

مرکز تحقیقات آبهای زیرزمینی (متآب)
Groundwater Research Center (GRC)

هیدروژئوشیمی و کیفیت منابع آب
Groundwater Geochemistry

فصل دوم

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Aqueous Geochemistry

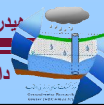
Why *geo*chemistry?

In natural waters, it is the interaction of the hydrosphere with the geosphere that controls the major ion chemistry of surface and groundwaters. Biological processes play a key role too, and so the *bio* prefix is often added.

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Geochemical Reactions

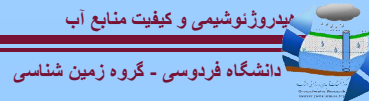
• **Acid-base reactions** involve the dissolution of minerals, hydrolysis, formation of complex ions, and sorption reactions, which are largely controlled by pH.

• **Redox reactions** involve the exchange of electrons between reactants, and have an effect on the solubility of many metals and compounds. The large changes in free energy can be used by different bacteria, which serve to catalyze redox reactions.

• **Physical reactions** involve a change of physical rather than chemical state, such as the evaporation or freezing of water, and solubility of many gases. All reactions, whether chemical or physical, involve the building and breaking of bonds.

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The Law of Mass Action

Geochemical reactions are written in terms of concentrations of reactants that are transformed into various products.

reactants → **products**

non-equilibrium – net mass transfer from reactants to products

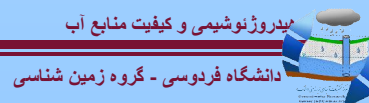
reactants ⇌ **products**

equilibrium – no net transfer of mass

The law of mass action holds that geochemical reactions will proceed to towards a state of equilibrium between reactants and products that is defined by a thermodynamic constant that is unique to that given reaction:

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The Law of Mass Action



Where the lower case refers to the number of moles of upper case constituents.

Equilibrium reaction constant K


$$K = \frac{\text{activity of products}}{\text{activity of reactants}} = \frac{[D]^d [E]^e}{[B]^b [C]^c}$$

Where K is the thermodynamic equilibrium constant or stability constant or equilibrium constant (not to be confused with the hydraulic conductivity); and the square brackets refer to **Activities** NOT concentrations.

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The Law of Mass Action



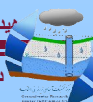
$$K = \frac{a_{Na^+} \cdot a_{Cl^-}}{a_{NaCl}} = 10^{1.58}$$

$$K = \frac{a_{Ca^{2+}} \cdot a_{F^-}^2}{a_{CaF_2}} = 10^{-10.96}$$

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Activity

Activity is essentially the “thermodynamically active concentration”, given by:

$$a_i = \gamma_i m_i$$

$$[D] = a_D = \gamma_D m_D$$

Where $[D]$ and a_D refer to the activity of constituent D , m_D is the molality and γ_D is the activity coefficient. The activity coefficient depends on the species being considered and on the ionic strength of the solution.

Ionic strength (I)

$$I = 1/2 \sum m_i z_i^2$$

Where:

- z_i is the valence (charge) of the i^{th} ionic species
- m_i is the molality of the i^{th} ion
- The summation takes place over all ionic species present in solution.

What is the ionic strength of a 1m solution of (a) NaCl (b) Na₂SO₄:

$$\begin{aligned} \text{NaCl} \quad I &= \frac{1}{2} (m_{\text{Na}^+} z_{\text{Na}^+}^2 + m_{\text{Cl}^-} z_{\text{Cl}^-}^2) \\ &= \frac{1}{2} (1 \times 1^2 + 1 \times 1^2) \\ &= 1 \end{aligned}$$

$$\begin{aligned} \text{Na}_2\text{SO}_4 \quad I &= \frac{1}{2} (m_{\text{Na}^+} z_{\text{Na}^+}^2 + m_{\text{SO}_4^{2-}} z_{\text{SO}_4^{2-}}^2) \\ &= \frac{1}{2} (2 \times 1^2 + 1 \times 2^2) \\ &= 3 \end{aligned}$$

What is the ionic strength of the following groundwater:

Ca²⁺ — 86 ppm

HCO₃⁻ — 280 ppm

Mg²⁺ — 33

SO₄²⁻ — 120

Na⁺ — 24

Cl⁻ — 37

K⁺ — 3.2

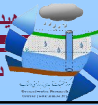
$$\begin{aligned} I &= \frac{1}{2} (4m_{\text{Ca}^{2+}} + 4m_{\text{Mg}^{2+}} + m_{\text{Na}^+} + m_{\text{K}^+} + m_{\text{HCO}_3^-} + 4m_{\text{SO}_4^{2-}} + m_{\text{Cl}^-}) \\ &= \frac{1}{2} (4[86/40.1/1000] + 4[33/24.3/1000] + \dots) \\ &= 0.013 \end{aligned}$$

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Debye-Hückel equation

The activity coefficient γ is calculated with the Debye-Hückel equation, which relates to γ , z and I .

