

2.2 Acid mine drainage

Problem 2.2 *The weathering of iron sulphide minerals produces acidified water, leading to major environmental problems from abandoned metal and coal mines. If the water is then diluted or neutralised such that the pH is raised sufficiently, a sludge is precipitated, consisting of $Fe(OH)_3$, which can discolour water systems and affect plant and animal life.*

The redox reaction in this acid mine drainage can be summarised by the equation (as yet unbalanced): $FeS_2 + \text{oxygen} + \text{water} \rightarrow \text{sludge} + H_2SO_4$

- *How many litres of water would be used up in a reaction with a cubic metre of pyrite and how much sulphuric acid is produced?*
 - *If this acid finds its way into a lake, how could you predict whether the sludge is likely to be formed?*
- Assume that the acid completely dissociates. This isn't completely true, there is an equilibrium point (as we will see in a later problem).
 - Pyrite has a density of 5.01 g cm^{-3} .
 - The sludge forms at a pH greater than 3.
 - Assume the lake contains a million cubic metres of water.

2.2.1 Notes

Do you know what pH is? Do you know what redox is? If not see if anyone in your group does.

1. First thing to do is create a balanced equation: $4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4$. Note that the oxygen is being used up, which has the effect of oxidising the Fe^{2+} in pyrite to Fe^{3+} in the hydroxide.
 - If we assume the acid completely dissociates then one mole of acid (H_2SO_4) gives two moles of H^+ ions. Note from the appendix that $pH = -\log_{10}[H^+]$ where $[H^+]$ is the concentration of H^+ ions (moles per litre).
 - Note, we shall work on 1 m^3 of pyrite.
 - With a density of 5.01 g cm^{-3} , 1 m^3 of pyrite is 5010 kg. The molecular weight of pyrite FeS_2 is $56 + 32 \times 2 = 120 \text{ g mole}^{-1}$ so the number of moles in 1 m^3 is $\frac{5.01 \times 10^6 \text{ g m}^{-3}}{120 \text{ g mole}^{-1}} = 4.175 \times 10^4$ moles.
 - From the balanced equation the amount of moles of water used is number of moles multiplied by $14/4$ so $4.175 \times 10^4 \times 14/4 \cong 1.46 \times 10^5$ moles. The molecular weight of water is 18 g mole^{-1} so the mass of water is $1.46 \times 10^5 \text{ moles} \times 18 \text{ g mole}^{-1} \cong 2.63 \times 10^6$ grams.
 - Since water has a density of 1000 kg m^{-3} the volume of the 2.63×10^6 grams of water is: $2.63 \times 10^6 \text{ g} \times 10^{-3} \text{ kg g}^{-1} \div 1000 \text{ kg m}^{-3} \cong 2.63 \text{ m}^3$ or 2630 litres.

- The amount of sulphuric acid produced is found in a similar way to the water: $4.175 \times 10^4 \times 8/4 \cong 8.35 \times 10^4$ moles. The molecular weight of H_2SO_4 is $1 + 1 + 32 + 16 \times 4 \cong 98$ so the mass of H_2SO_4 is $8.35 \times 10^4 \text{ moles} \times 98 \text{ g mole}^{-1} \cong 8.2 \times 10^6$ grams or 8.2 tonnes.
2. If the sulphuric acid finds its way into 1 million cubic metres of water then assuming complete dissociation $H_2SO_4 \rightarrow 2H^+SO_4^{2-}$:
- the molarity, M, (moles per litre) of SO_4^{2-} will be $\frac{8.35 \times 10^4 \text{ moles}}{1 \times 10^6 \times 10^3 \text{ litres}} \cong 8.35 \times 10^{-5}$ M.
 - Multiply this by two (both protons dissociate): $8.35 \times 10^{-5} \times 2 \cong 1.67 \times 10^{-4}$ M.
 - the pH is therefore $-\log_{10} 1.67 \times 10^{-4} \cong 3.8$. This is greater than 3 so the sludge is precipitated out.
 - You can also do the calculation if only one proton dissociates—what happens in that case?
3. Having said that, some of the 1 million cubic metres of water will be used up in the reaction. The number of moles of water in 1 million cubic metres is $\frac{1 \times 10^6 \text{ m}^3 \times 1000000 \text{ g m}^{-3}}{18 \text{ g mole}^{-1}} \cong 5.56 \times 10^{10}$ moles. This is way greater than the number of moles of water that need to be used up in the reaction, so we don't need to consider the fact that some water is used up.

