Aqueous Geochemistry and Stability of Minerals

Lecturer:

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Aquatic geochemistry is concerned with chemical processes affecting the distribution and circulation of chemical compounds in natural waters.

It aims to provide theoretical basis for the chemical behaviour of the Earth’s hydrosphere, including its main domains:

- ocean waters,
- estuaries (i.e. partly enclosed coastal bodies with brackish waters)
- river systems
- lakes and ponds
- groundwaters
- and soil water systems

Geochemistry of natural waters thus represents a research field where one needs knowledge of chemistry, mineralogy, geology and biology.
The **triple point** of a substance is the temperature and pressure at which three phases gas, liquid, solid coexist at equilibrium.

**Water triple point:**
- T = 0.01°C
- P = 611 Pa (0.006 atm)

At Earth’s surface:
- T = 20°C
- P = 101 kPa (1 atm)
Uniqueness of water: Importance of hydrogen bonds

Water (hydride of oxygen, $\text{H}_2\text{O}$) has much higher boiling point compared to other hydrides, hence it is commonly present in liquid form at the earth surface.

In contrast, other common hydrides such as ammonia (nitrogen hydride = $\text{NH}_3$), methane (carbon hydride = $\text{CH}_4$), (fluorine hydride = $\text{HF}$), that have their boiling points just below the room temperature, so they are all at Earth’s surface as gases.
Uniqueness of water: Importance of hydrogen bonds

Water is able to form four hydrogen bonds (i.e. attraction between positive hydrogen atoms and partially negative oxygen atom) because it possesses two hydrogens (bond donors) and a pair of negative charges on oxygen (acceptor)

Polar nature of water molecule

Structure of liquid water

Source: Principles of General Chemistry, Silberberg (2009)
Hydrogen bonding is what gives water its **adhesive and cohesive properties**, allowing water to form thin films as it spreads on smooth surfaces (adhesion), and stick together (cohesion) as droplets,

Thus, water has the **greatest surface tension** of any liquid on Earth’s surface

**Surface tension** is a contractive tendency of the surface of a liquid that allows it to resist an external force

*Source: Silberberg (2009), Misra (2012)*
H₂O is a very good solvent for ionic compounds, which are compounds that dissociate into positively and negatively charged ionic species (e.g. NaCl).

Hydration of Na⁺ and Cl⁻ ions thus provides a sort of protective shield around them, thus reducing the probability of their recombination.

The dipolar water molecule align their positive and negative ends in such a way that the ion attraction between Na⁺ and Cl⁻ is partially neutralized, and thus the attraction between these hydrated ions is weakened. This is the main reason for a high solubility of NaCl in water.
**Water as a solvent**

**H₂O is a very good solvent for ionic compounds**, which are compounds that dissociate into positively and negatively charged ionic species (e.g. NaCl).

The effectiveness of water (H₂O) as a solvent is reflected in its **high dielectric constant** ($\varepsilon_{H2O}$) which is the ability of a substance to insulate charges (ions) from each other.

Liquid water has a dielectric constant of 80.4 units, which means that charged ions in water are attracted to each other with a force of only 1/80 (~1.2%) as strong as in a vacuum.

In contrast, acetone (C₃H₆O) has a dielectric constant of 21 units, and acetic acid (C₂H₄O₂) of only 6 units.
Concept of Chemical Equilibrium

An example of a simple chemical reaction that achieves an equilibrium state:

\[ \text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^- \]

sodium chloride (table salt) being dissolved in pure water

when no more NaCl would dissolve in water the solution became *saturated* with respect to NaCl
Let’s consider a simple chemical reaction: \( A + B \rightleftharpoons C + D \)

The rate of the forward reaction \( (r_f) \) can be defined as: \( r_f = k_f (A) (B) \)

And the rate of the backward reaction \( (r_b) \) is then: \( r_b = k_b (C) (D) \)

where \( (A) \), \( (B) \), \( (C) \), and \( (D) \) are the concentrations of the elements, or compounds and \( k_{f,b} \) are the proportionality or rate constants (i.e. a relationship between “reaction rate“ and “concentrations of reactants“)

