

Chemistry 14 (Spring term 2024)

Midterm Examination

Distributed Thursday, May 2, 2024

Due Thursday, May 9, 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, including solving polynomial equations. Please note, though, that the problems can be worked with a quadratic equation as the most complex equation that needs to be solved.
- 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

$$T = 298.15 \text{ K} = 25^\circ\text{C}$$

$$P = 1 \text{ atm}$$

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

$$K_w = 10^{-14}$$

Debye-Huckel limiting expression, water, 25°C

$$\text{individual ionic activity coefficient } \log \gamma_i = -0.509 z_i^2 \sqrt{I}$$

$$\text{mean ionic activity coefficient } \log \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I}$$

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problem	points	
1a	5	
1b	5	<input type="checkbox"/>
2a	10	
2b	10	<input type="checkbox"/>
3a	5	
3b	10	<input type="checkbox"/>
3c	10	<input type="checkbox"/>
3d	10	<input type="checkbox"/>
3e	10	<input type="checkbox"/>
4a	10	
4b	10	<input type="checkbox"/>
5	5	
total	100	

1 Strong acids and strong bases

Nitric acid is a strong acid and barium hydroxide is a strong base. Assume activities equal concentrations in this problem.

1.1

Calculate the pH of solution containing 0.001M barium hydroxide ($\text{Ba}(\text{OH})_2$).

1.1.1 Answer

$$\begin{aligned}
 \text{Ba}(\text{OH})_2 &\longrightarrow \text{Ba}^{2+} + 2 \text{OH}^- \\
 [\text{Ba}(\text{OH})_2] &= 0.001 \text{ M} \rightarrow [\text{OH}^-] = 0.002 \text{ M} \\
 K_w &= [\text{H}^+][\text{OH}^-] = 10^{-14} \\
 [\text{H}^+] &= \frac{10^{-14}}{0.002} = 5 \times 10^{-12} \\
 \text{pH} &= -\log [\text{H}^+] = 11.3
 \end{aligned}$$

1.2

Calculate the pH of a solution containing 0.1M barium nitrate ($\text{Ba}(\text{NO}_3)_2$).

1.2.1 Answer

(Ba(NO₃)₂) is a salt of a strong acid and a strong base, so it will not affect the pH of the solution. The pH of the solution will be the same as the pH of the water, which is 7.

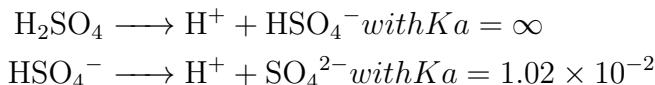
2 Weak acids and weak bases

2.1

Sulfuric acid completely dissociates to H⁺ and HSO₄⁻ in solutions more dilute than 0.1M. HSO₄⁻ further dissociates to H⁺ and SO₄²⁻ with K_a = 1.02 × 10⁻². Calculate the pH of a 0.05M solution of sulfuric acid. Since sulfuric acid is both a strong acid and a weak acid, start with the charge balance equation for this system. Assume activities equal concentrations.

2.1.1 Answer

We are interested in the two dissociation expressions for sulfuric acid:



We initially know that the concentration of protons is equal to the concentration of sulfuric acid, so [H⁺] = 0.05M and [HSO₄⁻] = 0.05M. We can then use the second dissociation to find the concentration of [SO₄²⁻]:

$$\begin{aligned} \text{HSO}_4^- &\longrightarrow \text{H}^+ + \text{SO}_4^{2-} \\ K_a &= \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \end{aligned}$$

Let us set the parameter x to be the concentration of [SO₄²⁻]. Then the final concentration of [HSO₄⁻] will be 0.05 - x and the final concentration of [H⁺] will be 0.05 + x . We can then solve for x . This suggests the expression:

