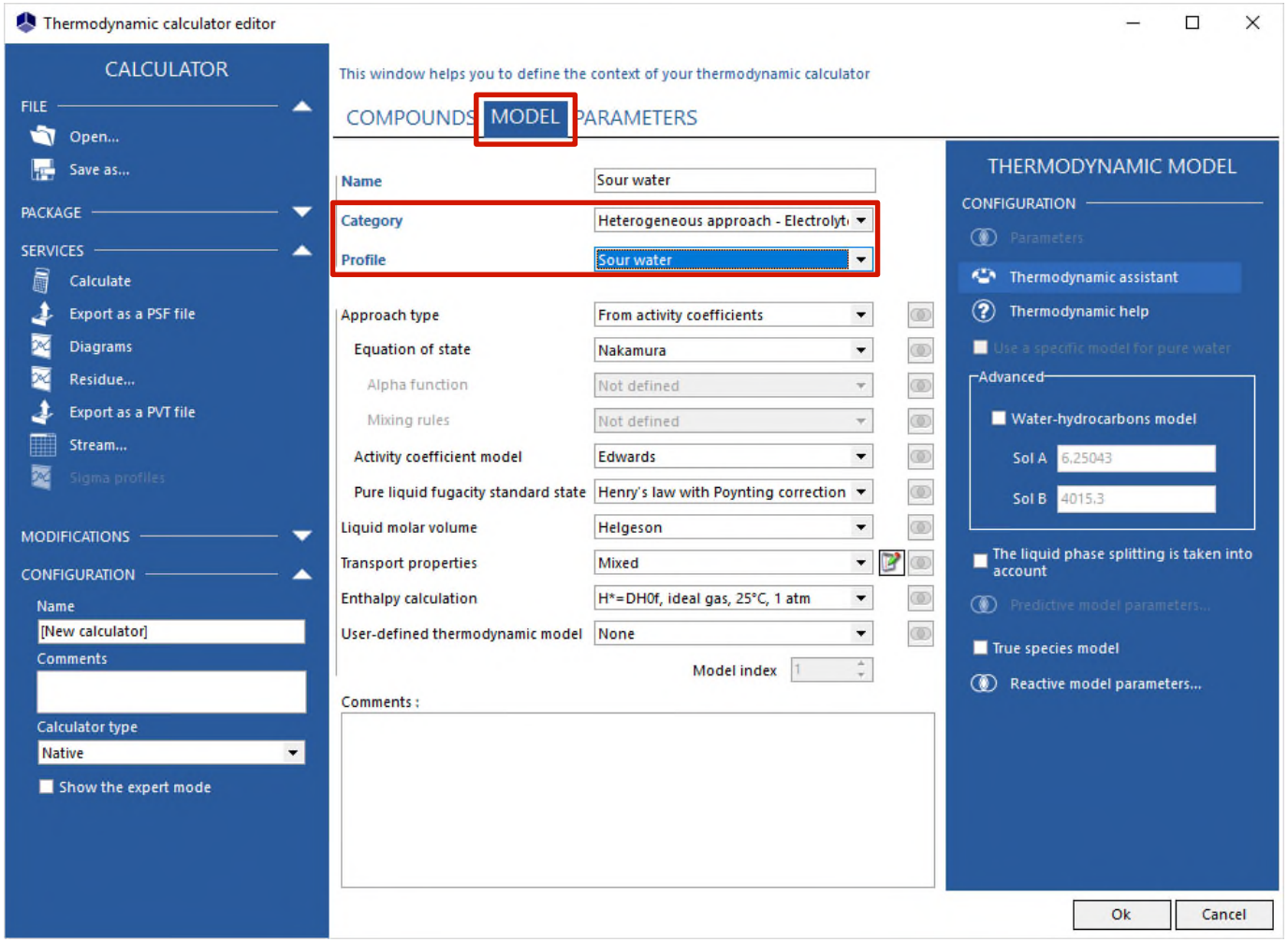
Simulis Thermodynamics: Visualization of parameters

- Step 1: in the calculator, define apparent species of the system



Simulis Thermodynamics: Visualization of parameters

- Step 2: choose an electrolyte thermodynamic model
  (in the category “Heterogeneous approach – Electrolytes”)

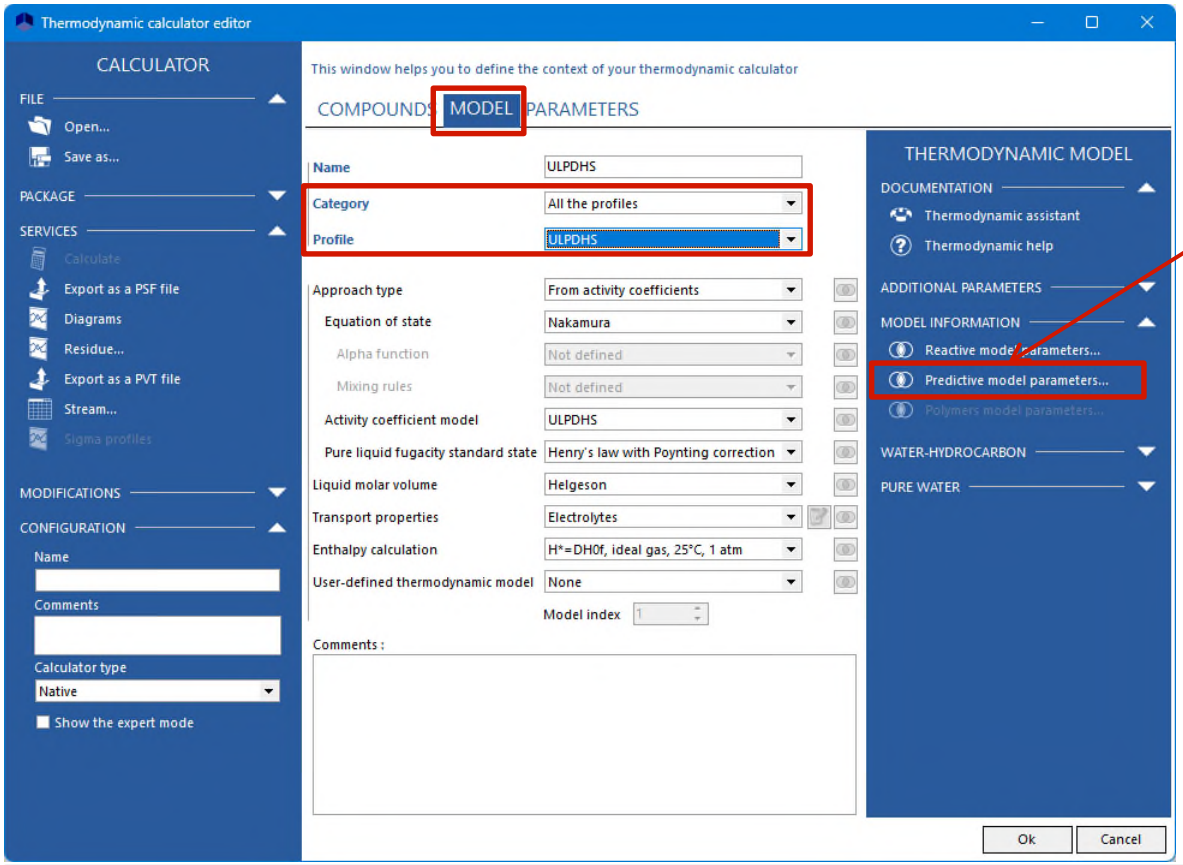


Simulis Thermodynamics: Visualization of parameters

- Simulis Thermodynamics (thermodynamic server of ProSim) offers several electrolyte or reactive thermodynamic models (cf. category of the models)
  - Sour Water
  - Pitzer
  - Amines and acid gases
  - e-NRTL
  - UNIQUAC electrolytes
  - ULPDHS
  - MSE
  - COSMO-UCAs
  - …

Simulis Thermodynamics: Visualization of parameters

- Step 2: case of a group contribution predictive electrolyte thermodynamic model, e. g. ULPDHS (in the category "Heterogeneous approach – Electrolytes - predictive models")