2.3 Problems

1. Balance the following chemical equations:

- Oxidation of galena to anglesite: $\text{PbS} + 2\text{O}_2 \rightarrow \text{PbSO}_4$.
- Oxidation of magnetite to hematite: $\text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$
- Weathering of alkali feldspar to kaolinite:

$$\text{KAlSi}_3\text{O}_8 + \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{K}^+ + \text{Si}(\text{OH})_4$$

orthoclase groundwater kaolinite groundwater
- Thermal metamorphism of sandy dolomitic limestone (i):

$$\text{CaMg}(\text{CO}_3)_2 + \text{SiO}_2 \rightarrow \text{CaMgSi}_2\text{O}_6 + \text{CO}_2$$

dolomite quartz diopside
- Thermal metamorphism of sandy dolomitic limestone (ii):

$$\text{CaMg}(\text{CO}_3)_2 + \text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 + \text{CaCO}_3 + \text{CO}_2$$

amphibole
- $$\text{NaAlSi}_3\text{O}_8 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Na}^+ + \text{HCO}_3^- + \text{H}_4\text{SiO}_4$$

albite kaolinite
- $$\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Ca}^{2+} + \text{HCO}_3^-$$

anorthite kaolinite

2. The compositions of an unknown mineral has been analysed and the percentages by weight of its constituent elements are now known. They are:

Cu 63.31%
 Fe 11.13%
 S 25.56%

How can you work out what the chemical formula of this mineral is?

3. A more common way of analysing mineral compositions is as a combination of simpler compounds. For example, for silicates the oxygen is no longer given separately but as part of stable, neutral oxides with each cation in turn. Can you adjust your method and thus find what this is:

CaO 37.35%
 Al₂O₃ 22.64%
 SiO₂ 40.02%

4. Write down a methodology of how to balance chemical equations.

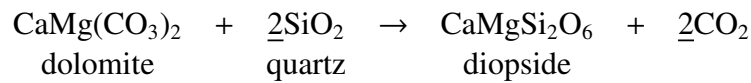
2.4 Notes on problems

1. Balance the following chemical equations:

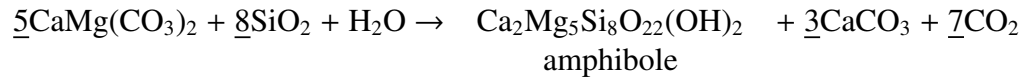
- Oxidation of galena to anglesite: $\text{PbS} + 2\text{O}_2 \rightarrow \text{PbSO}_4$.
- Oxidation of magnetite to hematite: $4\text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow 6\text{Fe}_2\text{O}_3$
- Weathering of alkali feldspar to kaolinite:

$$2\text{KAlSi}_3\text{O}_8 + 2\text{H}^+ + 9\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+ + 4\text{Si}(\text{OH})_4$$

orthoclase groundwater kaolinite groundwater
- Thermal metamorphism of sandy dolomitic limestone (i):



- Thermal metamorphism of sandy dolomitic limestone (ii):



- $\underline{2}\text{NaAlSi}_3\text{O}_8 + \underline{11}\text{H}_2\text{O} + \underline{2}\text{CO}_2 \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \underline{2}\text{Na}^+ + \underline{2}\text{HCO}_3^- + \underline{4}\text{H}_4\text{SiO}_4$
albite kaolinite
- $\text{CaAl}_2\text{Si}_2\text{O}_8 + \underline{2}\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Ca}^{2+} + \underline{2}\text{HCO}_3^-$
anorthite kaolinite

2. The compositions of an unknown mineral has been analysed and the percentages by weight of its constituent elements are now known. They are:

Cu 63.31%

Fe 11.13%

S 25.56%

How can you work out what the chemical formula of this mineral is?

- Solution is to divide each weight by its atomic weight:

Cu $63.31/63.5 \cong 0.997$

Fe $11.13/56 \cong 0.199$

S $25.56/32 \cong 0.799$

Then divide each by the smallest so the smallest denomination is ~1:

Cu $0.997/0.199 \cong 5$

Fe $0.199/0.199 \cong 1$

S $0.799/0.199 \cong 4$

So the empirical chemical formula is $\text{Cu}_5\text{Fe}_1\text{S}_4$. This is called bornite.

3. A more common way of analysing mineral compositions is as a combination of simpler compounds. For example, for silicates the oxygen is no longer given separately but as part of stable, neutral oxides with each cation in turn.

Can you adjust your method and thus find what this is:

CaO 37.35%

Al_2O_3 22.64%

SiO_2 40.02%

- Solution is to divide each weight by its molecular weight:

CaO $37.35/(40 + 16) \cong 0.667$

Al_2O_3 $22.64/(2 \times 27 + 3 \times 16) \cong 0.222$

SiO_2 $40.02/(28 + 2 \times 16) \cong 0.667$

Then divide each by the smallest so the smallest denomination is ~1:

CaO $0.667/0.222 \cong 3$

Al_2O_3 $0.222/0.222 \cong 1$

SiO_2 $0.667/0.222 \cong 3$

So the empirical chemical formula is $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. This is called grossular.

2.4.1 Homework and reading for next time

Background reading:

- Croft and Davison (2006, chapters on 'The exponential function', 'The logarithm function') OR 2.16,2.17,2.18,3.4,3.5 and 3.6 of the *Foundation Maths Support Pack*.

Do this weeks assessment on Blackboard:

- 'The exponential and the logarithm functions'.
- 'Acid mine drainage'.