Exercise 1: Ion activity

What are the activity and concentration of Na^+ in a solution of 1 mM NaCl?

Exercise 1: Solution

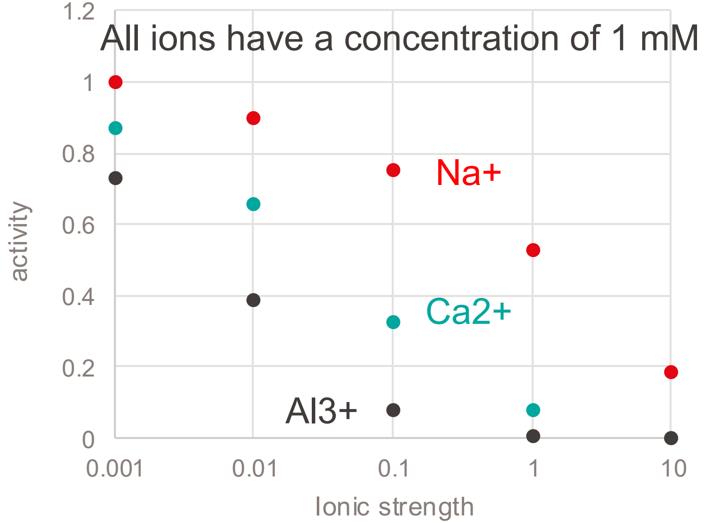
First, determine I. Before (example 1 from 2 slides ago), we found that in a 1 mM NaCl solution:

$I = 0.5 *(C_{Na+} * z^2_{Na+} + C_{Cl-} * z^2_{Cl-}) = 0.5*(10^{-3} * 1^2 + 10^{-3} * (-1)^2) = 10^{-3}$ M

$$\log\gamma_i = -A \cdot z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2 \cdot I \right) = -0.5 \cdot 1 \cdot \left(\frac{\sqrt{0.001}}{1+\sqrt{0.001}} - 0.2 \cdot 0.001 \right) = -0.01523$$

$\gamma_i = 10^{-0.01523} = 0.966$

Therefore, $\{Na^+\} = 0.966$ mM, whereas $[Na^+] = 1$ mM



Exercise 2: Freshwater vs. seawater

Freshwater and seawater have very different ion concentrations and thus, chemical species will have different activities. This exercise illustrates the effect of these differences on the dissolution of calcite ($CaCO_3$).

1. A lake is at 25°C and equilibrated with the atmosphere ($[CO_3^{2-}] = 1.153 * 10^{-5}$ M). The dissolved calcium concentration is 0.25 mM. Assume negligible ionic strength. The K_{s0} for calcite is $3.31 * 10^{-9}$. Determine if the water is over- or undersaturated with respect to calcite.

Exercise 2: Solution

IAP=$[Ca^{2+}][CO_3^{2-}]=(2.50*10^{-4})(1.153*10^{-5}) = 2.88\times10^{-9}$.

This value is below the K_{s0} for calcite, i.e., the system is undersaturated with respect to calcite and calcite will dissolve.

Exercise 2: Freshwater vs. seawater

2. Now consider surface seawater at 25°C with $[Ca^{2+}]$ = 10.3 mM and $[CO_3^{2-}]$ = 200 µM. Consider activity coefficients of γ_{Ca2+}= 0.23 and γ_{CO32-} = 0.1 in your calculations. The K_{s0} for calcite is $3.31 * 10^{-9}$. Determine if the water is over- or undersaturated with respect to calcite.

Exercise 2: Solution

$IAP=(\gamma_{Ca2+}[Ca^{2+}])(\gamma_{CO32-}[CO_3^{2-}])$

$= (0.23*10.3*10^{-3})(0.10*200*10^{-6}) = 4.74*10^{-8}$.

This value is above K_{s0} for calcite, i.e., the system is supersaturated with respect to calcite and calcite tends to precipitate.

