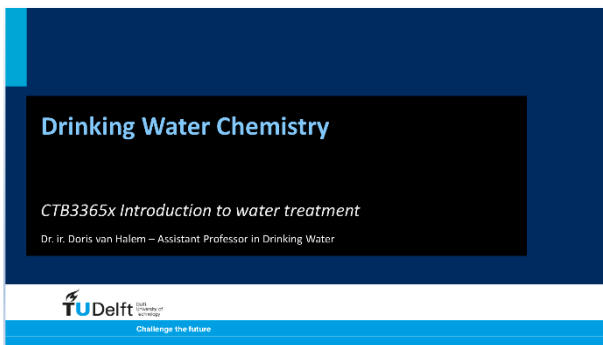


1c – Drinking water chemistry



Doris van Halem



Hi, great that you tuned in again for this water treatment lecture. My name is Doris van Halem and I am an Assistant Professor at Delft University of Technology. In this lecture I will introduce you to the most important parameters for drinking water chemistry. I will go through some basic water quality calculations, which are crucial for later design of water treatment plants. If you have a background in chemical engineering, or something alike, this lecture may be relatively easy for you. However, if you don't have a background in chemistry, for example like our civil engineering students, this course will provide you with a quick recap of the core chemical calculations needed for the design of water treatment processes.

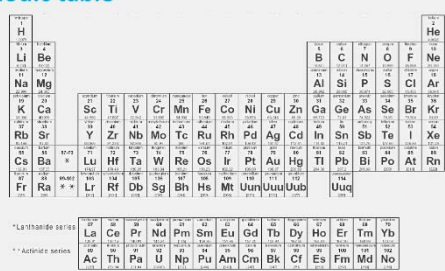
This lecture

- Ion balance
- pH
- Carbonic acid equilibrium
- Saturation index (SI)
- Hardness

We will focus on five different topics:

- Ion balance
- pH
- Carbonic acid equilibrium
- Saturation index
- Hardness

Periodic table



* Lanthanide series
** Actinide series

Before we get started I recommend that you download the periodic table, for example from the course platform. We will need it for many of the calculations during our course.

Ion balance

- **Electrical neutrality**
- **Major ions** usually represent most of the dissolved ions in water
- The **sum** of the **milliequivalents** of **major cations** and **anions** should be **nearly equal**

Let's get started with the ion balance of a water sample. The ion balance is based on the principle of electrical neutrality, meaning that the equivalent concentration of positively charged ions, the cations, is equal to the equivalent concentration of negatively charged ions, the anions. Major ions, such as sodium and chloride, usually represent most of the dissolved ions in water, so the sum in milliequivalents of major cations and anions should be nearly equal.

Why Ion Balance calculations?

- To check results of water quality analyses of the laboratory
- To assure that you included all major ions of your water sample in the analysis



This relatively simple calculation will help you to check if water quality analyses were performed correctly, and to assure that you included all relevant major ions in your water sample analyses.

Ion Balance

$$\sum \frac{C_i}{M_i * z_i} = \sum \frac{C_i}{M_i * z_i}$$

Cations Anions

With c = concentration (mg/L)
 M = molar mass (g/mol)
 z = valance (-)

This formula summarizes the ion balance, with the sum of cations on one side and the sum of anions on the other side. The milliequivalents can be calculated with concentration in your water sample, the molar mass and valence of the ion.

Calculating ion balance (pg. 225)

Cations	Concentration (mg/L)	Anions	Concentration (mg/L)
Na ⁺	63	Cl ⁻	73
K ⁺	5	HCO ₃ ⁻	151
Ca ²⁺	45	NO ₃ ⁻	1
Mg ²⁺	9	SO ₄ ²⁻	?
Fe ²⁺	4		
Mn ²⁺	1		
NH ₄ ⁺	2		

What is the sulfate concentration in this sample?

Let's practice with an exercise. This slide depicts the water composition of a sample, however, the sulfate analysis failed. Assuming that the major ions have all been measured, can you calculate what the sulfate concentration in this water is? You can take the time to calculate this for yourself by pausing this video, restart it when you are ready to hear the answer.

