

Ch14 Spring term 2024

Problem set 2

due April 18, 2024

please indicate length of time needed for this problem set

unless otherwise stated, assume $T = 25^{\circ}\text{C}$, that activities = concentrations and $K_w = 10^{-14}$. unless otherwise specified, give answers to 3 significant figures.

1

Calculate the pH to the nearest 0.01pH unit for Assume HCl is fully dissociated, and $K_w = 10^{-14}$.

If we assume that HCl is fully dissociated, then the concentration of H^+ is equal to the concentration of HCl, and the pH is given by $\text{pH} = -\log_{10}([\text{H}^+])$.

1.1

a 10^{-2}M solution of HCl

1.1.1 Answer

This translates to a concentration of H^+ of 10^{-2}M . Next, we can calculate the pH as follows:

$$\text{pH} = -\log_{10}(10^{-2}) = 2 \quad (1)$$

1.2

a 10^{-10}M solution of HCl

1.2.1 Answer

This translates to a concentration of H^+ of $10^{-10}M$. Next, we can calculate the pH as follows:

$$pH = -\log_{10}(10^{-10}) = 10 \quad (2)$$

2

for problems 2-4, assume that the concentrations are such that the "weak acid approximation" (H^+) $\sim \sqrt{K_a C_0}$ (or the corresponding "weak base approximation") is valid.

2.1

Calculate the pH to the nearest 0.01pH unit for the following solutions. Use $pK_a = 4.75$ for acetic acid, $pK_b = 4.75$ for ammonia, and $K_w = 10^{-14}$.

2.1.1

$10^{-2}M$ solution of acetic acid

2.1.2 Answer

Because the pK_a of acetic acid is 4.75, its K_a is $10^{-4.75}$. The concentration of acetic acid is $10^{-2}M$, so the concentration of H^+ is given by the equation

$$[H^+] = \sqrt{K_a C_0} = \sqrt{10^{-4.75} \times 10^{-2}} = 10^{-3.375} \quad (3)$$

Next, we can calculate the pH as follows:

$$pH = -\log_{10}(10^{-3.375}) = 3.375 \quad (4)$$

and with the correct number of significant figures, the pH is 3.38.

2.1.3

$10^{-2}M$ solution of NH_3

2.1.4 Answer

Because the pK_b of ammonia is 4.75, its K_b is $10^{-4.75}$. The concentration of ammonia is 10^{-2}M , so the concentration of OH^- is given by the equation

$$[\text{OH}^-] = \sqrt{K_b C_0} = \sqrt{10^{-4.75} \times 10^{-2}} = 10^{-3.375} \quad (5)$$

Next, we can calculate the pOH as follows:

$$\text{pOH} = -\log_{10}(10^{-3.375}) = 3.375 \quad (6)$$

and with the correct number of significant figures, the pOH is 3.38. Finally, we can calculate the pH as follows:

$$\text{pH} = 14 - \text{pOH} = 14 - 3.38 = 10.62 \quad (7)$$

3

In a 0.1M solution of NH_4Cl in water, calculate the concentrations of NH_4^+ and NH_3 . The pK_a of NH_4^+ is 9.25 .

3.1 Answer

The concentration of NH_4^+ is trivially 0.1M. As for the concentration of NH_3 , we can use equations to calculate K_b :

$$K_b = \frac{K_w}{K_a} \quad (8)$$

Then, we want to calculate the concentration of OH^- :

$$[\text{OH}^-] = \sqrt{K_b C_0} \quad (9)$$

Finally, we can calculate the concentration of NH_3 using the equilibrium equation:

$$[\text{NH}_3] = \frac{[\text{NH}_4^+][\text{OH}^-]}{K_b} \quad (10)$$

We end up with

$$[\text{NH}_3] = 7.50\text{M} \times 10^{-3} \quad (11)$$

```

1 # Constants for calculations
2 Ka = 10**(-9.25)
3 Kw = 10**(-14)
4 CO_NH4Cl = 0.1 # Molarity of NH4Cl, thus [NH4+]
5
6 # Calculate Kb for NH3
7 Kb = Kw / Ka
8
9 # Calculate [OH-] using the approximation for weak bases
10 OH_minus = (Kb * CO_NH4Cl)**0.5
11 H_plus = Kw / OH_minus
12
13 # Calculate [NH3] using the relation with OH- and NH4+
14 NH3 = (OH_minus * CO_NH4Cl) / Kb
15
16 NH3

```

4

The pH of a 0.10M solution of a certain amine, $R - NH_2$, is 11.80. What is the pK_b of this amine?

