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pH and Buffers

by

Richard B. Brandt, Ph.D.
Professor of Biochemistry & Molecular Biophysics,
and Preventive Medicine
MCV Station Box 980614
Richmond VA 23298-0614

Tel#(804) 828-0104

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INTRODUCTION

Man is a creature that only exists within certain narrow limits of hydrogen ion concentration (acidity). The normal pH (a measure of acidity) of blood and many other biological fluids is about 7.4. At a blood pH of 7.0, death in acidic coma results, while at blood pH of 7.8, death occurs from convulsive contractions (tetany). The body is equipped with physical and chemical means to maintain its pH within the physiological range. These controls of pH in healthy humans include respiration, digestion, the kidney and blood but will not be presented in detail in this package. The many cellular processes involving membranes, biochemical structures and enzymatic reactions that you will learn in Biochemistry will involve pH and will very often be strongly dependent on pH. The quantitative nature of the process of pH change and protection against change is important in understanding the biological processes. The chemical buffer system provides a partial explanation for the control of the body pH within the narrow limits required for life.

OBJECTIVES

The overall objective is to define and explain pH change and its control through the actions of buffers.

The Sub-objectives are:

define and explain qualitatively and quantitatively the action of H_3O^+ in water

define and explain qualitatively and quantitatively pH, weak acids, strong acids and buffers

solve problems involving buffers and pH

explain the importance of buffers in biological systems

PRE-TEST

(Please complete this prior to using the instructional package.)

1. What is the log of 1? What is the log of 0.1?
2. What is $10^{-2} \times 10^{-2}$? What is $10^{-10}/10^{-3}$?
3. Define: (a) pH
 (b) strong acid
 (c) weak acid
 (d) salt
 (e) buffer
4. What is the pH of 1.0×10^{-4} [H⁺]?
5. What is the pH change found by doubling the hydrogen ion concentration referred to in question 4?
6. What is the change in H⁺ concentration by increasing the pH 1.0 unit from that of question 4?
7. Is the solution in question 6 more acid than a 0.1 M solution of acetic acid ($pK_a = 5$)? Show proof.
8. What is the pH of a buffer composed of equal amounts of a weak acid ($pK_a = 5$) and its salt?

PRE-TEST ANSWERS

1. $\log 1 = 0$

$\log 0.1 = -1$

Whoops!! If you have forgotten this, please start the package at:

Appendix Section A.

2. $10^{-2} \times 10^{-2} = 10^{-4}$

$10^{-10}/10^{-3} = 10^{-7}$

If you did not get the above answer, start the package at:

Appendix Section B.

3. (a) $\text{pH} = -\log [\text{H}^+]$, a measure of H^+ concentration

(b) A strong acid is completely ionized in dilute solution so that the H^+ concentration is equal to the strong acid concentration.

(c) A weak acid is only partly dissociated in solution. The concentration of H^+ in solution will not be equal to the weak acid concentration, but is dependent on the K_a **and** the weak acid concentration.

(d) A salt is the product of an acid and a base. Most common salts are completely ionized in dilute solutions.

(e) A buffer is a mixture of a weak acid and its salt. For the effective range of a buffer (near the $\text{p}K_a$ of the weak acid) the addition of small amounts of acid or base will have little effect on the pH. A common biochemical and clinical equation that is used for the calculation of pH is the Henderson- Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{SALT}]}{[\text{WEAK ACID}]}$$

This package will treat many qualitative and quantitative properties of buffers.

4. pH for $1 \times 10^{-4} [\text{H}^+]$.

$\text{pH} = -\log [\text{H}^+]$.

$\text{pH} = -(\log 1 + \log 10^{-4})$.

$\log 1 = 0$ and $\log 10^{-4} = -4$. So that $\text{pH} = -(-4)$ and $\text{pH} = 4$.

5. pH for 2×10^{-4} $[H^+]$
 $-\log 2 + -\log 10^{-4}$
 $-0.30 + 4 = 3.7$

Therefore, in doubling $[H^+]$, there is only a change of 0.3 pH units.

6. pH of 5 has a $[H^+]$ of 10^{-5} .

7. A 0.1 M solution of HAc has a pH of about 3. $K_a = \frac{[H^+][Ac^-]}{[HAc]}$
and $10^{-5} = \frac{X^2}{0.1M}$ so that $X = 10^{-6} = 10^{-3}$. $[H^+]$ must equal $[Ac^-]$. The $[H^+]$ is therefore 10^{-3} and the pH = $-\log [H^+]$ which is 3.

The answer to the question is no, the solution from #6 with a pH of 5 is not more acid.

8. A solution of equal amounts of a weak acid and its salt is a buffer. The Henderson-Hasselbalch equation applies. (See 3c). So that using a pK of 5, and $[salt] = [weak\ acid]$:

$$pH = 5 + \log \frac{1}{1} \quad \text{and}$$

$$pH = 5 + \log 1. \quad \text{Since the log of 1 is zero, then } pH = 5.$$

If you have not been able to readily answer these questions, work through the packet. If you find your time exceeding three hours -- **QUIT!!** -- See an instructor!

If you get most of the questions, but want a brush-up, see: **Appendix E**, supplemental problems.

FEEDBACK 1a: From equation 1, the effect of increasing $[H_3O^+]$ would be to decrease $[OH^-]$ since equation 1 is written as an equilibrium and the product of $[H_3O^+]$ $[OH^-]$ is a constant at a particular temperature.

Equation 1 with H_2O predominantly undissociated, represents an equilibrium so that any change in $[H_3O^+]$ must also have a corresponding but opposite change in $[OH^-]$.

PRACTICE 1b: Now - we can be specific and have a $[H_3O^+]$ of 1×10^{-2} moles/liter. What is the $[OH^-]$? Write your answer with the mode of solution and then consult FEEDBACK 1b. [DON'T PEEK]!!

FEEDBACK 1b: using equation 2

$$K_w = [H_3O^+] [OH^-]$$

$$1 \times 10^{-14} = [1 \times 10^{-2}] [OH^-]$$

$$[OH^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-2}}$$

$$[OH^-] = 1 \times 10^{-12} \text{ moles/liter}$$

If you want to try a few more problems of the 1b type for determination of $[OH^-]$ when $[H_3O^+]$ is given:

- 1) 1×10^{-13}
 - 2) 5×10^{-2}
 - 3) 1×10^{-7}
- answers bottom of page 8

and for $[H_3O^+]$ when $[OH^-]$ given:

- 4) 1×10^{-7}
 - 5) 0.01
- answers bottom of page 8

If you understand, move to Cycle 2!!

If you are confused, you may not understand exponents. Try using exponents converted to decimals and perform the same operation. If you are still confused, see: **Appendix B** on exponents. Perhaps if you have forgotten the definition of some terms such as moles or moles/liter, M, or molar, you should also consult: **Appendix C** at this time.

PRACTICE CYCLE #2

pH

INPUT: Since $[H^+]$ can vary over a wide range, the accepted method of expression is in powers of 10 (scientific notation). For example, $[0.1]$ is $[10^{-1}]$ and $[0.01]$ is $[10^{-2}]$, etc. (all in moles/liter). The mathematical representation of hydrogen ion concentration used is the negative logarithm of $[H^+]$. This expression (eq.3), is called pH and will always give positive values rather than negative exponents.

$$pH = -\log [H^+] \quad \text{eq.3}$$

A pH of 1 would be very acid and correspond to a $[H^+]$ of 10^{-1} , while a pH of 14 would be very basic and correspond to a $[H^+]$ of 10^{-14} . Similar to the treatment in defining pH the negative log of K_w is pK_w . Looking back at equation 2 on page 6, the negative log of the whole expression gives another representation of pK_w as shown in equation 4.

$$pK_w = pH + pOH \quad \text{eq.4}$$

PRACTICE 2a: What is the pK_w at 24° ? Write your answer before continuing to FEEDBACK 2a!!

FEEDBACK 2a: The answer is 14 which is obtained from the $-\log$ of K_w , where $pK_w = -\log K_w$ and therefore $pK_w = -\log 10^{-14}$. Note that this is at 24° where $K_w = 1 \times 10^{-14}$. An increase in temperature would change the K_w (a different constant at each temperature) since the ionization increases as does most equilibrium reactions with increased temperature. However, for ease of calculation, 1×10^{-14} is used as the K_w throughout this package.

Continue to page 9!!

Answers from questions on page 7.

- | | |
|---------------------------------|--|
| 1) 0.1 (or 1×10^{-1}) | 4) 1×10^{-7} |
| 2) 2×10^{-13} | 5) 1×10^{-12} |
| 3) 1×10^{-7} | All in moles/liter. 1-3 $[OH^-]$; 4&5 $[H^+]$ |

If you did not get 14 as an answer, you had better review the **Appendix** material. If you cannot solve problems of this type and those involving eq. 3, see the **Appendix** and the problem solving unit. If you have this well understood--continue to PRACTICE 2b.

PRACTICE 2b: What is the $[H_3O^+]$ concentration at neutrality? What is the pH? Write your answer before continuing to FEEDBACK 2b!!