Ion balance

- Make a **table** with the **concentration** (c), **molar mass** (M) and **valency** (z) of all anions and cations (e.g., in spreadsheet)
- Calculate **total valence concentration** (meq/L) for the cations: $\sum C_i/M_i * z_i$

Example	
compound	Na ⁺
c	63 mg/L
M	23 g/mol
z	1

First you make a table with the concentration, molar mass and valence of all anions and cations, for example in a spreadsheet. For sodium, this is depicted in the slide. Then, calculate the valence concentration in milliequivalent per liter for all cations.

Calculating ion balance (pg. 225)

Cations	Concentration (mg/L)	Valence concentration (meq/L)
Na ⁺	63	2.74
K ⁺	5	0.13
Ca ²⁺	45	2.25
Mg ²⁺	9	0.73
Fe ²⁺	4	0.14
Mn ²⁺	1	0.04
NH ₄ ⁺	2	0.11
		TOTAL: 6.14 meq/L

This adds up to a total valence concentration of 6.14 meq/L.

Calculating ion balance

- Principle of **electrical neutrality**
- For anions: $\sum C_i / M_i * z_i = 6.14 \text{ meq/L}$
- $SO_4^{2-} = 6.14 - 2.06 - 2.48 - 0.01 = 1.60 \text{ meq/L}$
- $1.60 \text{ meq/L} = 160/2 = 0.80 \text{ mmol/L} = 76.8 \text{ mg/L}$

Now, based on the principle of electrical neutrality, also the anions should add up to 6.14 meq/L. When subtracting the valence concentration of the other anions, chloride, bicarbonate and nitrate, you end up with a valence concentration of 1.6 meq/L for sulfate. This equals 76.8 mg/L.

Ionisation of water

- Ionisation of water with **H⁺** and **OH⁻** ions
- $K_w = [H^+] \times [OH^-]$ (ion product of water)
- Neutral water solution:** $[H^+] = [OH^-] = 0.0001 \text{ mmol/L}$

One of the most important chemical properties of water is that it can be both an acid and a base, because water ionizes into H⁺ and OH⁻ ions. The ionization is an equilibrium reaction for which an equilibrium constant (K) can be determined. For a neutral solution H⁺ equals OH⁻ equals 0.0001 mmol/L.

pH

- Decimal logarithm**
- Neutral solution: $pH = 7$ (at 25°C)
- Simplified:

$$pH = -\log_{10}[H^+]$$

$$pOH = -\log_{10}[OH^-]$$

$$\text{At } 25^\circ\text{C: } pH + pOH = 14$$

The concentration of H⁺ is usually denoted as the negative logarithm pH. A neutral solution has a pH value of 7.0 at a temperature of 25°C. A lower pH, meaning a higher concentration of H⁺ ions, indicates an acid solution. Water with a pH above 7 is a base.

CO₂ dissociation

- $CO_2 + H_2O \rightleftharpoons H_2CO_3$
- $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
 $K_1 = [H^+][HCO_3^-] / [H_2CO_3] = 4.5 \cdot 10^{-7}$ (at 25°C)
- $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$
 $K_2 = [H^+][CO_3^{2-}] / [HCO_3^-] = 4.7 \cdot 10^{-11}$ (at 25°C)

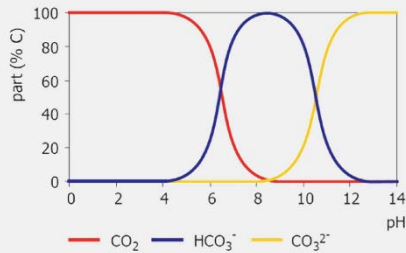
The most important acid-base reaction in water is related to the dissociation of carbon dioxide. This reaction takes a few seconds to complete. In practice, carbonic acid and carbon dioxide are considered identical and used as equivalents. The dissociation continues from carbonic acid to bicarbonate, as depicted in the slide. From these equilibrium formulas it can be calculated which ionic forms of CO₂ are present at a certain pH value. For this purpose it is convenient to rewrite the formulas in the pK form.

pK

- $pK = -\log(K)$
- $pK_1 = pH + \log \{ [H_2CO_3] / [HCO_3^-] \} = 6.35$ (at 25°C)
- $pK_2 = pH + \log \{ [HCO_3^-] / [CO_3^{2-}] \} = 10.33$ (at 25°C)
- If concentrations between '{}' are equal, $pK = pH$

pK equals to pH if the concentrations between brackets are equal, because $\log 1 = 0$.

