

Chemistry 14 (Spring term 2024)

Final Examination for Seniors

Distributed Thursday, May 30, 2024

Due Thursday, June 6, 2024 by 11:59 pm uploaded through Canvas

Conditions

- Open the midterm examination pdf when you are ready to take it.
- You have 4 hours to complete this examination (excluding a short break).
- You may use the Ch14 online lecture notes, problem sets and solutions, the course web site and a calculator. You may also use the Harris & Lucy text (or earlier editions). You may also use handwritten notes you have made from other books. You may not discuss the exam with others, use any other books (including those on Reserve), or other web sites.
- You may use Mathematica , Matlab , Excel® or equivalent program to get numerical solutions.
- Write your answers in the same sequential order as in the exam.
- After you have finished the exam, upload your answers through Canvas, just as you do for the problem sets.
- Show your work! Getting the right answer is not enough - the intermediate steps are needed for credit. If you use Mathematica ® or related program to get numerical solutions, be sure to clearly write out in the exam the specific equation being solved. Note: you do not need to derive equations that were derived in class.

- Unless otherwise instructed, you should report answers to 3 significant figures and assume that activities can be approximated by concentrations. You may use approximate formulas as long as you justify the particular approximation (ie in a sufficiently acidic solution, (OH^-) may be neglected relative to (H^+) , etc).

unless otherwise stated, you may assume:

aqueous solutions

$T = 298.15 \text{ K} = 25^\circ\text{C}$; $P = 1 \text{ atm}$, $\text{pH} = 7$; $K_w = 10^{-14}$

$R = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08206 \text{ liter atm mol}^{-1} \text{ K}^{-1}$

$F = 96.485 \text{ kJ mol}^{-1} \text{ V}^{-1}$

1

The pH of blood is regulated in part by the CO_2 / bicarbonate buffer system.

1.1

Calculate the expected pH if $[\text{HCO}_3^-] = 25\text{mM}$ and the concentration of CO_2 in the lungs = 0.038 atm . At 37°C , $K_{a1} = 7.94 \times 10^{-7}$ and $K_H = 0.030$. Assume that the CO_2 levels in the blood and in the lung are in equilibrium. The minor contribution of (CO_3^{2-}) may be neglected.

1.1.1 Answer

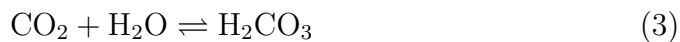
Using what we know about the first dissociation constant, we can use the concentration from the first dissociation product to relate to the bicarbonate and H^+ concentrations via

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \rightarrow [\text{H}^+] = \frac{K_{a1} \times [\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} \quad (1)$$

We know that Henry's law tells us that

$$[\text{CO}_2] = K_H \times P_{\text{CO}_2} \quad (2)$$

We know that there exists a rapid equilibrium between carbon dioxide and bicarbonate via hydration with water, so



and therefore

$$[\text{H}_2\text{CO}_3] = [\text{CO}_2] \quad (4)$$

Putting all of these ingredients together, we get that the pH is given by 7.44.

```
1 import sympy as sp
2
3 # Constants
4 k_a1 = 7.94e-7 # Acid dissociation constant
5 k_h = 0.03     # Henry's law constant at 37 degrees Celsius
6               # (M/atm)
7 p_co2 = 0.038  # Partial pressure of CO2 in the lungs (atm)
8 conc_hco3 = 0.025 # Concentration of bicarbonate in blood (M)
9
10 # Define symbols
11 H = sp.symbols('H')
12
13 # Calculation of [CO2] using Henry's law
14 conc_co2 = p_co2 * k_h
15
16 # Using the approximation that [H2CO3] \approx [CO2]
17 conc_h2co3 = conc_co2
18
19 # Ka expression for the first dissociation of carbonic acid
20 # H2CO3 -> H+ + HCO3-
21 equation = sp.Eq(H * conc_hco3, k_a1 * conc_h2co3)
22
23 # Solve for [H+]
24 H_concentration = sp.solve(equation, H)[0]
25
26 # Calculate pH
27 pH = -sp.log(H_concentration, 10)
28
29 # Simplify the expression for pH
30 pH_simplified = sp.simplify(pH)
31
32 # Displaying the pH expression and calculated value
33 pH_simplified.evalf()
```