**At equilibrium conditions:** \( r_f = r_b \) or \( k_f (A) (B) = k_b (C) (D) \)

Which can be rewritten as: \( \frac{k_f}{k_b} = \frac{(C) (D)}{(A) (B)} = K \)

where \( K \) is the *equilibrium constant* for this reaction
Fig. 4.1 A reaction, such as $X+Y=C+D$, is to have attained equilibrium when the rate of the forward reaction $X+Y \rightarrow C+D$ ($R_{\text{forward}}$) becomes equal to the rate of the reverse reaction $C+D \rightarrow X+Y$ ($R_{\text{reverse}}$). It is assumed that only $X$ and $Y$ were present at the start of the reaction. The properties of the system at equilibrium will not change with time.
Concentration vs. Activity Relationship

The concept of the **activity** of ions in aqueous geochemistry

**High activity** (no interfering ions)  **Low activity** (due to interferences)

Hence, also the concentration of our particle (i.e. car...) is same in both cases, the activity for this particle is very different for these two scenarios ...
Concentration vs. Activity Relationship

The Activity \(a\) of an ion in solution is related to its Molar Concentration \(c\) and its Activity Coefficient \(\gamma\), following the expression:

\[ a = \gamma \times c \]

How to calculate Activity Coefficient \(\gamma\) ...

Most popular method for the calculation of activity coefficients \(\gamma\), and thus activities \(a\), of ions in a solution is based on the Debye–Hückel theory:

\[
\log(\gamma) = -\frac{0.5 \cdot (Z)^2 \cdot \sqrt{I}}{1 + \sqrt{I}}
\]

Where:
- \(Z\) = oxidation number of the ion
- \(I\) = ionic strength of a solution

Ionic strength:

\[
I = \frac{1}{2} \sum c \cdot (Z)^2
\]

\(c\) = molar concentration
Debye–Hückel theory provides mathematical explanation for departures of ion activities from the “ideality” in a solutions.
# Practical Example of Calculations (Ionic Strength, Activities, etc.)

Chemical composition of water from Mississippi River (from Faure, page 140)

<table>
<thead>
<tr>
<th>Ion</th>
<th>ppm</th>
<th>mol/kg</th>
<th>Charge</th>
<th>log $\gamma$</th>
<th>$\gamma$</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>anion HCO3-</td>
<td>116</td>
<td>0.00190</td>
<td>-1</td>
<td>0.0310184</td>
<td>0.9311</td>
<td>0.001769</td>
</tr>
<tr>
<td>anion SO42-</td>
<td>25.5</td>
<td>0.00027</td>
<td>-2</td>
<td>0.1240738</td>
<td>0.7515</td>
<td>0.000199</td>
</tr>
<tr>
<td>anion Cl-</td>
<td>10.3</td>
<td>0.00029</td>
<td>-1</td>
<td>0.0310184</td>
<td>0.9311</td>
<td>0.000270</td>
</tr>
<tr>
<td>anion NO3-</td>
<td>2.7</td>
<td>0.00004</td>
<td>-1</td>
<td>0.0310184</td>
<td>0.9311</td>
<td>0.000040</td>
</tr>
<tr>
<td>cation Ca2+</td>
<td>34</td>
<td>0.00085</td>
<td>2</td>
<td>0.1240738</td>
<td>0.7515</td>
<td>0.000639</td>
</tr>
<tr>
<td>cation Mg2+</td>
<td>8.9</td>
<td>0.00037</td>
<td>2</td>
<td>0.1240738</td>
<td>0.7515</td>
<td>0.000278</td>
</tr>
<tr>
<td>cation Na+</td>
<td>11.9</td>
<td>0.00052</td>
<td>1</td>
<td>0.0310184</td>
<td>0.9311</td>
<td>0.000481</td>
</tr>
<tr>
<td>cation K+</td>
<td>1.9</td>
<td>0.00005</td>
<td>1</td>
<td>0.0310184</td>
<td>0.9311</td>
<td>0.000046</td>
</tr>
<tr>
<td>cation Fe2+</td>
<td>0.14</td>
<td>0.00000</td>
<td>2</td>
<td>0.1240738</td>
<td>0.7515</td>
<td>0.000002</td>
</tr>
<tr>
<td>neutral SiO2</td>
<td>11.7</td>
<td>0.00019</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Ionic Strength (I)**