FEEDBACK 2b: At neutrality $[H_3O^+] = [OH^-]$ and from equation 2, $K_w = [H_3O^+] [OH^-]$, so that $[H_3O^+] = 1 \times 10^{-7}$ moles/liter (i.e., if X is the concentration of each, then $X^2 = 1 \times 10^{-14}$, and $X = 1 \times 10^{-7}$ moles/liter). From eq.3 and eq.4, $pH = 7$ and so $14 = 7 + pOH$, therefore $pOH = 7$. If you wish to try a few more problems of this type, go back to the bottom of page 8 and use the $[H_3O^+]$ or $[OH^-]$ given there. Solve for both pH and pOH. Answers for additional problems are shown below:

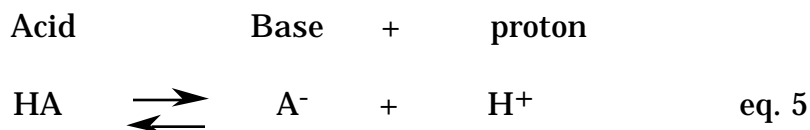
Answers

<u>pH</u>	<u>pOH</u>
1) 13	1
2) 1.3	12.7
3) 7	7
4) 7	7
5) 12	2

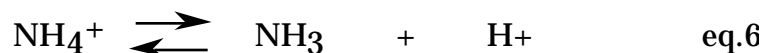
At this point if pH problems present difficulties, see: **Appendix D**, otherwise march on to Cycle #3.

PRACTICE CYCLE #3
Strong Acids

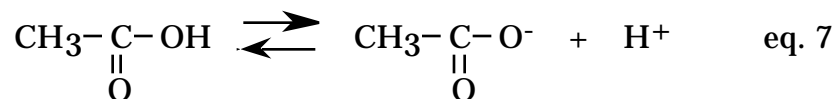
INPUT: The properties common to most acids, sour taste, ability to dissolve metals, to combine with or neutralize alkali (base) are all expressions of those acids furnishing protons [H⁺] (or more correctly hydronium ions, [H₃O⁺]) in solution.



This is the simplest definition of an acid according to Brønsted, that an acid is a proton donor. A base accepts protons. For example:



The ammonium ion is the acid and ammonia is the base.



Acetic acid is the acid and the acetate ion is the base (eq.7). Note in eq.5-7 the double arrow indicating an equilibrium. However, strong acids and strong bases are considered to be completely ionized in aqueous solutions and would have a single arrow directed toward protons released:



Therefore, the concentration of [H⁺] or [H₃O⁺] is equal to the concentration of the strong acid.

The quantitative addition of a base to a known amount of acid while measuring the change in pH is a titration. The pH values for the titration of 10.0 ml of 0.1 M HCl with increasing amounts of 0.1 M NaOH are shown in the last column of Table I.

A titration curve of a strong acid may be constructed by calculating the amount of hydrogen ion remaining at any point after the addition of measured amounts of base. Remember, the strong acid is always considered to be completely dissociated. A titration curve was drawn from the data shown in Table I and is shown in Figure 1. Note the general features: a) the slight increase in pH with increasing amounts of base (for example, addition of 5 ml of base has only increased the pH by 0.48 units); b) the larger increase in pH when the strong acid is nearly neutralized (an increase of 1.33 pH units from 90% neutralized to 99.5% neutralized); c) a still larger pH change occurs with the addition of a small increment of base to give 100% of the acid neutralized; d) further addition of base has the same effect as adding base to water, since the end point pH of the reaction shown in equation 9 is 7.0.



PRACTICE 3a: Solve for H^+ concentration for each step from Table I. Check your answers by solving for pH and comparing to the tabular values. Write your answer and check against FEEDBACK 3a before proceeding!!

FEEDBACK 3a: If your calculated pH values agree with pH values in Table I, skip to 3b. If they do not agree, did you (1) convert H^+ concentration to moles/liter? (2) use the log tables correctly? (3) use the correct volumes? See the example at the bottom of Table I.

PRACTICE 3b: Why is the H^+ concentration the same as the concentration of the strong acid? Write your answer and proceed to FEEDBACK 3b!!

FIGURE 1

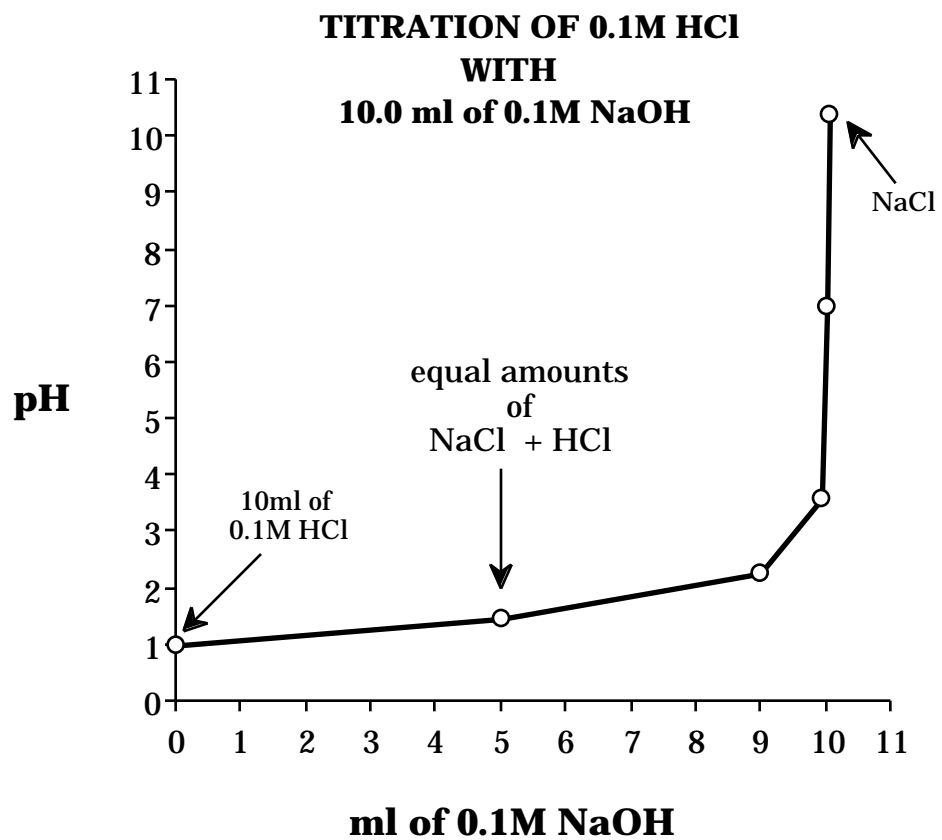


TABLE I

Titration of 0.1 M HCl with 0.1 M NaOH

Remaining HCl ² (mmoles)	Total Added Volume NaOH (ml)	Total Volume ¹ (ml)	pH
1.00	0	10.0	1.00
0.50	5.0	15.0	1.48
0.10	9.0	19.0	2.27
0.005	9.95	19.95	3.60
0	10.0	20.0	7.00
0	10.05	20.05	10.40

¹For example, after the addition of 5.0 ml of NaOH to 10 ml of HCl the total volume would be 15 ml, 5 ml of which would be 0.1 M HCl and 10 ml H₂O (NaCl was also produced, but this would not affect the pH). See also Cartoon Ia on pg. 15.

²One mole/liter is 1000 millimoles/liter. Using the formula, ml x molarity = mmoles, the number of millimoles of H₃O⁺ at any point in the titration may be determined. For example, after the addition of 5.0 ml of NaOH, there is 0.5 mmoles of HCl (5.0 ml HCl x 0.1 M) in a volume of 15 ml.

To solve for pH the hydrogen ion concentration must be found in moles/liter:

$$\frac{0.5 \text{ mmoles}}{15 \text{ ml}} = \frac{\text{mmoles}}{1000 \text{ ml}}$$

The H⁺ concentration is therefore 33.3 mmoles/1000 ml or 0.0333 moles/liter. The pH is - log 3.33 x 10⁻² which equals 1.48.

At exactly 10 ml of NaOH added to the strong acid, [OH⁻] = [H₃O⁺] and since K_w = [OH⁻] [H₃O⁺] then [OH⁻] & [H₃O⁺], each must be 1 x 10⁻⁷ moles/liter, so pH = 7.0.

At a volume of 10.05 ml of NaOH added all of the HCl has been titrated (used up). See the cartoon Ib on page 16. Note that there is now an excess of OH⁻. The concentration of OH⁻ can be determined. The total volume (see Table I page 13) is 20.05 ml. In this volume is 0.005 mmoles extra OH⁻ (0.05 ml NaOH x 0.1M).

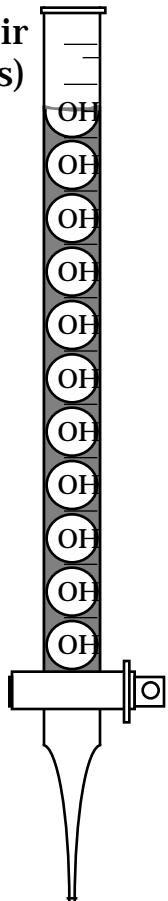
$$\frac{0.005 \text{ mmoles}}{20.05 \text{ ml}} = \frac{\text{mmoles}}{1000 \text{ ml}}$$

The OH⁻ concentration is therefore 0.25 mmoles/liter (0.25 x 10⁻³M). To determine the [H⁺] use equation 2, page 6. $K_w = [H_3O^+] [OH^-]$. The [H⁺] is calculated to be 4 x 10⁻¹¹M. The pH = -log [H⁺] and is 10.40 (as shown in Table I). See also Cartoon Ib. page 16.