$$1.02 \times 10^{-2} = \frac{(0.05 + x)x}{0.05 - x}$$

Solving gives a solution for x as 0.00753 M. This means that the concentration of $[H^+]$ is $0.05 + 0.00753 = 0.05753M$. The pH is then $-\log(0.05753) = 1.24$.

```

1 from sympy import symbols, Eq, solve
2
3 # Define the variable
4 x = symbols('x', real=True, positive=True)
5
6 # Given constants
7 Ka2 = 1.02e-2
8 initial_H2SO4 = 0.05 # Initial concentration of H2SO4 and
   hence HS04-
9
10 # Ka expression for the second dissociation of HS04-
11 equation_Ka = Eq((initial_H2SO4 + x) * x / (initial_H2SO4 - x
   ), Ka2)
12
13 # Solve the equation
14 x_value = solve(equation_Ka, x)
15 x_value

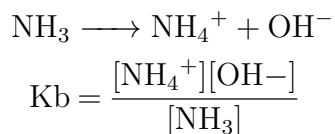
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2.2

Calculate the pH and the equilibrium concentrations of (NH_3) and (NH_4^+) present in a solution of NH_3 made to a total concentration of $1.0 \times 10^{-6}M (= (NH_3) + (NH_4^+))$. The pK_b of $NH_3 = 4.75$. Assume activities equal concentrations. Although this is a dilute NH_3 solution, you can reasonably neglect (H^+) in the charge balance equation.

2.2.1 Answer

We are interested in the expression for the equilibrium of NH_3 in water:



We know the pK_b of NH_3 is 4.75, so the K_b is $10^{-4.75}$. The relevant variables that we want to set up is the parameter x to be the concentration of $[OH^-]$ and $[NH_4^+]$ which will be present in equal amounts. If we were to set up a

charge balance equation for this process, it would reflect this fact. The final concentration of $[NH_3]$ will be $1.0 \times 10^{-6} - x$. This suggests the expression:

$$10^{-4.75} = \frac{x^2}{1.0 \times 10^{-6} - x}$$

Solving for x gives a value of $9.49 \times 10^{-7} M$.

```

1 from sympy import symbols, Eq, solve, log
2
3 # Define the variable
4 x = symbols('x', real=True, positive=True)
5
6 # Given constants
7 Kb = 10**(-4.75)
8 initial_NH3 = 1.0e-6 # Total initial concentration of NH3
9
10 # Kb expression for the reaction
11 equation_Kb = Eq(x**2 / (initial_NH3 - x), Kb)
12
13 # Solve the equation for x
14 x_value = solve(equation_Kb, x)
15 x_value

```

So the equilibrium concentrations of (NH_4^+) is $9.49 \times 10^{-7} M$. And that of (NH_3) is $1.0 \times 10^{-6} - 9.49 \times 10^{-7} = 0.51 \times 10^{-7} M$. The pOH is $-\log(9.49 \times 10^{-7}) = 6.02$ and the pH is $14 - 6.02 = 7.98$.

3 Maintaining a buffer

3.1

The titration curve of glycine was discussed in lecture 8. The pKa's of glycine are $pK_1 = 2.35$ and $pK_2 = 9.78$, respectively. Is glycine a better buffer when $pH = pK_1$ or when the pH equals the isoelectric point (pl) of glycine? Explain briefly.

3.1.1 Answer

We are given in the lecture that at the isoelectric point, the $[H^+] = \sqrt{K_1 K_2}$. This translates to an averaged out pH of 6.07, and is the point where it is in

the zwitterionic form. The lecture notes also give that the better buffer exist when the pH is closer to the pKa values. When this is the case, the glycine has a better chance to both accept and donate protons, and hence act as a better buffer. This means that glycine is a better buffer when the pH equals the pKa values of glycine, in this case, when the pH equals pK₁.

3.2

What are the fractions of glycine with 0, 1, and 2 protons bound in a solution of glycine when pH = pK₂? Assume activities equal concentrations.

3.2.1 Answer

We are interested in the quantity:

$$\bar{h} = \frac{K_1[H^+] + 2K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \quad (1)$$

We know that the pH is equal to the pK₂, so the concentration of protons is equal to 10^{-9.78}. We can then substitute this value into the equation.

As given in the lecture, the fractions of each form of glycine are given by:

$$\begin{aligned} f_{H_2A^+} &= \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2}, \\ f_{HA} &= \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2}, \\ f_{A^-} &= \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}. \end{aligned}$$

Because the last two fractions are the same, they give values of 0.5 and then because the K₂ = [H⁺] is much smaller than the K₁, the fraction of glycine with 0 protons is much smaller so we can approximate it as 0. The fractions of glycine with 0, 1, and 2 protons bound are 0, 0.5, and 0.5, respectively.

