Hydrogeochemistry

3. Processes in natural water
Spring 2022

ACID-BASE REACTIONS

Brønsted's definition of acids and bases

Acid

- A substance capable of transferring a proton to another substance.
- Proton donor.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Base

- A substance capable of accepting a proton from another substance.
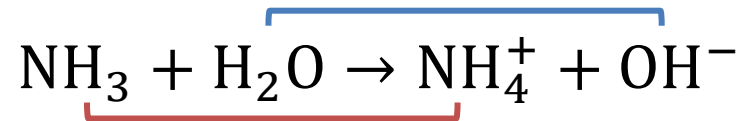- Proton acceptor.

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

- Arrhenius acids and bases are also acids and bases according to Brønsted's definition, but this is not the case retrospectively.

Conjugated pairs

- Acid - H^+ → base

- Base + H^+ → acid
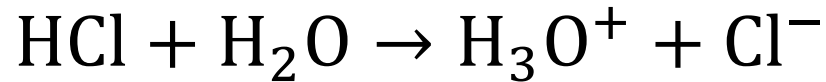
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$
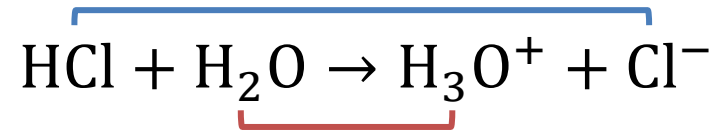
- The same substance can be an acid in one reaction and a base in another.

- The designation acid/base is relative and indicates the ability to bind/release a proton.

Dissociation of acids

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

- It does not run up to 100% and runs simultaneously forward and backwards (like all reactions).

- Dissociation leads to the establishment of protolytic equilibrium.

- Characterized by an equilibrium constant.

$$K_{eq} = \frac{[H_3O^+][Cl^-]}{[HCl][H_2O]}$$

Dissociation constant

- In an aqueous environment, we take water as a constant and include it directly in the constant, and then we talk about the *dissociation constant of* acid

$$K_A = \frac{[H_3O^+][Cl^-]}{[HCl]}$$

Dissociation of bases

- Quite analogous to acid dissociation, it is characterized by the equilibrium constant K_{eq} or the dissociation constant of base K

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

$$K_{eq} = \frac{[NH_4^+][OH^-]}{[NH_3][H_2O]} \qquad K_B = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Strength of acids and bases

- Dissociation constants determine the strength of acids and bases – the intensity of proton release/capture.

- For a strong acid, most molecules dissociate.

Strong $\quad$ K $_{A/B} > 10^{-2}$
Medium $\quad$ K $_{A/B} = 10^{-2} - 10^{-4}$
Weak $\quad$ K $_{A/B} < 10^{-4}$

The strength of acids

- The degree of dissociation depends on the structure of the acid molecules.
- Polybasic acids have multiple dissociation constants.
- The polarity of the molecule and its bonds determines the strength.
- Few acids dissociate completely and are very strong
  - HNO_3, H_2SO_4, $HClO_4$, HCl, HBr, HI
- Weak acids dissociate to smaller extent
  - H_2CO_3, organic acids

Water dissociation

- Water can behave as both acid and base.

$$H_2O + H_2O \rightarrow H_3O^+ + OH^-$$
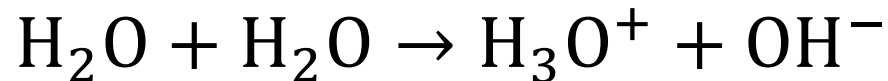
$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$
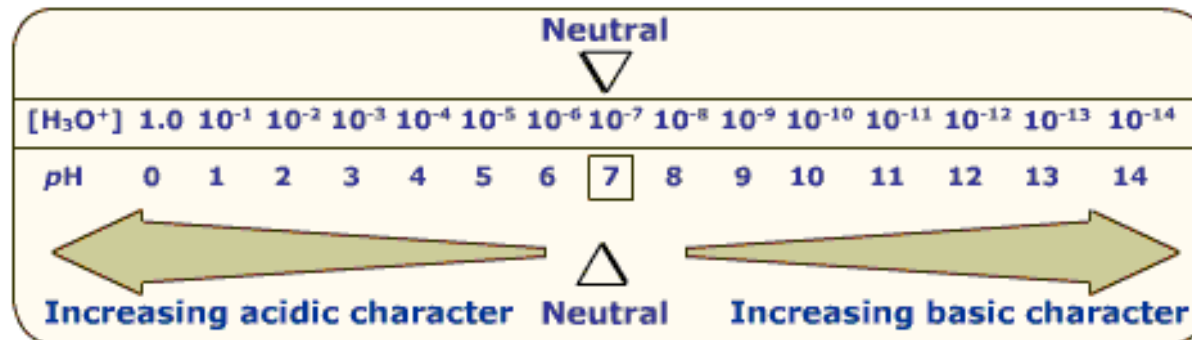
- The water concentration is considered to be constant and we derive the *ionic product of water* K_w

$$K_w = [H_3O^+][OH^-]$$

pH

- For clean water:
  - At 25 °C K_w = 10 $^{-14}$ pH is 7 (ie 100 ppb H$^+$)
  - At 0 °C K_W = 10 $^{-14.9}$ pH = 7.45
  - At 100 °C K_W = 10 $^{-13}$ pH = 6.50
- The concentration of H$_3$O$^+$ and OH$^-$ ranges from 10 to 10^{-15} mol L^{-1}
- For practical reasons, a logarithmic *pH scale has been introduced*
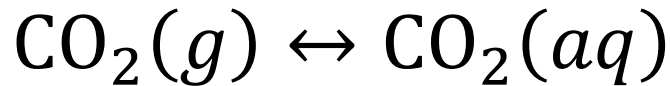
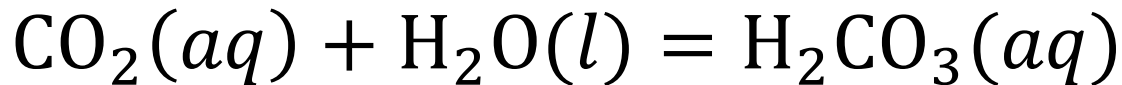$$\text{pH} = -log[\text{H}_3\text{O}^+]$$

CARBONATE SYSTEM

Carbonates

- The pH of most natural waters is controlled by reactions with carbonates
- $CO_2(g)$ dissolves in water to equilibrium in proportion to the partial pressure in air (P_{CO2})

$$CO_2(g) \leftrightarrow CO_2(aq)$$

- CO_2 reacts with water to form an acid

$$CO_2(aq) + H_2O(l) = H_2CO_3(aq)$$

- $CO_2(aq)$ is about 600 times more abundant, yet for simplicity we express all CO_2 as H_2CO_3*

$$H_2CO_3^*(aq) = CO_2(aq) + H_2CO_3(aq)$$
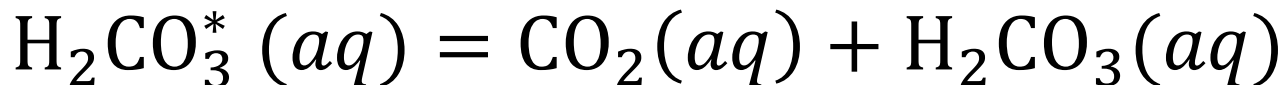
Carbonic acid

- We can therefore simplify the dissolution to:
$$CO_2(g) + H_2O(l) = H_2CO_3^*(aq)$$
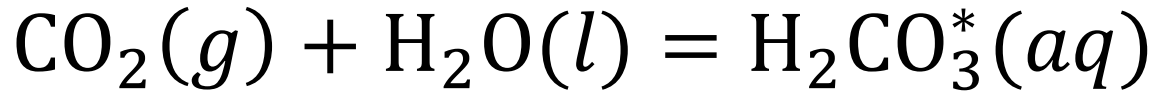
- With equilibrium constant
$$K_{CO_2} = \frac{a_{H2CO3(aq)}}{P_{CO2}}$$

- Each P_{CO2} thus corresponds to a specific a_{H2CO3*}

- The CO_2 content of water is therefore often expressed as P_{CO2} even if no gas phase is present

Dissociation

- Carbonic acid dissociates to the 1st degree:

$$H_2CO_3^* = HCO_3^- + H^+$$

$$K_1 = \frac{a_{HCO_3^-}\, a_{H^+}}{a_{H_2CO_3^*}} = 10^{-6.35}$$

- And to the 2nd degree:

$$HCO_3^- = CO_3^{2-} + H^+$$

$$K_2 = \frac{a_{CO_3^{2-}}\, a_{H^+}}{a_{HCO_3^-}} = 10^{-10.33}$$

Speciation

- The ratios a_{H2CO3*}/a_{HCO3-} and a_{HCO3-}/a_{CO32-} are pH dependent and can be simplified

$$\frac{a_{H_2CO_3^*}}{a_{HCO_3^-}} = \frac{a_{H^+}}{K_1} = 10^{+6,35}\, a_{H^+} \text{ at } 25\,°\,C$$

- Neglecting CO_3^{2-}, H_2CO_3* a HCO_3^- are in equilibrium at pH = 6.35

- **Ex .:** The total content of carbonates is 10^{-2} M, what is the distribution of H_2CO_3* a HCO_3^- going to be at **(a)** pH = 6.35 and **(b)** pH = 5.35

Speciation

- Analogously for a_{HCO3-} / a_{CO32-}

$$\frac{a_{\mathrm{HCO_3^-}}}{a_{\mathrm{CO_3^{2-}}}} = \frac{a_{\mathrm{H^+}}}{\mathrm{K_2}} = 10^{+10.33}\, a_{\mathrm{H^+}} \qquad \text{at 25 ° C}$$

- If H_2CO_3* is neglected, CO_3^{2-} and HCO_3^- are in equilibrium at pH = 10.33

Example

- What will be the pH of the water in equilibrium with atmospheric CO_2 at 25 °C, assuming ideal behavior and no other solutes?

- The CO_2 partial pressure is 4×10^{-4}

- $pK_{CO2} = 1.47$

- $pK_1 = 6.35$

- Charge balance equation

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

Distribution coefficients

$\alpha_0 = [H_2CO_3*] / c_T$ $\alpha_1 = [HCO_3^-] / c_T$ $\alpha_2 = [CO_3^{2-}] / c_T$

$c_T = [H_2CO_3*] + [HCO_3^-] + [CO_3^{2-}]$

$\alpha_0 + \alpha_1 + \alpha_2 = 1$

Combinations of expressions for equilibrium constants:

$$\frac{K_1}{[H^+]} = \frac{[HCO_3^-]}{[H_2CO_3*]} \qquad \frac{K_2}{[H^+]} = \frac{[CO_3^{2-}]}{[HCO_3^-]} \qquad \frac{K_1K_2}{[H^+]^2} = \frac{[CO_3^{2-}]}{[H_2CO_3*]}$$

Distribution coefficient α_0

$$\frac{1}{\alpha_0} = \frac{[H_2CO_3*]+[HCO_3^-]+[CO_3^{2-}]}{[H_2CO_3*]} \Rightarrow 1 + \frac{[HCO_3^-]}{[H_2CO_3*]} + \frac{[CO_3^{2-}]}{[H_2CO_3*]} \qquad \frac{1}{\alpha_0} = 1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}$$

$$\alpha_0 = \frac{1}{1 + \dfrac{K_1}{[H^+]} + \dfrac{K_1K_2}{[H^+]^2}} = \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2}$$

$$\frac{K_1}{[H^+]} = \frac{[HCO_3^-]}{[H_2CO_3*]}$$

$$\frac{K_2}{[H^+]} = \frac{[CO_3^{2-}]}{[HCO_3^-]}$$

$$\frac{K_1 K_2}{[H^+]^2} = \frac{[CO_3^{2-}]}{[H_2CO_3*]}$$

Distribution coefficient α_1

$$\frac{1}{\alpha_1} = \frac{[H_2CO_3*]+[HCO_3^-]+[CO_3^{2-}]}{[HCO_3^-]} \Rightarrow \frac{[H_2CO_3*]}{[HCO_3^-]} + 1 + \frac{[CO_3^{2-}]}{[HCO_3^-]}$$

$$\frac{1}{\alpha_1} = 1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}$$

$$\alpha_1 = \frac{1}{1 + \dfrac{[H^+]}{K_1} + \dfrac{K_2}{[H^+]}} = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1 K_2}$$

Distribution coefficient α_2

$$\frac{1}{\alpha_2} = \frac{[H_2CO_3*]+[HCO_3^-]+[CO_3^{2-}]}{[CO_3^{2-}]} \Rightarrow \frac{[H_2CO_3*]}{[CO_3^{2-}]} + \frac{[HCO_3^-]}{[CO_3^{2-}]} + 1$$

$$\frac{1}{\alpha_2} = 1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2}$$

$$\alpha_2 = \frac{1}{1 + \dfrac{[H^+]}{K_2} + \dfrac{[H^+]^2}{K_1 K_2}} = \frac{K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1 K_2}$$

Distribution coefficients

$$c_T = [H_2CO_3*] + [HCO_3^-] + [CO_3^{2-}]$$

$$\alpha\nu\delta_o = [H_2CO_3*] / c_T \qquad \alpha_o = 1 / (1 + K_1 / [H^+] + K_1 * K_2 / [H^+]\wedge 2)$$

$$\alpha\nu\delta_1 = [HCO_3^-] / c_T \qquad \alpha_1 = 1 / (1 + [H^+] / K_1 + K_2 / [H^+])$$

$$\alpha_2 = [CO_3^{2-}] / c_T \qquad \alpha_2 = 1 / (1 + [H^+] / K_2 + [H^+]\wedge 2 / K_1 * K_2)$$

$K_1 =$	4.45E − 07
$K_2 =$	4.69E − 11
$C_{T(1)} =$	1.00E − 03
$C_{T(2)} =$	1.00E − 04

pH	$[H^+]$	α_o	α_1	α_2	$[H_2CO_3*]$	$[HCO_3^-]$	$[CO_3^{2-}]$	$[H_2CO_3*]$	$[HCO_3^-]$	$[CO_3^{2-}]$
4	1.00E-04	9.96E–01	4.43E–03	2.08E–09	9.96E-04	4.43E-06	2.08E-12	9.96E-05	4.43E-07	2.08E-13
4.2	6.31E-05	9.93E–01	7.00E–03	5.20E–09	9.93E-04	7.00E-06	5.20E-12	9.93E-05	7.00E-07	5.20E-13
4.4	3.98E-05	9.89E–01	1.10E–02	1.30E–08	9.89E-04	1.10E-05	1.30E-11	9.89E-05	1.10E-06	1.30E-12
11	1.00E-11	3.95E–06	1.76E–01	8.24E–01	3.95E-09	1.76E-04	8.24E-04	3.95E-10	1.76E-05	8.24E-05
11.2	6.31E-12	1.68E–06	1.19E–01	8.81E–01	1.68E-09	1.19E-04	8.81E-04	1.68E-10	1.19E-05	8.81E-05
11.4	3.98E-12	7.01E–07	7.83E–02	9.22E–01	7.01E-10	7.83E-05	9.22E-04	7.01E-11	7.83E-06	9.22E-05
11.6	2.51E-12	2.87E–07	5.09E–02	9.49E–01	2.87E-10	5.09E-05	9.49E-04	2.87E-11	5.09E-06	9.49E-05
11.8	1.58E-12	1.17E–07	3.27E–02	9.67E–01	1.17E-10	3.27E-05	9.67E-04	1.17E-11	3.27E-06	9.67E-05
12	1.00E-12	4.70E–08	2.09E–02	9.79E–01	4.70E-11	2.09E-05	9.79E-04	4.70E-12	2.09E-06	9.79E-05

Carbonate speciation

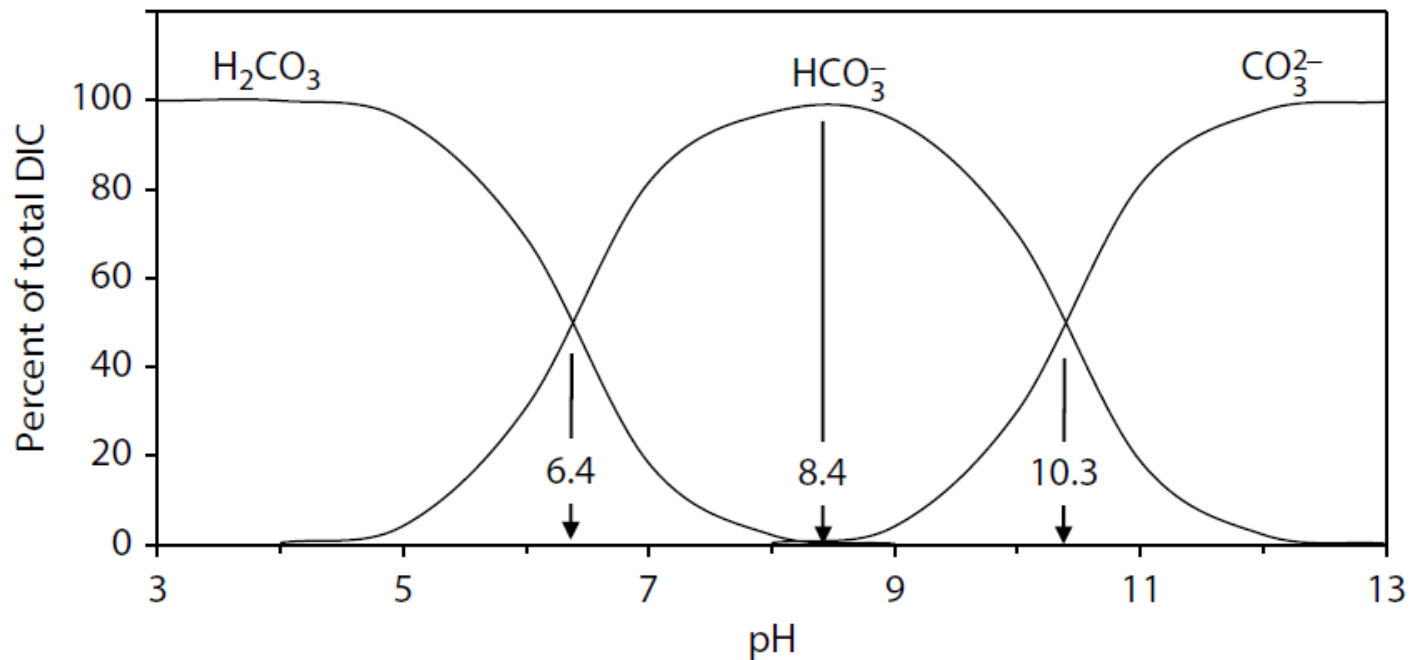- Natural waters contain mainly HCO_3^-

FIGURE 3.15 Relative distribution of dissolved inorganic carbon species in pure water as a function of pH, at 25°C.

