Chem 1B Objective 9:
Apply equilibrium principles to acids and bases

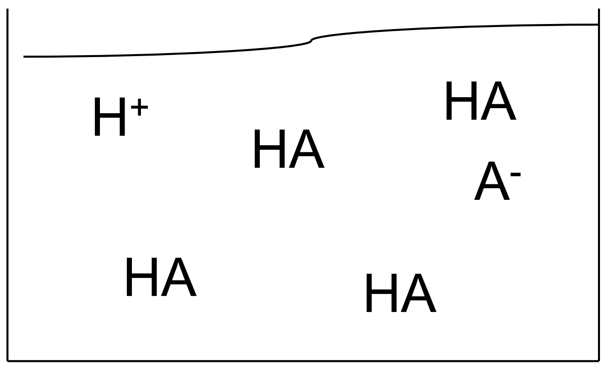
Key Ideas: A buffer is a substance that resists change in pH. Buffers are used in food preservatives, swimming pools, regulate pH in body.
A buffer consists of a weak acid and its conjugate base or weak base and its conjugate acid.

A titration curve helps us understand buffers. Buffer region is flat part 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 $[H^+]$

Buffers are used in food preservatives, blood, …

A Buffer Resists Change in pH

A Buffer contains a Weak Acid and its Conjugate Base
(or a weak base and its conjugate acid).

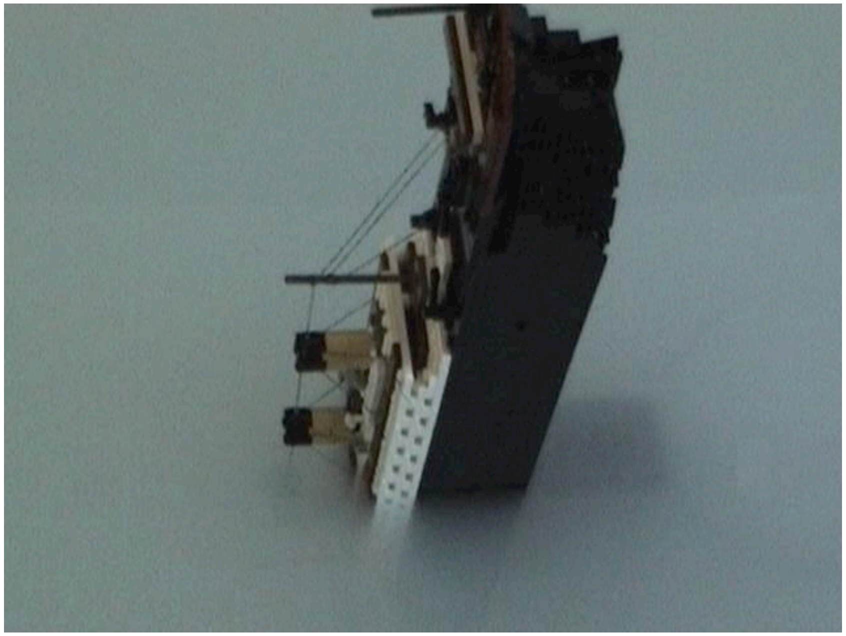


Why doesn’t a buffer contain a strong acid?

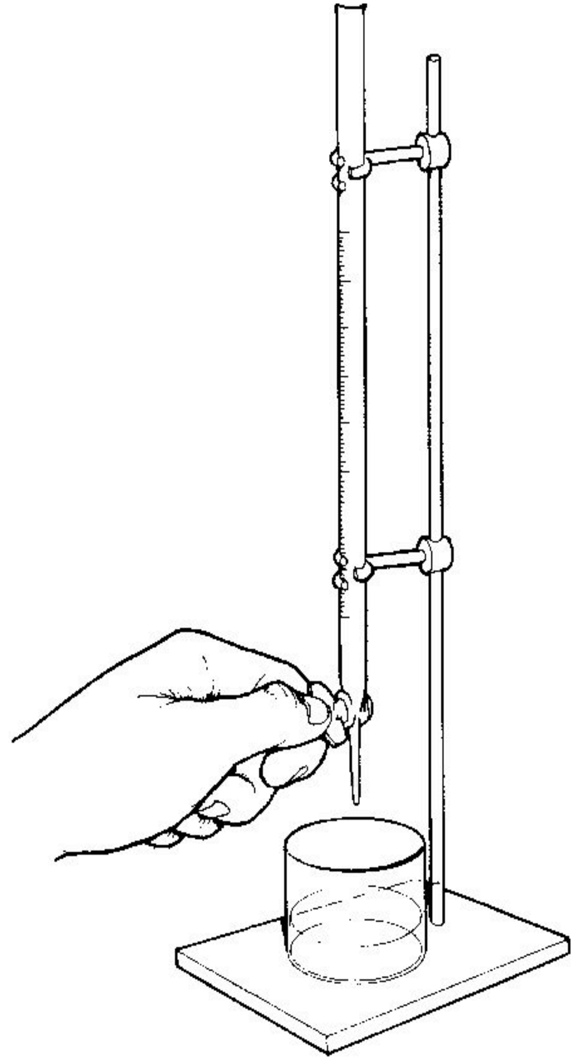
A Titration Curve helps us understand Buffers.

