Ch14 Winter term 2024

Problem set 4

due May 23, 2024

for Problems 1 and 2: for $CO_2, HCO_3^-, CO_3^{2-}, CaCO_3$ at 25°C, use $k_H = 0.035 \text{Matm}^{-1}$, $K_{a1} = 4.25 \times 10^{-7}$, $K_{a2} = 5.01 \times 10^{-11}$, $K_{sp} = 4.5 \times 10^{-9}$

1

Calculate the pH of the following solutions. The contribution of H_2CO_3 to the total concentration of dissolved CO_2-related species can be neglected in this analysis; these samples consist only of a solution, with neither gas phase CO_2 nor solid $CaCO_3$.

1.1

20mMNaHCO$_3$

1.1.1   Answer

This suggests that we have 20 mM of HCO_3^-. Now we have the equilibrium expression for the dissociation of a proton from HCO_3^-:

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \tag{1}$$

The equilibrium constant for this reaction is given by:

$$K_a = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \tag{2}$$

We can consider $0.02 - x$ as the concentration of HCO_3^- after dissociation and x as the concentration of H^+ and CO_3^{2-}. Substituting these values into the equilibrium constant expression, we get:

$$5.01 \times 10^{-11} = \frac{x^2}{0.02 - x} \tag{3}$$

Solving this equation, we get the pH of the solution is 6.00.

```
1  import sympy as sp
2
3  # Given constants
4  Ka2 = 5.01e-11
5  initial_HCO3 = 0.02
6  x = sp.symbols('x')
7  final_HCO3 = 0.02 - x
8  final_H = x
9  final_CO3 = x
10 eq = Ka2 - (final_H * final_CO3) / final_HCO3
11 x = sp.solve(eq, x)
12 # now get the pH
13 H = x[0]
14 pH = -sp.log(H, 10)
15 pH.evalf()
```
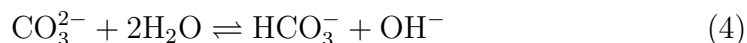
1.2

$20mMNa_2CO_3$

1.2.1 Answer

This suggests that we have 20 mM of CO_3^{2-}. We are interested in the hydrolysis of this ionic species in water:

$$CO_3^{2-} + 2H_2O \rightleftharpoons HCO_3^- + OH^- \tag{4}$$

We can use the given K_{a2} to determine the K_b for the hydrolysis of CO_3^{2-}:

$$K_b = \frac{K_w}{K_{a2}} \tag{5}$$

Then the equilibrium expression for this hydrolysis is:

$$K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} \tag{6}$$

We can then use the concentration of hydroxide to calculate the pH. This gives a pH of 11.3.

```python
import sympy as sp

# Given constants
Ka2 = 5.01e-11
# calculate the Kb from the Ka2
Kw = 1e-14
Kb = Kw / Ka2
initial_CO3 = 0.02
x = sp.symbols('x')
final_CO3 = 0.02 - x
final_OH = x
final_HCO3 = x
eq = Kb - (final_OH * final_HCO3) / final_CO3
x = sp.solve(eq, x)
# now get the pOH
OH = x[0]
pOH = -sp.log(OH, 10)
# convert this into a pH
pH = 14 - pOH
pH.evalf()
```

2

This problem is modified from the 2022 midterm, problem 6B "Is this a soluble problem?", which, ironically, was not soluble as it was written...