Electroneutrality

- Acid-base processes associated with ions
- The total charge of the solution is always zero (positive and negative are equalized)

$$\sum m_i z_i = 0$$

- At pH other than neutral, additional ions must be present
- For carbonate system:

$$[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$
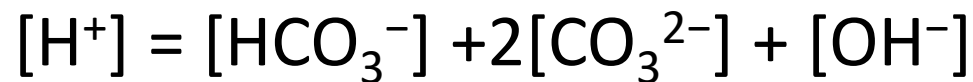
Electroneutrality

- In natural waters, concentrations of anions other than carbonates are often negligible
  - The concentration of cations corresponds to bicarbonates

- Not all species under normal conditions dependent on pH – conservative ions (Na^+, Ca^{2+}, Cl^-, SO_4^{2-} ...), the balance then:

$$\sum cons.\ cations - \sum cons.\ anions = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [H_3(SiO)_4^-] + [HS^-] + [organic\ anions] + [OH^-] - [H^+]$$

Alkalinity

- Ions involved in **total alkalinity**:
  - $[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [H_3(SiO)_4^-] + [HS^-] +$ [organic anions] $+ [OH^-] - [H^+]$
  - Anions that are consumed during titration with a strong acid – can easily turn into uncharged particles and balance the charge of the solution
- In natural waters, concentrations of anions other than carbonates are often negligible

    Carbonate alkalinity = $[HCO_3^-] + 2[CO_3^{2-}]$

- we assume

    Carbonate alkalinity ≈ total alkalinity

Alkalinity
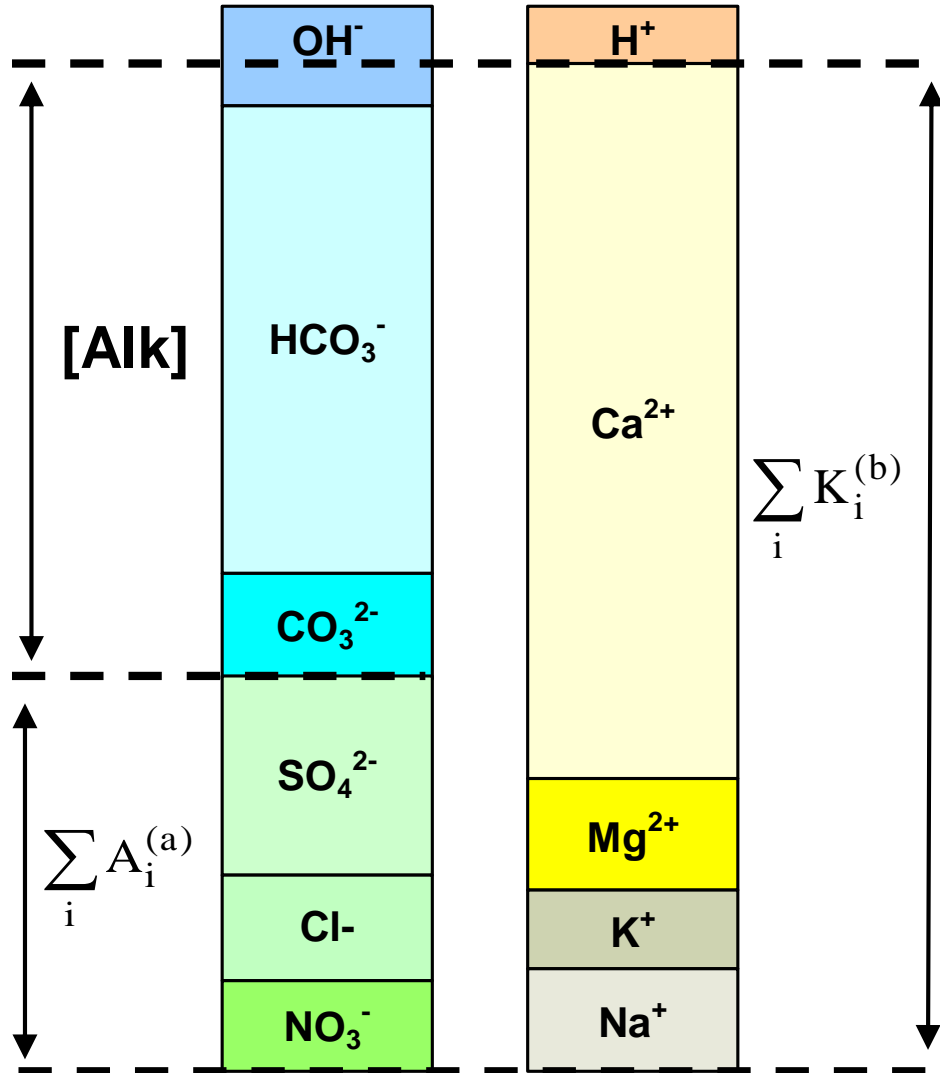
Alkalinity [Alk]: *sum*

Acidity: the sum of *free acid*

[Alk] = − [Acy]

[Acy] = BNC (basic neutralizing capacity)

[Alk] = ANC (acid neutralizing capacity)

BNC – capacity of the solution to accomodate equivalent of a strong acid to reaching neutrality (pH = 4.5)

ANC – capacity of the solution to accomodate equivalent of a strong base to reaching neutrality (pH = 4.5)

Alkalinity
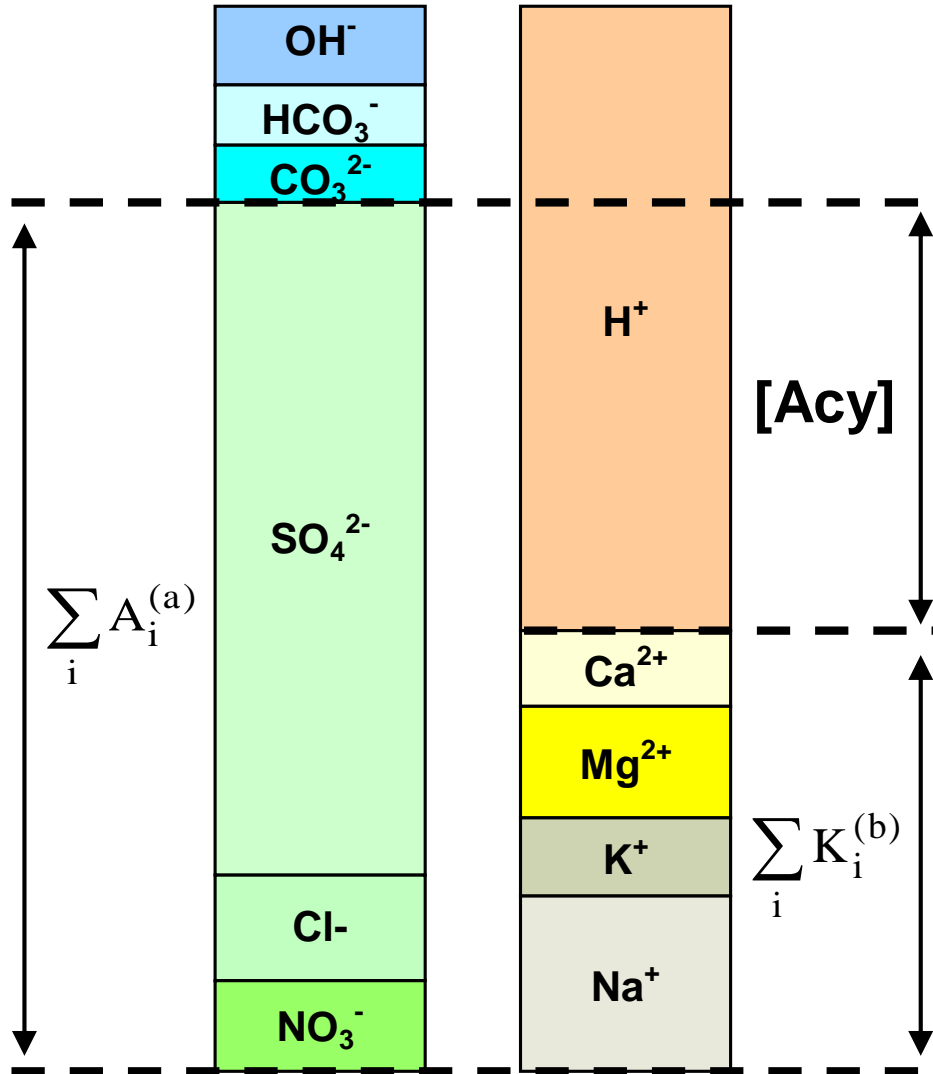

$$[Alk] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+]$$

$$[Alk] = \sum_i K_i^{(b)} - \sum_i A_i^{(a)}$$

$\sum_i K_i^{(b)}$ cations of strong bases

$\sum_i A_i^{(a)}$ strong acid ions

Conservative ions - complete dissociation, pH-independent concentration

Acidity

$$[\text{Acy}] = [\text{H}^+] - [\text{OH}^-] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}]$$

$$[\text{Acy}] = \sum_i A_i^{(a)} - \sum_i K_i^{(b)}$$

$$\Delta \sum_i K_i^{(b)} - \Delta \sum_i A_i^{(a)} = \Delta[\text{Alk}] = -\Delta[\text{Acy}]$$
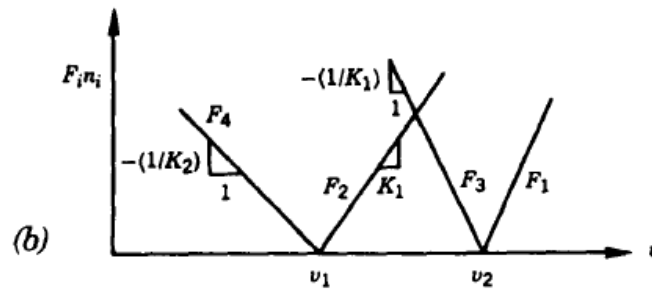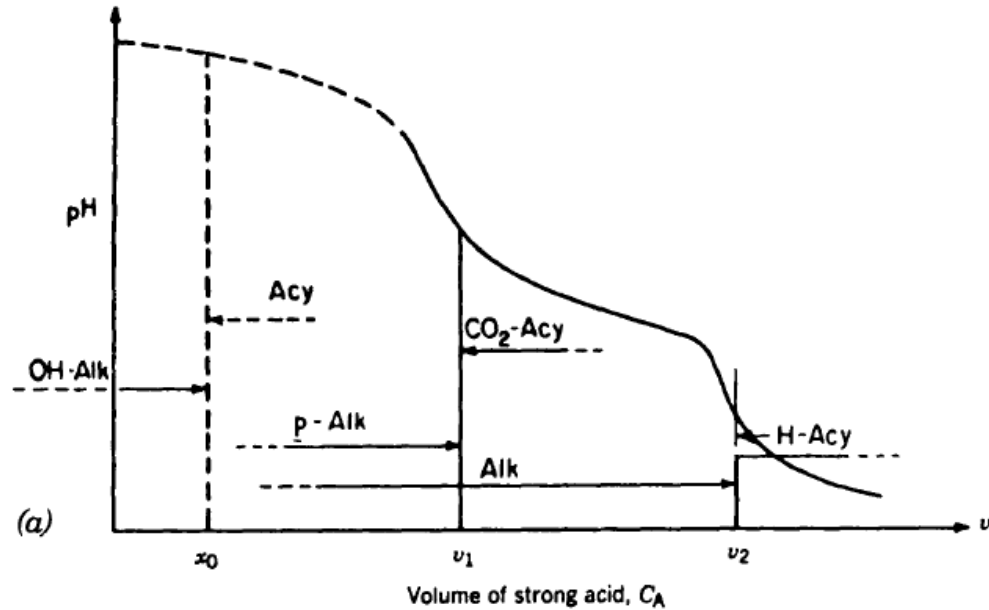
Titration curves

**Figure 4.12.** Sketch of an acidimetric titration curve (a). In (b) the results of (a) are plotted in terms of Gran functions: F_i is multiplied by scale factors n_i. The F_i values are defined by Equations 48 and 51–54. x_0, v_1, and v_2 are the volumes of strong acid corresponding to the equivalence points $f = 2$, $f = 1$, and $f = 0$, respectively.

INTERACTION WITH CARBONATE MINERALS

Calcium carbonates

$$CaCO_3(s) = CO_3^{2-} + Ca^{2+}$$
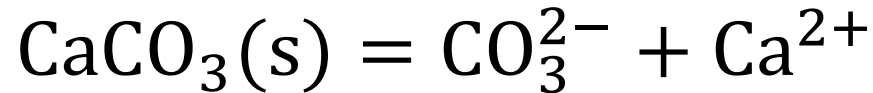
- The product of solubility is

$$K_c = a_{Ca^{2+}} \, a_{CO_3^{2-}} = 10^{-8,48} \text{ \textbf{calcite} } (25°C)$$

$$K_a = a_{Ca^{2+}} \, a_{CO_3^{2-}} = 10^{-8,34} \text{ \textbf{aragonite} } (25°C)$$

- We can solve the systems by adding the appropriate equations to the carbonate system
  - K_{CO2}, K_1, K_2, K_W, K_c, PEN and one other condition
    - Fixed P_{CO2} for open system or sum of carbonates for closed system

Example

- What will be the pH of the water in equilibrium with atmospheric CO_2 and calcite at 25°C, assuming ideal behavior and no other solutes?
  - 6 unknowns (P_{CO2}, $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[Ca^{2+}]$ and $[H^+]$)
  - 6 equations (P_{CO2}, K_{CO2}, K_1, K_2, K_C and PEN)

$$P_{CO2} = 10^{-3.4}$$

PEN: $[H^+] + 2[Ca^{2+}] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$

  - At neutral pH we simplify to

$$2\,[Ca^{2+}] = [HCO_3^-]$$

  - Substituting equations by expressing $[H^+]$

Example

- What will be the pH of the water in equilibrium with atmospheric CO_2 and calcite at 25°C, assuming ideal behavior and no other solutes?
    - 6 unknowns (P_{CO2}, $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[Ca^{2+}]$ and $[H^+]$)
    - 6 equations (P_{CO2}, K_{CO2}, K_1, K_2, K_C and PEN)

$$P_{CO2} = 10^{-3.4}$$

PEN: $[H^+] + 2[Ca^{2+}] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$

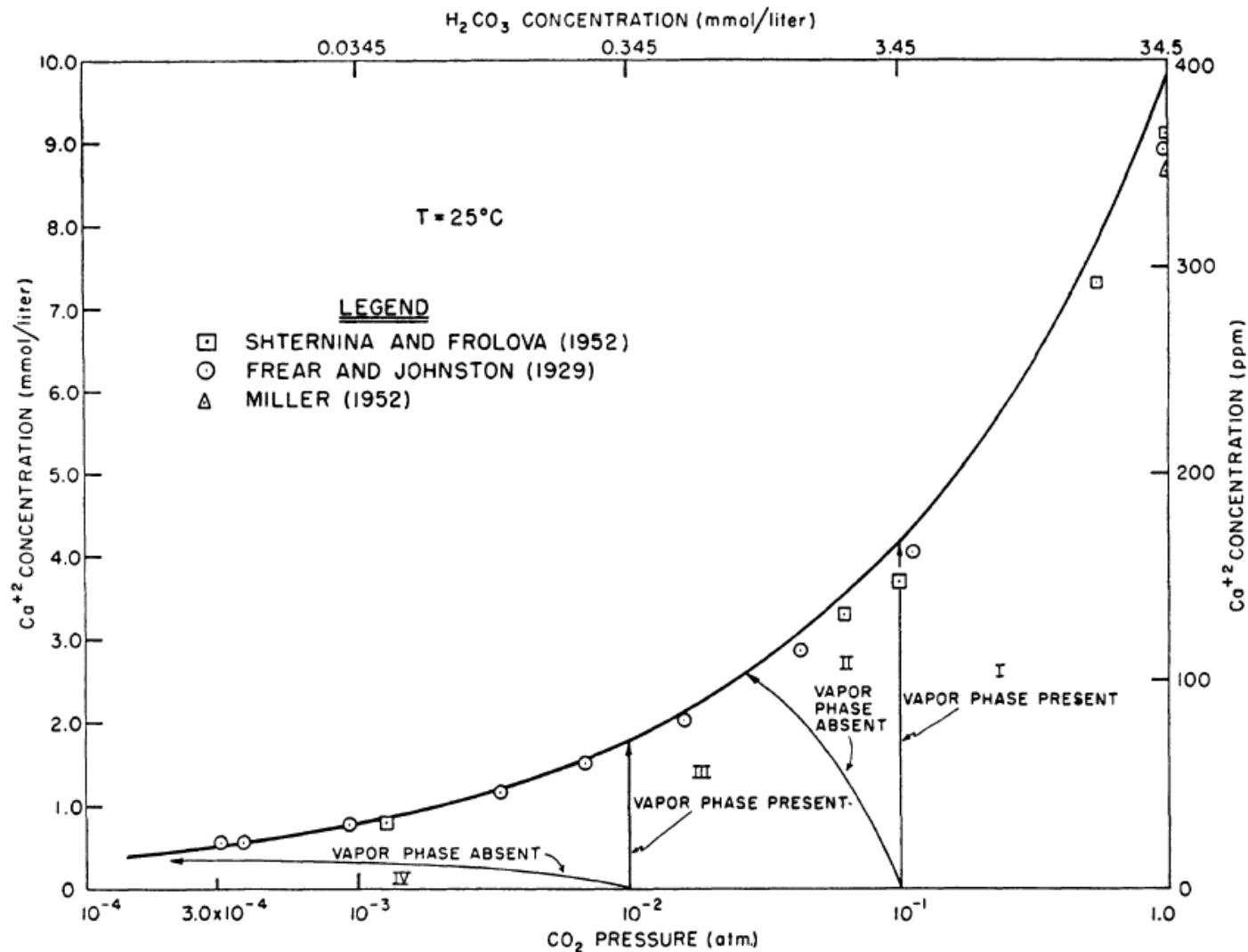 - At neutral pH we simplify to

$$2\,[Ca^{2+}] = [HCO_3^-]$$

  - Substituting equations by expressing $[H^+]$
  - $[H^+] = 10^{-8.5}$ ie pH = 8.5

Dependence of solubility on P_{CO2} and HCO_3^-

- $\dfrac{a_{\text{Ca}^{2+}}\, a^2_{\text{HCO}_3^-}}{a_{\text{H}_2\text{CO}_3^*}} = \dfrac{K_{cal}\, K_1}{K_2} = 10^{-4,30}$ for 25°C

- $\dfrac{a_{\text{Ca}^{2+}}\, a^2_{\text{HCO}_3^-}}{P_{\text{CO}_2}} = \dfrac{K_{cal}\, K_1\, K_{CO_2}}{K_2} = 10^{-5,97}$

- decrease in CO_2 leads to an increase in saturation and vice versa

- Respiration, decay, photosynthesis

- The dependence of $[Ca^{2+}]$ on P_{CO2} is nonlinear

FIG. 2.—Changes in composition of carbonated water during equilibration with calcite at 25° C. in the presence and in the absence of a vapor phase. Curves I and II describe the behavior of a solution which was originally in equilibrium with a vapor phase with a CO_2 pressure of 0.10 atm., curves III and IV describe the behavior of a solution that was originally in equilibrium with a vapor phase with a CO_2 pressure of 0.01 atm.