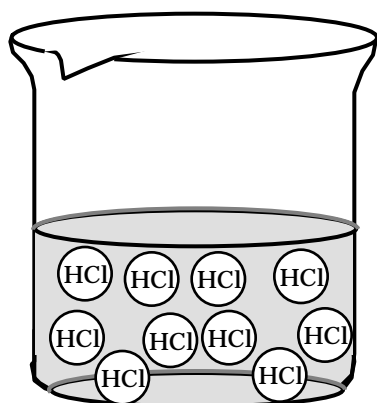
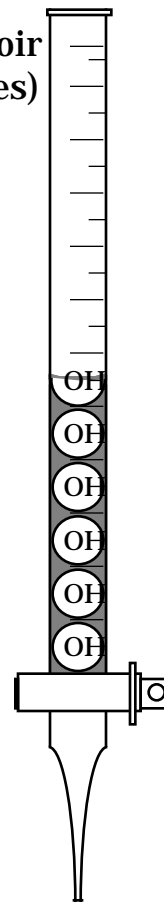
FEEDBACK 3b: The hydrogen ion concentration (expressed in moles/liter) is the same as the concentration of the acid because a strong acid was used and is completely ionized. This is a good generalization that is useful for dilute solutions of strong acids (or bases), even though the exact nature of the process is defined by the effective concentration of the strong acid present (activity) which may be less than the actual concentration added, due to solvation of ions and interaction of ions. However, in the treatment presented here, strong acids, salts and strong bases will always be assumed to be 100% ionized and the concentration used will be equal to the effective concentration (i.e.: 0.1M HCl equals 0.1M H⁺)

Cartoon Ia. Titration of Strong Acid with Base.

OH^- Reservoir
(1.05 mmoles)



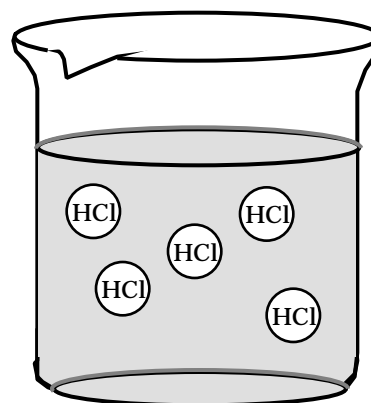
OH^- Reservoir
(0.55 mmoles)



Initial

pH 1.00

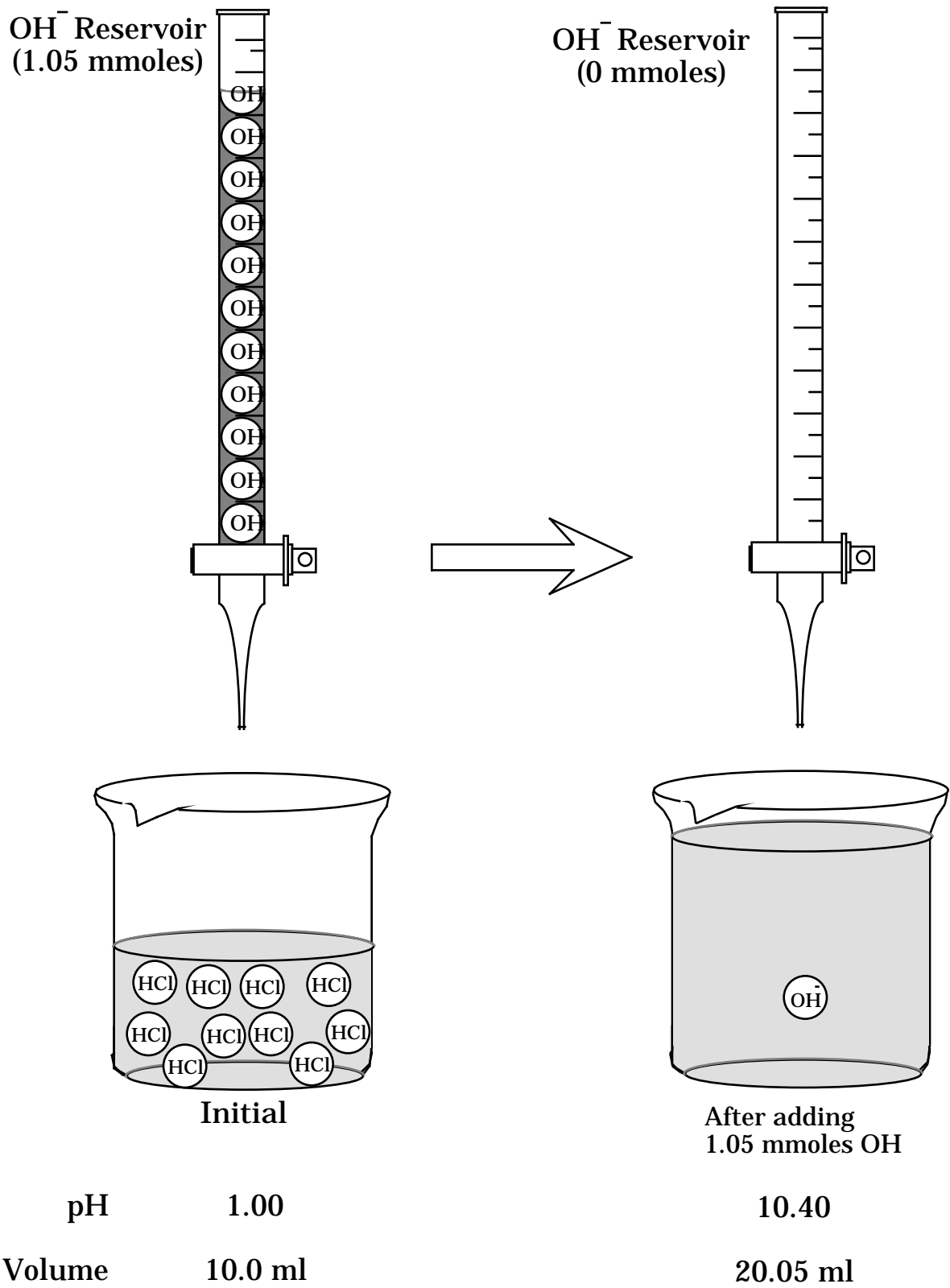
Volume 10.0 ml



After adding
0.5 mmoles OH^-
1.48

15.0 ml

Cartoon Ib. Titration of Strong Acid with Excess Base.



PRACTICE CYCLE #4

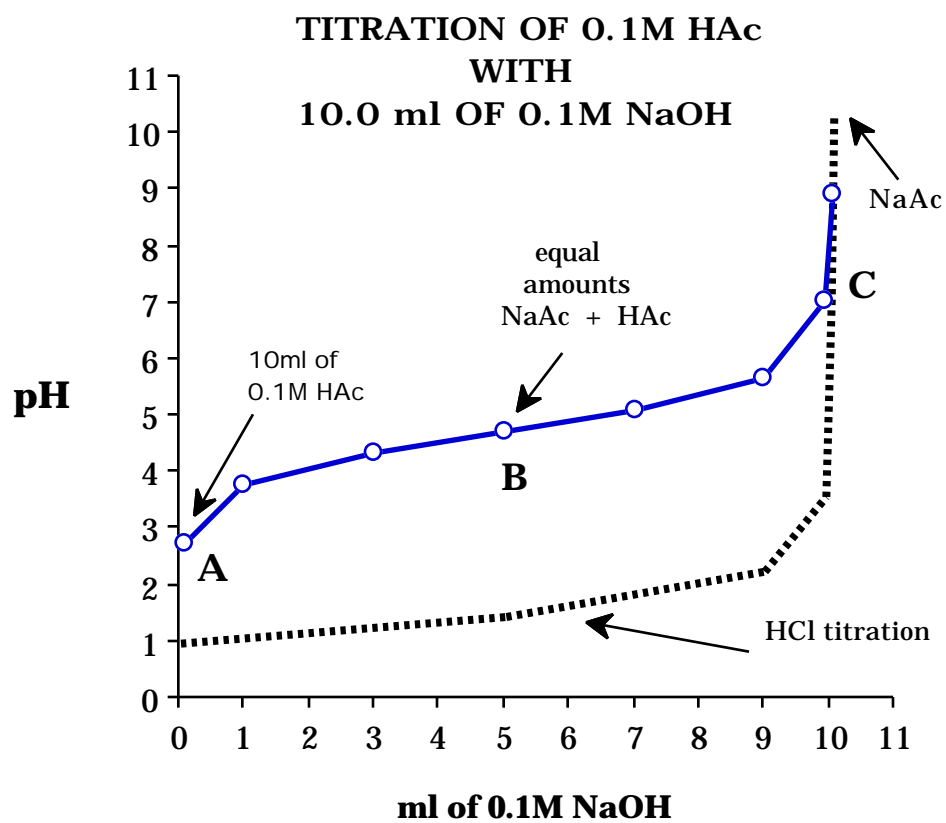
Weak Acids

INPUT: Biological buffers are usually a mixture of weak acids and their salts. To understand the theory and action of buffers the weak acid and its release of H^+ must be understood. For a weak acid the hydrogen ion concentration is determined both by the concentration of the weak acid and the dissociation of the weak acid to its salt $[A^-]$. However, this is only a partial ionization in solution to give a mixture of both the undissociated weak acid $[HA]$ and its ions $[A^-]$. The dissociation constant of a weak acid is the K_a and may be written as shown in eq. 10.

$$K_a = \frac{[A^-][H^+]}{[HA]} \quad \text{eq. 10}$$

The smaller the value of K_a , the greater the amount of the undissociated weak acid and the smaller the amount of protons in solution. Similar to the titration of a strong acid a weak acid may be titrated. The pH does not change in a uniform manner throughout the range of titration for the addition of each ml of NaOH. The greatest change occurs near the complete neutralization, while the least change of pH occurs at the midpoint of the dissociation of the weak acid. Table II gives the data for the titration of the weak acid (acetic acid) with sodium hydroxide. A graph prepared from this data is shown in Figure 2. The dotted line is the titration of HCl previously performed and is shown for contrast. Comparing the two curves (Figure 2) the weak acid is affected more by a small addition of base (at point A). The change in pH with added base is least at the region where the weak acid is half titrated (at point B). Another way of expressing this is that the change in pH is least when the concentration of the salt formed is equal to that of the weak acid remaining. The greatest change occurs at point C where very little undissociated weak acid remains.

