

CHEM 301

SOLUTIONS Assignment #2 Fall 2004

1. Hydrogen sulfide (H_2S) is considerably more toxic to fish than either HS^- or S^{2-} . If hydrogen sulfide concentrations greater than 0.15 mg/L (as S) are harmful to fish health, calculate the minimum safe pH, if the total sulfide concentration is determined to be 20 μM .

Solution: There are several ways to approach this problem, but in all of these we will need to know the K_a values for H_2S .

$$K_{a1}(\text{H}_2\text{S}) = 7.00 \quad pK_{a1} = 7.00$$

$$K_{a2}(\text{H}_2\text{S}) = 12.00 \quad pK_{a2} = 12.00$$

If we assume from inspection of the K_a values, that H_2S concentration will only be significant at pH near pK_{a1} , then the only chemical reaction we need consider is;

$$[\text{H}_2\text{S}]_{\text{critical}} = 0.15 \text{ mg S/L} \times 1 \text{ mol}/32,000 \text{ mg} = 4.69 \times 10^{-6} \text{ M}$$

$$[\text{S}]_{\text{T}} = 20 \times 10^{-6} \text{ M}$$



$$K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$\text{Rearranging for } [\text{H}^+] = K_{a1} [\text{H}_2\text{S}]/[\text{HS}^-]$$

Since, $[\text{HS}^-] = [\text{S}]_{\text{T}} - [\text{H}_2\text{S}] \cong 2.00 \times 10^{-5} - 4.69 \times 10^{-6} = 1.53 \times 10^{-5} \text{ M}$ (assuming $[\text{S}^{2-}] \lll [\text{HS}^-]$)

Therefore, $[\text{H}^+] = 3.10 \times 10^{-8} \text{ M}$

And, **pH = 7.51**

Alternately, we know that the total sulfide concentration (20 μM) is made up of contributions from three species.

$$[\text{S}]_{\text{T}} = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}] = 20 \text{ mM}$$

Since the critical value of H_2S toxicity is 4.69 μM , we need to calculate the pH at which

$$\alpha_{\text{H}_2\text{S}} = 4.69/20 = 0.234$$

$$\alpha_{\text{H}_2\text{S}} = \frac{[\text{H}_2\text{S}]}{[\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}]} = 0.234$$

Rearranging the K_{a1} and K_{a2} expressions this can be re-written as,

$$\alpha_{\text{H}_2\text{S}} = \frac{1}{1 + \frac{K_{a1}}{[\text{H}^+]} + \frac{K_{a1}K_{a2}}{[\text{H}^+]^2}} = 0.234$$

multiplying through by $[\text{H}^+]^2$ and rearranging yields;

$$[\text{H}^+]^2 = 0.23 [\text{H}^+]^2 + 0.23 K_{a1} [\text{H}^+] + 0.23 K_{a1} K_{a2}$$

Using the quadratic formula to solve for $[\text{H}^+] = 3.00 \times 10^{-8} \text{ M}$ and **pH = 7.51**

2. What is meant by the terms organic and inorganic carbon? Give examples of each. Using the diagram for the biogeochemical cycle of carbon (handout), calculate the average residence time for soluble organic carbon and soluble inorganic carbon. Comment on the similarity or difference of these results.

Solution: Inorganic carbon exists in several forms in aquatic systems, $\text{CO}_2(\text{aq})$, $\text{HCO}_3^-(\text{aq})$ and $\text{CO}_3^{2-}(\text{aq})$ as well as several inorganic minerals, eg CaCO_3 . All other carbon containing species can be considered organic carbon. You may notice that all forms of inorganic carbon in aquatic systems are in (+IV) oxidation state. Organic forms of carbon are in various lower oxidation states (-IV to +III).

Using the reservoir and flux rates given for soluble forms of carbon in the oceans,
 $R_t(\text{organic carbon}) = \text{amt}/\text{rate of loss} = 1000 \times 10^{12} \text{ kg}/0.04 \times 10^{12} \text{ kg yr}^{-1} = \mathbf{25,000 \text{ yr}}$

$R_t(\text{inorganic carbon}) = \text{amt}/\text{rate of loss} = 37,400 \times 10^{12} \text{ kg}/(100 + 0.15) \times 10^{12} \text{ kg yr}^{-1} = \mathbf{374 \text{ yr}}$

3. Using the pe-pH diagram for sulfur, estimate the pe and pH ranges for a water sample if H_2S is known to be the predominant form of inorganic sulfur in a water sample? What would you expect as the predominant forms for carbon and nitrogen under these conditions?

Solution:

Using the pe-pH diagram for sulfur (textbook, chap 10), it can be seen that if H_2S is the dominant form, the **pH < 7.0 and the pe < 4**. In most natural waters with pH 5 – 9, the pe < 0, if H_2S is dominant.

