CZECH REPUBLIC
DEVELOPMENT COOPERATION

Aqueous Geochemistry
and Stability of Minerals

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Basics of Aquatic Geochemistry

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**

Uniqueness of water physico-chemical properties
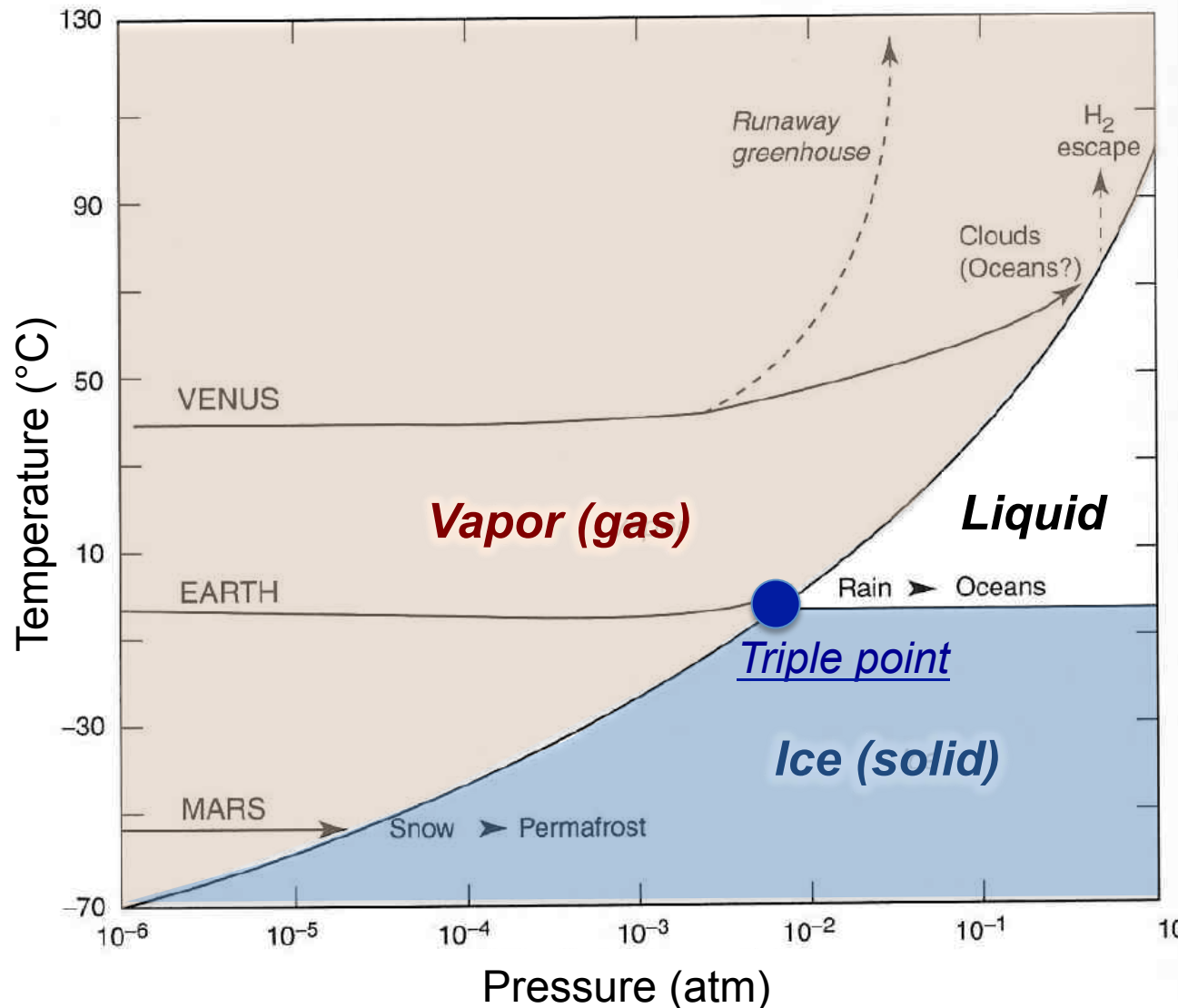
The **triple point** of a substance is the temperature and pressure at which three phases **gas, liquid, solid coexist** at equilibrium
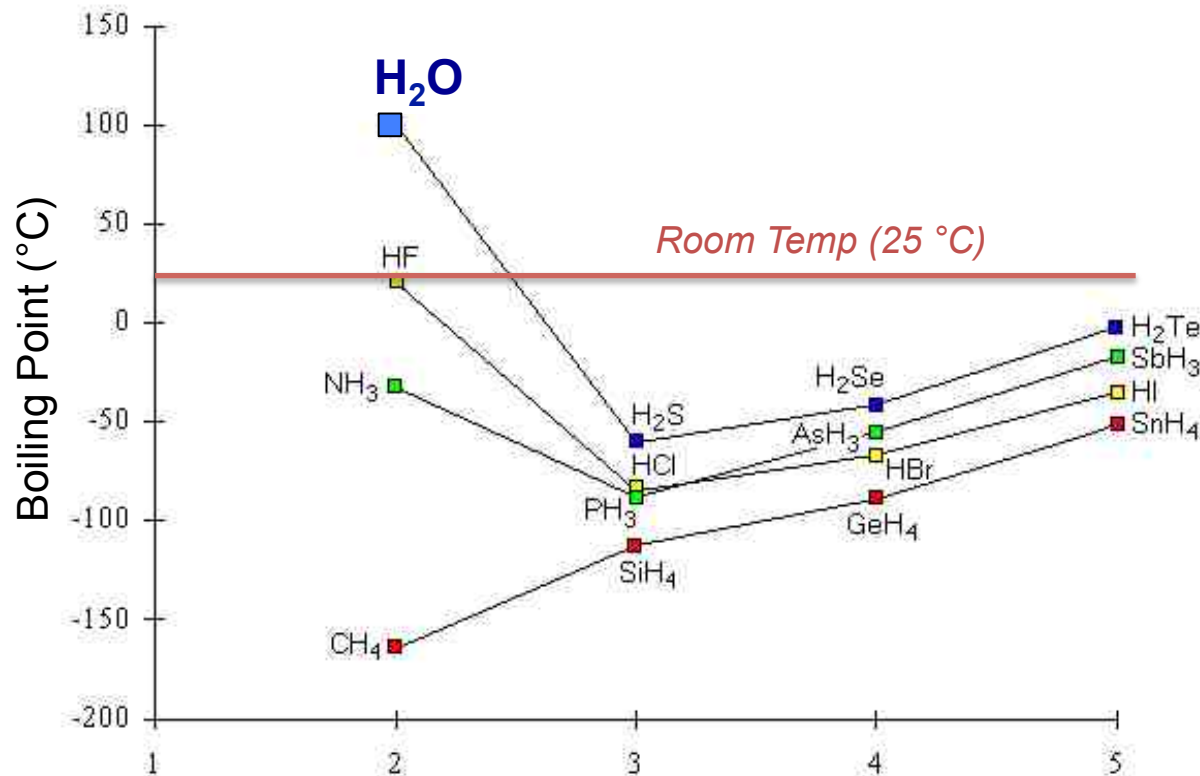
Water triple point:
T = 0.01°C
P = 611 Pa (0.006 atm)