The form of the Debye-Hückel equation depends on the salinity of the water. For fresh waters ($I < 0.01$) at temperatures up to about 50°C, the simplified form is fine:

$$\log \gamma_i = -0.5 z_i^2 \sqrt{I}$$

simplified Debye-Hückel equation

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Debye-Hückel equation

The Debye-Hückel model of an infinitely small charge interacting in solution breaks down in higher salinity waters, ($I > 0.01$ or $> \sim 1000$ mg/L TDS), and the hydrated radius of the ion, \hat{a} (in angstrom units, 10^{-8} cm) must be taken into account. This effect is taken into account by the extended Debye-Hückel equation including the Davies (1962) constant ($0.3I$), which is valid for solutions up to ionic strength of about 1 (i.e. greater than seawater, $I = 0.5$):

$$\log \gamma_i = \frac{-0.5 z_i^2 \sqrt{I}}{1 + 0.33 \hat{a}_i \sqrt{I}} + 0.3I$$

Values for the hydrated diameter of the ion of the common ions are:

- $\hat{a} = 2.5$ — NH_4^+
- 3.5 — K^+, Cl^-
- 4.0 — Na^+
- 5.0 — $\text{Ca}^{2+}, \text{SO}_4^{2-}, \text{Sr}^{2+}, \text{Ba}^{2+}$
- 5.5 — $\text{Mg}^{2+}, \text{HCO}_3^-, \text{CO}_3^{2-}$

Activity coefficients (γ)

Here is a plot for common ionic species in water.

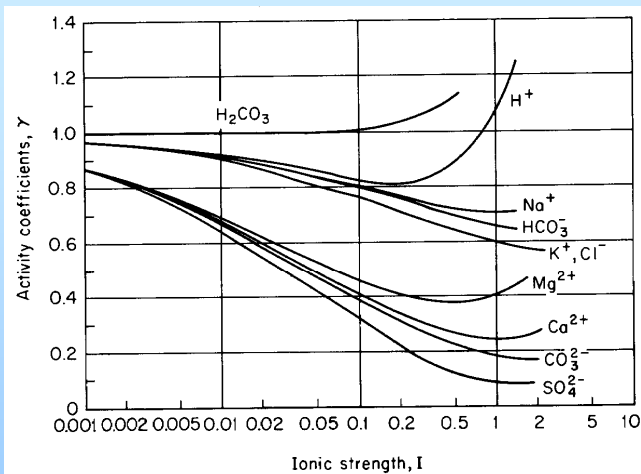


Figure 3.3 Activity coefficient versus ionic strength relations for common ionic constituents in groundwater.

Source: Freeze and Cherry, 1979. Groundwater

Dissociation and activity of water

$$K_w = \frac{[H^+][OH^-]}{[H_2O]} = [H^+][OH^-]$$

The second equation comes from the fact that the activity of pure water is 1.0.

To respect electroneutrality, we must have $[H^+] = [OH^-]$ in pure water, and therefore, $K_w = [H^+]^2$.

Recall that $\text{pH} = -\log [H^+]$, so:

$$\text{pH} = -1/2 \log K_w$$

So, from the table to the right,
 the **pH** of pure water at 25° is 7.00
 the **pH** of pure water at 5° is 7.367
 the **pH** of pure water at 55° is 6.568

Table 3.4 Equilibrium Constants for Dissociation of Water, 0–60°C

t (°C)	$K_w \times 10^{-14}$
0	0.1139
5	0.1846
10	0.2920
15	0.4505
20	0.6809
25	1.008
30	1.469
35	2.089
40	2.919
45	4.018
50	5.474
55	7.297
60	9.614

SOURCE: Garrels and Christ, 1965.

Source: Freeze and Cherry, 1979. Groundwater

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Mineral Dissolution and Solubility

Solubility: The mass of mineral that can be dissolved in a unit volume of water under specified conditions. Solubilities of different minerals in identical conditions vary over many orders of magnitudes.

