

ENV-200

Revision of basic concepts

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You should be able to:

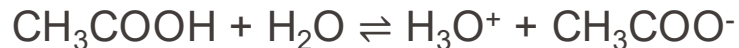
1. Recognize acids and bases and perform simple pH calculations.
2. Understand acidity and basicity constants as well as the ion product of water.
3. Recognize and balance simple redox reactions.
4. Understand the significance of solubility, solubility product and ion product.
5. Gain the ability to calculate the solubility of simple salts in natural waters.
6. Determine if solutions are over- or undersaturated with respect to a given salt.

Sigg, Behra, Stumm, Chimie des milieux aquatiques, pp.29-43 (acid-base), pp.271-272 (redox), 231-234 (dissolution and precipitation)

Essential points:

1. Acid-base reactions involve a proton transfer
2. The acidity of a system is determined by the concentration (activity) of protons on a pH scale
3. $\text{pH} = -\log[\text{H}^+]$

Are the following reactions acid-base reactions (do they involve a transfer of protons)?



Definition:

Bronsted acid: molecule that can liberate a proton

Bronsted base: molecule that can accept a proton

Examples of naturally occurring acids and bases:

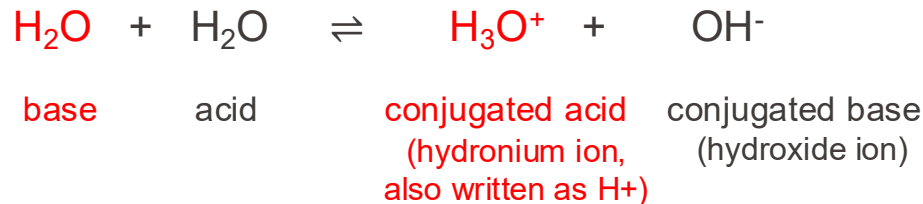
The most important base: $\text{HCO}_3^- / \text{CO}_3^{2-}$

Other bases: $\text{B}(\text{OH})_4^-$, PO_4^{3-} , NH_3 , AsO_4^{3-} , SO_4^{2-} , etc.

The most important acid: $\text{CO}_2(\text{aq})$ or H_2CO_3

Other acids: H_4SiO_4 , NH_4^+ , $\text{B}(\text{OH})_3$, H_2SO_4 , CH_3COOH (acetic), $\text{H}_2\text{C}_2\text{O}_4$ (oxalic), etc.

Autoprotolysis (self-ionization) of water



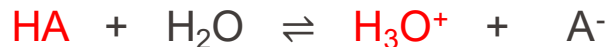
Equilibrium constant K_w = ion product of water

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14} \text{ at } 25 \text{ }^\circ\text{C} \text{ (} K_w \text{ changes with temperature!)}$$

$$\log K_w = \log[\text{H}_3\text{O}^+] + \log[\text{OH}^-]$$

$$14 = \text{pH} + \text{p}[\text{OH}^-]$$

Acid hydrolysis: dissociation of an acid HA in water



Equilibrium (or acidity) constant K_a = measure of the acidity of HA

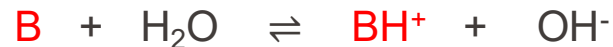
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$pK_a = -\log K_a$$

Some comments:

1. Strong acids have a low pK_a (often defined as < 2). Weak acids have a higher pK_a .
2. The concentration of water is constant and is included in K_a . It therefore does not show up in the equation.
3. The pK_a of water is NOT the same as the pK_w , so it is NOT 14. K_w is defined as $[\text{H}^+][\text{OH}^-]$. K_a is defined as $[\text{H}^+][\text{OH}^-]/[\text{H}_2\text{O}]$, with $[\text{H}_2\text{O}] = 55.4 \text{ M}$. So the pK_a of water is 15.75.

Base hydrolysis: dissociation of a base B in water



Equilibrium (or basicity) constant K_b = measure of the base strength of B

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$pK_b = -\log K_b$$

Some comments:

1. Strong bases have a low pK_b . Weak bases have a higher pK_b .
2. Note that bases are frequently negatively charged ($B^- + H_2O \rightleftharpoons BH + OH^-$)



The stronger the acid, the weaker the conjugated base.

Strong acids ($\text{p}K_a < 2$) and strong bases ($\text{p}K_b < 2$) fully ionize in water (irreversible reaction):



Weak acids ($\text{p}K_a > 2$) and weak bases ($\text{p}K_b > 2$) only partially ionize in water (reversible reaction):



Important questions: what is the pH of a solution containing an acid? At a given pH, does the acidic or basic species dominate?