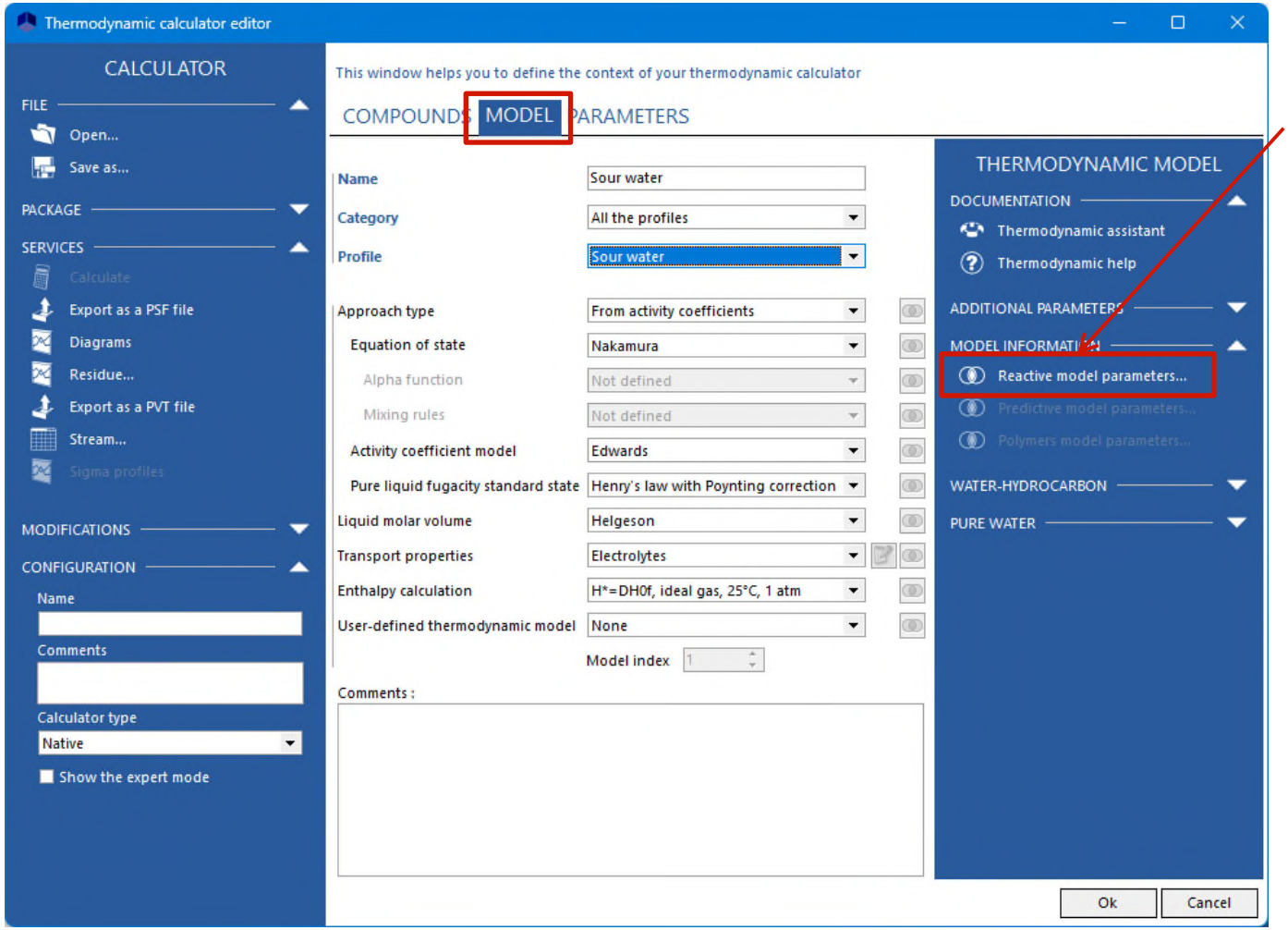


Click on the button "Predictive model parameters…"

Refer to "Getting started with Simulis Thermodynamics, Case 10" for more details concerning the use of group-contribution predictive models

Simulis Thermodynamics: Visualization of parameters

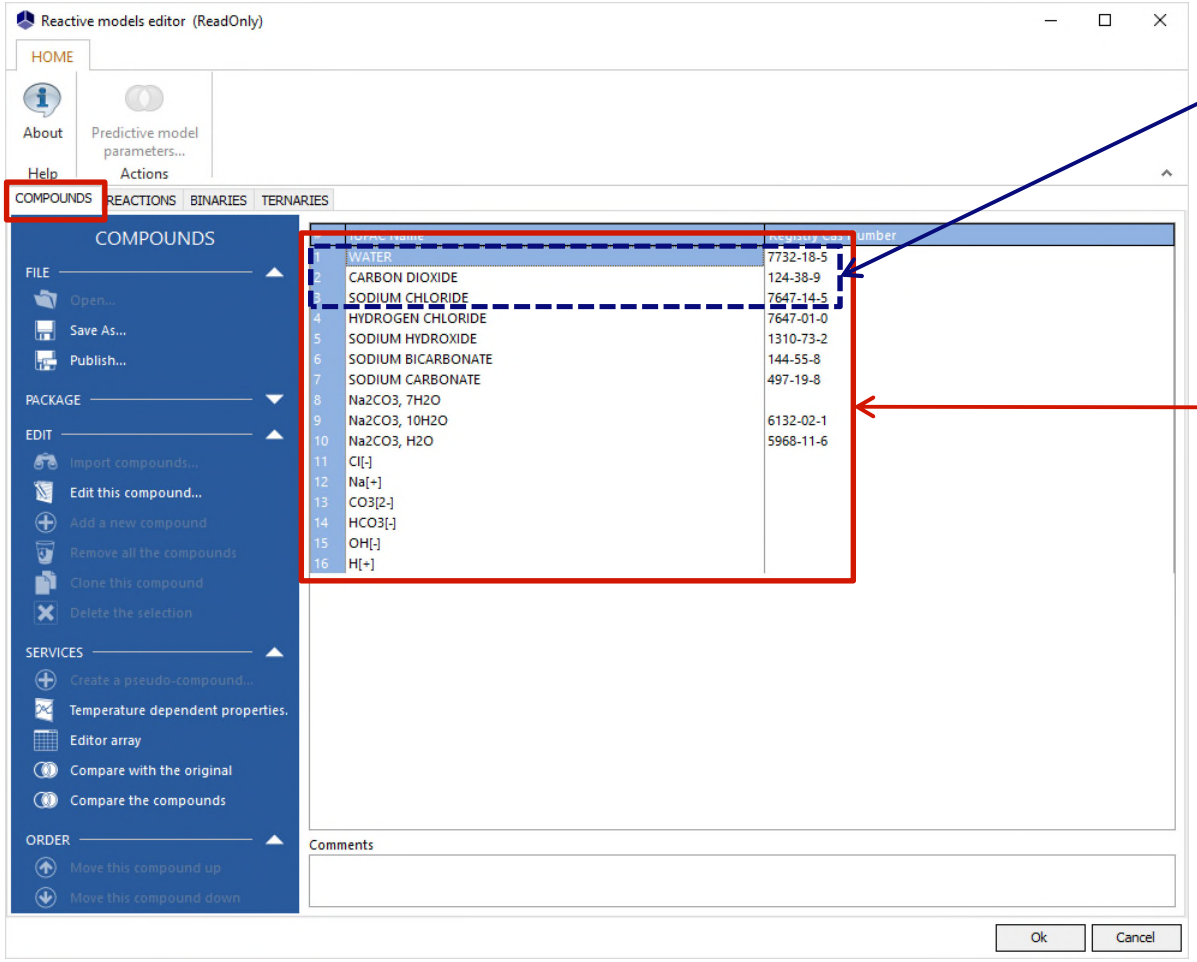
- Step 3: visualization of parameters of the chosen model for the selected system



Click on the button "Reactive model parameters…" (enabled only if the model is an electrolyte model)

Simulis Thermodynamics: Visualization of parameters

- Step 3a: list of true species that can exist in the system (apparent species + ionic species + salts + other species that can be recombined)



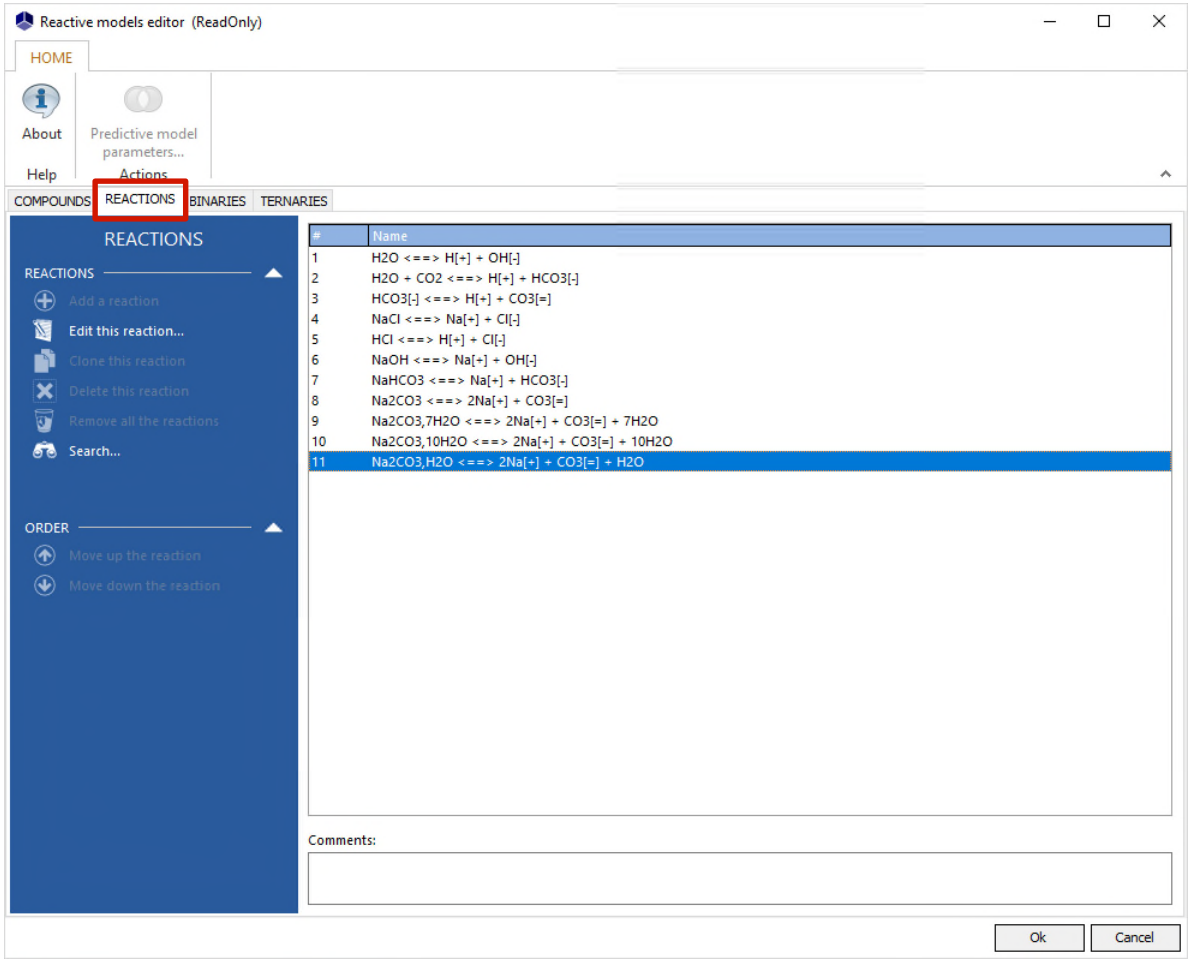
List of apparent species (defined by the user)

