9 Basic principles of chemical speciation calculations

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Summary

The distribution of components over the different forms ('species') in which they are present in different soil phases (speciation) can be calculated by solving mass balance equations. Soil phases include different species (complexes) in the water phase, gases in the gas phase, minerals, organic liquids (NAPL) and adsorbed components (surface species) in the solid phase. An overview of a system description is usually presented in the form of a so-called 'table of species'. Adsorption- and desorption processes are described by means of either the Langmuir- or the Freundlich sorption model. This chapter includes a few simple examples of speciation calculations.

9.1 Introduction

Chemical speciation comprises the distribution of chemical compounds over the different forms in which they are present in different phases of a soil-water system. In other words, it concerns both their distribution over different phases in a soil-water system (the solid-, water- and gas phases, and possibly also the biota phase) and the different forms in which they are present in these phases. Furthermore, the situation in a state of chemical equilibrium is considered, rather than how equilibrium is attained or how long it will take to attain equilibrium. With regard to speciation, the following text discusses only ionic compounds, although it also applies to organic chemicals.

Speciation calculations are used for determining the chemical equilibrium composition of soil-water systems, *i.e.* the total amounts or concentrations of the various species present in the system. In such calculations, physico-chemical processes such as complexation, hydrolysis, precipitation, dissolution, volatilization, oxidation, reduction, adsorption and desorption need to be considered. As far as the biota phase is involved, bioaccumulation or uptake by organisms should also be taken into account. However, there are no simple partition models for ionic compounds with regard to the biota phase and therefore uptake is often described as if it concerns adsorption onto cell walls (Plette et al. 1996).

Compounds may be present in the form of various species, such as:

- *in the water phase:*

free ions	: H^+, Cd^{2+}, OH^-, Cl^-, PO_4^{3-}, Al^{3+}
complexes (ion pairs)	: $CdCl^+$, $AlOH^{2+}$, $H_2PO_4^-$, chelates (EDTA)
metal-DOC complexes	: Cu-DOC (DOC = Dissolved Organic Carbon)

- *in the solid phase:*
  - minerals or solids : $CdS(s)$, $CdCO_3(s)$, $AlPO_4.2H_2O(s)$, $Fe(OH)_3(s)$
  - organic liquids : Benzeen, Tolueen, Tri, Per, oil, PAH, Tar
  - adsorbed to soil particles (surface species) : Various sorption models:
    - Langmuir, Freundlich, Ion Exchange
    - Variable charge models, heterogeneity models
- *in the gas phase:*
  - gases : $NH_3(g)$, $CO_2(g)$, $H_2S(g)$, $HCN(g)$
- *in the biota phase* : accumulated in organisms; no simple partition models are available, except models for organic chemicals.

It is often necessary to do speciation calculations, because there is a lack of proper analytical methods for the direct identification and determination of species concentrations. In most cases, only the total amounts of compounds can be determined by analytical methods, not the amounts of their specific forms (*e.g.* only the total amount of Cd can be determined, not the concentration of Cd^{2+}). Important exceptions are proton activity (pH) and redox potential (relative electron activity), which can easily be measured, whereas it is very difficult to estimate their total amounts in soil-water systems.

To give an example, speciation calculations need to be done in the case of risk assessments, as these require detailed information on the identities and concentrations of prevailing species because of differences in toxicity and/or behaviour in the soil-water system.

In other words, speciation calculations can supplement data which have been obtained by means of available analytical methods (*e.g.* total amounts of compounds). The remaining text explains how such calculations are done and what data they require. A few simple examples are included. For more information on the concerned systematic method for solving chemical equilibria, refer to the workbook 'Chemical Equilibria in Soil, Water, Sediment; Part B' (Keizer & van Riemsdijk 1992).

9.2 Arithmetic method

The first step of the systematic method for solving chemical equilibria consists of defining the system which contains all the relevant components. These components could be considered the 'building blocks' or 'basic entities' of the system. Many different species may be present; they are the reaction products of the components which react with each other. Components themselves are also considered species.

The equilibrium constant or formation constant (K^o) of an equilibrium reaction is defined as the species activity divided by the product of the component activities. For diluted solutions with very low salt concentrations, the activities of the components are equal to their concentrations.

Example of a system description:

Components : Cd^{2+} and Cl^-
Species : Cd^{2+}, Cl^-, $CdCl^+$ and $CdCl_2^o$

Equilibrium reactions:

$Cd^{2+} + Cl^{-} \quad <—> \quad CdCl^{+} \qquad \log(K^{o}) = 1.98$
$Cd^{2+} + 2\ Cl^{-} \quad <—> \quad CdCl_2^{o} \qquad \log(K^{o}) = 2.6$

$(CdCl^{+}) = (Cd^{2+}).(Cl^{-}).10^{1.98}$: activity of species $CdCl^{+}$
$(CdCl_2^{o}) = (Cd^{2+}).(Cl^{-})^2.10^{2.6}$: activity of species $CdCl_2^{o}$

Commonly, free cations and free anions are considered components of systems (*e.g.* H^{+}, Cd^{2+}, PO_4^{3-}, Al^{3+}, Cl^{-}).

