

Objective 9. Apply equilibrium principles to acid-base titrations and buffers.

Key ideas: A buffer is a substance that resists change in pH. Buffers are used in food preservatives, swimming pools, regulate pH in body.

Chem 1A: titration – add base to acid to determine amount.

Chem 1B: A titration curve helps us understand buffers. Buffer region is flat part of titration curve.

Want to know pH at starting point, half-way point, and endpoints of titration curve.

Starting pH: almost all weak acid present so use K_a to calculate $[H^+]$

half-way point pH = pK_a . From Henderson-Hasselbach equation, $pH = pK_a + \log [base]/[acid]$

endpoint pH: almost all conjugate base present so use K_b to calculate $[H^+]$

1. Aspirin and salicylic acid are pain relievers. Salicylic acid is not used as a pain reliever anymore because it is hard on a person's stomach. Salicylic acid is used to make aspirin. Aspirin has a pK_a of 3.5; salicylic acid has a pK_a of 2.98.

a. Aspirin is less hard on a person's stomach because it is a _____ acid than salicylic acid based on pK_a .

b. The purity of aspirin can be determined by titrating an aspirin solution with 0.1 M NaOH. Draw the titration curve (pH vs. volume of NaOH added) of aspirin. Calculate the starting pH (assume you have 20 ml of 0.1 M solution), the pH at the half-way point, and the pH at the end point.

(i) pH at starting point, only acid is present so use K_a of aspirin.

$pK_a = -\log K_a$.

Solve for $K_a = 10^{-pK_a} = 10^{-3.5} = 3.2 \times 10^{-4}$.

Acid dissociation reaction: $C_9H_8O_4 \rightarrow H^+ + C_9H_7O_4^-$

Initial	0.1	0	0
Reacts	x	x	x
Equilibrium	$0.1 - x$	x	x

Note: Since $K_a = 3.2 \times 10^{-4}$ (very small), we can assume $0.1 - x \approx 0.1$.

Set up your equilibrium constant equation and solve for $x = [H^+]$.

Then, use $pH = -\log[H^+]$ to calculate pH. (Answer: pH between 2.1 and 2.4)

(ii) at half-way point, the concentration of base (the conjugate base of aspirin) = the concentration of acid (the aspirin).

So use the Henderson-Hasselbach equation: $pH = pK_a + \log [base]/[acid]$

Since $[base] = [acid]$, $pH = pK_a$.

(iii) at end point, only base (conjugate base of aspirin) is present so use K_b of conjugate base of aspirin.

Calculate K_b of conjugate base of aspirin: $K_a K_b = K_w$ or $K_b = K_w / K_a = 1 \times 10^{-14} / 3.2 \times 10^{-4} = 3.2 \times 10^{-11}$.

Base hydrolysis reaction: $C_9H_7O_4^- + H_2O \rightarrow C_9H_8O_4 + OH^-$

Initial	0.05	0	0
Reacts	x	x	x
Equilibrium	$0.05 - x$	x	x

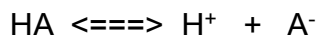
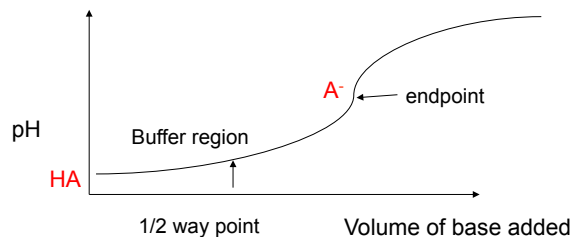
Note: the initial concentration of $C_9H_7O_4^-$ is 0.05 M because 20 ml of 0.1 M NaOH is required to neutralize 20 ml of 0.1 M aspirin. The volume of solution at the endpoint is 40 ml so using the dilution equation ($C_1V_1 = C_2V_2$), the concentration of $C_9H_7O_4^-$ is 0.05 M.

Set up your equilibrium constant equation and solve for $x = [OH^-]$.

Then, use $pOH = -\log[OH^-]$ to calculate pOH. (Answer: pOH between 5.7 and 6.0)

Last, use $pH + pOH = 14$ to calculate pH. (Answer: pH between 7.9 and 8.2)

Label the starting pH, half-way point pH, and endpoint pH values in your titration curve.