Solubility of metals in natural waters

- Which factors influence metal solubility?
- Does an increase/decrease of these factors have a positive or negative effect on solubility?

Solubility of metals in natural waters

- Temperature
  - Solubility of salts increases with increasing temperature
  - Entropy effect (heat provides energy to break bonds in the solid)
- Salinity
  - Solubility increases with increasing salinity
  - Due to inter-ionic interactions
- pH
  - Important for minerals that have anions that can be protonated/deprotonated
  - Protonation of basic anion (lower pH) increases solubility
- Complexation
  - Solubility increases with increasing complexation
  - Due to masking of metal ion

Exercise 3: Gypsum in natural waters

1. Is each water sample (water of Lake Zürich vs. groundwater in Glattfelden) undersaturated, at equilibrium, or supersaturated with respect to gypsum ($CaSO_4 \cdot 2H_2O$)? Assume $\gamma_i = 1$.

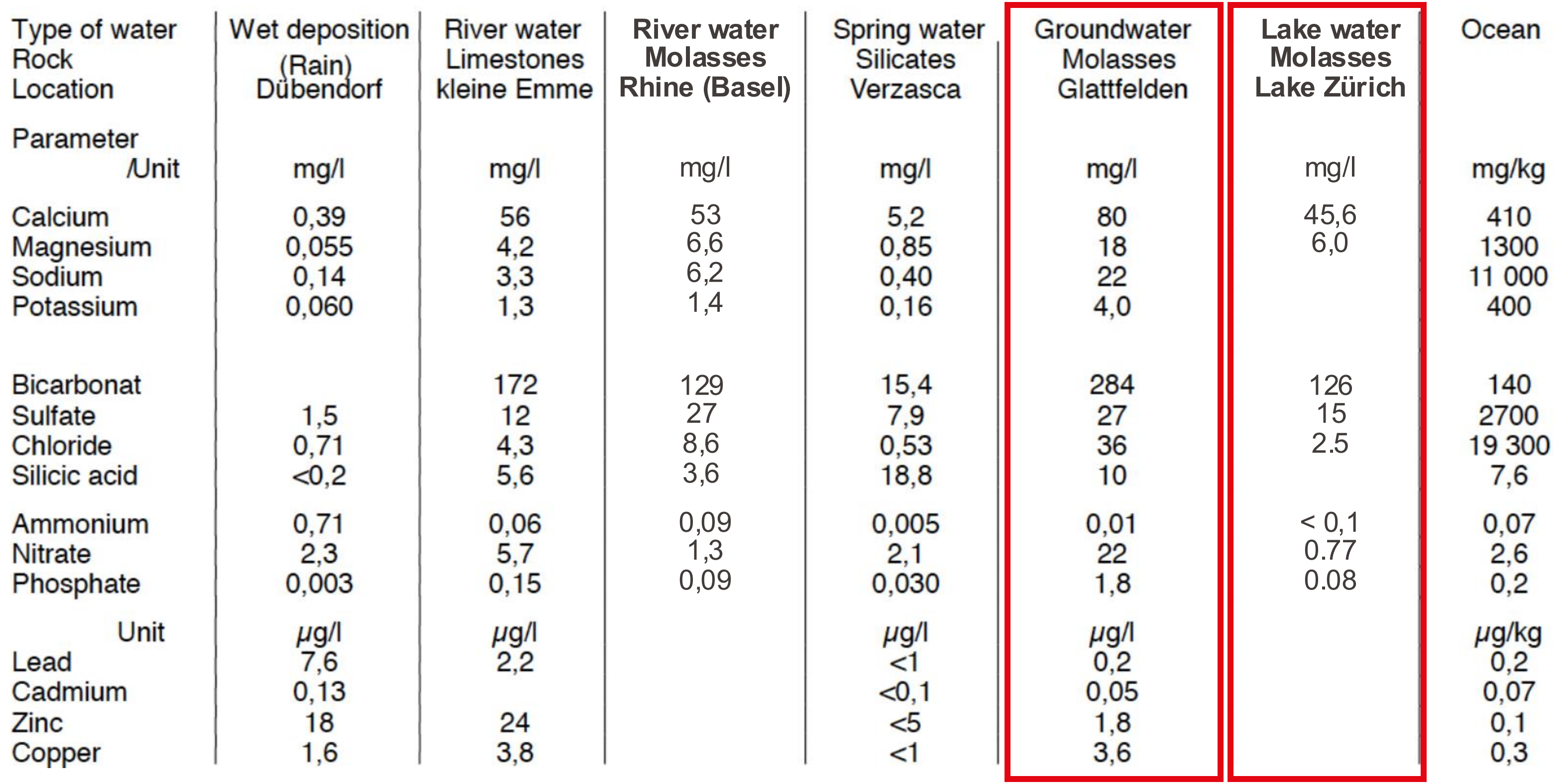
   $CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-}$ $K_{s0} = 10^{-4.58}$