A chemical equilibrium problem is solved by calculating the distribution of the components over all species present in the system. This requires knowledge of the concentrations or activities (*e.g.* pH) and/or the total amounts of the components (*e.g.* Cd(t)). The total amount of a component, distributed over several species, may be expressed in terms of the mass balance of that component.

Example of mass balance equations for the Cd-Cl system:

$Cd(t) = [Cd^{2+}] + [CdCl^{+}] + [CdCl_2^{o}]$: *total amount of Cd*
$Cl(t) = [Cl^{-}] + [CdCl^{+}] + 2\ [CdCl_2^{o}]$: total amount of Cl

In this text ( ) is used for the activities of species or components, and [ ] for their concentrations.

If mass balances are used, the calculations need to be done in terms of concentrations, and all species need to be expressed in terms of components and formation constants. However, such constants are normally defined in terms of activities. Therefore, activities need to be converted to concentrations. For such conversions, activity coefficients are used, as follows:

$$a_i = f_i.c_i \tag{1}$$

a_i : the activity of species i (mol/l)
c_i : the concentration of species i (mol/l)
f_i : the activity coefficient of species *i*

The activity coefficients can be readily calculated using the following Davies equation:

$$\log(f_i) = -0.51Z^2\left(\frac{\sqrt{U}}{1+\sqrt{U}}-0.2U\right) \tag{2}$$

Z_i : the valence of species i
U : ionic strength (mol/l)

The above formula can be used for calculating the activity coefficient for a given ionic strength, provided the latter does not exceed a value of approximately 0.5. In the case of higher values, the Davies equation needs to be adapted. The ionic strength is calculated using the following formula:

$$U = 0.5 \sum_{i=1}^{n} (C_i . Z_i^2) \tag{3}$$

n : the total number of species

This problem can be solved only by iteration. In many practical situations, a reasonably accurate estimate of the ionic strength can be made on the basis of known component concentrations and/or total amounts present in solution, and therefore this iteration procedure need not be applied.

Example: Estimate U on the basis of the total amounts of the components present in a solution containing 0.02 mol/l $CdCl_2$:

$U = 0.5\ (0.02 * 4 + 0.04 * 1) = 0.06$ mol/l

For values of f_i for ions with abs(z) = 1, 2, 3 and 4 for different values of U (0 - 0.5 mol/l), see Figure 9.1.

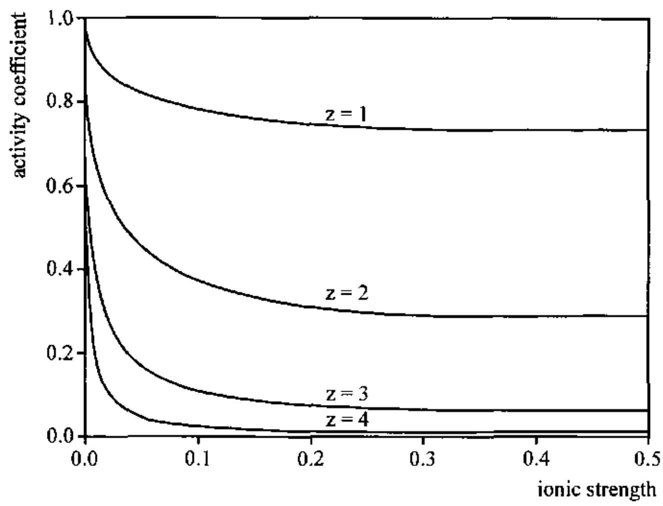

Figure 9.1. Activity coefficient versus ionic strength for z = 1, 2, 3 and 4.

In solving chemical equilibria, the following systematic approach is usually taken: Calculate the activity coefficients on the basis of an estimated ionic strength, and convert the equilibrium constants regarding the basic set of equilibrium reactions to 'concentration constants'. Thus, the 'concentration constants' apply to the given ionic strength.