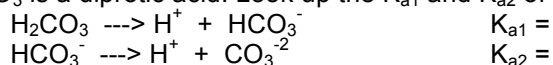
c. 20 ml of 0.1 M salicylic acid ($C_7H_6O_3$) is titrated with 0.1 M NaOH. Draw the titration curve (pH vs. volume of NaOH added) of salicylic acid. Calculate the starting pH (assume you have 20 ml of 0.1 M solution), the pH at the half-way point, and the pH at the end point. (Answers: starting pH between 1.8 and 2.1, pH at end point between 7.6 and 8.0)

2. From Lab 5, you know a buffer contains a weak acid and its conjugate base (or a weak base and its conjugate acid). The buffer pH is approximately the pK_a of the acid ± 2 . You can use the Henderson-Hasselbach equation to determine the ratio of the conjugate base to acid: $pH = pK_a + \log [base]/[acid]$. Aspirin has a pK_a of 3.5. Use the Henderson-Hasselbach equation to calculate the ratio of $[C_9H_7O_4^-]$ to $[C_9H_8O_4]$ to make a pH 3 buffer. Note: the buffer pH is less than the pK_a so there should be more acid than base.

3. Carbonic acid, H_2CO_3 , is formed when an acid reacts with a carbonate or bicarbonate (gas forming reaction from Chem 1A). It is the acid that forms when CO_2 (g) is bubbled into water at _____ pressure or _____ temperature.

20 ml 0.1 M solution of H_2CO_3 is titrated with 0.1 M NaOH.

a. H_2CO_3 is a diprotic acid. Look up the K_{a1} and K_{a2} of H_2CO_3 .



b. Draw the titration curve. Calculate the pH at starting point, each half-way point, and each end point.

(i) pH at starting point, only acid is present so use K_a of H_2CO_3 . (Answer: pH between 3.5 and 4.0)

(ii) at first half-way point, the concentration of base (HCO_3^-) = the concentration of acid (H_2CO_3).

So use the Henderson-Hasselbach equation: $pH = pK_{a1} + \log [base]/[acid]$

Since $[base] = [acid]$, $pH = pK_{a1}$.

(iii) at first end point, only base (HCO_3^-) is present but HCO_3^- also behaves like an acid (see K_{a2}).

Use $pH = 0.5(pK_{a1} + pK_{a2})$.

(iv) at second half-way point, the concentration of base (CO_3^{2-}) = the concentration of acid (HCO_3^-).

So use the Henderson-Hasselbach equation: $pH = pK_{a2} + \log [base]/[acid]$

Since $[base] = [acid]$, $pH = pK_{a2}$.

(v) at second end point, only base (CO_3^{2-}) is present so use K_b of CO_3^{2-} .

Calculate K_b of CO_3^{2-} : $K_a K_b = K_w$ or $K_b = K_w/K_a = 1 \times 10^{-14}/4.7 \times 10^{-11} = 2.1 \times 10^{-4}$. In this case, use K_a of HCO_3^- since HCO_3^- is the conjugate acid of CO_3^{2-} . (Answer: pH between 11.1 and 11.7)

(vi) Draw your titration curve. How does this titration curve (for a diprotic acid) look different than the titration curve in Question 1? Label the pH at starting point, each half-way point, and each end point.

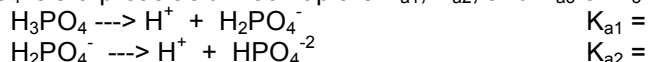
c. Could you make a pH 7.4 buffer using H_2CO_3 , HCO_3^- , or CO_3^{2-} ? If so, which substance serves as the acid and which serves as the base?

d. At what pH can baking soda be used as a buffer?

e. The pH of carbonated soda or water is between 3 and 4. At this pH, does the solution contain mostly H_2CO_3 , HCO_3^- , or CO_3^{2-} ? Hint: see your titration curve.

4. Phosphoric acid, H_3PO_4 , is added to soda to give it a tart taste.

a. H_3PO_4 is a triprotic acid. Look up the K_{a1} , K_{a2} , and K_{a3} of H_3PO_4 .



What is the acid dissociation reaction for K_{a3} ? $K_{a3} =$

b. Draw the titration curve. Calculate the pH at starting point, each half-way point, and each end point.

(i) pH at starting point, only H_3PO_4 is present. Which K_a should you use? (Answer: pH between 1.5 and 1.7)

(ii) pH at first half-way point, use Henderson-Hasselbach equation.

(iii) pH at first end point, only base ($H_2PO_4^-$) is present but $H_2PO_4^-$ also behaves like an acid (see K_{a2}).

Use $pH = 0.5(pK_{a1} + pK_{a2})$.

(iv) pH at second half-way point, use Henderson-Hasselbach equation.

(v) pH at second end point, only base (HPO_4^{2-}) is present but HPO_4^{2-} also behaves like an acid (see K_{a3}).

Use $pH = 0.5(pK_{a2} + pK_{a3})$.

(vi) pH at third half-way point, use Henderson-Hasselbach equation.

