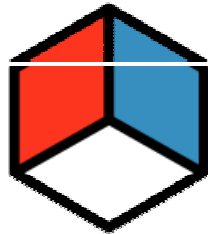




# **Electrolytes in ProSim software**



**ProSim**

## 1. Introduction

Representation of liquid-vapor equilibrium for electrolytic solutions is a complex operation, because it involves physico-chemical phenomena such as partial or complete dissociation of salts, electrostatic interaction between ions, ion solvation, .... The calculation is more complex if the liquid phase is a solvent mixture, with different dielectric characteristics. Furthermore, the presence of dissolved salt could have an important influence on the vapor phase composition (salt effect). For all these reasons, classical thermodynamic models (NRTL, UNIQUAC...), called physical models, do not represent liquid-vapor equilibrium in mixed solvent/salts solutions accurately.

This document presents several thermodynamic models applied to electrolyte solution implemented in ProSim thermodynamic library. It is important to note that for each electrolyte model, specific data are required in order to well represent a given system (reaction's stoichiometry, reaction's equilibrium constant, Heat of formation at infinite dilution, interaction parameters, Henry's law,...).

Nowadays, models parameters have been set in order to allow numerous systems modelisation. The performed developments allow to increase model accuracy and also model flexibility in order to be able to add quickly and easily new systems.

## 2. Some definitions

Some important definitions to bear in mind for electrolyte thermodynamic models conception are :

- *Phase*: The physical state of one or more chemical species.
- *Electrolyte*: A molecular or atomic species (gaseous, liquid, or solid) which has some solubility in water and reacts in water, to some significant extent, to one or more ionic (charged) species.  $\text{CO}_2(\text{g})$ , and  $\text{NaCl}(\text{s})$  are examples of electrolytes.
- *Nonelectrolyte*: A molecular or atomic species (gaseous, liquid, or solid) which has some solubility in water and remains nearly totally in the molecular form (uncharged) when dissolved in water.  $\text{Ar}(\text{g})$  and  $\text{C}_6\text{H}_{14}(\text{l})$  are examples of nonelectrolytes.
- *Ionic species*: A species dissolved in water and possessing a charge. Charged species are either termed cations (positive charge) or anions (negative charge).  $\text{Na}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  are examples of ionic species.
- *Molecular species*: A species dissolved in water and having no charge.  $\text{CO}_2(\text{aq})$  and  $\text{FeCl}_3(\text{aq})$  are examples of molecular species.
- *Complex, ion pair*: A species composed of both cationic and anionic portions. Complexes can be charged or uncharged.  $\text{FeCl}^{2+}(\text{aq})$  and  $\text{FeCl}_3(\text{aq})$  are examples of complexes.

- *Strong electrolyte*: A molecular or atomic species which completely dissociates to its constituent base ions, leaving virtually no uncharged molecular forms of species in water. NaCl(s) and KCl(s) at room temperature are examples of strong electrolytes.
- *Weak electrolyte*: A molecular or atomic species which partially dissociates in water to its constituent ions, leaving a significant concentration of the molecular form and/or other complexes.
- *Aqueous electrolyte equilibrium*: The thermodynamic equilibrium involving species, all of which are in the aqueous phase. An example of an electrolyte equilibrium is:



- *Aqueous phase equilibrium*: The thermodynamic description of the physical equilibrium between an aqueous phase and one other phase. The other phase can be, among others, gaseous, nonaqueous liquid, or an independent solid.  $\text{Ar} (\text{g}) \rightleftharpoons \text{Ar} (\text{aq})$  is an example of an aqueous phase equilibrium.
- *Solvent*: For aqueous systems, this refers to water.
- *Solute*: A substance dissolved in water. NaCl, present in water as  $\text{Na}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$ , is an example of solute.
- *Molality*: The customary unit of concentrations for all species in the aqueous phase other than  $\text{H}_2\text{O}(\text{aq})$ . Molality (abbreviated m) is defined as the moles of an aqueous phase species per kilogram (approximately 55.508 mol) of water. Molality is a more convenient unit of concentration than other concentration units (such as molarity), in that molality is independent of temperature.
- *Thermodynamic properties*: Aqueous-phase thermodynamic properties for all species other than water are usually expressed on a partial molal basis. This means that the property is per mole of solution. The principal properties we will be most concerned with are partial molal Gibbs free energy, enthalpy, entropy, heat capacity, and volume. Each species in solution possesses a value for each of these properties. Each of the partial molal thermodynamic properties is the sum of a standard-state term and an excess term.
- *Standard-state (term)*: This refers to the thermodynamic value ( $\bar{P}_i^0$ ) at a defined state (a specified concentration, temperature, and pressure). The nonideal (excess) contributions ( $\bar{P}_i^E$ ) are departures from this state. For aqueous systems, the standard state refers to a hypothetical 1 m solution of the species extrapolated to infinite dilution. For simplicity, this state is simply referred to as one of infinite dilution. It is quite important to realize that the standard state, as in most nonaqueous standard states, is a continuous function of temperature and pressure but not a function of composition. The difference between the sum of standard-state values for the products of chemical reaction multiplied by their stoichiometric coefficients and the sum of standard-state values for the reactants multiplied by their stoichiometric coefficients is related directly to the thermodynamic equilibrium constant for the reaction.
- *Reference state*: This is the thermodynamic value ( $\bar{P}_i^R$ ) at a specific standard state of 298.15 K and 1 atm. As noted above, the standard state is a continuous function of temperature and pressure. That means that for any choice of temperature and pressure there is a standard-state value. The reference state, on the other hand, refers to a specific temperature and pressure, as noted above.