For example, consider the formation of species A_mB_n from components A and B:

$$mA + nB \longrightarrow A_mB_n \qquad \log(K^o) \tag{4}$$

K^o is the formation constant for this reaction and is expressed in terms of activities (U = 0) :
K^c is the formation constant expressed in terms of concentrations (U = C).

$$K^o = \frac{(A_mB_n)}{(A)^m.(B)^n} \tag{5}$$

K^o is converted to K^c as follows:

$$K^o = \frac{(A)^m.(B)^n}{(A_mB_n)} = \frac{(f_A)^m.(f_B)^n[A]^m.[B]^n}{f_{A_mB_n}[A_mB_n]} = K^c.\frac{(f_A)^m.(f_B)^n}{f_{A_mB_n}} \tag{6}$$

f_A : the activity coefficient of component A
f_B : the activity coefficient of component B
f_{AB} : the activity coefficient of species A_mB_n

In order to solve the equilibrium problem - the distribution of A and B over the species A, B and A_mB_n - the mass balances of the components A and B need to be expressed in terms of component concentrations, as follows:

$$A(t) = [A] + m.[A_mB_n] \tag{7}$$

$$B(t) = [B] + n.[A_mB_n] \tag{8}$$

The concentration of species A_mB_n is equal to:

$[A_mB_n] = [A]^m.[B]^n.K^c$ Thus:

$$A(t) = [A] + m.[A]^m.[B]^n.K^c \tag{9}$$

$$B(t) = [B] + n.[A]^m.[B]^n.K^c \tag{10}$$

If A(t), B(t) and K^c are known, these two equations can be solved, because then only two unknown variables ([A] and [B]) are left. For solving such equations, usually a numerical solution method needs to be used (*e.g.* the Newton-Raphson method). Furthermore, for starting calculations, the component concentrations in the state of equilibrium ([A] and [B]) need to be estimated.

In the case of practical applications, it is necessary to know what components and species are relevant to the system concerned, and to have reliable $\log(K^o)$ values at one's disposal. Data on what species may be present and their $\log(K^o)$ values can be found in handbooks on stability constants (*e.g.* Sillen & Martell 1971; Smith & Martell 1976), soil chemistry (*e.g.* Lindsay 1979) and water chemistry (*e.g.* Stumm & Morgan 1981). These constants can also be found in the databases of many computer programs (*e.g.* MINEQL (Westall et al. 1976), GEOCHEM (Sposito & Mattigod 1980) and ECOSAT (Keizer & van Riemsdijk 1994)). For an overview see Loeppert et al. (1995).

9.3 Table of species

The classic method for describing the various mass balances of components, in which species concentrations are expressed in terms of component concentrations and K^o values (equations (9) and (10)), often leads to long, confusing equations, especially if they include the numerical values of the various formation constants.

A convenient alternative is a so-called 'table of species'. In a condensed form, such a table gives an almost complete overview of the system concerned. The structure of such a table is illustrated in Table 9.1, using the above example concerning a system with components A and B and species A, B and A_mB_n:

Table 9.1. Table of species.

Components	A	B	log (K)
species			
A	1	0	0
B	0	1	0
A_mB_n	m	n	log K^c
Total	A(t)	B(t)	

All species present in the system are listed in the column on the far left-hand side. Their charges are not indicated, however, so as to keep the table orderly. The selected components are given in the upper row of the table, as is log(K). The numbers in the columns below the components indicate how often these components are present in the species concerned (the stoichiometric coefficient). The log(K) column gives the log(K^c) values for the species concerned. For components, these values equal 0. The row at the bottom gives the total amounts for the components (mol/l).

The species concentration (mol/l), expressed in the concentrations of the components, may be derived directly from the table as:

Read the table horizontally:

$$[A] = [A]^1 . [B]^0 . 10^0 \quad \text{or} \quad \log[A] = 1.\log[A] + 0.\log[B] + 0 \qquad (11)$$
$$[B] = [A]^0 . [B]^1 . 10^0 \quad \text{or} \quad \log[B] = 0.\log[A] + 1.\log[B] + 0 \qquad (12)$$
$$[A_mB_n] = [A]^m . [B]^n . K^c \quad \text{or} \quad \log[A_mB_n] = m.\log[A] + n.\log[B] + \log(Kc) \qquad (13)$$

The expression for the mass balance for a certain component may also be derived directly from the table, as it is equal to the sum of the products of the numbers (stoichiometric coefficients) in the component column and the concentrations of the accompanying species, as follows :

Read the table vertically:

$$A(t) = 1.[A] + 0.[B] + m.[A_mB_n] \qquad (14)$$
$$B(t) = 0.[A] + 1.[B] + n.[A_mB_n] \qquad (15)$$

This table of species contains all information necessary for doing the calculations, namely:

- the components and species present
- the log K^c values for the species
- the total amounts of the components.

The ionic strength needs to be known (if it has not already been calculated), as well as the charges of the components (for calculating the activity coefficients) and the estimates of the component concentrations (for starting the iteration process).