List of true species (used by the electrolyte model)

A double-click on a component allows to access its properties

Simulis Thermodynamics: Visualization of parameters

- Step 3b: list of electrolyte reactions taken into account in the chosen reactive model for the selected system



A double-click on a reaction allows to access to parameters of the selected equilibrium

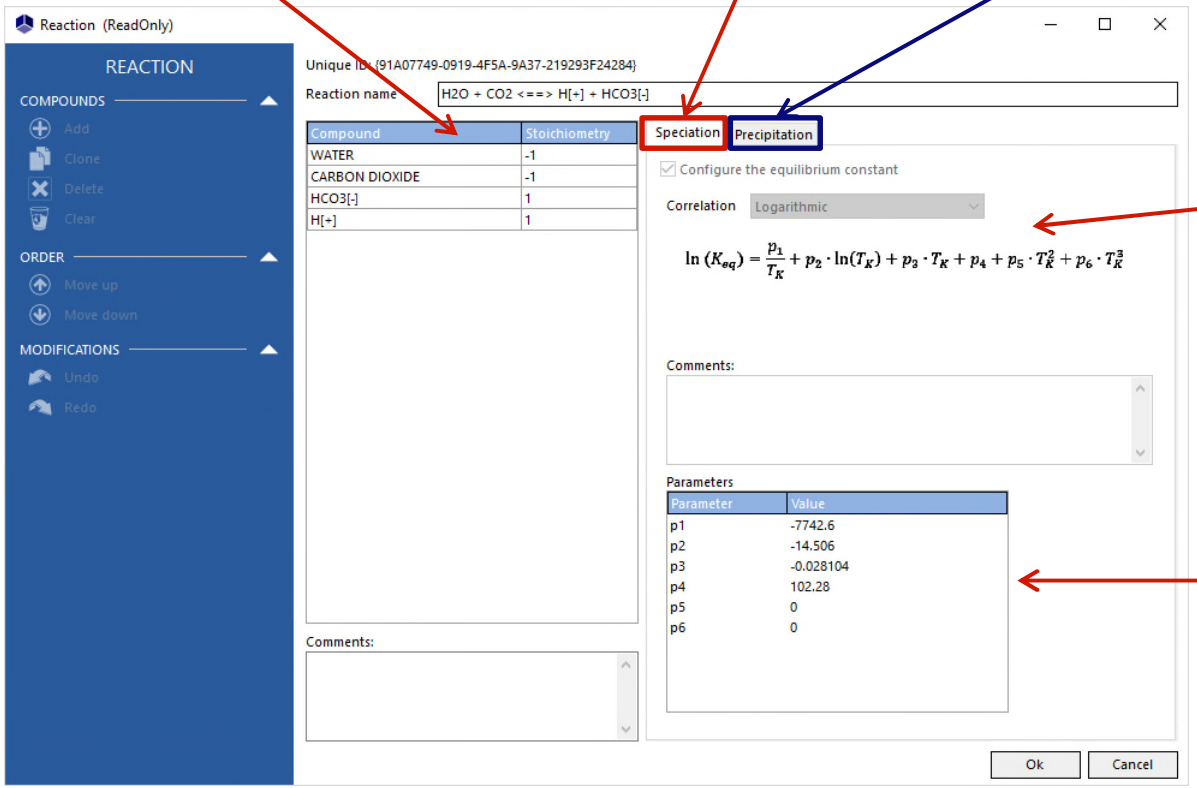
Simulis Thermodynamics: Visualization of parameters

- Step 3b: parameters of the selected electrolyte reaction (stoichiometry, speciation, possible precipitation)

Stoichiometry of the reaction

Parameters of the speciation (or dissociation)

Parameters of the precipitation (or solubility)

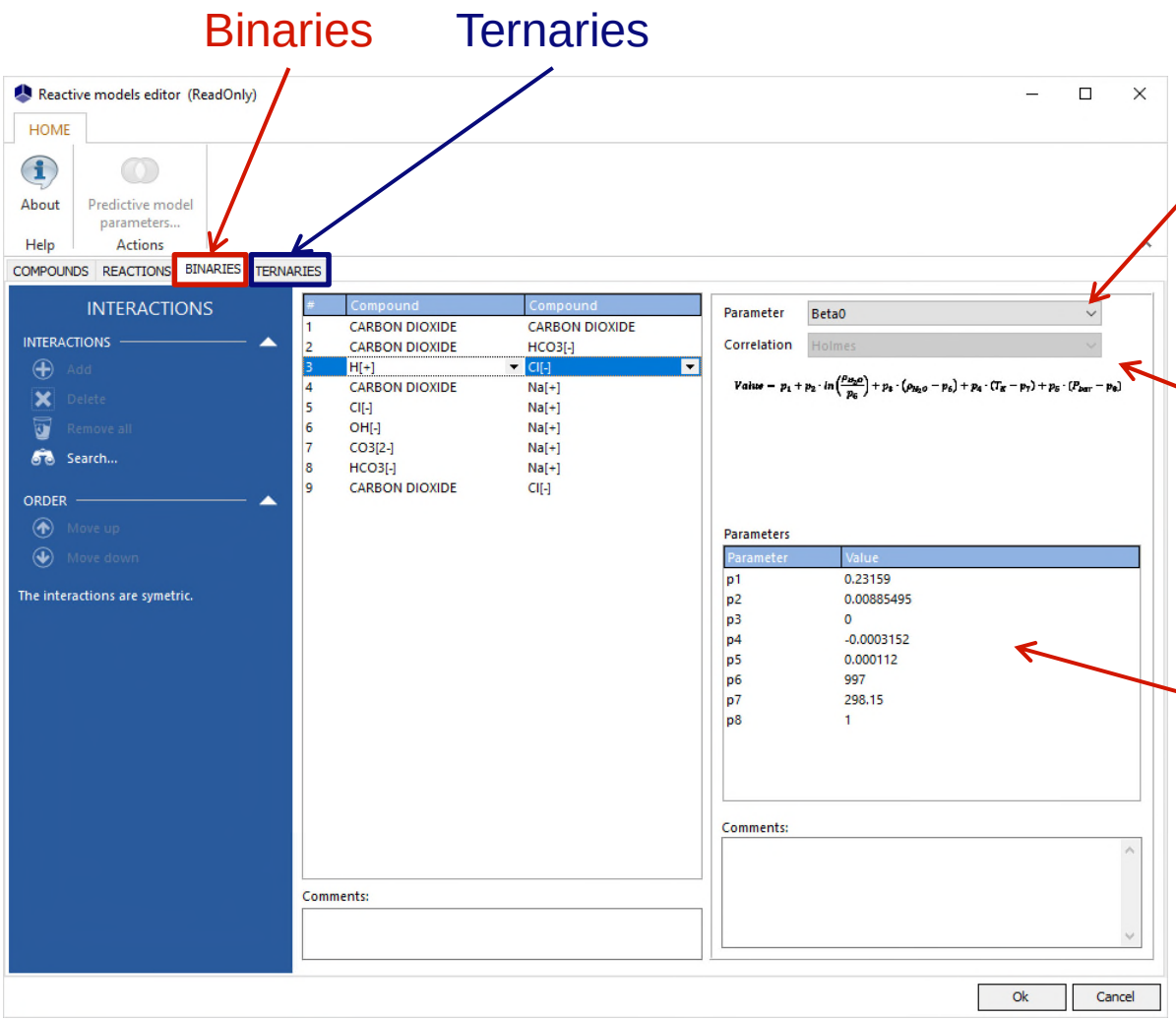


Correlation for speciation equilibrium constant (or for precipitation)

Parameters

Simulis Thermodynamics: Visualization of parameters

- Step 3c: interaction parameters of the chosen model between true species (binaries, possibly ternaries)



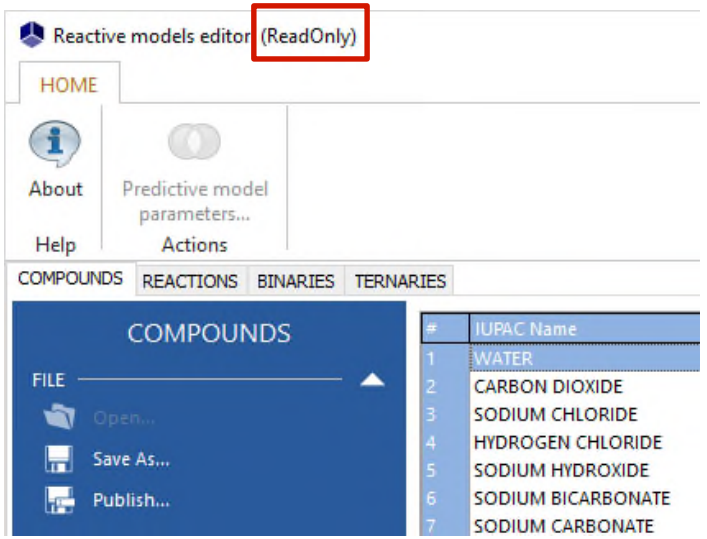
List of parameters of the chosen model

Correlation for the selected binary (or ternary) interaction parameter

Parameters

Simulis Thermodynamics: Visualization of parameters

- Parameters of the chosen model for the selected system, accessible from the "Reactive model parameters…" button, are "Read Only" (no possible modification)



