

The Properties of Buffers

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&

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LAST WEEK E1 EXPERIENCE

This week lab care

- SAFETY ISSUES
- pH METER CARE & MEASUREMENTS
- MAKE UP SOLUTIONS
- LABEL SAMPLES
- MEASURING VOLUMES
- WASHING & RINSING
- HOW MANY SAMPLES, EACH STUDENT, EACH GROUP

OBJECTIVES

- Develop an understanding of the pH scale.
- Examine the differences between strong and weak acids.
- Investigate how buffers work.
- Prepare a buffer solution with a target concentration and pH.
- Determine the buffer capacity of a solution.

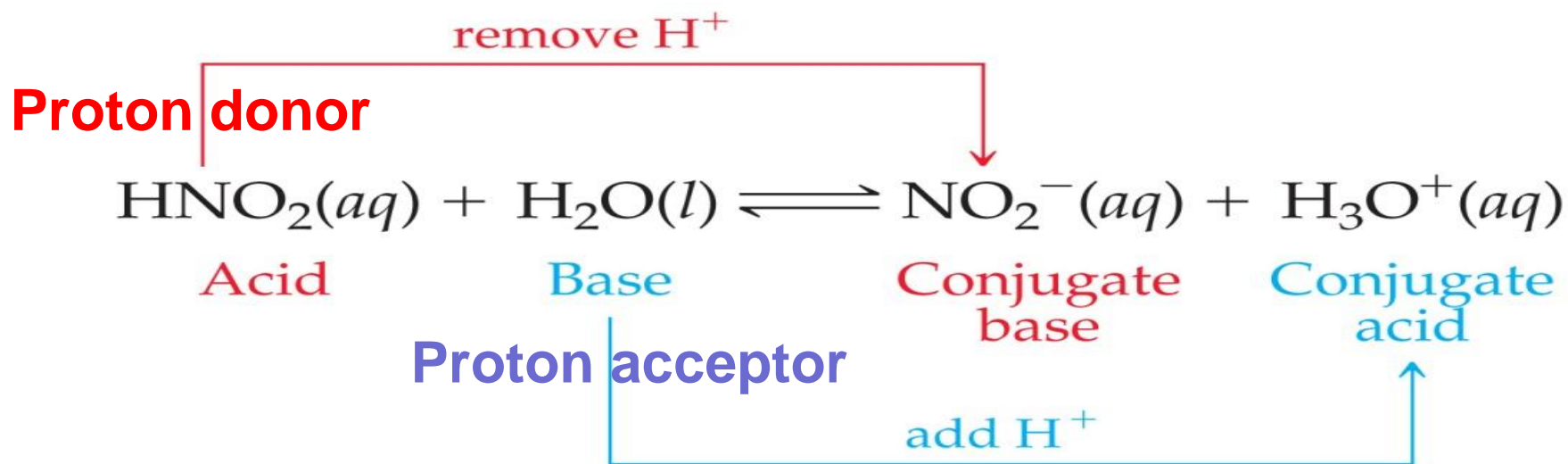
What are buffers



- **Buffers** are solutions of a **weak conjugate acid–base** pair
- HAc/NaAc
- HF/NaF
- Etc.
- They are particularly **resistant to pH changes**, even when strong acid or base is added.

Buffers are solutions of a weak conjugate acid–base pair

- Buffer means lessen the impact of external force. Remember Le Châtelier's
- They resist pH changes when H^+ or OH^- added. Example: Weak Nitrous Acid HNO_2



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- **Water acts** as a **Brønsted–Lowry base** and abstracts a proton (H^+) from the acid (the acid acts as a Bronsted-Lowry acid).
- Important applications: Controlling pH of human blood (Carbonic acid buffer $\text{H}_2\text{CO}_3/\text{HCO}_3^-$)

BACKGROUND

- Calculating the pH of weak acid
- Preparing a buffer
- The properties of buffers
- Capacity of Buffers

Calculating the pH of weak acid



	[HCOOH], M	[H ₃ O ⁺], M	[HCOO ⁻], M
Initially	c	0	0
Change	-x	x	x
At equilibrium	c-x	x	x

c = initial conc. of weak acid HA & x is concentration H₃O⁺ or A⁻ formed from partial dissociation of weak acid (c-x ≈ c)

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$x = [\text{H}^+] = \sqrt{K_a^\theta c}$$

$$K_a = \frac{x^2}{c-x} \approx x^2/c$$

$$\text{pH} = -\log[\text{H}^+] = \frac{1}{2} \text{p}K_a^\theta - \frac{1}{2} \log c$$

The properties of buffers (1)---

Depicting Buffer Action

Water

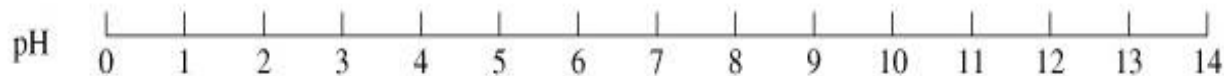
1.00 L water + 0.010 mol OH^-



1.00 L water



1.00 L water + 0.010 mol H_3O^+



Buffer solution

1.00 L buffer + 0.010 mol OH^-



1.00 L buffer



1.00 L buffer + 0.010 mol H_3O^+



The properties of buffers (2)---

Common Ion Effect Illustrated
(**La Chatelier's Principle**)