Particular attention should be paid to the values of log K^c. Sometimes, there is confusion over which value is correct, for example, in the case of minerals for which the solubility values are unknown. Sometimes, even the correct values are unknown, *e.g.* in the case of metal-DOC complexes (DOC = Dissolved Organic Matter) or surface species (parameters of a sorption model).

9.4 H_2O dissociation equilibrium

Up until now, the solvent water (H_2O) has not explicitly been taken into account, although it is an essential part of the systems in which we are interested. Even more important is the fact that H_2O participates in many equilibrium reactions, such as the dissociation of H_3PO_4 and the formation of hydrolysis products. This means that the dissociation equilibrium of H_2O also belongs to the basic set of equations describing the system. Its equation is as follows:

$$H_2O <\!\!-\!\!-\!\!> H^+ + OH^- \qquad \log(K^o) = -14.0 \tag{16}$$

As the activity of water in many diluted solutions is practically equal to 1, the expression for the ion product of water can be simplified as indicated in equation (17).

$$K^o = \frac{(H^+).(OH^-)}{(H_2O)} \approx (H^+).(OH^-) = 10^{-14.0} \tag{17}$$

The mass balances for the components H^+ and OH^- (H(t) and OH(t)) now include the concentration of water ($[H_2O]$) as a term. It is equal to 1000/18 = 55.56 mol/l at 25 °C. The H_2O phase now appears in a separate part of the table of species, designated by 'phases' (see Table 9.2). The log(K) column now contains the dissociation constant instead of the formation constant. Horizontally, the table now includes an expression for the ion product of water (equation (17)) instead of the concentration of water. Vertically, the total amounts of the components are still expressed, including the components present in H_2O. The same procedure can be applied to minerals. In this, the solubility constant (K_s) is placed in the log(K) column (see section 9.6).

The complexation of Cd^{2+} with Cl^- and OH^- is given here as an example. Assume that 0.02 mol/l $CdCl_2$ and 0.01 mol/l HCl have been dissolved in water. For convenience, U is assumed to be equal to 0 ($\log(K^c) = \log(K^o)$).

The following equilibrium reactions are relevant:

log(K°)

$H^+ + OH^- \longleftrightarrow H_2O$ 14.0 (18)

$Cd^{2+} + Cl^- \longleftrightarrow CdCl^+$ 1.98 (19)

$Cd^{2+} + 2\ Cl^- \longleftrightarrow CdCl_2^o$ 2.60 (20)

$Cd^{2+} + OH^- \longleftrightarrow Cd(OH)^+$ 3.90 (21)

$Cd^{2+} + 2\ OH^- \longleftrightarrow Cd(OH)_2^o$ 7.70 (22)

The table of species belonging to this system is represented in Table 9.2.

Mass balance equations :

$Cd(t) = [Cd^{2+}] + [CdCl^+] + [CdCl_2^o] + [Cd(OH)^+] + [Cd(OH)_2^o] = 0.02$ mol/l (23)

$Cl(t) = [Cl^-] + [CdCl^+] + 2\ [CdCl_2^o] = 0.05$ mol/l (24)

$H(t) = [H^+] + [H_2O] = 0.01 + 55.56 = 55.57$ mol/l (25)

$OH(t) = [OH^-] + [H_2O] + [Cd(OH)^+] + 2\ [Cd(OH)_2^o] = 55.56$ mol/l (26)

Table 9.2. Table of species: 0.02 mol/l $CdCl_2$ + 0.01 mol/l HCl; U = 0.

Components	Cd	Cl	H	OH	log(K)
Species					
Cd	1	0	0	0	0
Cl	0	1	0	0	0
H	0	0	1	0	0
OH	0	0	0	1	0
CdCl	1	1	0	0	1.98
$CdCl_2$	1	2	0	0	2.6
CdOH	1	0	0	1	3.9
$Cd(OH)_2$	1	0	0	2	7.7
Phases					
H2O	0	0	1	1	-14.0
Total	Cd(t) 0.02	Cl(t) 0.05	H(t) 55.57	OH(t) 55.56	

$[H_2O]$ appears in the mass balances for H and OH. *In both cases,* this term is multiplied by one, because H_2O is composed of a combination of one H^+ unit and one OH^- unit.

The concentration of a species may be expressed as a product of component concentrations and K^c values. However, this does not apply to the water phase. For diluted systems, the concentration of water is practically constant. In such a case, the activity coefficient of water is unity. This approximation may be used for most environmental systems.

