

SOIL AND AQUATIC CHEMISTRY

EXAMPLES CLASS – 2018-19

Acid-base equilibria – diprotic acids

1. Construct a plot of $-\log$ (species concentration) vs pH for a diprotic acid, H_2A , in water. Label the graph to show, pK_1 , pK_2 , C, and the equilibrium pH for solutions containing the acid (H_2A).

2.(a) Explain what is meant by a closed system for carbonic acid.

(b) Write expressions for each dissolved inorganic carbon species ($H_2CO_3^*$, HCO_3^- , CO_3^{2-}) in solution in terms of constants and $[H^+]$ only.

(c) Write a charge balance expression for an aqueous solution of carbonic acid.

(d) Sketch a plot of $-\log []$ vs pH and annotate to show the equilibrium pH of the solution in (c).

3.(a) Write down the equations that are required to completely characterise the open carbonate system (assuming no solid phases).

(b) Write an expression that defines the equilibrium pH of a solution containing sodium hydrogen carbonate in water. (Hint: $C = [Na^+]$)

(c) Write an expression that defines the carbonate alkalinity of a natural water and explain why the addition or removal of carbon dioxide does not cause a change in alkalinity.

4.(a) Calculate the alkalinity of the following solutions (Hint: use only the appropriate part of the alkalinity expression):

(i) 10^{-3} M KOH

(ii) 10^{-3} M $NaHCO_3$

(iii) 5×10^{-4} M Na_2CO_3

(iv) 5×10^{-4} M MgO

(b) Calculate the total concentration of dissolved inorganic carbon, C, where $[Alk] = 2.3 \times 10^{-4}$ eq L^{-1} , $K_1 = 10^{-6.35}$, $K_2 = 10^{-10.35}$ and the pH of solution is 8.6.

5. For the water described below ($CaCO_{3(s)}-CO_{2(aq)}-H_2O_{(l)}$ system), calculate whether it is over- or under-saturated with respect to $CaCO_3$. Use the equilibrium constant data provided (Hint: start by calculating C...finally calculate the ion product $\{Ca^{2+}\}\{CO_3^{2-}\}$).

pH	7.5
$[Ca^{2+}]$	1.6×10^{-3} M
[Alk]	4×10^{-3} M
pK_1	6.52
pK_2	10.56
$\log K_{SP} (CaCO_3)$	-8.35

Redox equilibria

6. Calculate the pE of the following (assume $I = 0$ M):

(i) a solution (pH = 2) containing 10^{-5} M Fe^{3+} and 10^{-3} M Fe^{2+} ($\log K = 13.0$)

(ii) a solution (pH = 7.5) in equilibrium with the atmosphere ($p_{O_2} = 0.21$ atm; $O_{2(g)} + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $\log K = 83.1$)

(iii) a solution (pH = 8) containing 10^{-5} M Mn^{2+} in equilibrium with $Mn(IV)O_{2(s)}$ ($MnO_{2(s)} + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$ $\log K = 40.84$)

Complexation equilibria

7. Write equilibria for the stepwise complexation of Cu(II) by Cl^- ($K_1 = 10^{0.46}$, $K_2 = 10^{0.16}$) Calculate the cumulative stability constants β_1 and β_2 .

Given $\Sigma Cu(II) = 2 \times 10^{-2}$ M and $\Sigma Cl(I) = 2$ M, what is the main species of Cu(II) in solution?

Level 11

Lectures – acid-base equilibria

1. Derive an expression which leads to the full numerical solution for $\{H^+\}$ for a dilute aqueous solution of a diprotic acid.
2. Given the following information for the open carbonate system (initial equilibrium pH = 8.13), calculate the new equilibrium pH of seawater if p_{CO_2} increased from 3.5×10^{-4} atm to 7.1×10^{-4} atm.

$$[Alk] = 2.47 \times 10^{-3} \text{ eq l}^{-1}$$

$$K_H = 4.8 \times 10^{-2} \text{ M atm}^{-1}$$

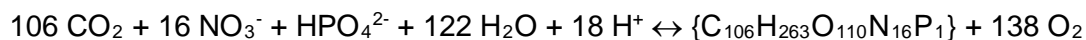
$$K_1 = 8.8 \times 10^{-7}$$

$$K_2 = 5.6 \times 10^{-10}$$

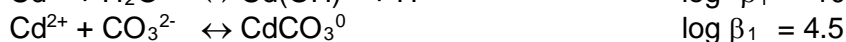
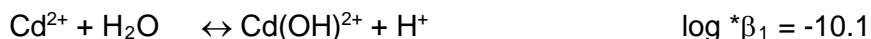
Hint: Use the approximation $[Alk] \sim [HCO_3^-] + 2 [CO_3^{2-}]$ together with the information above

NB for a quadratic equation: $x = [-b \pm \sqrt{(b^2 - 4ac)}] / 2a$

3. As a result of photosynthesis with nitrate assimilation (see equilibrium below), a surface water with an initial alkalinity of $8.5 \times 10^{-4} \text{ eq l}^{-1}$ showed a pH variation from 9.0 to 9.5 over a 3 hour period. Calculate the rate of net CO_2 fixation assuming a closed system and no deposition of $CaCO_3$. Use $pK_1 = 6.3$ and $pK_2 = 10.2$. (Hint: use $[Alk]$ at pH 9.0 in calculation; then write down two expressions for $[Alk]$ at pH 9.5)



4. Given the following information about a natural water:



$$[CO_3^{2-}] = 3.65 \times 10^{-6} \text{ M}; \text{ pH} = 7.8; \Sigma Cd(II) = 1 \times 10^{-9} \text{ M}$$

- (i) in which form does Cd(II) mainly occur?
- (ii) is there a possibility that $CdCO_{3(s)}$ or $Cd(OH)_{2(s)}$ will precipitate?

Paper to be Read

Remediation of groundwater contaminated with arsenic through enhanced natural attenuation: Batch and column studies. Hafeznezami et al. Water Research 122 (2017) 545-556. (Summary of main points will be given in the tutorial answers).