

Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET 6 SOLUTIONS

DUE NOV. 7, 2007

1. Consider a 0.005M solution of Na_2CO_3 at 25°C. Assuming ideality and that the system is closed,
a. What is the pH of this solution?

We can write the following equations:

$$\text{Proton Balance: } [\text{H}^+] + [\text{HCO}_3^-] + 2[\text{H}_2\text{CO}_3] = [\text{OH}^-] \quad (3.1)$$

A reasonable guess would be that the concentration of carbonic acid can be neglected, so the proton balance equation is:

$$[\text{H}^+] + [\text{HCO}_3^-] = [\text{OH}^-] \quad (3.2)$$

The charge balance equation is:

$$[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (3.3)$$

The conservation equation is (again neglecting carbonic acid):

$$[\text{Na}^+] = 2\Sigma\text{CO}_3 = 2([\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3]) = 2 \times 0.005 = 0.010 \text{ M} \quad (3.4)$$

and the mass balance equation becomes:

$$\Sigma\text{CO}_3 = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] \quad (3.5)$$

Manipulating the equilibrium constant expression, we have:

$$[\text{CO}_3^{2-}] = \frac{K_2[\text{HCO}_3^-]}{[\text{H}^+]} \quad (3.6)$$

Substituting this into the mass balance equation we have:

$$\Sigma\text{CO}_2 = \frac{K_2[\text{HCO}_3^-]}{[\text{H}^+]} + [\text{HCO}_3^-] \quad (3.7)$$

Doing some algebra this becomes:

$$[\text{HCO}_3^-] = \frac{\Sigma\text{CO}_2}{1 + K_2/[\text{H}^+]} \quad (3.8)$$

This expression can be substituted into the proton balance equation (3.2) to obtain:

$$[\text{H}^+] = [\text{OH}^-] - \frac{\Sigma\text{CO}_2}{1 + K_2/[\text{H}^+]} \quad (3.9)$$

Substituting for $[\text{OH}^-]$, we have:

$$[\text{H}^+] = \frac{K_w}{[\text{H}^+]} - \frac{\Sigma\text{CO}_2}{1 + K_2/[\text{H}^+]} \quad (3.10)$$

Doing some algebra, this becomes:

$$[\text{H}^+]^3 + (K_2 + \Sigma\text{CO}_2)[\text{H}^+]^2 - K_w[\text{H}^+] - K_wK_2 = 0 \quad (3.11)$$

Neglecting any terms here is dangerous, since all are small. This is a cubic equation, and one approach is to use the standard solution to the cubic equation. The cubic equation solution can have multiple real roots, and we would have to

Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET 6 SOLUTIONS

DUE NOV. 7, 2007

eliminate the irrelevant ones. So perhaps the best way to solve it is through successive guess, or using the Solver in Excel. **The result is a pH of 10.97.**

b. What is the pH of this solution when titrated to the bicarbonate equivalence point?

At the equivalence point we have $[H_2CO_3] = [CO_3^{2-}]$

Both can be related to bicarbonate ion concentration through equilibrium constant expressions:

$$[H_2CO_3] = [H^+][HCO_3^-]K_1$$

$$[CO_3^{2-}] = K_2[H^+]/[HCO_3^-]$$

Substituting these expressions into the above, then solving for $[H^+]$, we have

$$[H^+] = \sqrt{K_1 K_2} = 10^{-8.4}$$

Thus the pH of the bicarbonate equivalence point, 8.4, is independent of composition.

2. Make a plot similar to Figure 6.1, but for water in equilibrium with atmospheric CO_2 ($P_{CO_2} = 10^{-3.43}$). Assume ideality and that there are no other species present in solution but those shown on the graph. What is the pH of the CO_2 equivalence point in this case? What is the pH of the bicarbonate equivalence point?

The three equations we need are:

$$K_{sp} = \frac{a_{H_2CO_3}}{f_{CO_2}} = -1.47 \quad 6.18$$

$$K_1 = \frac{a_{H^+} a_{HCO_3^-}}{a_{H_2CO_3}} = -6.35 \quad 6.19$$

$$K_2 = \frac{a_{H^+} a_{CO_3^{2-}}}{a_{HCO_3^-}} = -10.33 \quad 6.20$$

Solving 6.18 for $[H_2CO_3]$:

$$\log(a_{H_2CO_3}) = \log f_{CO_2} - pK_{sp} = -3.43 - 1.47 = -4.90 \quad (a)$$

Combining 6.18 and 6.19 and solving for HCO_3^- :

$$\log a_{HCO_3^-} = \log a_{H_2CO_3} - pK_1 + pH = -4.90 - 6.35 + pH = -11.25 + pH \quad (b)$$

Combining all 3 equations and solving for CO_3^{2-} :

$$\log a_{CO_3^{2-}} = -pK_2 + \log a_{HCO_3^-} + pH = -10.33 - 11.25 + 2pH = -21.58 + 2pH \quad (c)$$

Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET 6 SOLUTIONS

DUE NOV. 7, 2007

Bicarbonate equivalence point is the same as in problem 1: **pH=8.34**.