(vii) pH at third end point, only base (PO_4^{3-}) is present so use K_b of PO_4^{3-} . (Answer: pH between 12.7 and 13)

c. Coca-Cola has a pH of 2.5. At this pH, does Coke contain mostly H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , or PO_4^{3-} ?
Hint: see your titration curve.

d. At the pH of Coke, phosphoric acid works as a buffer. Calculate the ratio of [base] to [acid]. Identify the phosphorus containing acid (H_3PO_4 or H_2PO_4^- or HPO_4^{2-} or PO_4^{3-}) and base (H_3PO_4 or H_2PO_4^- or HPO_4^{2-} or PO_4^{3-}) at this pH.

5. Citric acid ($\text{pK}_1 = 3.13$, $\text{pK}_2 = 4.76$, $\text{pK}_3 = 6.40$) is the acid in lemon juice. Lemon juice has a pH of 2.4.
a. Draw the structure of citric acid. Circle the acidic protons and write the pK_a of that proton next to your circle.

b. At pH 2.4, calculate the ratio of the acid and its conjugate base present.

c. Draw the structure and show the charge of the acid and base at this pH.

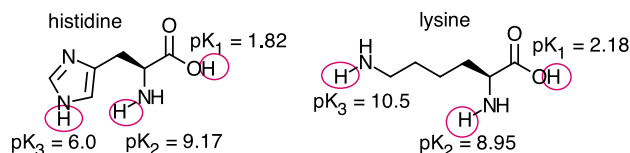
6. EDTA ($\text{pK}_1 = 2.0$, $\text{pK}_2 = 2.7$, $\text{pK}_3 = 6.2$, $\text{pK}_4 = 10.0$), oxalic acid ($\text{pK}_1 = 1.2$, $\text{pK}_2 = 4.2$), and citric acid ($\text{pK}_1 = 3.13$, $\text{pK}_2 = 4.76$, $\text{pK}_3 = 6.40$) bind to metals, are used as chelating agents, and are used as buffers.

a. Oxalic acid is the strongest acid because _____.

b. Draw a titration curve (pH vs. volume of base) of EDTA. Calculate the starting pH (assume a 0.1 M solution), the pH at each half-way point, and the pH at each end point. Label each pH on your titration curve.

c. Which substance would you use to make a pH 6 buffer? Calculate the ratio of [base]/[acid] to make this buffer.

7. You are given a 0.1 M mixture of two amino acids, histidine and lysine, and want to separate the amino acids by electrophoresis. The Lewis structures of each amino acid, the acidic protons, and pK_a 's are shown.



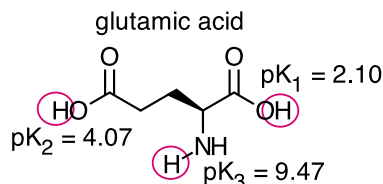
a. Draw a titration curve of each amino acid if titrated with 0.1 M NaOH. Calculate the pH at each half-way point and each end point. Show the charge of each amino acid at each half-way point and each end point.

b. What pH would you use in an electrophoresis experiment to separate these two amino acids? Give reasons.

c. What is the isoelectric point of glutamic acid?

d. Identify the amino acid and salt (conjugate base) combination you would use to make a pH 5 buffer. Describe how you would make this buffer.

8. (From Lab 5) MSG (monosodium glutamate) is used as a flavor enhancer in foods. MSG can be made from glutamic acid (an amino acid).



a. Draw a titration curve of each amino acid if titrated with 0.1 M NaOH. Calculate the pH at each half-way point and each end point. Show the charge of the amino acid at each half-way point and each end point.

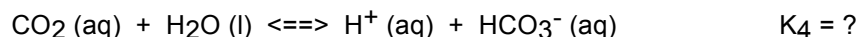
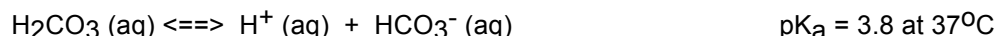
b. At what pH is glutamic acid in the form of glutamate? Give reasons.

c. What is the isoelectric point of glutamic acid?

9. Based on your knowledge of acids and bases, you know that a buffer is effective only in the region of its pK_a . Blood has a normal pH of 7.35-7.45 and contains two major buffer systems. It is important that the pH of blood remains relatively constant because at pH below 6.8 or greater than 8.0, cells cannot function properly and death may result. The $\text{HCO}_3^-/\text{CO}_2$ (aq) blood buffer *in vivo* is an *open system* in which the concentration of dissolved CO_2 is maintained constant. Any excess CO_2 produced by the reaction $\text{H}^+ +$

$\text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_2$ is expelled by the lungs. Note that a typical laboratory buffer is a *closed system*. The concentration of conjugate acid increases when H^+ reacts with the conjugate base.

a. Calculate the K_{eq} and pK of Reaction (4) from the following reactions and K values.



b. The $[\text{HCO}_3^-] = 0.024 \text{ M}$ in blood at pH 7.4. Calculate the $[\text{CO}_2 (\text{aq})]$ in blood at this pH.