At Earth's surface:
T = 20°C
P = 101 kPa (1 atm)

Water (hydride of oxygen, H_2O) has much **higher boiling point** compared to other hydrides, hence it is commonly present in liquid form at the earth surface

Water molecules are drawn together by hydrogen bonds
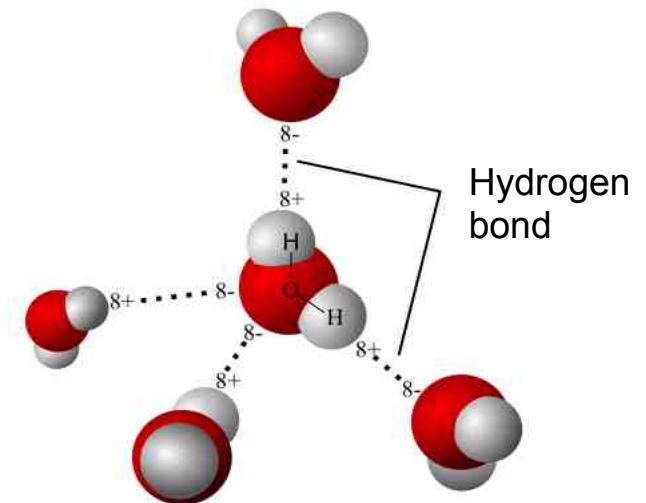
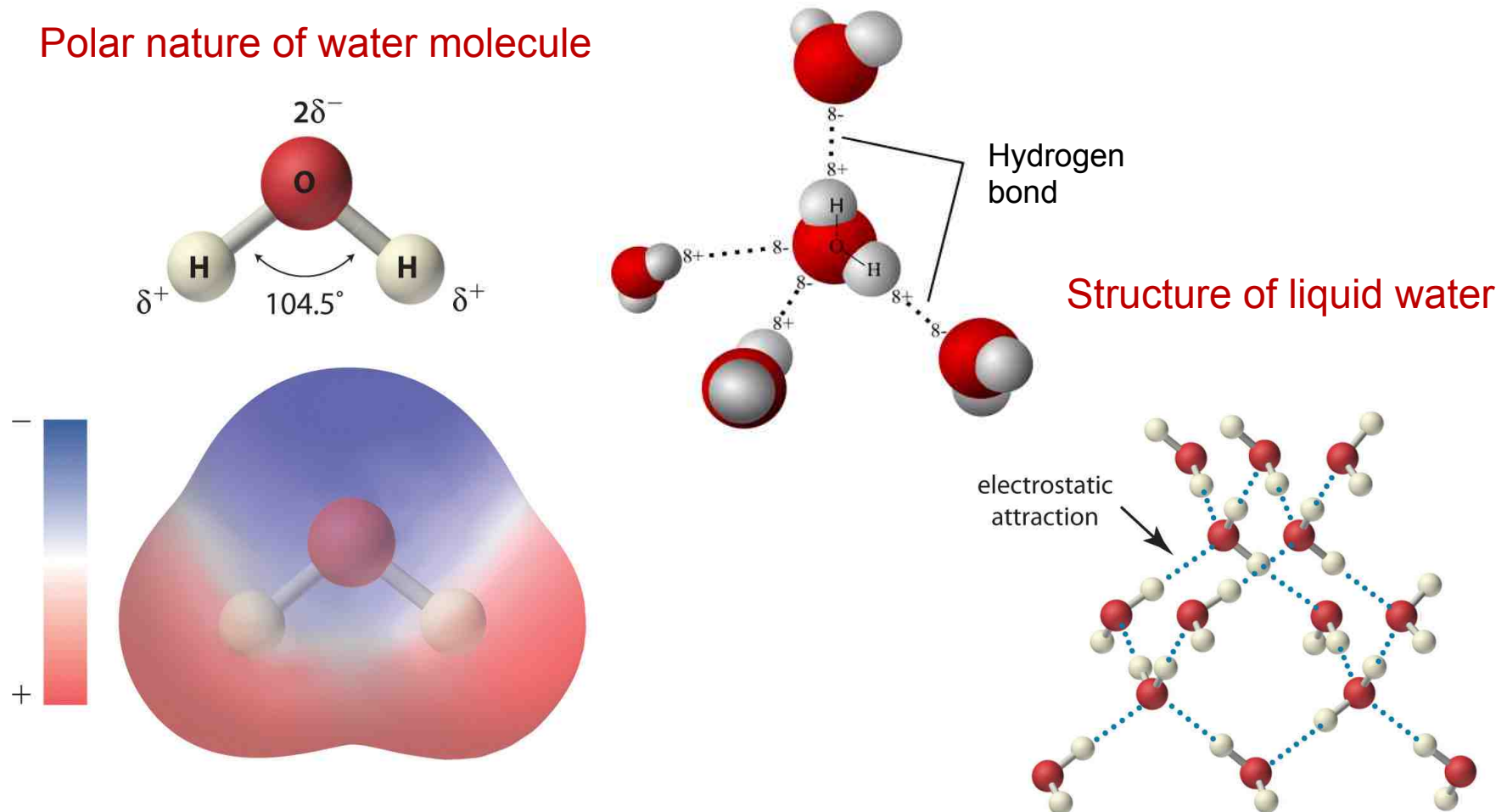In contrast, other common hydrides such as ammonia (nitrogen hydride = NH_3), methane (carbon hydride = CH_4), (fluorine hydride = HF), that have their boiling points just below the room temperature, so they are all at Earth's surface as gases