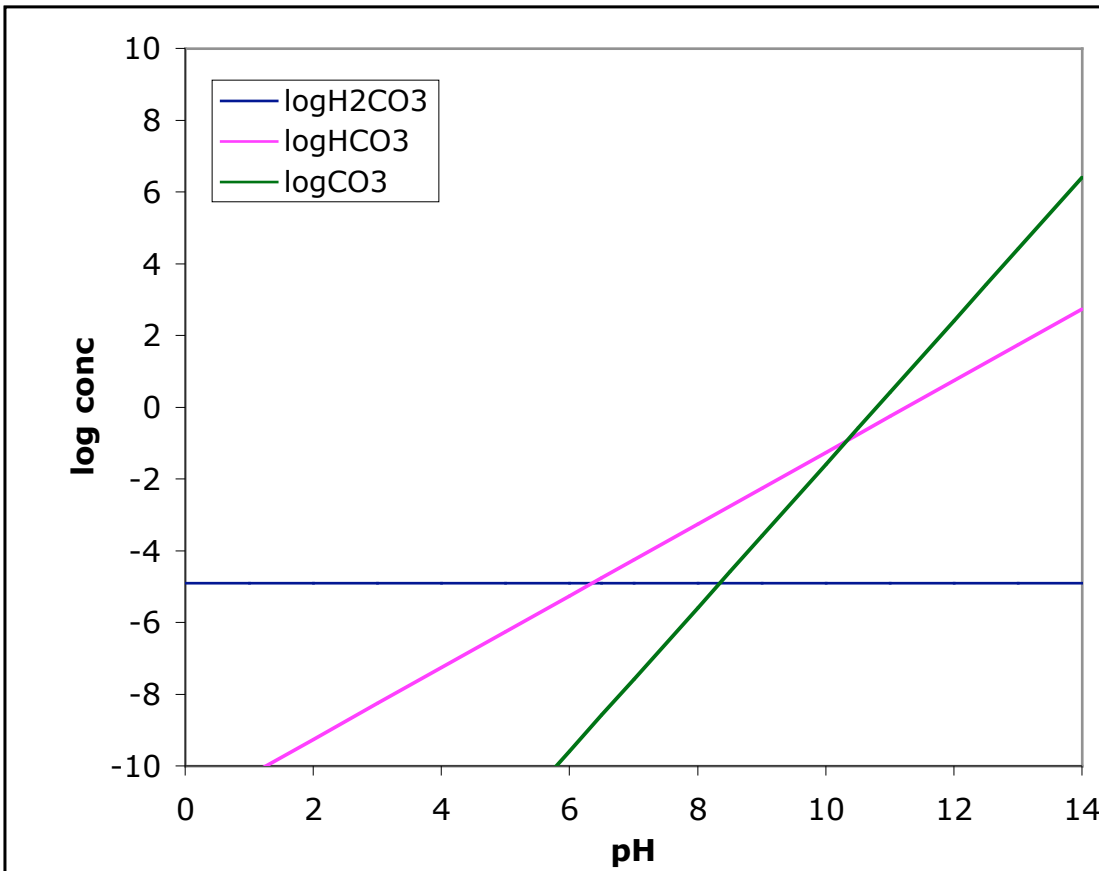
CO₂ equivalence point is where [HCO₃]=[H⁺]. From equation (b) above, we have:

$$\log a_{\text{HCO}_3^-} = -11.25 + \text{pH}$$

Solving this relationship: $\text{pH} = \frac{11.25}{2} = 5.625$

The CO₂ equivalence point depends, in this case, on the partial pressure of CO₂.