One of the principal purposes for a reference state is that this state becomes the most common condition for experimental measurements. Compilations of experimental data for aqueous systems are usually comprised of measurements of the reference-state partial molal free energy, enthalpy, entropy, heat capacity, and volume.

- *Excess (term)*: This measures the departure of a partial molal thermodynamic property from the standard state. This term is customarily a function of temperature, pressure, and composition. This term is related directly to the activity, and in turn, to the activity coefficient and concentration of the species in question.
- *Activity*: The activity of a species ( $a_i$ ), is a thermodynamic property of the species which relates directly to the excess Gibbs free energy ( $G_i^E$ ). Specifically,

$$\bar{G}_i^E = RT \ln(a_i)$$

where R is the gas constant and T is the absolute temperature.

- *Activity coefficient*: The activity coefficient of a dissolved species ( $\gamma_i$ ), is defined as the thermodynamic property of the species which relates directly to the activity by

$$a_i = \gamma_i m_i$$

where  $m_i$  is the concentration of the species in units of molality. Defined this way, the aqueous activity coefficient is said to conform to the asymmetric convention. The asymmetric convention means that the activity coefficient of the species approaches unity as the concentration of the species approaches zero (infinite dilution). This is quite different from the more familiar symmetric conventionst, in which the species activity coefficient approaches unity as the species mole fraction approaches unity.

### 3. Models available in the ProSim software

#### 3.1. Mixed solvents UNIQUAC electrolytes (UQMS)

The UQMS model (extended version of UNIQUAC model) has been especially developed for the thermodynamic treatment of mixed solvent/salts solutions. The calculation of the activity coefficient using this model includes the following elements :

- a Debye-Huckel contribution, in order to take into account the electrostatic effects of ions in the solution.
- a combinatorial term which takes into account the form and size differences for the species present.
- a residual term that takes into account interactions between the various present species. It is calculated from fitted parameters, called binary interaction parameters which, in this case, depend on the composition.

Mathematical expressions used can be consulted in the literature [1].

#### Use

All binary interaction parameters of ion-solvent and salt-solvent are "pre coded" for all the electrolytic reactions hereafter. It is possible to add quickly new systems, please consult.

$\text{HCl} \rightleftharpoons \text{H}^{+} + \text{Cl}^{-}$	$\text{NaHCO}_3 \rightleftharpoons \text{Na}^{+} + \text{HCO}_3^{-}$
$\text{NaBr} \rightleftharpoons \text{Na}^{+} + \text{Br}^{-}$	$\text{Na}_2\text{CO}_3 \rightleftharpoons 2\text{Na}^{+} + \text{CO}_3^{2-}$
$\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}^{+} + \text{HCO}_3^{-}$	$\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^{-}$
$\text{HCO}_3^{-} \rightleftharpoons \text{H}^{+} + \text{CO}_3^{2-}$	$\text{KCl} \rightleftharpoons \text{K}^{+} + \text{Cl}^{-}$
$\text{NH}_3 + \text{HCO}_3^{-} \rightleftharpoons \text{H}_2\text{O} + \text{NH}_2\text{COO}^{-}$	$\text{NaF} \rightleftharpoons \text{Na}^{+} + \text{F}^{-}$
$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^{+} + \text{HSO}_4^{-}$	$\text{CaCl}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{Cl}^{-}$
$\text{HSO}_4^{-} \rightleftharpoons \text{H}^{+} + \text{SO}_4^{2-}$	$\text{KI} \rightleftharpoons \text{K}^{+} + \text{I}^{-}$
$\text{Na}_2\text{SO}_4 \rightleftharpoons 2\text{Na}^{+} + \text{SO}_4^{2-}$	$\text{NaI} \rightleftharpoons \text{Na}^{+} + \text{I}^{-}$
$(\text{NH}_4)_2\text{SO}_4 \rightleftharpoons 2\text{NH}_4^{+} + \text{SO}_4^{2-}$	$\text{KBr} \rightleftharpoons \text{K}^{+} + \text{Br}^{-}$
$\text{NaCl} \rightleftharpoons \text{Na}^{+} + \text{Cl}^{-}$	$\text{K}_2\text{CO}_3 \rightleftharpoons 2\text{K}^{+} + \text{CO}_3^{2-}$
$\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_4^{+} + \text{Cl}^{-}$	$\text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{+} + \text{NO}_3^{-}$
$\text{NaOH} \rightleftharpoons \text{Na}^{+} + \text{OH}^{-}$	$2\text{HNO}_3 \rightleftharpoons \text{H}_2\text{O} + \text{NO}_3^{-} + \text{NO}_2^{+}$
$\text{NaC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{Na}^{+} + \text{CH}_3\text{COO}^{-}$	$\text{Mg}(\text{NO}_3)_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{NO}_3^{-}$
$\text{CuCl}_2 \rightleftharpoons \text{Cu}^{2+} + 2\text{Cl}^{-}$	

#### Range of application

This model applies to salt concentration up to 10 mol/kg for salts 1:1 (NaCl, KCl,...) and 6,5 mol/kg for salts 2:1 (CaCl<sub>2</sub>,...).