FIGURE 2



PRACTICE 4a: For two solutions of equal concentrations of a weak acid and a strong acid, which has more protons in solution? Solve and write your answer and then go to FEEDBACK 4a!!

FEEDBACK 4a: The strong acid has more protons in solution since the H^+ concentration is equal to the concentration of the strong acid. The weak acid is mostly undissociated and its H^+ concentration depends on its K_a . The larger the K_a the more H^+ in solution. See Cartoon IIa & IIb on page 22. Go to PRACTICE 4b!!

PRACTICE 4b: For separate solutions of a strong acid and a weak acid ($K_a = 1 \times 10^{-5}$) both at 0.1 moles/liter: what is the $[H_3O^+]$ for each? You might as well get some practice and solve for pH also. Solve and write your answer. Go to FEEDBACK 4b!!

FEEDBACK 4b: The weak acid has a $[H^+]$ of 1×10^{-3} moles/liter and the strong acid 1×10^{-1} moles/liter. This is a quantitative example of the type mentioned in FEEDBACK 4a. If you got this right, skip to PRACTICE 4c. If you did not get the correct $[H^+]$ for the weak acid, the following may apply: 1) did you use equation 10 (remember a weak acid is only partly dissociated); 2) did you use the K_a of 1×10^{-5} ; 3) do you know that the 1×10^{-6} is 1×10^{-3} ? Additional problems for weak acid pH may be found in the **Appendix** section. Now go to PRACTICE 4c!!

PRACTICE 4c: How many ml of 0.1 M NaOH are required to react completely with 10 ml of each of the weak and strong acids? Solve, write and proceed to FEEDBACK 4c!!

FEEDBACK 4c: Using 0.1 M NaOH, 10.0 ml would be required to react with both the strong and weak acid. The total acidity available from each for equal concentrations is the same. A solution of the weak acid would have fewer H^+ in solution at any one time and in order to maintain the K_a , more weak acid must dissociate to produce more H^+ from that weak acid as the OH^- reacts with the protons in solution. Eventually all the weak acid will have been dissociated as its salt NaA is formed. See Cartoon III page 23. Proceed to PRACTICE 4d!!

PRACTICE 4d: Which is a stronger weak acid, one with a K_a of 1×10^{-3} or one with a K_a of 1×10^{-9} ? Solve and write your answer and proceed to FEEDBACK 4d!!

FEEDBACK 4d: The larger K_a (1×10^{-3}) is for a stronger acid than the lower K_a (1×10^{-9}). The larger the K_a , the more the acid is dissociated. Work this through using equation 10 and solving for $[H^+]$, using a 0.1 M weak acid if you do not agree to the above statement. Only 10^{-5} $[H^+]$ from the weak acid which was 10^{-1} $[HA]$ for a K_a of 1×10^{-9} , while 10^{-2} $[H^+]$ from the weak acid, K_a 1×10^{-3} .

TABLE II**Titration of 0.1 M Acetic Acid with 0.1 M NaOH**

HAc mmoles (remaining)	Total Added Volume NaOH (ml)	Total Volume (ml)	Ratio Ac/HAc	pH ¹
1.0	0	10.0	--	2.86
0.90	1.0	11.0	1/9	3.77
0.70	3.0	13.0	3/7	4.36
0.50	5.0	15.0	1/1	4.73
0.30	7.0	17.00	7/3	5.10
0.10	9.0	19.00	9/1	5.68
0.005	9.95	19.95	9.95/0.05*	7.03
0	10.0	20.0	---	8.70
0	10.05	20.05	--	10.40

¹pH for 1 mmole of HAc was calculated on the basis of K_a of

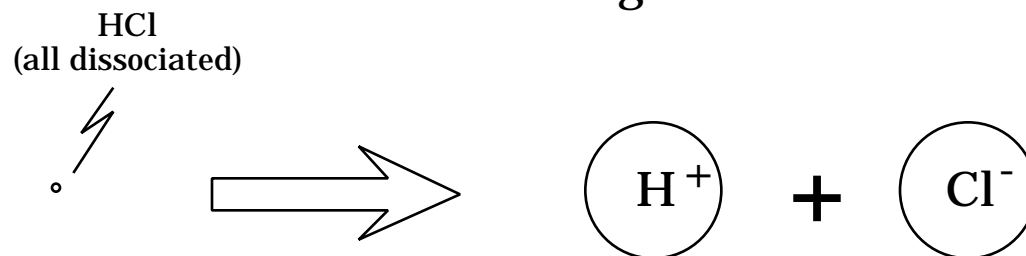
$$1.86 \times 10^{-5} = \frac{[\text{H}^+][\text{Ac}^-]}{[0.1]} \quad \text{and } [\text{H}^+] = [\text{Ac}^-], \text{ so that } [\text{H}^+]^2 = 1.86 \times 10^{-6}$$

and $[\text{H}^+] = 1.36 \times 10^{-3}$ moles/liter. The other pH values were calculated using equation 13, cycle 5. The pH at the end point (10.0 ml NaOH added) depends on the concentration of sodium acetate which is briefly mentioned in APPENDIX D. With an excess of OH^- the pH depends only on the H^+ remaining with an increase to pH 10.40 as seen in Table I.

*Very poor buffering when the ratio of salt to weak acid is so large.