Remember the Titration!

http://analytical.wikia.com/wiki/Burette



http://www.monsterprelaunch.com/surf2b/1

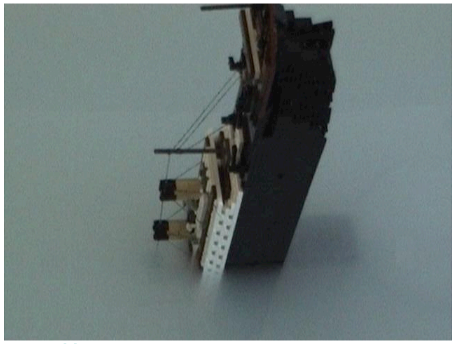


Acids React With Bases!

Acid + Base →

Remember the Titration!

http://analytical.wikia.com/wiki/Burette



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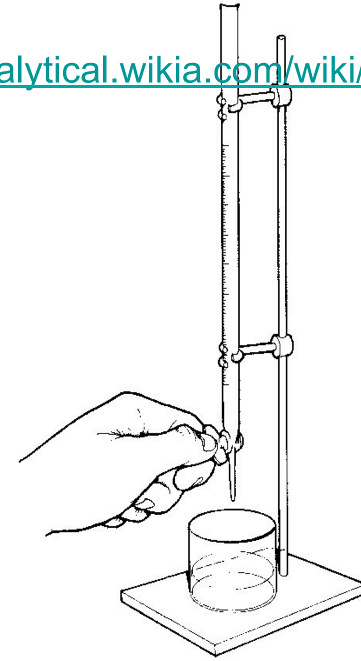
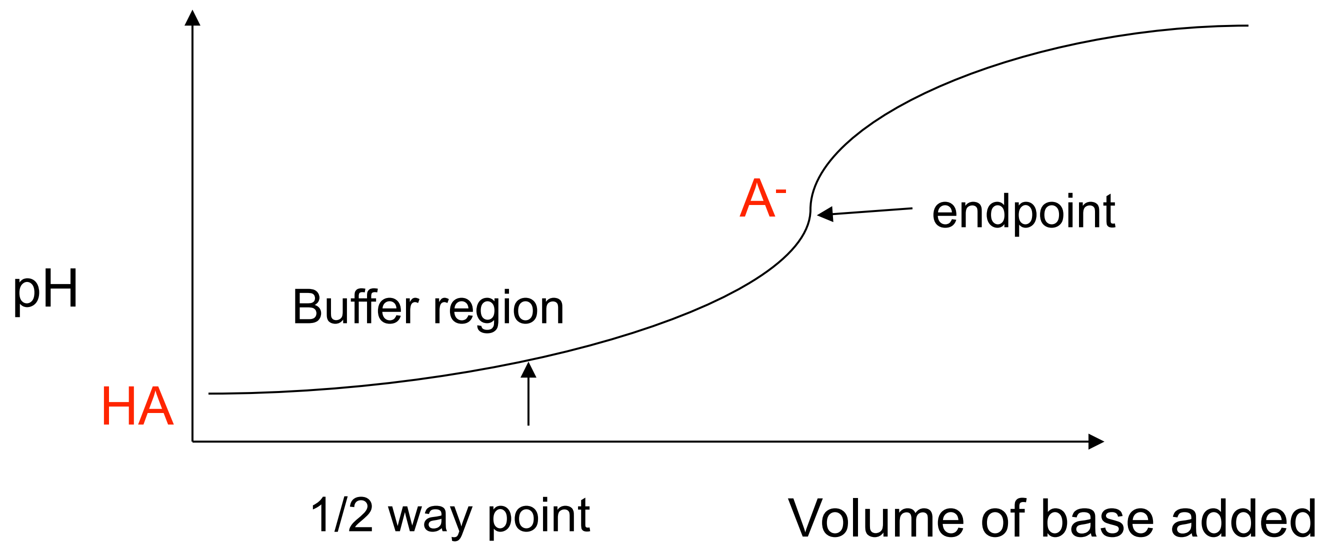


Acids React With Bases!