$$I = \frac{1}{2} \cdot \sum c_i \cdot Z_i^2$$

$$\log(\gamma) = -\frac{0.5 \cdot (Z_i)^2 \cdot \sqrt{I}}{1 + \sqrt{I}}$$

so

$$\gamma = 10^{-\log(\gamma)}$$
1\textsuperscript{st} Step:  
Measure the \textbf{concentrations (molar)} of cations and anions in your solution

2\textsuperscript{nd} Step:  
From the concentrations (\(c\)) and ion charges (\(Z\)) calculate the \textbf{Ionic Strength (I)}

3\textsuperscript{th} Step:  
Using the ionic strength (\(I\)) and charges (\(Z\)) calculate the \textbf{Activity Coeff. (\(\gamma\))}

4\textsuperscript{th} Step:  
Using the concentrations and activity coefficients calculate the ionic \textbf{Activity (a)}

\textit{Then you are done ... you have your activities !}
The oxidation number of an element indicates the number of electrons lost, gained, or shared as a result of chemical bonding.
In general, the activities of ions progressively decrease with an increasing Ionic Strength (I) of a solution (due to more interferences).
Ionic Strength (I) for Selected Natural Waters

<table>
<thead>
<tr>
<th>Water</th>
<th>Typical Ionic Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rivers and lakes</td>
<td>0.001 - 0.005</td>
</tr>
<tr>
<td>Potable groundwater</td>
<td>0.001 - 0.02</td>
</tr>
<tr>
<td>Seawater</td>
<td>0.7</td>
</tr>
<tr>
<td>Oil field brines</td>
<td>&gt;5</td>
</tr>
</tbody>
</table>

Note that the **Debye–Hückel theory** provides reliable results only for solutions with lower Ionic Strength, e.g. \( I < 0.1 \)

For solutions with higher Ionic Strength (I), other theories are proposed, e.g. **extended Debye-Hückel**, or **Davies theory**, which give reliable results for \( I > 0.5 \) or 1

Increase of activity coefficients in highly saline solution (I > 1) can be attributed to “crowding“ of ions, which counteracts the interferences.
Dissolution of gypsum in pure water can be represented by the reaction:

\[
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2+} + \text{H}_2\text{O}
\]
Solubility of Gypsum in Pure water

\[ \text{Reactants} \quad \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \quad \xrightleftharpoons{} \quad \text{Products} \quad \text{Ca}^{2+} + \text{SO}_4^{2+} + \text{H}_2\text{O} \]

Solubility = the ability of a substance or mineral to dissolve

At the chemical equilibrium (at 25°C and 1 atm):

\[ K_{eq} = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{SO}_4^{2-}} \cdot a^2_{\text{H}_2\text{O}}}{a_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}} \]

Note that we always write Products over Reactants

\( K_{eq} = \) this constant (also called Solubility Product constant, \( K_{sp} \)) reflects equilibrium conditions for a solid (mineral) and its respective ions in a solution; and it identifies the ability of a substance or mineral to dissolve in water

This constant can be used as reference to estimate if some mineral will precipitate (or rather dissolve) in a specific water solution
**Solubility of Gypsum in Pure water**

\[
K_{eq} = \frac{a_{Ca^{2+}} \cdot a_{SO_{4}^{2-}} \cdot a_{H_{2}O}^2}{a_{CaSO_{4} \cdot 2H_{2}O}}
\]

Since, H\(_2\)O and CaSO\(_4\)\(_2\)H\(_2\)O are neutral species (their \(a = 1\)), so we can write:

\[
K_{eq \ (gypsum)} = a_{Ca^{2+}} \cdot a_{SO_{4}^{2-}} = (\gamma \cdot C)_{Ca} \cdot (\gamma \cdot C)_{SO_{4}} = 10^{-4.59}
\]