Cartoon IIa. Dissociation of a Strong Acid

0.1 M Strong Acid

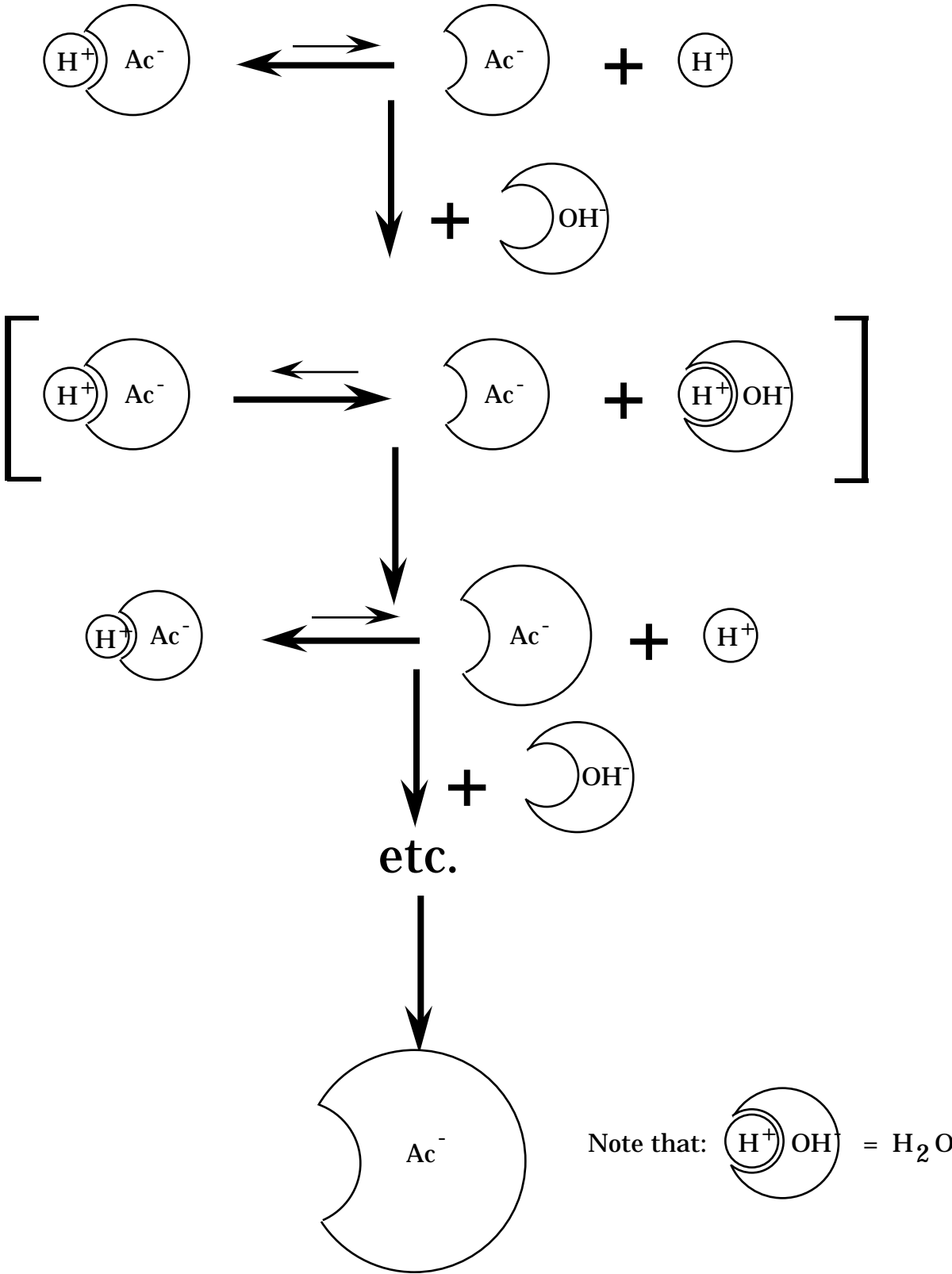


Cartoon IIb. Dissociation of a Weak Acid

0.1 M Weak Acid



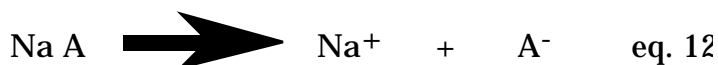
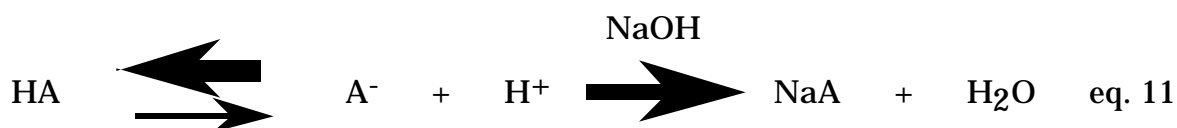
Cartoon III. Addition of Base to Weak Acid



PRACTICE CYCLE #5

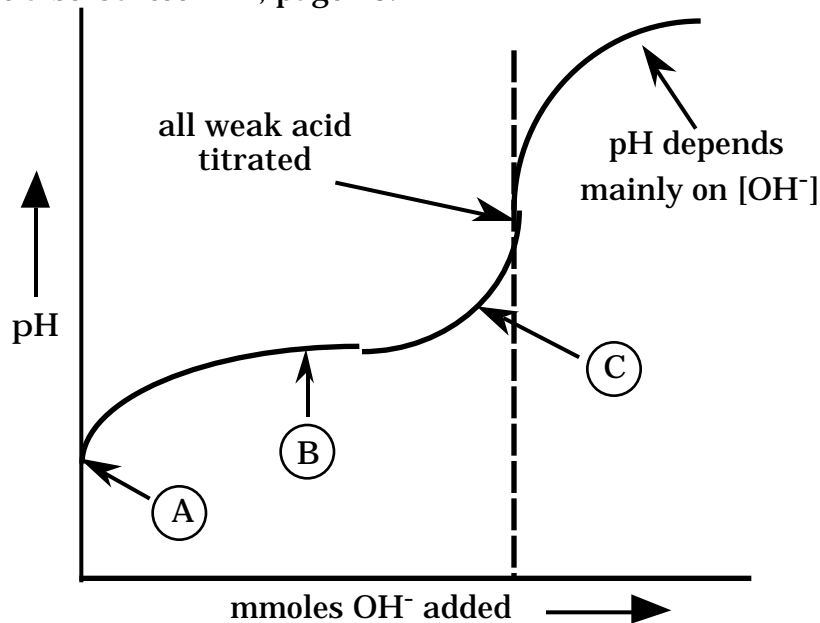
Buffers

INPUT: A buffer is a mixture of a weak acid and its salt that resists change in pH upon the addition of acid or base. In order to understand the effect of the action of buffers in maintaining pH remember that a weak acid is only slightly ionized while its salt is completely ionized. Refer to figure 3 below which is a representation of a weak acid at various pH ranges. At point (A) there is all weak acid so that the addition of a small amount of base shows a large pH change. The reactions occurring are represented by eq. 11 and eq. 12.



The amount of A^- (the ionized salt) and HA (the undissociated weak acid) yield the pH for a specific weak acid. At point (B) the HA is present at 50% of its original value and the A^- (salt) is equal to the concentration of the weak acid (i.e. the ratio of salt to weak acid is 1). The pH of the solution varies least at this point with added base (or strong acid). At point (C) the ratio of salt to weak acid is large and small amounts of base will cause greater changes in the pH than at (B). See also Cartoon III, page 23.

FIGURE 3



The $[H^+]$ in solution from a weak acid at any time depends on the K_a of the weak acid, so that a buffer solution will have a quantitative relationship based on the ratio of $\frac{A^-}{HA}$ and on the K_a . This quantitative relationship is known as the Henderson-Hasselbalch equation (shown in equation 13).

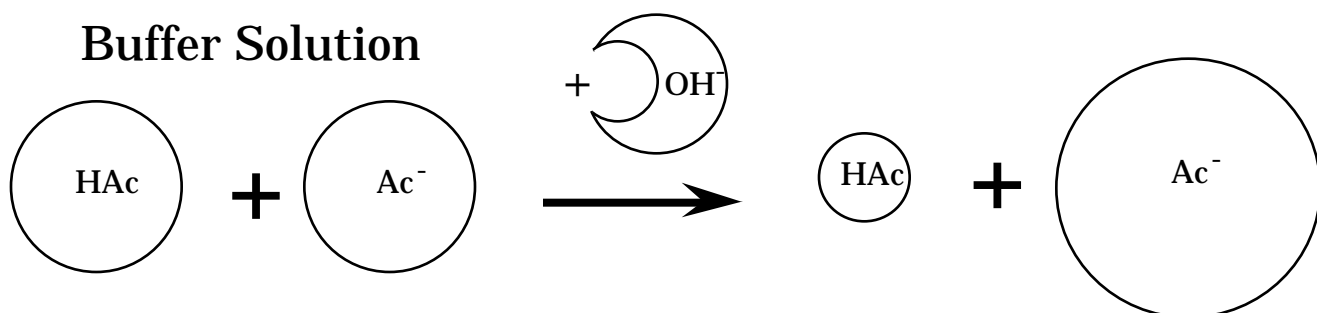
$$pH = pK_a + \log \frac{[\text{salt of weak acid}]}{[\text{weak acid}]} \quad \text{eq. 13}$$

The pK_a is the negative log of K_a . This is both a quantitative formula and a tool for understanding buffer action (the formula is derived in the [Appendix E, c](#)) but the derivation is not required for its use).

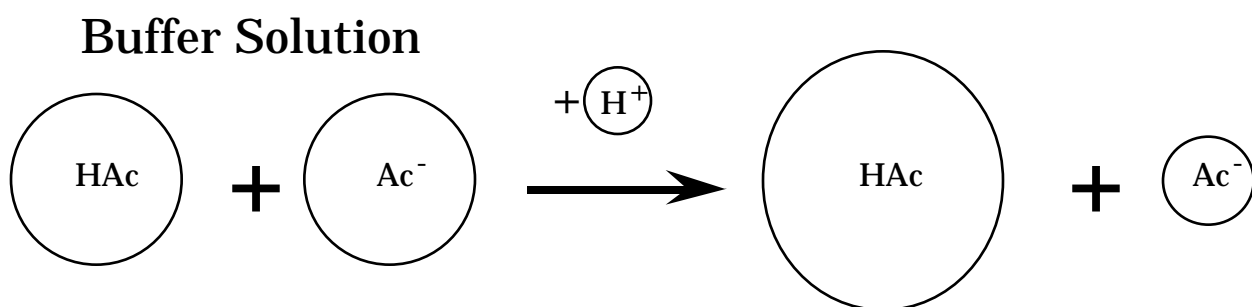
From equation 11 when a weak acid is present, it is predominantly in the undissociated form. From equation 12, the salt NaA is completely dissociated to A^- (and of course Na^+) so the mixture of HA and A^- would have essentially all of the A^- from the added NaA. Also essentially all of the HA is from the weak acid. The pH for a known ratio of salt/weak acid may be calculated if the pK_a of the weak acid is known. The action of addition of OH^- to a buffer may be explained by formation of the salt from the weak acid by removal of H^+ as shown in equation 11, driving the reaction to the right decreasing the $[HA]$ and increasing the $[A^-]$. This will increase the ratio of salt/weak acid in equation 13 and only slightly increase the pH, since the pH will change as a function of the \log of $\frac{\text{salt}}{\text{weak acid}}$.

Conversely the addition of a strong acid removes A^- from solution (equation 11 reaction driven to the left) to form the weak acid, HA and thus decreases the ratio of $\frac{\text{salt}}{\text{weak acid}}$, slightly decreasing the pH. (See [Cartoon IVa IVb](#), page 26). The effect of added strong acid or base depends on the concentration of the weak acid and salt as well as the ratio of $\frac{\text{salt}}{\text{weak acid}}$. The best buffering action occurs when the ratio of the $\frac{\text{salt}}{\text{weak acid}}$ is one. This corresponds to (B) in [Figure 3](#) (i.e., at a ratio of 1 then $[\text{salt}] = [\text{weak acid}]$).