	HA	+	B	$\rightarrow$	HB	+	A^-
Initial	1		0.1				
Reacts			0.1				
Leftover							

How much HA and A^- leftover?

A **<u>Titration Curve</u>** Tells us about a Buffer



$$HA \Longleftrightarrow H^+ + A^-$$

Henderson-Hasselback equation: $pH = pK_a + \log \dfrac{[A^-]}{[HA]}$

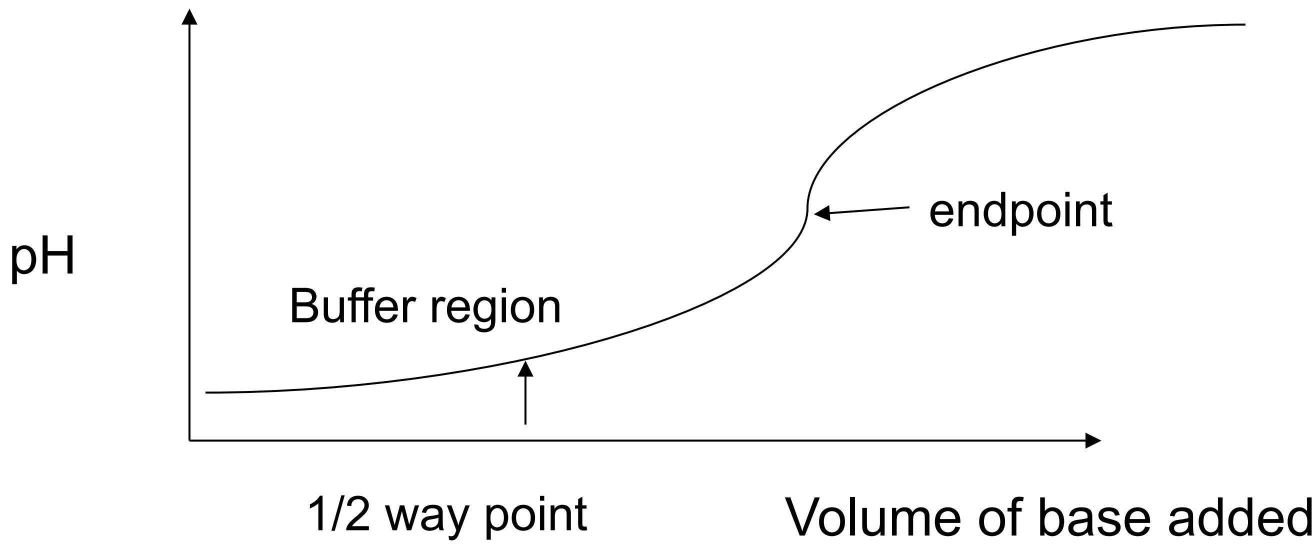
At starting point: only HA present ==> use K_a

At 1/2 way point: $[A^-] = [HA]$ ==> $pH = pK_a$

At end point: only A^- present ==> use K_b

Use Henderson-Hasselbach equation to make a Buffer

1. Find acid with pK_a **NEAR** pH of buffer you want to make.
2. ID conjugate base of acid.
3. Use H-H equation to calculate [base]/[acid] ratio.
4. Calculate % acid and % base to use.



Before 1/2 way point:

(i) $[A^-] < [HA]$ (ii) $[A^-] = [HA]$ (iii) $[A^-] > [HA]$

After 1/2 way point:

(i) $[A^-] < [HA]$ (ii) $[A^-] = [HA]$ (iii) $[A^-] > [HA]$

On the Titration Curve, show where the buffer capacity is exceeded.

Objective: draw titration curve and determine pHs

A Titration Curve Gives Us A Lot Of Information About Acids, Bases, Buffers, and Charge

20 ml of 0.1 M aspirin (monoprotic acid) solution is titrated with 0.1 M NaOH.
Calculate the pH at the start, half-way point, and end point.
Draw a titration curve.
At what pH can aspirin be used as a buffer?