Under these conditions; **carbon** is predominantly **CH_4** and **nitrogen** is predominantly **NH_4^+**

4. Para-hydroxy benzoic acid (HO-C₆H₄-CO₂H) is a diprotic acid (H₂B) with pK_{a1} = 4.48 and pK_{a2} = 9.32.

- Derive an expression for the fractional abundance for the HB⁻
- Identify the HB⁻ species
- Construct a fully labeled pH speciation diagram for this species over the range of 0 to 14 using Excel.

Solution:

$$a) \alpha_{HB^-} = \frac{[HB^-]}{[H_2B]_T} = \frac{[HB^-]}{[H_2B] + [HB^-] + [B^{2-}]}$$

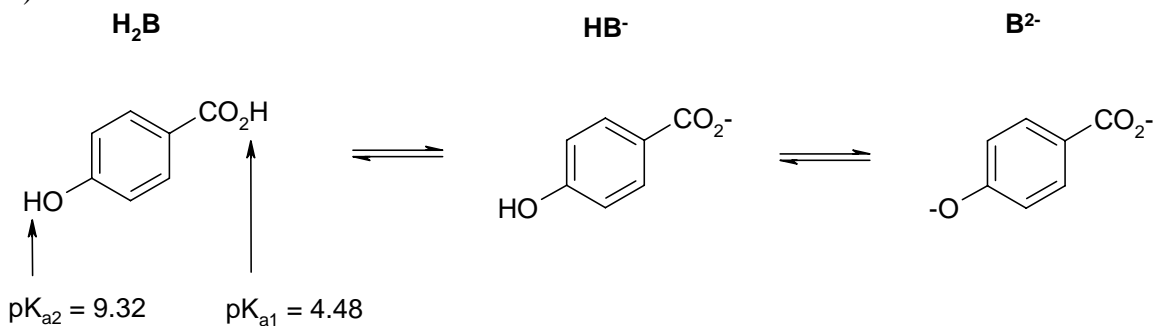
$$K_{a1} = \frac{[H^+][HB^-]}{[H_2B]} \quad \text{and} \quad [H_2B] = \frac{[H^+]}{K_{a1}}[HB^-]$$

$$K_{a2} = \frac{[H^+][B^{2-}]}{[HB^-]} \quad \text{and} \quad [B^{2-}] = \frac{K_{a2}}{[H^+]}[HB^-]$$

Substituting into the expression above yields,

$$\alpha_{HB^-} = \frac{[HB^-]}{\frac{[H^+][HB^-]}{K_{a1}} + [HB^-] + \frac{K_{a2}[HB^-]}{[H^+]}} = \frac{1}{\frac{[H^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[H^+]}} = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

b)



c) (see attached spreadsheet)

5. A treated wastewater sample has been analyzed to contain the following species.

$$[\text{HOCl}]_{\text{T}} = 2.0 \times 10^{-4} \text{ M}$$

$$[\text{NH}_3]_{\text{T}} = 7.9 \times 10^{-4} \text{ M}$$

Using Excel, construct an overlay plot of log C vs pH for four species involved between pH 4 and 10. The pK_a values for HOCl and NH₄⁺ are 7.60 and 9.25, respectively.

Solution: (see attached spreadsheet)

6. Kennedy Lake has a measured pH of 5.81 and an ORP = 290 mV using an ORP probe with an internal silver/silver chloride reference electrode. Standard E_h values are referenced to a standard saturated hydrogen electrode (SHE). Look up the standard reduction potential for the AgCl(s) + e⁻ → Ag(s) + Cl⁻ half reaction and correct the field ORP reading to an E_h value.

a) Report the pe value of Kennedy Lake.

b) Using the appropriate pe-pH (Pourbaix) diagrams, predict the dominant forms of iron, copper and zinc.

Solution:

a) The E^o for the AgCl/Cl half reaction is given as 0.221 V (vs SHE), therefore the measured ORP needs to be corrected to E_h = 0.290 + 0.221 V = 0.511 V.

So, pe = 0.511/0.0591 = **8.65**

b) Depending on the particular Pourbaix diagrams used, the dominant speciation at pH = 5.81 and pe = 8.65 are as follows.

Iron: Fe(OH)₃ or Fe₂O₃

Copper is predicted to be in the form of cupric ion, Cu²⁺

Zinc present as Zn²⁺

7. a) Write the balanced half reaction for the boundary between SeO_4^{2-} and HSeO_3^- and calculate the slope of the line dividing these two species on a pe-pH diagram.