Holland et al. (1964)

Water mixing
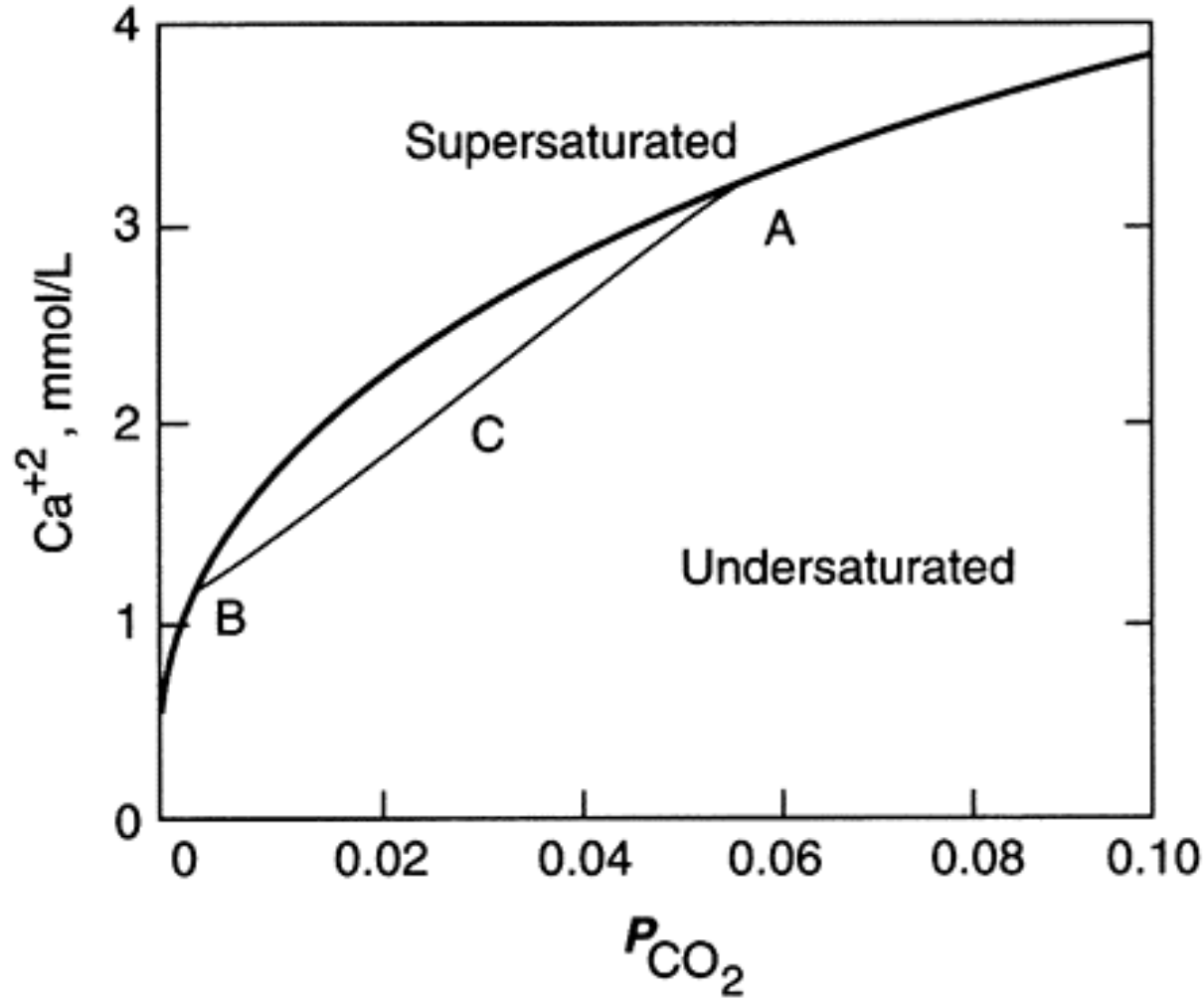
Drever (1997)

- Mixing usually produces unsaturated solutions

Dolomite

$$CaMg(CO_3)_2(s) = CO_3^{2-} + Ca^{2+} + Mg^{2+}$$
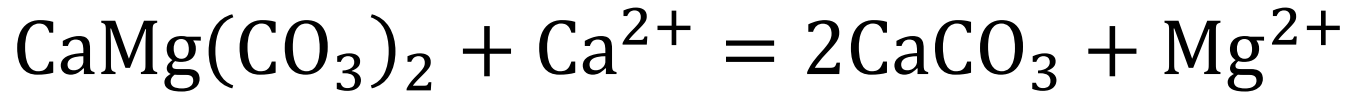
- The product of solubility is

$$K_D = a_{Ca^{2+}} a_{Mg^{2+}} a_{CO_3^{2-}} = 10^{-17,2}(25°C)$$

- The value of K_D is quite uncertain and can vary greatly for dolomites of various origins

- At normal temperatures it dissolves only slowly and hardly grows (very unsaturated/supersaturated solutions)

Formation of dolomite

- Dolomite is often formed by alteration of calcite

$$CaMg(CO_3)_2 + Ca^{2+} = 2CaCO_3 + Mg^{2+}$$

$$K_{CD} = \frac{a_{Mg^{2+}}}{a_{Ca^{2+}}}$$

- In solutions where the Mg/Ca ratio is greater than K_{CD}, dolomite is more stable than calcite and vice versa

- However, the process is kinetically very slow

- Calcite changes to dolomite only under conditions of a very large excess of magnesium

Dissolution of dolomite

- Analogous to calcite
- Significantly slower
- The need for extreme retention times to achieve "balance" (thousands of years)
  - equilibrium
- At low temperatures, it should dissolve uncongruently due to kinetics and thermodynamics

Magnesium calcite

$$\mathrm{Ca}_{(1-x)}\mathrm{Mg}_x\mathrm{CO}_3(s) = \mathrm{CO}_3^{2-} + (1-x)\mathrm{Ca}^{2+} + x\mathrm{Mg}^{2+}$$
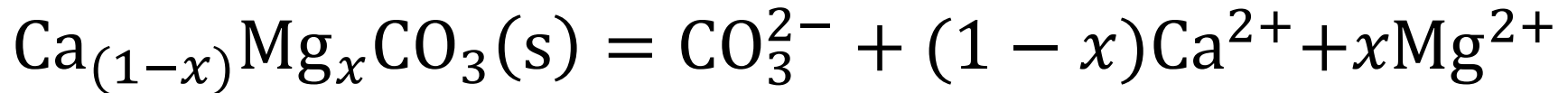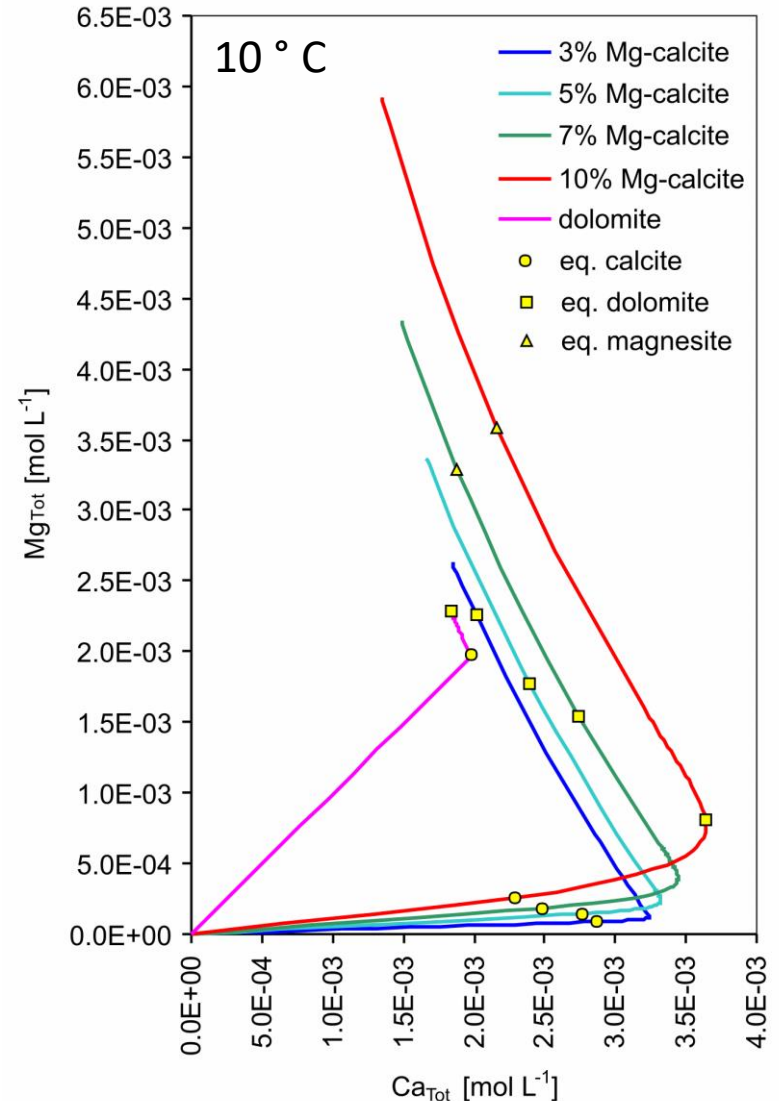
- Low magnesium Mg-calcite (<5%)
- High-magnesium Mg-calcite (> 10%) – recent deep-sea sediments
- All high-magnesium are unstable (conversion to dolomite and low-magnesium), but under surface conditions it inhibits the growth kinetics of dolomite
- Mg-calcite in seawater more stable than pure calcite
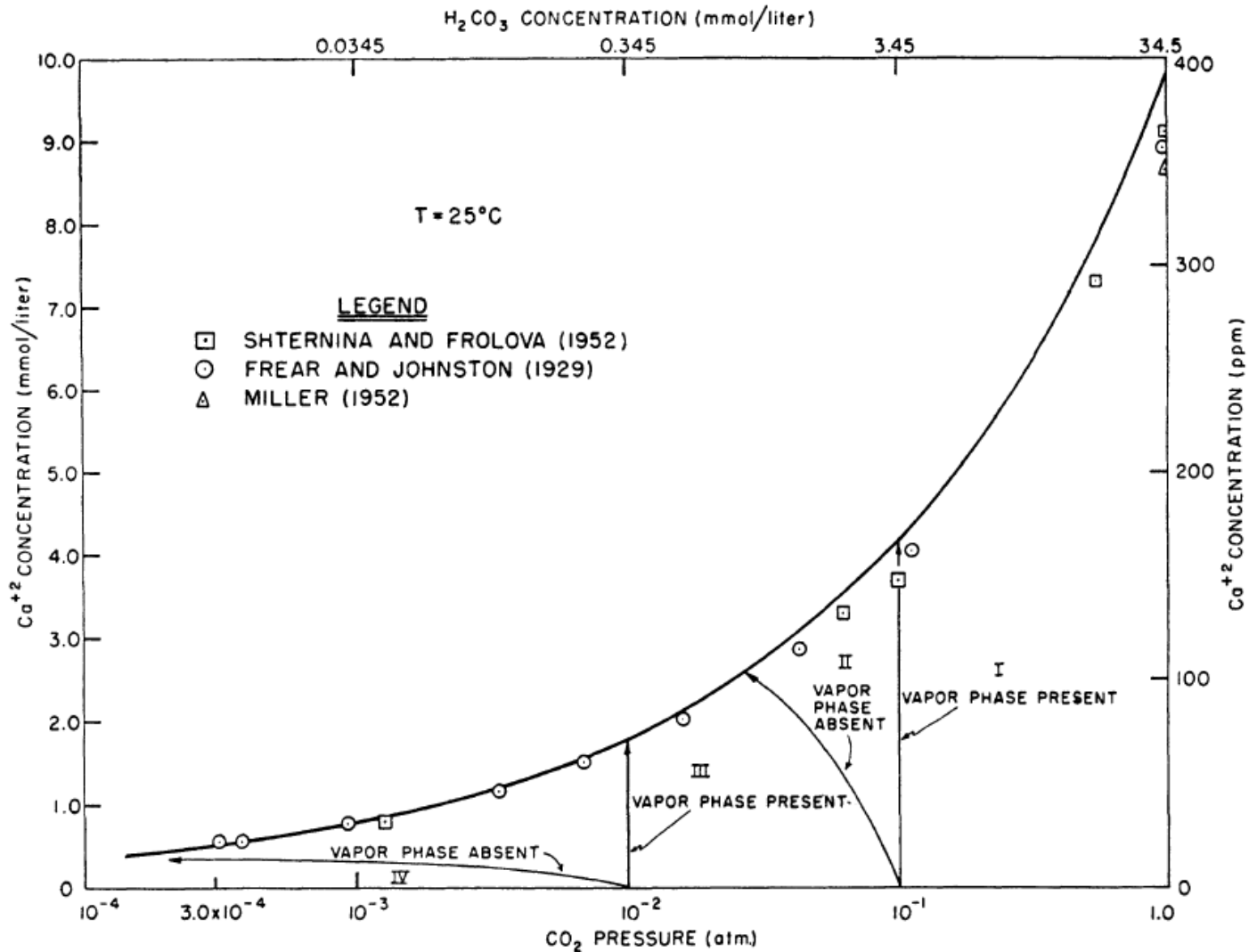
Dissolution of Mg-calcite

- Equilibrium with solution definable as cation exchange or dissolution
  - As a result, both processes must be in balance
- The correctness of the approaches is not clarified, the relationships are very complex
- The determination of K is complicated by a combination of congruent and non-congruent dissolution

10 °C

Legend:
- 3% Mg-calcite
- 5% Mg-calcite
- 7% Mg-calcite
- 10% Mg-calcite
- dolomite
- eq. calcite
- eq. dolomite
- eq. magnesite

Mg_{Tot} [mol L^{-1}]

Ca_{Tot} [mol L^{-1}]

Pracny et al. 2017

Properties of water in carbonate aquifers

- Major ions Ca^{2+} and HCO_3^-
- Close to balance with calcite
- The total mineralization depends mainly on the P_{CO2} in the system
  - More CO_2 in the soil than in the air
  - Decisive role of CO_2 replenishement in to the solution
  - With the exception of water of deeper circulation mixed with other sources of minerals

- The ammount of dissolved calcite is critically dependent on available CO_2 gas phase during dissolution

FIG. 2.—Changes in composition of carbonated water during equilibration with calcite at 25° C. in the presence and in the absence of a vapor phase. Curves I and II describe the behavior of a solution which was originally in equilibrium with a vapor phase with a CO_2 pressure of 0.10 atm., curves III and IV describe the behavior of a solution that was originally in equilibrium with a vapor phase with a CO_2 pressure of 0.01 atm.

Holland et al. (1964)

Example

- Pure water in equilibrium with $P_{CO_2} = 10^{-2}$
  a) How much calcite dissolves in a closed system?

     6 unknowns (P_{CO_2}, $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[Ca^{2+}]$ and $[H^+]$)

     6 equations (K_{CO_2}, K_1, K_2, K_C, PEN and ΣCO_2)

     $\Sigma CO_2 = \Sigma CO_2^o + \Sigma CO_{2diss}$

     $\Sigma CO_2 = [H_2CO_3^*]^o + [Ca^{2+}]$

     We assume negligible $[CO_3^{2-}]$ in ΣCO_2 and obtain

     $[H_2CO_3^*]^o = [HCO_3^-] + [H_2CO_3^*] - [Ca^{2+}]$

Example

- Pure water in equilibrium with $P_{CO2} = 10^{-2}$
    a) How much calcite dissolves in a closed system?

    6 unknowns (P_{CO2}, $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[Ca^{2+}]$ and $[H^+]$)

    6 equations (K_{CO2}, K_1, K_2, K_C, PEN and ΣCO_2)

    $\Sigma CO_2 = \Sigma CO_2^o + \Sigma CO_{2diss}$

    $\Sigma CO_2 = [H_2CO_3^*]^o + [Ca^{2+}]$

    We assume negligible $[CO_3^{2-}]$ in ΣCO_2 and obtain

    $[H_2CO_3^*]^o = [HCO_3^-] + [H_2CO_3^*] - [Ca^{2+}]$

    Substituting the rest of the equations we get

    $$[Ca^{2+}] = 3.34 \times 10^{-4} \ mol/L$$

    Dissolve approximately 33.4 mg of calcite per liter of water

Example

- Pure water in equilibrium with $P_{CO2} = 10^{-2}$

  b) How much does it dissolve in an open system?

  – The system we have already solved

  6 unknowns (P_{CO2}, $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[Ca^{2+}]$ and $[H^+]$)

  6 equations (P_{CO2}, K_{CO2}, K_1, K_2, K_C and PEN)

  $$P_{CO2} = 10^{-2}$$

Example

- Pure water in equilibrium with $P_{CO_2} = 10^{-2}$

    b) How much does it dissolve in an open system?

    – The system we have already solved

    6 unknowns (P_{CO_2}, $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[Ca^{2+}]$ and $[H^+]$)

    6 equations (P_{CO_2}, K_{CO_2}, K_1, K_2, K_C and PEN)

    $$P_{CO_2} = 10^{-2}$$

    From the equations we express $[Ca^{2+}]$ and substitute the parameters

    $$[Ca^{2+}] = 1.39 \times 10^{-3} \text{ mol/L}$$

    Dissolve approximately 139 mg of calcite per liter of water

		Punkva Cave					Býčí skála		
		TC1	TC2	CP 1	RD1	Angel	BS1	BS2	ZD1
conductivity	mS/m (25 °C)	28.1	54.8	62.5	56.1	61.1	25.7	33.3	49.3
ZNK 8.3	mmol/l	<0.2	<0.2	<0.2	<0.2	<0.2	-	-	-
KNK 4.5	mmol/l	1.91	5.14	6.21	5.78	6.27	2.45	2.6	3.72
total hardness	mmol/l	1.43	2.99	3.48	3.15	3.38	1.35	1.7	2.65
Na	mg/l	2.1	2.1	1.9	2.3	3	3.8	3.5	-
K	mg/l	0.86	0.57	0.77	0.71	<0.5	0.5	1.2	-
Ca	mg/l	54.7	117.5	137.2	124.1	133.5	47.5	61.9	-
Ca from the cave	mg/l	52.8	124	144	-	137.6	52.8	65.6	-
Mg	mg/l	1.6	1.4	1.4	1.3	1.2	4	3.8	-
SO4	mg/l	40.1	38.6	45.6	30.6	30.2	13.9	43	-
Cl	mg/l	9	7	4	5	3	7	4	-
NO3	mg/l	6.5	3.7	<3	<3	<3	-	6.5	-
Sum of cations		2.97	6.08	7.06	6.42	6.89	2.88	3.59	-
Sum of anions		3.1	6.2	7.27	6.56	6.98	2.94	3.71	-
HCO3-	mg/l	117	314	379	353	382	149	159	-
alkalinity from the cave	meq/l	1.83	5.28	6.25	-	6.153561	2.585	3.446667	-
HCO3-	mg/l	111.8	322.1	381.6	-	375.5	157.7	210.3	-
Al	µg/l	<20	<20	<20	<20	<20	-	155	-
Mn	mg/l	<0.05	<0.05	<0.05	<0.05	<0.05	-	-	-
Fe	mg/l	<0.1	<0.1	<0.1	<0.1	<0.1	-	0.17	-
Sr	µg/l	77.6	77.9	86	75.9	87.2	77.9	80.8	-
Si	µg/l	2055	1805	2225	1782	1847	4038	3787	-
Li	mg/l	<0.1	<0.1	<0.1	<0.1	<0.1	-	-	-
pH		7.7	7.92	7.78	7.89	7.61	8.34	8.5	8.33
discharge	drops/ min	51	39	117	167	Surface flow	Surface flow	Surface flow	8
PCO2	ppm	640	640	630	820	720	730	710	-