At starting point:	only HA present ==> use K_a
At 1/2 way point:	$[A^-] = [HA]$ ==> $pH = pK_a$
At end point:	only A^- present ==> use K_b

"Milk Does a Body Good"

87.3% water
3.9 % fat
8.8% solids-not-fat
  protein 3.25% (3/4 casein)
  lactose 4.6%
  minerals 0.65% - Ca, P, Mg, K, Na, Zn, Cl, Fe, Cu, .
  vitamins - A, C, D, thiamine, riboflavin, others

http://www.npr.org/blogs/money/2012/12/27/168147765/understanding-the-milk-cliff

http://blog.fooducate.com/2011/06/26/if-milk-is-white-why-is-cheese-yellow/

Milk pH = 6.6

What substance in milk makes it an acid?

Is milk a buffer?

Protein precipitates at pH 4.6

How to make cheese from milk?

- Coagulation and precipitation
- Concentration of curd
- Ripening

http://pubs.acs.org/isubscribe/journals/cen/82/i42/html/8242sci1.html CEN, 10/18/04, p. 47)

CHEESE WHIZZES: Food scientists plumb the depths of this ancient food, which overflows with chemistry

≈ 10 lb of milk to make 1 lb of cheese

≈ 400 flavor compounds in cheddar (from metabolism of bacteria, mold, and yeast, as well as from chemical reactions involving other ingredients as cheese develops and ages)

YUM!

Flavor compounds lend a distinctive note to the different styles of cheese

FLAVOR COMPOUND	CHEESE VARIETY
Methanethiol	Cheddar, Limburger
3-(Methylthio)propanal	Emmental
Methyl ketones	Roquefort
1-Octen-3-ol	Camembert, buffalo mozzarella
2-Methylpropanoic acid ethyl ester	Bovine mozzarella
Butanoic, hexanoic, and octanoic acids	Parmesan, provolone, Romano
2-Methylpropanoic and 3-methylbutanoic acids	Brie
4-Methyloctanoic and 4-ethyloctanoic acids	Goat milk cheese

SOURCE: Michael H. Tunick, USDA

http://pubs.acs.org/isubscribe/journals/cen/82/i42/html/8242sci1.html CEN, 10/18/04, p. 47)

CHEESE WHIZZES: Food scientists plumb the depths of this ancient food, which overflows with chemistry

≈ 10 lb of milk to make 1 lb of cheese

Method:

1. Starter culture of bacteria:

- converts lactose to lactic acid, citric acid, (and other metabolic products)
- reduces pH from 6.7 to 5.3

2. Rennet added to break down casein and coagulate curds.

3. Heat, stir, drain whey, salt and season, curing.

Medium cheddar: 60 days

XSharp cheddar: 15 months

http://cen.acs.org/articles/90/i52/Shooting-Fish-Barrel-Extreme-Cheese.html

12/24/12, CEN, p. 48 “Extreme Cheese Making”

Bacteria, e.g., Lactobacillus, is used to make typical cheese.

Bacteria ferments the lactose --> lactic acid --> curds (protein)

Researchers swabbed their armpits, hands, noses, and feet to collect starter bacteria cultures for cheese fermentation.

Armpit cheese is especially pleasant smelling and tastes like a fresh farmer’s cheese.

Avoid the foot cheese.

http://www.npr.org/sections/thesalt/2015/07/15/391927036/hey-yogurt-maker-whered-you-get-those-microbes

Making Yogurt is Like Making Cheese

By law, anything called "yogurt" must be made from a few common ingredients:

milk

two species of bacteria - *Lactobacillus bulgaricus* and *Streptococcus thermophilus*

A Titration Curve Gives Us A Lot Of Information About Acids, Bases, Buffers, and Charge

20 ml of 0.1 M $H_2C_2O_4$ (diprotic acid) is titrated with 0.1 M NaOH.
Calculate pH at start, 1/2 way points, and end points.

At 1st endpoint: $pH = 0.5\,(pK_{a1} + pK_{a2})$

Draw titration curve and show buffer region(s).
Show the carbon compound and charge at each point.
At what pH is oxalate present?

Spinach contains oxalate
Oxalate ion + Ca^{2+} --> kidney stones

http://www.apartmenttherapy.com/-2910

Objective: draw titration curve and determine pHs

A Titration Curve Gives Us A Lot Of Information About Acids, Bases, Buffers, and Charge

20 ml of 0.1 M H_3PO_4 (triprotic acid) is titrated with 0.1 M NaOH.
Calculate pH at start, 1/2 way points, and end points.

At 1st and 2nd endpoints: $pH = 0.5\,(pK_{ai} + pK_{a(i+1)})$

Draw titration curve and show buffer region(s).
Show the phosphorus compound and charge at each point.

