

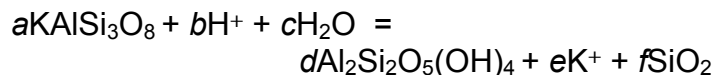
Practical 1

Weathering and Carbonate Equilibria

How to balance complicated reactions:

Suppose you needed to write a balanced reaction for the weathering of potassium feldspar KAlSi_3O_8 to kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and quartz (SiO_2):

First, write out the reaction assuming it involves water and protons. It doesn't matter which side you put them on:



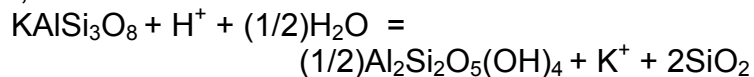
The coefficients a , b , c , etc. are the unknown quantities we will determine. Next write out the mass and charge balance equations. We have 6 unknowns and can write 5 eqns:

$$\begin{aligned} a &= e \quad (\text{to balance K}) \\ b + 2c &= 4d \quad (\text{to balance H}) \\ a &= 2d \quad (\text{to balance Al}) \\ 3a &= 2d + f \quad (\text{to balance Si}) \\ b &= e \quad (\text{to balance charge}) \end{aligned}$$

We are only interested in the relative coefficients so simply set $a = 1$:

$$\begin{aligned} a &= e \text{ thus } e = 1; \\ a &= 2d \text{ thus } d = 1/2; \\ 3a &= 2d + f \text{ thus } 3 = 1 + f \text{ or } f = 2; \\ b &= e \text{ thus } b = 1, \\ b + 2c &= 4d \text{ or } 1 + 2c = 2 \text{ or } c = 1/2 \end{aligned}$$

To give,



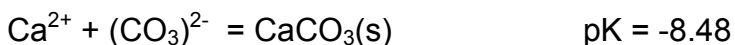
1. Oxidation of pyrite (FeS_2) is the source of acid mine drainage. As we will learn, the fast step in this reaction is the oxidation of FeS_2 by dissolved Fe^{+3} (not by $\text{O}_2(\text{g})$). The Fe^{+3} is generated by chemolithoautotrophic oxidation of dissolved Fe^{+2} . Work out a balanced reaction for the oxidation of pyrite (FeS_2) by Fe^{3+} to give Fe^{+2} , H^+ and SO_4^{-2}

2. Work out a balanced chemical reaction for the weathering of sodium feldspar ($\text{NaAlSi}_3\text{O}_8$) by H_2CO_3 to kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and dissolved Na^+ , HCO_3^- and $\text{Si}(\text{OH})_4(\text{aq})$. Given the following thermodynamic data, calculate the equilibrium constant for this reaction.

Formula	Name	ΔG_f (kJ/mol)
$\text{NaAlSi}_3\text{O}_8$	Feldspar	-3698.7
H_2O	Water	-237.2
H_2CO_3	Carbonic acid	-623.4
$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	Kaolinite	-3776.9
$\text{Na}^+(\text{aq})$	Sodium	-261.9
$\text{HCO}_3^-(\text{aq})$	Bicarbonate	-587.0
$\text{Si}(\text{OH})_4$	Silicic acid	-1308.8

If the concentration of $\text{Si}(\text{OH})_4$ is buffered by the dissolution of quartz, then at $\text{pH} < 9$ we have $\text{pSi}(\text{OH})_4 = 2.7$. The system is exposed to the atmosphere so that $\text{pH}_2\text{CO}_3 = 4.94$. Assume that $[\text{Na}^+] = [\text{HCO}_3^-]$; what is $[\text{Na}^+]?$ Given $[\text{Na}^+]$, how many kg of water must be flushed through the system to dissolve 1 mole of feldspar if the water is allowed to always come to equilibrium with the feldspar?

3. Given the following carbonate equilibria, plot a pC-pH diagram of the open-carbonate system for the doomsday scenario of $P_{\text{CO}_2} = 0.01$ bar (31 times current CO_2 content). What would be the pH of rain? What would be the pH of the oceans and the solubility of CaCO_3 if $[\text{Ca}^{2+}] = [\text{HCO}_3^-]$?



4. Below is the chemical analysis (in mg/kg) of seawater and rainwater in Cumbria in the late 1980s (Sutcliffe, 1998). The pH of the rain water was 4.9. Calculate the excess ions (relative to Cl) for the rain. Is there any evidence for acid-rain pollution by H_2SO_4 ?

	Seawater mg/kg	Rain ($\mu\text{g}/\text{kg}$)	Excess ($\mu\text{g}/\text{kg}$) relative to seawater Cl
Cl^-	19344	4935	0
Na^+	10773	2553	-195
Mg^{+2}	1294	328	2.1
SO_4^{-2}	2717	2832	2138
Ca^{+2}	412	581	475
K^+	399	234	132
Alkalinity	142 (as HCO_3^-)	-1014 (= H_2CO_3)	