# 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

Hydrogen bond

Structure of liquid water

electrostatic attraction
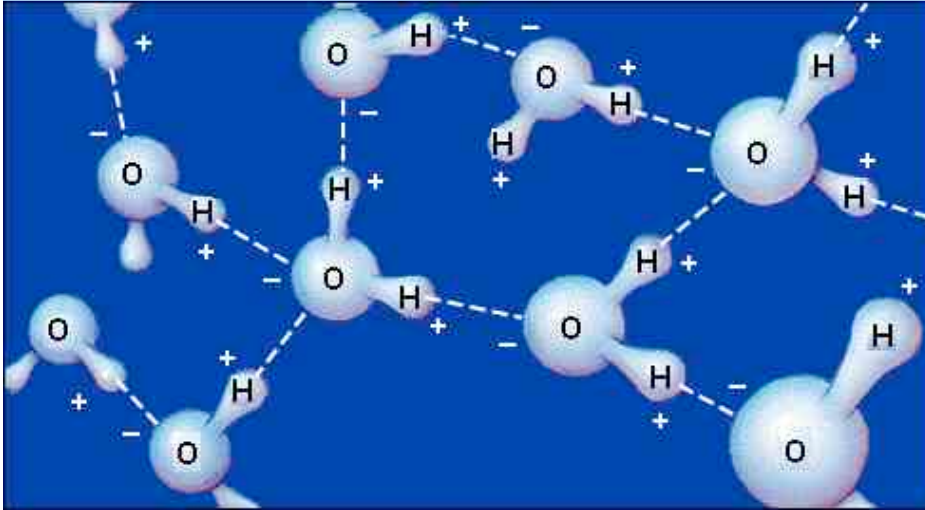
Hydrogen bonding is what gives water its **adhesive and cohesive properties**, allowing water to form thin films as it spreads of smooth surfaces (adhesion), and stick together (cohesion) as droplets,

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)

Water as a solvent

H₂O is a very good solvent for ionic compounds, which are compound that dissociate into positively and negatively charged ionic species (e.g. NaCl)
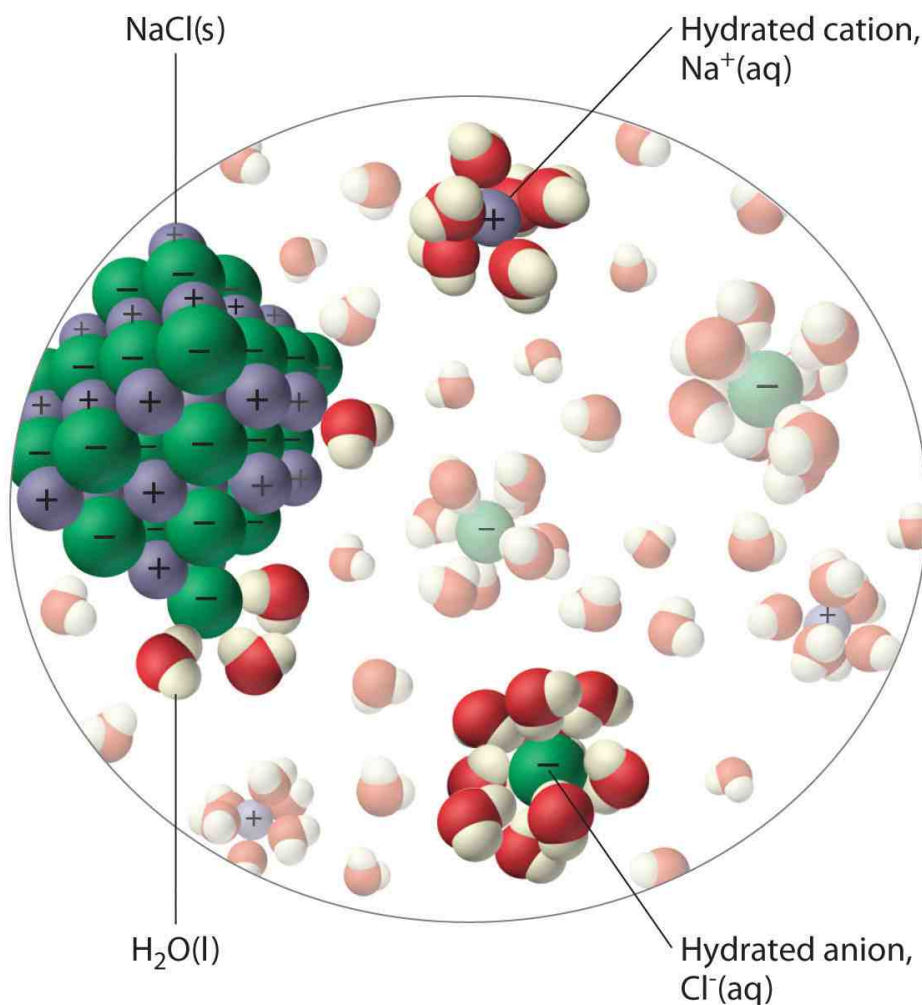
Hydration of Na^+ and Cl^- ions thus provides a sort of protective shield around them, thus reducing the probability of their recombination.