Effect of Ionic Strength: Generally, increased salinity (ionic strength) increases solubility (Ionic strength effect). e.g. gypsum:

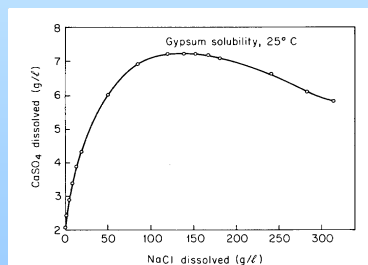


Figure 3.6 Solubility of gypsum in aqueous solutions of different NaCl concentrations, 25°C, and 1 bar (after Stermna, 1960).

Source: Freeze and Cherry, 1979. Groundwater

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Saturation Index

When a reaction is not at equilibrium we can calculate the Ion Activity Product (IAP) from the activities measured in the system:



Ion Activity Product

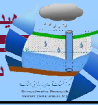
$$IAP = \frac{[D]^d [E]^e}{[B]^b [C]^c} \neq K$$

where the quantities in *IAP* are measured activities and *K* is the equilibrium constant (available from tables).

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Saturation Index

$$SI = \frac{IAP}{K_{sp}}$$

SI > 1 or log SI > 0

mineral is supersaturated and can precipitate

SI = 1 or log SI = 0

mineral is in equilibrium with the solution

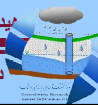
SI < 1 or log SI < 0

mineral is undersaturated, and will dissolve if present

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Gibb's free energy and determination of K

$$\Delta G_r^\circ = \sum \Delta G_{\text{products}}^\circ - \sum \Delta G_{\text{reactants}}^\circ$$

$$\Delta G_r^\circ = -RT \ln K$$

$$\log K = -\frac{\Delta G_r^\circ}{5.708} \quad (\Delta G \text{ in kJ/mol})$$

$$\log K = -\frac{\Delta G_r^\circ}{1.364} \quad (\Delta G \text{ in kcal/mol})$$

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What is the solubility product K_{sp} for gypsum?



$$\begin{aligned} \Delta G_r^\circ &= \Delta G_{\text{Ca}^{2+}}^\circ + \Delta G_{\text{SO}_4^{2-}}^\circ + 2 \Delta G_{\text{H}_2\text{O}}^\circ - \Delta G_{\text{gypsum}}^\circ \\ &= (-552.8) + (-744.0) + 2(-237.14) - (-1797.36) \\ &= 26.28 \text{ kJ/mol} \end{aligned}$$

$$\log K_{\text{gypsum}} = -\frac{\Delta G_r^\circ}{5.708}$$

$$\log K_{\text{gypsum}} = -\frac{26.28}{5.708} = -4.60$$

$$\text{Thus, } K_{\text{gypsum}} = 10^{-4.60}$$

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What is the dissociation constant of water?



$$\Delta G^\circ = 0 + (-157.2) - (-237.14) = 79.94 \text{ kJ/mol}$$

$$\begin{aligned} \log K_{\text{H}_2\text{O}} &= -\frac{\Delta G^\circ_r}{5.708} \\ &= \frac{-79.89}{5.708} = -14.00 \end{aligned}$$

$$K_{\text{H}_2\text{O}} = 10^{-14.00}$$

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Example: *Determining the state of saturation of low temperature minerals. For a groundwater with the following geochemical analysis, determine the saturation indices for calcite and gypsum.*

T = 25°C	Na ⁺ = 180 ppm	HCO ₃ ⁻ = 250 ppm
pH = 7.65	K ⁺ = 18 ppm	CO ₃ ²⁻ = 0.8 ppm
	Ca ²⁺ = 60 ppm	SO ₄ ²⁻ = 85 ppm
	Mg ²⁺ = 22 ppm	Cl ⁻ = 280 ppm

Step 1 Determine K_{calcite} and K_{gypsum} ($\text{DG}^\circ_{\text{r calcite}} = 48.37 \text{ kJ/mol}$ and $\text{DG}^\circ_{\text{r gypsum}} = 26.28 \text{ kJ/mol}$)

Step 2 Calculate m , for input species and then calculate I

Step 3 Using I , calculate γ for all ions using the simplified Debye Hückel equation, and a for each

Step 4 Determine $\log \text{SI}_{\text{calcite}}$ and $\log \text{SI}_{\text{gypsum}}$

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