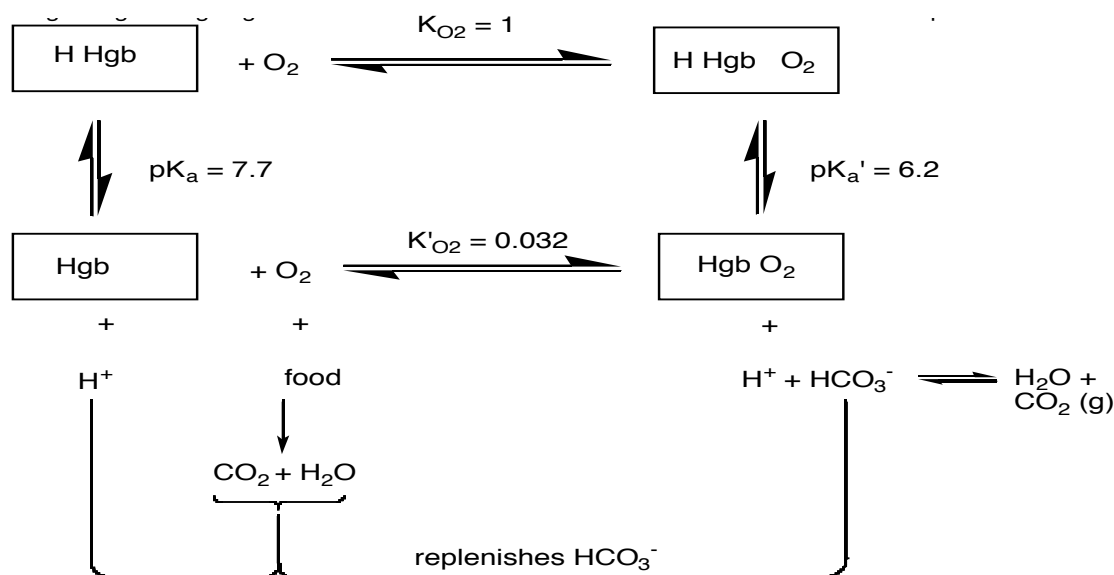
c. 0.01 M H^+ is added to blood. Calculate the pH of blood under conditions such that the increased $[\text{CO}_2 (\text{aq})]$ can not be released as $\text{CO}_2 (\text{g})$. In other words, assume that the blood buffer is a closed system.

d. 0.01 M H^+ is added to blood. Calculate the pH of blood under conditions such that the increased $[\text{CO}_2 (\text{aq})]$ can be released as $\text{CO}_2 (\text{g})$. In other words, assume that the blood buffer is an open system.

Remember that the $[\text{CO}_2 (\text{aq})]$ remains constant in this open buffer system.

e. Your pH calculations should show a large decrease in pH in part c and a small decrease in pH in part d. Based on these calculations, it would appear that HCO_3^- should be quickly depleted in an open system when acid is added. How is HCO_3^- replenished in blood?

10. The diagram below represents a simplified version of the buffering action of hemoglobin as a buffer and the uptake and release of oxygen (Reference: I.H. Segel, "Biochemical Calculations", 2nd ed., Wiley, 1976, p. 88). Hemoglobin is the oxygen carrier in blood that transports oxygen from our lungs to tissues. Diffusion due to partial pressure differences is one mechanism by which oxygen transport occurs.



In lecture, we will discuss the relevant equilibrium reactions involving the four different forms hemoglobin.

a. When hemoglobin is oxygenated, H Hgb O_2 forms. Draw a titration curve of H Hgb O_2 . Assume you have 20 ml of 0.1 M acid and 0.1 M NaOH as the base. Calculate the pH at the starting point, half-way point, and end point.

b. At pH 7.4, will there be more H Hgb O_2 present or Hgb O_2 ? Calculate the ratio of Hgb O_2 to H Hgb O_2 .

c. When the acid form of oxygenated hemoglobin dissociates into the base form of oxygenated hemoglobin, what happens to the pH? How is the pH buffered when the pH changes?

Since hemoglobin is a protein, it exists in two acid forms, H Hgb ($\text{pK}_a = 7.7$) and H Hgb O_2 ($\text{pK}_a = 6.2$), and two base forms, Hgb and Hgb O_2 . At the blood pH of 7.4, which form of the oxygenated hemoglobin is present in the higher amount? Give reasons.

a. Calculate the ratio of $\text{H Hgb}/\text{Hgb}$ and $\text{H Hgb O}_2/\text{Hgb O}_2$ present at pH 7.4. (You want to calculate two ratios.) Of the four forms of hemoglobin present, which form is present in the highest amount at pH 7.4?

c. Does the acid form of hemoglobin (H Hgb) have a higher, lower, or same affinity for oxygen than its conjugate base (Hgb)? Give reasons.