The dipolar water molecule align their positive and negative ends in such 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

H_2O is a very good solvent for ionic compounds, which are compound that dissociate into positively and negatively charged ionic species (e.g. NaCl)
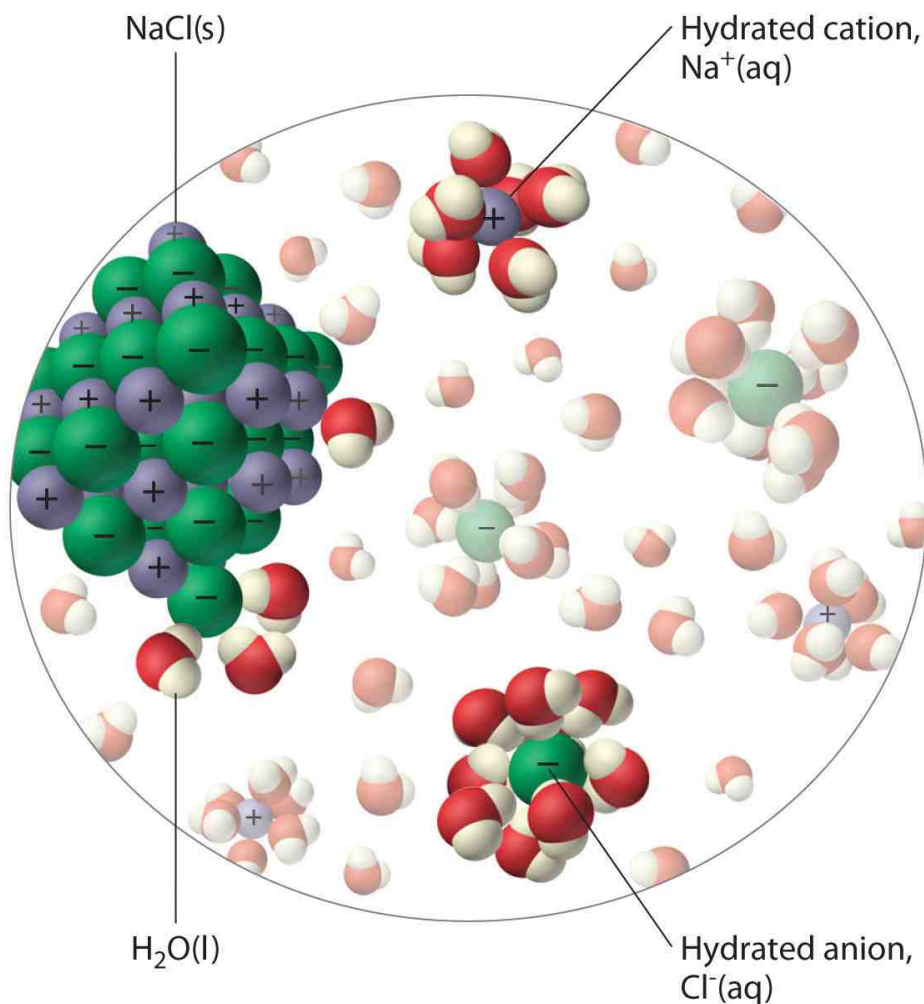
NaCl(s)

Hydrated cation, $Na^+(aq)$

$H_2O(l)$

Hydrated anion, $Cl^-(aq)$

The effectiveness of water (H_2O) as solvent is reflected in its **high dielectric constant (ε_{H2O})** which is the ability of a substance to insulate charges (ions) from each other

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

In contrast, acetone (C_3H_6O) has dielectric constant of 21 units, and acetic acid ($C_2H_4O_2$) of only 6 units

