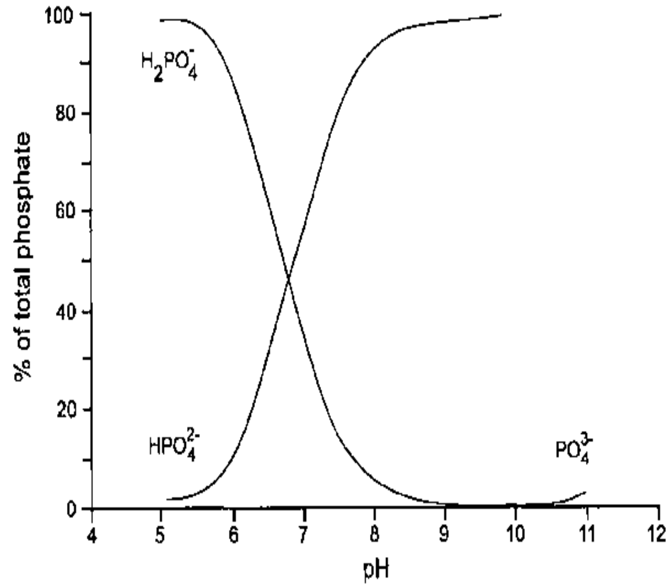
Acid-base reactions

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 $H_2PO_4^-$?

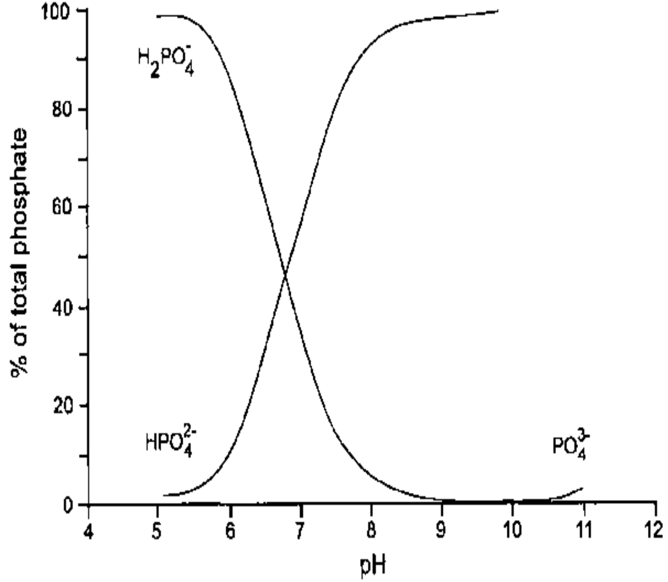


Acid-base reactions

Exercise 1 - Solution

The dominant species is HPO_4^{2-}.

The pK_a is the pH where the acidic species and its conjugated base are at equal concentrations, so $[H_2PO_4^-]=[HPO_4^{2-}]$. This is the case where the two lines for these species intersect, i.e. at around 7.



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°C
$pK_a(NH_4^+)$ at 15 °C = 9.57.

Acid-base reactions

Exercise 2 - Solution

We have 2 unknowns ($[NH_4^+]$,$[NH_3]$) and thus need 2 equations:

1. total ammonium = $[NH_4^+]+[NH_3]$; so $[NH_3]$ = total ammonium – $[NH_4^+] = 3x10^{-5} – [NH_4^+]$
2. $pH = pK_a - \log([NH_4^+]/[NH_3])$

Substitute 1. into 2.:

$8.5 = 9.57 – \log([NH_4^+]/(3x10^{-5} – [NH_4^+])$

$-1.07 = - \log([NH_4^+]/(3x10^{-5} – [NH_4^+])$

$10^{1.07} = [NH_4^+]/(3x10^{-5} – [NH_4^+])$

$10^{1.07}x3x10^{-5} = [NH_4^+] + 10^{1.07} x [NH_4^+]$

$3.52x10^{-4} = 12.75 [NH_4^+]$

$[NH_4^+]$= 2.75x10^{-5} M (the pH is ca. 1 unit < pK_a, so this should be about right).

$[NH_3]$= 3x10^{-5} - 2.75x10^{-5} = 0.25 x 10^{-5} M

Redox reactions

Exercise 3

Equilibrate the following reaction:

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

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

Exercise 3 - solution

Step 1: divide equation into half-reactions and balance each half reaction for mass and charge

$Fe^{2+} = Fe^{3+} + 1e-$

$1/4O_2 + H^+ + e- = ½ H_2O$

Step 2: equalize the number of e- transferred

Multiply each half reaction by 4:

$4Fe^{2+} = 4Fe^{3+} + 4e-$

$O_2 + 4H^+ + 4e- = 2H_2O$

Consider precipitation of $Fe(OH)_3$ and multiply by 4:

$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$

$4Fe^{3+} + 12 H_2O = 4Fe(OH)_3 + 12H^+$

Step 3: add half-reactions and precipitation reaction together

$4Fe^{2+} + O_2 + 4 H^+ + 12H_2O = 4Fe(OH)_3 + 12 H^+ + 2H_2O$

Step 4: balance H+ and H_2O

$\mathbf{4Fe^{2+} + O_2 + 10H_2O = 4Fe(OH)_3 + 8 H^+}$

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 4 - solution

(a) AgI

$AgI(s) \rightleftharpoons Ag^{+}(aq) + I^{-}(aq)$; $K_s = \{Ag^{+}\}\{I^{-}\}$; $S = \sqrt[1+1]{\frac{K_s}{1^1 1^1}} = \sqrt{K_s}$

(b) $Ca(OH)_2$

$Ca(OH)_2 \rightleftharpoons Ca^{2+}(aq) + 2\,OH^{-}(aq)$; $K_s = \{Ca^{+}\}\{OH^{-}\}^2$

$$S = \sqrt[1+2]{\frac{K_s}{1^1 2^2}} = \sqrt[3]{\frac{K_s}{4}}$$

(c) $Ca_5(PO_4)_3OH$

$Ca_5(PO_4)_3OH \rightleftharpoons 5\,Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^{-}(aq)$

$K_s = \{Ca^{+}\}^5\{PO_4^{3-}\}^3\{OH^{-}\}$

$$S = \sqrt[5+3+1]{\frac{K_s}{5^5 3^3 1^1}} = \sqrt[9]{\frac{K_s}{84375}}$$

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:

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

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 5 - Solution

$PbI_2 \rightleftharpoons Pb^{2+} (aq) + 2 I^- (aq)$; $S = 0.0117$ M

If the concentration of Pb^{2+} in saturated solution is 0.0117 M, this implies that the solubility S of PbI_2 is also 0.0117 M. To find K_s, consider that the stoichiometry is 1:2. So at equilibrium with the solid, we have 0.0117 M Pb^{2+}, and 0.0234 M I^- in solution. Now use this to find:

$K_s = [Pb^{2+}][I^-]^2 = 6.4 \times 10^{-6}\ M^3$

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 $Ca(OH)_2$?

Dissolution and precipitation

Exercise 6 - solution

The dissolution equation and solubility product expression are

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

$K_S=[Ca^{2+}][OH^{-}]^2$

The solubilty of $Ca(OH)_2$:

$$S = \sqrt[1+2]{\frac{K_s}{1^1 2^2}} = \sqrt[3]{\frac{K_s}{4}} = (1.3 \times 10^{-6} / 4)^{1/3} = 0.007\ M$$

Each mol of $Ca(OH)_2$ will release 1 mol of Ca^{2+} and 2 mol of OH^-.

So the maximal (i.e., saturation) concentration of OH^- is $2 \times 0.007\ M = 0.014\ M$