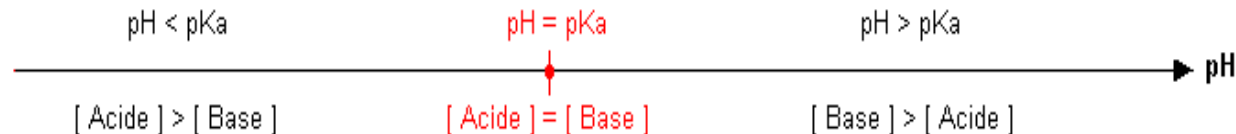
To answer these questions, consider the **Henderson-Hasselbach equation**:

$$pH = pK_a - \log \frac{[HA]}{[A^-]}$$

If $pH < pK_a$: the acidic form dominates

If $pH > pK_a$: the basic form dominates

If $pH = pK_a$: the acid and base are present in equal concentrations ($[HA] = [A^-]$)



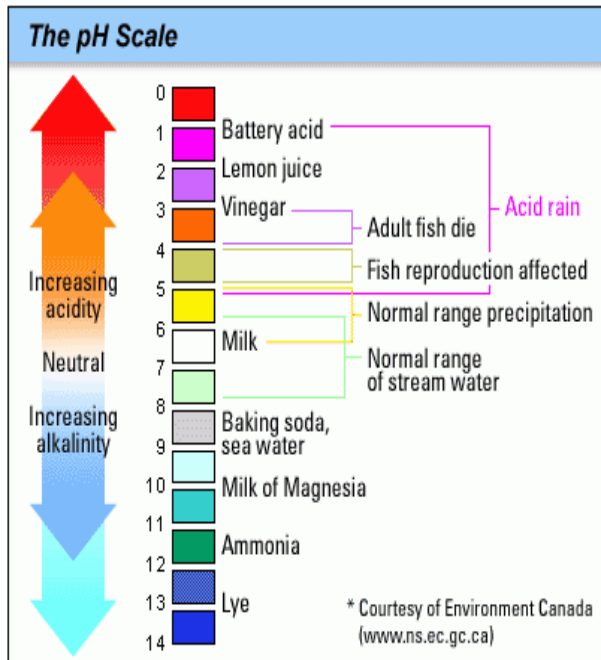
The pH scale

$\text{pH} < 7$, the solution is acidic

$\text{pH} = 7$, the solution is neutral

$\text{pH} > 7$, the solution is basic

The pH influences many environmental processes. In natural waters, the pH is typically between 5.5 and 9. It is mainly determined by the carbonate equilibrium and by biological processes (respiration and photosynthesis).

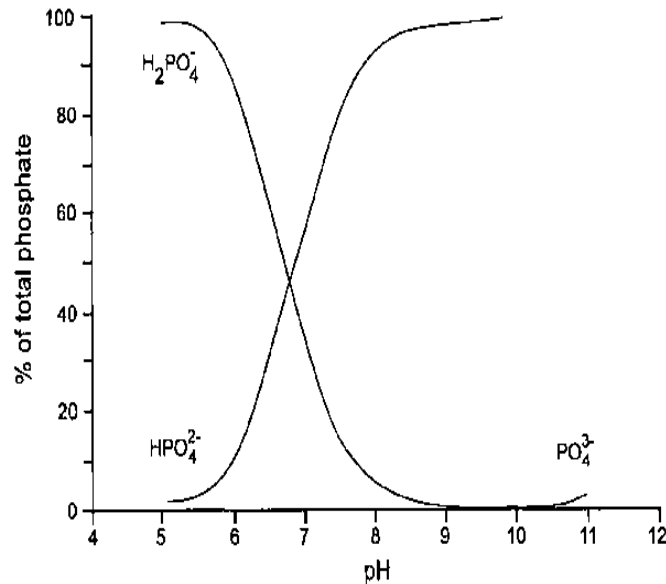


Exercise 1

Phosphates are macropollutants that are partially responsible for the eutrophication of lakes.

What are the dominant phosphate species in a lake with pH 8?

What is the pK_a of $H_2PO_4^-$?



Exercise 2

Free ammonia (NH_3) is a species that is toxic to fish. In a river, you measured a concentration of 3×10^{-5} M total ammonium ($[\text{NH}_4^+] + [\text{NH}_3]$). How much NH_3 is in the water?

$$\text{pH} = 8.5$$

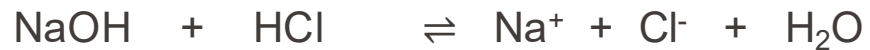
$$T = 15^\circ\text{C}$$

$$\text{pK}_a(\text{NH}_4^+) \text{ at } 15^\circ\text{C} = 9.57.$$

Essential points:

1. Redox reactions involve the transfer of an electron
2. A redox reaction is composed of two half reactions
3. The half reaction in which a loss of electrons occurs is called an oxidation
4. The half reaction in which the uptake of electrons occurs is called a reduction
5. The tendency to accept or donate electrons is given by the reduction potential (E)

Are the following reactions redox reactions?