Reconstruction of P $_{CO2}$

Pracny et al. 2016

$$SI_{calcite} = -log(P_{CO_2}) + 3log(Ca^{2+}) + log\,C$$
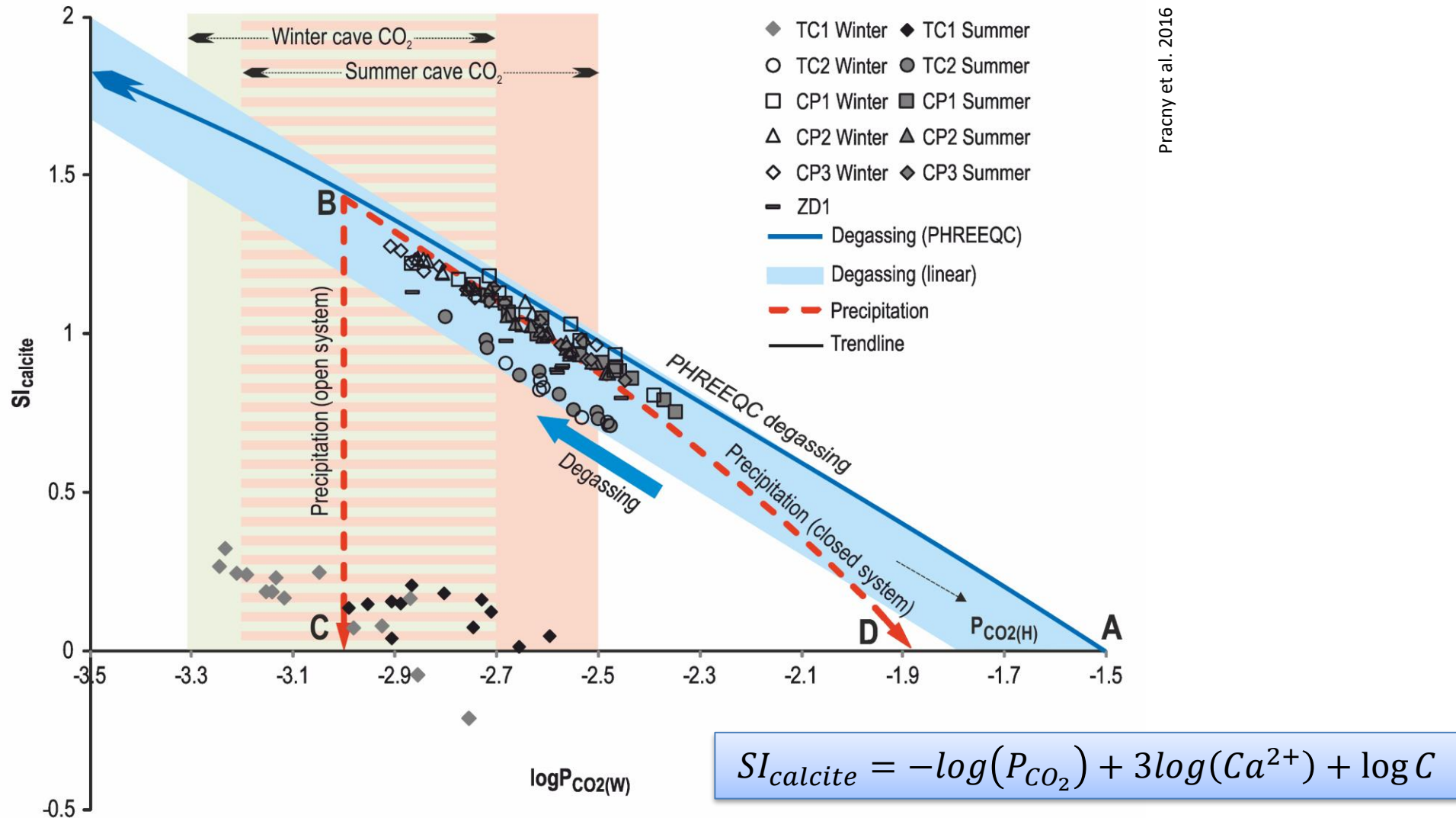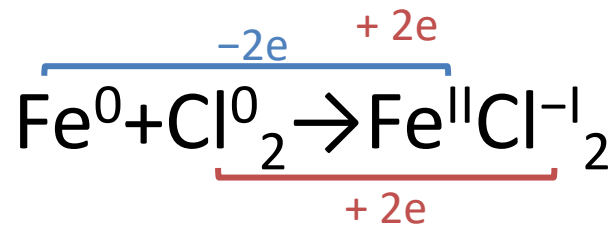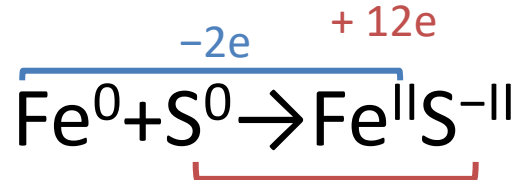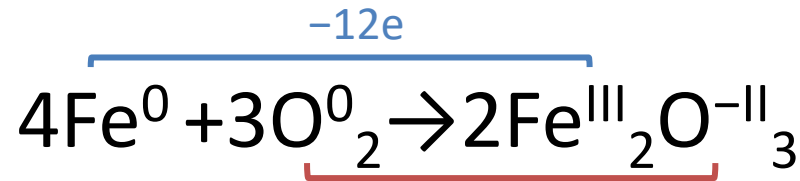
REDOX

Themes

- Redox processes
- Standard hydrogen electrode
- Electron activity
- Redox potential
- Thermodynamic derivation Eh
- **pe-pH diagrams**
- **Redox conditions in natural waters**
- **Buffering redox conditions in nature**

Oxidation and reduction

- Historically, oxidation is the reaction of a substance with oxygen.
- Today, a broader definition of oxidation:

  "The process by which a substance loses electrons in a chemical reaction."

- The opposite process is the reduction:

  "The process by which a substance gains electrons in a chemical reaction."

- The processes of oxidation and reduction always take place simultaneously, and therefore are combined into one process.

Oxidation-reduction reactions

- Any reaction in which electron transfers occur between reactants.

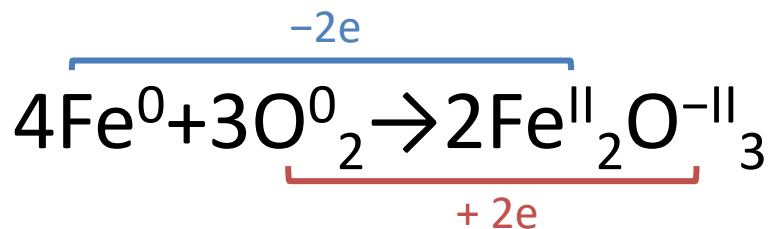- Redox reactions are reactions in which electrons are transferred.

$$4Fe^0 + 3O^0_2 \rightarrow 2Fe^{III}_2O^{-II}_3$$

−12e

+ 12e

$$Fe^0 + S^0 \rightarrow Fe^{II}S^{-II}$$

−2e

+ 2e

$$Fe^0 + Cl^0_2 \rightarrow Fe^{II}Cl^{-I}_2$$

−2e

+ 2e

Redox reagents

Oxidizing agent

- It causes oxidation by accepting electrons from the second reactant.
- It **reduces itself**.

Reducing agent

- It causes reduction by donating electrons to the second reactant.
- It **oxidizes itself**.

$$4Fe^0 + 3O^0_2 \rightarrow 2Fe^{II}_2O^{-II}_3$$

$-2e$

$+ 2e$

- The same substance may be an oxidizing agent in one reaction and a reducing agent in another reaction.
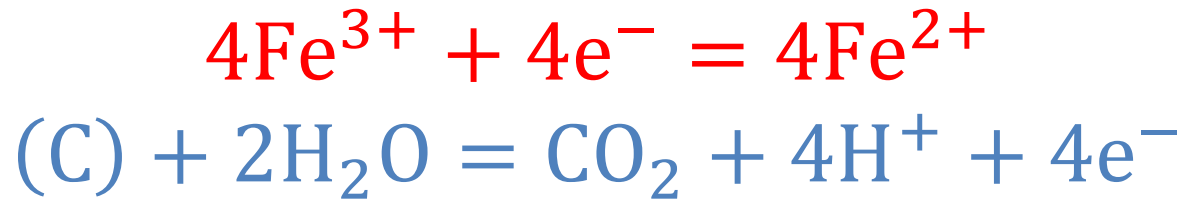
REDOX BALANCE

Redox reactions

$$Fe^{3+} + e^- = Fe^{2+}$$
$$3Fe_2O_3 + 2H^+ + 2e^- = 2Fe_3O_4 + H_2O$$
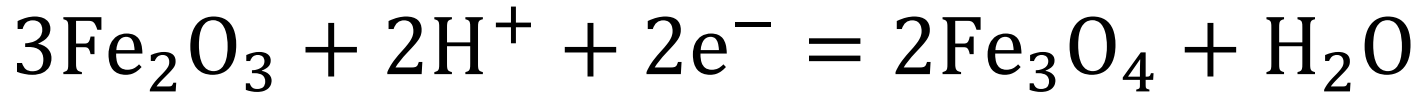
- Equations are not complete reactions

- There are **no free electrons** in the solution

- A complementary reaction is always needed
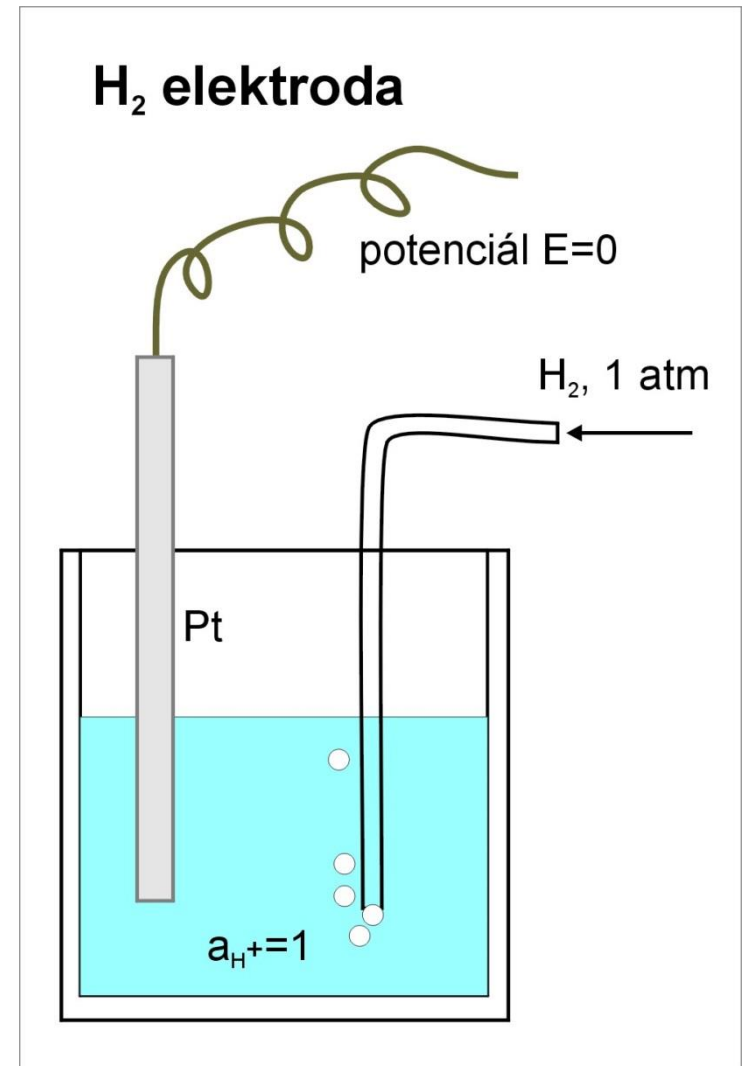
Redox reactions

- Reduction of iron by organic matter (C)

$$4Fe^{3+} + (C) + 2H_2O = 4Fe^{2+} + CO_2 + 4H^+$$

- Could be rewritten as:

$$\color{red}{4Fe^{3+} + 4e^- = 4Fe^{2+}}$$
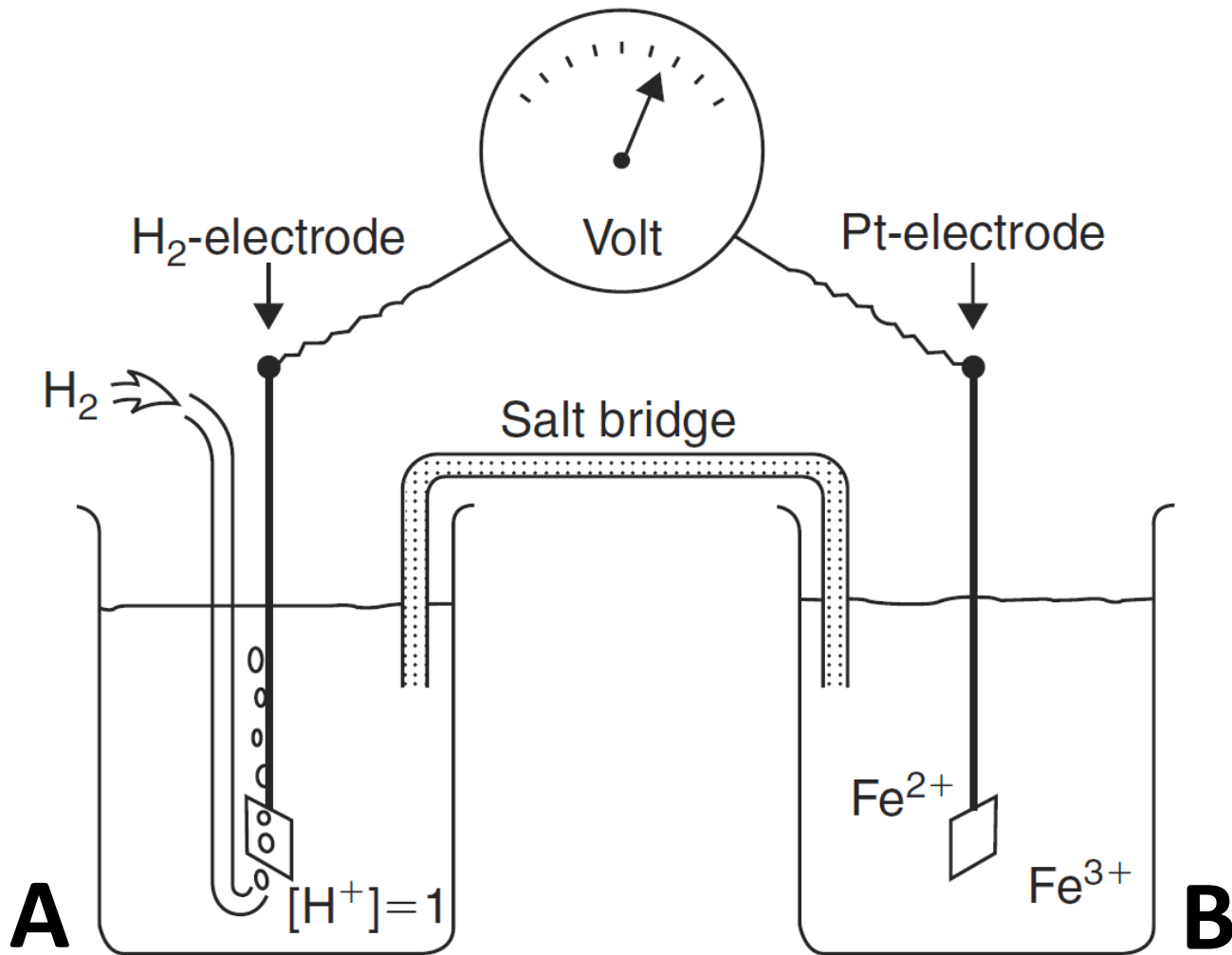
$$\color{blue}{(C) + 2H_2O = CO_2 + 4H^+ + 4e^-}$$

- *The standard hydrogen electrode* allows individual assessment of each half of the reaction

Standard hydrogen electrode

- Pt wire in contact with a solution with electron activity $a_{e^-} = 1$ and fugacity $H_2(g) = 1$ (at 25°C)
- **The following conventions apply**:
1. The electric potential difference between the metal electrode and the solution is 0
2. The Gibbs function of formation of H^+ is zero
3. The Gibbs function of formation of e^- is zero
- We introduce a scale that can be utilized to determine G_f^o of other species in solution

H_2 elektroda

potenciál E=0

H_2, 1 atm

Pt

$a_{H^+}=1$

Redox balance

Half-cell B

$$Fe^{3+} + e^- \Rightarrow Fe^{2+}$$
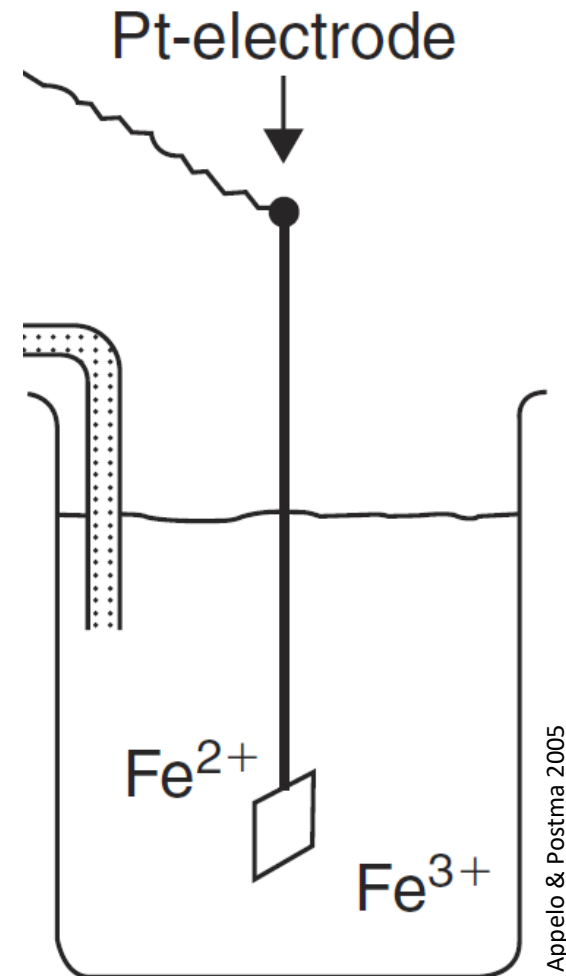
We need to source e^-

$$Fe^{2+} \Rightarrow Fe^{3+} + e^-$$

We need to sink e^-

- Without a source or a sink of e^- the overall reaction does not take place
- A potential forms on the electrode – the tendency to leave the solution

Pt-electrode
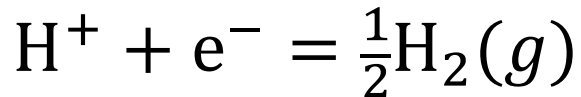
Fe^{2+}

Fe^{3+}

Half-cell B

$$\mathrm{Fe}^{3+} + \mathrm{e}^- = \mathrm{Fe}^{2+}$$

- A potential is established on the Pt electrode reflecting the tendency of e^- to leave the solution

$$K_{eq} = \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}\ a_{e^-}}$$

$$a_{e^-} = \frac{1}{K_{eq}} \times \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

- e^- activity is a proportional ratio of reduced to oxidized species
- This is not a conventional concentration/activity – a useful form for expressing redox reactions
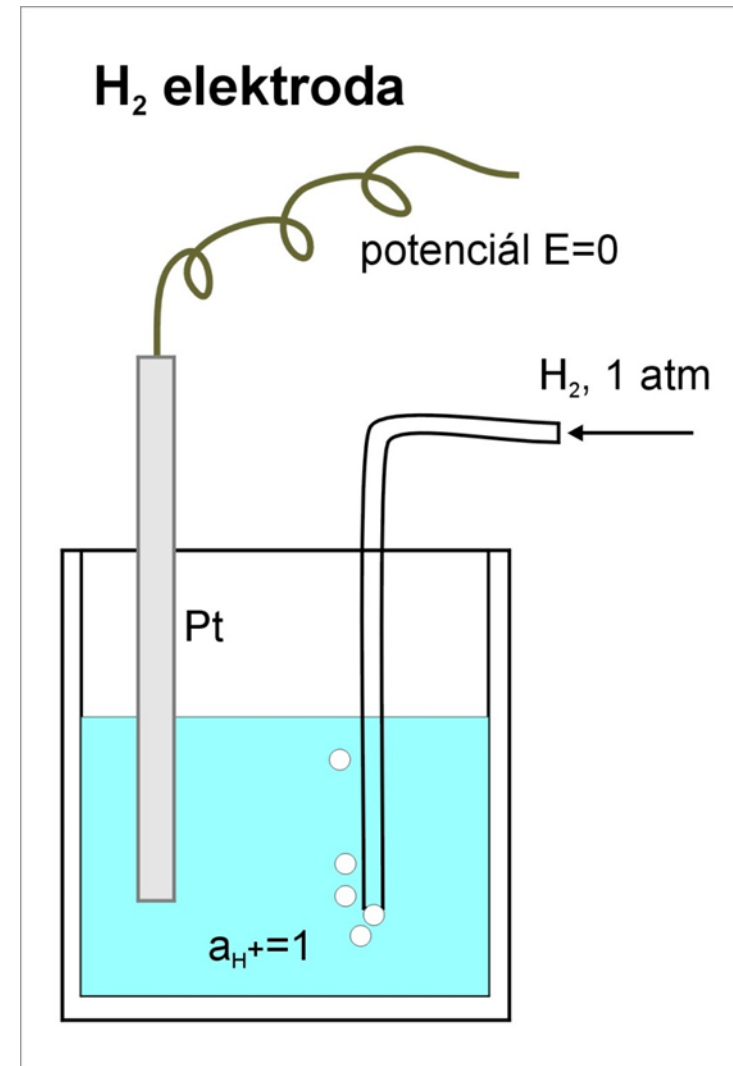
Half-cell A

$$H^+ + e^- = \frac{1}{2}H_2(g)$$

- Standard hydrogen electrode
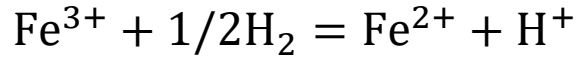- A potential is established on the Pt electrode reflecting the tendency of e^- to leave the solution

$$K_{eq} = \frac{P_{H_2^{0.5}}}{a_{H^+}\, a_{e^-}}$$

- e^- activity on the hydrogen electrode is conventionally set to 1

H₂ elektroda

potenciál E=0

H₂, 1 atm

Pt

$a_{H^+}=1$

Redox potential

Total equation at circuit closure:
$$Fe^{3+} + 1/2H_2 = Fe^{2+} + H^+$$

Electrons flow from a half-cell with higher activity to the lower. The hydrogen electrode has a standard potential = 0 and the voltmeter therefore shows the potential E corresponding to the potential on the half-cell B