- Composition of a buffer solution**

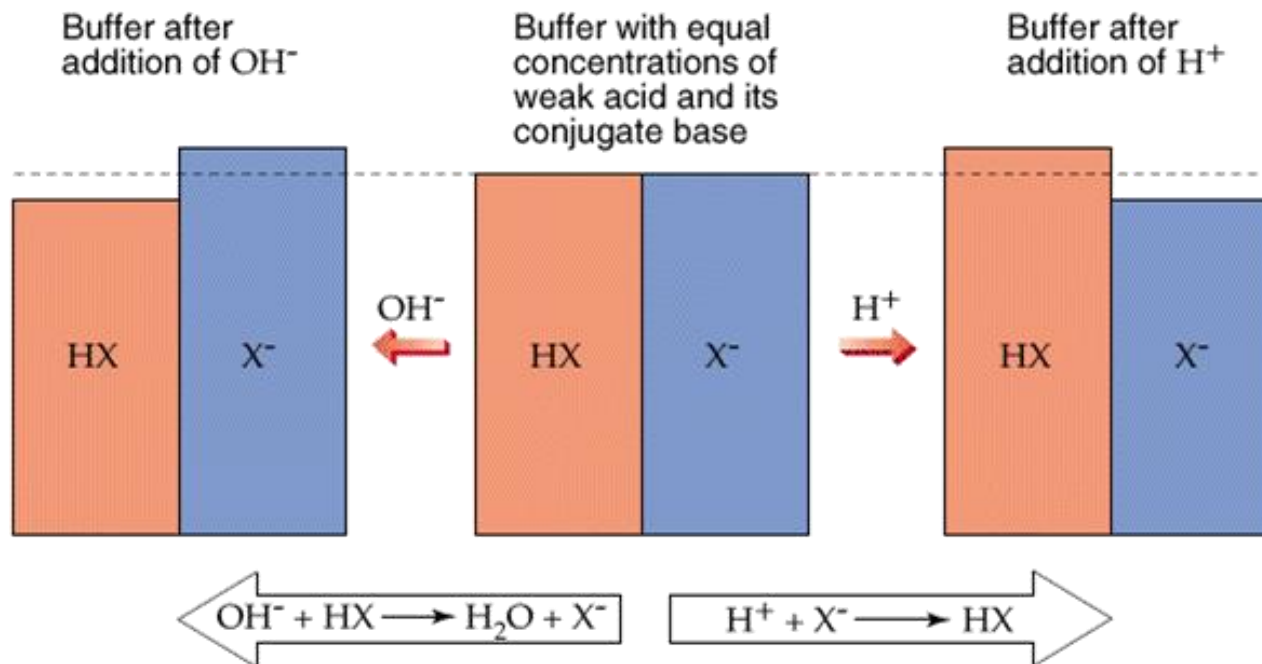
a weak acid /conjugate base or

a weak base /conjugate acid

$\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$; $\text{NH}_3 \cdot \text{H}_2\text{O}/\text{NH}_4\text{Cl}$

The essential components of a buffer consists of high concentrations of weak acid & its conjugate base so they neutralize added small amounts of H^+ or OH^- and the buffer components stay the same (pH remains constant)

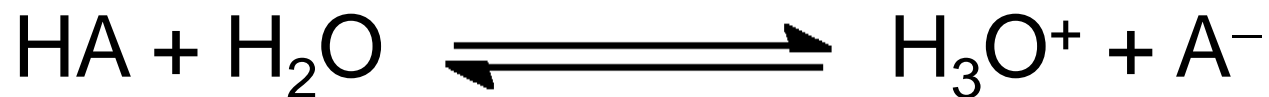
Preparation of a buffer (3)



$$[\text{H}^+] = K_a \cdot \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

Buffer Calculations

Consider the equilibrium constant expression for the dissociation of a generic acid, HA:



**AT EQUILIBRIUM
(AFTER REACTION):**

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Buffer Calculations

Rearranging slightly, this becomes

**AT EQUILIBRIUM
(AFTER REACTION):**

$$K_a = [\text{H}_3\text{O}^+] \frac{[\text{A}^-]}{[\text{HA}]}$$

Taking the negative log of both side, we get

$$-\log K_a = -\log [\text{H}_3\text{O}^+] + -\log \frac{[\text{A}^-]}{[\text{HA}]}$$

The diagram illustrates the derivation of the Henderson-Hasselbalch equation. It shows the equation $-\log K_a = -\log [\text{H}_3\text{O}^+] + -\log \frac{[\text{A}^-]}{[\text{HA}]}$ with blue arrows pointing from labels to specific terms. An arrow from pK_a points to $-\log K_a$. An arrow from pH points to $-\log [\text{H}_3\text{O}^+]$. An arrow from acid points to $[\text{HA}]$ in the denominator of the fraction. An arrow from base points to $[\text{A}^-]$ in the numerator of the fraction.

Buffer Calculations

- So at equilibrium:

$$\text{p}K_a = \text{pH} - \log \frac{[\text{base}]}{[\text{acid}]}$$

- Rearranging, this becomes

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]_{\text{eq}}}{[\text{acid}]_{\text{eq}}}$$

- This is the **Henderson–Hasselbalch equation.**

Buffer Calculations: very important

NEXT EXAMPLE SHOWS THAT:

Henderson–Hasselbalch equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]_{\text{eq}}}{[\text{acid}]_{\text{eq}}}$$

$[\text{acid}]_{\text{eq}}$ = weak acid

$[\text{base}]_{\text{eq}}$ = strong electrolyte of the acid

IS ABOUT THE SAME AS:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]_{\text{initial}}}{[\text{acid}]_{\text{initial}}}$$

Because K_a is small and a common ion is present, we expect x to be small relative to either weak acid initial molarity or its initially added electrolyte molarity. Thus, our equation can be simplified to give

Henderson–Hasselbalch Equation

EMPHASIZE

What is the pH of a buffer that is 0.12 *M* in lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, and 0.10 *M* in sodium lactate? K_a for lactic acid is 1.4×10^{-4} .

a. Use Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

b. Compare with previous calculations

Henderson–Hasselbalch Equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\text{pH} = -\log (1.4 \times 10^{-4}) + \log \frac{(0.10)}{(0.12)}$$

$$\text{pH} = 3.85 + (-0.08)$$

$$\text{pH} = 3.77$$

**NEXT: VERIFY USING
PREVIOUS ANALYSIS FROM
START OF CHAPTER**

Sample Exercise 17.3 Calculating the pH of a Buffer

EMPHASIZE

What is the pH of a buffer that is 0.12 *M* in lactic acid [$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, or $\text{HC}_3\text{H}_5\text{O}_3$] and 0.10 *M* in sodium lactate [$\text{CH}_3\text{CH}(\text{OH})\text{COONa}$, or $\text{NaC}_3\text{H}_5\text{O}_3$]? For lactic acid, $K_a = 1.4 \times 10^{-4}$.