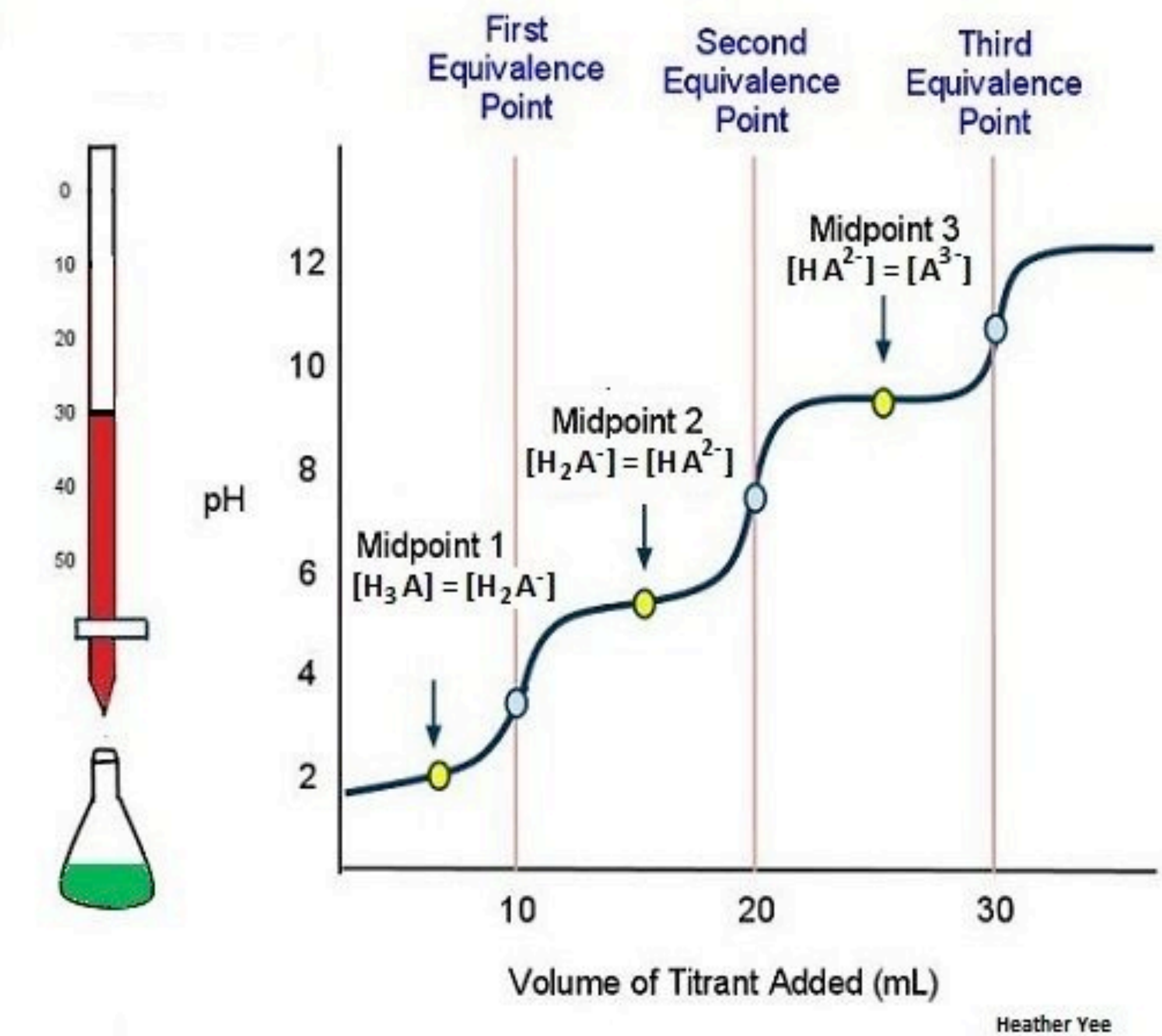


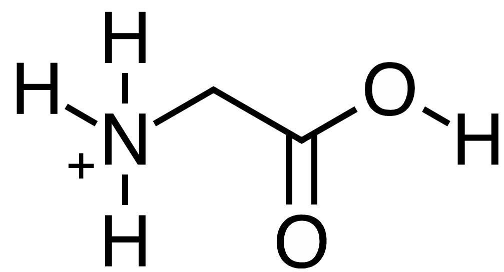
Figure 3.3 Titration of a Weak Polyprotic Acid. The final equivalence point is attained by adding another 10 mL, or a total of 30 mL, of the titrant to the weak polyprotic acid. Image created by Heather Yee.

	pH
start	Use K_{a1}
1st 1/2 way pt	pK_{a1}
1st end point	$0.5(pK_{a1}+pK_{a2})$
2nd 1/2 way pt	pK_{a2}
2nd end point	$0.5(pK_{a2}+pK_{a3})$
3rd 1/2 way pt	pK_{a3}
3rd end point	Use K_{b3}

http://chemwiki.ucdavis.edu/Analytical_Chemistry/Quantitative_Analysis/Titration/Titration_Of_A_Weak_Polyprotic_Acid

Glycine is the simplest amino acid.