Solution:



$$\text{In general, } pe = pe^o - \frac{n_H}{n_e} pH - \frac{1}{n_e} \log \frac{\{\text{Red}\}}{\{\text{Ox}\}}$$

$$\text{And at the boundary, where } \{\text{Red}\} = \{\text{Ox}\}, pe = pe^o - \frac{n_H}{n_e} pH$$

So slope of pe vs pH = **-3/2**



So slope of pe vs pH = **-2**

b) A water sample with a pH 6.0 was analyzed and found to contain 0.5 mmol/L nitrate ion and 5 μmol/L of ammonium ion. Calculate the pe of this water and predict the ratio of $[\text{HSO}_4^-]$ to $[\text{H}_2\text{S}]$ in the same sample.

Solution: Use the conc given for $\text{NO}_3^-/\text{NH}_4^+$ system to calculate a pe for the water. Then use this value to calculate the conc ratio for $\text{SO}_4^{2-}/\text{H}_2\text{S}$. Note, that at pH = 6, $[\text{HSO}_4^-]$ is negligible relative to that of SO_4^{2-} . We will calculate $[\text{SO}_4^{2-}]/[\text{H}_2\text{S}]$ first and then relate $[\text{SO}_4^{2-}]$ to $[\text{HSO}_4^-]$ using K_{a2} .



$$pe = pe^o - \frac{n_H}{n_e} pH - \frac{1}{n_e} \log \frac{\{\text{Red}\}}{\{\text{Ox}\}}$$

$$pe = 14.9 - \frac{10}{8} pH - \frac{1}{8} \log \frac{\{5.0 \times 10^{-6}\}}{\{0.5 \times 10^{-3}\}} = 7.65$$

where $pe^o = 14.9$ (Appendix 11, text)

Now use this value for the sulfur system.



$$pe = pe^o - \frac{n_H}{n_e} pH - \frac{1}{n_e} \log \frac{\{\text{Red}\}}{\{\text{Ox}\}}$$

$$pe = 4.20 - \frac{10}{8} pH - \frac{1}{8} \log \frac{\{H_2S\}}{\{SO_4^{2-}\}}$$

where $pe^0 = 4.20$ (Appendix 11, text) and $pe = 7.65$ (from above)

solving for $[SO_4^{2-}]/[H_2S] = 10^{87.6}$

We can use K_{a2} for the H_2SO_4 system to relate $[SO_4^{2-}]$ and $[HSO_4^-]$

$$K_{a2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} \quad \text{and} \quad [SO_4^{2-}] = \frac{K_{a2}[HSO_4^-]}{[H^+]}$$

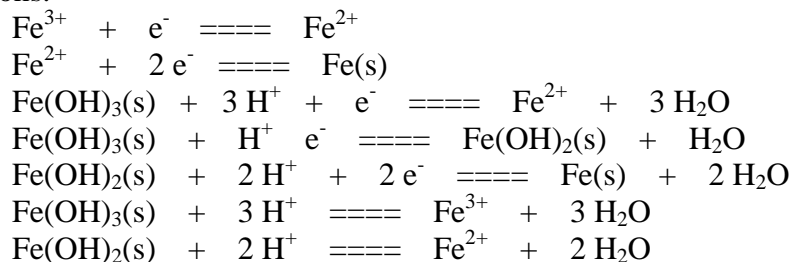
Substituting this into the ratio above yields,

$$\frac{[HSO_4^-]}{[H_2S]} = \frac{10^{87.6}[H^+]}{K_{a2}} = 4 \times 10^{83}$$

where $[H^+] = 10^{-6}$ and $K_{a2} = 1 \times 10^{-2}$

8. Considering the following reactions and boundary conditions, construct a pe-pH speciation diagram for the iron system consisting of $Fe(s) - Fe^{2+} - Fe(OH)_2(s) - Fe^{3+} - Fe(OH)_3$ in freshwater. Use 1.0×10^{-5} M as the maximum soluble $[Fe^{2+}]$ or $[Fe^{3+}]$.

Reactions:



Thermodynamic Data:

$$\begin{aligned} K_{sp}(Fe(OH)_2) &= 4.8 \times 10^{-17} \\ K_{sp}(Fe(OH)_3) &= 1.0 \times 10^{-38} \end{aligned}$$

Standard Free Energy of Formation (ΔG_f^0) in kJ/mol

e^- (aq)	H^+ (aq)	OH^- (aq)	$H_2O(l)$	$H_3O^+(aq)$	$Fe(s)$	$Fe^{2+}(aq)$	$Fe^{3+}(aq)$	$Fe(OH)_2(s)$	$Fe(OH)_3(s)$
0	0	-157.3	-237.2	-237.2	0	-78.9	-4.60	-486.6	-699

Solution: (see attached)