Relationship pH and C



This graph shows the relationship between pH and different CO₂ related species. In the low pH ranges, carbon dioxide contributes for 100% to the carbon in the water, while in the highest pH ranges 100% consists of carbonate. Around neutral pH a combination of carbon dioxide and bicarbonate is present in the water. The amount of carbonic acid or bicarbonate can be determined with titration methods. Well, this must have given you a quick introduction to acid-base reactions in water, which will return in the lectures about aeration and softening.

Calculating pH

pH of soda if 4.4g of CO₂ is added to 1L of demineralized water



Let's get active again with a few exercises. First we will calculate the pH in 1 liter of demineralized water if 4.4g of carbon dioxide is added. Again, feel free to pause this video to take your time for calculation; in the next slide I will explain the calculation steps.

Calculating pH

- Added CO₂ (or H₂CO₃) = 4.4 / 44 = 0.1 mol
- x mol CO₂ dissociates, making x mol H⁺, x mol HCO₃⁻ and (1-x) mol CO₂ (neglecting HCO₃⁻ transformation to CO₃²⁻)
- Use $K_1 = x \cdot x / (0.1-x) = 4.5 \cdot 10^{-7}$
- $x = 0.21$ mmol/L
- $pH = -\log(0.00021) = 3.68$

First calculate how much carbon dioxide was added to the water in mol/L. Then use the equation of K₁ to calculate how much carbon dioxide dissociates. In this exercise, 0.21 mmol/L carbon dioxide dissociates. The pH equals to the minus log of H⁺ concentration, and is therefore 3.68.

pH if 1 mmol/L HCO₃⁻ is dosed?

- $pH = pK_1 - \log \{ [H_2CO_3] / [HCO_3^-] \}$
= 6.35 - log(99.79 / (0.21+1))
= 6.35 - 1.92
= 4.43

What happens to the pH if 1 mmol/L bicarbonate is dosed to the water? Well, for this calculation you can use the equation of pH that equals pK₁ minus log of carbonic acid divided by bicarbonate. The carbonic acid (or carbon dioxide) concentration is 100 minus 0.21 equals 99.79 mmol/L. The bicarbonate concentration is 0.21 plus 1 equals 1.21 mmol/L. With a pK₁ of 6.35 this leaves a pH of 4.43. I hope these exercises have shown you how the pH with acid-base equilibrium reactions.

Calcium carbonate equilibrium

- Calcium carbonate is difficult to dissolve in water:
 - $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3$
 - $K_s = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 3.8 \cdot 10^{-9}$ (at 25°C)

If CO_3^{2-} is removed from water, more CaCO_3 can dissolve

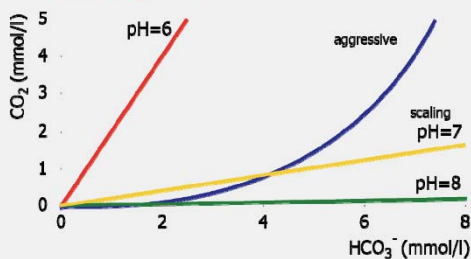
The next topic in this lecture is the calcium carbonate equilibrium. In general, calcium carbonate is difficult to dissolve in water. From a chemical perspective this is a precipitation reaction, but in natural water also acid-base reactions with carbonic acid are involved. From the solubility constant, K_s , it is clear that the more carbonate is removed from the water – for example by dosing an acid – the more calcium carbonate can dissolve into the water.

Calcium carbonate equilibrium

- Through CO_2 calcareous rock and lime stone can be dissolved:
 - $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$
 - $K = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2] = 3.6 \cdot 10^{-5}$ (at 25°C)
- If all calcium originates from CaCO_3 : $[\text{Ca}^{2+}] = [\text{HCO}_3^-] / 2$

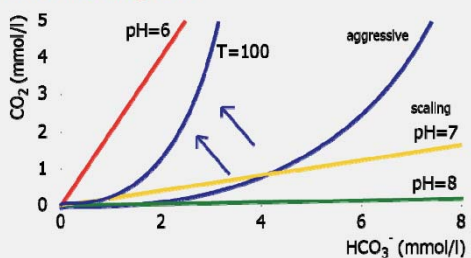
In nature, calcium enters the water because the calcium carbonate in the soil reacts with the carbon dioxide in water, which is produced through dissimilation processes in the subsurface. When all calcium in the water has originated from calcium carbonate (and not calcium sulfate), it holds that calcium equals bicarbonate divided by two. Therefore a third power relationship between carbon dioxide and bicarbonate holds for this equilibrium.