The plot is shown below:



3. Using the composition given below, calculate the alkalinity of seawater at 25°C.

Na ⁺	0.481 M	Cl ⁻	0.560 M
Mg ²⁺	0.0544 M	SO ₄ ²⁻	0.0283 M
Ca ²⁺	0.0105 M	HCO ₃ ⁻	0.00238 M
K ⁺	0.0105 M		

It is most convenient to use equation 6.35 for this calculation, since we have the concentrations of the conservative cations and anions. All the above are conservative except for bicarbonate. First we convert concentrations to

Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET 6 SOLUTIONS

DUE NOV. 7, 2007

equivalents, then the alkalinity is the difference between the sum of the cations and the sum of the anions. A spreadsheet is shown below:

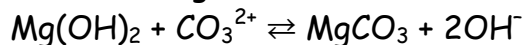
ion	z	conc	meq
Na+	1	0.481	481
Mg2+	2	0.0544	108.8
Ca2+	2	0.0105	21
K+	1	0.0105	10.5
		cation sum	621.3
Cl-	1	0.56	560
SO4	2	0.0283	56.6
		anion sum	616.6
Alk=	cations- anions	4.7	meq

4. Using the following reactions and equilibrium constants for this problem:



a. Calculate the pH of the boundary between the regions of stability brucite and magnesite (e.g., Figure 6.14a), for a fixed ΣCO_2 activity of $10^{-2.5}$, and assuming that $\Sigma\text{CO}_2 \approx \text{CO}_3^{2-}$.

The conversion of brucite to magnesite can be written as:



This reaction is obtained by subtracting the second reaction above from the first. So the log equilibrium constant can be obtained in a similar manner:

$$\log K_{\text{bru-mag}} = \log K_{\text{bru}} - \log K_{\text{mag}} = -11.6 - -7.5 = -4.1$$

Assuming magnesite and brucite are pure solids:

$$\log K_{\text{bru-mag}} = 2\log a_{\text{OH}^-} - \log a_{\text{CO}_3}$$

The activity of hydroxyl is related to pH as

$$\log a_{\text{OH}^-} = \log K_w + \text{pH}$$

Substituting this, we have:

$$\log K_{\text{bru-mag}} = 2\log K_w + 2\text{pH} - \log a_{\text{CO}_3}$$

Rearranging:

$$\text{pH} = (\log K_{\text{bru-mag}} - 2\log K_w + \log a_{\text{CO}_3})/2$$

If $\Sigma\text{CO}_2 = 10^{-2.5}$ and $\text{CO}_3^{2-} = \Sigma\text{CO}_2$ then

$$\text{pH} = -4.1 - 2(-14) + -2.5 = 21.4/2 = \mathbf{10.7}$$

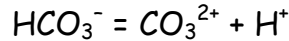
Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET 6 SOLUTIONS

DUE NOV. 7, 2007

b. Perform the same calculation, but this time assume that $\Sigma\text{CO}_2 \approx \text{HCO}_3^-$.

Now we also need to consider the reaction:



The equilibrium constant expression for this is:

$$\log K_2 = \log a_{\text{CO}_3} - \text{pH} - \log a_{\text{HCO}_3}$$

Rearranging: $\log a_{\text{CO}_3} = \log K_2 + \text{pH} + \log a_{\text{HCO}_3}$

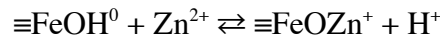
Substituting this into our equilibrium constant expression for brucite-magnesite

$$\log K_{\text{brucite-mag}} = 2 \log K_w + 2\text{pH} - (\log K_2 + \text{pH} + \log a_{\text{HCO}_3})$$

or $\log K_{\text{brucite-mag}} = 2 \log K_w + \text{pH} - \log K_2 - \log a_{\text{HCO}_3}$

$$\text{pH} = (\log K_{\text{brucite-mag}} - 2 \log K_w + \log K_2 + \log a_{\text{HCO}_3}) = 11.07$$

5. For the adsorption of Zn^{2+} on hydrous ferric oxide:



the apparent equilibrium constant is $10^{0.99}$. For this problem, use the surface acidity constants (i.e., equilibrium constants for adsorption and desorption of H^+) given in equations 6.98 and 6.99 (Example 6.10). Make a plot of Θ_{Zn} (fraction of sites occupied by Zn) vs. the aqueous concentration of Zn^{2+} at pH 7 and a total concentration of surface sites of 10^{-3} M. Assume that Zn^{2+} forms no complexes in solution.