   M_w Ca^{2+} = 40.08 g/mol

   M_w SO_4^{2-} = 96.06 g/mol

2. Why do lake water and groundwater differ in their chemical composition and degree of mineral saturation?

Exercise 3: Gypsum in natural waters



Type of water Rock Location	Wet deposition (Rain) Dübendorf	River water Limestones kleine Emme	**River water** **Molasses** **Rhine (Basel)**	Spring water Silicates Verzasca	Groundwater Molasses Glattfelden	**Lake water** **Molasses** **Lake Zürich**	Ocean
Parameter /Unit	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/kg
Calcium	0,39	56	53	5,2	80	45,6	410
Magnesium	0,055	4,2	6,6	0,85	18	6,0	1300
Sodium	0,14	3,3	6,2	0,40	22		11 000
Potassium	0,060	1,3	1,4	0,16	4,0		400
Bicarbonat		172	129	15,4	284	126	140
Sulfate	1,5	12	27	7,9	27	15	2700
Chloride	0,71	4,3	8,6	0,53	36	2.5	19 300
Silicic acid	<0,2	5,6	3,6	18,8	10		7,6
Ammonium	0,71	0,06	0,09	0,005	0,01	< 0,1	0,07
Nitrate	2,3	5,7	1,3	2,1	22	0.77	2,6
Phosphate	0,003	0,15	0,09	0,030	1,8	0.08	0,2
Unit	µg/l	µg/l		µg/l	µg/l		µg/kg
Lead	7,6	2,2		<1	0,2		0,2
Cadmium	0,13			<0,1	0,05		0,07
Zinc	18	24		<5	1,8		0,1
Copper	1,6	3,8		<1	3,6		0,3

Exercise 3: Solution

1. Step 1: Convert concentrations to molar concentrations

   Lake Zürich:

   $[Ca^{2+}] = 45.6/40.08 = 1.13 * 10^{-3}$ mol/L

   $[SO_4^{2-}] = 15/96.06 = 1.56*10^{-4}$ mol/L

   Glattfelden:

   $[Ca^{2+}] = 80/40.08 = 2.00 * 10^{-3}$ mol/L

   $[SO_4^{2-}] = 27/96.06 = 2.81*10^{-4}$ mol/L

   Step 2: Calculate IAP

   Lake Zürich: $(1.13*10^{-3})(1.56*10^{-4}) = 1.76*10^{-7}$

   Glattfelden: $(2.00*10^{-3})(2.81*10^{-4}) = 5.62*10^{-7}$

   Step 3: Compare IAP to K_{s0} ($K_{s0} = 10^{-4.58}$)

   Lake Zürich: IAP $<<$ K_{s0} undersaturated

   Glattfelden: IAP $<$ K_{s0} undersaturated

2. Both waters are **undersaturated** with respect to gypsum. The **groundwater** is **closer to saturation**, reflecting its longer residence time and greater mineral contact.

Exercise 4: Multiple solid phases

Consider an anoxic water at pH 6.8 and $\{HCO_3^-\} = 10^{-4}$ eq L^{-1} (= 10^{-4} M). Assume $\gamma_i = 1$.