```

1 import math
2
3 # Constants
4 pK1 = 2.35
5 pK2 = 9.78
6

```

```

7 # Equilibrium constants
8 K1 = 10**(-pK1)
9 K2 = 10**(-pK2)
10
11 # Proton concentration at pH = pK2
12 H_plus = 10**(-pK2)
13
14 # Fractions of each form of glycine
15 f_H2A_plus = H_plus**2 / (H_plus**2 + K1 * H_plus + K1 * K2)
16 f_HA = K1 * H_plus / (H_plus**2 + K1 * H_plus + K1 * K2)
17 f_A_minus = K1 * K2 / (H_plus**2 + K1 * H_plus + K1 * K2)
18
19 print(f"Fraction of H2A+ (glycine with 2 protons): {
    f_H2A_plus:.4f}")
20 print(f"Fraction of HA (glycine with 1 proton): {f_HA:.4f}")
21 print(f"Fraction of A- (glycine with 0 protons): {f_A_minus
    :.4f}")

```

3.3

What are the concentrations of HAc and Ac^- in a 0.1M acetate buffer (i.e., $[\text{HAc}] + [\text{Ac}^-] = 0.1\text{M}$) at pH4.76? The $\text{p}K_a$ of HAc is 4.76. Assume activities equal concentrations.

3.3.1 Answer

The relevant equation for this equilibrium process is:

$$K_a = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} \quad (2)$$

We are given the pH, which implies a proton concentration of $[\text{H}^+] = 10^{-4.76}$. This is the same value as the K_a . Since the total mass of the buffer must be conserved, we can define $[\text{HAc}] = x \rightarrow [\text{Ac}^-] = 0.1 - x$. We can then substitute these values into the equation and solve for x . That script gives a value of 0.05 M for $[\text{HAc}]$ and 0.05 M for $[\text{Ac}^-]$.

```

1 from sympy import symbols, Eq, solve
2
3 # Define the variable
4 x = symbols('x')
5
6 # Given constants

```



```

7 total_concentration = 0.1 # Total concentration of HAc + Ac-
8 pH = 4.76
9 Ka = 10**(-pH) # Ka equals [H+] at pH 4.76
10
11 # Set up the equation from the given relationship
12 equation = Eq(Ka * x / (total_concentration - x), Ka)
13
14 # Solve the equation
15 concentration_HAc = solve(equation, x)
16 concentration_Ac_minus = total_concentration -
    concentration_HAc[0]
17
18 concentration_HAc, concentration_Ac_minus

```

3.4

Calculate the volumes of glacial acetic acid (17.4 M) and 2.54MNaOH needed to make 2 liters of 0.2M acetate buffer, pH 5.0 (i.e., $(\text{HAc}) + (\text{Ac}^-) = 0.2M$). Assume activities equal concentrations.

3.4.1 Answer

Let us use the Henderson-Hasselbalch equation to solve this problem. The equation is given by:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{Ac}^-]}{[\text{HAc}]} \right) \quad (3)$$

In the previous part of the problem, we are given that the $\text{p}K_a$ of HAc is 4.76 and then we know that the pH is 5.0. So, the equation simplifies to:

$$0.24 = \log \left(\frac{[\text{Ac}^-]}{[\text{HAc}]} \right) \quad (4)$$

This allows us to compute the ratio $[\text{Ac}^-]/[\text{HAc}]$. If we set x to be the number of moles of HAc, the total number of moles is 2 liters * 0.2 M = 0.4 moles. This gives us the relation $[\text{moles}_{\text{Ac}^-}] = 0.4 - x$. We can then substitute these values into the equation and solve for x . Then it is straightforward to solve for the volumes needed, as we can use the definition of molarity:

$$\text{Molarity} = \frac{\text{moles solute}}{\text{liters solution}} \quad (5)$$

That script gives a value of 8.40 mL for the volume of glacial acetic acid and 100. mL for the volume of 2.54MNaOH.

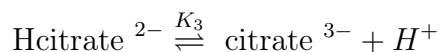
```