(a) The quantity that we want is $[\equiv\text{FeOZn}^+]/[\Sigma\equiv\text{FeO}]$

We start with a conservation equation for surface sites:

$$\Sigma \equiv \text{FeO} = [\equiv \text{FeOZn}^+] + [\equiv \text{FeOH}_2^+] + [\equiv \text{FeOH}] + [\equiv \text{FeO}^-] \quad (\text{a})$$

Our equilibrium constant expressions are:

$$K_{ad} = \frac{[\equiv \text{FeOZn}^+][\text{H}^+]}{[\equiv \text{FeOH}^0][\text{Zn}^{2+}]}$$

$$K_1 = \frac{[\equiv \text{FeOH}]^0[\text{H}^+]}{[\equiv \text{FeOH}_2^+]}$$

$$K_2 = \frac{[\equiv \text{FeO}^-][\text{H}^+]}{[\equiv \text{FeOH}^0]}$$

From these we can derive the following:

$$[\equiv \text{FeOZn}^+] = \frac{[\equiv \text{FeOH}^0][\text{Zn}^{2+}]K_{ad}}{[\text{H}^+]} \quad (\text{b})$$

$$[\equiv \text{FeOH}_2^+] = \frac{[\equiv \text{FeOH}^0][\text{H}^+]}{K_1} \quad (\text{c})$$

$$[\equiv \text{FeO}^-] = \frac{K_2[\equiv \text{FeOH}^0]}{[\text{H}^+]} \quad (\text{d})$$

Substituting these into (a) and rearranging, we have

Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET 6 SOLUTIONS

DUE NOV. 7, 2007

$$\Sigma \equiv FeO = [\equiv FeOH^0] \left(\frac{[Zn^{2+}]K_{ad}}{[H^+]} + \frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]} \right) \quad (e)$$

Dividing (b) by (e), we have:

$$\frac{[\equiv FeOZn^+]}{\Sigma \equiv FeO} = \frac{[Zn^{2+}]K_{ad}}{\left([Zn^{2+}]K_{ad} + \frac{[H^+]^2}{K_1} + [H^+] + K_2 \right)} \quad (e)$$

Calculated values are:

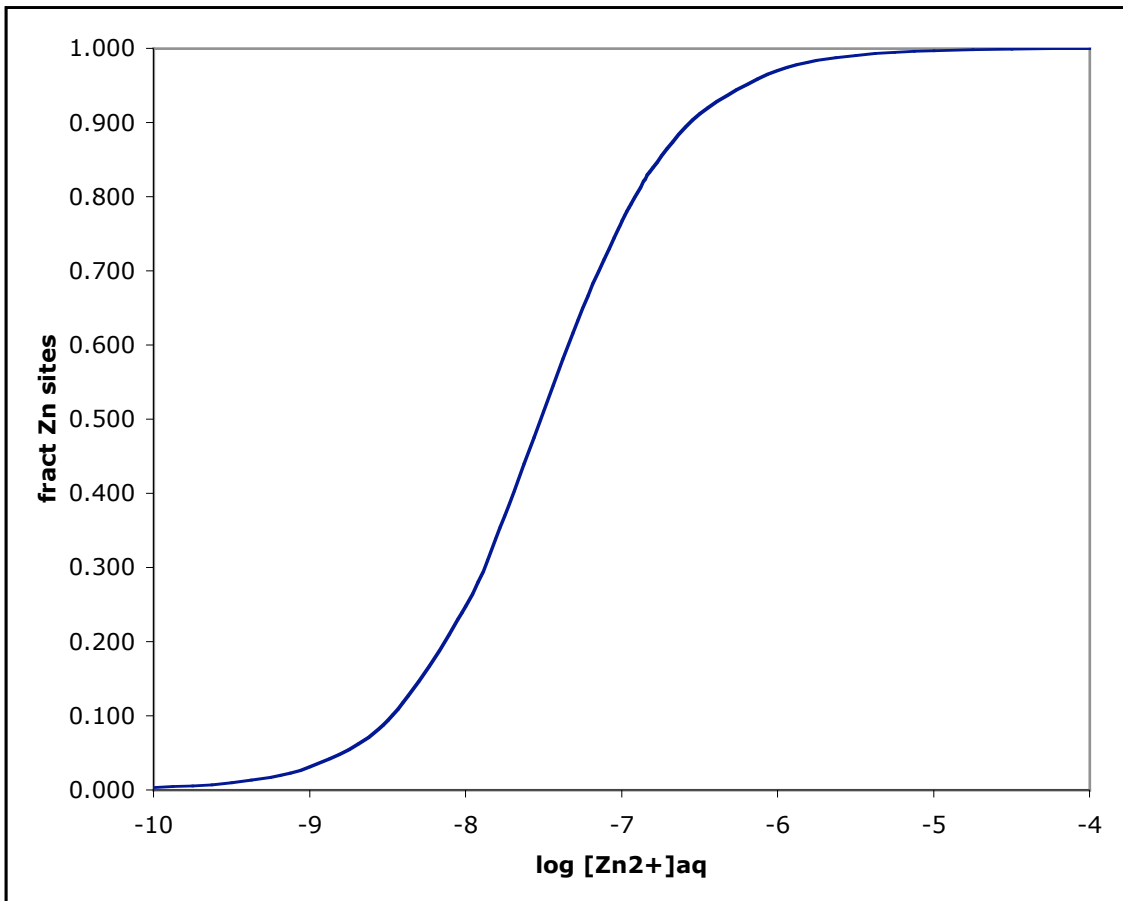
log ZnZn	fract Zn sites
-101.0E-10	0.003
-9.53.2E-10	0.010
-91.0E-09	0.032
-8.53.2E-09	0.094
-81.0E-08	0.248
-7.751.8E-08	0.370
-7.53.2E-08	0.511
-7.255.6E-08	0.650
-71.0E-07	0.767
-6.91.3E-07	0.806
-6.81.6E-07	0.839
-6.53.2E-07	0.913
-61.0E-06	0.971
-5.53.2E-06	0.991
-51.0E-05	0.997
-4.53.2E-05	0.999
-41.0E-04	1.000