This value represents the **Solubility Product constant (K\(_{sp}\))** for gypsum mineral

**Rule of thumb:** the lower K\(_{sp}\) value, the less soluble a mineral is in the water
## Selected Minerals and their $K_{sp}$ Values

### Solubility-Product Constants for Compounds at 25°C

<table>
<thead>
<tr>
<th>NAME</th>
<th>FORMULA</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium carbonate</td>
<td>BaSO$_4$</td>
<td>$5.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>Barium chromate</td>
<td>BaCrO$_4$</td>
<td>$2.1 \times 10^{-10}$</td>
</tr>
<tr>
<td>Barium fluoride</td>
<td>BaF$_2$</td>
<td>$1.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>Barium oxalate</td>
<td>BaC$_2$O$_4$</td>
<td>$1.6 \times 10^{-6}$</td>
</tr>
<tr>
<td>Barium sulfate</td>
<td>BaSO$_4$</td>
<td>$1.1 \times 10^{-10}$</td>
</tr>
<tr>
<td>Cadmium carbonate</td>
<td>CdCO$_3$</td>
<td>$1.8 \times 10^{-14}$</td>
</tr>
<tr>
<td>Cadmium hydroxide</td>
<td>Cd(OH)$_2$</td>
<td>$2.5 \times 10^{-14}$</td>
</tr>
<tr>
<td>Cadmium sulfide*</td>
<td>CdS</td>
<td>$8.0 \times 10^{-28}$</td>
</tr>
<tr>
<td>Calcium carbonate (calcite)</td>
<td>CaCO$_3$</td>
<td>$4.5 \times 10^{-9}$</td>
</tr>
<tr>
<td>Calcium chromate</td>
<td>CaCrO$_4$</td>
<td>$7.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Calcium fluoride</td>
<td>CaF$_2$</td>
<td>$3.9 \times 10^{-11}$</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>Ca(OH)$_2$</td>
<td>$6.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>Calcium phosphate</td>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td>$2.0 \times 10^{-29}$</td>
</tr>
<tr>
<td>Calcium sulfate</td>
<td>CaSO$_4$</td>
<td>$2.4 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Mineral Saturation and Ion Activity Product

The Ion Activity Product (IAP) has basically the same form as the Equilibrium Constant ($K_{sp}$), but IAP involves the actual (measured) ion activities

\[
IAP_{(gypsum)} = (a_{Ca^{2+}})_{\text{actual}} \times (a_{SO_{4}^{2-}})_{\text{actual}}
\]

Saturation Index (SI) quantifies if a certain mineral or solid will precipitate (or dissolve) in a solution, and SI is defined as:

\[
SI_{(gypsum)} = \log \frac{IAP_{\text{actual}}}{K_{sp}}
\]

- **SI = 0**, the solution is just saturated ($IAP = K_{sp}$), neither dissolve nor precipitate
- **SI > 0**, the solution is supersaturated ($IAP > K_{sp}$), mineral will precipitate
- **SI < 0**, the solution is undersaturated ($IAP < K_{sp}$), mineral will dissolve
Practical Calculation of Mineral Saturation in Waters

Suppose, the concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\) in a sample of water are 5 \times 10^{-2} \, m and 7 \times 10^{-3} \, m, respectively. Let’s find out the saturation state of the solution with respect to gypsum. For simplicity, we will assume that \(a_{\text{Ca}^{2+}} = m\) and \(a_{\text{SO}_4^{2-}} = m\).

\[
IAP \text{ (solution)} = a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}} = (5 \times 10^{-2}) (7 \times 10^{-3})
\]

\[
= 3.5 \times 10^{-5} = 10^{-3.5}
\]

\[K_{sp \, (\text{CaSO}_4)} = 10^{-4.59}\]

Since \(IAP \text{ (solution)} > K_{sp \, (\text{gypsum})}\), the water sample is oversaturated with respect to gypsum, and some gypsum should precipitate out of this solution to restore equilibrium.