Solution

Analyze We are asked to calculate the pH of a buffer containing lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) and its conjugate base, the lactate ion ($\text{C}_3\text{H}_5\text{O}_3^-$).

Plan We will first determine the pH using the method described in Section 17.1. Because $\text{HC}_3\text{H}_5\text{O}_3$ is a weak electrolyte and $\text{NaC}_3\text{H}_5\text{O}_3$ is a strong electrolyte, the major species in solution are $\text{HC}_3\text{H}_5\text{O}_3$, Na^+ , and $\text{C}_3\text{H}_5\text{O}_3^-$. The Na^+ ion is a spectator ion. The $\text{HC}_3\text{H}_5\text{O}_3$ – $\text{C}_3\text{H}_5\text{O}_3^-$ conjugate acid–base pair determines $[\text{H}^+]$ and, thus, pH; $[\text{H}^+]$ can be determined using the acid-dissociation equilibrium of lactic acid.

Solve The initial and equilibrium concentrations of the species involved in this equilibrium are

$$\text{HC}_3\text{H}_5\text{O}_3(aq) \rightleftharpoons \text{H}^+(aq) + \text{C}_3\text{H}_5\text{O}_3^-(aq)$$

Initial	0.12 <i>M</i>	0	0.10 <i>M</i>
Change	− <i>x M</i>	+ <i>x M</i>	+ <i>x M</i>
Equilibrium	(0.12 − <i>x</i>) <i>M</i>	<i>x M</i>	(0.10 + <i>x</i>) <i>M</i>

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The equilibrium concentrations are governed by the equilibrium expression:

$$K_a = 1.4 \times 10^{-4} = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{x(0.10 + x)}{(0.12 - x)}$$

Because K_a is small and a common ion is present, we expect x to be small relative to either 0.12 or 0.10 *M*. Thus, our equation can be simplified to give

$$K_a = 1.4 \times 10^{-4} = \frac{x(0.10)}{0.12}$$

Sample Exercise 17.3 Calculating the pH of a Buffer

Continued

a. TRADITIONAL METHOD

Solving for x gives a value that justifies our approximation:

$$[\text{H}^+] = x = \left(\frac{0.12}{0.10} \right) (1.4 \times 10^{-4}) = 1.7 \times 10^{-4} M$$
$$\text{pH} = -\log(1.7 \times 10^{-4}) = 3.77$$

Alternatively, we can use the Henderson-Hasselbalch equation to calculate pH directly:

b. Henderson–Hasselbalch Eq.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 3.85 + \log \left(\frac{0.10}{0.12} \right)$$
$$= 3.85 + (-0.08) = 3.77$$

Practice Exercise

Calculate the pH of a buffer composed of 0.12 M benzoic acid and 0.20 M sodium benzoate. (Refer to Appendix D.)

Answer: 4.42

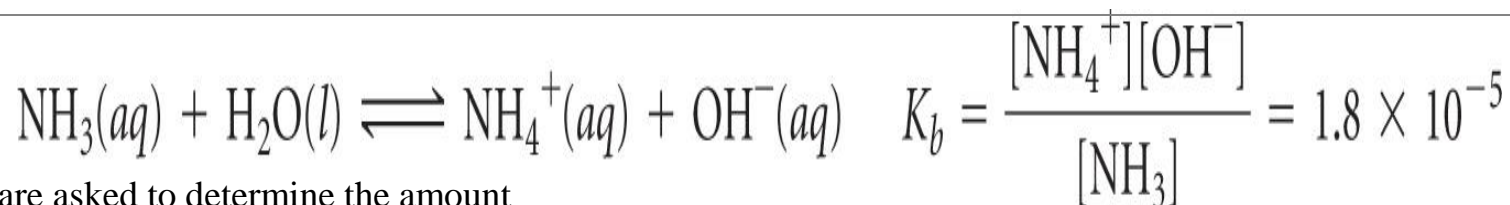
a. or b. SAME RESULTS

Sample Exercise 17.4 Preparing a Buffer

EMPHASIZE

How many moles of NH_4Cl must be added to 2.0 L of 0.10 M NH_3 to form a buffer whose pH is 9.00?
(Assume that the addition of NH_4Cl does not change the volume of the solution.)

Solution



Analyze We are asked to determine the amount of NH_4^+ ion required to prepare a buffer of a specific pH.

Plan The major species in the solution will be NH_4^+ , Cl^- , and NH_3 . Of these, the Cl^- ion is a spectator (it is the conjugate base of a strong acid). Thus, the NH_4^+ – NH_3 conjugate acid–base pair will determine the pH of the buffer. The equilibrium relationship between NH_4^+ and NH_3 is given by the base-dissociation reaction for NH_3 :

The key to this exercise is to use this K_b expression to calculate $[\text{NH}_4^+]$.

Solve We obtain $[\text{OH}^-]$ from the given pH:

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.00 = 5.00$$

and so

$$[\text{OH}^-] = 1.0 \times 10^{-5} M$$

Because K_b is small and the common ion $[\text{NH}_4^+]$ is present, the equilibrium concentration of NH_3 essentially equals its initial concentration:

$$[\text{NH}_3] = 0.10 M$$

Preparation of a buffer (1)---

Henderson-Hasselbalch Equation

$$K_a^\theta = \frac{[H^+][A^-]}{[HA]} = \frac{cx \cdot cx}{c(1-x)} \approx cx^2$$

$$[H^+] = K_a \cdot \frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = pK_a + \log \frac{[ConjugateBase]}{[WeakAcid]}$$

If [weak acid] = [conjugate base], $pH = pK_a$

Preparation of a buffer (2)---

Henderson-Hasselbalch Equation

Requirements:

- ❖ The ratio of [conjugate base] to [weak acid] is between 0.10 and 10

$$pH = pK_a \pm 1$$

Preparation of a buffer (4)---

Related Calculation: Example

1. How to prepare 100mL buffer solution with a pH=4.0 and total concentration of 0.10M, starting with: x mL of [HA]= 5.0M. & y mL of [Ac⁻] = 2.0M?
a. Find X & Y, b. Find ? g AcNa added

a. Analysis: $K_a=1.8 \times 10^{-5}$, $pK_a(\text{HAc})=4.75$,
therefore, HAc+NaAc can be chosen.