Cartoon IVa. Addition of Base to a Buffer



Cartoon IVb. Addition of Acid to a Buffer



PRACTICE 5a: What happens to the ratio of $\frac{\text{salt}}{\text{weak acid}}$ in a buffer solution when a strong acid is added to a buffer? Write your answer and proceed to FEEDBACK 5a!!

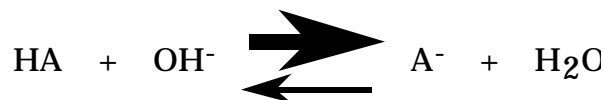
FEEDBACK 5a: The ratio of $\frac{\text{salt}}{\text{weak acid}}$ decreases with the addition of a strong acid $[\text{H}_3\text{O}^+]$ to the buffer, since some of the salt A^- is converted to the weak acid (the equation driven to the right as written below).



Thus $[\text{A}^-]$ decreases and $[\text{HA}]$ increases. Using the Henderson-Hasselbalch equation 13, if the ratio of $\frac{\text{salt}}{\text{weak acid}}$ decreases there will be some decrease in pH. See also Cartoon IVb. Go to PRACTICE 5b!!

PRACTICE 5b: What happens to the ratio of $\frac{\text{salt}}{\text{weak acid}}$ in a buffer solution upon addition of a strong base? Write your answer and proceed to FEEDBACK 5b!!

FEEDBACK 5b: The ratio of $\frac{\text{salt}}{\text{weak acid}}$ increases by addition of a strong base to the buffer, since the reaction below is driven to the right, decreasing the $[\text{weak acid}]$ and increasing the $[\text{salt}]$. The pH will increase (see also equation 13 and cartoon IVa).



Go to PRACTICE 5c!!

PRACTICE 5c: What does the Henderson-Hasselbalch equation reduce to when the ratio of $\frac{\text{salt}}{\text{weak acid}}$ is one? Write your answer and proceed to FEEDBACK 5c!!

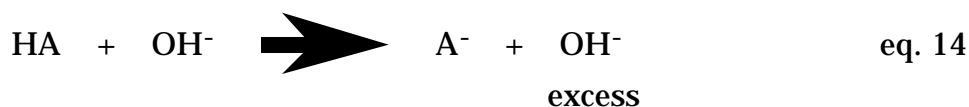
FEEDBACK 5c: Using equation 13, the $\text{pH} = \text{pK} + \log 1$. Since the $\log 1$ is zero then $\text{pH} = \text{pK}$. At this ratio of one, the salt concentration equals the weak acid concentration. This is, of course, the region of best buffer action. Go back to Cycle #4 and look at Figure 2 for the weak acid, acetic acid. Notice there, that at the half titration of the weak acid (when 50% of the original weak acid is used) the mixture in solution is 0.5 mmoles of acetic acid and 0.5 mmoles of sodium acetate. Since at this point $\text{pH} = \text{pK}$, the pK can be determined from the graph. It is found to be 4.73. If you look at Table II, the pH change upon addition of 2.0 ml of base at half titration of the weak acid (pH 4.73) is only 0.37 pH units to pH 5.10. At 10% titration (when 1.0 ml of OH^- has been added to acetic acid) and the pH is 3.77, addition of 2.0 ml of base gives a 0.59 pH change to pH 4.36. The least change in pH upon added base (or acid) is shown to occur at the pK .

****Read this last paragraph again working with both Figure 2 and Table 2.****

PRACTICE CYCLE #6

Buffers (Concentration Effects)

INPUT: Given the pK_a of a weak acid (HA) and the ratio of its salt to weak acid, $\frac{[A^-]}{[HA]}$ the pH may be calculated using the Henderson-Hasselbalch equation (see equation 13, Cycle #5). A third factor, the concentration of the salt and the weak acid is important, since a buffer becomes less effective as the ratio of salt to weak acid changes from a ratio of 1. If the weak acid were very dilute and a large amount of a strong base were added, the net result would be a failure to maintain a buffer system since there would be an excess of OH^- .



The pH for equation 14 is then dependent essentially on rearrangement of the equation 4 previously shown in Cycle #2,

$$pH = pK_w - pOH \quad \text{eq. 15}$$

Of course combination of equations 2 and 3 would also give the same result.

PRACTICE 6a: Calculate the pH for a solution which is 0.05 M in acetic acid, pK_a 4.7, and 0.1 M in sodium acetate. Before solving, will the pH be higher or lower than the pK_a ? Write your answer and proceed to FEEDBACK 6a!!

FEEDBACK 6a: I hope you decided that the pH would be higher than the pK_a since by using the Henderson-Hasselbalch equation, inspection would show a ratio greater than 1 for $\frac{\text{salt}}{\text{weak acid}}$.

Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{weak acid}]}$$

$$\text{pH} = 4.7 + \log \frac{[0.1]}{[0.05]}$$

$$= 4.7 + \log 2 \text{ (a good trick to work with whole numbers)}$$

$$= 4.7 + 0.3$$

$$\text{pH} = 5.0$$

If you wish, solve some of the additional problems below for pH of various weak acids, given the concentration of salt and concentration of weak acid (in moles/liter) and the pK_a .

	pK_a	$[\text{A}^-]$	$[\text{HA}]$	pH
1)	4.7	0.1	0.01	answers at the bottom of this page
2)	4.7	0.01	0.1	
3)	6.8	0.05	0.05	
4)	6.8	0.05	0.005	
5)	6.8	0.01	0.005	

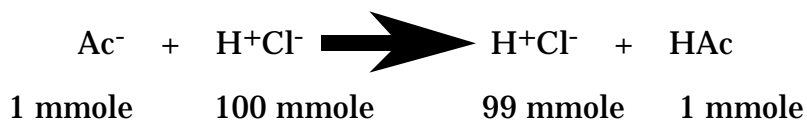
Go to PRACTICE 6b!!

PRACTICE 6b: If 10 ml of the buffer described in 6a was treated with 1000 ml of 0.1 M HCl, is this still a buffer system? What would the pH be? Write your answer and proceed to FEEDBACK 6b!!

Answers to additional questions 6a:

- 1) 5.7 3) 6.8 5) 7.1
2) 3.7 4) 7.8

FEEDBACK 6b: A very large amount of strong acid (1000 ml x 0.1 M = 100 mmoles H⁺) has been added to a buffer which is a mixture of 0.5 mmoles of acetic acid (0.05 M x 10 ml) and 1 mmole of acetate (0.1 M x 10 ml). The final solution will consist of 1010 ml containing 99 mmoles of H⁺ and 1.5 mmoles of acetic acid. What happened to the acetate? (Reacted with H⁺ to give HAc, see Cartoon III, page 23)

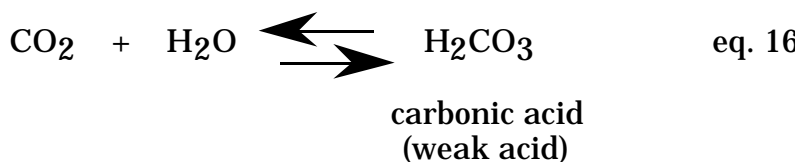


The pH is therefore dependent only on the H⁺ in solution and not the weak acid, so that [H⁺] is $\frac{0.099 \text{ moles}}{1010 \text{ ml}} = \frac{x \text{ moles}}{1000 \text{ ml}}$, which is about 10⁻¹M (0.098, but close enough) and the pH is 1. We no longer have a buffer solution, since a large excess of strong acid was added. See page 38, question 3c for another question of this type.

CYCLE FOR OVERALL OBJECTIVE

Buffers are used for controlling pH of reactions such as those catalyzed by enzymes and are important to us by maintaining pH levels consistent with life. The main buffers in mammalian systems are the bicarbonate⁻/carbonic acid, $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$, hemoglobin⁻/protonated hemoglobin and the proteinate⁻/protein systems. One of the most important buffers due to its high concentration and its control through respiration is the bicarbonate⁻/carbonic acid system. The body is able to maintain its pH environment through excretion (or retention) by the kidney of HCO_3^- , which controls the $[\text{H}^+]$ of plasma and restores the buffer systems that are required to prevent drastic changes in pH. The pH requirement for life involves the maintenance of conformation of proteins. Loss of or change of protein structure would influence the enzymatic activity of proteins involved in different phases of life support (for example metabolism, muscle contraction, blood clotting, respiration and membrane stability) as well as the structural elements of membranes.

PRACTICE: Using the following equation and the Henderson-Hasselbalch equation predict the effect of slower breathing on blood pH.



FEEDBACK: Slower breathing would tend to expel less CO_2 . Since CO_2 is always being formed from metabolism of many food components (glucose, triacylglycerols, amino acids), then by not expelling the CO_2 , more weak acid (H_2CO_3) is formed (driven to the right as written). The salt of carbonic acid (HCO_3^-) would be essentially unchanged in this time period (also remember weak acids are poorly dissociated), thus the ratio of $\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$ is involved and decreased.

Using the Henderson-Hasselbalch equation, a decrease in pH is found and may be quantitatively predicted if the parameters of $[\text{HCO}_3^-]$ and $[\text{H}_2\text{CO}_3]$ are known, since the pK_a of H_2CO_3 is a constant (6.1). This is only one example of buffer control of pH. Obviously reactions of weak acids are constantly taking place in the cells as well as loss of salts and protons through urinary excretion.