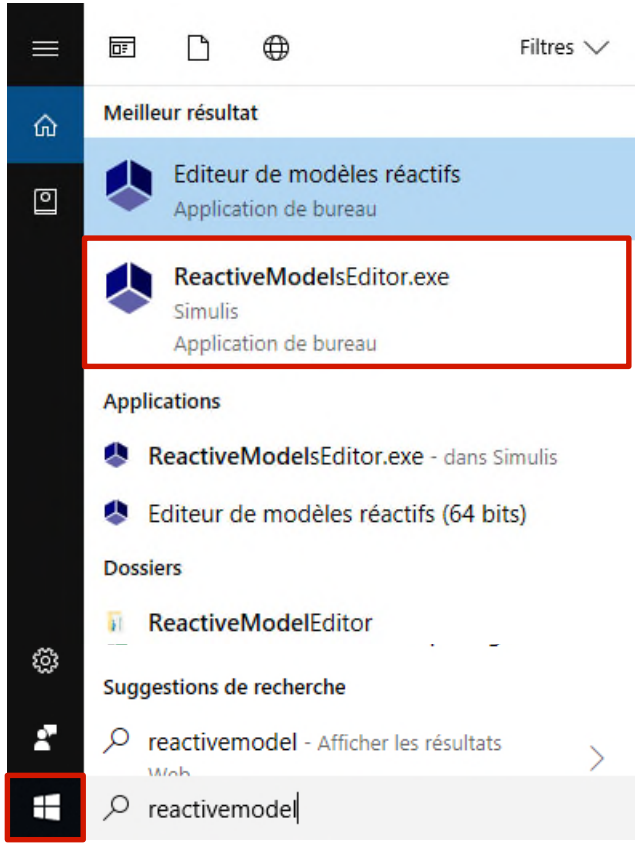
- Visualization of species, equilibrium reactions and interactions taken into account by the model

- Possibility to add systems or to modify parameters of existing systems

→ Use of the reactive models editor

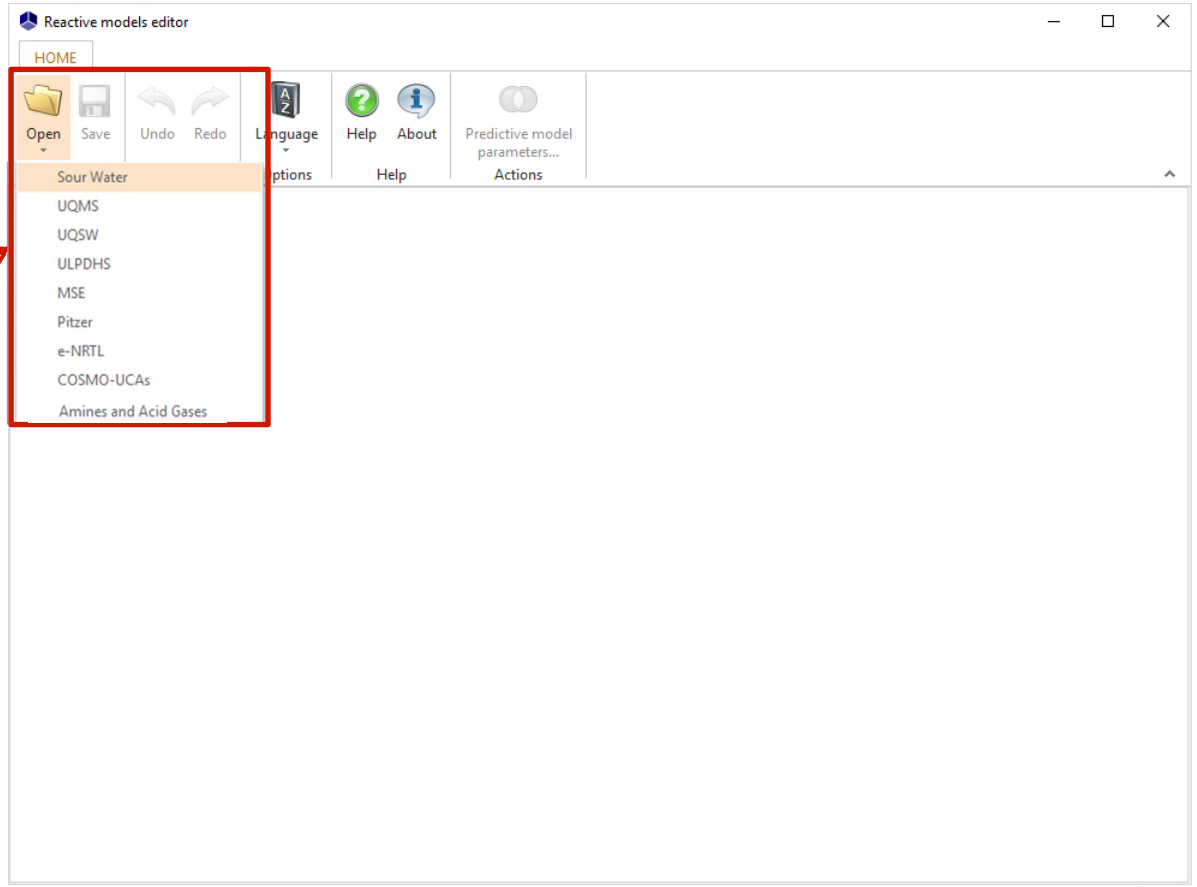
Reactive Models Editor

- Reactive models editor: “ReactiveModelsEditor.exe”
  - Accessible from “Start” menu of WINDOWS
  - Or in directory: C:\Program Files (x86)\Simulis
  - Or in directory: C:\Program Files\Simulis



Reactive Models Editor

- Reactive models editor: "ReactiveModelsEditor.exe"
  - Open a database associated to a model

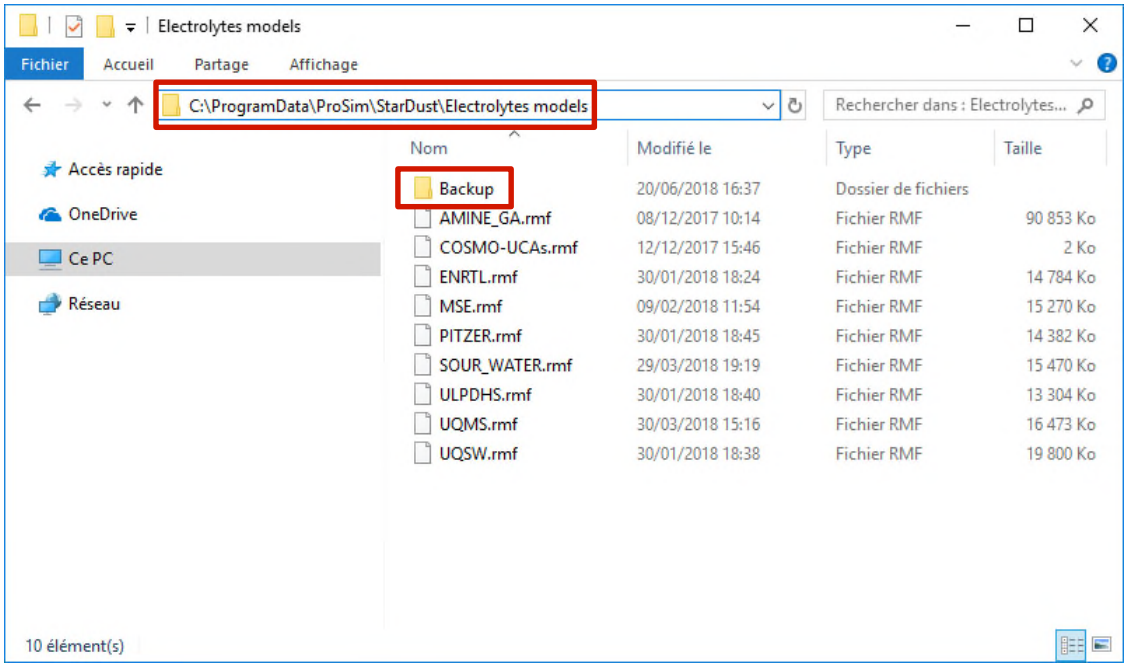


Access to databases of reactive model parameters

Reactive Models Editor

- Data file of reactive model parameters (**rmf**)
  - In C:\ProgramData\Prosim\Stardust\Electrolytes models
  - 1 rmf file for each electrolyte model

It is strongly recommended to save original rmf files as well as the different versions created by the user

