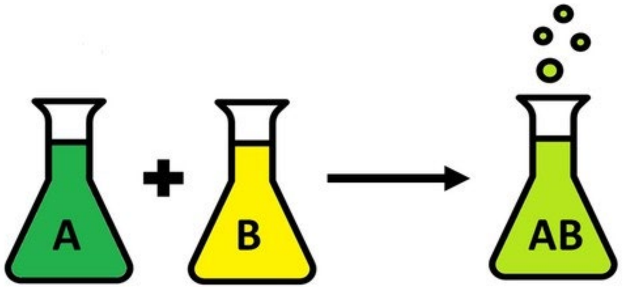

ENV-200 Revision of basic concepts

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Learning objectives

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.

Resources

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

Acid-base reactions

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. $pH = -\log[H^+]$

Acid-base reactions

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

$$CH_3COOH + H_2O \rightleftarrows H_3O^+ + CH_3COO^-$$

$$PO_4^{3-} + H_2O \rightleftarrows HPO_4^{2-} + OH^-$$

Definition:

Bronsted acid: molecule that can liberate a proton

Bronsted base: molecule that can accept a proton

Acid-base reactions

Examples of naturally occurring acids and bases:

The most important base: HCO_3^- / CO_3^{2-}

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

The most important acid: $CO_2(aq)$ or H_2CO_3

Other acids: H_4SiO_4, NH_4^+, $B(OH)_3$, H_2SO_4, CH_3COOH (acetic), $H_2C_2O_4$ (oxalic), etc.

Acid-base reactions

Autoprotolysis (self-ionization) of water

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$$

base — acid — conjugated acid (hydronium ion, also written as H+) — conjugated base (hydroxide ion)

Equilibriuim constant K_w = ion product of water

$K_w = [H_3O^+][OH^-] = 10^{-14}$ at 25 ^oC (K_w changes with temperature!)

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

$14 = pH+p[OH^-]$

Acid-base reactions

Acid hydrolysis: dissociation of an acid HA in water

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

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

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

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 $[H^+][OH^-]$. K_a is defined as $[H^+][OH^-]/[H_2O]$, with $[H_2O]$ = 55.4 M. So the pK_a of water is 15.75.

Acid-base reactions

Base hydrolysis: dissociation of a base B in water

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Equilibriuim (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 ($B^- + H_2O \rightleftharpoons BH + OH^-$)

Acid-base reactions

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad K_a$$

$$A^- + H_2O \rightleftharpoons OH^- + HA \qquad K_b$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad \boxed{K_w = K_a * K_b}$$

The stronger the acid, the weaker the conjugated base.

Strong acids ($pK_a < 2$) and strong bases ($pK_b < 2$) fully ionize in water (irreversible reaction):

$$HA + H_2O \rightarrow H_3O^+ + A^-$$

$$B + H_2O \rightarrow BH^+ + OH^-$$

Weak acids ($pK_a > 2$) and weak bases ($pK_b > 2$) only partially ionize in water (reversible reaction):

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Acid-base reactions

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

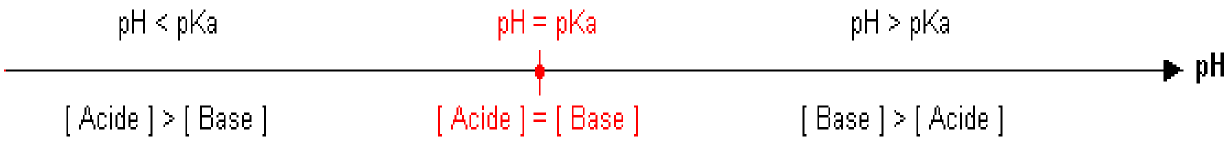
To answer these questions, consider the Henderson-Hasselbach equation:

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

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^-])

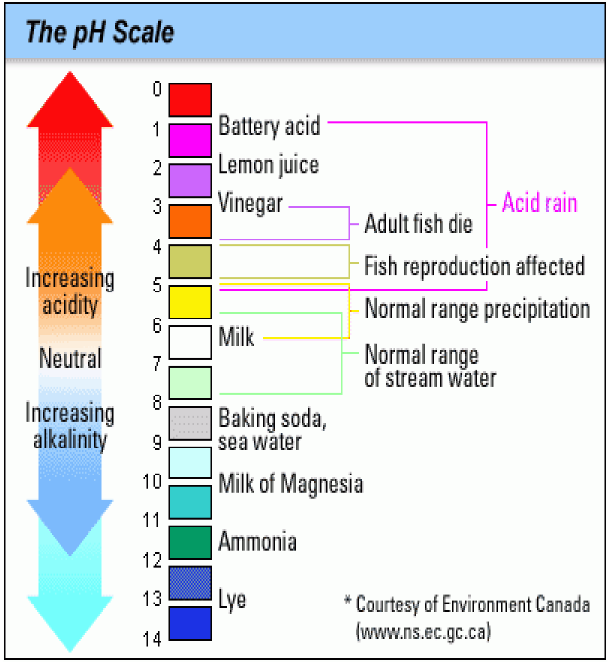


Acid-base reactions

The pH scale

pH<7, the solution is acidic
pH=7, the solution is neutral
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).