PRACTICE: Predict the effect of very rapid breathing on blood pH.

FEEDBACK: Rapid breathing would expel more CO_2 and thus the weak acid $[\text{H}_2\text{CO}_3]$ would decrease, so that the ratio of $\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$

would increase and the blood pH would thus increase. In contrast holding your breath or other failure to exchange CO_2 through the lungs would decrease the pH.

Many additional problems are given in Appendix F, questions 1-8.

APPENDIX

A. Logarithms - The logarithm of any number is the exponent of the power to which 10 must be raised to produce the number. The logarithm X of the number N to the base 10 is the exponent of the power to which 10 must be raised to give N (for example, $\log_{10} N = X$). Logarithms consist of two parts. First there is the "characteristic" which is determined by the position of the first significant figure of the number in relation to the decimal point. If we count leftwards from the decimal as positive and rightwards as negative the characteristic is equal to the count ending at the right of the first significant figure. Thus, the characteristic of the logarithm of 2340 is 3, of and of 0.00234 is -3. The second part of the logarithm is the "mantissa." It is always positive and is found in logarithm tables (or a part of the "magic button" on the calculator ($\log X$) and depends only on the sequence of significant figures. Thus, the mantissa for the two numbers is the same, namely 0.3692. The logarithm of a number is the sum of the characteristic and the mantissa. Thus: $\log 2340 = 3.3692$, while $\log 0.00234 = -3 + 0.3692 = -2.6308$.

The logarithms of the whole integers 1 to 10 are given below.

$\log 1.0 = 0.000$	$\log 6.0 = 0.778$
$\log 2.0 = 0.301$	$\log 7.0 = 0.845$
$\log 3.0 = 0.477$	$\log 8.0 = 0.903$
$\log 4.0 = 0.602$	$\log 9.0 = 0.954$
$\log 5.0 = 0.699$	$\log 10.0 = 1.000$

Useful rules in understanding logarithms.

- 1) The logarithm of a product is equal to the sum of the logarithms of the factors. Thus the $\log ab = \log a + \log b$. Check this out by solving for $\log 6$. This is $\log 2 \times 3$, which is $\log 2 + \log 3$).
- 2) The logarithm of a fraction is equal to the logarithm of the numerator minus the logarithm of the denominator. Thus the $\log \frac{a}{b} = \log a - \log b$ (example: $\log \frac{10}{2} = \log 10 - \log 2$, which is the same as $\log 5$ and is 0.699). (How about $\log 2.5$? Answer from a log table is 0.398).

3) The logarithm of the reciprocal of a number is the negative logarithm of the number. $\log \frac{1}{a} = \log 1 - \log a$. Since $\log 1 = 0$, then $\log \frac{1}{a} = -\log a$ (example: $\log \frac{1}{2} = -\log 2$ which is -0.301).

4) The logarithm of a number raised to a power is the logarithm of the number multiplied by the power. $\log a^b = b \log a$ (example: $\log 2^2 = 2 \log 2 = 0.603$). (This is the same as $\log 4$, since 4 is 2^2 .)

B. Exponents - It is convenient to express large numbers as 10^x , where x represents the number of places that the decimal must be moved to place it after the first significant figure. This also represents $10 \cdot 10$ for x times. For example 1,000,000 may be expressed as 1×10^6 ; 3663 as 3.663×10^3 and so on. To multiply numbers, the exponents are added, but coefficients are multiplied. To divide, the exponents are subtracted, but coefficients are divided.

Multiplying: $(1 \times 10^a) \cdot (1 \times 10^b) = 1 \times 10^{a+b}$
For example, $(4 \times 10^2) \cdot (2 \times 10^3) = 8 \times 10^5$

Numbers less than 1 are 10^{-x} . For example, 0.000001 is 1×10^{-6}

Multiplying numbers less than 1 are $(1 \times 10^{-a}) \cdot (1 \times 10^{-b}) = 1 \times 10^{-(a+b)}$. For example, $(4 \times 10^{-2}) \cdot (2 \times 10^{-3}) = 8 \times 10^{-5}$

Multiplying a large number and a small number. For example, $(4 \times 10^{-2}) \cdot (2 \times 10^3) = 8 \times 10^1$

Dividing: $(1 \times 10^a) \div (1 \times 10^b) = 1 \times 10^{a-b}$
For example, $(4 \times 10^2) \div (2 \times 10^3) = 2 \times 10^{-1}$

C. Miscellaneous Definitions : A mole of a compound is the weight which contains Avogadro's number of molecules (6.023×10^{23}). The weight in grams is one gram molecular weight (MW). For example, the MW in grams of HCl is 36.5 g. A solution containing 36.5 g of HCl/liter of solution would be 1 molar or 1M, which means 1 mole/liter. For this solution 1 ml would contain 0.001 moles or 1 mmole (1×10^{-3} moles).

An equivalent weight is that weight in grams which combines with or liberates one gram of protons. For example, 36.5 gms of HCl/liter of solution is a 1 normal or 1N solution (1000 meq). One ml would contain 0.001 equivalents or 1 meq (1×10^{-3} equivalents).

D. pH of Salts (informational)

For the salt of acetic acid (Na acetate) a combination of equations shown in eq. 1 must be used to determine the pH. Since NaAc is the salt of a strong base and a weak acid the pH will be greater than 7 upon hydrolysis.

$$\text{pH} = \text{pK} + \log \frac{[\text{Ac}^-]}{[\text{HAc}]} \quad \text{and} \quad \text{pH} = 14 - \text{pOH} \quad \text{eq.1}$$

$$\text{pH} = 4.7 + \log \frac{[\text{Ac}^-]}{[\text{HAc}]} + \text{pH} = 14 - \text{pOH} \quad \text{eq.2}$$

pH = 14 - pOH is also the same as:

$$\text{pH} = 14 + \log [\text{OH}^-] \quad \text{eq. 3}$$

The sum then of eq. 3 and $\text{pH} = 4.7 + \log \frac{[\text{Ac}^-]}{[\text{HAc}]}$ is

$$2\text{pH} = 18.7 + \log[\text{Ac}^-] - \log[\text{HAc}] + \log[\text{OH}^-] \quad \text{eq.4}$$

The concentration of [HAc] and [OH⁻] are equal and thus cancel out so that eq. 4 is $2\text{pH} = 18.7 + \log[\text{Ac}^-]$ or

$$\text{pH} = \frac{18.7 + \log[\text{Ac}^-]}{2} \quad \text{eq.5}$$

For a 0.1M solution of NaAc the pH may be determined from eq. 5 and is 8.85 for acidic salts (NH₄Cl for example) the pH is in the acid region upon hydrolysis. Salts formed from the reaction of a strong acid and a strong base are neutral

E. Problem Solving:

a) Given the hydrogen ion concentration calculate pH. Example: $[\text{H}^+] = 0.00003 = 3 \times 10^{-5}$ moles/liter. The characteristic is -5 and the mantissa of 3 from a logarithmic table (or the "magic button", log X on the calculator) table is 0.477. Using the definition of pH:

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{pH} = -\log [3 \times 10^{-5}]$$

$$= -\log 3 + -\log 10^{-5}$$

$$= -0.477 + (-)(-) 5$$

$$= -0.477 + 5$$

$$\text{pH} = 4.52$$

b) Given the pH, calculate the hydrogen ion concentration. Example:

$$\text{pH} = 6.35$$

$$6.35 = -\log [\text{H}^+]$$

$$-6.35 = \log [\text{H}^+]$$

$$-7 + .65 = \log [\text{H}^+]$$

$$10^{-7} \times 10^{.65} = [\text{H}^+]$$

Look up the mantissa 0.65 in the logarithm table (or the "magic button" (INVlog) and find the number 4.47.

$$[\text{H}^+] = 4.47 \times 10^{-7} \text{ moles/liter}$$

c) Derivation of the Henderson Hasselbalch equation (see cycle 5)

Writing the dissociation constant for a weak acid (HA):

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{rearranging: } [\text{H}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]}$$

Taking the logarithm of both sides of the equation:

$$\log [\text{H}^+] = \log K_a + \log [\text{HA}] - \log [\text{A}^-]$$

multiplying by -1:

$$-\log [\text{H}^+] = -\log K_a - \log [\text{HA}] + \log [\text{A}^-]$$

Since $-\log [\text{H}^+] = \text{pH}$ and $-\log K_a = \text{p}K_a$ then

$$\text{pH} = \text{p}K_a - \log [\text{HA}] + \log [\text{A}^-]$$

which is the same as:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

RECALL: $[\text{A}^-]$ is the conjugate base of the weak acid, $[\text{HA}]$. Also $[\text{A}^-]$ is the salt of the weak acid, $[\text{HA}]$.

F. Questions: (Supplemental)

1. What is the pH of the following where the hydrogen ion concentration is given in moles/liter: 0.01, 0.000005, 2×10^{-11} ?

Answers: 2, 5.3, 10.7 (See Appendix E, Problem Solving if you do not get these answers.)

2. Calculate the hydrogen ion concentration in moles/liter where the pH is given as: 1.00, 4.50, 13.30.

Answers: 1×10^{-1} , 3.16×10^{-5} , 5×10^{-14} (See Appendix E Problem Solving if you do not get these answers).