Generalized representation of a redox reaction:



Ox: oxidized species, Red: reduced species, m: number of H⁺; n: number of electrons

Note that the pH (H⁺) influences the reaction!

Some more definitions:

- Reductant: species that gives up an electron (gets oxidized)
- Oxidant: species that accepts an electron (gets reduced)
- Electron donor: species that gives up an electron (same as reductant)
- Electron acceptor: species that accepts an electron (same as oxidant)

Example of important redox reactions

Oxidation of hydrocarbons by microorganisms:

the oxidation of hydrocarbons produces different products, depending on the availability of oxygen:

- aerobic conditions:



- low O_2 conditions ($< 0.5 - 1.0 \text{ mgL}^{-1}$):



- anoxic conditions (no oxygen):



Can you identify the electron donors and acceptors in each equation?

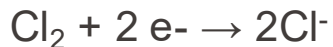
Equilibrating a redox reaction



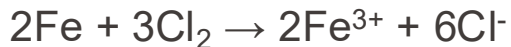
1: Determine the oxidation number in each element.



2: Determine the number of electrons gained or lost for each reactant.



3: Make the cross product, such that the number of electrons lost corresponds to the number of electrons gained.



4: Verify the mass and charge balance.

Exercise 3

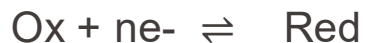
Equilibrate the following reaction:



Fe^{2+} exists in anoxic ground water. When such waters are used from drinking water supplies and the water becomes exposed to the atmosphere, the Fe^{2+} is oxidized by O_2 to Fe(III) (ferric iron), which is insoluble at neutral pH and precipitates as $\text{Fe}(\text{OH})_3(\text{s})$.

Electrochemical potential, Nernst's law

E = measure of the tendency of a species to accept electrons. It is always defined for a reduction (oxidant on the left).



$$E = E_o - \frac{RT}{nF} \ln \frac{\{\text{Red}\}}{\{\text{Ox}\}}$$

E is the potential in Volt

E° is the standard potential

R is the universal gas constant, 8.314 J/mol/K

T is the absolute temperature in Kelvin

n is the number of electrons transferred

F is the Faraday constant, 96'487 coulombs/mol

$\{\}$ indicate activity rather than concentration (see next week)

Standard potential E^0

The electrochemical potential cannot be measured in absolute terms, only relative to a reference potential.

Typically, a **standard hydrogen electrode** (SHE) is used as the reference. Its potential is defined as $E_{\text{SHE}}^0 = 0.0 \text{ V}$

For all other substances, the standard potential of the half reaction is measured with respect to the SHE, at standard conditions (**all soluble substances present at 1M, all gases at 1 bar**)

The half reactions are ordered according to E^0 , either by increasing oxidizing or reducing power (**electrochemical series**)

The electrochemical series allows to **determine if a redox reaction will occur spontaneously ($E > 0$)** between two redox partners (under standard conditions)

Electrochemical series

Electrode reaction	E^0/V	
$\text{Au}^{3+} + 3\text{e}^- \rightleftharpoons \text{Au}$	+1.43	Good oxidant, poor reductant
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	+0.80	
$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$	+0.34	
$\text{H}^+ + \text{e}^- \rightleftharpoons \text{H}$	0	Reference!
$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$	-0.13	
$\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn}$	-0.14	
$\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni}$	-0.25	
$\text{Cd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cd}$	-0.40	
$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$	-0.44	
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	-0.76	
$\text{Ti}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ti}$	-1.63	
$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}$	-1.66	
$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}$	-2.37	
$\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na}$	-2.71	
$\text{K}^+ + \text{e}^- \rightleftharpoons \text{K}$	-2.93	
$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}$	-3.05	Good reductant, poor oxidant

<http://labspace.open.ac.uk/mod/resource/view.php?id=391135>

Essential points:

1. **Precipitation** is the process by which a dissolved compound passes into the solid phase.
2. **Dissolution** is the process by which a solid substance passes into solution.
3. The **solubility S** indicates the maximal amount of a solid that can be dissolved per L of water (saturated solution). Solubility is expressed in M or g/L.
4. The **solubility product K_s** describes the equilibrium between a solid and its dissolved ions.

Dissolution and precipitation

Generalized representation of the solubility equilibrium:



Solubility product: $K_s = \{M_{(\text{aq})}\}^n \{X_{(\text{aq})}\}^m$

M is usually a (transition) metal ion, usually a cation.

X is an organic or inorganic ligand, often an anion.

The **solubility product** is an equilibrium constant between a solid salt and its ions in **saturated solution**.