Because the activity coefficient of water is unity, it is possible to eliminate one of the components (H^+ or OH^-) from the set by expressing one in terms of the other. Here, the component OH^- is eliminated. The set of mass balance equations can now be reduced by one in order to calculate the concentrations of the remaining components. In other words, the system loses one degree of freedom. This reduction of the number of mass balance equations is done in such a way that the concentration of water (which is not unity!) is eliminated from the set of equations. This is possible by combining the mass balances of H^+ and OH^- as follows:

$$H(t) - OH(t) \;=\; [H^+] - [OH^-] - [Cd(OH)^+] - 2\,[Cd(OH)_2^0] \;=\; 0.01 \text{ mol/l} \qquad (27)$$

$$\text{or with : } [OH^-] \;=\; [H^+]^{-1}.10^{-14.0} \qquad (28)$$

$$H(t) - OH(t) \;=\; [H^+] - [H^+]^{-1}.10^{-14.0} - [Cd^{2+}].[H^+]^{-1}.10^{-10.1} - 2[Cd^{2+}].[H^+]^{-2}.10^{-20.3} \qquad (29)$$

The last equation shows that the coefficients in the H^+ column of the table of species (Table 9.2) have been changed by subtracting the coefficient in the OH^- column from the one in the H^+ column. The log(K^c) values have been adjusted by adding -14.0 times the coefficient in the OH^- column. The value of H(t) - OH(t) is equal to the total amount of component H^+ minus the total amount of component OH^- (mol/l). The result of this operation is shown in Table 9.3.

In contrast to ordinary mass balances, H(t) - OH(t) may have negative values or be equal to 0, because it is a linear combination of two ordinary mass balances.

Table 9.3. Table of species. 0.02 mol/l $CdCl_2$ + 0.01 mol/l HCl; U = 0. Reduction based on the H_2O dissociation equilibrium.

Components	Cd	Cl	H	log(K)
Species				
Cd	1	0	0	0
Cl	0	1	0	0
H	0	0	1	0
OH	0	0	-1	-14.0
CdCl	1	1	0	1.98
$CdCl_2$	1	2	0	2.6
CdOH	1	0	-1	-10.1
$Cd(OH)_2$	1	0	-2	-20.3
Total	Cd(t) 0.02	Cl(t) 0.05	H(t) - OH(t) 0.01	

If precipitates (pure solid phases or minerals) are formed, a situation arises which is completely analogous to the one encountered in the case of reduction with the H_2O dissociation equilibrium (see section 9.6).

9.5 Constant component concentrations or activities

If the concentration or activity of a component is known, that is, if it has a constant value (*e.g.* pH), the set of mass balance equations can be further reduced. In the table of species, the column of the component with known concentration (if the activity is known, it should be converted to concentration) is then omitted, and the log(K) column is adjusted.

In many practical situations, the pH has a constant, known (measured) value. The total amount of H(t) - OH(t) is then not relevant to the solution of the chemical equilibrium problem.

Consider, for example, the dissociation of H_3PO_4. The relevant equilibrium reactions are as follows:

			log(K°)	
$H^+ + OH^-$	<—>	H_2O	14.0	(30)
$H^+ + PO_4^{3-}$	<—>	HPO_4^{2-}	12.35	(31)
$2\ H^+ + PO_4^{3-}$	<—>	$H_2PO_4^-$	19.55	(32)
$3\ H^+ + PO_4^{3-}$	<—>	$H_3PO_4^o$	21.70	(33)

The table of species for this system is presented in Table 9.4. It is assumed that U = 0, H(t) - OH(t) = 0.02 mol/l and PO_4(t) = 0.01 mol/l.

Table 9.4. Table of species. Reduction based on the H_2O dissociation equilibrium; U = 0.

Components	H	PO_4	log(K)
Species			
H	1	0	0
OH	-1	0	-14.0
PO_4	0	1	0
HPO_4	1	1	12.35
H_2PO_4	2	1	19.55
H_3PO_4	3	1	21.70
Total	H(t) - OH(t) 0.02	PO_4(t) 0.01	

From Table 9.4, it can be deduced that:

$$[H_3PO_4^o] = [H^+]^3.[PO_4^{3-}].10^{21.70}$$

Replace, for example, $[H^+]$ by 10^{-6}, *i.e.* pH = 6 (U = 0). This results in the following:

$$[H_3PO_4^o] = [PO_4^{3-}].10^{21.70}.10^{-18} = [PO_4^{3-}].10^{3.70}$$

Thus, the log(K) column should be adjusted by adding the product of the coefficient of the 'known' component column and the logarithm of the actual component concentration to the original log(K) value. In Table 9.5, this situation is elaborated upon for the given example with a concentration of H^+ which is assumed to be known.

Table 9.5. Table of species. Reduction based on the H_2O dissociation equilibrium; known value for $[H^+]$; U = 0.

