

Exercise 1: Contaminated wetland



Consider a contaminated wetland soil containing Sr^{2+} , Co^{2+} , and Hg^{2+} . Soil flooding results in soil reduction and in the release of bicarbonate (HCO_3^-) and sulfide (HS^-) into soil solution.

- a. Which of the metals would you expect to mainly interact via complexation and precipitation with bicarbonate and which one predominantly with sulfide?
- b. For which trace metal is it most difficult to anticipate its preference for one of the two anions?





a. Use the hard-soft concept

Sr^{2+} : hard cation

Co^{2+} : intermediate cation

Hg^{2+} : soft cation

HCO_3^- : hard ligand

HS^- : soft ligand

We would expect Sr^{2+} to preferentially react with HCO_3^- and Hg^{2+} to primarily react with HS^- .

b. For Co^{2+} , it is most difficult to anticipate a preference for one of the two ions.

Exercise 2: Silver speciation



For a system with Ag^+ and NH_3 , what is the silver speciation at pH 7?

We know: $[\text{Ag}^+]_{\text{tot}} = 10^{-6} \text{ M}$, $[\text{NH}_4^+]_{\text{tot}} = 10^{-2} \text{ M}$, $K_1 = 10^{3.2}$, $K_2 = 10^{3.83}$, $K_a = 10^{-9.3}$

1. Identify species present at equilibrium
2. Write out equilibrium equations
3. List mass balance equations
4. Solve equations
5. Apply simplifications
6. Calculate silver speciation

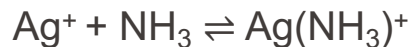
Exercise 2: Solution



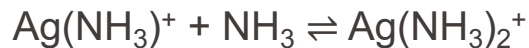
1. Species at equilibrium:



2. Equilibrium equations



$$K_1 = \frac{[\text{Ag}(\text{NH}_3)]}{[\text{Ag}^+][\text{NH}_3]} \quad \text{eq. 1}$$



$$K_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]} \quad \text{eq. 2}$$

$$\beta_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} \quad \text{eq. 3}$$



$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \quad \text{eq. 4}$$

3. Mass balance equations

$$[\text{Ag}^+]_{\text{tot}} = \text{Ag}^+ + \text{Ag}(\text{NH}_3)^+ + \text{Ag}(\text{NH}_3)_2^+ \quad \text{eq. 5}$$

$$[\text{NH}_4^+]_{\text{tot}} = [\text{NH}_3] + [\text{NH}_4^+] \quad \text{eq. 6}$$

Exercise 2: Solution



4. Use eqs. 1-6 to obtain an expression of $[Ag^+]$ as a function of given values

Express eq. 5 by substituting $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$ using eqs. 1-3:

$$[Ag^+]_{tot} = [Ag^+] (1 + [NH_3]K_1 + [NH_3]^2\beta_2) \quad \text{eq. 7}$$

Express NH_3 as a function as a function of $[NH_4^+]_{tot}$ and K_a using eq. 6:

$$[NH_3] = \frac{K_a[NH_4^+]_{tot}}{10^{-pH} + K_a} \quad \text{eq. 8}$$

Solve eq. 7 for $[Ag^+]$ and substitute $[NH_3]$ using eq. 8 to get

$$[Ag^+] = \frac{[Ag^+]_{tot}}{1 + \left(\frac{K_a[NH_4^+]_{tot}}{10^{-pH} + K_a}\right) K_1 + \left(\frac{K_a[NH_4^+]_{tot}}{10^{-pH} + K_a}\right)^2 \beta_2} \quad \text{eq. 9}$$

5. Apply simplifications: ligand is in excess, we do not consider complexes in the total ligand concentration

6. Calculate silver speciation

for $[Ag^+]$: fill numbers into eq. 9

for $[Ag(NH_3)^+]$: use $[Ag^+]$ and eq. 1 with $[NH_3]$ from eq. 8

for $[Ag(NH_3)_2^+]$: use mass balance eq. 5

Exercise 3: Zn(II) speciation in the presence of several ligands



Consider a system with Zn(II). Zn forms both hydroxo-complexes and carbonato-complexes. You have the following information:

- pH 8.5
- $Zn_{tot} = 10^{-8} \text{ M}$
- Total carbonate: $C_{tot} = 2 \cdot 10^{-3} \text{ M}$

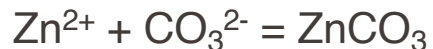
Calculate the concentrations of Zn^{2+} , $Zn(OH)^+$, $Zn(OH)_2$ and $ZnCO_3$



$$K_1 = 10^{-9.1}$$



$$\beta_2 = 10^{-17}$$



$$K_2 = 10^{4.52}$$



$$K_a = 10^{-10.2}$$

Exercise 3: Solution



$$\begin{aligned}
 [\text{Zn}_{\text{tot}}] &= [\text{Zn}^{2+}] + [\text{Zn}(\text{OH})^+] + [\text{Zn}(\text{OH})_2] + [\text{ZnCO}_3] \\
 &= [\text{Zn}^{2+}] + \frac{K_1}{[\text{H}^+]} [\text{Zn}^{2+}] + \frac{\beta_2}{[\text{H}^+]^2} [\text{Zn}^{2+}] + K_2 [\text{CO}_3^{2-}] [\text{Zn}^{2+}] \\
 &= [\text{Zn}^{2+}] \left(1 + \frac{K_1}{10^{-\text{pH}}} + \frac{\beta_2}{10^{-2\text{pH}}} + K_2 [\text{CO}_3^{2-}] \right)
 \end{aligned}
 \tag{eq. 1}$$

Find expression for $[\text{CO}_3^{2-}]$

$$C_{\text{tot}} = [\text{CO}_3^{2-}] + [\text{HCO}_3], \text{ i.e., } [\text{HCO}_3] = C_{\text{tot}} - [\text{CO}_3^{2-}]$$

$$K_a = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{C_{\text{tot}} - [\text{CO}_3^{2-}]}, \text{ thus } [\text{CO}_3^{2-}] (K_a + [\text{H}^+]) = K_a C_{\text{tot}}$$

$$[\text{CO}_3^{2-}] = \frac{K_a C_{\text{tot}}}{K_a + [\text{H}^+]} \tag{eq. 2}$$

Fill eq. 2 into eq. 1 and solve for $[\text{Zn}^{2+}]$ to get $[\text{Zn}^{2+}] = 2.8 \cdot 10^{-9} \text{ M}$

Calculate the concentrations of $\text{Zn}(\text{OH})^+$, $\text{Zn}(\text{OH})_2$ and ZnCO_3 using the equilibrium constants.

$$\text{Zn}(\text{OH})^+ = \frac{K_1}{[\text{H}^+]} [\text{Zn}^{2+}], \text{Zn}(\text{OH})_2 = \frac{\beta_2}{[\text{H}^+]^2} [\text{Zn}^{2+}], \text{ZnCO}_3 = K_2 [\text{CO}_3^{2-}] [\text{Zn}^{2+}]$$