$$pH = pK_a + \log \frac{[Ac^-]}{[HAc]}$$

$$4.0 = 4.75 + \log \frac{[Ac^-]}{[HAc]}$$

NOTE: Eq. 1 next, has 2 unknowns

$$10^{(4.00-4.75)} = [Ac^-]/[HAc] = C_b/C_a$$

..... **Eq. 1**

Log (C_b/ C_a)= - 0.75 , then C_b/C_a = 10^{-0.75}

or: C_b/C_a = 0.178 Eq.1

Preparation of a buffer (5)--- Related Calculation: Weak Acid conc. $[HAc] = C_a$, Conjugate Base Conc. $[Ac^-] = C_b$

but: $C_a + C_b = 0.10M$ **Eq.2** $C_a = [HAc] = 0.085M$

$C_a + (0.178 C_a) = 0.10$, then: $C_b = [Ac^-] = 0.015M$

$$X (5.0M) = 100 \text{ mL } (0.085M), X = 1.7 \text{ mL} = V_a$$

$$Y (2.0M) = 100 \text{ mL } (0.015M), Y = 0.75 \text{ mL} = V_b$$

b. $m_{AcNa} = ? \text{ g}$

$$? \text{ moles NaAc} = V_b \times 2.0M = 0.75 \text{ mL} \times 2.0 \text{ moles/1000mL}$$

$$m_{AcNa} = (0.75 \times 2.0) \text{ moles} \times 83 \text{ (g/mole)} = 0.12 \text{ g AcNa}$$

SEE DETAILED CALCULATIONS IN PROCEDURE

Each student must prepare one buffer. “Show TA your buffer design table to get his approval to start the experiment”

- **Design four Buffer Solutions:** V_a & V_b to be calculated (see next slide) assuming desired buffer pH. Prepare 1 buffer per student, 4 buffers (not 5) per group.
- Make 0.100L of a 0.100M ($0.100M = C_a + C_b$) buffer solution in a 100-mL volumetric flask using V_a mL 5.00M CH_3COOH and V_b mL 2.00M CH_3COONa solutions, diluted with deionized H_2O). * **See example slide, answers on last slide**

Buffer	Target pH	C_b/C_a	V_a (mL) 5.00M HA_c	V_b (mL) 2.00M A_c^-
Example*	4.00	0.178*	1.70*	0.75*
1	4.15			
2	4.57			
3	4.75			
4	5.35			

SUMMARY OF E2 PROCEDURES:

(best to follow datasheet after pH meter calibration)

1. **PART A:** Measure pH of: 0.50M HCl, 0.50M HAc (diluted from 5.0M HAc), and unknown molarity of HAc sample. Then test their strength in dissolving Mg strip. (3 pH measurements & 2 Mg strips tested /group). **GROUP EFFORTS**
2. **PART B:** Design 4 buffers with different pH using same stock solutions of HAc & AcNa but each buffer is diluted to 100 mL (use different volumes of each stock that will be calculated to give designed pH). (1buffer/student, 4buffers/group)
3. **PART C:** Test the initial pH of each buffer to compare with target pH. Then add 5 drops of 0.50M HCl to one 20mL buffer sample then add 5 drops of 0.50M NaOH to another 20mL sample of same buffer. Add 5ml de-ionized water to the 3rd beaker of of 20mL sample of same buffer. Measure pH to conclude that pH remains about constant. Measure pH for the remaining 2 water beakers of 20mL distilled water before and after using 5drops of 0.5M HCl for one beaker & 5drops 0.50M NaOH for the other beaker. If only 100-mL beakers available then use 30mL samples. **Note: Datasheet pH columns not in order as procedure.**
4. (3beakers/buffer/student, 12beakers/group, plus 2beakers of distilled water/group). **PART D:** Test the total capacity of a buffer using the previous sample from Part C when 5drops of 0.50M HCl were added (not NaOH) by also adding more drops until pH starts dropping rapidly. Make sure you account for the initial drops of 0.50M HCl added at start of Part C, to find volume added to capacity. (1 buffer sample/student, 4buffer samples/group).
5. **Data Errors:** not following procedure, temperature effect on K_{eq} , contamination, pH meter errors & mishandling (electrode saturated), stock solutions, readings & dilutions, etc.

TABULATED DATASHEET

(pH meter calibration with buffer pH=4.003 or as provided)

1. pH meter calibration (**see instructions later**): Use standard buffer of pH = 4.003 or as available. In all pH measurements measure 30 mL desired solution and pour into 50-mL a beaker so height of liquid is enough to cover sensor of pH meter electrode. If 100-mL beaker is used then carefully tilt beaker to cover electrode.
2. Prepare dilution of 5.0 M to 0.50M in a 100-mL volumetric flask, measure pH1, pH2, & pH3 of each of: 0.50M HCl, 0.50M Hac, ?M HA_c of unknown concentration. Mg observation: two Mg strips add 5-10 drops 0.50M HCl to one strip and then 0.50 M HA_c to the other.
3. Prepare Buffers Target pH: Target pH, Calculated C_b/C_a, Calculated V_a (to measure & add to 100mL volumetric flask), Calculated V_b (to measure & add to the same 100mL volumetric flask), pH4&pH5 of distilled water in 2 separate beakers, pH6&pH7: Add 5drops of 0.50M HCl one beaker, and 5 drops of 0.50M NaOH to the other beaker.
4. pH8, pH9: measure pH of 30 mL buffer in a 50-mL beaker, then add 5 mL distilled water and measure pH again. pH10& pH11: Using same stock buffer pour measured 30mL each into two separate beakers and measure the pH after adding 5 drops of 0.5M NaOH to one beaker and another 5 drops of 0.5M HCl to another beaker. pH12: add another 5 drops of the 0.5M HCl into the last beaker that of pH11 then measure the pH12 (keep track of the initial volume of 0.50M HCl before adding more drops to test buffer capacity (Part C), final volume after adding more drops of 0.50M HCl to capacity point, change in volume at capacity point, end pH reading at capacity point. Make enough measurements to conclude when buffer capacity is reached within a reasonable time before end of lab session). Instructor/TA will give you directions if you should use HCl or NaOH to reach buffer capacity. **Note: Datasheet pH columns are not in the same order as Procedure Part C.**
5. Discuss results & complete the post lab report for the experiment. All information in the ALR report must be completed as instructed in manual.
6. Inconsistent Data Errors: not following procedure, temperature effect on K_{eq}, contamination, pH meter errors & mishandling (electrode saturated), stock solutions, inaccurate readings & dilutions, etc.