### 3.2. Sour Water UNIQUAC electrolytes (UQSW)

An other electrolytic version of the UNIQUAC model is described in [2], [3], [4]. This model has been specially developed for electrolytes in aqueous solution with different kind of equilibria : ionic, solid-liquid and liquid vapour. As for the UQMS model, it is an electrolyte model formed by combining:

- a Debye-Huckel contribution, in order to take into account the electrostatic effects of ions in the solution;
- Classical UNIQUAC combinatorial term which takes into account the form and size differences for the species present;

Classical UNIQUAC residual term that takes into account interactions between the various present species

The combinatorial and the residual terms of the UNIQUAC excess Gibbs energy function are based on the rational, symmetrical activity convention. The Debye-Hückel electrostatic term is expressed in term of the rational, symmetrical convention for water and the rational, asymmetrical convention for the solutes.

#### Use

All the description parameters of the chemical reactions and/or physical balances are "pre coded" for all the electrolytic reactions hereafter. It is possible to add quickly new systems, please consult.

$H_2O \Leftrightarrow H[+] + OH[-]$	$Na_2CO_3 \Leftrightarrow 2Na[+] + CO_3[=]$
$H_2O + NH_3 \Leftrightarrow NH_4[+] + OH[-]$	$Na_2SO_4, 10H_2O \Leftrightarrow Na_2SO_4 + 10 H_2O$
$H_2O + CO_2 \Leftrightarrow H[+] + HCO_3[-]$	$KCl \Leftrightarrow K[+] + Cl[-]$
$HCO_3[-] \Leftrightarrow H[+] + CO_3[=]$	$K_2SO_4 \Leftrightarrow 2K[+] + SO_4[=]$
$NH_3 + HCO_3[-] \Leftrightarrow H_2O + NH_2COO[-]$	$HNO_3 + H_2O \Leftrightarrow H_3O[+] + NO_3[-]$
$HCl \Leftrightarrow H[+] + Cl[-]$	$NaNO_3 \Leftrightarrow Na[+] + NO_3[-]$
$H_2SO_4 \Leftrightarrow H[+] + HSO_4[-]$	$KNO_3 \Leftrightarrow K[+] + NO_3[-]$
$HSO_4[-] \Leftrightarrow H[+] + SO_4[=]$	$(NH_4)NO_3 \Leftrightarrow NH_4[+] + NO_3[-]$
$Na_2SO_4 \Leftrightarrow 2Na[+] + SO_4[=]$	$K_2CO_3 \Leftrightarrow 2K[+] + CO_3[=]$
$(NH_4)_2SO_4 \Leftrightarrow 2NH_4[+] + SO_4[=]$	$H_2O + SO_2 \Leftrightarrow H[+] + HSO_3[-]$
$NaCl \Leftrightarrow Na[+] + Cl[-]$	$HSO_3[-] \Leftrightarrow H[+] + SO_3[=]$
$NH_4Cl \Leftrightarrow NH_4[+] + Cl[-]$	$2HSO_3[-] \Leftrightarrow S_2O_5[=] + H_2O$
$NaOH \Leftrightarrow Na[+] + OH[-]$	$Na_2S_2O_5 \Leftrightarrow 2Na[+] + S_2O_5[=]$
$(NH_4)_2CO_3 \Leftrightarrow 2NH_4[+] + CO_3[=]$	$Na_2S_2O_5, 7H_2O \Leftrightarrow 2Na[+] + S_2O_5[=] + 7H_2O$
$(NH_4)HCO_3 \Leftrightarrow NH_4[+] + HCO_3[-]$	$Na_2SO_3 \Leftrightarrow 2Na[+] + SO_3[2-]$
$NaHCO_3 \Leftrightarrow Na[+] + HCO_3[-]$	$Na_2SO_3, 7H_2O \Leftrightarrow 2Na[+] + SO_3[2-] + 7H_2O$

### **3.3. Sour Water**

The complexity of electrolytes aqueous solutions is even more obvious for the systems  $\text{H}_2\text{O-NH}_3\text{-CO}_2\text{-H}_2\text{S}$ ... (known as "Sour Water" systems) where the dissociation of weak electrolytes ( $\text{NH}_3$ ,  $\text{CO}_2$ ,...) is strongly linked to the pH value. As a matter of fact, absorption of acid gases ( $\text{H}_2\text{S}$ ,  $\text{CO}_2$ ,...) will be easier if there is ammonia in the solution. Thus, it became necessary to develop a specific model in order to take into account the involved phenomena, as classical models were not adapted.

The Sour Water model has been specifically developed for thermodynamic representation of the above described solutions. This model is based on the following concepts :

- partial dissociation of electrolytes;
- chemical equilibrium between ions and undissociated species;
- physical equilibrium between the species in vapor phase (all the components except ions) and the undissociated molecules in liquid phase;
- non ideal behavior of the liquid phase.

The model automatically takes into account all information relating to the acido-basic reactions associated to these components.

Furthermore, the Sour Water model enables to take into account the contribution to the mixture of strong electrolytes.