Components	PO_4	log(K)
Species		
H	0	0 + log(H)
OH	0	-14.0 - log(H)
PO_4	1	0
HPO_4	1	12.35 + log(H)
H_2PO_4	1	19.55 + 2 log(H)
H_3PO_4	1	21.70 + 3 log(H)
Total	PO_4(t) 0.01	

The species H^+ and OH^- may be omitted from the table, because their values are known or can be calculated directly (the coefficient in the PO_4 column equals 0).

9.6 Equilibria with minerals

It is typical of minerals that their quantities do not affect the equilibrium composition of the solution of the system in which they are present. In other words, the activity of pure minerals is equal to 1 (compare this situation with that of the water phase in section 9.4). Based on the equilibrium reaction, the solubility constant K_s of minerals may be defined as follows (the equilibrium reaction for gibbsite is given as an example):

$$\begin{array}{llll}
Al(OH)_3(s) & \longleftrightarrow & Al^{3+} + 3\,OH^- & \log K_s = -33.96 \\
3\,H^+ + 3\,OH^- & \longleftrightarrow & 3\,H_2O & \log K = 42.0 \\
\hline
Al(OH)_3(s) + 3\,H^+ & \longleftrightarrow & Al^{3+} + 3\,H_2O & \log K_s = 8.04
\end{array} \quad (34)$$

$$K_s = (Al^{3+}).(H^+)^{-3} = 10^{8.04} \quad (35)$$

The product $(Al^{3+}).(H^+)^{-3}$ is called the ion activity product (IAP).

Equation (35) may be written as follows:

$$\log [Al^{3+}] = 8.04 - 3\ pH \quad (36)$$

This simple relation can be plotted in a so-called 'solubility diagram' (Figure 9.2).

At equilibrium, the ion activity product (IAP) equals K_s. If IAP > K_s, the solution is supersaturated with respect to gibbsite, and the mineral will be formed (precipitation). If IAP < K_s, the solution is undersaturated with respect to gibbsite, and the gibbsite present will dissolve until either IAP equals K_s, or all gibbsite has dissolved (see Figure 9.2).

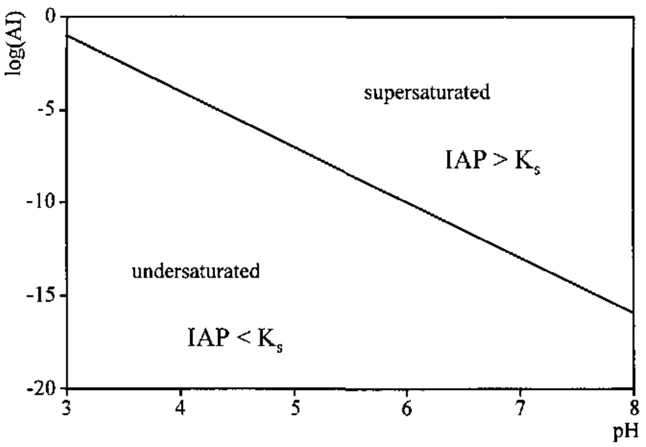

Figure 9.2. The solubility diagram for gibbsite, in which log(Al^{3+}) is plotted against pH.

The calculation of chemical equilibria may be complicated as a result of slow reaction rates, especially if solid phases are involved. Reaction rates for species in solution are generally rather high, so that the calculated equilibrium composition for a system without solid phases, gas phase or surface sorption sites is normally reached within seconds.

One mineral is usually converted very slowly into another (dissolution and precipitation of minerals). In fact, sometimes the conversion rate is so low that the system may be described on the basis of a partial equilibrium. Similar problems may arise in the case of adsorption and desorption processes, although higher conversion rates are involved in this.

Handbooks on stability constants sometimes give many different log(K_s^o) values for relationships which are basically the same, *e.g.* for the solubility product of $Al(OH)_3(s)$: $(Al^{3+}).(OH^-)^3$, or for $Fe(OH)_3(s)$: $(Fe^{3+}).(OH^-)^3$. For the relevant equilibrium reactions and log(K_s^o) values, refer to Table 9.6.

Table 9.6. Equilibrium reactions and log(K_s^o) values for $Al(OH)_3(s)$ and $Fe(OH)_3(s)$.