H_2-electrode   Volt   Pt-electrode

H_2

Salt bridge

AND $[H^+]=1$

Fe^{2+}

Fe^{3+} B
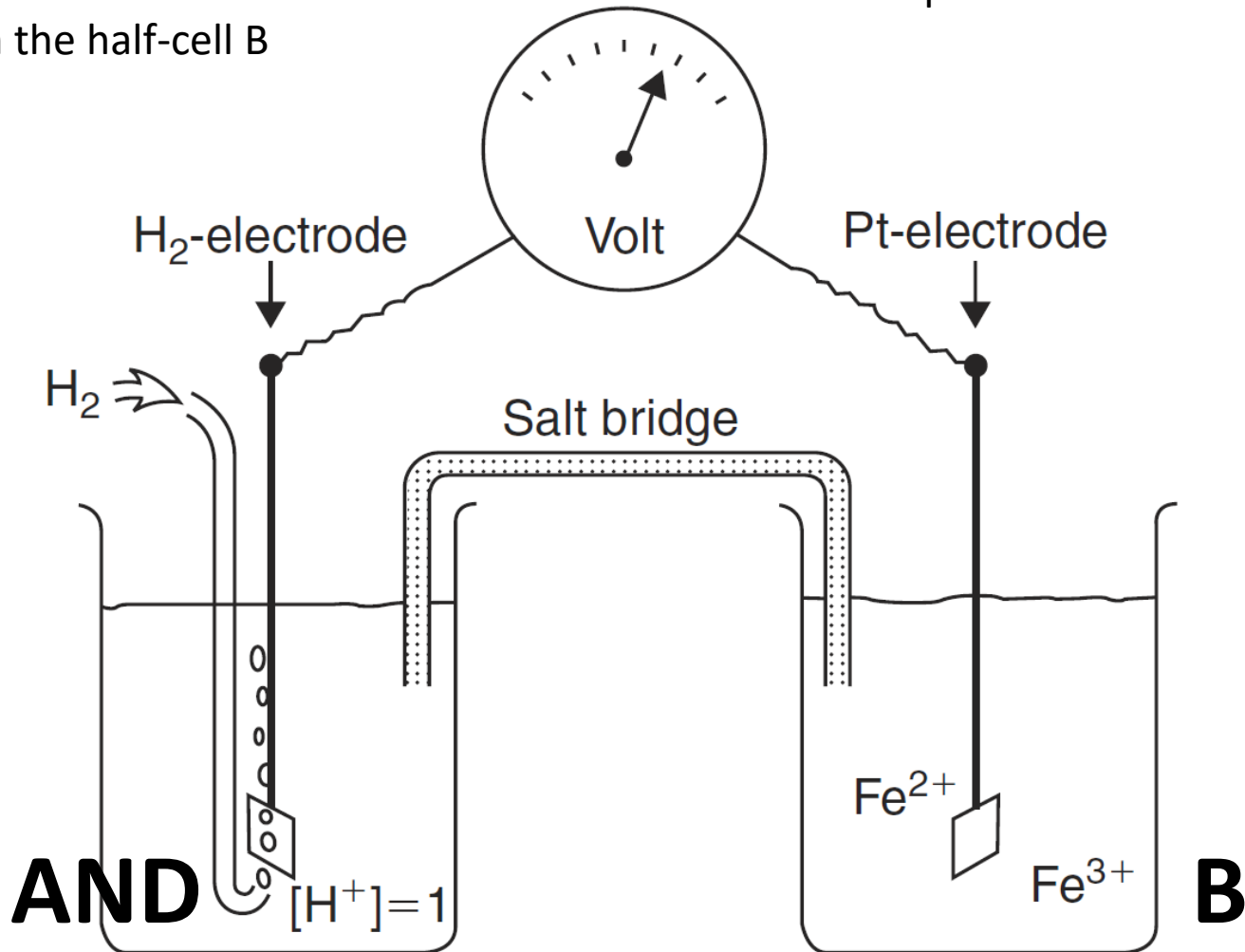
Eh

- Eh – potential compared to hydrogen electrode (h)

- Conventionally, it is positive if the e⁻ activity of half-cell B is lower than on the hydrogen electrode

- In the background is the principle that the equations are thermodynamically equivalent:

$$Fe^{3+} + 1/2H_2 = Fe^{2+} + H^+$$

$$Fe^{3+} + e^- = Fe^{2+}$$
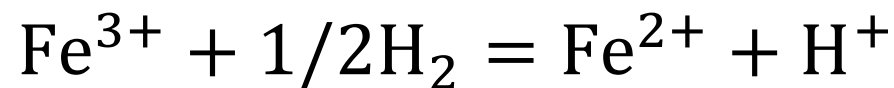
Electron activity

- pe (similar to pH), where pe = $-log\ a_{e-}$
- Eh (V)

$$p e = \frac{F}{2,303 RT} \text{Eh}$$

$$\text{Eh} = 0.059\ p e \qquad \text{For 25 ° C}$$

F... Faraday constant

Thermodynamic derivation of pe

$$\mathrm{Fe^{3+} + e^- = Fe^{2+}}$$

$$K_{eq} = \frac{a_{Fe^{2+}}}{a_{Fe^{3+}} \; a_{e^-}}$$

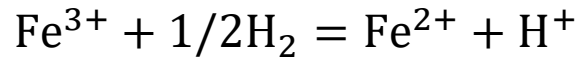$$a_{e^-} = \frac{1}{K_{eq}} \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

Let's invert the value

$$\frac{1}{a_{e^-}} = K_{eq} \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

$$\frac{1}{a_{e^-}} = a_{e^-}{}^{-1}$$

We're logging out

$$\mathrm{p}e = logK_{eq} + log\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

Thermodynamic derivation Eh

$$Fe^{3+} + 1/2H_2 = Fe^{2+} + H^+$$

$$\Delta G_r = \Delta G_r^o + RT ln \frac{a_{Fe^{2+}}\, a_{H^+}}{a_{Fe^{3+}}\, P_{H_2}^{1/2}}$$

Because $a_{H+} = P_{H2} = 1$

$$\Delta G_r = \Delta G_r^o + RT ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

$$\frac{\Delta G_r}{-nF} = \frac{\Delta G_r^o}{-nF} - \frac{RT}{nF} ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

$$Eh = E^o - \frac{RT}{nF} ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

$$\Delta G_r = -nFEh$$

$$Eh = \frac{\Delta G_r}{-nF}$$

Example

What is the pe for a solution at neutral pH with a sulfate activity, $a_{SO_4^{2-}} = 10^{-2}$ (~960 ppm) and sulfide activity, $a_{H_2S_{(aq)}} = 10^{-3}$ (34 ppm)?

Write the half-reaction: $SO_4^{2-} + 8e^- \rightarrow H_2S_{(aq)}$

Balance it: $SO_4^{2-} + 8e^- + 10H^+ \rightarrow H_2S_{(aq)} + 4H_2O$

Determine K: $\Delta G_r^\circ = -27.83 + 4(-237.14) - (-744.0) = -232.39 \text{ kJ/mol}$

$$\log K = -\frac{\Delta G_r^\circ}{5.708} = -\frac{-232.39}{5.708} = 40.7$$

$$K = \frac{a_{H_2S}}{a_{SO_4^{2-}} \times a_{e^-}^8 \times a_{H^+}^{10}} = 10^{40.7}$$

substituting redox species activities:

$$\log K = \log a_{H_2S} - \log a_{SO_4^{2-}} - 8 \log a_{e^-} - 10 \log a_{H^+}$$

$$8 \log a_{e^-} = \log a_{H_2S} - \log a_{SO_4^{2-}} - 10 \log a_{H^+} - 40.7$$

$$= \log(0.001) - \log(0.01) - 10(-7) - 40.7$$

$$= 28.3$$

$$\log a_{e^-} = 3.54$$

$$pe = -3.54$$

Definition of redox pairs

- Potential independent of electrode presence
- Defined whenever both members of a redox pair are in solution
- Solution with more redox pairs
  - Each pair defines pe (Eh) – may not be the same
  - Same only in equilibrium (which is not often in nature)
  - Without equilibrium, one cannot speak of an Eh of solution but only of partial pairs
- In waters, we usually measure mixed Eh
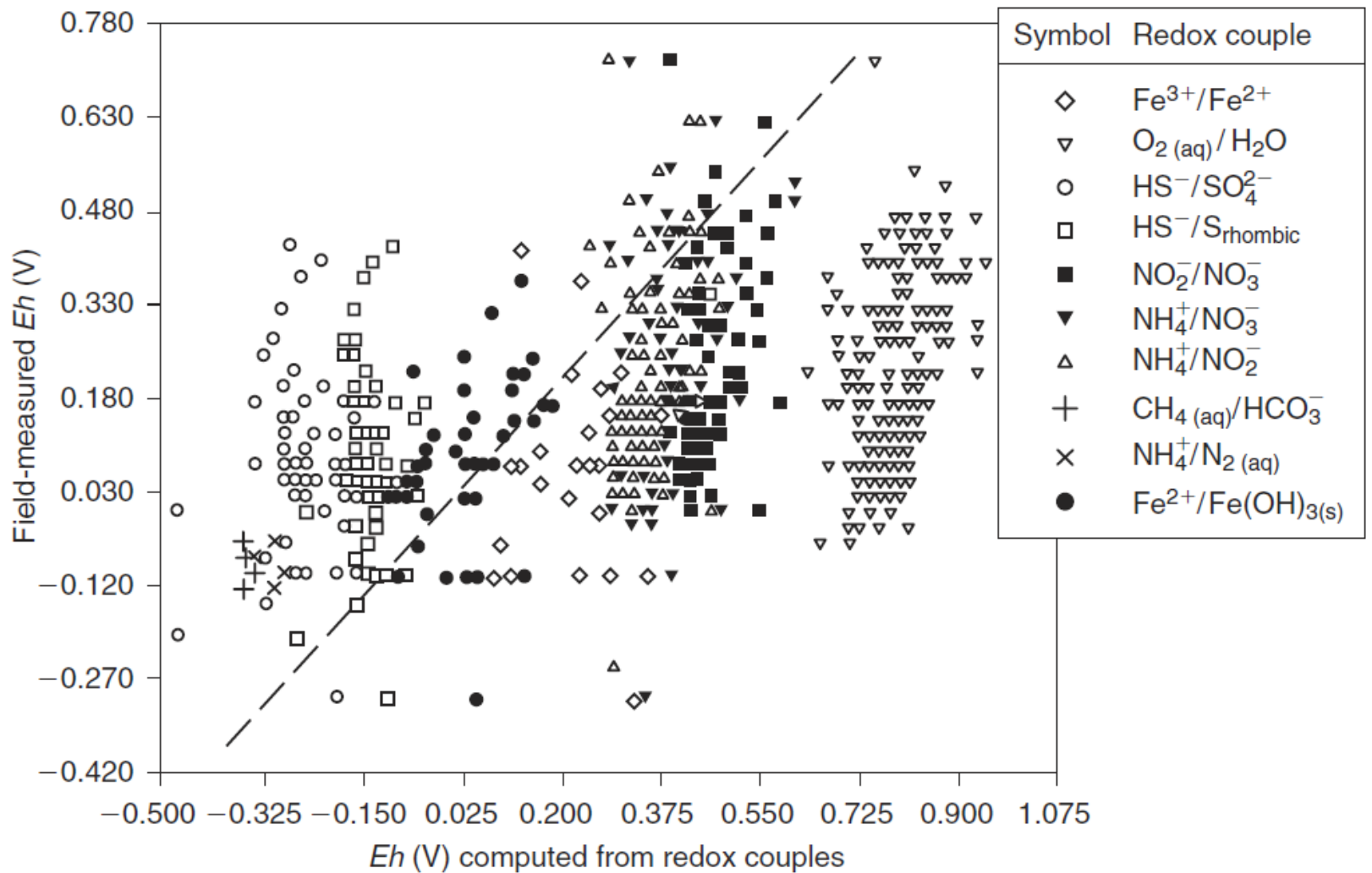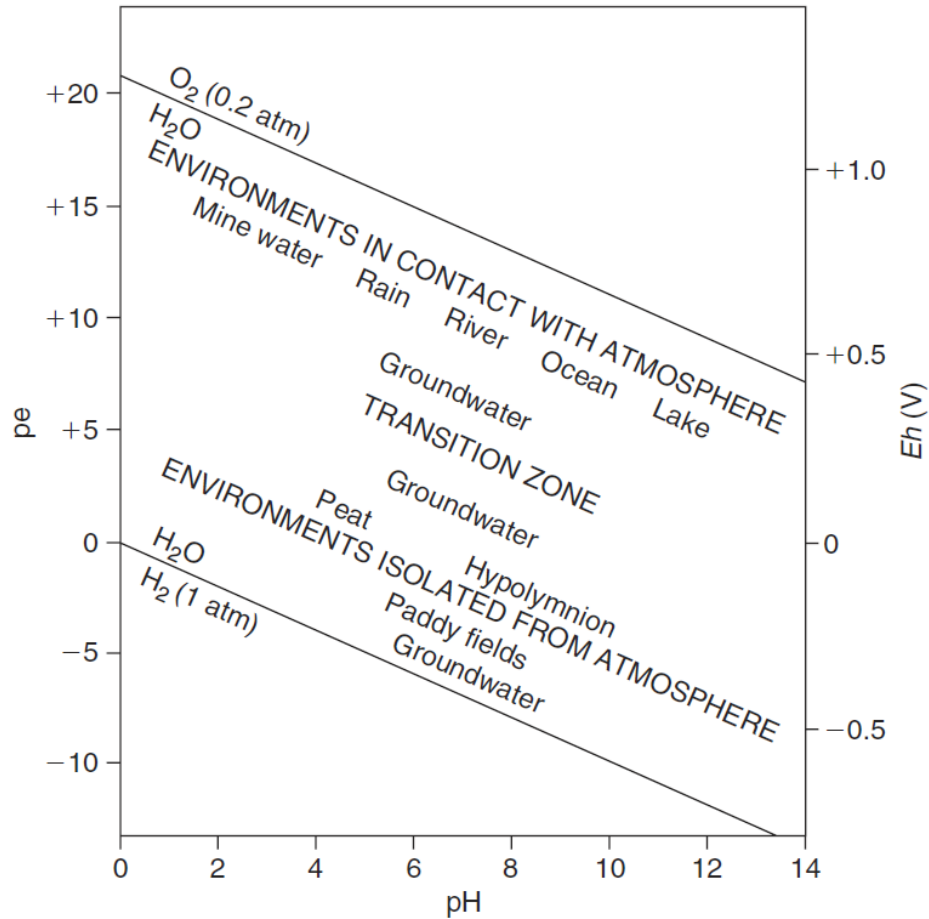 - Indicates redox conditions in water

Figure 9.3.   Comparison of groundwater field Eh measurements with potentials calculated for individual redox species (Lindberg and Runnels, 1984, Science, 225, 925–927 Copyright 1985 by the AAAS).

Legend:

Symbol	Redox couple
◇	Fe^{3+}/Fe^{2+}
▽	$O_{2\,(aq)}/H_2O$
○	HS^-/SO_4^{2-}
□	$HS^-/S_{rhombic}$
■	NO_2^-/NO_3^-
▼	NH_4^+/NO_3^-
△	NH_4^+/NO_2^-
+	$CH_{4\,(aq)}/HCO_3^-$
×	$NH_4^+/N_{2\,(aq)}$
●	$Fe^{2+}/Fe(OH)_{3(s)}$