The Sour Water model also enables to take into account non condensable gases that will be considered as chemically inert. These components are : Argon ,Nitrogen, Oxygen, Hydrogen, Carbon monoxide, Methane, Ethane, Propane, Carbonyl Sulfide.

Any other component will be considered as inert and possible interactions with water will not be taken into account. Activity coefficient calculation is based on the Pitzer method, modified by Edwards and Maurer.

#### **Use**

All the description parameters of the chemical reactions and/or physical balances are "pre coded" for all the electrolytic reactions hereafter. It is possible to add quickly new systems, please consult.

$\text{H}_2\text{O} \rightleftharpoons \text{H}^{[+]} + \text{OH}^{[-]}$	$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^{[+]} + \text{CH}_3\text{COO}^{[-]}$
$\text{H}_2\text{O} + \text{NH}_3 \rightleftharpoons \text{NH}_4^{[+]} + \text{OH}^{[-]}$	$(\text{NH}_4)_2\text{CO}_3 \rightleftharpoons 2\text{NH}_4^{[+]} + \text{CO}_3^{[=]}$
$\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}^{[+]} + \text{HCO}_3^{[-]}$	$\text{NH}_4\text{HCO}_3 \rightleftharpoons \text{NH}_4^{[+]} + \text{HCO}_3^{[-]}$
$\text{HCO}_3^{[-]} \rightleftharpoons \text{H}^{[+]} + \text{CO}_3^{[=]}$	$\text{NaHCO}_3 \rightleftharpoons \text{Na}^{[+]} + \text{HCO}_3^{[-]}$
$\text{H}_2\text{S} \rightleftharpoons \text{H}^{[+]} + \text{HS}^{[-]}$	$\text{Na}_2\text{CO}_3 \rightleftharpoons 2\text{Na}^{[+]} + \text{CO}_3^{[=]}$
$\text{HS}^{[-]} \rightleftharpoons \text{H}^{[+]} + \text{S}^{[=]}$	$\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{[2+]} + 2\text{OH}^{[-]}$
$\text{H}_2\text{O} + \text{SO}_2 \rightleftharpoons \text{H}^{[+]} + \text{HSO}_3^{[-]}$	$\text{Ca}(\text{Cl})_2 \rightleftharpoons \text{Ca}^{[2+]} + 2\text{Cl}^{[-]}$
$\text{HSO}_3^{[-]} \rightleftharpoons \text{H}^{[+]} + \text{SO}_3^{[=]}$	$\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O} \rightleftharpoons 2\text{Na}^{[+]} + \text{SO}_4^{[=]} + 10 \text{H}_2\text{O}$
$\text{HCN} \rightleftharpoons \text{H}^{[+]} + \text{CN}^{[-]}$	$\text{KCl} \rightleftharpoons \text{K}^{[+]} + \text{Cl}^{[-]}$
$\text{NH}_3 + \text{HCO}_3^{[-]} \rightleftharpoons \text{H}_2\text{O} + \text{NH}_2\text{COO}^{[-]}$	$\text{K}_2\text{SO}_4 \rightleftharpoons 2\text{K}^{[+]} + \text{SO}_4^{[=]}$
$\text{HCl} \rightleftharpoons \text{H}^{[+]} + \text{Cl}^{[-]}$	$\text{CH}_3\text{COONa} \rightleftharpoons \text{Na}^{[+]} + \text{CH}_3\text{COO}^{[-]}$
$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^{[+]} + \text{HSO}_4^{[-]}$	$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{[2+]} + \text{CO}_3^{[=]}$
$\text{HSO}_4^{[-]} \rightleftharpoons \text{H}^{[+]} + \text{SO}_4^{[=]}$	$\text{CaSO}_4 \rightleftharpoons \text{Ca}^{[2+]} + \text{SO}_4^{[=]}$
$\text{DEA} + \text{H}_2\text{O} \rightleftharpoons \text{DEAH}^{[+]} + \text{OH}^{[-]}$	$\text{CaSO}_4, 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{[2+]} + \text{SO}_4^{[=]} + 2\text{H}_2\text{O}$
$2\text{DEA} + \text{CO}_2 \rightleftharpoons \text{DEAH}^{[+]} + \text{DEACOO}^{[-]}$	$\text{CaHCO}_3^{[+]} \rightleftharpoons \text{Ca}^{[2+]} + \text{HCO}_3^{[-]}$
$\text{MEA} + \text{H}_2\text{O} \rightleftharpoons \text{MEAH}^{[+]} + \text{OH}^{[-]}$	$\text{CaCl}^{[+]} \rightleftharpoons \text{Ca}^{[2+]} + \text{Cl}^{[-]}$
$2\text{MEA} + \text{CO}_2 \rightleftharpoons \text{MEAH}^{[+]} + \text{MEACOO}^{[-]}$	$\text{FeSO}_4 \rightleftharpoons \text{Fe}^{[2+]} + \text{SO}_4^{[=]}$
$\text{MDEA} + \text{H}_2\text{O} \rightleftharpoons \text{MDEAH}^{[+]} + \text{OH}^{[-]}$	$\text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons 2\text{Fe}^{[3+]} + 3\text{SO}_4^{[=]}$
$\text{Na}_2\text{SO}_4 \rightleftharpoons 2\text{Na}^{[+]} + \text{SO}_4^{[=]}$	$\text{Fe}(\text{OH})_3 \rightleftharpoons \text{Fe}^{[3+]} + 3\text{OH}^{[-]}$
$(\text{NH}_4)_2\text{SO}_4 \rightleftharpoons 2\text{NH}_4^{[+]} + \text{SO}_4^{[=]}$	$\text{Fe}(\text{OH})_2 \rightleftharpoons \text{Fe}^{[2+]} + 2\text{OH}^{[-]}$
$\text{NaCl} \rightleftharpoons \text{Na}^{[+]} + \text{Cl}^{[-]}$	$\text{FeSO}_4, 7\text{H}_2\text{O} \rightleftharpoons \text{Fe}^{[2+]} + \text{SO}_4^{[=]} + 7\text{H}_2\text{O}$
$\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_4^{[+]} + \text{Cl}^{[-]}$	$\text{Na}_2\text{SO}_3 \rightleftharpoons 2\text{Na}^{[+]} + \text{SO}_3^{[2-]}$
$\text{NaOH} \rightleftharpoons \text{Na}^{[+]} + \text{OH}^{[-]}$	$\text{Na}_2\text{SO}_3, 7\text{H}_2\text{O} \rightleftharpoons 2\text{Na}^{[+]} + \text{SO}_3^{[2-]} + 7\text{H}_2\text{O}$
	$\text{HI} \rightleftharpoons \text{H}^{[+]} + \text{I}^{[-]}$
	$\text{I}_2 \rightleftharpoons 2\text{I}^{[-]}$