Tilmanns' diagram



The graphic presentation of this is known as Tilmanns' diagram. The blue equilibrium line separates the aggressive water, or calcium carbonate dissolving (above the line) and the calcium carbonate precipitating water (below the line). The curve is temperature dependent and will shift upwards at higher temperatures

Tilmanns' diagram



This illustrates that when water in equilibrium is heated, for example in a water cooker, it may become calcium carbonate precipitating, causing scaling on the equipment.

Aggressive water

Increasing pH by the removal of CO_2 , through:

- Gas transfer
- Adding a base (e.g., lime)
- or, by reaction with CaCO_3 (e.g., marble filtration)

The pH of aggressive water can be increased by the removal of CO_2 , for example by gas transfer, adding a base or reaction with calcium carbonate (like during marble filtration).

Calcium carbonate equilibrium constants

	pK		
	10°C	25°C	100°C
K_s	8.36	8.42	9.20
K_1	6.46	6.35	6.45
K_2	10.49	10.33	10.16
K_w	14.53	14.00	11.27

For calcium carbonate equilibrium calculations you will frequently need the constants as depicted in this table.

Saturation Index (SI)

- The **degree of over- or undersaturation** of calcium carbonate:
 - $SI = pH - pH_s = \log \left(\frac{[Ca^{2+}] \cdot [CO_3^{2-}]}{K_s} \right)$
 - $pH_s = pK_2 - pK_s - \log ([Ca^{2+}][HCO_3^-])$

Before we start the exercise I want to introduce one last term, namely the Saturation Index or SI. The Saturation Index is the degree of over- or undersaturation of calcium carbonate. SI equals pH-pH_s. pH_s is the pH at which water is in equilibrium and can be calculated with the equilibrium constants and calcium and bicarbonate concentrations.

Parameter	Unit	Value
K ⁺	mg/L	7
Na ⁺	mg/L	46
NH ₄ ⁺	mg/L	1
Fe ²⁺	mg/L	4
Mg ²⁺	mg/L	9.5
Ca ²⁺	mg/L	78
Cl ⁻	mg/L	63.5
HCO ₃ ⁻	mg/L	200
SO ₄ ²⁻	mg/L	95
CO ₂	mg/L	36
O ₂	mg/L	0
pH	-	7.1

What is the Saturation Index (SI) of this sample?

Let's put this knowledge into practice. On this slide the water composition of a groundwater sample is depicted. And the question for you is: calculate the Saturation Index. I advice that you pause the video here until you have performed the calculation, simply press restart when you want to continue.

Saturation Index (SI)

- $pH_s = pK_2 - pK_s - \log ([HCO_3^-][Ca^{2+}])$
- in mol/L (!): $[HCO_3^-][Ca^{2+}] = 6.39 \cdot 10^{-6}$
- $pH_s = 10.49 - 8.36 - \log(6.39 \cdot 10^{-6})$
- $SI = pH - pH_s = 7.06 - 7.32 = -0.26$

Well, I hope you started with the calculation of the pH_s, where it is crucial to use the mol/L unit for bicarbonate and calcium. With the pH_s of 7.32 and a water pH of 7.06 it can be calculated that the Saturation Index is minus 0.26. Have you figured out if this is calcium carbonate aggressive or precipitating? Yes, you are right, this water is calcium carbonate aggressive, because the SI is below zero.