PE-PH DIAGRAMS
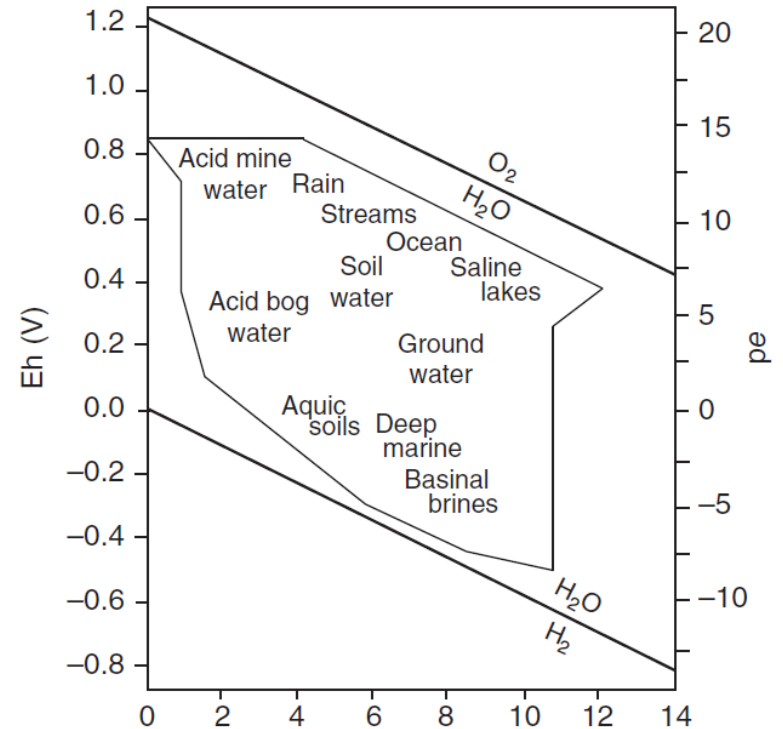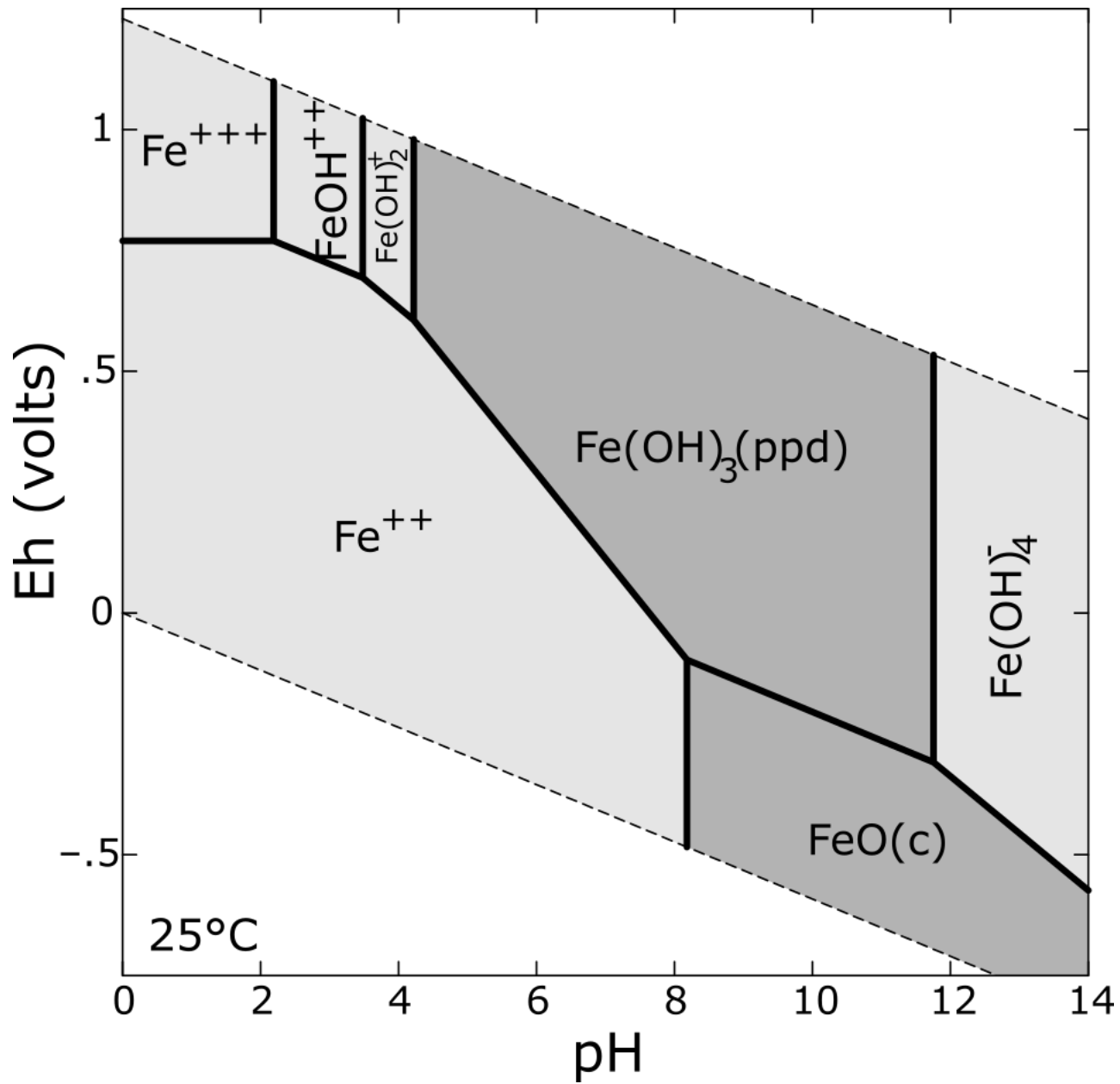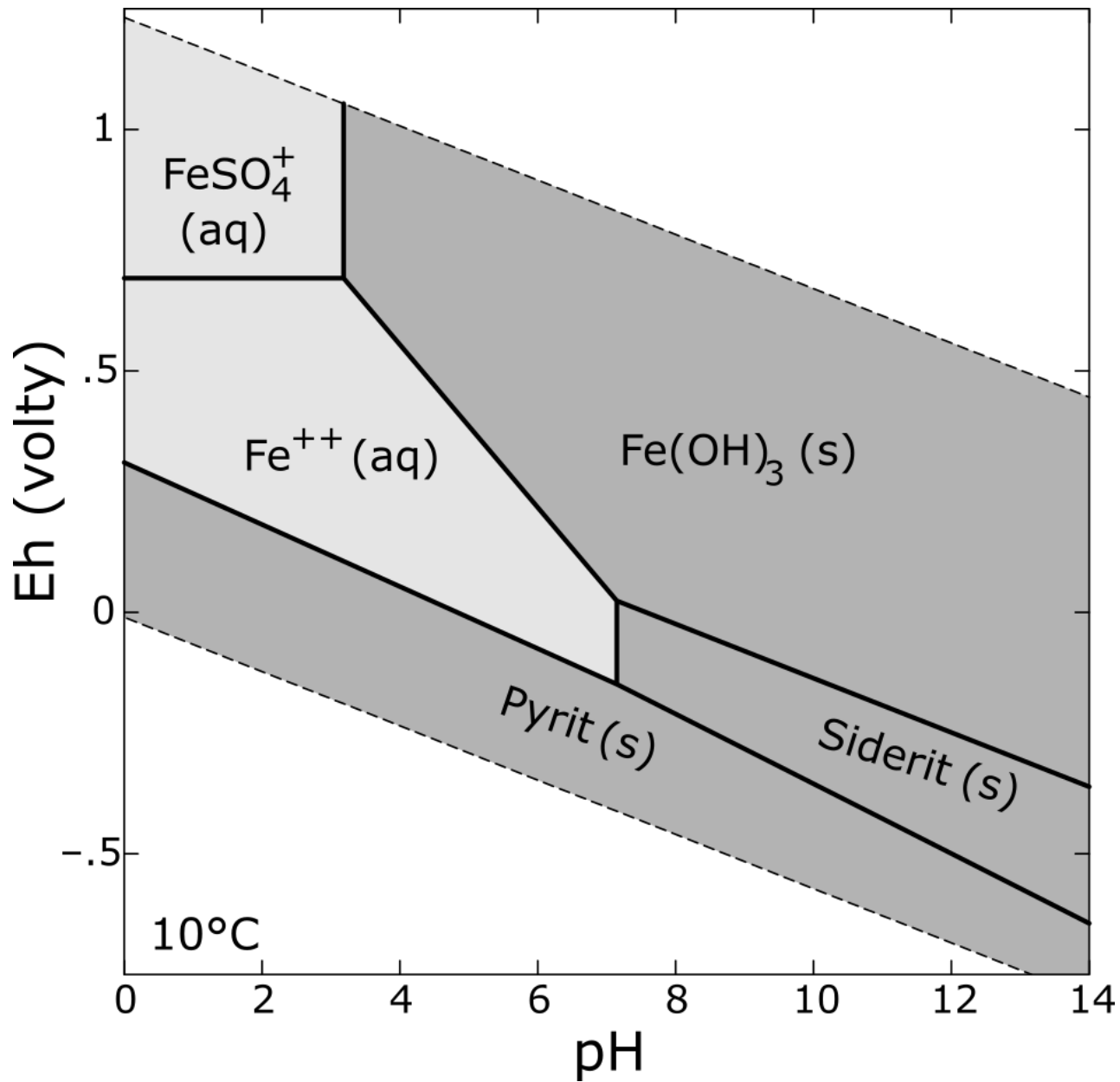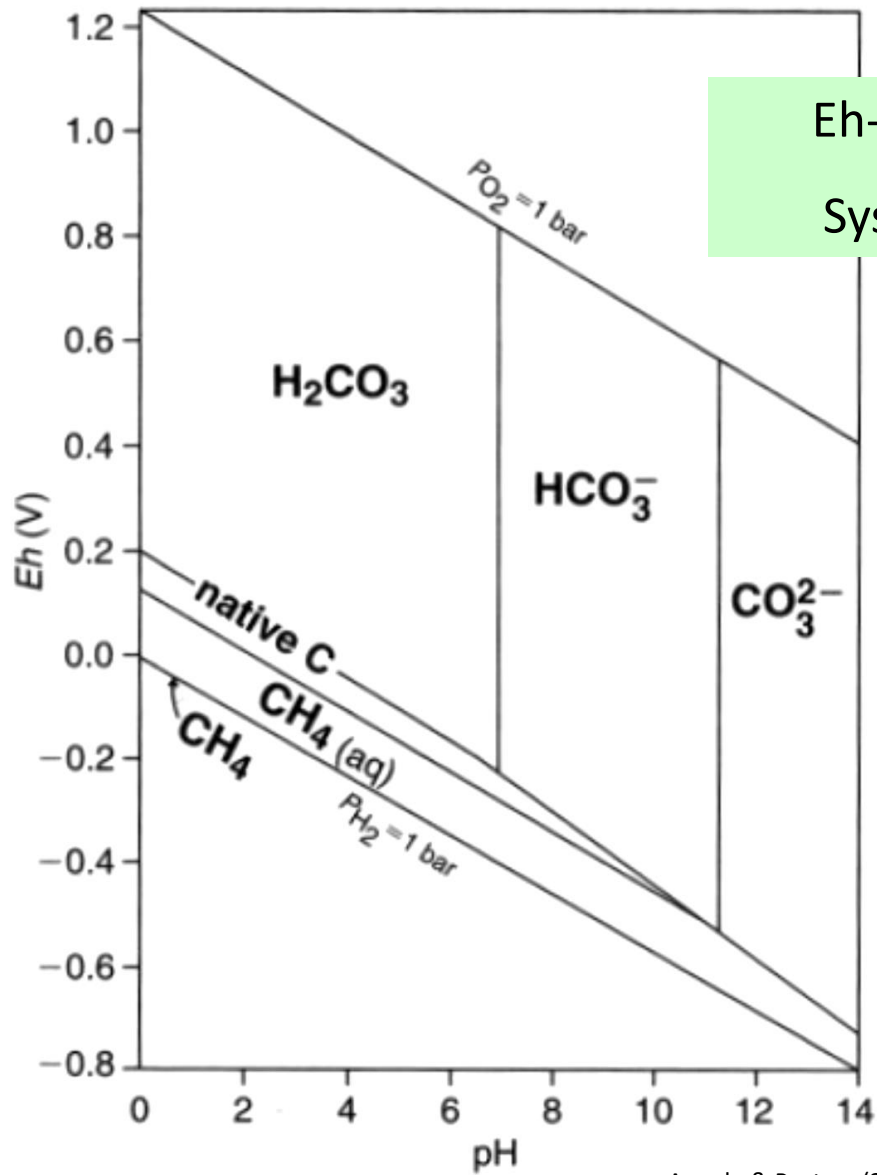
Natural conditions

Appelo & Postma (2005)

Fig. 4.12 Approximate locations of selected natural systems as a function of reduction–oxidation potential and pH. Note that redox units are given in terms of Eh (left) and pe. The thin line bounding the natural environments indicates the limits of nearly all natural waters (after Bass Becking et al. 1960).
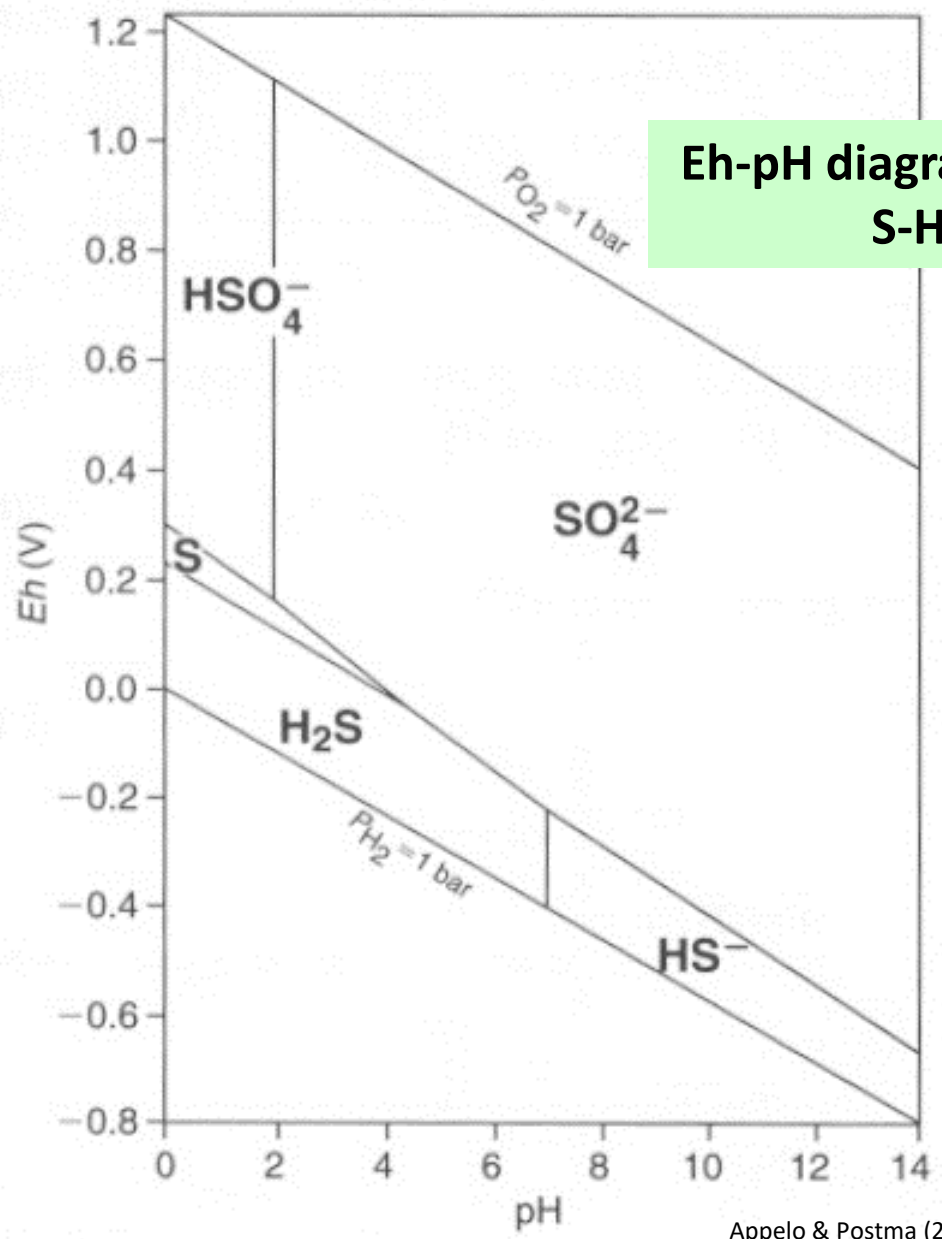
Taken from Ryan (2014)

Eh-pH diagram

System C-H_2O

Appelo & Postma (2005)

Eh-pH diagram. System S-H$_2$O

Appelo & Postma (2005)

At the entrance to a wetland, sampled water has an Eh of 0.9 V and a pH of 2
At the output, the values change to Eh 0.2 V and pH 8.5
Describe, using diagrams, what happens in the wetland.
How will the situation change if the decay in the wetland intensifies and Eh drops even more to, -0.2 V?
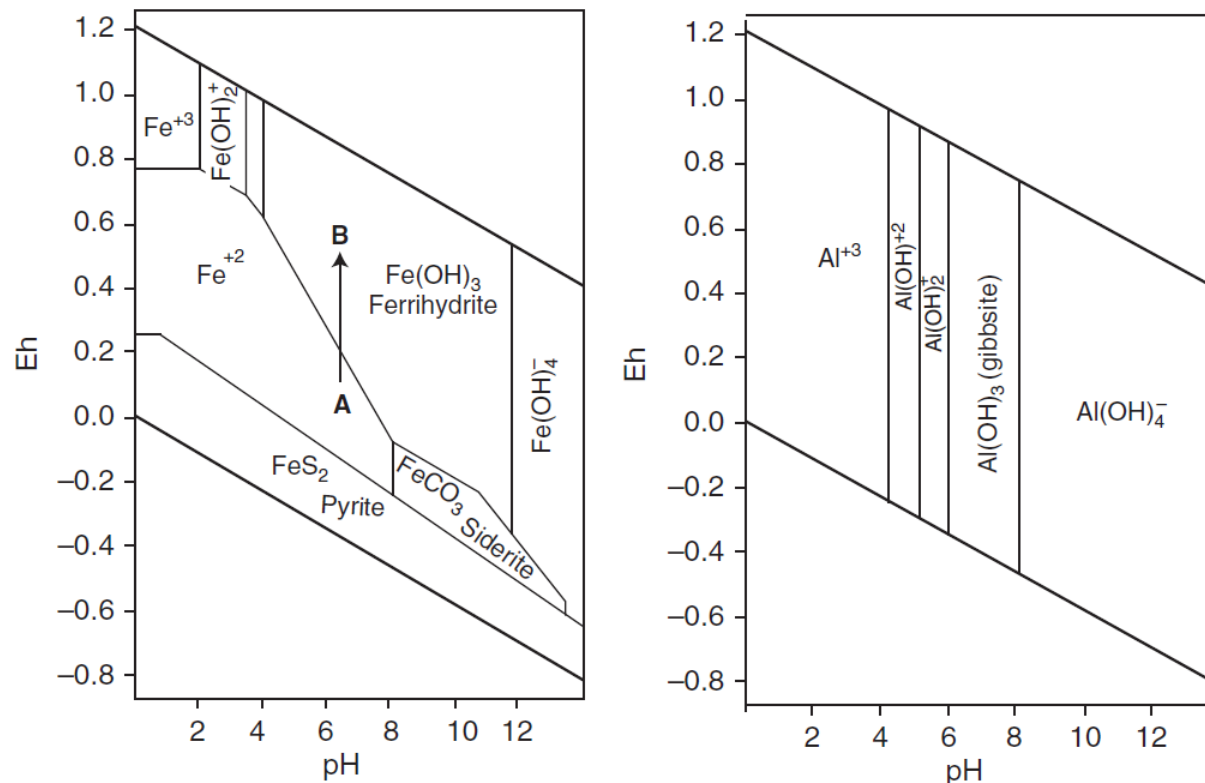

Fig. 4.15 Eh–pH diagram for iron and aluminum. For the iron diagram, activity of Fe = 10^{-6} mol/L, S = 10^{-2} mol/L and CO_2 = $10^{-3.4}$ atm. For aluminum diagram, Al = 10^{-9} mol/L. Note that iron speciation is influenced by both Eh and pH; conversely, aluminum speciation is controlled by pH but not Eh. The arrow A to B represents oxidation as shown in Plate 5.