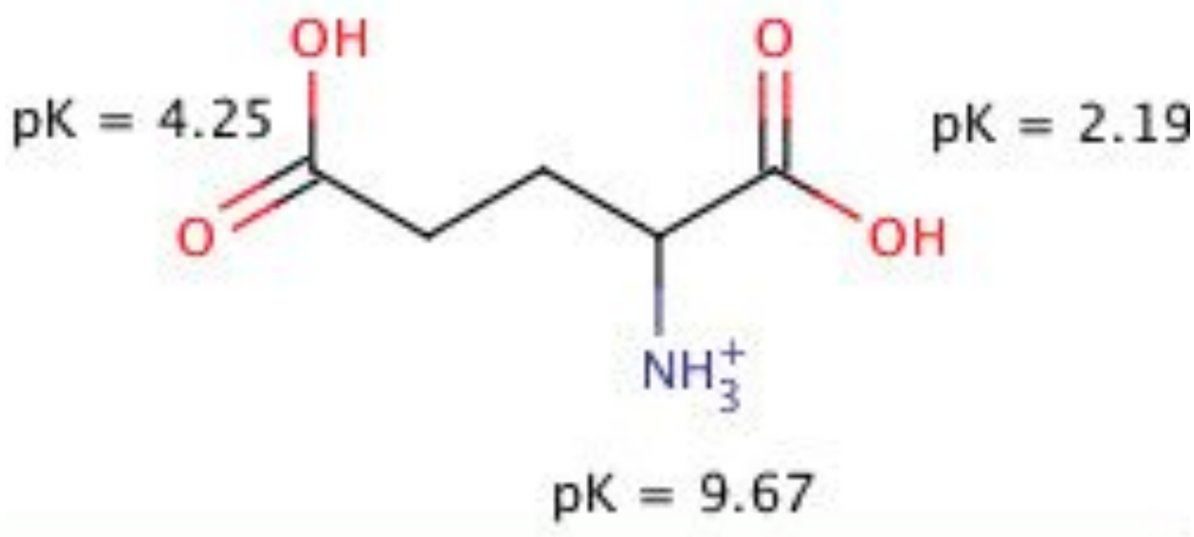
$pK_a = 9.60$



$pK_a = 2.34$

a. Circle the H’s that are acidic in glycine. Which H is the strongest acid? Give reasons.
b. Draw a titration curve of glycine. Label the pH at the starting point, each half way point, and each end point. Assume a 0.1 M solution of glycine is titrated with 0.1 M base.
c. What is the isoelectric point of glycine? Show the pI on your titration curve.
d. Could glycine be used for a pH 5 buffer? Give reasons.

__Bring MSG to Lab on Thursday__ (MSG = Accent)
What's That Stuff? MSG – monosodium glutamate. MSG is a flavor enhancer made from glutamic acid (amino acid).



a. Circle the H's that are acidic in glutamic acid. Which H is the strongest acid? Give reasons.
b. Draw a titration curve of glutamic acid. Label the pH at each end and half way point. Assume a 0.1 M solution.
c. At what pH is MSG prepared? Draw the structure of MSG at this pH.

Weak Acids and Bases Are Found in Biology!

Electrophoresis is a lab technique used to separate and purify substances based on charge. This technique is used to separate and purify amino acids and proteins.
Glutamic acid and glycine are amino acids.
a. Draw the structure of each amino acid.
b. How many protons are donated by each amino acid?
Amino acid pKa values:

http://homepage.smc.edu/kline_peggy/Organic/Amino_Acid_pKa/Amino_Acid_pKa.htm

c. At low pH, what is the charge?
d. At what pH does the AA have a charge = 0 (isoelectric point)?
e. How would you use electrophoresis to separate a mixture of these two amino acids?

What pH would you use to separate a glutamic acid and glycine mixture using electrophoresis?