The plot is shown below:

Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET 6 SOLUTIONS

DUE NOV. 7, 2007



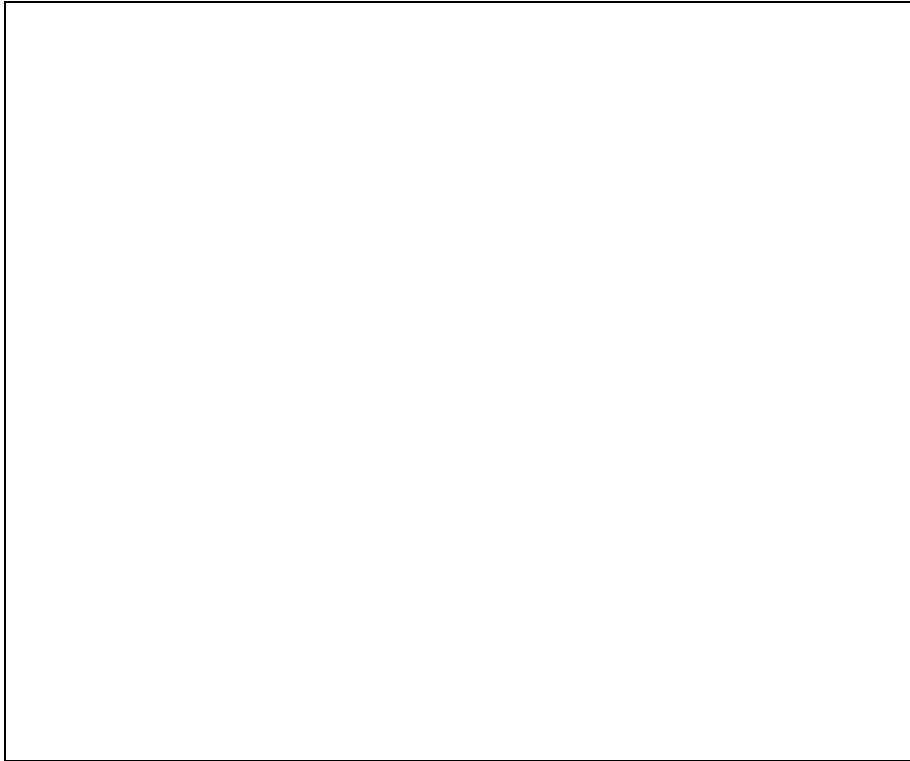
6. Make rare earth plots for the following two samples (concentrations in ppm), interpolating missing values. For the granite, plot it normalized to one of the chondritic values in Table 7.3. For the Mn nodule, make one plot normalizing it to chondrites and one plot normalizing it to average shale. Describe the features of the REE patterns.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Granite	41	75		25	3.6	0.6	2.7		1.3					0.4
Mn-nodule	110	858		116	24	4.9	24		24.1		14.4		13	1.92

Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET 6 SOLUTIONS

DUE NOV. 7, 2007



On this plot, both the granite and Mn-nodule show negative Eu anomalies, the Mn-nodule also shows a positive Ce anomaly. The Mn-nodule is somewhat LRE enriched, and overall has high REE. The granite shows strong LREE enrichment and HREE depletion.



Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET 6 SOLUTIONS

DUE NOV. 7, 2007

On this plot, the Mn nodule appears enriched relative to shales, has a positive Ce anomaly, and only a slight negative Eu anomaly. It is more or less flat, except for these features.