4.1 Answer

From the pH, we calculate the concentration of H^+ as follows:

$$[H^+] = 10^{-pH} \quad (12)$$

Using this, the concentration of OH^- is determined by the water ion-product, K_w :

$$[OH^-] = \frac{K_w}{[H^+]} \quad (13)$$

Assuming that all the amine is initially present as $R - NH_2$ and the solution is 0.10 M, the concentration of $R - NH_3^+$ formed by the reaction of $R - NH_2$ with water is equal to $[OH^-]$. The equilibrium constant for the base, K_b , is then:

$$K_b = \frac{[OH^-]^2}{0.10} \quad (14)$$

Finally, the pK_b is calculated using:

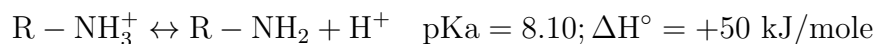
$$pK_b = -\log_{10}(K_b) \quad (15)$$

This gives us a pK_b of 3.40.

```
1 import math
2 # Constants
3 pH = 11.80
4 CO_amine = 0.10 # Molarity of the amine
5 Kw = 10**-14
6
7 # Calculate [H+]
8 H_plus = 10**(-pH)
9
10 # Calculate [OH-]
11 OH_minus = Kw / H_plus
12
13 # Assuming [OH-] equals the amount of amine that reacted and
14   [R-NH2] is approximately equal to the initial
15   concentration
16 Kb = (OH_minus**2) / CO_amine
17
18 # Calculate pKb
19 pKb = -math.log10(Kb)
```

5

Tris(hydroxymethyl)aminomethane (Tris) is a frequently used buffer component for biochemical studies. The structure of Tris in the basic form will be abbreviated in this problem as $R - NH_2$. The acid dissociation equilibrium may be represented as



where $pK_a = -\log_{10} K_a$, and K_a is the equilibrium constant for this acid dissociation reaction. K_a is a function of temperature since ΔH° is non-zero.

Although Tris is widely used, it has the serious drawback that the pH of a buffered solution varies significantly with temperature. Based on the van't Hoff equation that we've discussed in class, numerically evaluate $\partial pK_a / \partial T$, the change in pK_a with a change in temperature, for Tris buffer at $T = 25^\circ\text{C}$.

If this derivative is assumed to be constant, independent of temperature (this is not actually true, but is a reasonable approximation), calculate the expected pK_a of Tris buffer at 0°C .

5.1 Answer

The van't Hoff equation in our case is given by:

$$\left(\frac{\partial \ln K_a}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \quad (16)$$

The relationship between K_a and pKa is given by:

$$pKa = -\log_{10}(K_a) \quad (17)$$

Differentiating this equation with respect to T gives:

$$\frac{\partial pKa}{\partial T} = -\frac{1}{\ln(10)} \frac{\partial \ln K_a}{\partial T} \quad (18)$$

Substituting the van't Hoff equation into this gives:

$$\frac{\partial pKa}{\partial T} = -\frac{\Delta H^\circ}{RT^2 \ln(10)} \quad (19)$$

Evaluating this at $T = 25^\circ\text{C}$ gives:

$$\frac{\partial pKa}{\partial T} = -\frac{50000}{(8.314 \times 298.15^2) \ln(10)} = -0.0294 \frac{1}{K} \quad (20)$$

Finally, we can calculate the expected pKa at 0°C as follows:

$$pKa_{0^\circ\text{C}} = pKa_{25^\circ\text{C}} + \left(\frac{\partial pKa}{\partial T}\right) \times (0 - 25) \quad (21)$$

This one gives us a pKa of 8.83 at 0°C .

```
1 import numpy as np
2
3 # Constants
4 R = 8.314 # J/(molxK)
5 Delta_H = 50000 # J/mol
6 T = 298.15 # K
7 pKa_25 = 8.10
8
9 # Calculate the partial derivative of pKa with respect to
   temperature
10 partial_pKa_partial_T = -1 / np.log(10) * (Delta_H / (R * T
   **2))
```

```

11
12 # Calculate the pKa at 0 degrees Celsius (273.15 K)
13 Delta_T = 273.15 - 298.15
14 pKa_0 = pKa_25 + partial_pKa_partial_T * Delta_T
15
16 partial_pKa_partial_T, pKa_0