Is the solubility of Fe(II) dominated by siderite ($FeCO_3(s)$) or $Fe(OH)_2(s)$? Note that the solid that gives the lowest concentration of soluble Fe(II) controls the solubility for a given set of conditions.

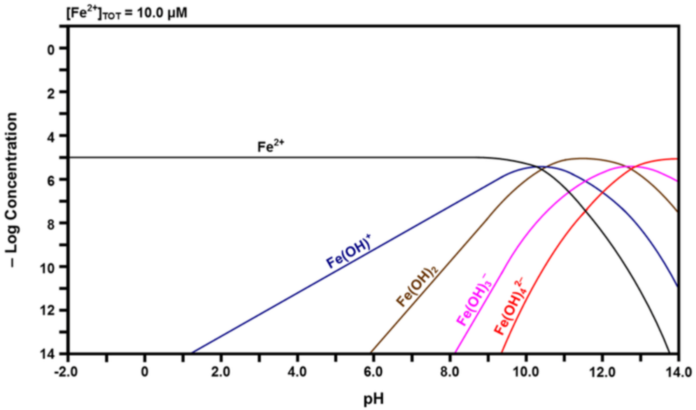
(Fe(II) encompasses all soluble iron species with an oxidation state of (+II); at pH 6.8, the dominant species is free aqueous Fe^{2+}, so we neglect any hydroxo- or carbonato complexes)

$FeCO_3(s) = Fe^{2+} + CO_3^{2-}$ $\log K_{s0} = -10.4$

$H^+ + CO_3^{2-} = HCO_3^-$ $-\log K_{a2} = +10.33$

$Fe(OH)_2(s) = Fe^{2+} + 2OH^-$ $\log K_{s0} = -14.5$

$2H^+ + 2OH^- = 2H_2O$ $-2\log K_w = +27.8$



Exercise 4: Solution

For Siderite $FeCO_3(s)$:

1. Combine the equations

   $(Fe^{2+})(CO_3^{2-}) = K_{s0}$
   $(HCO_3^-)/(H^+)(CO_3^{2-}) = 1/K_{a2}$; or $(CO_3^{2-}) = K_{a2}*(HCO_3^-)/(H^+)$
   Insert the second equation into the first to get:
   $(Fe^{2+})*K_{a2}*(HCO_3^-)/(H^+) = K_{s0}$

2. Solve for Fe^{2+}

   $(Fe^{2+}) = K_{s0}/K_{a2} *(H^+)/(HCO_3^-)$
   and on a log scale
   $\log (Fe^{2+}) = \log K_{s0} - \log K_{a2} - pH - \log(HCO_3^-)$
   $\underline{\log (Fe^{2+})} = -10.4 + 10.33 - 6.8 + 4 = \underline{-2.87}$

Exercise 4: Solution

For $Fe(OH)_2(s)$:

1. Combine the equations

   $(Fe^{2+})(OH^{-})^2 = K_{s0}$

   H_2O / $(H^+)(OH^-) = 1/K_w$; or $(OH^-) = K_w{*}(H_2O)/(H^+)$

   Insert the second equation into the first to get:

