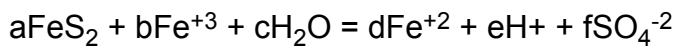


Solutions to Environmental Geochemistry Practical 1

Weathering and Carbonate Equilibria

1. Write out a balanced equation for the oxidation of pyrite (FeS_2) to Fe^{+2} , H^+ and SO_4^{-2} by Fe^{+3}

Solution:



Fe balance gives

$$a + b = d$$

S balance give

$$2a = f$$

H balance gives

$$2c = e$$

O balance gives

$$c = 4f$$

charge balance gives

$$3b = 2d + e - 2f$$

Set $a = 1$ to get

$$1 + b = d$$

$$2 = f$$

$$2c = e$$

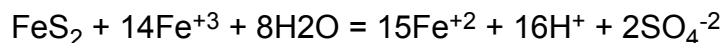
$$c = 8 \text{ (since } f = 2) \text{ hence } e = 16$$

$$3b = 2d + 16 - 4 = 2d + 12$$

This gives

$$3b = 2b + 2 + 12 \text{ or } b = 14$$

$$d = 15$$

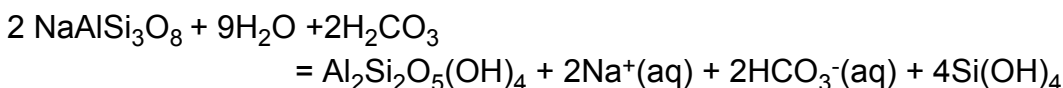


2. Work out a balanced chemical reaction for the weathering of sodium feldspar ($\text{NaAlSi}_3\text{O}_8$) by H_2CO_3 to kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and dissolved Na^+ , HCO_3^- and $\text{Si}(\text{OH})_4(\text{aq})$. Given the following thermodynamic data, calculate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

Formula	Name	ΔG (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 equilibrate with the rock?

Solution: the balanced reaction is



The change in free energy is then +69.1 kJ.

Hence, $K = \exp(-\Delta G/RT) = \exp(-69.1/(0.0083147 \times 298\text{K})) = 7.9 \times 10^{-13}$
or $\text{pK} = 12.1$.

The equilibrium constant is $K = \frac{[\text{Na}^+]^2 [\text{HCO}_3^-]^2 [\text{Si}(\text{OH})_4]^4}{[\text{H}_2\text{CO}_3]^2}$

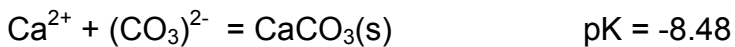
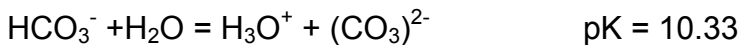
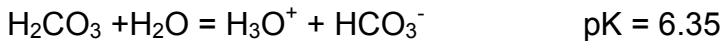
If $\text{p}[\text{H}_2\text{CO}_3]$ is 4.94 (buffered by atmosphere with $P_{\text{CO}_2} = 10^{-3.5}$) and $\text{p}[\text{Si}(\text{OH})_4]$ is 2.7, we get $\text{p}[\text{Na}^+] = 2.795$.

Water in equilibrium with $\text{NaAlSi}_3\text{O}_8$ will have $[\text{Na}] = 10^{-2.796}$ moles/kg.

To dissolve 1 mole of feldspar must require

1 mole $\text{NaAlSi}_3\text{O}_8 \times (\text{kg water}/10^{-2.795} \text{ moles Na}) \times (1 \text{ mole Na}/\text{mole NaAlSi}_3\text{O}_8) = 624 \text{ kg of water}$. That is, this is the amount of water needed to flush through the rock to dissolve 1 mole of $\text{NaAlSi}_3\text{O}_8$ assuming the water has fully reached equilibrium with the feldspar. In fact, this condition will seldom be reached since the dissolution rate of feldspar is slow. Far more water will be required to dissolve 1 mole of feldspar.