2.1

What partial pressure (in atm) of gas phase CO_2 exists in equilibrium with a solution saturated with $CaCO_3$ at pH $= 7.5$? The problem originally specified that the free Ca^{2+} concentration $= 0.001$ M, but this constraint is inconsistent with the relevant equilibrium constants.
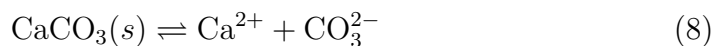
2.1.1 Answer

Since we are given the pH of the solution, we can calculate the concentration of H^+ ions in the solution. The solubility product constant for $CaCO_3$ is

given by:
$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] \tag{7}$$

The relevant equilibrium expression for this reaction would be:
$$\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} \tag{8}$$

So due to stoichiometry, we know that the concentration of Ca^{2+} should be approximately equal to the concentration of CO_3^{2-}. We can use this fact to substitute into the solubility product expression and then solve for the concentration of CO_3^{2-}:
$$4.5 \times 10^{-9} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = x^2 \tag{9}$$

Now that we have the concentration of CO_3^{2-}, we can calculate the concentration of HCO_3^- using the dissociation expression:
$$K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \tag{10}$$

Now that we have solved for the concentration of HCO_3^-, we can now use this information to solve for the concentration of H_2CO_3 using the equilibrium expression:
$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \tag{11}$$

Then, we know that there exists a rapid equilibrium between H_2CO_3 and CO_2, so we can say that their concentrations will be roughly equal. Now we can solve for the partial pressure of CO_2 using the Henry's law constant:
$$k_H = \frac{[\text{CO}_2]}{P_{\text{CO}_2}} \tag{12}$$

This gives a partial pressure of CO_2 of 0.0900 atm.

```python
import sympy as sp
import numpy as np

# defined the symbols
h_plus, co3_2_minus, hco3_minus, h2co3, co2 = sp.symbols('
    h_plus co3_2_minus hco3_minus h2co3 co2')

# Given equilibrium constants
```

```
 8 pH = 7.5
 9 # use this to compute the futon concentration
10 h_plus = 10**-pH
11 ksp = 4.5e-9
12 co3_2_minus = np.sqrt(ksp)
13 # now we have all of the ingredients to compute hco3_minus
14 ka1 = 4.25e-7
15 hco3_minus = (h_plus * co3_2_minus) / ka1
16 # now we can compute h2co3
17 ka2 = 5.01e-11
18 h2co3 = (h_plus * hco3_minus) / ka2
19 # this will be equal to the concentration of carbon dioxide
20 co2 = h2co3
21 # now come we want to solve for the partial pressure of
       carbon dioxide using henry's law
22 kh = 0.035
23 p_co2 = co2 / kh
24 p_co2
```

3

A protein P binds to DNA according to the following reaction

$$P^{ZP\pm} + DNA^{Z-} \overset{K_A}{\rightleftharpoons} P \cdot DNA^{Z-ZP\pm}$$
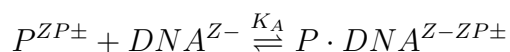
where K_A is the association constant for the binding of P to DNA. P has multiple positively charged amino groups and multiple negatively charged carboxylate groups, with an overall charge of ZP±. Due to the titration of these ionizable residues, the overall charge ZP± is a function of pH as shown below:
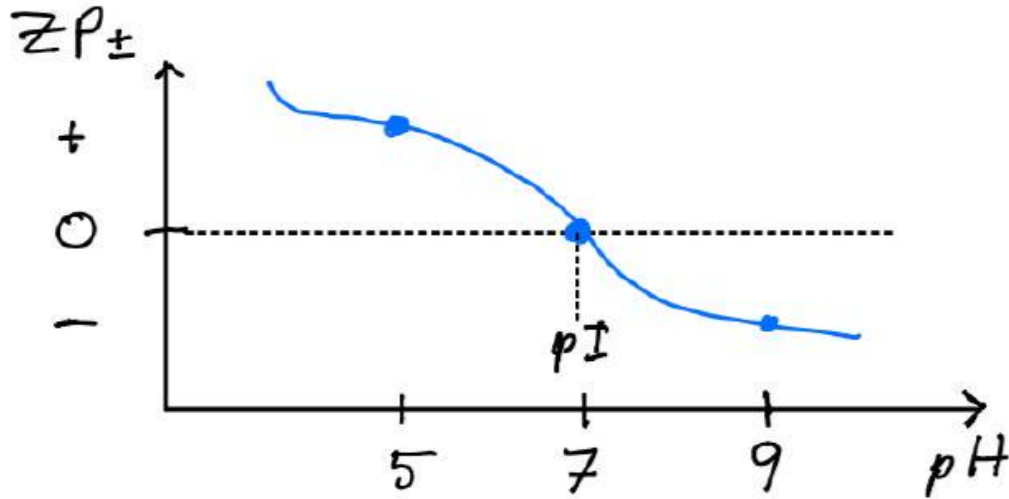
At the isoelectric point, pl, the positively charged residues are balanced by the negatively charged residues, so that the net charge is 0 . The DNA remains negatively charged at all pHs. The association of P and DNA has a strong electrostatic component based on the net charges of P and DNA; i.e., at pHs lower than the pl, P has a net positive charge, so there is an attractive electrostatic contribution stabilizing complex formation with the negatively charged DNA, while at pHs above the pl, P has a net negative charge so there is a repulsive electrostatic contribution destabilizing complex formation with DNA. At every pH, the charge of the complex is the sum of the charges on the protein at that pH, plus the negative charge on DNA.