   $(Fe^{2+}){*}(K_w/H^+)^2 = K_{s0}$

2. Solve for Fe^{2+}

   $(Fe^{2+}) = K_{s0}/K_w^2 \, {*}(H+)^2$

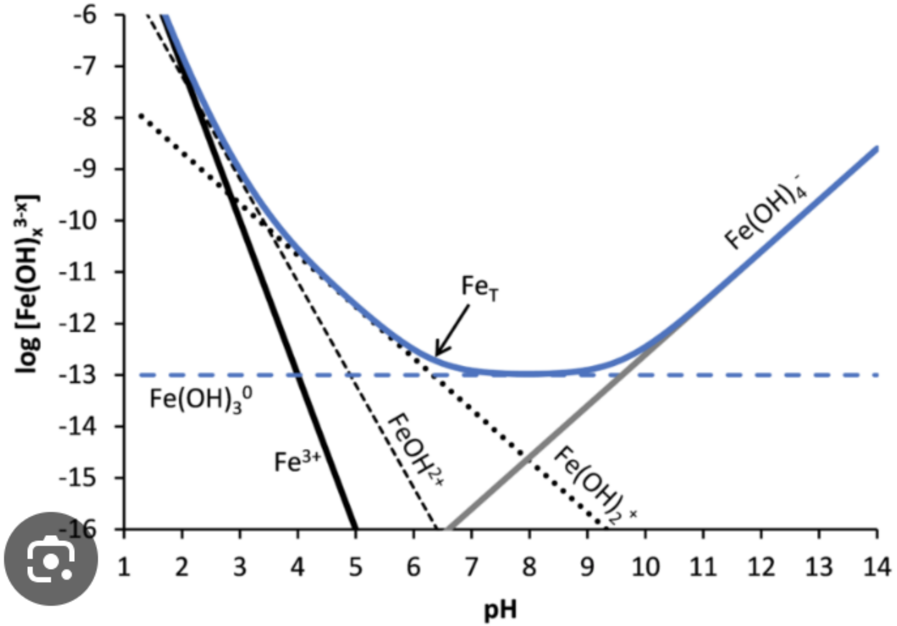
   And on a log scale

   $\log (Fe^{2+}) = \log K_{s0} – 2\log K_w – 2pH$

   $\underline{\log (Fe^{2+})} = -14.5 + 27.8 – 2{*}6.8 = \underline{-0.32}$

Exercise 4: Solution

Because [Fe(II)] is smaller for hypothetical equilibrium with $FeCO_3$(s) than with $Fe(OH)_2$, $FeCO_3$(s) is more stable than $Fe(OH)_2$(s).



Exercise 5: Flocculation

Flocculation is a process by which a chemical coagulant added to the water acts to facilitate bonding between particles, creating larger aggregates which are easier to separate. The method is widely used in water treatment plants.

Example by Urs Von Gunten

Exercise 5: Flocculation

Aluminium is often used as a flocculant in water treatment. To achieve the best results, the pH of minimum solubility should be used. To identify the pH of minimum solubility, sketch the aluminum speciation as a function of pH in a log-log plot.

$Al(OH)_3(s) = Al^{3+} + 3\ OH^-$	$\log K_{s0} = -33.9$	eq. 1
$Al^{3+} + H_2O = Al(OH)^{2+} + H^+$	$\log {}^*K_1 = -5$	eq. 2
$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$	$\log {}^*\beta_2 = -10.13$	eq. 3
$Al^{3+} + 3H_2O = Al(OH)_3(aq) + 3H^+$	$\log {}^*\beta_3 = -16.63$	eq. 4
$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$	$\log {}^*\beta_4 = -22.2$	eq. 5
$H_2O = H^+ + OH^-$	$\log K_w = -14.0$	eq. 6

Exercise 5: Solution

From eq. 6 it follows that $K_w = [OH^-][H^+]$, thus $[OH-] = K_w / [H^+]$

Fill this expression into eq. 1 to get $[Al^{3+}] = K_{s0} [H^+]^3 / K_w^3$

Taking logs: $\log [Al^{3+}] = \log(K_{s0} K_w^{-3}) - 3\,pH = \underline{8.1 - 3\,pH}$

From eq. 2 it follows that $[Al(OH)^{2+}] = [Al^{3+}] {}^*K_1 / [H^+] = K_{s0} {}^*K_1 [H^+]^2 / K_w^3$

And thus $\log [Al(OH)^{2+}] = \log(K_{s0} K_w^{-3} {}^*K_1) - 2\,pH = \underline{3.1 - 2\,pH}$

$Al(OH)_2^+ = [Al^{3+}] {}^*\beta_2 / [H^+]^2 = K_{s0} {}^*\beta_2 [H^+] / K_w^3$