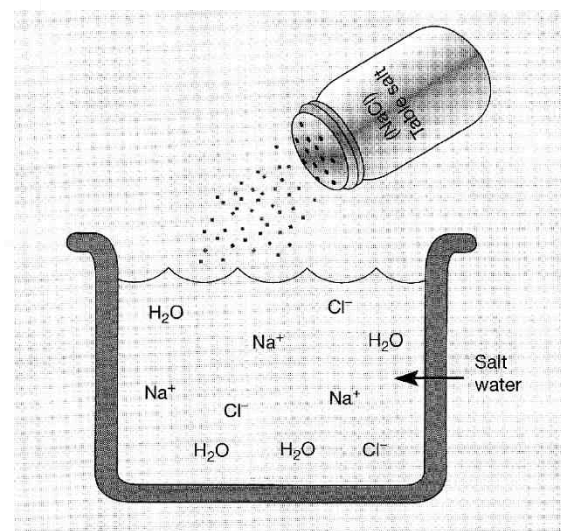## Concept of Chemical Equilibrium

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

$$NaCl \rightleftarrows Na^+ + Cl^-$$ sodium chloride (table salt) being dissolved in pure water
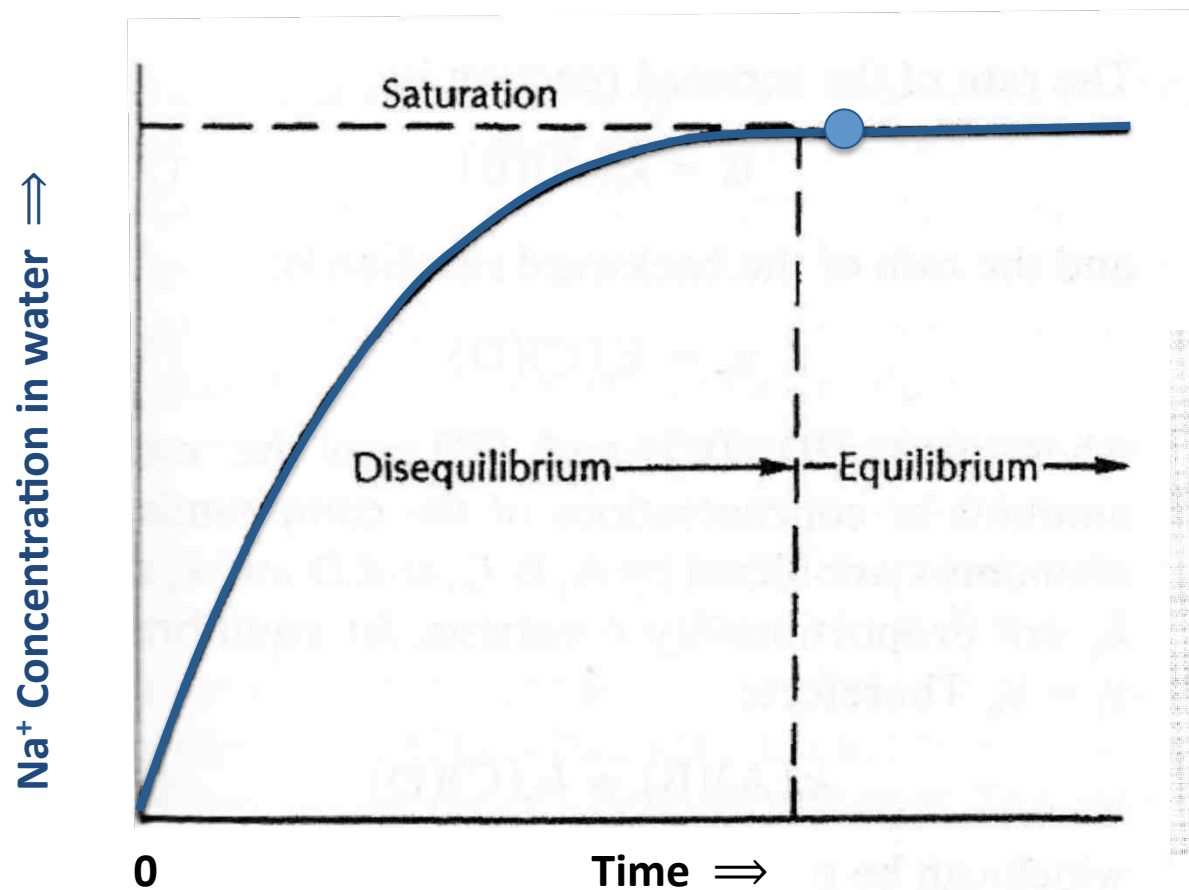
when no more NaCl would dissolve in water the solution became **saturated** with respect to NaCl

Basics of Chemical Reactions – Law of Mass Action

Let's consider a simple chemical reaction: $A + B \rightleftarrows C + D$

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) 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: $\dfrac{k_f}{k_b} = \dfrac{(C)*(D)}{(A)*(B)} = K$

where K is the *equilibrium constant* for this reaction

Law of Mass Action and Equilibrium Constant (K)
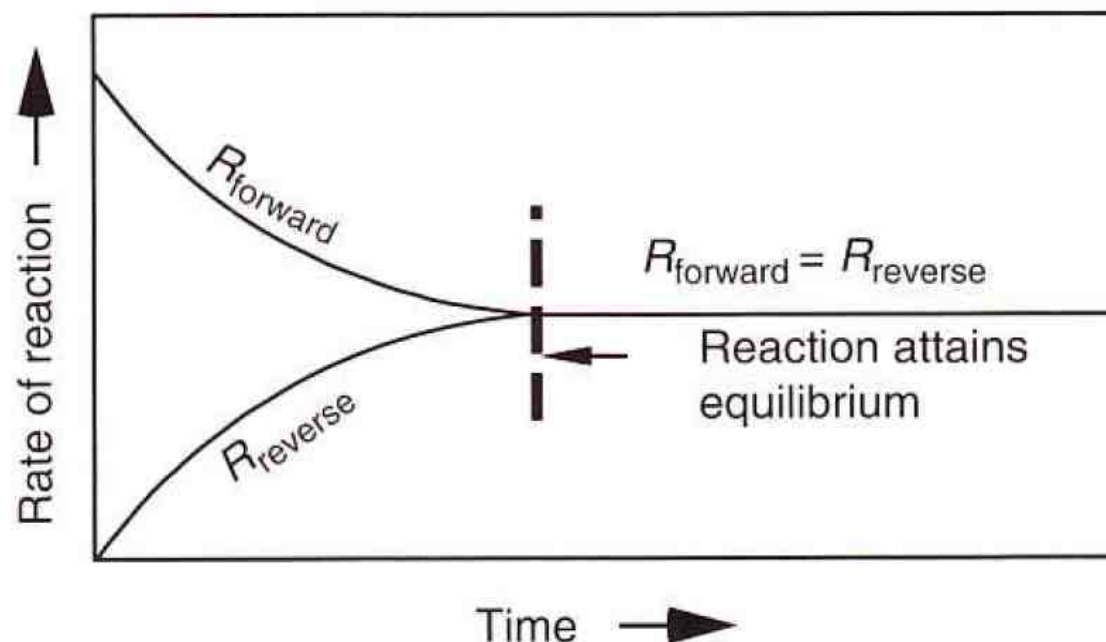
Fig. 4.1 A reaction, such as X+Y=C+D, is to have attained equilibrium when the rate of the forward reaction X+Y → C+D ($R_{forward}$) becomes equal to the rate of the reverse reaction C+D → X+Y ($R_{reverse}$). It is assumed that only X and Y were present at the start of the reaction. The properties of the system at equilibrium will not change with time.

Apparent Equili. Constant

$$\frac{[C]^c_{eq}\ [D]^d_{eq}\cdots}{[X]^x_{eq}\ [Y]^y_{eq}\cdots} = K^{app}$$

Concentrations

True Equili. Constant

$$\frac{a^c_C\ a^d_D\ \cdots}{a^x_X\ a^y_Y\ \cdots} = K_{eq}$$

Activities (a)

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 ...

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

$$a = \gamma * c$$

How to calculate Activity Coefficient (γ) ...