Nr.	Mineral	Reaction		log(K_s^o)
1	amorphous $Al(OH)_3$	$Al(OH)_3(s)$	$<\!\!-\!\!-\!\!>$ $Al^{3+} + 3\ OH^-$	-32.34
2	boehmite	$Al(OH)_3(s)$	$<\!\!-\!\!-\!\!>$ $Al^{3+} + 3\ OH^-$	-33.87
3	bayerite	$Al(OH)_3(s)$	$<\!\!-\!\!-\!\!>$ $Al^{3+} + 3\ OH^-$	-33.49
4	gibbsite	$Al(OH)_3(s)$	$<\!\!-\!\!-\!\!>$ $Al^{3+} + 3\ OH^-$	-33.96
5	amorphous $Fe(OH)_3$	$Fe(OH)_3(s)$	$<\!\!-\!\!-\!\!>$ $Fe^{3+} + 3\ OH^-$	-38.46
6	hematite	$0.5\alpha\text{-}FeOOH(s) + 1.5\ H_2O$	$<\!\!-\!\!-\!\!>$ $Fe^{3+} + 3\ OH^-$	-41.91
7	goethite	$\alpha\text{-}Fe_2O_3(s) + H_2O$	$<\!\!-\!\!-\!\!>$ $Fe^{3+} + 3\ OH^-$	-42.02

The reason that these values are different is that the minerals concerned have a slightly different crystal lattice. It will be obvious that the composition of a solution in equilibrium with $Al(OH)_3(s)$ can correspond to only one of the four above-mentioned solubility relations. At complete equilibrium, the system will in principle be characterised by the most stable mineral.

Any mixture of amorphous $Al(OH)_3(s)$, boehmite and bayerite in contact with water will finally convert to gibbsite. The reactions involved are extremely slow. A conversion may be disregarded, if its reaction rate is low compared to the time scale of interest. The conversion of amorphous $Al(OH)_3(s)$ into gibbsite will in general take months, or even years. The equilibrium composition of the system containing water and amorphous $Al(OH)_3(s)$ can thus be predicted using equation (1) of Table 9.6, as long as the equilibrium between dissolved aluminium species and amorphous $Al(OH)_3(s)$ is established relatively quickly.

9.7 Adsorption and desorption equilibria

The behaviour of compounds in soil-water systems is often strongly influenced by adsorption and desorption processes. The most important reactive surfaces are located on clay minerals, metal (hydr)oxides and organic matter.

For the description of the relationship between a dissolved substance and its adsorbed form, various model equations may be used, such as the Langmuir equation, the Freundlich equation, various ion-exchange equations, and (electrostatic) models which take into account the (variable) charge of the reactive surfaces and the charge of the sorbing substance (species).

The systematic method for solving chemical equilibria presented in the previous sections may also be applied to these sorption models. By considering the amount of a component adsorbed on the solid-phase as a species 'dissolved' in the soil solution, it is possible to treat adsorption and desorption equilibria in the same way that chemical equilibria for species in the water phase are treated.

Equations describing adsorption or desorption processes, or describing ion exchange reactions, should be changed in such a way that they become comparable to 'normal' chemical equilibrium equations. Therefore, they need to be expressed in terms of the components of the system, and characterized by an equilibrium constant. This is elaborated upon below for two adsorption/desorption models (Langmuir and Freundlich). Regarding ion-exchange, an approach can be taken which is similar to the Langmuir model (Keizer & van Riemsdijk 1992).

9.7.1 Langmuir model

The Langmuir model may be represented by:

$[Q_i]$: the concentration of the adsorbed component i in mol/kg

$$[Q_i] = \frac{K_i . Q(t) . [i]}{(1 + K_i . [i])} \qquad (37)$$

$[i]$: concentration of component i (mol/l)

$Q(t)$: the total amount of surface sites available for adsorption (mol/kg)

K_i : the Langmuir sorption constant for component i (l/mol)

with $Q(t) = [Q] + [Q_i]$

[Q] : the concentration of surface sites still available for adsorption (mol/kg)

After substituting Q(t) in (37), the Langmuir model may be formulated as:

$$[Q_i] = K_i.[Q].[i] \qquad (38)$$

This equation is comparable to the equation for the concentration of dissolved species expressed in terms of component concentrations and formation constants. If the surface sites available for adsorption (Q) are considered a component and the adsorbed amount of component i is considered a species (Q_i), this type of adsorption/desorption equilibrium can be treated as a normal chemical equilibrium. Q(t) equals the mass balance for component Q.

The concentrations of Q, Q_i and Q(t) (expressed in mol/kg) need to be converted into concentrations expressed in mol/l using either the soil solution ratio (kg/l), or the soil moisture content (l/kg). This is necessary in order to calculate the mass balance of the adsorbing component.

If several components compete for the same sorption sites, different K_i values for the various adsorbed components may be assumed to exist (multicomponent Langmuir model). The parameter values K_i and Q(t) can be derived from measurement data of adsorption or desorption experiments, or can be estimated by applying linear regression analyses to the linearized Langmuir equation, as follows:

$$\frac{[i]}{[Q_i]} = \frac{1}{K_i.Q(t)} + \frac{[i]}{Q(t)} \qquad (39)$$

Table 9.7. Table of species. Cd sorption from a $CdCl_2$ solution according to the Langmuir model. U = 0. The species are similar to those in Table 9.3. Reduction based on the H_2O dissociation equilibrium.