REDOX CONDITIONS IN NATURAL WATERS

Photosynthesis

- Photosynthetic organisms convert CO_2 to organic matter and release oxygen

$$CO_2 \xrightarrow{sunlight} C_{org} + O_2$$
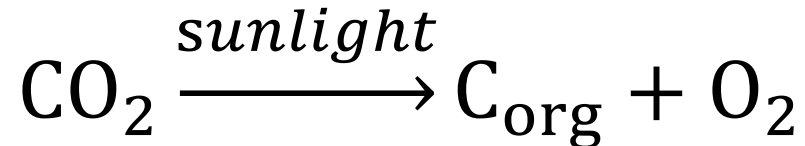
- Thanks to energy from the Sun, thermodynamically stable CO_2 is converted into unstable organic substances
  - If photosynthesis stopped, all oxygen would be consumed over time and C_{org} would decompose

Photosynthesis

- Plants need more substances
  - Nitrates and phosphates – a limiting factor for algae
  - Trace elements – necessary, but not usually limiting
- Averaging of photosynthesis to the average plankton composition:

$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O$$
$$+ 18H^+ + \text{Energie} + trace\ elements$$
$$= C_{106}H_{263}O_{110}N_{16}P + 138O_2$$

- The importance of phosphorus in water

Respiration and decomposition processes

- The opposite process of photosynthesis – when oxygen is available
- The release of CO_2 increases the pH of the water
- Without oxygen, the decomposition is a series of reactions representing gradually decreasing pe
- Organic oxidation is generally:
$$C_{org} + 2H_2O = CO_2 + 4H^+ + 4e^-$$
- The main difference is in the **final acceptor of e$^-$**

Decomposition processes

- **Various oxidizing agents:**
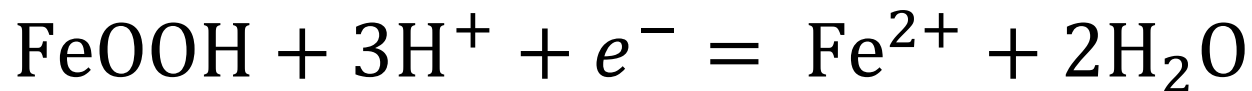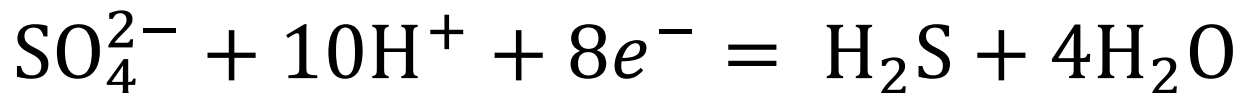
A. Aerobic metabolism
$$O_2 + 4H^+ + 4e^- = 2H_2O$$

B. Denitrification
$$2NO_3^- + 12H^+ + 10e^- = N_2 + 6H_2O$$
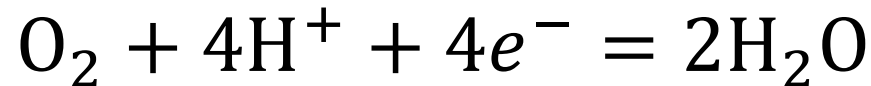
C. Fe^{3+} reduction
$$FeOOH + 3H^+ + e^- = Fe^{2+} + 2H_2O$$

D. Sulphate reduction
$$SO_4^{2-} + 10H^+ + 8e^- = H_2S + 4H_2O$$

# Nitrate reduction

- Bacterial decomposition: N^{+V} as e^- acceptor
- Denitrification = reduction to biologically inert N_2
$$C_{org} + 4NO_3^- + 4H^+ = 2N_2 + 5CO_2 + 2H_2O$$
- Other bacteria reduce to NO_2^- or up to NH_3
- Ammonia reacts with water
$$NH_3 + H_2O = NH_4^+ + OH^-$$
  - Alkalization of the aquatic environment
  - Possible precipitation of $CaCO_3$

Iron reduction

- In particular oxides and hydroxides with Fe^{3+}

$$C_{org} + 4Fe(OH)_3 + 8H^+ = CO_2 + 4Fe^{2+} + 10H_2O$$
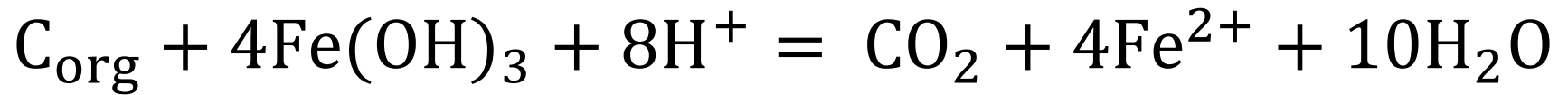
- Little significance in surface water – important in groundwater (order of magnitude more FeOOH)

- The resulting Fe^{2+} is transported or precipitated (eg siderite)

- Very reducing conditions (reduction of sulphates) – iron sulphides are formed
  - Microbial interaction

Sulphate reduction

- Bacteria use SO_4^{2-} as an oxidizing agent

$$2C_{org} + SO_4^{2-} + 2H_2O = H_2S + 2HCO_3^-$$
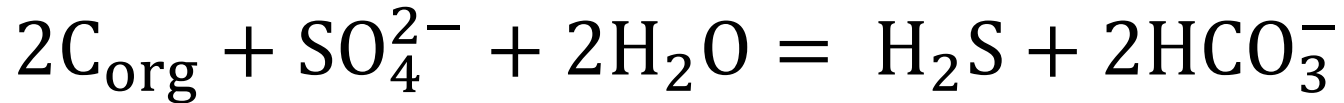
- Various S species may be formed – the final product is always sulphides/sulphane (according to available cations)

- Bacteria can use only simple molecules (up to 20 C)

  - Additional fission processes producing shorter chains

- H_2S and HS^- toxic – effect on biota

Consequences of Fe^{3+} and SO_4^{2-} reduction

- Fe reduction – color change from red and brown to gray and black

- Release of substances sorbed on iron oxohydroxide surfaces (arsenic in Bangladesh)

- Heavy metals soluble in oxidizing conditions (Cu, Zn, Mo, Pb, Hg) insoluble in the presence of S^{2-} (forms sulphides)

Fermentation and methanogenesis

- Without external e⁻ acceptors, bacteria use the transformation of organic matter as a source of energy

- Complex organic substances to simpler to CO_2 and H_2

- Other organisms use fermentation products to obtain energy producing CH_4

- We will simplify both processes to general:
$$2C_{org} + 2H_2O = CO_2 + CH_4$$
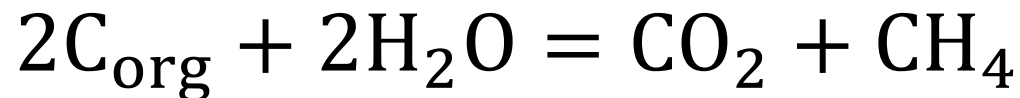
Anaerobic decomposition

- In general, the way in which microorganisms obtain energy by decomposing the products of photosynthesis
- Organisms catalyze the decomposition of thermodynamically unstable substances into more stable ones
- In general, each reaction has its own organisms and takes place gradually (with some overlap)
- First, the most energy efficient processes:

Consumption of O_2 => consumption of SO_4^{2-} => formation of CH_4

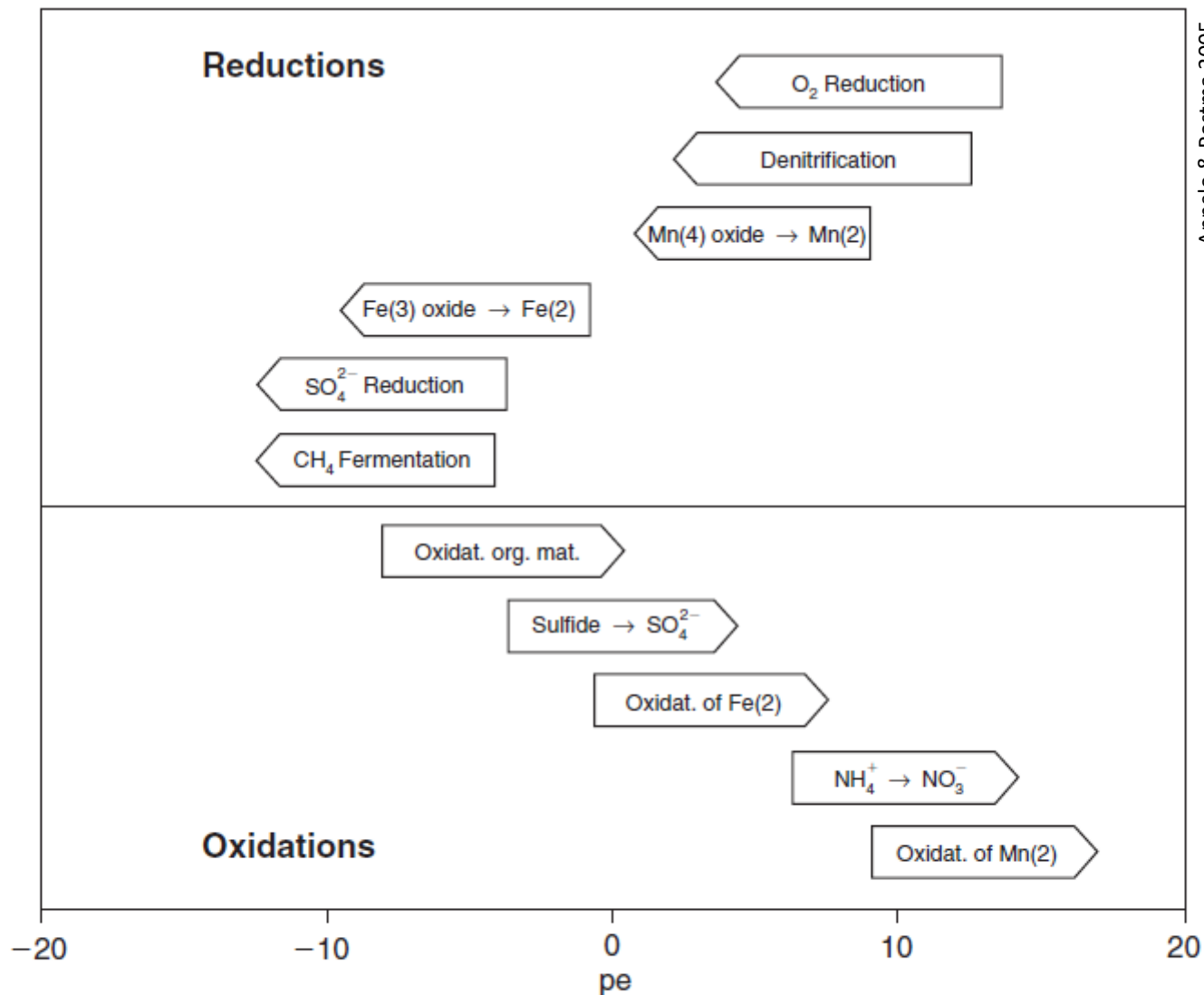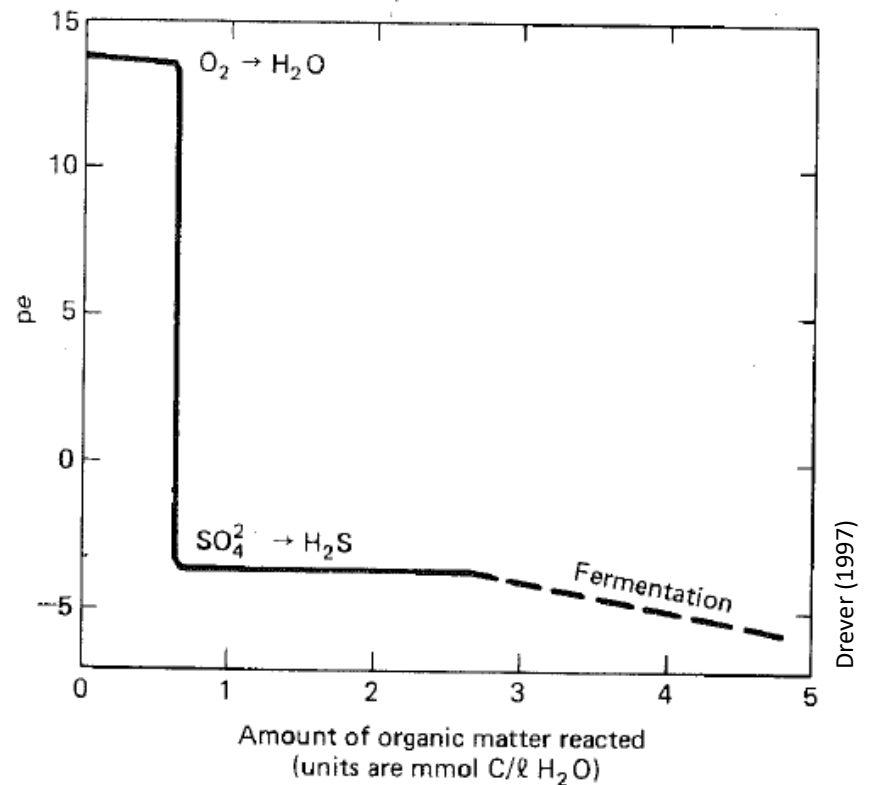- O_2 toxic to many bacteria – must be consumed first

Figure 9.15. Sequences of important redox processes at pH = 7 in natural systems (modified and corrected after Stumm and Morgan, 1996).

Buffering redox conditions

- Observation: pe of groundwater decreases very slowly, then jumps to a lower level and stagnates again.

- The system buffers redox if oxidizable and reducible substances are present which would prevent a significant change in pe with the addition of a small amount of strong oxidizing or reducing agent

- pe remains stable while consuming a certain oxidant

Buffering redox conditions

- In natural **surface** waters, O_2 maintains oxidizing conditions

- During consumption, they fall sharply and are held by another redox pair (especially SO_4^{2-}, because there usually are very few nitrates)

  - The values of pe in water are usually within the ranges given by the buffers redox pairs – stable values

Plot with pe on the y-axis (from about −5 to 15) versus "Amount of organic matter reacted (units are mmol C/ℓ H_2O)" on the x-axis (0 to 5). Curve labeled $O_2 \rightarrow H_2O$ at top, $SO_4^{2-} \rightarrow H_2S$ lower, and dashed line labeled Fermentation.

Drever (1997)

Buffering redox conditions

- The solid phase also plays an important role in **groundwater** and sediments - especially oxides of Mn and Fe


Froehlich et al. (1979)
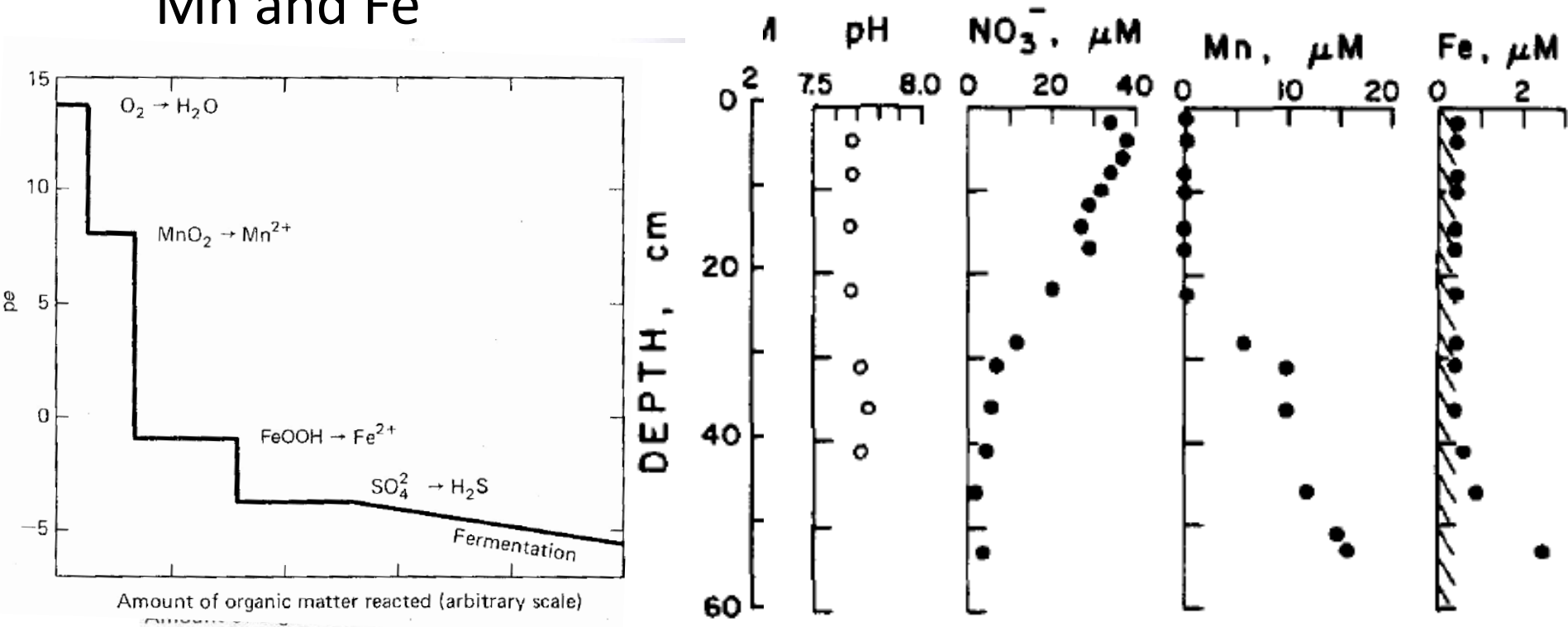
Redox conditions in a lake environment

- Given by the balances of the decomposition of organic matter and the supply of oxygen
- Water circulation in lakes controlled by differences in density (consequence of temperature)
- Epilimnion
- Metalimnion (thermocline)
- Hypolimnion
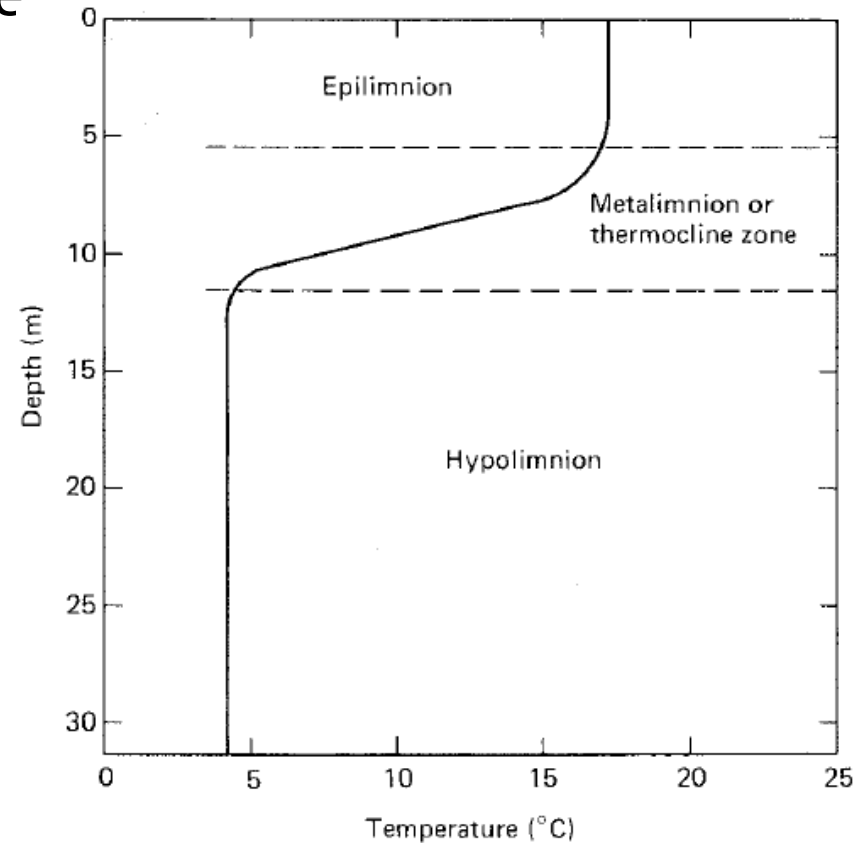
Redox conditions in a lake environment

- When equilibrating (mixing) the O_2 content is given by equilibrium with the atmosphere
- During stratification, the O_2 content in the hypolimnion gradually decreases (aerobic decomposition of organic matter from the epilimnion)
- The amount of organic matter is limited by nutrients - especially phosphates
- Large supply of organic matter - achieving anaerobic conditions
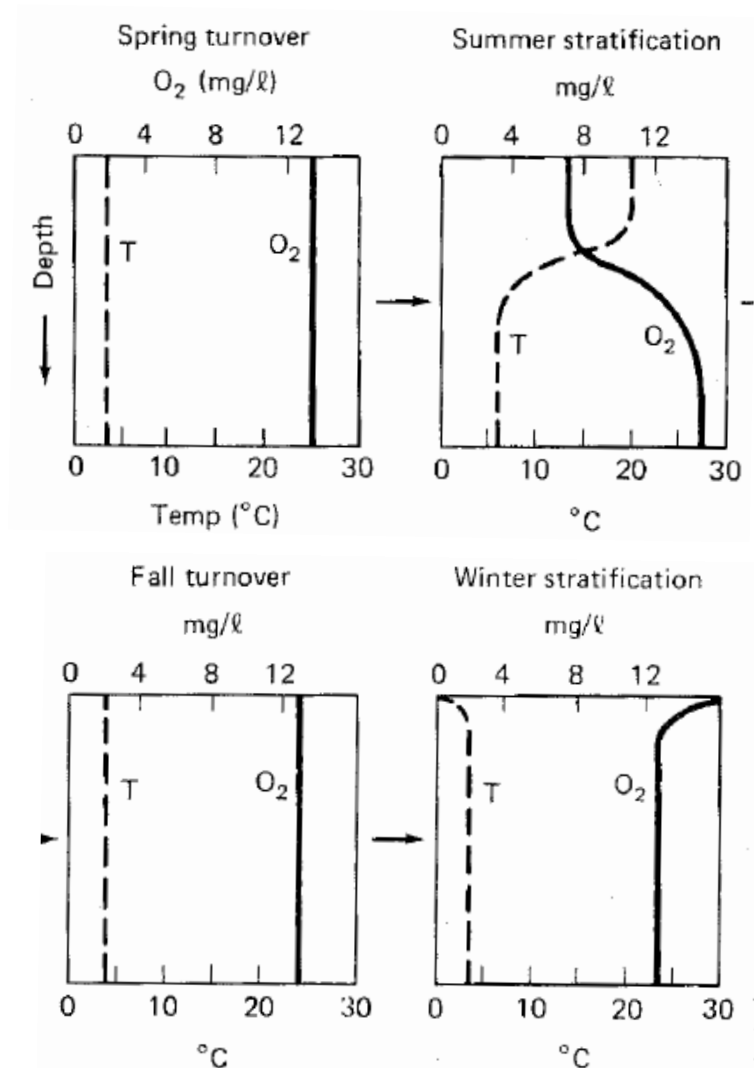
Redox conditions in a lake environment