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

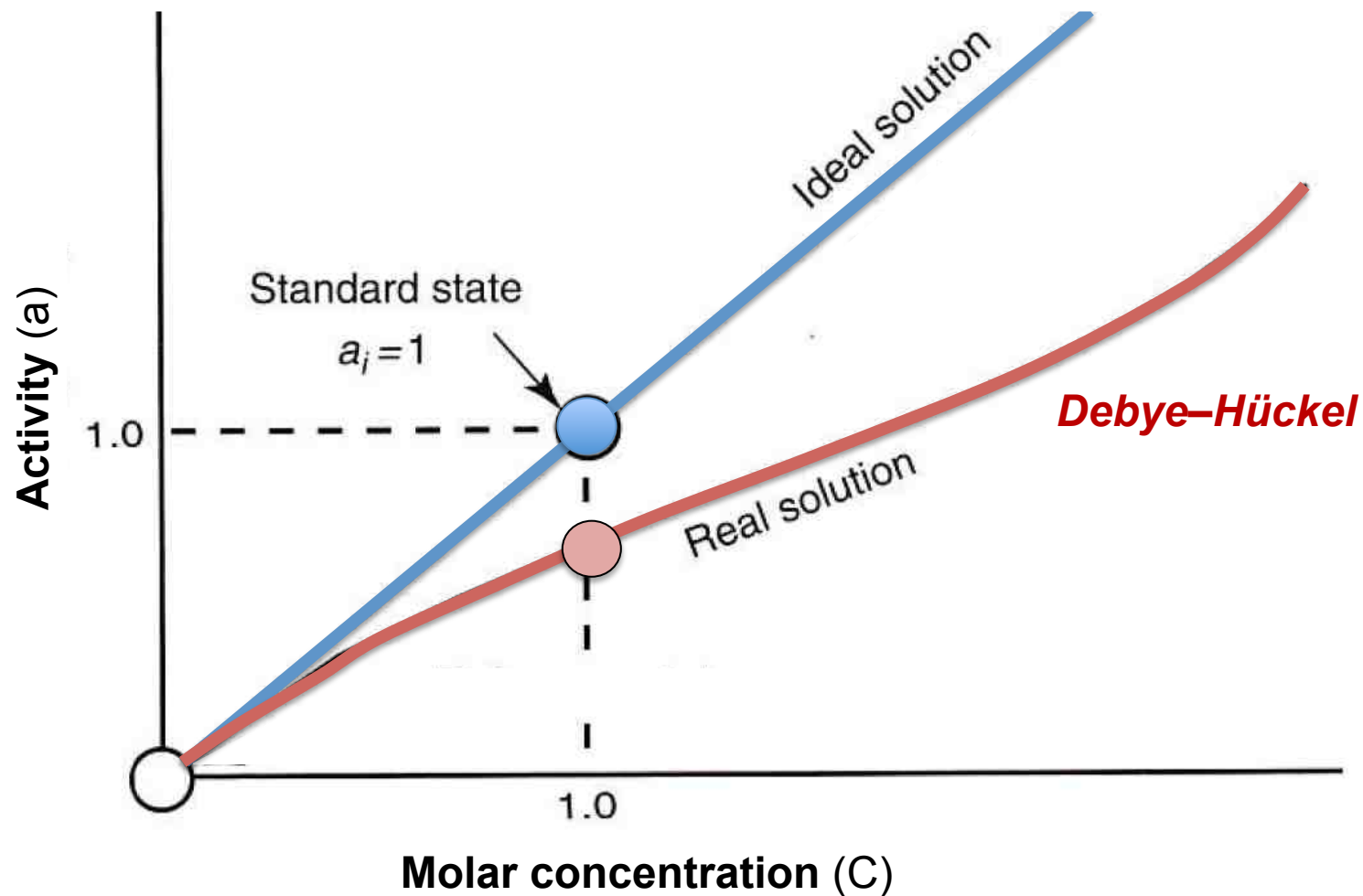$$\log(\gamma) = -\frac{0.5 \cdot (Z)^2 \cdot \sqrt{I}}{1 + \sqrt{I}}$$

Where:

Z = oxidation number of the ion

I = ionic strength of a solution

Ionic strength: $\quad I = \dfrac{1}{2} \sum c \cdot (Z)^2$

c = molar concentration

Concentration vs. Activity Relationship

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)

		c	z	log γ	γ	a
	Ion	ppm	mol/kg	Charge	Activity Coefficient		Activity
anion	HCO3-	116	0,00190	-1	-0,0310184	0,9311	0,001769
anion	SO42-	25,5	0,00027	-2	-0,1240738	0,7515	0,000199
anion	Cl-	10,3	0,00029	-1	-0,0310184	0,9311	0,000270
anion	NO3-	2,7	0,00004	-1	-0,0310184	0,9311	0,000040
cation	Ca2+	34	0,00085	2	-0,1240738	0,7515	0,000639
cation	Mg2+	8,9	0,00037	2	-0,1240738	0,7515	0,000278
cation	Na+	11,9	0,00052	1	-0,0310184	0,9311	0,000481
cation	K+	1,9	0,00005	1	-0,0310184	0,9311	0,000046
cation	Fe2+	0,14	0,00000	2	-0,1240738	0,7515	0,000002
neutral	SiO2	11,7	0,00019	0	0		

Ionic Strength (I)   0,0044   mol per kg

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

$$\log(\gamma) = -\frac{0.5 \cdot (Z_i)^2 \cdot \sqrt{I}}{1 + \sqrt{I}} \quad \text{so} \quad \gamma = 10^{-\log(\gamma)}$$

Step-By-Step Approach to Calculate Ion Activities

1st Step:

Measure the **concentrations (molar)** of cations and anions in your solution

2nd Step:

From the concentrations (c) and ion charges (Z) calculate the **Ionic Strength (I)**

3th Step:

Using the ionic strength (I) and charges (Z) calculate the **Activity Coeff. (γ)**

4th Step:

Using the concentrations and activity coefficients calculate the ionic **Activity (a)**

Then you are done … you have your activities !

