# 1 Methodology

A **chemical species** is a *"[s]pecific form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure."* (IUPAC 2019). An example would be the species couple of $[NH_4^+]$ and $[NH_3]$, whose total concentration c_T is commonly termed total ammonia nitrogen (TAN). The concentration of both species at a given TAN $= c_T = 5\,\mathrm{mmol\,L^{-1}}$ is a function of pH and can be calculated if the pH and the dissociation constant K of the reaction

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \tag{1}$$
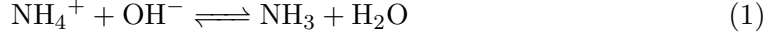
is known.

The saturation concentration of a cation in solution is determined by the least soluble salt that can be formed with the present anion(s) in solution. The concentration of the salt-forming anion, on the other hand, is not reflected by its total concentration c_T that is used for the formulation of nutrient solutions such as the Hoagland solution (see Tab. 1) but determined by the pH due to speciation reactions. Thus, the true concentration of the species that is causing precipitation has to be calculated.

Table 1: Concentrations of plant nutrients in the nutrient solution after Hoagland and Arnon Resh 2016.

Nutrient	$\gamma[\mathrm{mg\,L^{-1}}]$	$c[\mathrm{mmol\,L^{-1}}]$
Anions		
NH_4^+-N	14	0.78
NO_3^--N	196	3.16
PO_4^{3-}-P	31	0.33
SO_4^{2-}-S	64	0.67
Cations		
K^+	234	5.98
Ca^{2+}	160	3.99
Mg^{2+}	48	1.97
Fe^{3+}	0.6	10.74×10^{-3}
Mn^{2+}	0.5	9.1×10^{-3}
Cu^{2+}	0.02	0.55×10^{-3}
Zn^{2+}	0.05	0.76×10^{-3}
Mo^{6+}	0.01	0.1×10^{-3}

1.1 Calculation of Nutrient Species Concentrations

Being directly pH-dependent, the **hydroxide** concentration can be calculated by Eq. 2.

$$[OH^-] = 10^{\mathrm{pH}-14} \tag{2}$$

The concentration of **diprotic acids** $[A^{2-}]$ such as carbonic acid H_2CO_3 and sulphuric acid H_2SO_4 or **triprotic acids** $[A^{3-}]$ such as phosphoric acid H_3PO_4 can be calculated by using Eq. 3 and 4, respectively.

$$[A^{2-}] = c_T \cdot \left(\frac{1}{\frac{[H^+]^2}{K_{a1}K_{a2}} + \frac{[H^+]}{K_{a2}} + 1} \right) \tag{3}$$

$$[A^{3-}] = c_T \cdot \left(\frac{1}{\frac{[H^+]^3}{K_{a1}K_{a2}K_{a3}} + \frac{[H^+]^2}{K_{a2}K_{a3}} + \frac{[H^+]}{K_{a3}} + 1} \right) \tag{4}$$

Here, $K_{a,n}$ represents the acidity dissociation constants of the corresponding deprotonation levels.

In the case of carbonate, it is assumed that all carbonate species in the water are originating from atmospheric CO_2 ($p = 5.4 \times 10^{-2}$ atm), neglecting the use of carbonate buffers in aquaculture. The initial **carbon dioxide concentration in water** is thus calculated by applying Henry's law.

$$[CO_{2(aq)}] = p(CO_{2(g)}) \cdot K_H \tag{5}$$

Eventually, the concentrations of $CO_{2(aq)}$ and H_2CO_3 resulting from the reaction

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \tag{6}$$
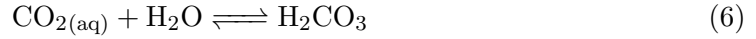
are summed up as

$$[CO_{2(aq)}] + [H_2CO_3] = [H_2CO_3 \cdot] \tag{7}$$

as it is common practice (see e.g. Sigg and Stumm 2011). In all equations, c_T is denoting for the total molar concentration of an element and brackets are denoting for molar concentrations of the individual species. No correction for activities was done. The numeric values used for the calculations are stated in Tab. 2.