1.2

By holding your breath for an extended period of time, the CO_2 levels in the lungs and blood will increase. How will this qualitatively change the pH of

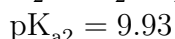
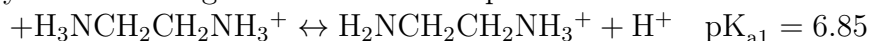
the CO₂/ bicarbonate buffer system if the bicarbonate concentration remains unchanged?

1.2.1 Answer

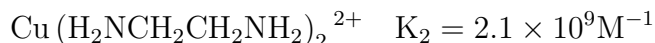
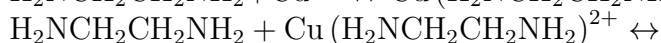
When the levels of carbon dioxide in your blood stream increase, this increases the concentration of bicarbonate, which therefore increases the concentration of protons and thus decreases the pH. This is why you can get as an athlete a lot of lactic acid buildup after exercise because the carbon dioxide levels in your body are increasing, and thus there is a more acidic environment.

2

Ethylenediamine (H₂NCH₂CH₂NH₂) is a bidentate chelating ligand that displays the following acid dissociation equilibria:



Fully deprotonated ethylenediamine chelates Cu²⁺ with the following stepwise association constants:



10⁻⁵M Cu²⁺ is mixed with 0.01M ethylenediamine at pH5.0. Calculate the fractions of Cu²⁺ with 0,1 and 2 bound ethylenediamine ligands under these conditions. You may assume that the ethylenediamine is in large excess relative to Cu²⁺.

2.0.1 Answer

We can sort by defining the 2 acid dissociation equations

$$K_{a1} = \frac{[H^+][H_2NCH_2CH_2NH_3^+]}{[+H_3NCH_2CH_2NH_3^+]} \quad (5)$$

and

$$K_{a2} = \frac{[\text{H}^+][\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2]}{[\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_3^+]} \quad (6)$$

We can then use the equilibrium constant for the chelation of the copper ions to the ethylenediamine ligands, which is given by

$$K_1 = \frac{[\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2][\text{Cu}^{2+}]}{[\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2^{2+}]} \quad (7)$$

and

$$K_2 = \frac{[\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2][\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2^{2+}]}{[\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2^{2+}]} \quad (8)$$

In order to compute the fractions, we want to see the concentrations of the species divided by the total copper concentration initially at 10^{-5}M . So

$$n_1 = \frac{[\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2^{2+}]}{10^{-5}} \quad (9)$$

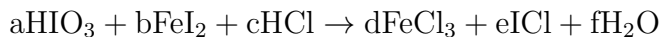
and

$$n_2 = \frac{[\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2^{2+}]}{10^{-5}} \quad (10)$$

while $n_0 = 1 - n_1 - n_2$.

3

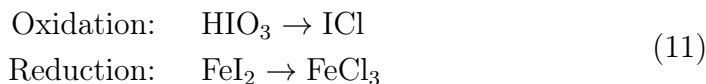
Balance the following redox reaction (i.e., determine the values of the stoichiometric coefficients a, b, c, d, e, and f):



Hint: the oxidation states of iodine in HIO_3 , FeI_2 , and ICl are +5, -1, and +1, respectively, while the oxidation states of O, Cl, and H in this reaction may be taken as -2, -1, and +1, respectively, and are unchanged in this reaction.