Typical Oxidation (valence) Number of Elements

Legend:
- Non-Metals
- Transition Metals
- Rare Earth Metals
- Halogens
- Alkali Metals
- Alkali Earth Metals
- Other Metals
- Inert Elements

Periodic Table of Elements

Oxidation Number (Ionic Charges)

Cations +1 +2   Variable Charges   +3 +/.4 -3 -2 -1 0 **Anions**

The **oxidation number** of an element indicates the number of electrons lost, gained, or shared as a result of chemical bonding

# Relationship between Activity of Ions and Ionic Strength (I)
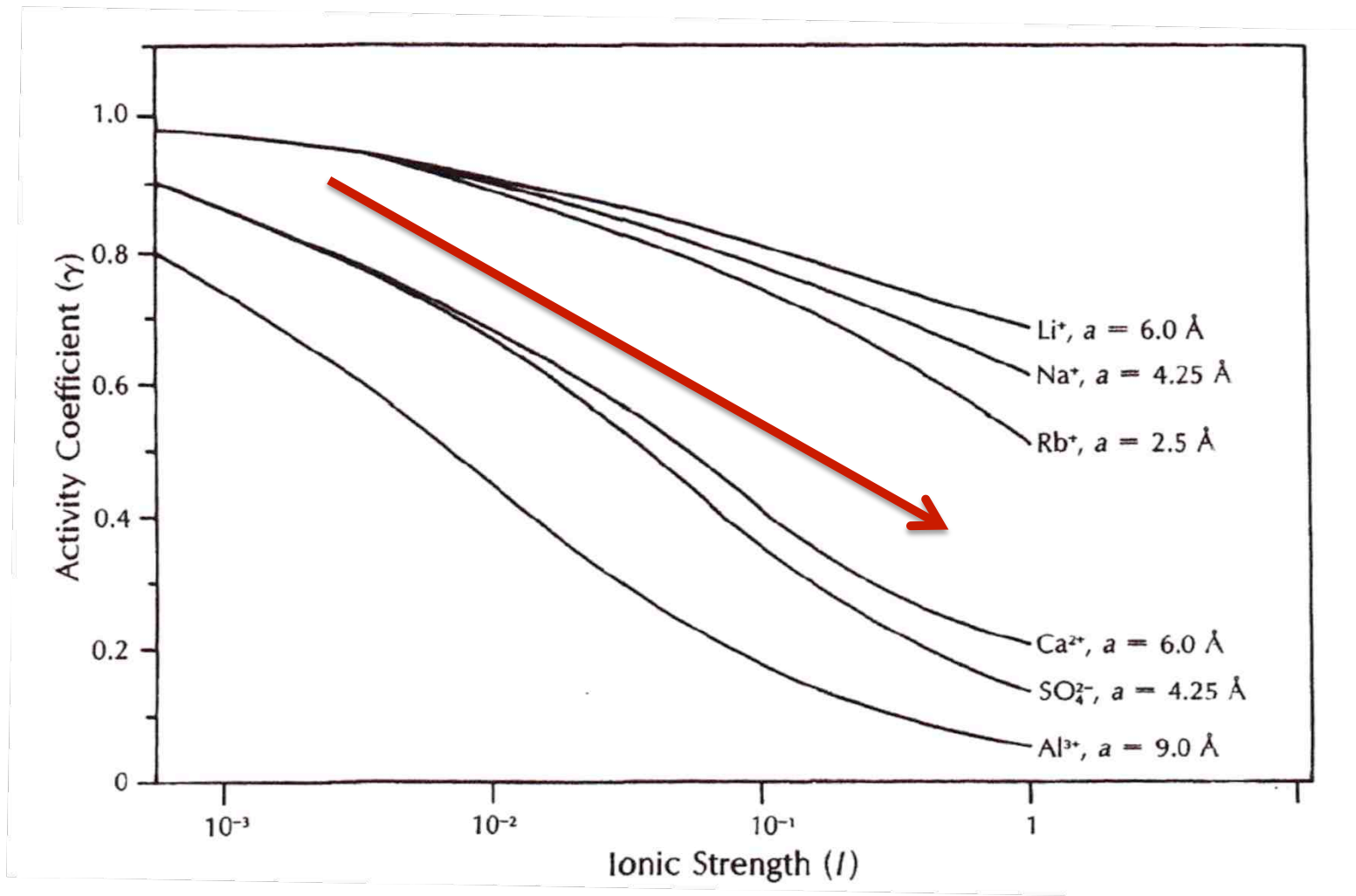
In general, the activities of ions progressively decrease with
an increasing Ionic Strength (I) of a solution (due to more interferences)

Ionic Strength (I) for Selected Natural Waters

Water	Typical Ionic Strength
Rivers and lakes	0.001 - 0.005
Potable groundwater	0.001 - 0.02
Seawater	0.7
Oil field brines	>5

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*
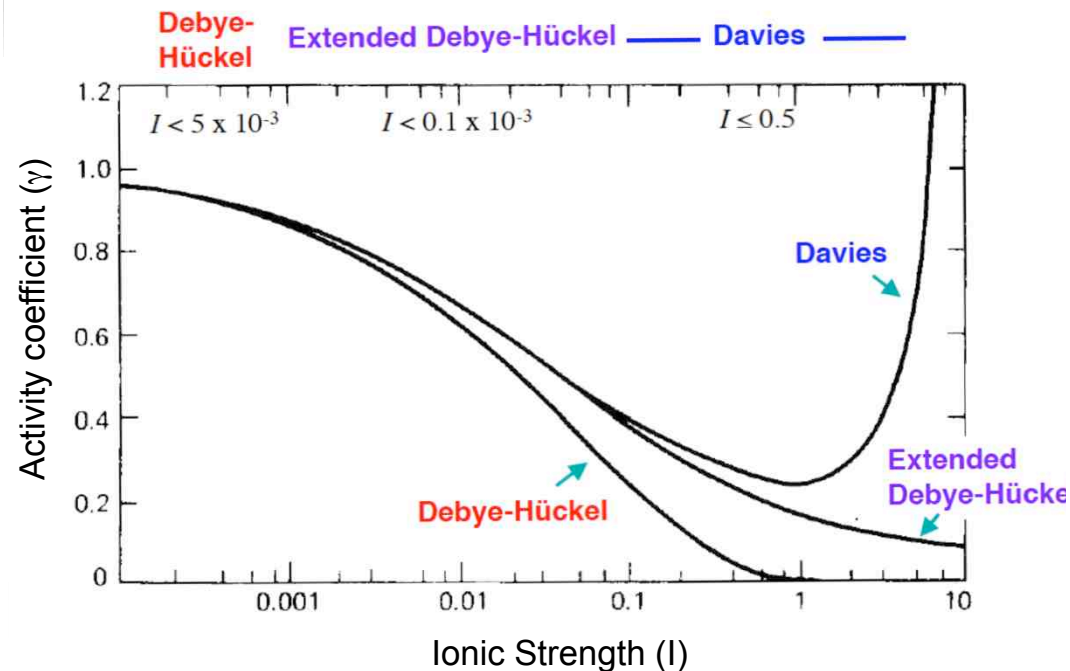
Increase of activity coefficients in highly saline solution (I > 1) can be attributed to "crowding" of ions, which counteracts the interferences