```

6

A solution with the following composition is prepared
 0.15 liter of 1.0M ammonium hydroxide (NH_4^+OH^-)
 0.10 liter of 0.5M ammonium chloride (NH_4^+Cl^-)
 0.10 liter of 1.0M acetic acid ($\text{CH}_3\text{CO}_2\text{H}$)
 distilled H_2O is added to a final volume of 1.0 liter.

Using either graphical (such as Excel[®]) or numerical (such as Mathematica[®]) methods, calculate the pH of this solution without any approximations. You may wish to start from the charge balance equation, incorporating mass balance and equilibrium relationships to get an equation that may be solved for (H^+).

The pKa's of acetic acid and ammonium are $\text{pK}_1 = 4.75$ and $\text{pK}_2 = 9.25$, respectively. Hint: the final pH is ~ 9 .

6.1 Answer

We want to start by setting up mass balance equations. First we are interested in the total concentration of NH_4^+ in the solution. There are two sources for this; the ammonium hydroxide and the ammonium chloride. The total concentration of NH_4^+ is given by:

$$[\text{NH}_4^+] = [\text{NH}_4^+]_{\text{hydroxide}} + [\text{NH}_4^+]_{\text{chloride}} \quad (22)$$

and then, we are interested in the concentration of $\text{CH}_3\text{CO}_2\text{H}$ in the solution. The total concentration of $\text{CH}_3\text{CO}_2\text{H}$ is given by:

$$[\text{CH}_3\text{CO}_2\text{H}] = [\text{CH}_3\text{CO}_2\text{H}] \quad (23)$$

```

1 # Initial concentrations
2 V_total = 1.0 # Total volume in liters

```

```

3 C_NH4OH = 0.15 * 1.0 / V_total # Concentration of NH4+ from
  NH4OH
4 C_NH4Cl = 0.10 * 0.5 / V_total # Concentration of NH4+ from
  NH4Cl
5 C_CH3COOH = 0.10 * 1.0 / V_total # Initial concentration of
  CH3COOH
6
7 # Total NH4+ concentration
8 C_NH4_plus_total = C_NH4OH + C_NH4Cl

```

We also know the constance of

```

1 # Constants
2 Kw = 10**-14 # Water ionization constant
3 Ka_acetic = 10**-4.75 # Acetic acid dissociation constant
4 Ka_ammonium = 10**-9.25 # Ammonium hydrolysis constant

```

Next, we can set up the charge balance equation. The total charge in the solution is given by:

$$[H^+] + [NH_4^+] = [OH^-] + [CH_3CO_2^-] + [Cl^-] \quad (24)$$

```

1 eq1 = H_plus + NH4_plus - OH_minus - CH3COO_minus -
  C_Cl_minus # Charge balance

```

Then we want to use the mass balance for ammonium

```

1 eq2 = NH4_plus + NH3 - C_NH4_plus_total # Total NH4 balance

```

and the mass balance for acetic acid

```

1 eq3 = CH3COOH + CH3COO_minus - C_CH3COOH # Total acetic acid
  balance

```

Then, we want to consider the auto-ionization of water

```

1 eq4 = H_plus * OH_minus - Kw # Water ionization

```

the equilibrium for the ammonia

```

1 eq5 = NH3 * H_plus - NH4_plus * Ka_ammonium # Ammonium
  hydrolysis

```

and the equilibrium for acetic acid

```

1 eq6 = CH3COO_minus * H_plus - CH3COOH * Ka_acetic # Acetic
  acid dissociation

```

Finally, we can solve the system of equations given our knowledge of initial values


```

1 # Initial guesses for [H+], [NH4+], [NH3], [OH-], [CH3COOH],
  [CH3COO-]
2 initial_guesses = [1e-7, C_NH4_plus_total, 0.01, 1e-7,
  C_CH3COOH, 0.01]
3 solution = fsolve(equations, initial_guesses)

```

Then we use the following to get the pH

```

1 pH = -np.log10(solution[0])

```

This gives a final value of $\text{pH} = 8.77$.