### Range of application

- Temperature : 0 to 200°C.
- Pressure : 100 mbars to 50 bars.
- Concentration : 0 to 10 in molality (nb of moles per kg of water) for dissociating species.

### 3.4. ULPDHS

ULPDHS model has been developed in 1992 by ACHARD and al. [5]. The model combines a term of Debye-Hückel type with a modified UNIFAC equation and is based on the solvation concept. This model has advantage over the former ones due to its predictive aspect based on a group contribution method.

The number of molecule of water fixed around the ion is named hydration number. In this model, it is assumed that solvation phenomena are constant with temperature and ionic strength. Accordingly the limit of validity of the model is the inclusion of all the water molecules in clusters.

Mixture non ideality characterisation is made with an hydrated reference state for the ULS part of the model and with a non hydrated reference state for the PDH term.

#### Use

All the description parameters of the chemical reactions and/or physical balances are "pre coded" for all the electrolytic reactions hereafter. It is possible to add quickly new systems, please consult.

$\text{H}_2\text{O} \rightleftharpoons \text{H}^{+} + \text{OH}^{-}$	$\text{NH}_4\text{HCO}_3 \rightleftharpoons \text{NH}_4^{+} + \text{HCO}_3^{-}$
$\text{H}_2\text{O} + \text{NH}_3 \rightleftharpoons \text{NH}_4^{+} + \text{OH}^{-}$	$\text{NaHCO}_3 \rightleftharpoons \text{Na}^{+} + \text{HCO}_3^{-}$
$\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}^{+} + \text{HCO}_3^{-}$	$\text{Na}_2\text{CO}_3 \rightleftharpoons 2\text{Na}^{+} + \text{CO}_3^{=}$
$\text{HCO}_3^{-} \rightleftharpoons \text{H}^{+} + \text{CO}_3^{=}$	$\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^{-}$
$\text{H}_2\text{S} \rightleftharpoons \text{H}^{+} + \text{HS}^{-}$	$\text{Ca}(\text{Cl})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{Cl}^{-}$
$\text{HS}^{-} \rightleftharpoons \text{H}^{+} + \text{S}^{=}$	$\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O} \rightleftharpoons 2\text{Na}^{+} + \text{SO}_4^{=} + 10 \text{H}_2\text{O}$
$\text{H}_2\text{O} + \text{SO}_2 \rightleftharpoons \text{H}^{+} + \text{HSO}_3^{-}$	$\text{KCl} \rightleftharpoons \text{K}^{+} + \text{Cl}^{-}$
$\text{HSO}_3^{-} \rightleftharpoons \text{H}^{+} + \text{SO}_3^{=}$	$\text{K}_2\text{SO}_4 \rightleftharpoons 2\text{K}^{+} + \text{SO}_4^{=}$
$\text{HCN} \rightleftharpoons \text{H}^{+} + \text{CN}^{-}$	$\text{CH}_3\text{COONa} \rightleftharpoons \text{Na}^{+} + \text{CH}_3\text{COO}^{-}$
$\text{NH}_3 + \text{HCO}_3^{-} \rightleftharpoons \text{H}_2\text{O} + \text{NH}_2\text{COO}^{-}$	$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{=}$
$\text{HCl} \rightleftharpoons \text{H}^{+} + \text{Cl}^{-}$	$\text{CaSO}_4 \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{=}$
$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^{+} + \text{HSO}_4^{-}$	$\text{CaSO}_4, 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{=} + 2\text{H}_2\text{O}$
$\text{HSO}_4^{-} \rightleftharpoons \text{H}^{+} + \text{SO}_4^{=}$	$\text{CaHCO}_3^{+} \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^{-}$
$\text{Na}_2\text{SO}_4 \rightleftharpoons 2\text{Na}^{+} + \text{SO}_4^{=}$	$\text{CaCl}^{+} \rightleftharpoons \text{Ca}^{2+} + \text{Cl}^{-}$
$(\text{NH}_4)_2\text{SO}_4 \rightleftharpoons 2\text{NH}_4^{+} + \text{SO}_4^{=}$	$\text{FeSO}_4 \rightleftharpoons \text{Fe}^{2+} + \text{SO}_4^{=}$
$\text{NaCl} \rightleftharpoons \text{Na}^{+} + \text{Cl}^{-}$	$\text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons 2\text{Fe}^{3+} + 3\text{SO}_4^{=}$
$\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_4^{+} + \text{Cl}^{-}$	$\text{Fe}(\text{OH})_3 \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^{-}$
$\text{NaOH} \rightleftharpoons \text{Na}^{+} + \text{OH}^{-}$	$\text{Fe}(\text{OH})_2 \rightleftharpoons \text{Fe}^{2+} + 2\text{OH}^{-}$
$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^{+} + \text{CH}_3\text{COO}^{-}$	$\text{FeSO}_4, 7\text{H}_2\text{O} \rightleftharpoons \text{Fe}^{2+} + \text{SO}_4^{=} + 7\text{H}_2\text{O}$
$(\text{NH}_4)_2\text{CO}_3 \rightleftharpoons 2\text{NH}_4^{+} + \text{CO}_3^{=}$	$\text{KOH} \rightleftharpoons \text{K}^{+} + \text{OH}^{-}$
$\text{NH}_4\text{HCO}_3 \rightleftharpoons \text{NH}_4^{+} + \text{HCO}_3^{-}$	$\text{NaBr} \rightleftharpoons \text{Na}^{+} + \text{Br}^{-}$
$\text{NaHCO}_3 \rightleftharpoons \text{Na}^{+} + \text{HCO}_3^{-}$	$\text{NaNO}_3 \rightleftharpoons \text{Na}^{+} + \text{NO}_3^{-}$
$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^{+} + \text{CH}_3\text{COO}^{-}$	$\text{HI} \rightleftharpoons \text{H}^{+} + \text{I}^{-}$
$(\text{NH}_4)_2\text{CO}_3 \rightleftharpoons 2\text{NH}_4^{+} + \text{CO}_3^{=}$	$\text{I}_2 \rightleftharpoons 2\text{I}^{-}$