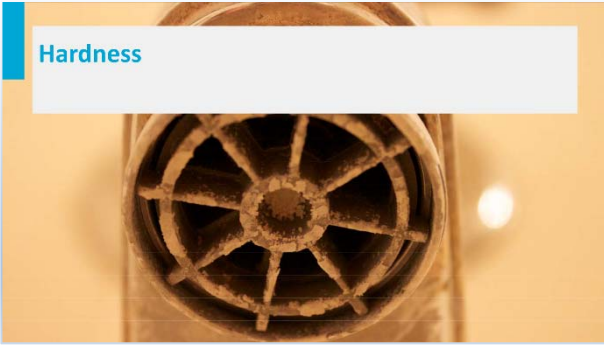
Saturation Index (SI)

- $SI > 0$: CaCO₃ precipitating
- $SI < 0$: CaCO₃ dissolving (aggressive)

Drinking water should be slightly precipitating to prevent dissolution of (cement-bound) materials during distribution

A Saturation Index above 0 is calcium carbonate precipitating and an SI below zero will dissolve calcium carbonate. For drinking water it is preferred to have water that is slightly precipitating to prevent dissolution of materials during distribution.

Hardness



Apart from the pH and the saturation index, also the hardness of water is of importance for the scaling potential.

Hardness

- The sum of dissolved **calcium & magnesium ions**
- Typically expressed in **mmol/L**
- In the Netherlands the term '**German hardness**' is also used
- **1 °GH or 1 °D = 0.178 mmol/L**

Hardness is the sum of calcium and magnesium ions in water. This is typically expressed in mmol/L, but also the term "german hardness" is practiced. 1 degree german hardness equals to 0.178 mmol/L.

Calculating hardness 'Spa Reine'

Mineral		Concentration (mg/L)
Sodium	Na ⁺	3
Calcium	Ca ²⁺	5
Magnesium	Mg ²⁺	1
Chloride	Cl ⁻	5
Sulfate	SO ₄ ²⁻	4
Nitrate	NO ₃ ⁻	2
Bicarbonate	HCO ₃ ⁻	15



The last exercise of this lecture is to calculate the hardness of mineral water, as depicted in the table. Take the

Calculating hardness 'Spa Reine'

Mineral		Concentration (mg/L)
Sodium	Na ⁺	3
Calcium	Ca²⁺	5
Magnesium	Mg ²⁺	1
Chloride	Cl ⁻	5
Sulfate	SO ₄ ²⁻	4
Nitrate	NO ₃ ⁻	2
Bicarbonate	HCO ₃ ⁻	15



calcium and

Calculating hardness 'Spa Reine'

Mineral		Concentration (mg/L)
Sodium	Na ⁺	3
Calcium	Ca ²⁺	5
Magnesium	Mg²⁺	1
Chloride	Cl ⁻	5
Sulfate	SO ₄ ²⁻	4
Nitrate	NO ₃ ⁻	2
Bicarbonate	HCO ₃ ⁻	15



magnesium concentration and calculate the concentration in mmol/L.

Calculating hardness 'Spa Reine'

Calcium = concentration / molar mass
= 5 mg/L / 40.078
= 0.125 mmol/L

Magnesium = concentration / molar mass
= 1 mg/L / 24.305
= 0.041 mmol/L

Total hardness = 0.17 mmol/L or 0.93 °GH

For calcium this equals to 0.125 mmol/L and for magnesium to 0.041 mmol/L. In total this amounts to a hardness of 0.17 mmol/L or 0.93 degrees german hardness.

Guidelines for tap water

- Dutch Decree of Water Supply: >1 and <2.5 mmol/L
- Water should be **non-aggressive** and **non-scaling** (during heating)
- pH: >7.0 and <9.5
- Saturation Index (SI) = >-0.2

The guidelines for tap water are not the same around the world, but now I will briefly summarize the guidelines in the Dutch Decree of Water Supply. These standards include that the hardness should be between 1 and 2.5 mmol/L, because if the hardness is too low it may result in locally aggressive waters. From a health perspective it is also desirable to have some hardness in the water. If the hardness is too high it may result in scaling once heated, as described with the Tilmanns' curve. So, the water should neither be aggressive nor scaling. The pH should be within the range of 7 and 9.5 and the Saturation Index should not be lower than -0.2.

Drinking Water Chemistry

CTB3365x Introduction to water treatment

Dr. ir. Doris van Halem – Assistant Professor in Drinking Water



Challenge the Future

We have come to the end of this lecture about basic water quality calculations. I thank you for watching and recommend to practice the homework exercises to get more familiar with these basic, but crucial parameters.