From Ch14, we know that equilibrium concentrations involving charged species will depend on ionic strength (I) due to the ionic strength dependence of the activity coefficients. Based on the ionic strength dependence of the activity coefficients captured in the Debye-Hückel limiting law, answer the following questions and provide a brief (1 sentence) explanation.

3.1

The Debye-Hückel limiting law is given by:

$$\log \gamma_{\pm} = -0.509 z_{\pm}^2 \sqrt{I} \tag{13}$$
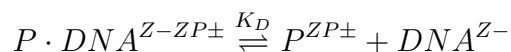
3.1.1 Question

Will the association constant K_A increase or decrease with increasing I at pH5 ?

3.1.2 Answer

As we

- Will the association constant K_A increase or decrease with increasing I at pH5 ?

- Will the association constant K_A increase or decrease with increasing I at pH 9?

This reaction can also be modeled as a dissociation reaction, where K_D is the dissociation constant.

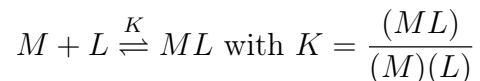$$P \cdot DNA^{Z-ZP\pm} \overset{K_D}{\rightleftharpoons} P^{ZP\pm} + DNA^{Z-}$$

3b. (10 pts)

- Will the dissociation constant K_D increase or decrease with increasing I at pH5 ?

- Will the dissociation constant increase or decrease with increasing I at pH9 ?

4   Problem 4 (20 points total)

M and L interact to form a complex ML with association constant K.

$$M + L \overset{K}{\rightleftharpoons} ML \text{ with } K = \frac{(ML)}{(M)(L)}$$

In our analysis of ligand binding, we typically have assumed that the ligand, L, is in vast excess over the metal, M, so that the binding of ligand to M to form ML does not appreciably impact the concentration of free L. Under these conditions, when $(L) = \frac{1}{K}$

Eq. A

7

$$\bar{n} = \frac{(ML)}{(M)+(ML)} = \frac{K(L)}{1+K(L)} = \frac{1}{2}$$

In the case of tight binding systems where the total ligand concentration is comparable to the total metal concentration, however, the formation of ML will influence the amount of free L left in solution. The following example illustrates this point.

Define the total concentrations of the metal and ligand as (M_{tot}) and (L_{tot}), respectively:

$$(M)+(ML) = (M_{tot})$$
$$(L)+(ML) = (L_{tot})$$

Taking into account the effect of (ML) on free (L), calculate the numerical value of $\bar{n}$ to 3 significant figures for the case where

$$(M_{tot}) = (L_{tot}) = \frac{1}{K}$$

(continued on next page!)