$\log [Al(OH)_2^+] = \log(K_{s0} K_w^{-3} {}^*\beta_2) - pH = \underline{-2.0 - pH}$

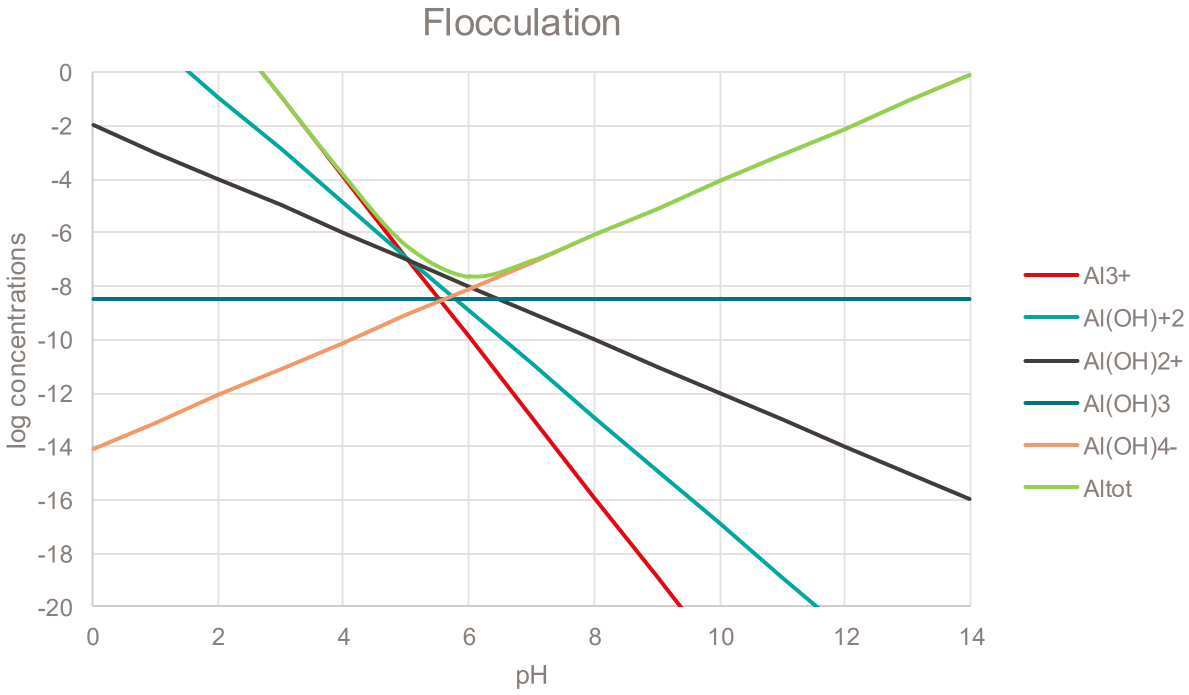
$Al(OH)_3 = [Al^{3+}] {}^*\beta_3 / [H^+]^3 = K_{s0} {}^*\beta_3 / K_w^3$

$\log [Al(OH)_3] = \log(K_{s0} K_w^{-3} {}^*\beta_3) = \underline{-8.5}$

$Al(OH)_4^- = [Al^{3+}] {}^*\beta_4 / [H^+]^4 = K_{s0} {}^*\beta_4 [H^+]^{-1} / K_w^3$

$\log [Al(OH)_4^-] = \log(K_{s0} K_w^{-3} {}^*\beta_4) + pH = \underline{-14.1 + pH}$

Exercise 5: Solution



The best results will be obtained at pH 6 when Al_{tot} is lowest.

Flint water crisis- before 2014

Phosphate (PO_4^{3-}) was added to precipitate all metal cations and inhibit corrosion in the Detroit plant.

a. What reactions can phosphate (use Na_3PO_4) undergo with $FeCl_2(aq)$ and $Pb(NO_3)_2(aq)$ in solution?

b. What effect does the addition of PO_4^{3-} have on pH?