### **3.5. Engels**

The Engels model [6] has been specially designed for the calculation of phase equilibrium (liquid-vapor equilibrium) and of thermodynamic properties (entropy and enthalpy) of strong acids aqueous solutions.

The modelisation of this kind of mixture proves to be particularly critical because the following physical phenomena have to be taken into account :

- acid dissociation in the liquid phase;
- liquid-vapor equilibrium involving numerous azeotropes (water-HCl, water-HBr, water HNO<sub>3</sub>, water-H<sub>2</sub>SO<sub>4</sub>, ...);
- significant, even very important, heat of dilution (or enthalpy of mixing).

The simultaneous resolution of the model equations gives the molar fractions “after solvation” and then all the thermodynamic properties necessary in the ProSim software (activity coefficient, enthalpy, ...).

The combination of an adequate solvation model and of a model of calculation of activity coefficient based on the concept of local composition gives rise to a great flexibility concerning the simultaneous fitting of equilibrium and enthalpy data. So this model is particularly suitable to the treatment of strong acid aqueous solutions.

In order to generalize its use and because the theory allows it, this model has been extended to the following solutions :

- water-strong acid-inerts ;
- water-multiple strong acids. In this case, few tests could have been done and so it is recommended to stay in the field of important water concentrations..

#### **Use**

The user has simply to select the Engels model in the list of thermodynamic models available in all the ProSim software. An automatic treatment is then done to determine the number of reactions to calculate and the number of "complexes" to be taken into account. It has to be noted that the user has not to specify the presence of “complexes” at the level of the components definition and has not to give the binary interaction coefficient. All is automatically managed, only if the components used are issued from standard ProSim database.

## Range of application

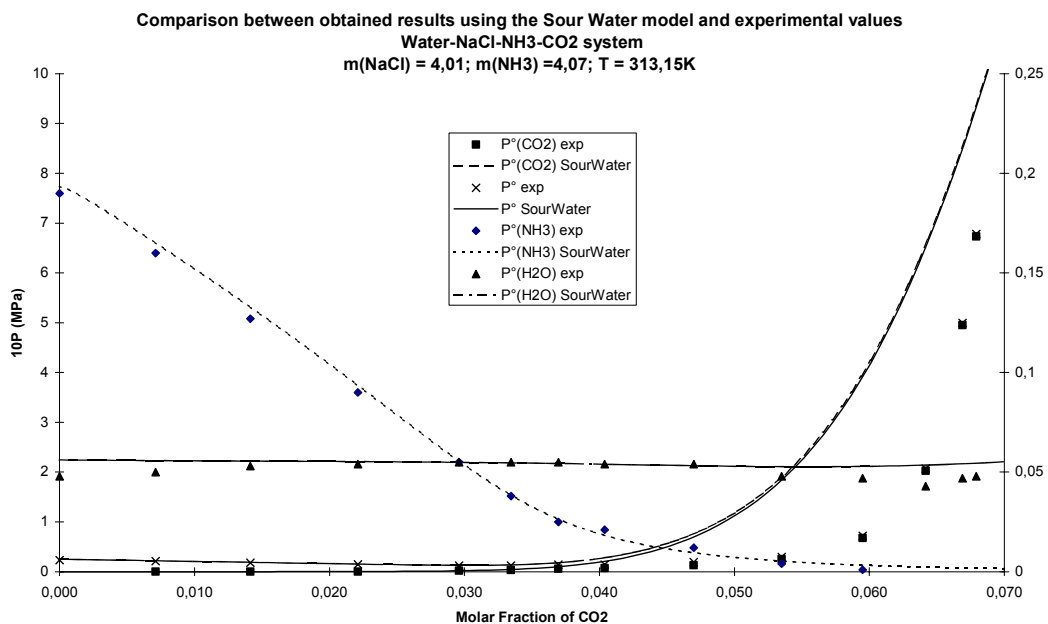
According to the calculation of the activity coefficients, either calculated using NRTL or using WILSON, the studied mixtures are the following ones :