Hint: incorporate the conservation of mass relations into the association constant expression and solve for (ML) when $(M_{\text{tot}}) = (L_{\text{tot}}) = \frac{1}{K}$; i.e.

$$K = \frac{(ML)}{(M)(L)} = \frac{(ML)}{[(M_{tot})-(ML)]\,[(L_{tot})-(ML)]}$$

Explain briefly why $\bar{n}$ for the tight binding case when $(L) = \frac{1}{K}$ is less than that observed when $(L) = \frac{1}{K}$ for the weak binding case of Eq. A.

4.0.1   Answer

We start with the expression for the association constant K:

$$K = \frac{(ML)}{(M)(L)} \tag{14}$$

But now in the denominator, we can use the conservation of mass relations that were given:

$$K = \frac{(ML)}{[(M_{\text{tot}})-(ML)]\,[(L_{\text{tot}})-(ML)]} \tag{15}$$

Now we can substitute the given values of $(M_{\text{tot}}) = (L_{\text{tot}}) = \frac{1}{K}$ into this equation:

$$K = \frac{(ML)}{\left[\frac{1}{K} - (ML)\right]\left[\frac{1}{K} - (ML)\right]} \tag{16}$$

Solving for (ML), we get $(ML) = \frac{3 \pm \sqrt{5}}{2K}$. The definition of $\bar{n}$ is given by:

$$\bar{n} = \frac{(ML)}{(M) + (ML)} \tag{17}$$

But we know that $(M) = (M_{\text{tot}}) - (ML)$, so we can substitute this into the equation for $\bar{n}$:

$$\bar{n} = \frac{(ML)}{(M_{\text{tot}} - (ML)) + (ML)} = \frac{(ML)}{(M_{\text{tot}})} = \frac{\frac{3 \pm \sqrt{5}}{2K}}{\frac{1}{K}} = \frac{3 \pm \sqrt{5}}{2} = 0.382 \tag{18}$$

Note that we have only used the $-$ of the $\pm$ because we need for the fraction of $\frac{(ML)}{(M + (ML))}$ to be less than 1 since the (M) must be positive.

```python
import sympy as sp

# Define the symbols
ml, k = sp.symbols('ml k')

# Define the equation
eq = sp.Eq(k, ml / ((1 / k - ml)**2))

# Solve the equation for ml
ml_solution = sp.solve(eq, ml)

# Select the physically meaningful solution
ml_solution = ml_solution[0]  # typically the positive root

# Define the total metal concentration
M_tot = 1 / k

# Calculate the value of bar_n
n_bar = ml_solution / M_tot

# Simplify the expression for n_bar
n_bar = sp.simplify(n_bar)

# Display the simplified n_bar
n_bar.evalf()
```

9

For the tight binding case, the formation of the complex ML significantly reduces the free ligand concentration, unlike in the weak binding case where the ligand concentration remains largely unaffected. This results in a lower $\bar{n}$ value because fewer complexes can form when the ligand concentration is appreciably reduced.
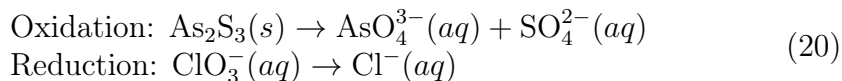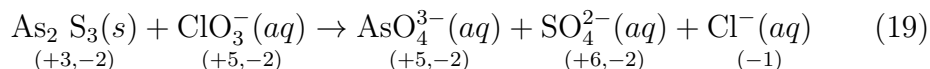
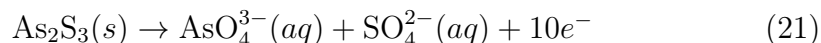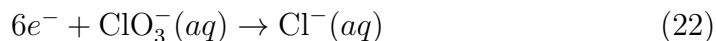# 5 Problem 5 (20 points total)