DATASHEET SUMMARY OF E2

[illegible]

LAB ROOM:

Start with (x) mL 5.0 M HAc & (y) mL 2.0 M AcNa. TA will compare "pH Design"

to measured "pH8" of each buffer made by a student

D

-----INDIVIDUAL EFFORTS -----

TER pH: H_2O , NaOH , & $\text{HCl} \rightarrow$

0	N ₂ OH	HCl	HCl	101	7
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H0	-H10	-H11	-H12	V(HCP)
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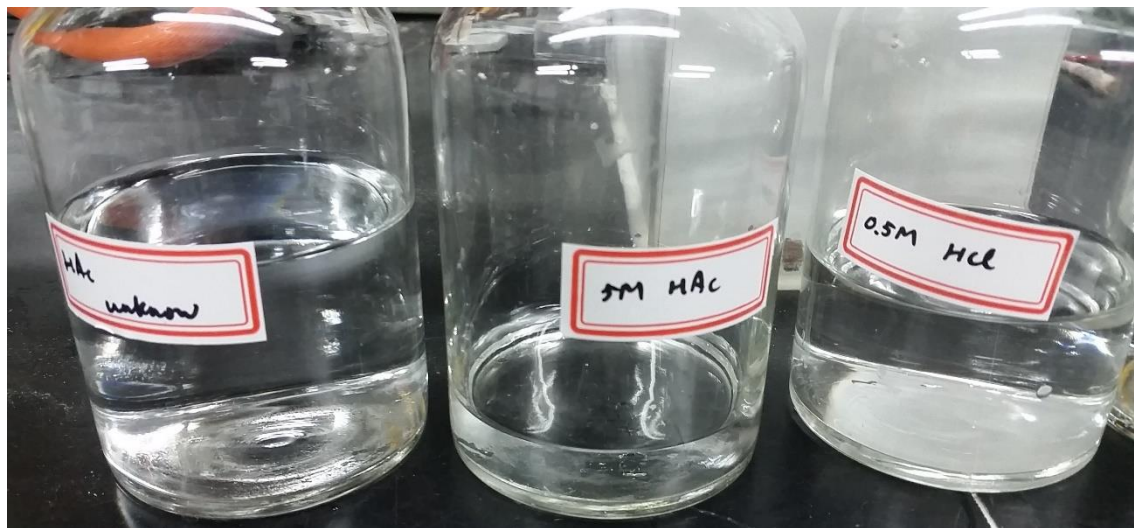
$$V_{A1} = V_{A2} \times C_{A2}/C_{A1} \text{ or } V_{A1} = 100\text{mL} \times 0.085/5.0 = 1.7\text{mL, \& } V_{B1} = V_{B2} \times C_{B2}/C_{B1} = 100\text{mL} \times 0.015/2.0 = 0.75\text{mL}$$

(pH meter calibration with buffer pH=4.003 or as provided)

1. pH meter calibration (see instructions later): Use standard buffer of pH = 4.003 or as available. In all pH measurements measure 30 mL desired solution and pour into 50-mL beaker so height of liquid is enough to cover sensor of pH meter electrode. If 100-mL beaker is used then carefully tilt beaker to cover electrode.
2. Prepare dilution of 5.0 M to 0.50M in a 100-mL volumetric flask, measure pH1, pH2, & pH3 of each of: 0.50M HCl, 0.50M HAc, 7M HAc, of unknown concentration. Mg observation: two Mg strips add 5-10 drops 0.50M HCl to one strip and then 0.50 M HAc to the other.
3. Prepare Buffers Target pH: Target pH, Calculated C_b/C_a , Calculated V_a (to measure & add to 100mL volumetric flask), Calculated V_b (to measure & add to the same 100mL volumetric flask), pH4&pH5 of distilled water in 2 separate beakers, pH6&pH7: Add 5drops of 0.50M HCl one beaker, and 5 drops of 0.50M NaOH to the other beaker.
4. pH8, pH9: measure pH of 30 mL buffer in a 50-mL beaker, then add 5 mL distilled water and measure pH again. pH10& pH11: Using same stock buffer pour measured 30mL each into two separate beakers and measure the pH after adding 5 drops of 0.5M NaOH to one beaker and another 5 drops of 0.5M HCl to another beaker. pH12: add another 5 drops of the 0.5M HCl into the last beaker that of pH11 then measure the pH12 (keep track of the initial volume of 0.50M HCl before adding more drops to test buffer capacity (Part C), final volume after adding more drops of 0.50M HCl to capacity point, change in volume at capacity point, and pH reading at capacity point. Make enough measurements to conclude when buffer capacity is reached within a reasonable time before end of lab session). Instructor/TA will give you directions if you should use HCl or NaOH to reach buffer capacity. Note: Datasheet pH columns are not in the same order as Procedure Part C.
5. Discuss results & complete the post lab report for the experiment. All information in the ALR report must be completed as instructed in manual.
6. Inconsistent Data Errors: not following procedure, temperature effect on K_a , contamination, pH meter errors & mishandling (electrode saturated), stock solutions, inaccurate readings & dilutions, etc.