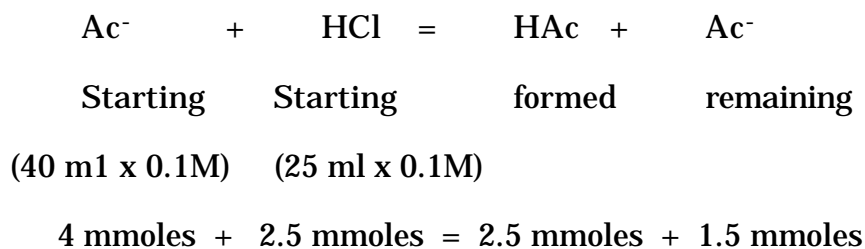
3. Calculate the pH of a solution:

(a) of 0.05M in sodium acetate and 0.04M in acetic acid, pK 4.7.

Answer: 4.8 (See Cycle 6, FEEDBACK 6a for this type)

(b) of 40 ml of 0.1 M sodium acetate and 25 ml of 0.1 M HCl.

Answer: 4.48 (See Cycle 5 , Cycle 6, Appendix E and footnote to Table I).
The simplest approach is to write the reactions

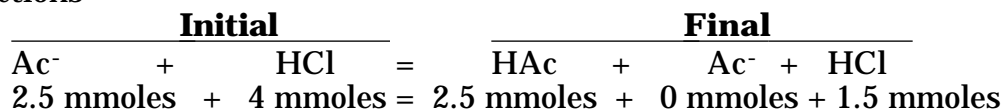


Then use the Henderson-Hasselbalch equation, and $\text{pH} = 4.7 + \log \frac{1.5}{2.5}$.

This is the same as $\log \frac{3}{5}$.

(c) of 25 ml of 0.1 M sodium acetate and 40 ml of 0.1 M HCl (Hint: how much HCl in moles/liter remains after reaction with the acetate?)

Answer: pH is 1.64 (See Cycle 6 FEEDBACK 6b and Table I). Write the reactions



The total volume is 65 ml which has 1.5 mmoles of H⁺ (HAc is neglected since this is mostly undissociated). Calculate H⁺ in moles/liter and use the equation pH = -log [H⁺].

4. The K_a of acetic acid is 2 x 10⁻⁵, HCN is 7 x 10⁻¹⁰, H₂PO₄⁻ is 2 x 10⁻⁷.

(a) Which is the stronger weak acid? (In other words which is more ionized?)

Answer: acetic acid strongest, HCN weakest (See Cycle 4.)

(b) What are the pK_a 's?

Answer: acetic acid 4.7, HCN 9.2, H₂PO₄⁻ 6.7 (All found by taking the -log K_a)

(c) Which has the lower pK_a , the weaker or stronger acid?

Answer: the stronger acid (See Cycle 4).

(d) What is the approximate pH of a 0.1 N solution of acetic acid?

Answer: 2.86 (See Cycle 4 and Table II footnote) Compare to the pH of a 0.1 M solution of HCl, which is 1.0 (See Cycle 3).

5. (a) What is the calculated [H⁺] for water at 24°C? (Show calculations).

Answer: 10⁻⁷ moles/liter (See Cycle 1 and 2.)

(b) Why is pH 7.0 for water neutral at 24°C?

Answer: at pH 7, $K_w = 10^{-14}$, so $[H^+][OH^-]$ must equal 10^{-14} and $[H^+] = 10^{-7}$ (See Cycle 2 FEEDBACK 2b).

6. What is the % decrease in $[H^+]$ of blood serum during a pH change of 7.4 to 7.7?

Answer: 50% (Cycle 2 and Appendix E,b)

- $\log [H^+] = 7.4$, so $[H^+] = 4 \times 10^{-8}$ moles/liter

- $\log [H^+] = 7.7$, so $[H^+] = 2 \times 10^{-8}$ moles/liter

7. (a) List the best weak acid from 7b for preparing a buffer at pH 4.7, 6.8, and 12.4.

Answer: acetic acid, $H_2PO_4^-$, HPO_4^{2-} . Each is the weak acid with its pK closest to the pH desired. (See Cycle 5).

(b) Show the chemical forms involved and the ratio of salt to weak acid. Given the acetic acid pK 4.7, phosphate pK₂ 6.8, phosphate pK₃ 12.4.

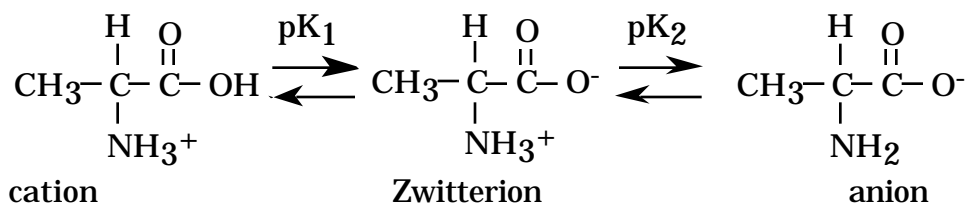
Answer: each 1/1, Ac^-/HAc , $HPO_4^{2-}/H_2PO_4^-$ and PO_4^{3-}/HPO_4^{2-}

(c) At what ratio of salt to weak acid is the buffer most effective in maintaining pH?

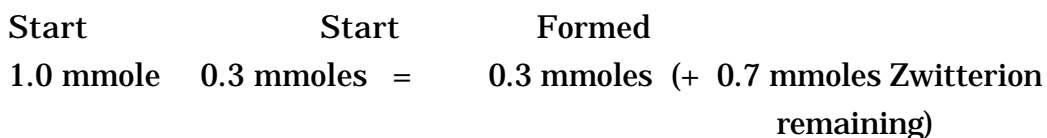
Answer: One (See Cycle 5 and 6)

8. (a) Calculate the pH of a mixture of 10 ml of 0.1 M alanine in its Zwitterion form (pK_1 2.5 and pK_2 9.5) and 3.0 ml of 0.1 M HCl. (Hint: amino acids are ampholytes that may act as weak acids or bases).

Write the chemical reaction involved starting with the zwitterion.



Treat like any buffer problem



So the weak acid is the cation and the salt is the Zwitterion. Use H-H equation!

Answer: 2.87

(b) Calculate the pH of a mixture of 10 ml of 0.1 M alanine in its Zwitterion form and 3.0 ml of 0.1 M NaOH.

Answer: 9.13, same type of treatment as above but now the Zwitterion is the weak acid and the anion is the salt.

POST-TEST

(Show all the steps in your calculations.)

1. What is a buffer?
2. What does a buffer do?
3. How does a buffer function in a chemical sense?
4. How do buffers relate to life?
5. a) What is the effect of a pH change of 1.0 units on H^+ in solution?
b) What is the effect of a pH change of 0.30 units on H^+ in solution?
6. What is the % decrease in $[H^+]$ of blood serum during a pH change of 7.4 to 7.7?
7. How does question 5 relate to question 4?
8. In plasma the bicarbonate concentration is about 0.025 M and the carbonic acid concentration is 0.00125. Using pK_1 carbonic acid of 6.1, what is the pH?
9. Given a lethal organism that attacks humans and is sensitive to change in pH (only viable between pH 7.35 and 7.45). Why would a crying baby, an uncontrolled diabetic and aspirin "addict" all survive infection? (see for example *Andromeda Strain* by M. Crichton).

Post Test Answers

1. A buffer is a mixture of a weak acid (or weak base) and its salt. Its action may be explained in a quantitative manner using the Henderson-Hasselbalch equation, where the $\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$.
2. A buffer resists change in pH depending on the ratio of salt to weak acid, the concentration of salt and weak acid and the pK_a of the weak acid.
3. The addition of a strong acid to a buffer causes an increase in the weak acid portion and an equivalent decrease in the salt of the weak acid. The addition of OH^- causes an increase in the salt and a decrease in the weak acid. Neither case produces a large increase in $[\text{H}^+]$ or $[\text{OH}^-]$ in the effective buffer range.
4. The body maintains a tight control of pH around 7.4, by respiratory exchange of CO_2 , kidney function and various buffers including proteins. Failure to maintain pH leads to serious complications or death.
5. a) A factor of 10 change in $[\text{H}^+]$ for each pH of 1.0 (example: changing from pH 2.0 to 3.0, $[\text{H}^+]$ is 10^{-2} to 10^{-3} M).
b) A change of 0.30 in pH is a change in $[\text{H}^+]$ by a factor of 2 ($\log 2 = 0.30$).
6. 50% ($[\text{H}^+]$ at 7.4 is 4×10^{-8} and at pH 7.7 is 2×10^{-8}).
7. The apparent tight regulation in pH reflects the fact that this is a log change, so even a change of 0.3 pH units represent a two fold change in $[\text{H}^+]$ which will disrupt proteins, enzymes, etc.
8. $\text{pH} = 6.1 + \log \frac{0.025}{0.00125}$
 $= 6.1 + \log 20$, therefore the $\text{pH} = 7.4$.
9. Crying baby - (Increased pH since loss of CO_2 by increased breathing)
Diabetic - acidotic (if uncontrolled due to increased metabolism of fat instead of glucose)
Aspirin Addict - acidotic (aspirin is acetyl salicylic acid, a weak acid).
All potentially, outside range of normal for this viable lethal organism.