3.0.1 Answer

We identify the oxidation and reduction half-reactions as follows:



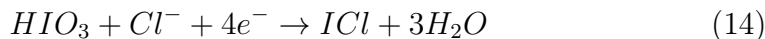
The first thing that we do is to add some electrons to the left side of the oxidation reaction



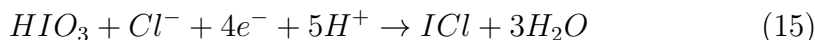
Then, we balance the number of elements other than oxygen and hydrogens



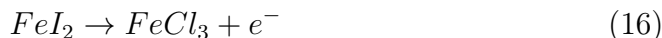
Then, we balance the number of oxygens by adding 3 waters to the right side



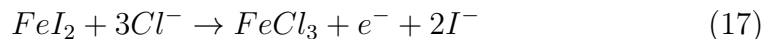
Then, we balance the number of hydrogens by adding 5 protons to the left



Next, we turn to the reduction half-reaction. We start by adding 1 electron to the right side



Then, we balance the number of elements other than oxygen and hydrogens by adding 3 chloride ions to the left side and 2 iodides to the right side



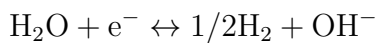
At this point, normally one would multiply one of the half-reactions by some factor and add it to the other one, but I am not sure how to proceed here with the extra factor of 2I^- on the right side of the reduction half-reaction.

4

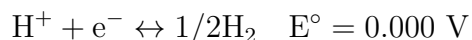
Oxidation-reduction reactions are typically described in terms of an acidic standard state (ie, pH0 where the H^+ activity = 1M). This choice is arbitrary and we could equally as well have used an alkaline standard state where

the OH^- activity = 1M (ie, pH 14). Under these conditions, the hydrogen electrode reduction potential may be written as

Eq A



From the definitions of $K_w (= 10^{-14})$ and the standard hydrogen electrode at pH0 :



calculate E° in Volts for the Eq A half cell reaction.

4.0.1 Answer

We can achieve equation A by adding to it the ionization of water



which we know has the K_w value of 10^{-14} . We can therefore find the free energy change using the relation

$$\Delta G^\circ = -RT \ln K_w \quad (19)$$

We can use the change in free energy to find the associated potential using the relation

$$\Delta E^\circ = \frac{\Delta G^\circ}{nF} \quad (20)$$

where n is the number of electrons transferred in the reaction, which is 1 in this case. The last step will be to find out how this potential change relates to the standard hydrogen electrode potential at pH0.

$$E_A^\circ = E_{\text{standard hydrogen electrode}}^\circ - \Delta E^\circ \quad (21)$$

This gives $E_A^\circ = -0.828$ Volts.

```
1 import numpy as np
2 import sympy as sp
3
4 # Constants
5 R = 8.314 # J/(mol K)
6 T = 298 # Kelvin
7 F = # C/mol
```

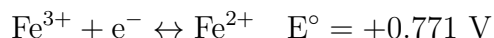
```

8 Kw = 10**-14
9
10 # Calculate change in Gibbs free energy for ionization of
    water
11 delta_G = -R * T * np.log(Kw)
12
13 # Convert delta G to delta E
14 delta_E = delta_G / F
15
16 # Calculate the new E for the Eq A half-cell reaction
17 E_standard_acid = 0.000 # V for the standard hydrogen
    electrode
18 E_standard_alkaline = E_standard_acid - delta_E #
    Subtracting because we are moving from acid to alkaline
19
20 E_standard_alkaline

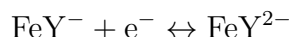
```

5

Given the following half-cell reaction:



and that the formation constants β for the binding of full deprotonated EDTA (abbreviated as Y^{4-}) to Fe^{2+} and Fe^{3+} to yield FeY^{2-} and FeY^- are 2.1×10^{14} and 1.3×10^{25} , respectively, calculate the standard reduction potential E° in Volts for the following half cell:



5.0.1 Answer

We can make use of the formation constants. We have the reactions



and



By adding the first one to the initial half-cell reaction and then the reverse of the second one to this, we get the desired half-cell reaction. Now, we are left

with the task to convert the formation constants into reduction potentials. We can relate the Gibbs free energy to the formation constant by

$$\Delta G^\circ = -RT \ln \beta \quad (24)$$

We can then use the relation

$$\Delta E^\circ = \frac{\Delta G^\circ}{nF} \quad (25)$$

to find the reduction potential. We can then use the relation

$$E_{\text{desired}}^\circ = E_{\text{given}}^\circ - \Delta E_1^\circ + \Delta E_2^\circ \quad (26)$$

where we have defined ΔE_1° and ΔE_2° as the changes in free energy for the first and second reactions, respectively. This gives $E_{\text{desired}}^\circ = 0.133$ Volts.

```

1 import numpy as np
2 import sympy as sp
3
4 # Constants
5 R = 8.314 # J/(mol K)
6 T = 298 # Kelvin
7 F = 96485 # C/mol
8
9 # Given data
10 E0_Fe3_to_Fe2 = 0.771 # V, standard potential for Fe3+ to
    Fe2+
11 beta_Fe2_EDTA = 2.1e14 # formation constant for Fe2+ with
    EDTA
12 beta_Fe3_EDTA = 1.3e25 # formation constant for Fe3+ with
    EDTA
13
14 # Calculate delta G for both formation reactions using the
    formation constants
15 delta_G1 = -R * T * np.log(beta_Fe2_EDTA) # For FeY^2-
16 delta_G2 = -R * T * np.log(beta_Fe3_EDTA) # For FeY^-
17
18 # Convert delta G to delta E
19 delta_E1 = delta_G1 / F # Corresponds to Fe2+ + Y4- -> FeY2-
20 delta_E2 = delta_G2 / F # Corresponds to Fe3+ + Y4- -> FeY^-
21
22 # Calculate the desired E0 for the reaction FeY^- + e^- ->
    FeY^2-
23 E0_desired = E0_Fe3_to_Fe2 - delta_E1 + delta_E2
24
25 E0_desired

```

6

The solutions of two Cu^{+2}/Cu half-cells are connected through a salt bridge, while the two copper electrodes are connected with a voltmeter. One of the solutions contains $0.1\text{M}\text{CuSO}_4$, while the other contains $1.0\text{M}\text{CuSO}_4$. What is the potential difference (if any), in Volts, generated by this system, and which half-cell has the positive electrode (i.e. is the positive Cu electrode in the 0.1M or 1.0M solution?)?

6.0.1 Answer

As given in the May 21st lecture, there will be indeed a potential difference caused by this difference in concentrations. The concentration of the copper sulfate would give rise to an oxidation to Cu^{2+} . The cell will seek to achieve a configuration where the concentration of Cu^{2+} is the same in both solutions, so the electrons will move from the lower to the higher concentration to achieve this, and thus the half-cell with the higher concentration will have the positive electrode. To make this more rigorous, we know that in a negatively charged cell, the relevant redox reaction is



where $[B_{\text{ox}}] = 1.0\text{M}$ and $[B_{\text{red}}] = 0.1\text{M}$. For the other cell, we have the same thing happening with $[A_{\text{ox}}] = 1\text{M}$ and $[A_{\text{red}}] = 1.0\text{M}$. The potential difference is given by

$$\Delta E = \Delta E^\circ - \frac{RT}{nF} \ln \left(\frac{[A_{\text{red}}][B_{\text{ox}}]}{[A_{\text{ox}}][B_{\text{red}}]} \right) = 0 - \frac{RT}{2F} \ln \left(\frac{1.0 \times 0.1}{1.0 \times 1.0} \right) \quad (28)$$