Lab **Objective**: Determine the pK_a's and pI (isoelectric point) of Milk

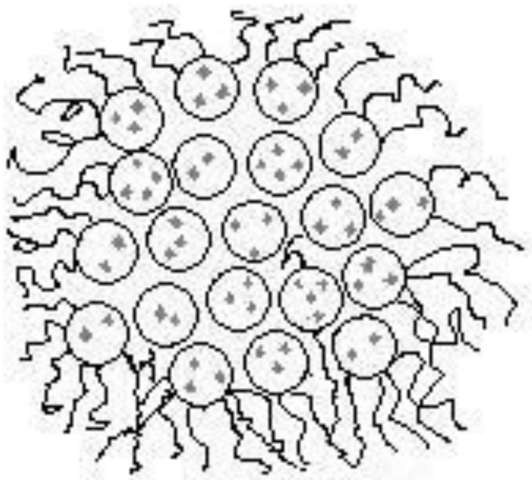


Figure 2. Casein Micelle
submicelle
calcium phosphate
k-casein peptide chain

http://www.milkfacts.info/Milk%20Composition/Protein.htm

Milk pH = 6.6
protein = calcium caseinate

What is the charge on the caseinate ion at pH 6.6?

Protein precipitates at pH 4.6
protein = casein

What is the charge on casein at pH 4.6?

How would you use the titration curve of milk to find pI?

Application: ***Baking Soda*** Buffers Our Blood
One Blood Buffer Consists of HCO_3^-/CO_2

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 HCO_3^-/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

$$H^+ + HCO_3^- \text{--->} H_2O + CO_2$$

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.

In the HCO_3^-/CO_2 blood buffer, what is the acid?
What is the base?

Baking Soda Buffers our Blood: The HCO_3^-/CO_2 Blood Buffer

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

CO_2 (g) <==> CO_2 (aq) $K_1 = 3 \times 10^{-5}$ at 37°C.
CO_2 (aq) + H_2O (l) <==> H_2CO_3 (aq) $K_2 = 5 \times 10^{-3}$ at 37°C
H_2CO_3 (aq) <==> H^+ (aq) + HCO_3^- (aq) $pK_a = 3.8$ at 37°C
CO_2 (aq) + H_2O (l) <==> H^+ (aq) + HCO_3^- (aq) $K_4 = ?$

(i) $K_4 = K_1 + K_2 + K_a = 5.21 \times 10^{-3}$
(ii) $K_4 = K_1 K_2 K_a = 2.38 \times 10^{-11}$
(iii) $K_4 = K_2 + K_a = 5.16 \times 10^{-3}$
(iv) $K_4 = K_2 K_a = 7.92 \times 10^{-7}$

b. The $[HCO_3^-] = 0.024$ M in blood at pH 7.4. Calculate the $[CO_2\text{ (aq)}]$ in blood at this pH.
(i) Use K_1 for Rxn (1); $[CO_2\text{ (aq)}] = 5.21 \times 10^{-3}$ M
(ii) Use H-H equation for Rxn (2); $[CO_2\text{ (aq)}] = 5.16 \times 10^{-3}$ M
(iii) Use H-H equation for Rxn (4); $[CO_2\text{ (aq)}] = 1.2 \times 10^{-3}$ M