Debye-Hückel   Extended Debye-Hückel ——— Davies ———

$I < 5 \times 10^{-3}$ $I < 0.1 \times 10^{-3}$ $I \leq 0.5$

Activity coefficient (γ)

Davies

Debye-Hückel

Extended Debye-Hückel

Ionic Strength (I)

Solubility of Minerals in Aqueous Solutions
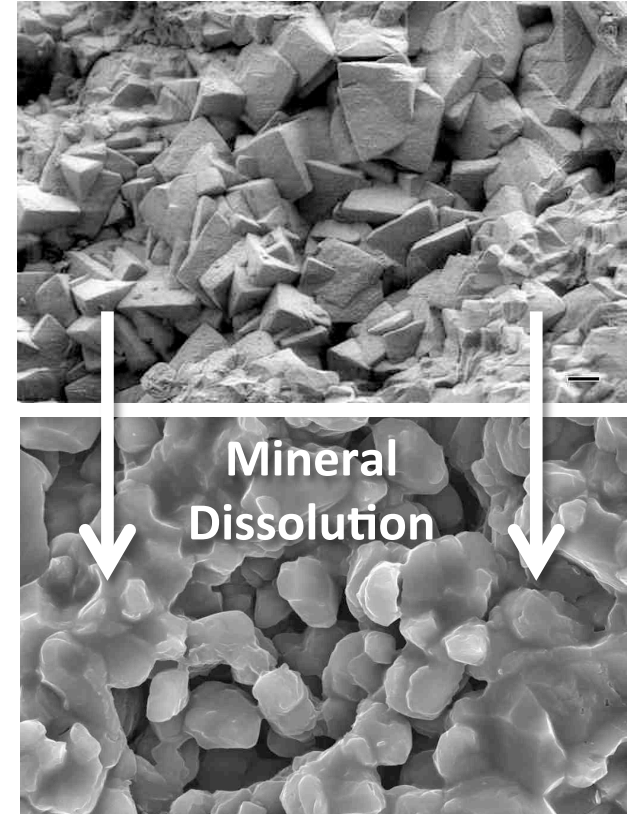
Photo: M. Brook

Dissolution of gypsum in pure water can be represented by the reaction:

$$CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2+} + H_2O$$

Solubility of Gypsum in Pure water

Reactants   **Products**

$$CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2+} + H_2O$$

Solubility = the ability of a substance or mineral to dissolve

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

$$K_{eq} = \frac{a_{Ca2+} * a_{SO42-} * a^2_{H2O}}{a_{CaSO4*2H2O}}$$

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

$$K_{eq} = \frac{a_{Ca2+} * a_{SO42-} * \boxed{a^2_{H2O}}}{\boxed{a_{CaSO4*2H2O}}}$$

Since, H_2O and $CaSO_4 2H_2O$ are neutral species (their **a = 1**), so we can write:

$$K_{eq\,(gypsum)} = a_{Ca2+} * a_{SO42-} = (\gamma *C)_{Ca} * (\gamma *C)_{SO4} = 10^{-4.59}$$

This value represents the **Solubilit 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		
NAME	FORMULA	K_{sp}
Barium carbonate	$BaSO_4$	5.0×10^{-9}
Barium chromate	$BaCrO_4$	2.1×10^{-10}
Barium fluoride	BaF_2	1.7×10^{-6}
Barium oxalate	BaC_2O_4	1.6×10^{-6}
Barium sulfate	$BaSO_4$	1.1×10^{-10}
Cadmium carbonate	$CdCO_3$	1.8×10^{-14}
Cadmium hydroxide	$Cd(OH)_2$	2.5×10^{-14}
Cadmium sulfide*	CdS	8.0×10^{-28}
Calcium carbonate (calcite)	$CaCO_3$	4.5×10^{-9}
Calcium chromate	$CaCrO_4$	7.1×10^{-4}
Calcium fluoride	CaF_2	3.9×10^{-11}
Calcium hydroxide	$Ca(OH)_2$	6.5×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2$	2.0×10^{-29}
Calcium sulfate	$CaSO_4$	2.4×10^{-5}

Less Soluble — $CaCO_3$ (4.5×10^{-9})

Least Soluble — CaF_2 (3.9×10^{-11})

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**

$$IAP_{(gypsum)} = (a_{Ca2+})_{actual} * (a_{SO42-})_{actual}$$

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

$$SI_{(gypsum)} = log \frac{IAP_{actual}}{K_{sp}}$$

SI = 0, the solution is **just saturated** (IAP=Ksp), neither dissolve nor precipitate

SI > 0, the solution is **supersaturated** (IAP > Ksp), mineral will precipitate

SI < 0, the solution is **undersaturated** (IAP < Ksp), mineral will dissolve

Practical Calculation of Mineral Saturation in Waters

Suppose, the concentrations of Ca^{2+} and SO_4^{2-} in a s[...] water are 5×10^{-2} m and 7×10^{-3} m, respectively. Le[...] find out the saturation state of the solution with re[...] gypsum. For simplicity, we will assume that $a_{Ca^{2+}} = m$[...] $a_{SO_4^{2-}} = m_{SO_4^{2-}}$

Real-life applications ...

$$IAP \text{ (solution)} = a_{Ca^{2+}} \, a_{SO_4^{2-}} = (5 \times 10^{-2}) \, (7 \times 10^{-3})$$

$$= 35 \times 10^{-5} = 10^{-3.5}$$ **Ion Activity Product (IAP)**

$$K_{sp \, (CaSO_4)} = 10^{-4.59}$$ **Solubility Product Constant (Ksp)**

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