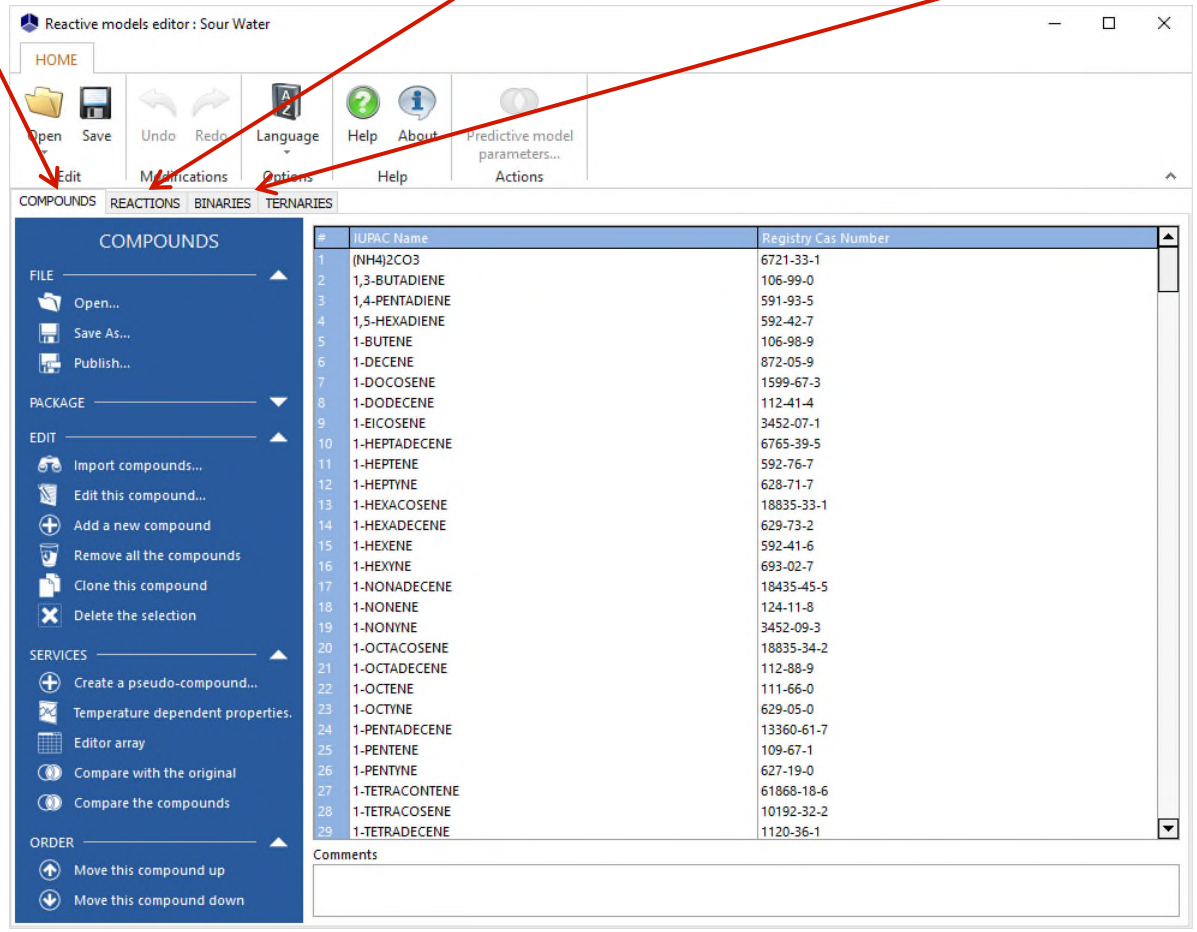


Reactive Models Editor

List of compounds taken into account for the selected model (true species)

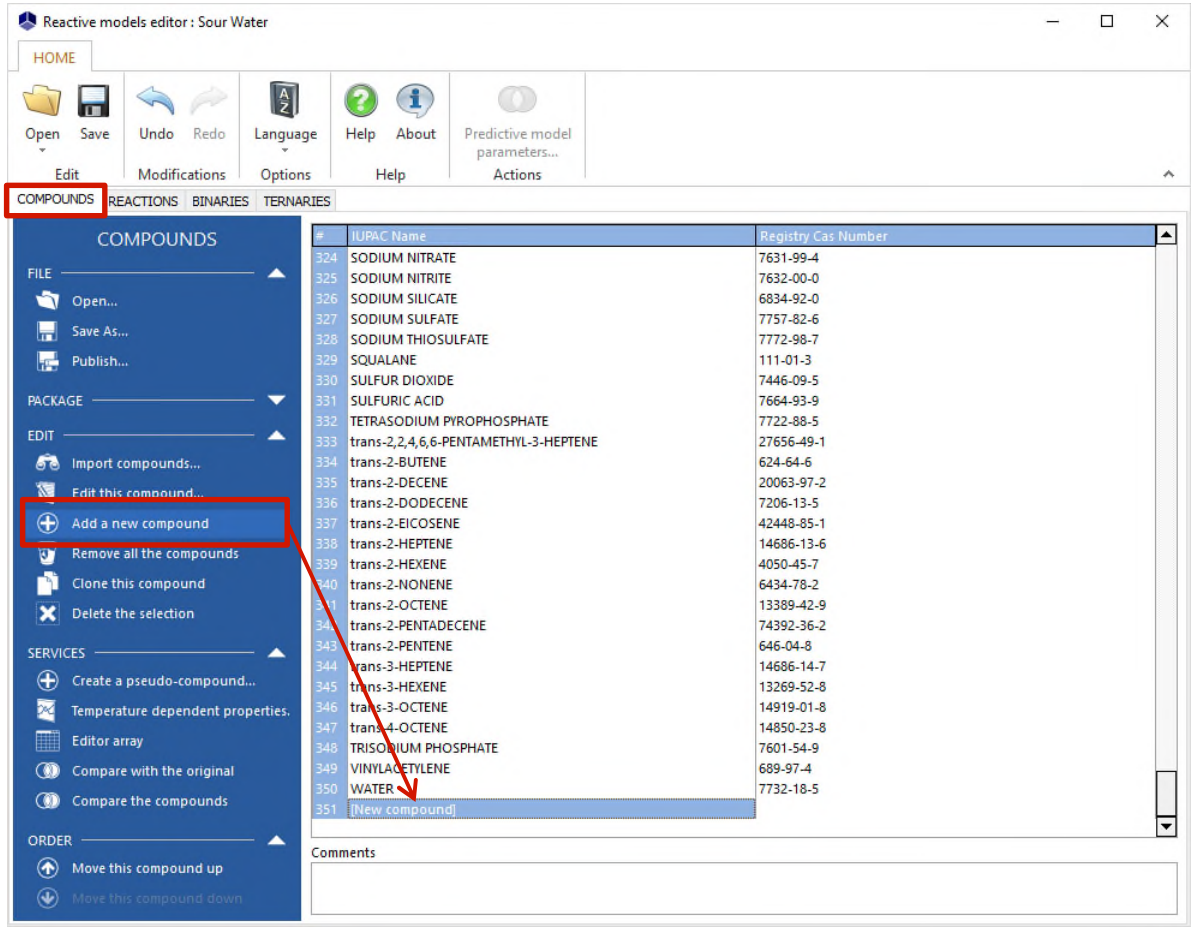
List of reactions taken into account for the selected model (access to speciation and precipitation constants)

Access to binary (possibly ternary) interaction parameters available for the selected model



Reactive Models Editor

- Add a species



Reactive Models Editor

- Add a ionic species: required properties
  - Name
  - CAS number or intrinsic number (negative value not used yet < -1000)
  - Molecular weight
  - Charge
  - Born constant
  - Thermal conductivity contribution (electrolyte solution)
    (only if the Jamieson-Thudope model is used)
  - Helgeson coefficients: A_1, A_2, A_3, A_4, C_1, C_2
    (only if the Helgeson model is used)
  - Standard entropy at 25°C – infinite dilution
  - Standard specific heat at 25°C – infinite dilution
  - Standard state enthalpy of formation – infinite dilution
  - Standard state Gibbs energy of formation – infinite dilution
  - Temperature dependent properties: those of water

Reactive Models Editor

- Add a salt: required properties
  - Name
  - CAS number or intrinsic number (negative value not used yet < -1000)
  - Chemical formula
  - Molecular weight
  - Physical state at 25°C: solid
  - Physical state in aqueous solution at 25°C
    (must be different from “completely soluble”)
  - Solid standard state enthalpy of formation
  - Solid specific heat (temperature dependent)
  - Vapor pressure: non volatile (equation #101 with A=-30)
  - Enthalpy of vaporization: null (equation #100 with A=B=C=D=E=0)
  - Other temperature dependent properties: those of water

Reactive Models Editor

- Add another component: required properties
  - Name
  - CAS number
  - Chemical formula
  - Molecular weight
  - Physical state at 25°C
  - Standard state enthalpy of formation at 25°C
  - Standard state Gibbs energy of formation at 25°C
  - Standard state absolute entropy at 25°C
  - Nakamura coefficients (A, B, C, D, A0, A1, B0, B1) (only if Nakamura equation of state is used)
  - All temperature dependent properties
  - Particularly Henry's law constant for solutes