Components	Cd	Cl	H	Q	log(K)
Species					
Cd	1	0	0	0	0
Cl	0	1	0	0	0
H	0	0	1	0	0
OH	0	0	-1	0	-14
Q	0	0	0	1	0
CdCl	1	1	0	0	1.98
$CdCl_2$	1	2	0	0	2.6
CdOH	1	0	-1	0	-10.1
$Cd(OH)_2$	1	0	-2	0	-20.3
Q_{Cd}	1	0	0	1	$\log(K_{Cd})$
Total	Cd(t)	Cl(t)	H(t)-OH(t)	Q(t)	

The values found for K_i and Q(t) apply only to the specific experimental conditions used. Important variables are, for instance: ionic strength, temperature, pH, soil type, other competing components, and soil/solution ratio.

The speciation is illustrated in Table 9.7 in the form of the table of species for cadmium adsorption from a $CdCl_2$ solution (see Table 9.3).

In soil systems, the value of H(t) - OH(t) is usually unknown. Therefore, pH should be measured and used as an input variable in order to eliminate the H^+ column in the table of species (see also section 9.5).

9.7.2 Freundlich model

The Freundlich sorption model is very similar to a 'normal' chemical equilibrium equation, as follows:

$$[Q_i] = K_i.[i]^n \qquad (40)$$

$Q_i]$: the concentration of the adsorbed component i in mol/kg
[i] : the concentration of component i (mol/l)
K_i : the Freundlich sorption constant for component i ($l^n.kg^{-1}.mol^{1-n}$)
n : model parameter

The adsorbed amount of component i may be considered a 'dissolved' species. No extra components need to be introduced. The concentration of Q_i (expressed in mol/kg) needs to be converted into concentration expressed in mol/l, using either the soil solution ratio (kg/l), or the soil moisture content (l/kg), in order to make it possible to calculate the mass balance.

The values for the model parameters K_i and n can be obtained using the linearized Freundlich equation, which is formulated as follows:

$$\log([Q_i]) = \log(K_i) + n \log([i]) \qquad (41)$$

The values can be estimated on the basis of measurement data of adsorption or desorption experiments using linear regression analyses. The values found for K_i and n apply only to the specific experimental conditions used. Important variables are, for instance: ionic strength, temperature, pH, soil type, other competing components, and soil/solution ratio.

Because the value of n is usually not equal to 1 (except in the case of a linear adsorption model), it is difficult to calculate the mass balance for component i. The species Q_i has been formed by adsorption of ***1*** mol of i per mol of Q_i, and not by adsorption of ***n*** mol of i per mol of Q_i. This means that in calculating the species concentration of Q_i, the actual value of n needs to be used, but in calculating the total amount of component i (mass balance), n should be equal to 1. To do this with a computer program, the calculation procedure needs to be slightly adapted (as is done in the ECOSAT computer program).

Many adsorption and desorption processes (especially those of heavy metals) are pH dependent and can be described by a pH-dependent Freundlich model, according to the following formula:

$$[Q_i] = K_i.[H]^m[i]^n \qquad (42)$$

In this case, information about the effect of adsorption or desorption of component i on the mass balance H(t) - OH(t) is also necessary. Even without adsorption or desorption processes, the value of H(t) - OH(t) is usually unknown in soil systems. Therefore, the pH-dependent Freundlich model can only be applied to known (measured at equilibrium) pH values (see also section 9.5). In most soils, pH will be buffered to a constant value upon metal adsorption or desorption.

The above is illustrated in the form of the table of species for Cd adsorption from a $CdCl_2$ solution in Table 9.8.

Table 9.8. Table of species. Cd sorption from a $CdCl_2$ solution according to the pH-dependent Freundlich model. U = 0. The species are similar to those in Table 9.3. Reduction based on H_2O dissociation equilibrium.

Components	Cd	Cl	H	log(K)
Species				
Cd	1	0	0	0
Cl	0	1	0	0
H	0	0	1	0
OH	0	0	-1	-14
CdCl	1	1	0	1.98
$CdCl_2$	1	2	0	2.6
CdOH	1	0	-1	-10.1
$Cd(OH)_2$	1	0	-2	-20.3
Q_{Cd}	n*	0	m	$\log(K_{Cd})$
Total	Cd(t)	Cl(t)	H(t) - OH(t)	

* read horizontally : n = n; m = m
read vertically : n = 1; m = o

This table can be reduced further, using the known pH value (see section 9.5).

9.8 References

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