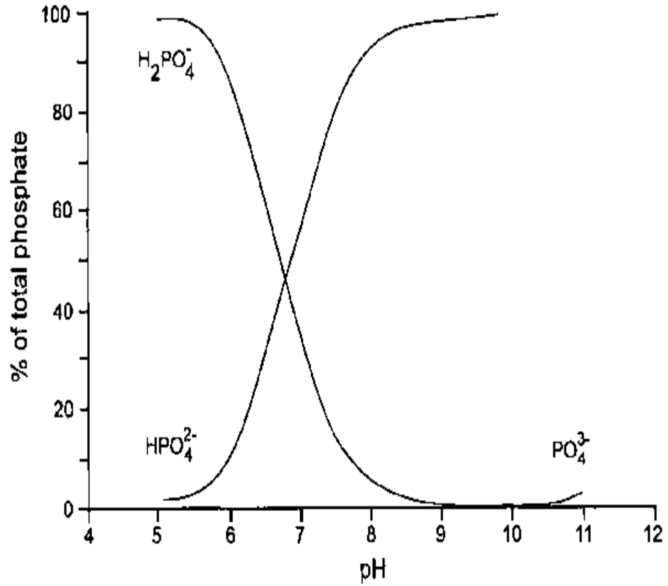
Acid-base reactions

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 $H_2PO_4^-$?



Acid-base reactions

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 ($[NH_4^+]+[NH_3]$). How much NH_3 is in the water?

pH = 8.5
T = 15^{o}C
$pK_a(NH_4^+)$ at 15^{o}C = 9.57.

Redox reactions

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)

Redox reactions

Are the following reactions redox reactions?

$$NaOH + HCl \rightleftharpoons Na^+ + Cl^- + H_2O$$

$$2\,HCl(aq) + FeS(s) \rightleftharpoons H_2S(aq) + FeCl_2(aq)$$

$$2\,KI + 2\,FeCl_3 \rightleftharpoons I_2 + 2\,FeCl_2 + 2\,KCl$$

Redox reactions

Generalized representation of a redox reaction:

$$Ox + mH^+ + ne^- \rightleftharpoons Red$$

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)

Redox reactions

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:

  $$6\ CH_2O + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$$

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

  $$2\ CH_2O + 2\ NO_3^- \rightarrow 2\ CO_3^{2-} + 2\ H_2O + N_2$$

- anoxic conditions (no oxygen):

  $$6\ CH_2O \rightarrow 3\ CH_4 + 3\ CO_2$$

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

Redox reactions

Equilibrating a redox reaction

$Fe(s) + Cl_2 \rightarrow Fe^{3+} + 2Cl^-$

1: Determine the oxidation number in each element.

$Fe^o + Cl_2^o \rightarrow Fe^{3+} + 2Cl^-$

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

$Fe^o - 3\ e- \rightarrow Fe^{3+}$

$Cl_2 + 2\ e- \rightarrow 2Cl^-$

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

$2Fe + 3Cl_2 \rightarrow 2Fe^{3+} + 6Cl^-$

4: Verify the mass and charge balance.

Redox reactions

Exercise 3

Equilibrate the following reaction:

Fe^{2+} + O_2 + $H_2O \leftrightarrow Fe(OH)_3$

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 $Fe(OH)_3$(s).

Redox reactions

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).

Ox + ne- $\rightleftarrows$ Red

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

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)

Redox reactions

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 $E_{SHE}^0 = 0.0$ 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 to redox partners (under standard conditions)

Redox reactions

Electrochemical series

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

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

Dissolution and precipitation

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:

$$M_nX_m(\text{solid}) \rightleftharpoons nM(aq) + mX(aq)$$

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

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

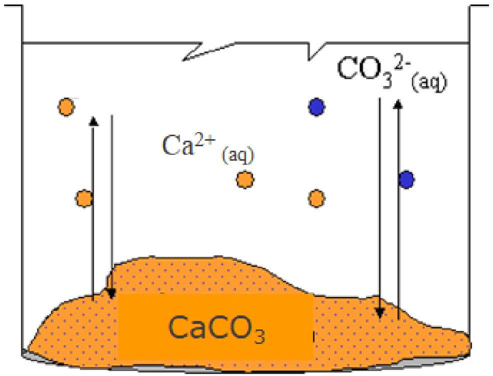
Oxides and hydroxides: $Fe(OH)_3(s)$, FeOOH, Fe_2O_3
Gibbsite($Al(OH)_3$) , Mn oxides

Carbonates: calcite $CaCO_3$ (s)

Silicates: kaolinite, albite, SiO_2 (quartz)

Phosphates: hydroxyapatite

Sulfides: e.g., pyrite (FeS_2)



$CaCO_3\,(s) \leftrightarrow Ca^{2+} + CO_3^{2-}$

$K_s = \{Ca^{2+}\}\{CO_3^{2-}\}$

$S_{CaCO3} = \sqrt[1+1]{\frac{K_s}{1^1 1^1}} = \sqrt{K_s}$

Dissolution and precipitation

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

Example $CaCO_3$: $CaCO3(s) \leftrightarrow Ca^{2+} + CO_3^{2-}$

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

$$K_s = \{M_{(aq)}\}^n \{X_{(aq)}\}^m = \{Ca^{2+}\}\{CO_3^{2-}\}$$

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

$$IP = \{Ca^{2+}\}\{CO_3^{2-}\}$$

If IP > K_s: the solution is oversaturated, the salt will precipitate
If IP = K_s: the solution is saturated
If 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) $Ca(OH)_2$, calcium hydroxide, a mineral used to raise the pH in water treatment

(c) $Ca_5(PO_4)_3OH$, 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:

$$PbI_2 \rightleftarrows Pb^{2+} (aq) + 2\ I^- (aq)$$

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?

Dissolution and precipitation

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 is quite soluble and therefore a good source of OH^-. $Ca(OH)_2$ has a K_s of 1.3×10^{-6} M^3. What is the maximum OH^- concentration that can be reached by the addition of $Ca(OH)_2$?

Summary

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.