1.2 Calculation of Solubility

The dissolution of a salt consisting of cations C and anions A in H_2O can be described with Eq. 8.

$$C_iA_j + n\,H_2O \rightleftharpoons i\,C^{a+}(aq) + j\,A^{b-}(aq) \tag{8}$$
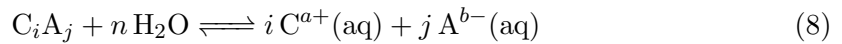
Using the law of mass action and considering the concentrations of H_2O and the salt being constant ($c = 1$), the solubility product K_{sp} can be simplified as shown in Eq. 9.

$$K_{sp} = [C^{a+}]^i \cdot [A^{b-}]^j \tag{9}$$

With K_{sp} of a salt and the concentration of one of the ions in solution being known, the saturation concentration S of the other ion up to which no precipitation of the salt occurs can be calculated.

In all equations, brackets are denoting for molar concentrations. The solubility products used for the calculation of theoretical maximum solubilities of pure salts are given in Table 3.

2 Constants

Table 2: Equilibrium constants of dissociation reactions.

Reaction	Abbrev.	Value	Reference
$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$	K_W	1.0×10^{-13}	
$CO_2 + H_2O \rightleftharpoons H_2CO_3*$	K_H	3.4×10^{-2}	Sigg and Stumm 2011
$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$	K_{a1}	4.46×10^{-7}	Sigg and Stumm 2011
$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$	K_{a2}	4.16×10^{-11}	Sigg and Stumm 2011
$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$	K_{a1}	7.52×10^{-3}	Küster 2011
$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$	K_{a2}	6.23×10^{-8}	Küster 2011
$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$	K_{a3}	3.5×10^{-13}	Küster 2011
$H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$	K_{a1}	1.0×10^{3}	Küster 2011
$HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+$	K_{a2}	1.2×10^{-2}	Küster 2011

Table 3: Solubility products (K_{sp}) of some poorly soluble salts of relevant plant nutrients at 25 °C.

Compound	Solubility product	Reference
$CaCO_3$	3.36×10^{-9}	De Rijck and Schrevens 1998
$Ca(OH)_2$	5.02×10^{-6}	Lide 2007
$Ca_3(PO_4)_2$	1.00×10^{-26}	Lide 2007
$Cu_3(PO_4)_2$	1.40×10^{-37}	Lide 2007
$FePO_4 \cdot 2\,H_2O$	9.91×10^{-16}	Lide 2007
$MgCO_3$	6.82×10^{-6}	Lide 2007
$Mg(OH)_2$	5.61×10^{-12}	Lide 2007
$Mg_3(PO_4)_2$	1.04×10^{-24}	Lide 2007
$MnCO_3$	2.24×10^{-11}	Lide 2007
$Ni_3(PO_4)_2$	4.74×10^{-32}	Lide 2007
$ZnCO_3$	1.46×10^{-10}	Lide 2007
$Zn(OH)_2$	3.00×10^{-17}	Lide 2007
$Zn_3(PO_4)_2$	9×10^{-33}	Lide 2007

References

De Rijck, G. and E. Schrevens (1998). "Elemental Bioavailability in Nutrient Solutions in Relation to Precipitation Reactions". In: *Journal of Plant Nutrition* 21.10, pp. 2103–2113.

IUPAC (2019). *Compendium of Chemical Terminology*. Ed. by Victor Gold. 2nd. the "Gold Book". Oxford: International Union of Pure and Applied Chemistry (IUPAC). ISBN: 0-9678550-9-8. DOI: 10.1351/goldbook.

Küster, Friedrich W. (2011). *Rechentafeln für die Chemische Analytik: Basiswissen für die Analytische Chemie (German Edition)*. De Gruyter, p. 412. ISBN: 978-3-11-022962-2.

Lide, David R. (2007). *CRC Handbook of Chemistry and Physics*. 88th. CRC Press, p. 2640. ISBN: 978-0-8493-0488-0.

Resh, Howard M. (Apr. 2016). *Hydroponic Food Production*. Taylor & Francis Ltd. 560 pp. ISBN: 978-1-4398-7869-9.

Sigg, Laura and Werner Stumm (2011). *Aquatische Chemie*. 5th. Zurich: vdf Hochschulverlag. ISBN: 978-3-8252-8463-3.