

Acid-base reactions

Exercise 1

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

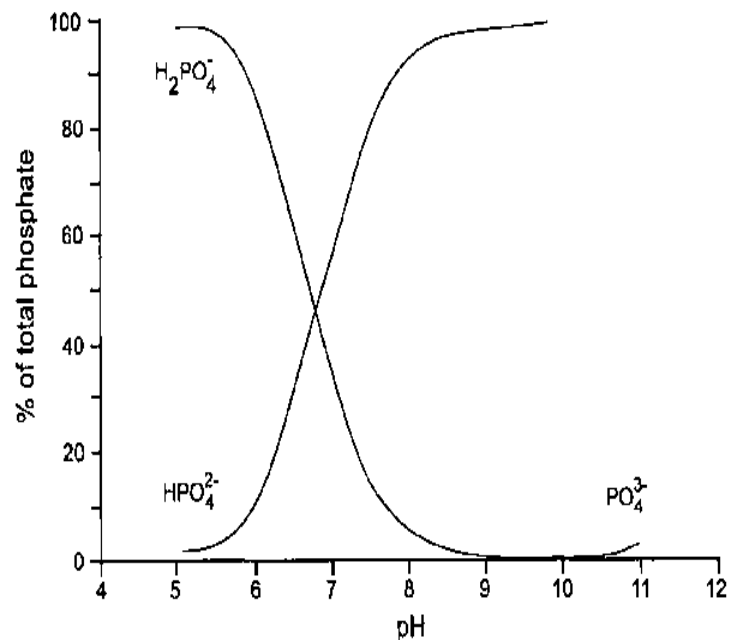
What are the dominant phosphate species in a lake with pH 8?

What is the pKa of H_2PO_4^- ?

Answer:

The dominant species is HPO_4^{2-} .

The pKa is the pH where the acidic species and its conjugated base are at equal concentrations, so $[\text{H}_2\text{PO}_4^-] = [\text{HPO}_4^{2-}]$. 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 ($[\text{NH}_4^+] + [\text{NH}_3]$). How much NH_3 is in the water?

$$\text{pH} = 8.5$$

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

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

Acid-base reactions

Exercise 2 - solutions

We have 2 unknowns ($[\text{NH}_4^+]$, $[\text{NH}_3]$) and thus need 2 equations:

1. total ammonium = $[\text{NH}_4^+] + [\text{NH}_3]$;

so $[\text{NH}_3] = \text{total ammonium} - [\text{NH}_4^+] = 3 \times 10^{-5} - [\text{NH}_4^+]$

2. $\text{pH} = \text{pKa} - \log([\text{NH}_4^+]/[\text{NH}_3])$

$$8.5 = 9.57 - \log([\text{NH}_4^+]/(3 \times 10^{-5} - [\text{NH}_4^+]))$$

$$-1.07 = -\log([\text{NH}_4^+]/(3 \times 10^{-5} - [\text{NH}_4^+]))$$

$$10^{1.07} = [\text{NH}_4^+]/(3 \times 10^{-5} - [\text{NH}_4^+]))$$

$$10^{1.07} \times 3 \times 10^{-5} = [\text{NH}_4^+] + 10^{1.07} \times [\text{NH}_4^+]$$

$$3.52 \times 10^{-4} = 12.75 [\text{NH}_4^+]$$

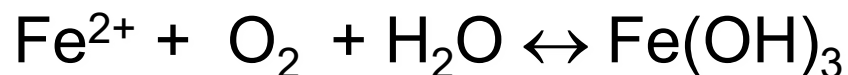
$[\text{NH}_4^+] = 2.75 \times 10^{-5} \text{ M}$ (the pH is ca. 1 unit < pKa, so this should be about right).

$$\textbf{[NH}_3\textbf{]} = 3 \times 10^{-5} - 2.75 \times 10^{-5} = 0.25 \times 10^{-5} \textbf{ M}$$

Redox reactions

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 $\text{Fe}(\text{OH})_3(\text{s})$.