Baking Soda Buffers our Blood: The HCO_3^-/CO_2 Blood Buffer

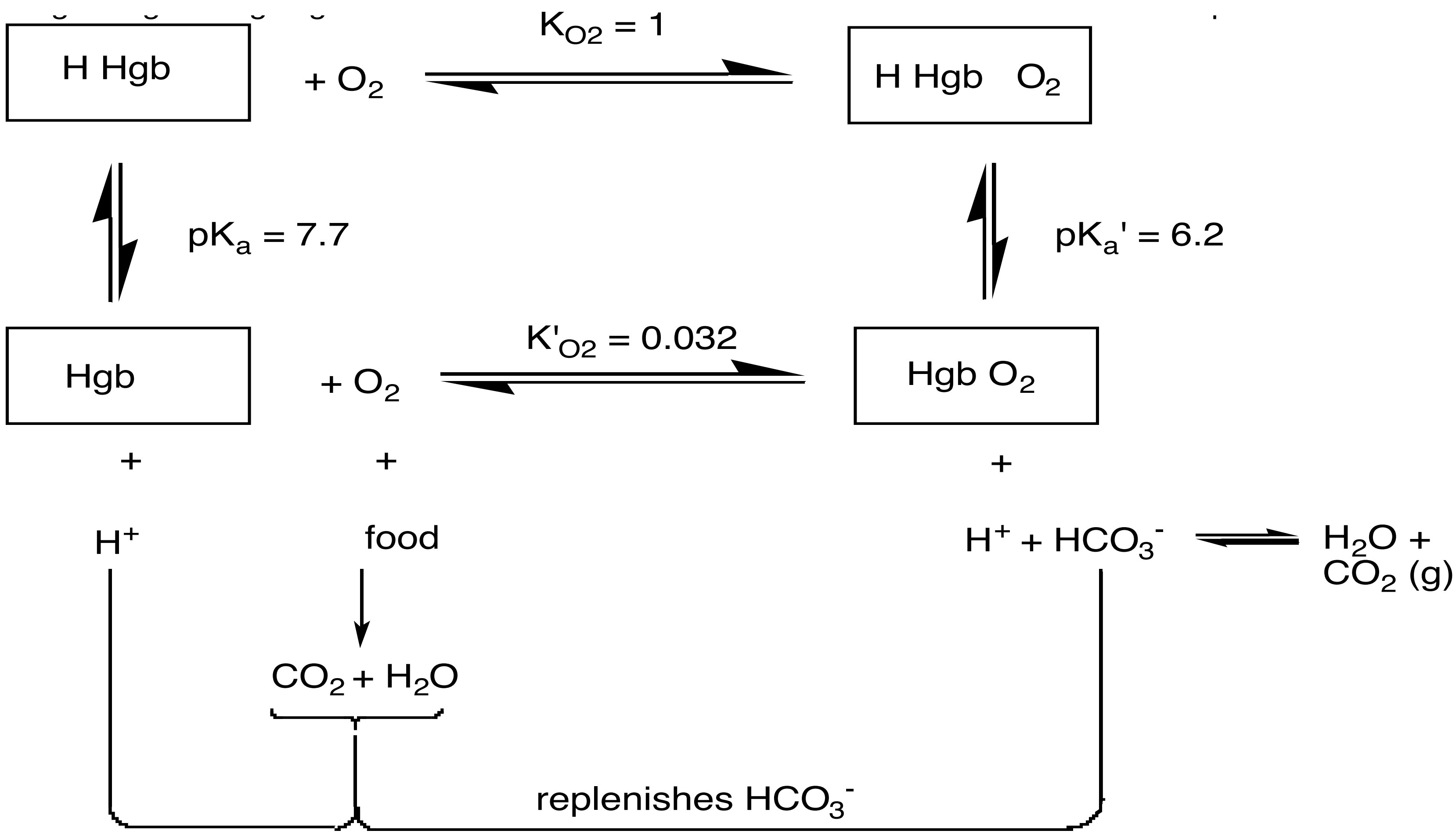
c. 0.01 M H^+ is added to blood. Calculate the pH of blood under conditions such that the increased [CO_2 (aq)] can <u>not</u> be released as CO_2 (g). In other words, assume that the blood buffer is a closed system. (Hint: do stoichiometry calculation, then use H-H equation)

d. 0.01 M H^+ is added to blood. Calculate the pH of blood under conditions such that the increased [CO_2 (aq)] can be released as CO_2 (g). In other words, assume that the blood buffer is an open system. Remember that the [CO_2 (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?

Hemoglobin Gives Blood its Red Color and is a ***Blood Buffer***

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.



Hemoglobin is a ***Blood Buffer***

a. Does the conjugate acid of hemoglobin (H Hgb) have a higher, lower, or same affinity for oxygen than its conjugate base (Hgb)? Give reasons.
b. In the lungs, is the conjugate acid or conjugate base of hemoglobin formed? Give reasons.
c. In the tissues, is the conjugate acid or conjugate base of hemoglobin formed? Give reasons.
d. When O_2 is released, which equilibrium reaction is affected? In which direction does this reaction shift?
e. How does eating (metabolic pathway) replenish HCO_3^- in blood? Give reasons. What other effect does eating have on the buffering action of hemoglobin?

Eggshells are composed mostly of calcium carbonate ($CaCO_3$) formed by the reaction

$$Ca^{2+} (aq) + CO_3^{2-} (aq) <==> CaCO_3 (s)$$

The carbonate ions are supplied by CO_2 produced as a result of metabolism. Explain why eggshells are thinner in the summer, when the rate of chicken panting is greater. Suggest a remedy for this situation. (Chang, 6th ed., p. 539, Problem 15.71)

If you have an upset stomach, should you chew on egg shells or drink milk?