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



Solution:

Write out the equilibrium expressions, take p ($= -\log$) function of everything

$$\text{pH}_2\text{CO}_3 - \text{pCO}_2 = 1.46$$

$$\text{Since } \text{pP}_{\text{CO}_2} = -\log(0.01) = 2, \text{ we get } \text{pH}_2\text{CO}_3 = 3.46.$$

$$\text{pHCO}_3 + \text{pH} - \text{pH}_2\text{CO}_3 = 6.35$$

$$\text{Since, } \text{pH}_2\text{CO}_3 = 3.46 \text{ we get } \text{pHCO}_3 = 9.81 - \text{pH}$$

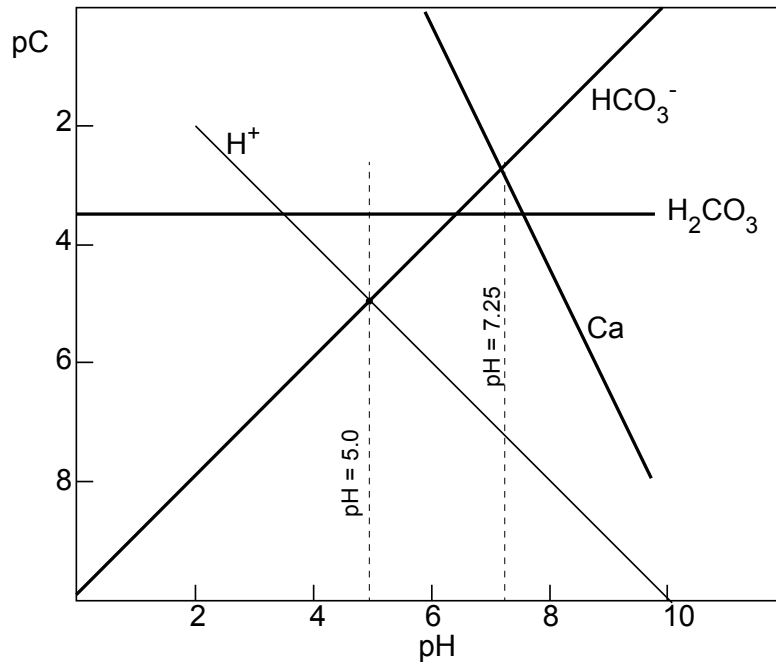
$$\text{pCO}_3 + \text{pH} - \text{pHCO}_3 = 10.33$$

$$\text{Since, } \text{pHCO}_3 = 9.81 - \text{pH} \text{ we get } \text{pCO}_3 = 20.14 - 2\text{pH}$$

$$\text{pCa} + \text{pCO}_3 = 8.48$$

$$\text{Since, } \text{pCO}_3 = 20.14 - 2\text{pH} \text{ we get } \text{pCa} = -11.66 + 2\text{pH}$$

Now plot these equilibrium expressions along with $pC=pH$:



From the plot, we find that the pH of calcite-free water (where $pHCO_3 = pH$) will be ~ 5.0 . The pH of seawater (saturated in calcite) will be when $pCa = pHCO_3 + 0.301 = 7.25$. The solubility of $CaCO_3$ will be $10^{-2.8}$ mole/kg water.

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)	

If we do the calculation by mole ratios..

	Seawater mol/kg	Rain ($\mu\text{mol}/\text{kg}$)	Excess ($\mu\text{mol}/\text{kg}$) relative to seawater Cl
Cl^-	0.546	141	0
Na^+	0.467	111	-9.6
Mg^{+2}	0.053	14	0.3
SO_4^{-2}	0.028	30	28
Ca^{+2}	0.01	15	12.4
K^+	0.01	6	3.4
Alkalinity	0.002 (as HCO_3^-)	-13 (= H_2CO_3)	-14

Either way, we find that there is excess sulphate in the rain relative to what would be expected from marine aerosol input. This may come from H_2SO_4 . The presence of a negative Na excess component means that there must actually be a small excess Cl relative to marine aerosols.