This gives $\Delta E = 0.0296$ Volts.

```
1 import math
2
3 # Constants
4 R = 8.314 # Gas constant, J/(mol K)
5 T = 298   # Temperature in Kelvin
6 F = 96485 # Faraday constant, C/mol
7 n = 2     # Number of electrons transferred in the reaction
8
9 # Concentrations
10 C_high = 1.0 # Molarity of CuSO4 in the high concentration
                half-cell
```

```

11 C_low = 0.1      # Molarity of CuSO4 in the low concentration
    half-cell
12
13 # Nernst Equation to calculate the potential difference
14 delta_E = -(R * T / (n * F)) * math.log(C_low / C_high)
15
16 delta_E

```

7

A one meter column has 500 theoretical plates. The elution volumes of two solutes are 100 and 105mls, respectively. All things being equal (flow rate, crosssectional area, etc.), the elution volumes and the number of theoretical plates will both be proportional to the column length. How long (in meters) would the column need to be to separate these two solutes by $R = 1$?

7.0.1 Answer

We know that the resolution is given by

$$R = \frac{2(t_2 - t_1)}{w_1 + w_2} \quad (29)$$

where t_1 and t_2 are the elution volumes of the two solutes, and w_1 and w_2 are the widths of the two peaks. Since the peak is given by a Gaussian distribution, we know that the width can be approximated As

$$w = \frac{4\sigma}{\sqrt{N}} \quad (30)$$

But then, in the lecture, we found the form for the effective number of plates As

$$N = \left(\frac{V_E}{\sigma}\right)^2 \rightarrow \sigma = \frac{V_E}{\sqrt{N}} \quad (31)$$

where V_E is the elution volume. So we can plug in to solve for N since we no the ventilation is 1, and then we can use the relationship between the number of plates and the length of the column as 500 plates for 1 meter to solve for the length of the column.

$$N = 500L \quad (32)$$

This gives $L = 0.164$ meters.

```

1 import sympy as sp
2
3 # Define symbols
4 L = sp.symbols('L', real=True, positive=True) # Column
   length
5 R = 1 # Target resolution
6
7 # Given values
8 V1 = 100 # Elution volume of solute 1 in mL
9 V2 = 105 # Elution volume of solute 2 in mL
10 plates_per_meter = 500 # Number of theoretical plates per
   meter
11
12 # Calculate the effective number of plates N based on length
   L
13 N = 500 * L
14
15 # Compute the standard deviation sigma for each solute
16 sigma1 = V1 / sp.sqrt(N)
17 sigma2 = V2 / sp.sqrt(N)
18
19 # Compute the widths of the peaks
20 w1 = 4 * sigma1 / sp.sqrt(N)
21 w2 = 4 * sigma2 / sp.sqrt(N)
22
23 # Set up the resolution equation
24 resolution_eq = sp.Eq(2 * (V2 - V1) / (w1 + w2), R)
25
26 # Solve for L
27 length_solution = sp.solve(resolution_eq, L)
28
29 length_solution[0].evalf()

```

8

8.1

What is the nearest pH of a 10^{-1}M HCl solution?

- i. -1
- ii. 0
- iii. +1

8.1.1 Answer

We know that the pH is given by

$$\text{pH} = -\log_{10}[\text{H}^+] \quad (33)$$

So we can plug in the concentration of H^+ to find that the pH is 1.

8.2

What is the nearest pH of a 10^{-9}M HCl solution?

- i. 5
- ii. 7
- iii. 9

8.2.1 Answer

At neutral pH in water, the concentration of protons is 10^{-7} , so the addition of 10^{-9} moles of protons will not change the pH significantly. Therefore, the pH will be 7.

9

9.1

What was the most memorable Ch14 field trip that you participated in this term? Explain briefly.

9.1.1 Answer

I enjoyed visiting Scott Virgil's lab and specifically seeing the robots being put to use. Also, I thought the machine from Japan which got all of the little beads into the vials was pretty neat.

9.2

What campus facilities would you have liked to have visited? Explain briefly.

9.2.1 Answer

This is not really relevant to the class, but it would be nice to see the high-performance computing center on campus, to speak a bit with the staff and for them to talk about what resources they provide.