1 import math
2 from sympy import symbols, Eq, solve
3
4 # Define the variable
5 x = symbols('x', positive=True, real=True)
6
7 # Given data
8 pH = 5.0
9 pKa = 4.76
10 total_concentration = 0.2 # M
11 total_volume = 2 # liters of solution
12 conc_acetic_acid = 17.4 # M
13 conc_NaOH = 2.54 # M
14
15 # Calculate the ratio from the Henderson-Hasselbalch equation
16 ratio_Ac_minus_to_HAc = 10**(pH - pKa)
17
18 # Total moles in solution
19 total_moles = total_concentration * total_volume # 0.4 moles
20
21 # Equation for moles of HAc
22 equation = Eq(x + ratio_Ac_minus_to_HAc * x, total_moles)
23
24 # Solve for x
25 moles_HAc = solve(equation, x)[0]
26 moles_Ac_minus = ratio_Ac_minus_to_HAc * moles_HAc
27
28 # Calculate volumes needed for each component
29 volume_HAc = moles_HAc / conc_acetic_acid
30 volume_NaOH = moles_Ac_minus / conc_NaOH
31
32 volume_HAc, volume_NaOH

```

3.5

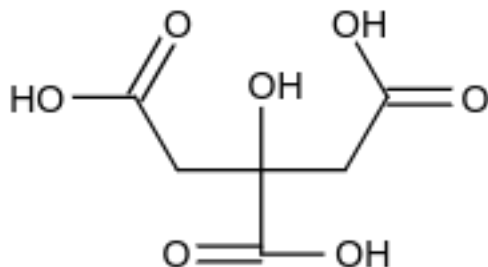
A citrate buffer is made up of 0.01MNa₂H citrate and 0.01MNa₃ citrate, where the relevant pK₃ = 6.40 for this reaction:



Using the Debye-Huckel limiting law and the Henderson-Hasselbalch equa-

tion, estimate the actual pH of this buffer. You can neglect the contribution of H^+ and OH^- to the ionic strength.

(citrate is a tricarboxylic acid with the following structure:



Hcitrate $^{2-}$ and citrate $^{3-}$ have 2 and 3 dissociated protons, respectively.)

3.5.1 Answer

The Henderson-Hasselbalch equation is given by:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{citrate}^{3-}]}{[\text{Hcitrate}^{2-}]} \right) \quad (6)$$

so since we know that the concentrations what be the same, in the ideal case $\text{pH} = \text{p}K_a$. However, we are asked to estimate the actual pH of the buffer, which will be mortified by the activities. The Debye-Huckel limiting law is given by:

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I} \quad (7)$$

where I is the ionic strength of the solution. The ionic strength is given by:

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (8)$$

where m_i is the molarity of the ion and z_i is the charge of the ion. The ionic strength is then given by:

$$I = \frac{1}{2} (0.01 \times 2^2 + 0.01 \times 3^2) = 0.065 \quad (9)$$

We can then use the Debye-Huckel limiting law to estimate the activity coefficients of the ions as $\gamma_{\text{citrate}} = 0.0679$ and $\gamma_{\text{Hcitrate}} = 0.303$. This means that

the actual concentrations that enter into the Henderson-Hasselbalch equation are 0.01×0.0679 and 0.01×0.303 . The actual pH of the buffer is then $6.40 + \log(0.01 \times 0.0679 / 0.01 \times 0.303) = 5.75$.

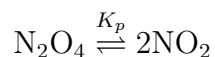
```