- Calculation of the activity coefficients using WILSON method :
    - \* water-HBr
    - \* water-HI
    - \* water-HCl
    - \* water-NaCl
  
  - Calculation of the activity coefficients using NRTL method :
    - \* water-HNO<sub>3</sub>
    - \* water-HF
    - \* water-H<sub>2</sub>SO<sub>4</sub>
- all the concentration field (except for the water-NaCl binary). It has to be noted that this model does not take into account the presence of the “Coulombic” strength in the field of infinite dilution, which may give erroneous results for low compositions of electrolytes;
- pressure: 0 to 20 bars.

## 4. Some application examples

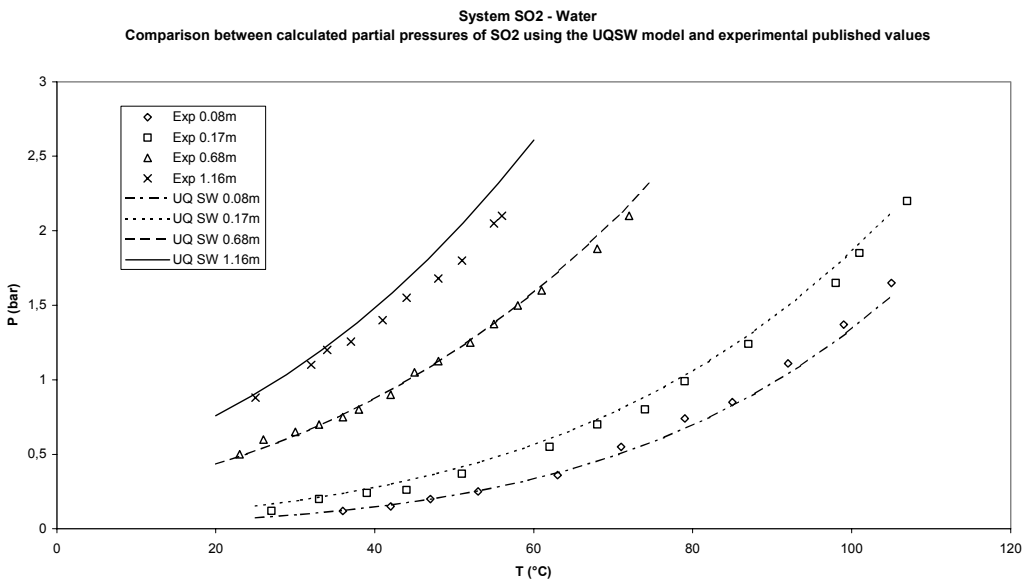
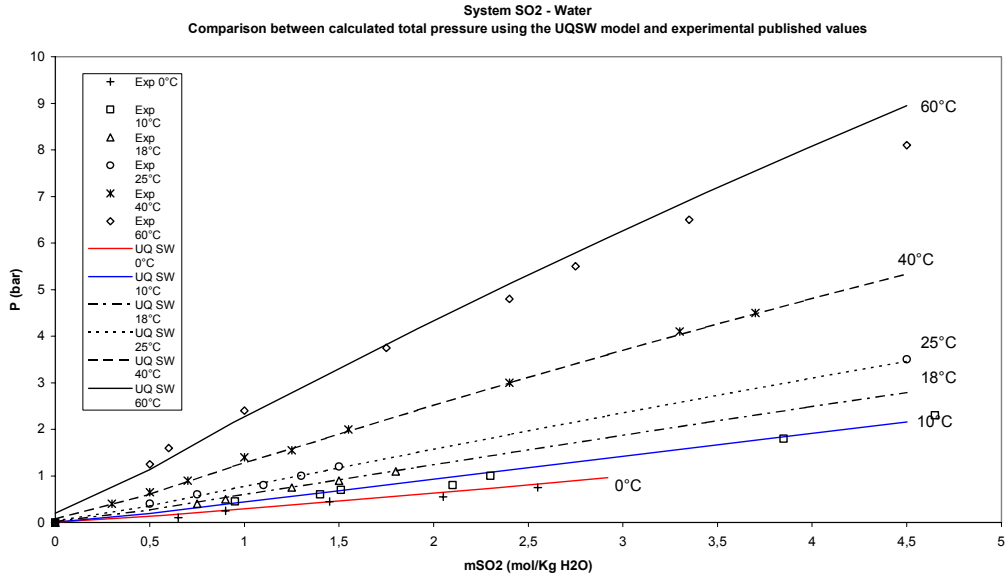
### 4.1. Water-NaCl-NH<sub>3</sub>-CO<sub>2</sub> system

The graph hereafter presents a comparison between obtained results using the Sour Water model and experimental values.