Balance the following reaction,

$$As_2\,S_3(s) + ClO_3^-(aq) \rightarrow AsO_4^{3-}(aq) + SO_4^{2-}(aq) + Cl^-(aq)$$
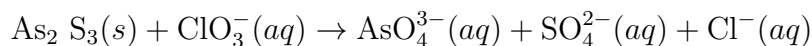
5.0.1 Answer

We start by assigning oxidation states to the compounds in the unbalanced reaction:

$$\underset{(+3,-2)}{As_2\,S_3(s)} + \underset{(+5,-2)}{ClO_3^-(aq)} \rightarrow \underset{(+5,-2)}{AsO_4^{3-}(aq)} + \underset{(+6,-2)}{SO_4^{2-}(aq)} + \underset{(-1)}{Cl^-(aq)} \tag{19}$$

$$\begin{aligned} \text{Oxidation: } & As_2S_3(s) \rightarrow AsO_4^{3-}(aq) + SO_4^{2-}(aq) \\ \text{Reduction: } & ClO_3^-(aq) \rightarrow Cl^-(aq) \end{aligned} \tag{20}$$
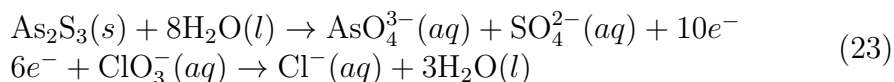
For the oxidation reaction, we need to add 10 electrons to the right side to balance the charge. For the reduction reaction, we need to add 6 electrons to the left side to balance the charge:
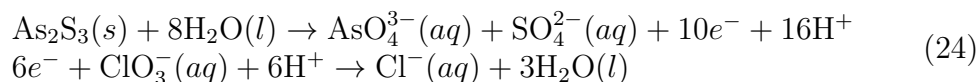
$$As_2S_3(s) \rightarrow AsO_4^{3-}(aq) + SO_4^{2-}(aq) + 10e^- \tag{21}$$

and

$$6e^- + ClO_3^-(aq) \rightarrow Cl^-(aq) \tag{22}$$

Next, we want to balance the number of oxygens by adding water:

$$\begin{aligned} & As_2S_3(s) + 8H_2O(l) \rightarrow AsO_4^{3-}(aq) + SO_4^{2-}(aq) + 10e^- \\ & 6e^- + ClO_3^-(aq) \rightarrow Cl^-(aq) + 3H_2O(l) \end{aligned} \tag{23}$$

Finally, we balance the hydrogens by adding protons:

$$\begin{aligned} & As_2S_3(s) + 8H_2O(l) \rightarrow AsO_4^{3-}(aq) + SO_4^{2-}(aq) + 10e^- + 16H^+ \\ & 6e^- + ClO_3^-(aq) + 6H^+ \rightarrow Cl^-(aq) + 3H_2O(l) \end{aligned} \tag{24}$$

Now, we can multiply the oxidation reaction by 3 and the reduction reaction by 5 to balance the electrons:

$$3As_2S_3(s) + 24H_2O(l) \rightarrow 3AsO_4^{3-}(aq) + 3SO_4^{2-}(aq) + 30e^- + 48H^+$$
$$30e^- + 5ClO_3^-(aq) + 30H^+ \rightarrow 5Cl^-(aq) + 15H_2O(l) \tag{25}$$
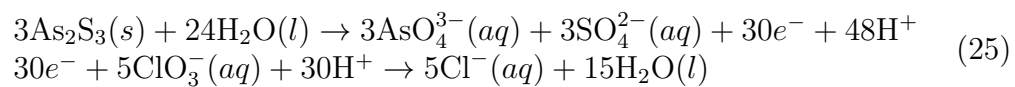
Finally, we can add the two reactions together to get the balanced reaction and cancel common factors:

$$3As_2S_3(s) + 9H_2O(l) + 5ClO_3^-(aq) \rightarrow 3AsO_4^{3-}(aq) + 3SO_4^{2-}(aq) + 5Cl^-(aq) + 18H^+ \tag{26}$$