Reactive Models Editor

- Properties of the species

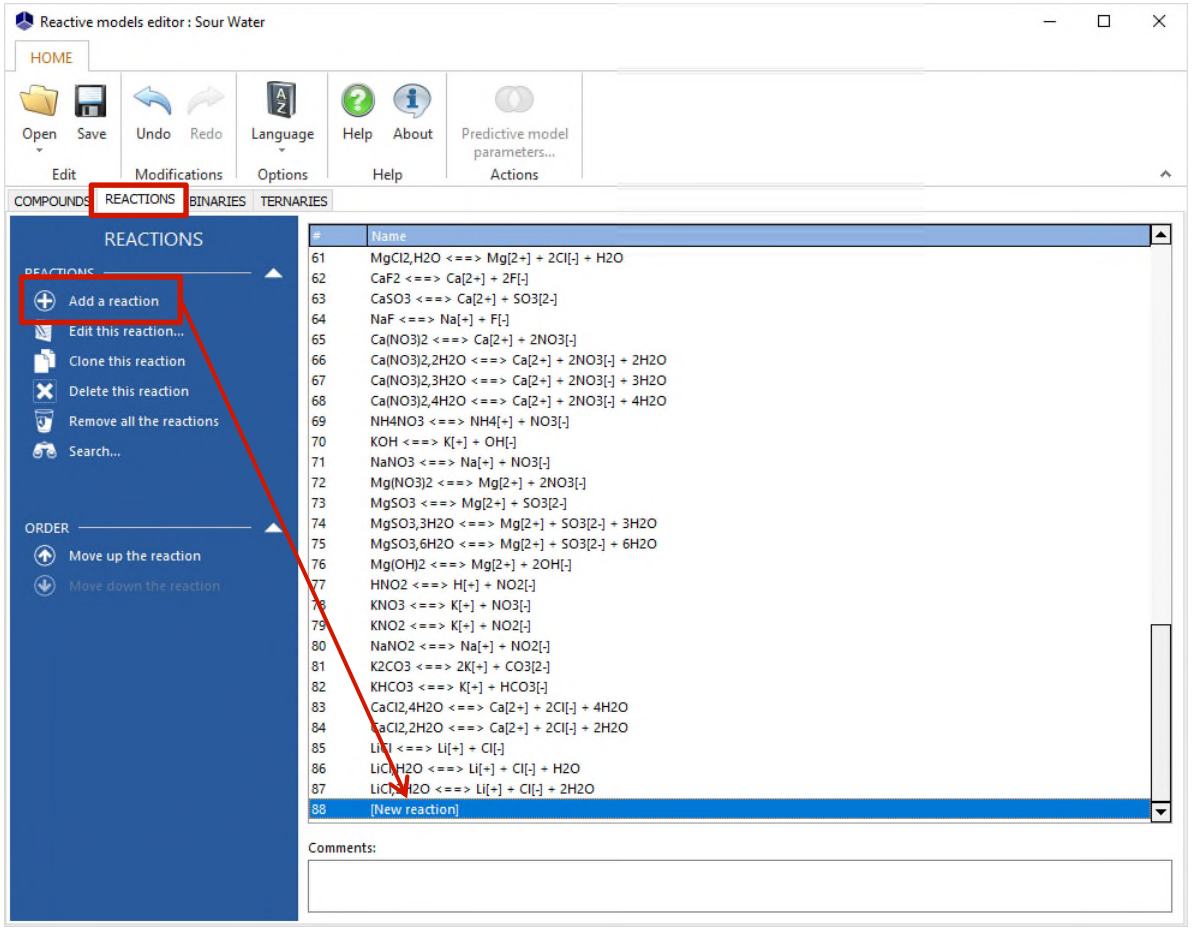
As part of the use of a reactive model, all properties of a component coming from the reactive models editor have priority compared to properties of a component selected in the calculator

- Except for the following properties:
  - Physical state at 25°C
  - Physical state in aqueous solution at 25°C

(it allows to impose or not, directly in the components of the calculator, a possible precipitation for systems with many salts)

Reactive Models Editor

- Add an electrolyte reaction



Reactive Models Editor

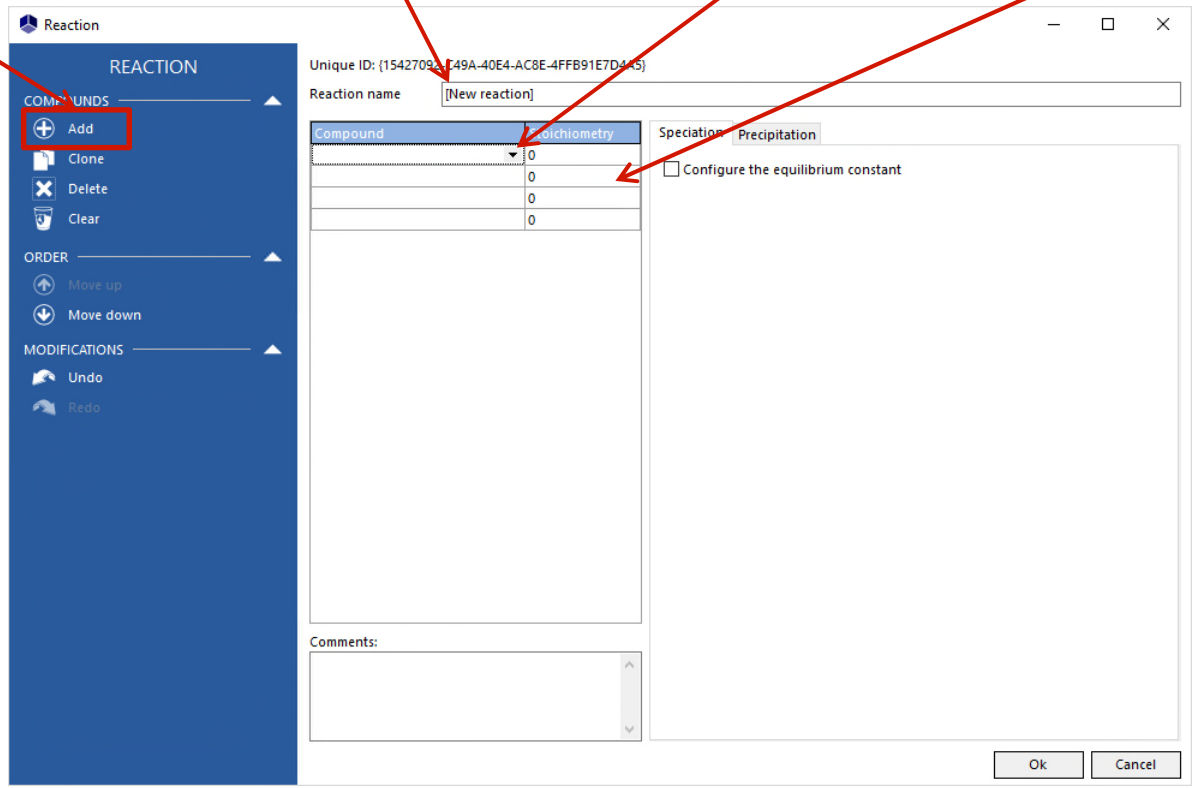
- Add an electrolyte reaction

1. Name of the reaction (e.g. A + B <==> C + D)

2. Add components of the reaction

3. Select each component concerned by the reaction from the dropdown list of species

4. Enter stoichiometric coefficients of the reaction



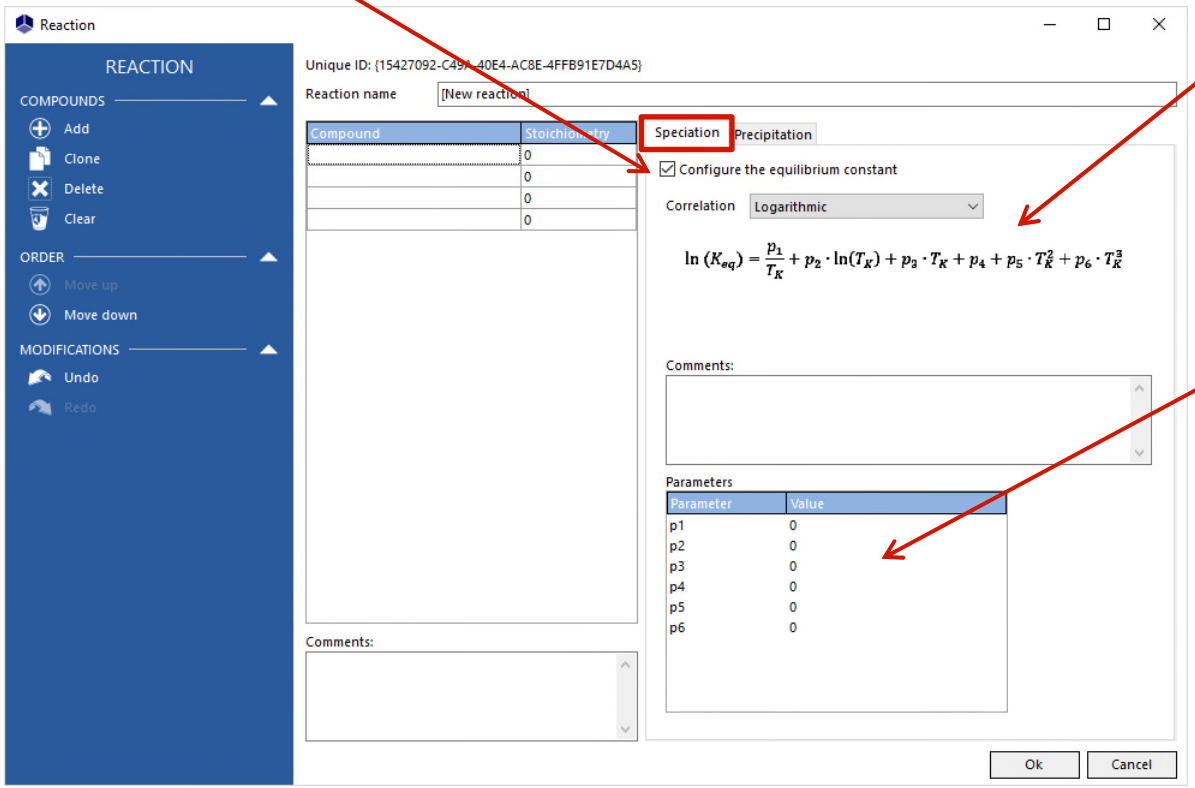
Reactive Models Editor

- Add an electrolyte reaction (speciation constant)