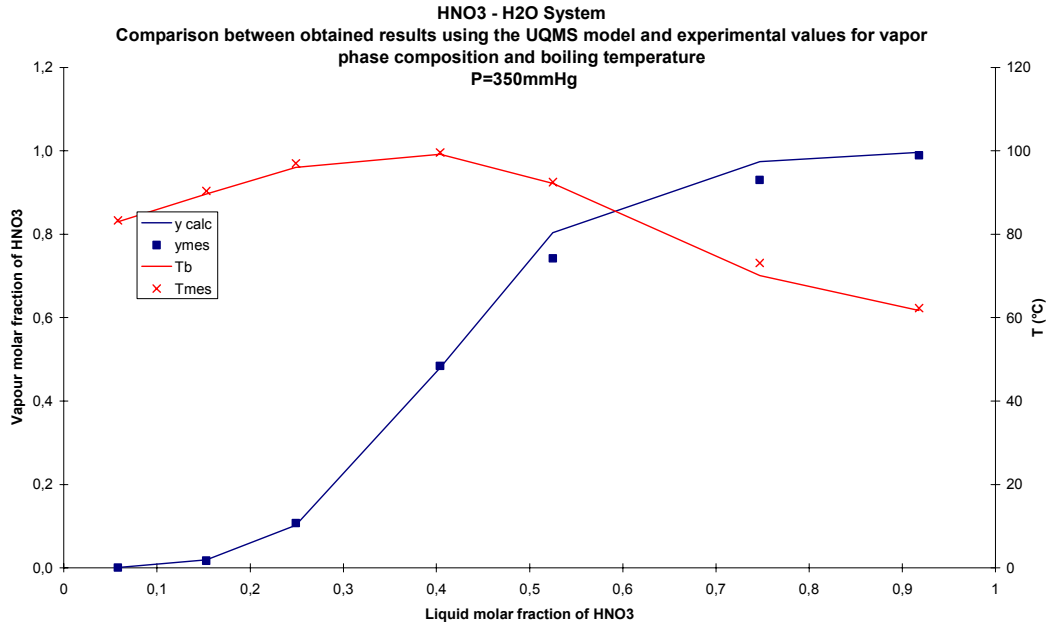
## 4.2. SO<sub>2</sub>-Water system

The two graphs hereafter present comparison between calculated partial and total pressures using the UQSW model and experimental published values.

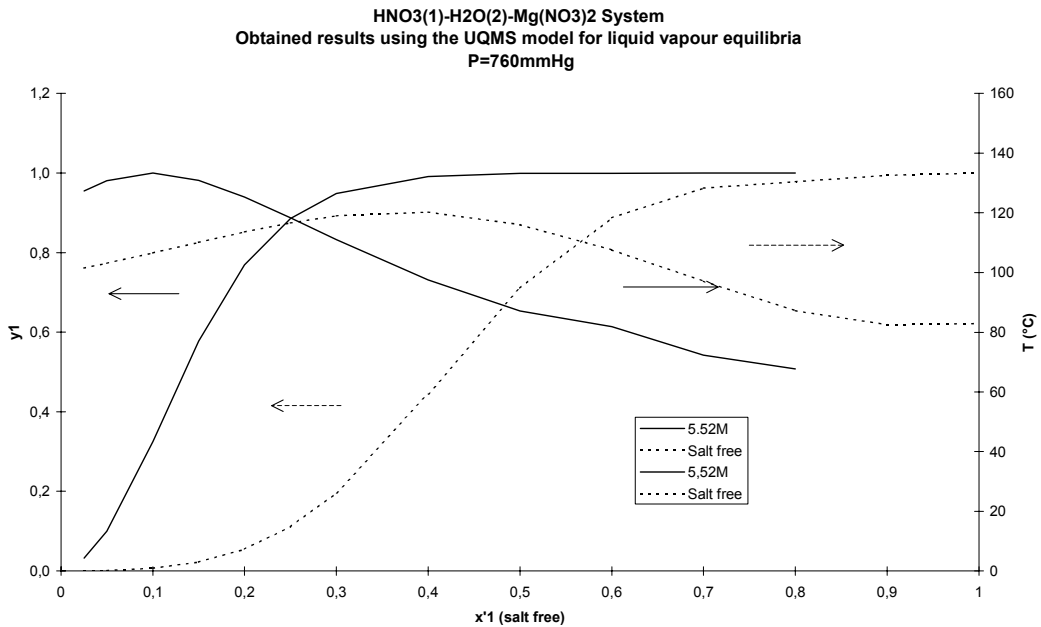


### 4.3. $\text{HNO}_3\text{-H}_2\text{O-MgNO}_3$ system

The graph hereafter presents a comparison between obtained results using the UQMS model and experimental values for vapor phase composition and boiling temperature.



The hereunder graph points the salt effect of the magnesium nitrate on the Water-HNO<sub>3</sub> azeotrope.



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