Flint water crisis- before 2014

a. Phosphate formed solid phases with Fe(II) and Pb(II) which resulted in the formation of a passivation layer in the pipes:

$2Na_3PO_4 + 3FeCl_2 \rightleftharpoons Fe_3(PO_4)_2(s) + 6NaCl$

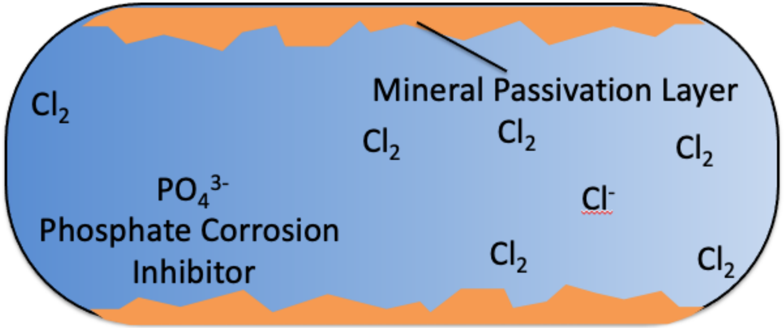
$2Na_3PO_4 + 3Pb(NO_3)_2 \rightleftharpoons Pb_3(PO_4)_2(s) + 6NaNO_3$

b. Furthermore, phosphate buffered pH

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

$PO_4^{3-} + H^+ \rightleftharpoons HPO_4^{2-}$

$Pb^{2+} + 2OH^- \rightleftharpoons Pb(OH)_2(s)$



Flint water crisis- after 2014

Flint's water supply was switched to the city's own water treatment plant on the Flint River. Phosphate was NOT added to the Flint River water in the new plant.

a. What effects does this have on the passivation layer in the pipes and why?

b. In the absence of a passivation layer, what other chemical reactions can occur between the water and metals in the pipes?

Flint water crisis- after 2014

a. Effect of phosphate removal:
  - Removal of dissolved $Fe^{2+/3+}$ and $Pb^{2+/4+}$ no longer possible
  - Acidic river water directly dissolves passivation layer by neutralizing OH^-
  - Result: The passivation layer dissolved, exposing the metal pipes.

b. This lead to corrosion of the pipes as metals came in contact with oxidants O_2 and Cl^-
  - Pb is oxidized by O_2 to Pb^{2+} which is mobile
  - Iron corrosion (reaction with O_2) leads to rust-colored water
  - Exposed iron reduced free chlorine (Cl_2) which is used as disinfectant in this system

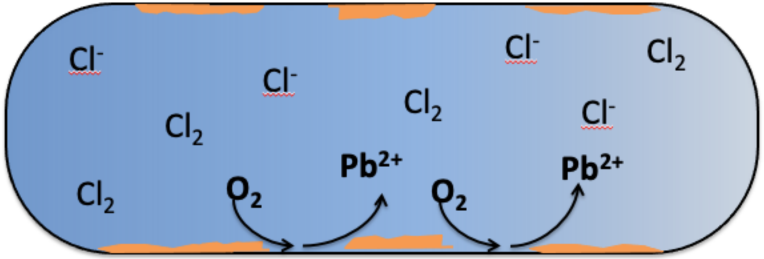
Flint water crisis- after 2014

Redox reactions will be the topic of the next class!

Lead pipes: lead is oxidized by dissolved oxygen

$2Pb(s)\ + O_2 + 4H^+ \rightleftharpoons 2Pb^{2+}(aq) + 2H_2O$

$2Fe(s)\ + O_2 + 4H^+ \rightleftharpoons 2Fe^{2+}(aq) + 2H_2O$



Iron pipes: iron is oxidized by dissolved oxygen and chlorine. Precipitation of iron oxides turns water rust colored.

$Fe(s)\ + Cl_2 \rightleftharpoons FeCl_2$