1. Configure the equilibrium constant

2. Choice of the correlation

3. Parameters of the correlation



For a total dissociation

$\ln(K_{eq}) = 35$

$(i.\ e.\ p_4 = 35)$

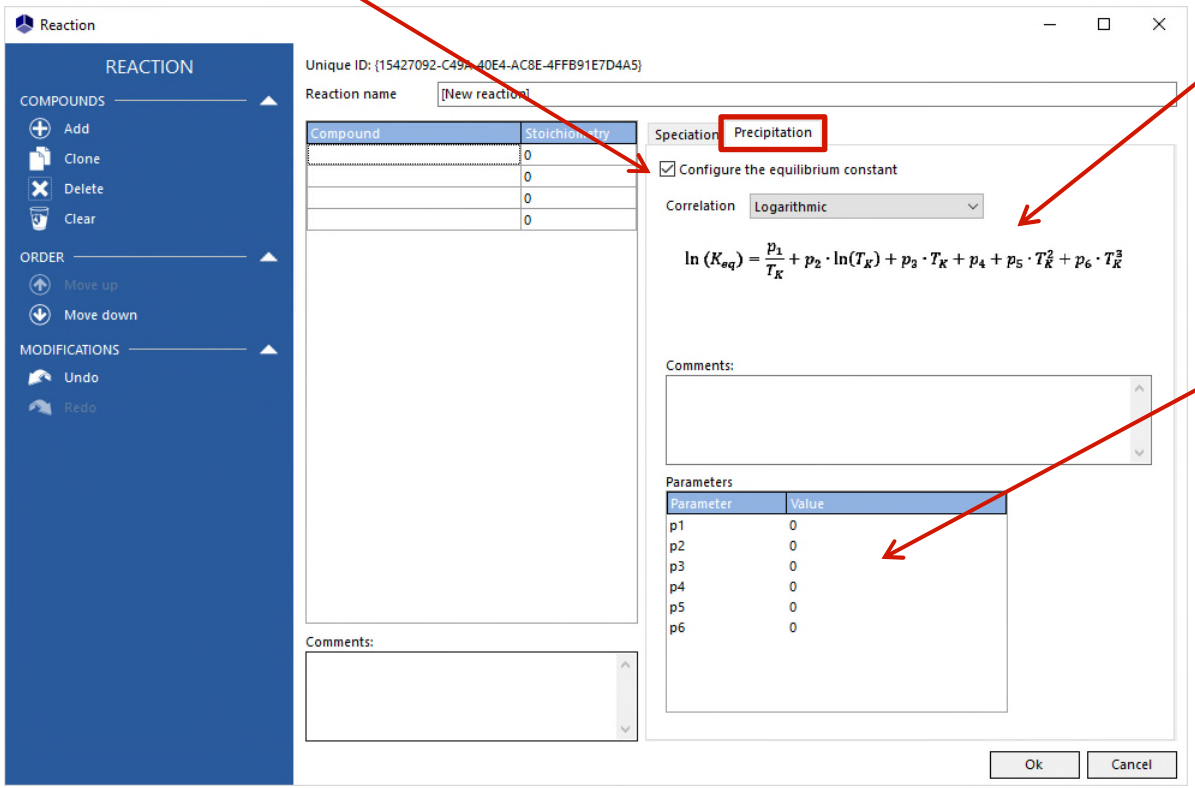
Reactive Models Editor

- Add an electrolyte reaction (precipitation constant, if necessary)

1. Configure the equilibrium constant

2. Choice of the correlation

3. Parameters of the correlation



Reactive Models Editor

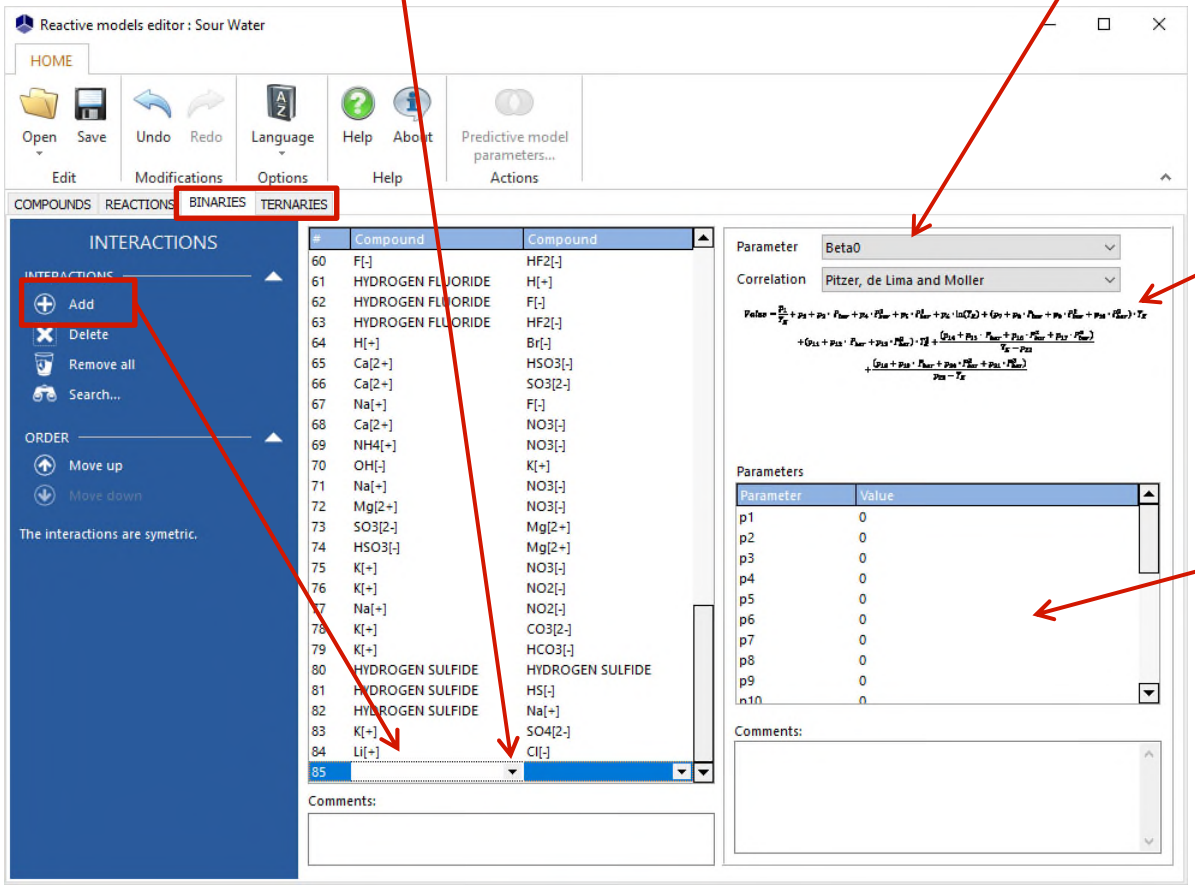
- Add binary or ternary interaction parameters

1. Select the concerned species from the dropdown list of species

2. Select the interaction parameter of the model

3. Choice of the correlation

4. Parameters of the correlation

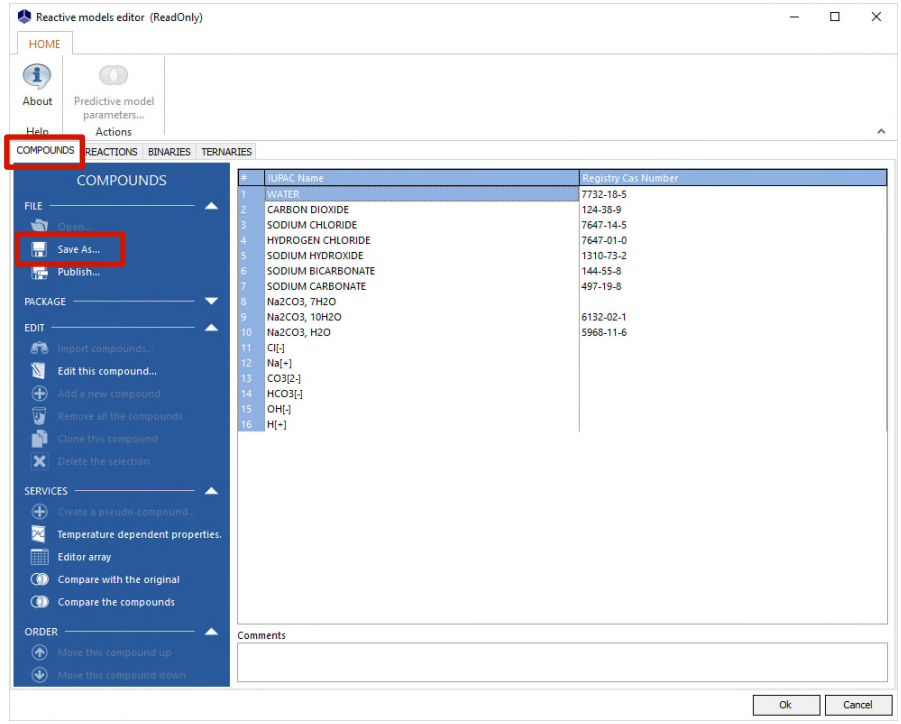


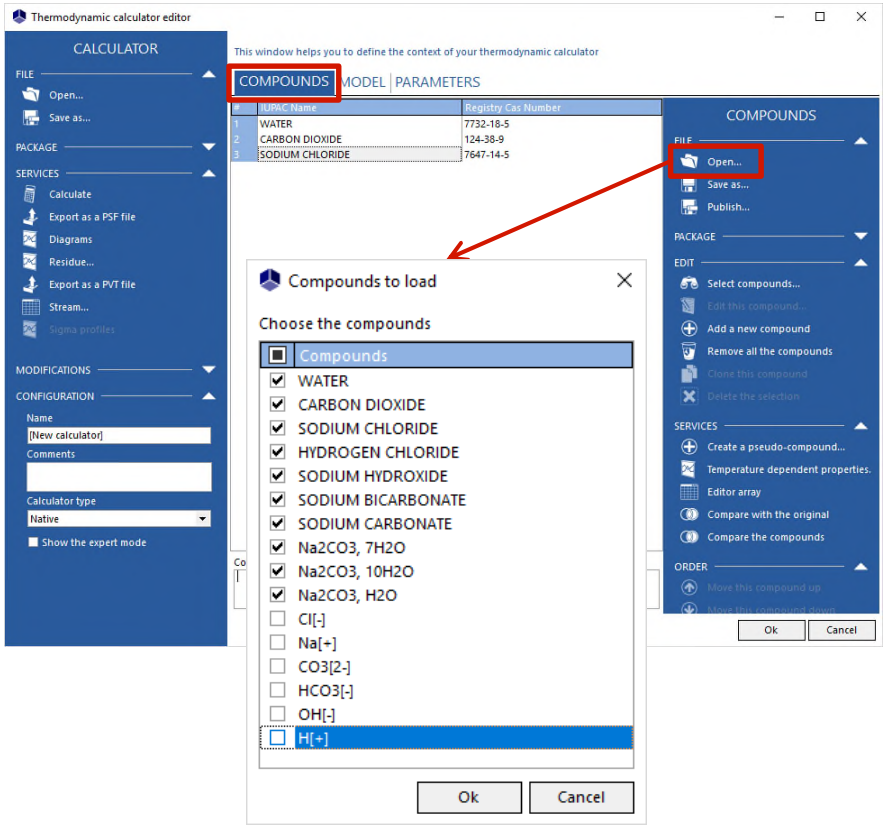
Reactive Models Editor vs Calculator

- Add in the calculator all species that are able to precipitate or to be recombined