- Oligotrophic lakes - low supply of nutrients, little organic matter, water generally oxygenated

- Eutrophic lakes - large supply of nutrients, a lot of organic, anaerobic hypolimnion
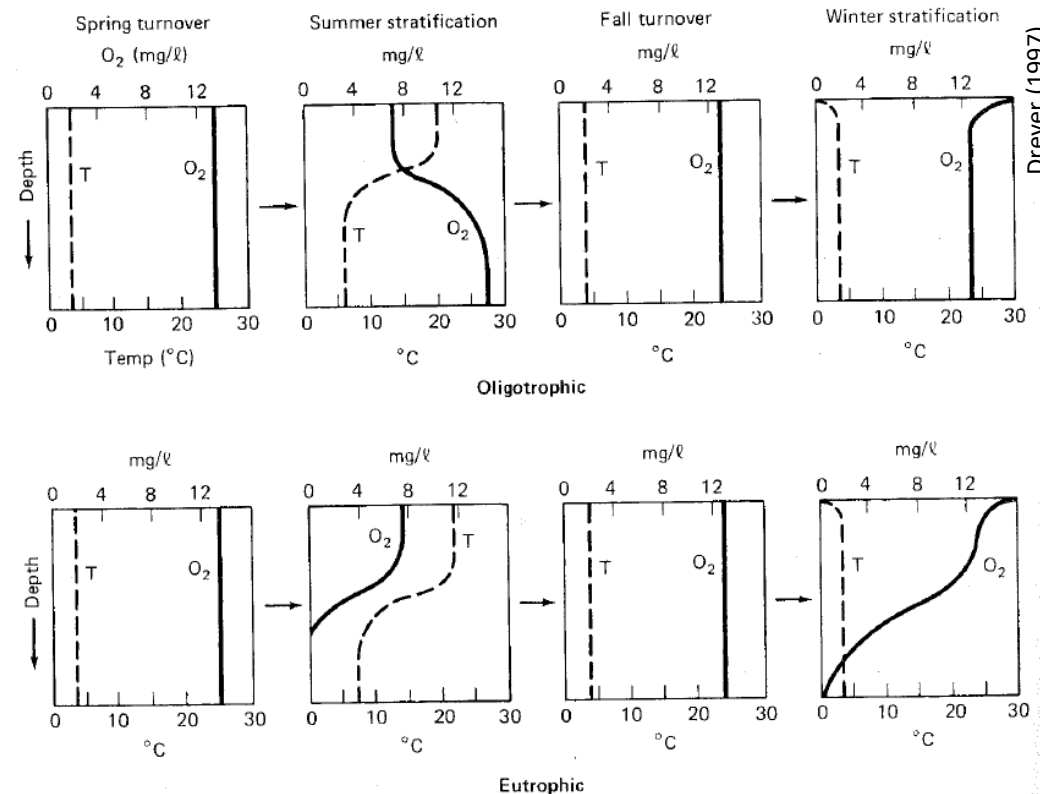

Drever (1997)

FIGURE 8-8 Idealized distributions of temperature and dissolved oxygen in oligotrophic and eutrophic lakes. The increase in dissolved O_2 with depth in the oligotrophic case in summer is due to the greater solubility of O_2 at lower temperatures (after Wetzel, 1983).

BOD & COD

- Organic matter significantly affects redox conditions in water, the total content is expressed by analytical terms:

Biochemical oxygen demand
- The amount of oxygen that water consumes in a given period of time (approx. 5 days)
- Estimation of how much O_2 pollutant directly consumes
- It better expresses the consumption of O_2 in the environment

Chemical oxygen demand
- Measured by the addition of strong ox. reagents
- The total concentration of org. materials (reactive and non-biodegradable)
- Better to determine

Eutrophication

- Easy adjustment of BOD and COD in WWTP
- Nitrates and phosphates problematic
- Phosphates sorb to FeOOH
  - It is released under reducing conditions
  - It often overlooks the effect of sedimentation
  - Eutrophication potentiates itself

Redox conditions in the oceans

- Different from lakes – continuous water mixing
- Nutrient content controlled by internal circulation (tributaries in lakes)
- Subsurface zone – O_2 from the atmosphere and photosynthesis
- Below it, the zone of oxygen minimum – decomposition of organic matter
- Below, the O_2 content rises again
- Organic production is not large enough to consume all O_2
- Most of the C_{org} decompose before hitting the bottom
- Oxygenated water sinks to the depths at the poles
- Most of the water in the ocean is well oxygenated
  - Except for closed basin (Black Sea)
  - Sediments with organic on the shelf
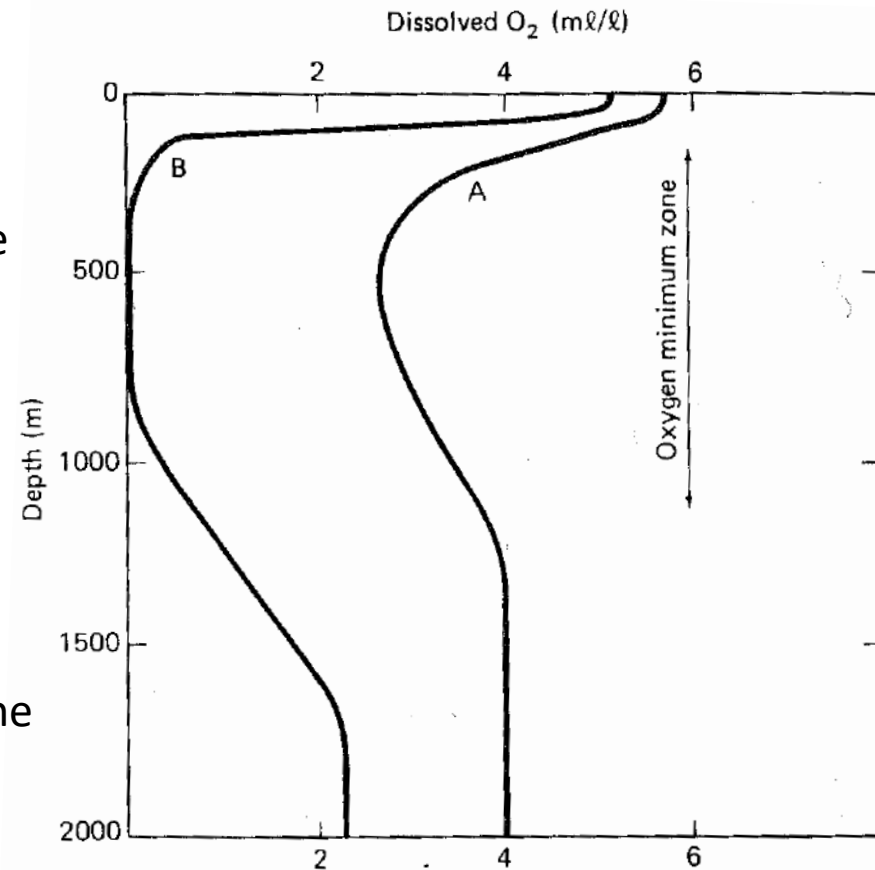
Redox conditions in groundwater

- Redox conditions are given by the ratio of the oxygen input and its consumption by the decomposition of organic matter and some minerals
- The main variables include:
1. O_2 content in replenished water
   - Water seeping directly through cracks vs. seeping through a thick layer of soil
2. Distribution and reactivity of organics (and other reducible phases)
   - Availability for organisms – organics in sediments are often refractory (influence of diagenesis), eg coal
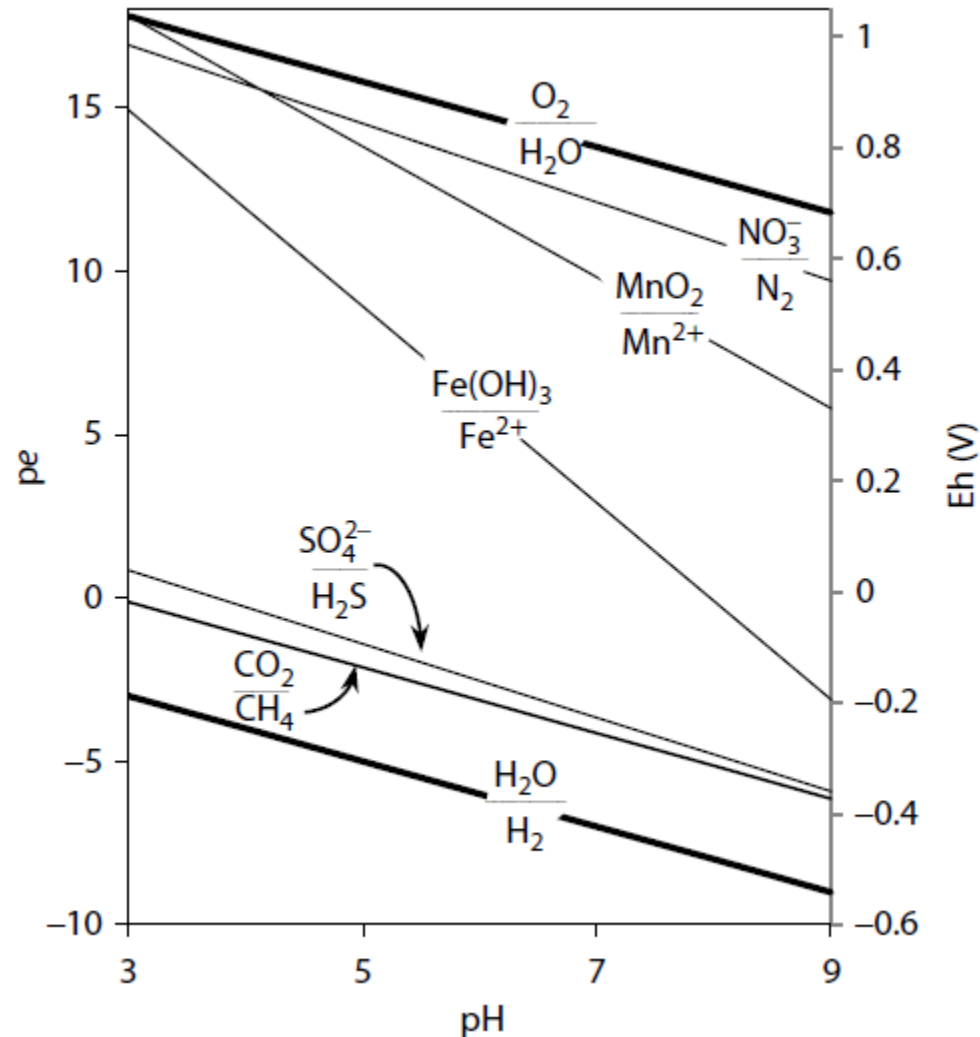
Redox conditions in groundwater

3. Distribution of redox buffers
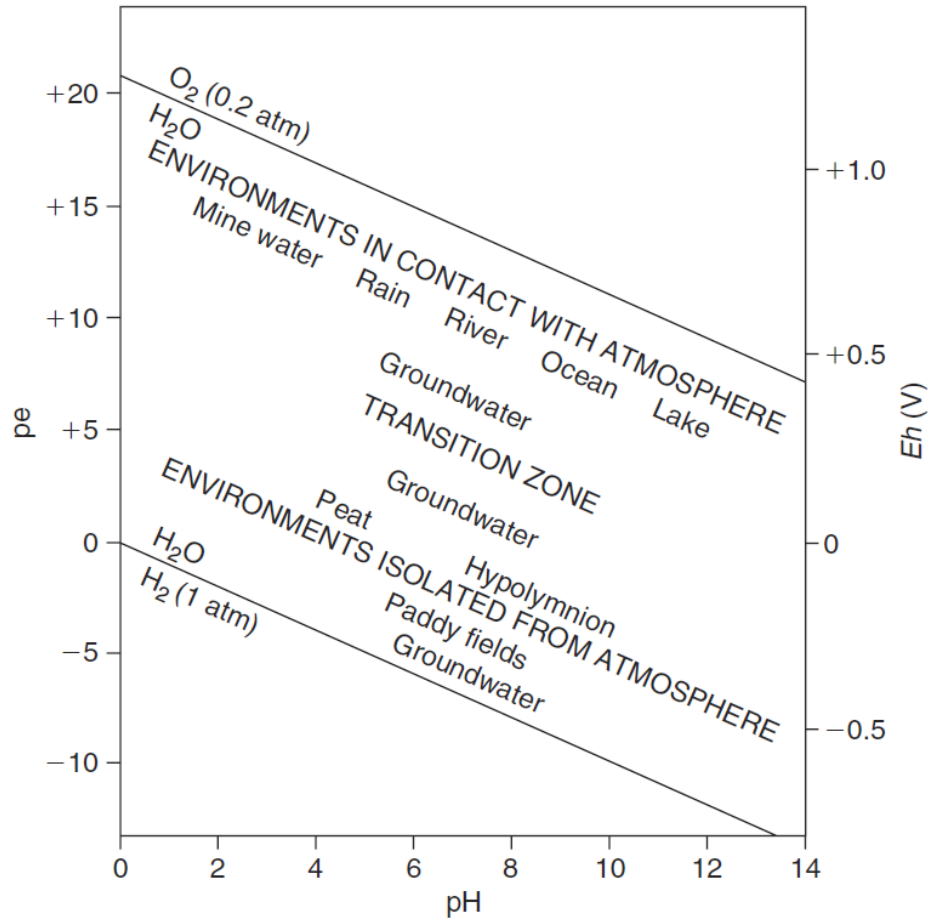   - Large amounts of buffers and slow interactions -> very slow pe decrease
   - In particular Fe(OH)$_3$, MnO$_2$ and Fe$_2$O$_3$

4. Groundwater flow rate
   - Bacterial redox processes are slow – the effect of residence time and reservoir size on the resulting pe

Clark 2015

Natural conditions
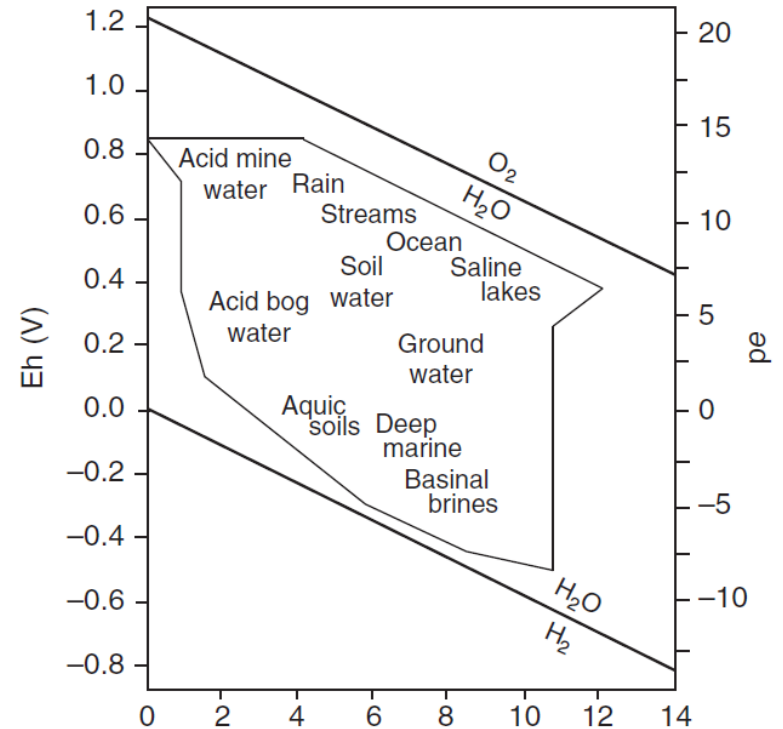

Appelo & Postma (2005)

Fig. 4.12 Approximate locations of selected natural systems as a function of reduction–oxidation potential and pH. Note that redox units are given in terms of Eh (left) and pe. The thin line bounding the natural environments indicates the limits of nearly all natural waters (after Bass Becking et al. 1960).

Taken from Ryan (2014)

Summary

- Redox conditions of natural waters are usually determined by the balance of O_2 supply from the atmosphere and its consumption by microbial decomposition of organic matter.

- After O_2 consumption , pe decreases progressively with the advancing sequence of reactions (reduction of Fe^{3+}, SO_4^{2-} and fermentation).

- Organic production in lakes and the ocean is significantly controlled by the availability of inorganic nutrients (phosphates and nitrates).

- Changes in pe have a great influence on the solubility and mobility of many metals.

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie
č. CZ.02.2.69/0.0/0.0/16_018/0002593

References

- APPELO, CAJ and Dieke POSTMA. *Geochemistry , groundwater and pollution :. _* 2nd ed . Leiden: AA Balkema publishers , c2005. ISBN 0-415-36421-3.

- CLARK, I. (2015): Groundwater Geochemistry and Isotopes.BocaRaton , Florida: CRC Press.

- DREVER, James I. *The geochemistry of natural waters: surface and groundwater environments* . 3rd ed. Upper Saddle River, NJ: Prentice Hall, c1997. ISBN 0-13-272790-0.

- Ryan, P. (2014). Environmental and low temperature geochemistry. John Wiley and Sons. 402p. ISBN 978-1-4051-8612-4 (pbk .)

- Froelich , PN, et al. "Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic : suboxic diagenesis . " *Geochimica et Cosmochimica Acta* 43.7 (1979): 1075-1090.

References

- Unmarked images are author's or taken over with the permission of doc. Zemana and doc. Faimona
- Clark , I. (2015). Groundwater Geochemistry and Isotopes . CRC Press . 442p. ISBN 978-1-4665-9174-5 (eBook - PDF)
- Drever , J. (1997): The geochemistry of natural waters : surface and groundwater environments . (I have a book from our library with me on a long-term loan)
- Dreybrodt , W. & Eisenlohr , L. (2000): Limestone dissolution rates in karst environments . - In: Klimchouk , AB (ed .): Speleogenesis evolution of karst aquifers . - National speleological society. Huntsville , Alabama. 527 s.
- Holland HD, Kirsipu T V., Huebner JS, Oxburgh UM (1964) On Some Aspects of the Chemical Evolution of Cave Waters. J Geol 72: 36–67. doi : 10.1086 / 626964
- Plummer LN, Parkhurst DL, Wigley TML (1979) Critical review of the kinetic of calcite dissolution and precipitation.
- Plummer LN, Wigley TML, Parkhurst DL (1978) The kinetics of calcite dissolution in CO_2 -water systems at 5 degrees to 60 degrees C and 0.0 to 1.0 atm CO_2. Am J Sci 278: 179–216. doi : 10.2475 / ajs.278.2.179
- Pracný P, Faimon J, Všianský D, Handbag L (2017) Evolution of Mg / Ca Ratios During Limestone Dissolution Under Epicarstic Conditions. Aquat Geochemistry 1–21. doi : 10.1007 / s10498-017-9313-y
- Pracný P, Faimon J, Kabelka L, Hebelka J (2016) Variations of carbon dioxide in the air and dripwaters of Punkva Caves (Moravian Karst, Czech Republic). Carbonates and Evaporites 31: 375–386. doi : 10.1007 / s13146-015-0259-0
- Stumm , W. and Morgan, J. (1995): Aquatic chemistry: chemical equilibrium and rates in natural waters.