Redox reactions

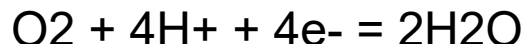
Exercise 3 - solutions

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

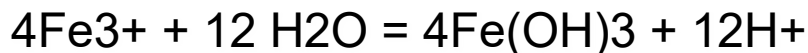
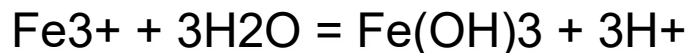


Step 2: equalize the number of e⁻ transferred

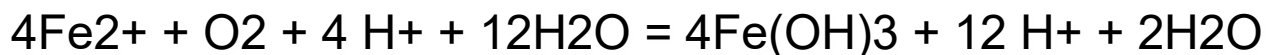
Multiply each half reaction by 4:



Consider precipitation of Fe(OH)₃ and multiply by 4:



Step 3: add half-reactions together



Step 4: balance H⁺ and H₂O



Dissolution and precipitation

Exercise 4

Solubility (S) and solubility product (K_s) expressions

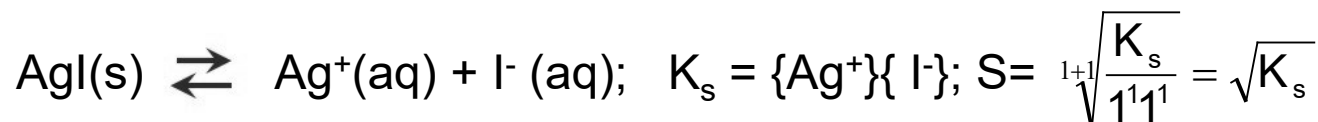
Write the solubility S and the solubility product K_s for each of the following slightly soluble ionic compounds:

- (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

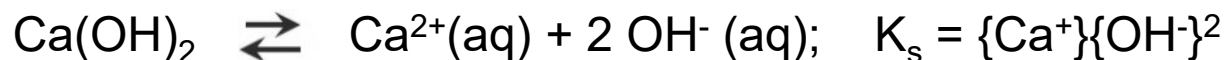
Dissolution and precipitation

Exercise 4 - solutions

(a) AgI



(b) Ca(OH)_2



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

(c) $\text{Ca}_5(\text{PO}_4)_3\text{OH}$



$$K_s = \{\text{Ca}^+\}^5 \{\text{PO}_4^{3-}\}^3 \{\text{OH}^-\}$$

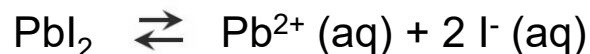
$$S = \sqrt[5+3+1]{\frac{K_s}{5^5 3^3 1^1}} = \sqrt[9]{\frac{K_s}{84375}}$$

Dissolution and precipitation

Exercise 5

Calculate K_s from Equilibrium Concentrations

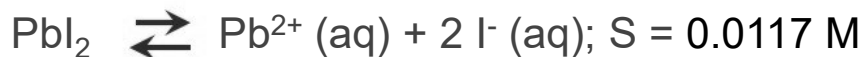
Lead Iodide, PbI_2 , is used as yellow paint pigment, and in the production of solar cells. It dissolved according to the equation:



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 - solutions



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:

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

Dissolution and precipitation

Exercise 6

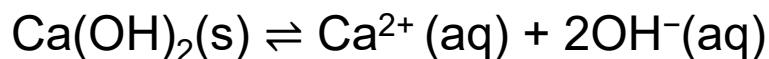
Determine molar solubility from K_s

Calcium hydroxide, $\text{Ca}(\text{OH})_2$, 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. $\text{Ca}(\text{OH})_2$ is well-suited for this, because it is quite soluble and therefore a good source of OH^- . $\text{Ca}(\text{OH})_2$ 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 $\text{Ca}(\text{OH})_2$?

Dissolution and precipitation

Exercise 6 - solutions

The dissolution equation and solubility product expression are



$$K_s = [\text{Ca}^{2+}][\text{OH}^{-}]^2$$

The solubility of Ca(OH)_2 :

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

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 $2 \times 0.007 \text{ M} = 0.014 \text{ M}$