Visualization of parameters:
Save all true species of the system as a *.compounds file

Calculator:
Open the *.compounds file and choose non ionic species



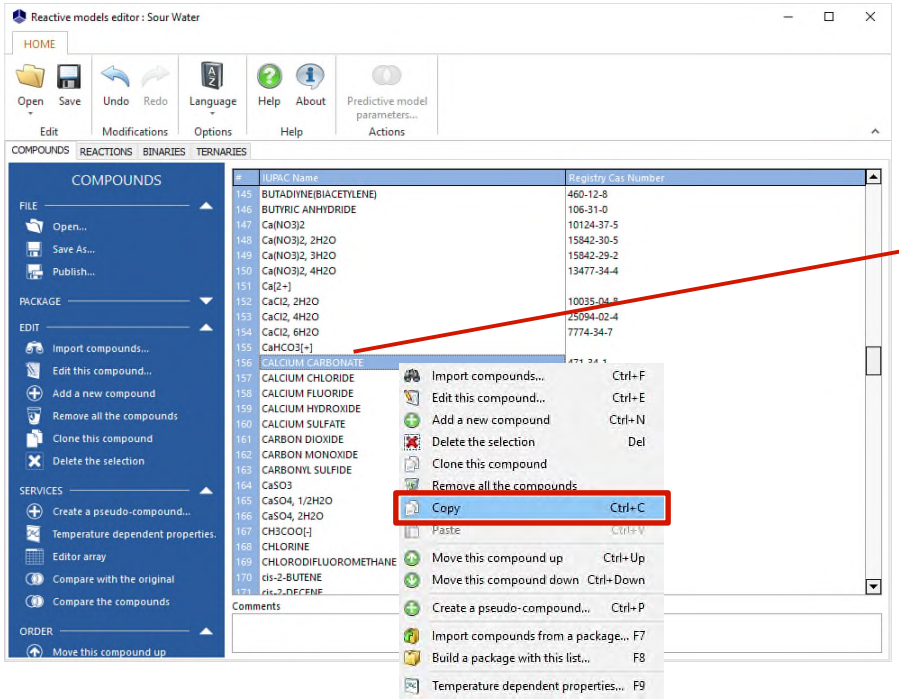


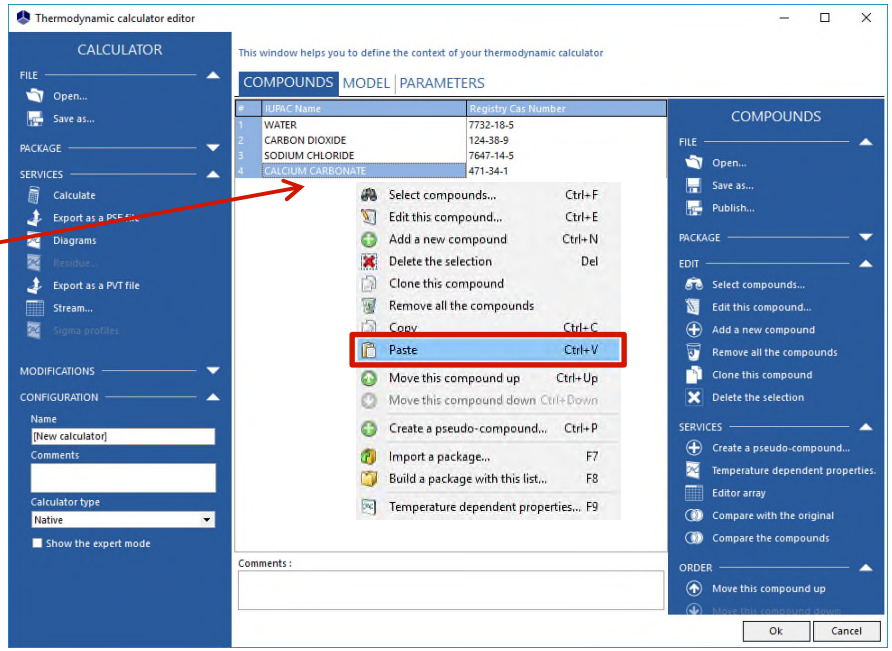
Reactive Models Editor vs Calculator

- Add species of the reactive models editor to the calculator

Reactive models editor:
Right click on a species,
Copy (or CTRL + C)

Calculator:
Right click in the component list,
Paste (or CTRL + V)

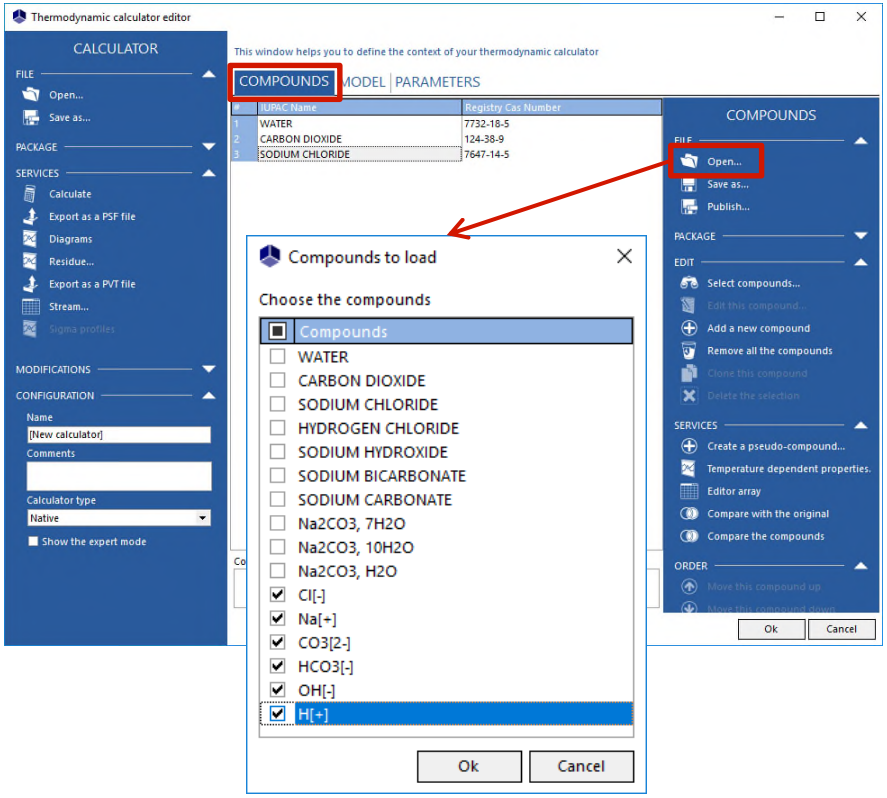




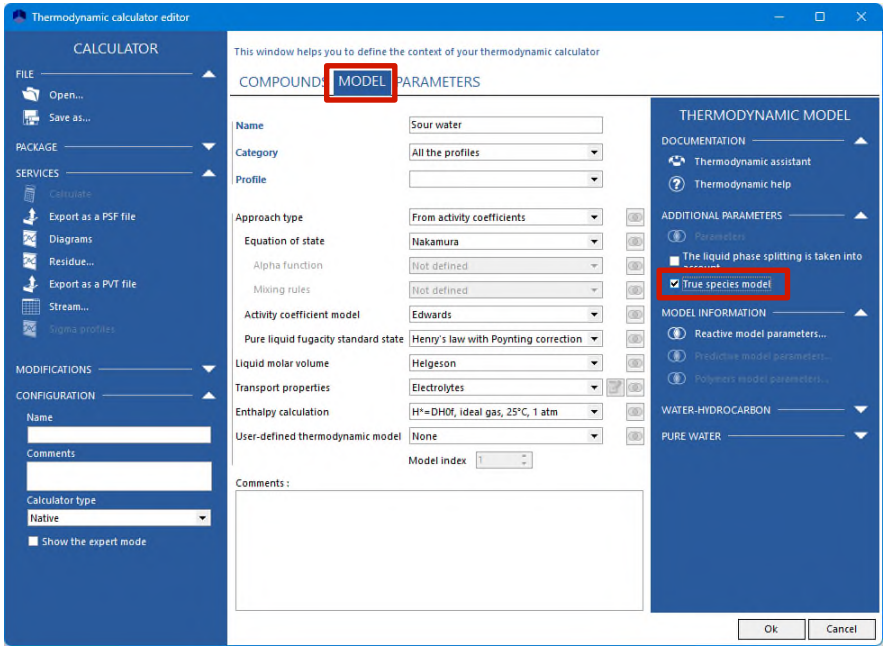
Reactive Models Editor vs Calculator

- Working directly with true species

Calculator - Compounds:
Open the *.compounds file and choose ionic species in addition to apparent species defined by the user



Calculator - Model:
Select the “true species model” option (no reaction taken into account)



Allows reaction description with controlled kinetics that are managed externally (e.g. ProSimPlus, Excel, Matlab…)

ProSim

Software & Services In Process Simulation

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