PROCEDURE-- Part A.1

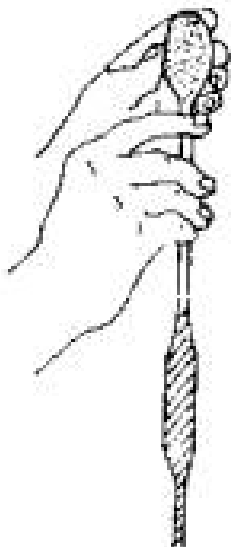
- ***Strong and Weak Acids***
- 1. Prepare 0.50M CH_3COOH solution in a 50-mL volumetric flask solution by using 5-mL graduated pipette and adding 5.00mL of 5.0M CH_3COOH into the volumetric flask



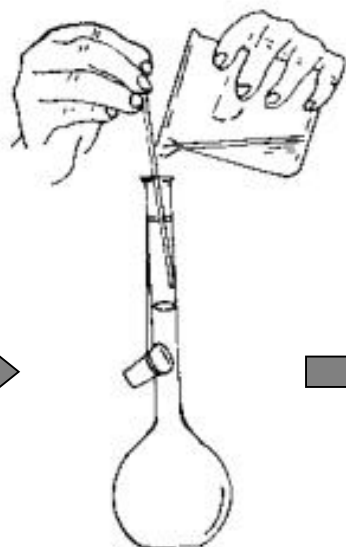
Procedure

Part A.1

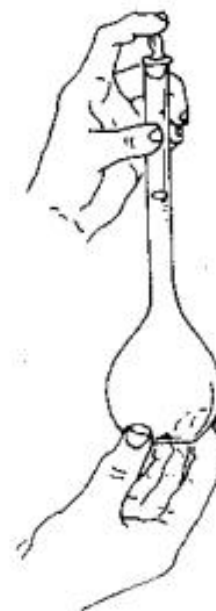
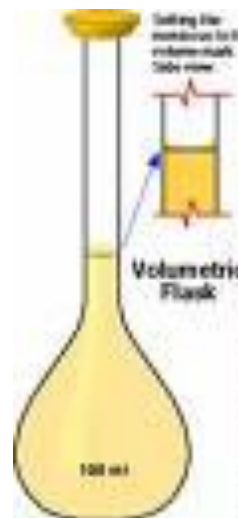
Attention!
Add drop-wise
with a pipet!



Pipet
5.00mL
5.0M HAc



Dilute the solution to
50.00mL



Invert
>20 times

PROCEDURE-- Part A.2

- ***Strong and Weak Acids***

2. Use the pH meter to record the pH of the 0.50 M HCl solution, the 0.50 M HAc solution and one of the unknown HAc solutions. **This part: Students work in group, measure 3 pH readings total.**

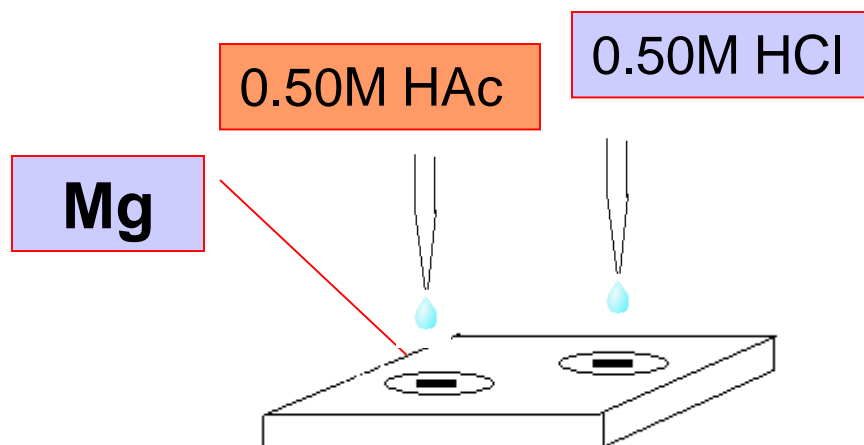


PROCEDURE-- Part A.3

- ***Strong and Weak Acids***

2Mg strips tested /group

3. Sand two short Mg strips with a piece of abrasive paper and put each in the bottom of the 2 empty wells of a porcelain spot plate, add 5-10 drops 0.50M HCl solution to one well & equal amount of HAc solution to the other well just to cover the Mg, record your observations.



PROCEDURE--- Part B.1 (ANSWERS LAST SLIDE)

- **Designing a Buffer** : V_a & V_b to be calculated (see next slide) assuming desired buffer pH. Prepare 1 buffer per student, 4 buffers (not 5) per group.
1. Make 0.100L of a 0.100M ($0.100M = C_a + C_b$) buffer solution in a 100-mL volumetric flask using V_a mL 5.00M CH_3COOH and V_b mL 2.00M CH_3COONa solutions, diluted with deionized H_2O .

Buffer	Target pH	V_a (mL) 5.00M HA_c	V_b (mL) 2.00M A_c^-
Example	4.00	1.70 see example	0.75 see example
1	4.15	?	?
2	4.57	?	?
3	4.75	?	?
4	5.35	?	?

SAMPLE CALCULATION

a. Prepared Buffer must be: Total volume = 0.100L, 0.100M

$$\text{pH} = \text{pK}_a + \log ([\text{A}_c^-]/[\text{HA}_c])$$

b. Start with: V_a mL of $[\text{A}_c^-] = 2\text{M}$ & V_b mL of $[\text{HA}_c] = 5\text{M}$,

To find V_a & V_b : Set $V_a = \text{volume } 5.00\text{M HA}_c$, $V_b = \text{volume } 2.00\text{M A}_c^-$

c. Then prepared Buffer: 5.00 V_a (mmole HA_c) & 2.00 V_b (mmole A_c^-)

$$10^{\text{pH}-\text{pK}_a} = [\text{A}_c^-]/[\text{HA}_c] = C_b/C_a$$

Example Buffer 1: Desired pH = 4.15:

$$\bullet C_b/C_a = 10^{\text{pH}-\text{pK}_a} = 10^{4.00-4.75} = 0.178 = C_b/C_a$$

$$\bullet \text{or } C_b = 0.178C_a, \text{ substitute value of } C_a \text{ into: } C_a + C_b = 0.100$$

• Then $C_a = 0.085\text{M}$ & $C_b = 0.015\text{M}$, But:

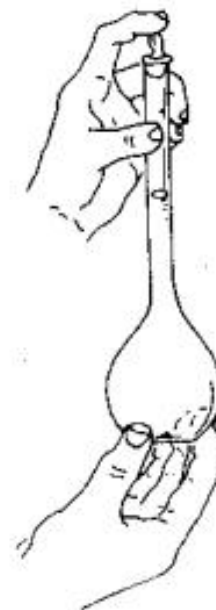
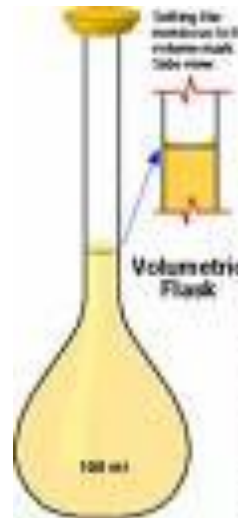
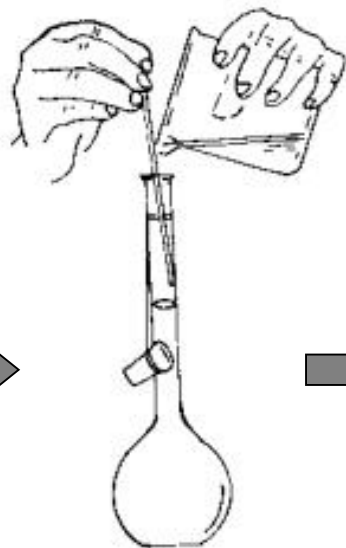
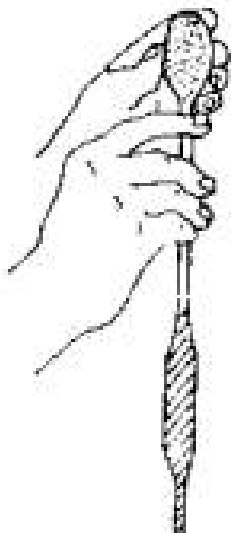
$$\bullet 5.00 \text{ M} \times V_a (\text{mL}) = 100 \text{ mL} \times 0.085\text{M}, \quad V_a = 1.7 \text{ mL}$$

$$\bullet \text{Similarly: } 2.00 \text{ M} \times V_b = 100 \text{ mL} \times 0.015\text{M}, \quad V_b = 0.75 \text{ mL}$$

**•USE VOLUMES CALCULATED TO MAKE THE BUFFER
THEN MEASURE pH TO COMPARE WITH TARGET pH**

Procedure Part B

Attention!
Add drop-wise
with a pipet!



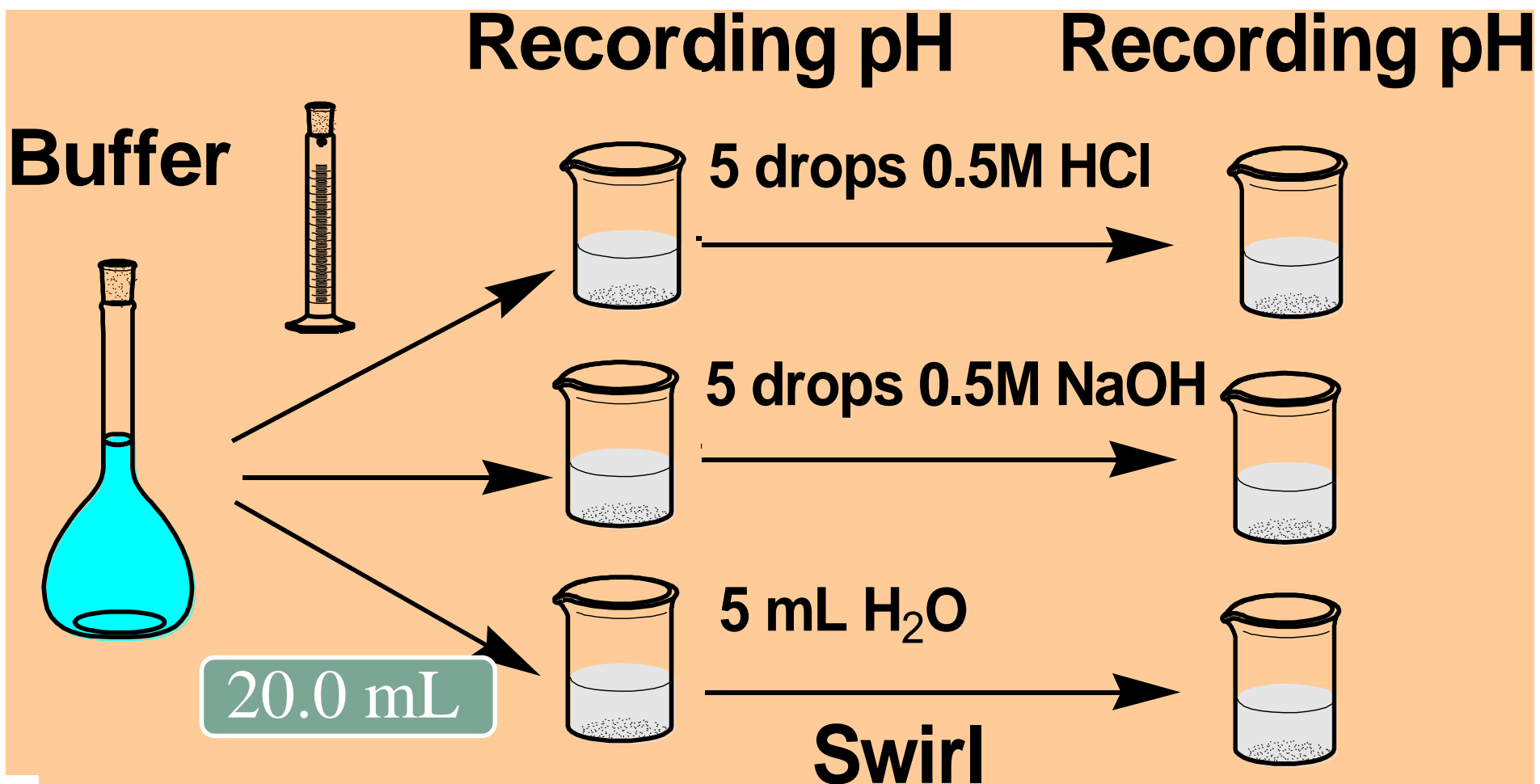
Pipet x mL
5.00M HAc
and y mL
2.00M NaAc