1
2 import math
3 # Constants and values from the problem statement
4 pKa = 6.40
5 concentration_Hcitrate = 0.01 # M
6 concentration_citrate = 0.01 # M
7 ionic_strength = 0.065 # calculated in the problem statement
8
9 # Constants for Debye-Huckel equation
10 A = 0.509
11 z_citrate = 3
12 z_Hcitrate = 2
13
14 # Calculating activity coefficients using Debye-Huckel
    limiting law
15 gamma_citrate = 10 ** (-A * z_citrate**2 * math.sqrt(
        ionic_strength))
16 gamma_Hcitrate = 10 ** (-A * z_Hcitrate**2 * math.sqrt(
        ionic_strength))
17
18 # Calculating effective concentrations
19 effective_concentration_citrate = concentration_citrate *
    gamma_citrate
20 effective_concentration_Hcitrate = concentration_Hcitrate *
    gamma_Hcitrate
21
22 # Calculating the actual pH using the Henderson-Hasselbalch
    equation
23 actual_pH = pKa + math.log10(effective_concentration_citrate
    / effective_concentration_Hcitrate)
24
25 gamma_citrate, gamma_Hcitrate, actual_pH

```

4 Keep your equilibrium - it's a gas.

The gases N_2O_4 and NO_2 interconvert through the following equilibrium



4.1

The free energies of formation at 298 K for N_2O_4 and NO_2 are 99.8 and 51.3 kJ mol^{-1} , respectively. Calculate the equilibrium constant K_p for this reaction at 298 K.

4.1.1 Answer

The equilibrium constant is given by:

$$\Delta G = -RT \ln K \quad (10)$$

We are given the differences of the free energies of formation, so we have that $\Delta G = 2 \times 51.3 - 99.8 = 2.8 \text{ kJ mol}^{-1}$. We can then substitute this value into the equation to get the equilibrium constant $K_p = 0.323$.

```
1 import math
2
3 # Constants
4 R = 8.314 # J/(mol*K), gas constant
5 T = 298 # K, temperature
6
7 # Given free energies of formation (in kJ/mol, convert to J/
  mol)
8 delta_G_f_N2O4 = 99.8 * 1000 # J/mol
9 delta_G_f_NO2 = 51.3 * 1000 # J/mol
10
11 # Calculate delta G for the reaction
12 delta_G_reaction = 2 * delta_G_f_NO2 - delta_G_f_N2O4 # J/
  mol
13
14 # Calculate the equilibrium constant Kp using the formula:
  Delta G = -RT ln Kp
15 Kp = math.exp(-delta_G_reaction / (R * T))
16
17 Kp
```

4.2

What are the partial pressures of N_2O_4 and NO_2 (in atm) at equilibrium when the total pressure is 1 atm ? If you are unsure of your answer to 4a, you may use $K_{eq} = 1$ (accurate to within a factor of 100)

4.2.1 Answer

The equilibrium constant is given by:

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} \quad (11)$$

We are given that the total pressure is 1 atm, so if we define x to be the partial pressure of N_2O_4 , then the partial pressure of NO_2 is $2(1 - x)$. Now, we can use the equilibrium expression from the previous part:

$$0.323 = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \quad (12)$$

Solving gives a value of 0.753 atm for the partial pressure of N_2O_4 and 0.493 atm for the partial pressure of NO_2 .

```
1 import sympy as sp
2
3 # Define the unknowns
4 x = sp.symbols('x')
5
6 # Given equilibrium constant K_p
7 K_p = 0.323
8
9 # Total pressure
10 total_pressure = 1 # atm
11
12 # Define the equilibrium relationships
13 P_N2O4 = x
14 P_NO2 = 2 * (total_pressure - x)
15
16 # Set up the equation based on K_p
17 equilibrium_equation = sp.Eq(K_p, (P_NO2 ** 2) / P_N2O4)
18
19 # Solve for x (the partial pressure of N2O4)
20 solution = sp.solve(equilibrium_equation, x)
21
22 # Get the partial pressures of N2O4 and NO2 at equilibrium
23 P_N2O4_eq = solution[0]
24 P_NO2_eq = 2 * (total_pressure - P_N2O4_eq)
25
26 # Display the results
27 P_N2O4_eq, P_NO2_eq
```

5 Getting blasted

What is the role of the argon plasma in the inductively coupled plasma mass spectrometry (ICP-MS) instrument we discussed in the Water and Environment Laboratory tour?

5.0.1 Answer

Argon is the candidate element for this instrument because it is an inert gas and thus will not react with the sample that is being measured. The reason for turning the argon into plasma is to heat up the sample sufficiently so that it ionizes, allowing us to determine masses with mass spectrometry.