Relation between **solubility S** and the **solubility product**:

$$S = \sqrt[n+m]{\frac{K_s}{n^n m^m}}$$

Dissolution and precipitation

Examples of important solid phases in the environment

Oxides and hydroxides: $\text{Fe}(\text{OH})_3(\text{s})$, FeOOH , Fe_2O_3

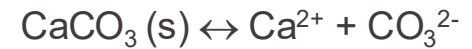
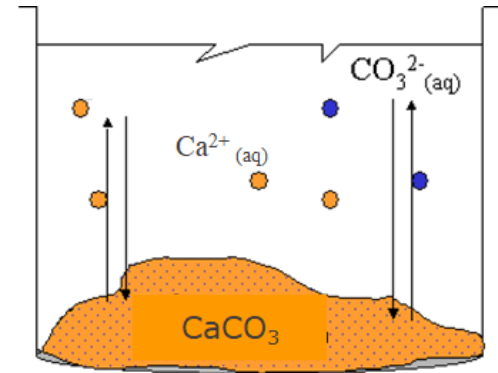
Gibbsite $\text{Al}(\text{OH})_3$, Mn oxides

Carbonates: calcite $\text{CaCO}_3(\text{s})$

Silicates: kaolinite, albite, SiO_2 (quartz)

Phosphates: hydroxyapatite

Sulfides: e.g., pyrite (FeS_2)



$$K_s = \{\text{Ca}^{2+}\} \{\text{CO}_3^{2-}\}$$

$$S_{\text{CaCO}_3} = \sqrt[1+1]{\frac{K_s}{1111}} = \sqrt{K_s}$$

Dissolution and precipitation

Solubility product (K_s) and ion product (IP): is a solution saturated?



The **solubility product** K_s is the product of the ion concentrations / activities **in equilibrium with the solid** (solution is saturated):

$$K_s = \{M_{(\text{aq})}\}^n \{X_{(\text{aq})}\}^m = \{\text{Ca}^{2+}\} \{\text{CO}_3^{2-}\}$$

The **ion product** IP is the product of the **actual** ion concentrations / activities (solution not necessarily saturated):

$$\text{IP} = \{\text{Ca}^{2+}\} \{\text{CO}_3^{2-}\}$$

If $\text{IP} > K_s$: the solution is **oversaturated**, the salt will precipitate

If $\text{IP} = K_s$: the solution is **saturated**

If $\text{IP} < K_s$: the solution is **undersaturated**, the salt will dissolve

Dissolution and precipitation

Exercise 4

Solubility (S) and solubility product (K_s) expressions:

Write the solubility S and the solubility product K_s for each of the following slightly soluble ionic compounds:

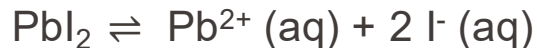
- (a) AgI, silver iodide, a solid with antiseptic properties
- (b) $\text{Ca}(\text{OH})_2$, calcium hydroxide, a mineral used to raise the pH in water treatment
- (c) $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, the mineral apatite, a source of phosphate for fertilizers

Dissolution and precipitation

Exercise 5

Calculate K_s from equilibrium concentrations:

Lead iodide, PbI_2 , is used as yellow paint pigment, and in the production of solar cells. It dissolved according to the equation:



In a saturated solution of PbI_2 the concentration of Pb^{2+} corresponds to 0.54 g/100 mL, or 0.0117 M. What is the K_s of PbI_2 ?

Exercise 6

Determine molar solubility from K_s :

Calcium hydroxide, Ca(OH)_2 , is often used in water treatment to lower water hardness, and to increase the pH (by releasing OH^- into solution) before discharging the treated drinking water into the distribution system. Ca(OH)_2 is well-suited for this, because it is quite soluble and therefore a good source of OH^- . Ca(OH)_2 has a K_s of $1.3 \times 10^{-6} \text{ M}^3$. What is the maximum OH^- concentration that can be reached by the addition of Ca(OH)_2 ?

Acid / base

- Acid-base reactions involve the transfer of a proton between the acid and the conjugated base.
- The strength of an acid (acidity) or base (basicity) is determined by the equilibrium constant (K_a or K_b) for its reaction with water.
- The acidity of a solution is measured in terms of pH. The pH influences a large number of environmentally relevant chemical and biological processes.

Redox

- Redox reactions involve the transfer of an electron. Each oxidation is accompanied by a reduction.
- The movement of electrons creates an electrochemical potential, which is determined by the activities of the oxidized and reduced substances, and can be calculated by the Nernst equation.

Precipitation / dissolution

- The tendency of a substance to dissolve or precipitate is determined by its solubility.
- The solubility product K_s is given by the equilibrium constant of the dissolution reaction. The bigger the K_s , the more soluble the salt.
- Dissolution and precipitation play a major role in regulating the concentration of environmentally important substances.