Dilute the solution to
100.00mL

Invert
>20 times

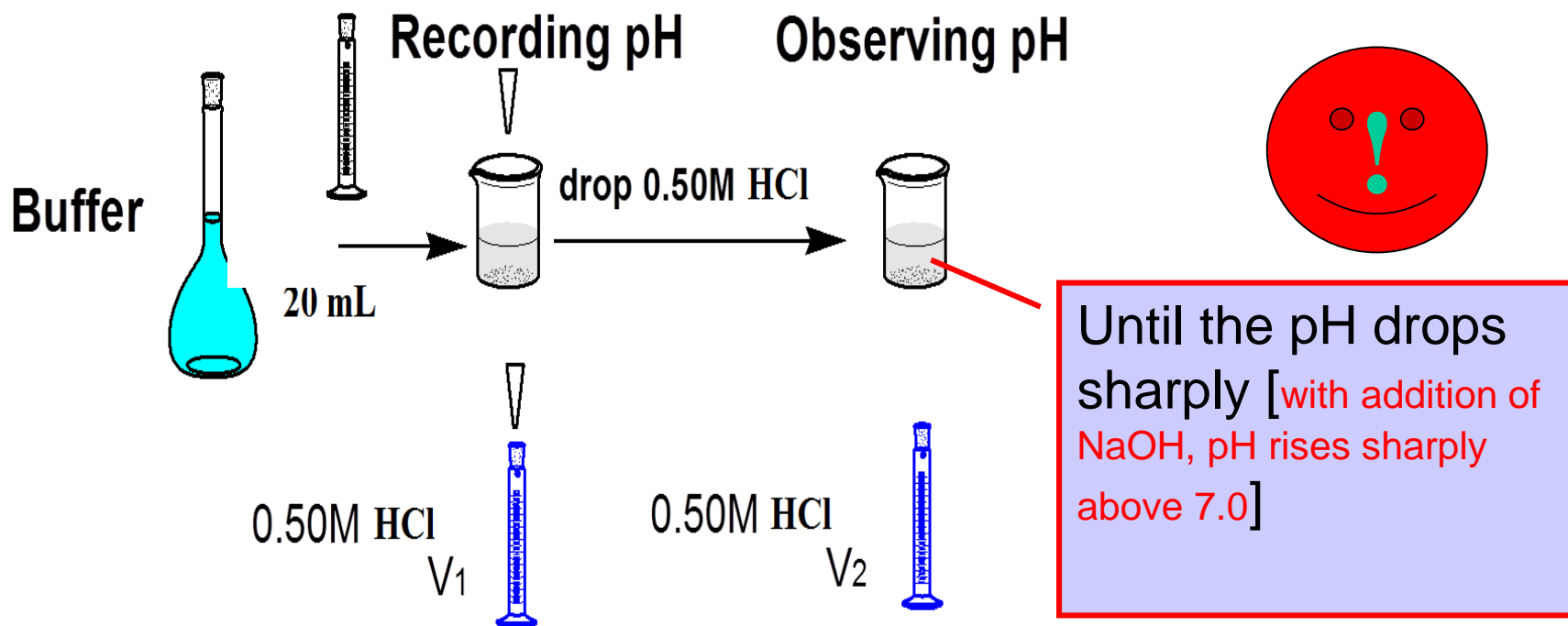


Procedure Part C: Properties of Buffer



PROCEDURE--- Part D.

- Determination of Buffer Capacity***
(use 0.50M HCl only & not NaOH)



After lab

- Exchange data with the others in your team who had a different buffer.
- Mark the solution you prepared and measured.
- **Discuss in ALR why some data inconsistent? Inconsistent Data Causes: not following procedure, temperature effect on K_{eq} , contamination, pH meter errors & mishandling (electrode saturated), stock solutions, inaccurate readings & dilutions, etc.**
- **Example next: K_a Temperature corrections**

Temperature Effect from CH19, Eq. 19-19:

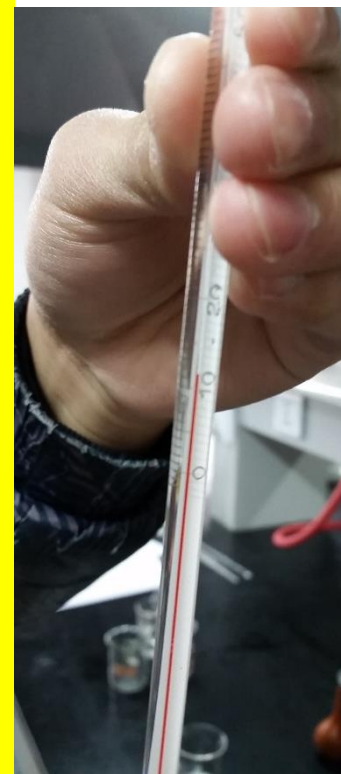
$$\Delta G = \Delta G^\circ + RT \ln Q$$

At equilibrium: $\Delta G = 0$ & $Q = K_{eq}$

Then: $\Delta G^\circ = -RT \ln K_{eq}$

or $K_{eq} = e^{-\Delta G^\circ/RT}$

Where: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$



All the values for various substances
& solutions are typically tabulated in
handbook of chemistry or
appendices of VC210 chemistry book

TABLE 19.2 • Conventions Used in Establishing Standard Free Energies

For E, H & S, elements in standard states at 25°C & 1atm.

State of Matter

Standard State

Solid

Pure solid

ΔG° [J/mol]

Liquid

Pure liquid

Gas

1 atm pressure

Solution

1 M concentration

Element

$\Delta G_f^\circ = 0$ for element
in standard state

$\Delta G_f^\circ = 0$ for elements (incl. N_2 , F_2 ,
 Br_2 , I_2 , Cl_2 , O_2 in standard state)

NOTE: For substances in solution, the standard state is a concentration of 1M, for gas 1atm all at a given T that does not have to be 298 K. $\Delta G_f^\circ = 0$ only for elements in their standard state (at 25°C & 1atm)

pH meter

❖ Calibrating a Digital pH Meter

1. Switch on the pH meter.
2. Press the “校准” “RESET” button to begin the new calibration.
3. Remove the electrode from the bottle of storage solution. Rinse with de-ionized water & dry the electrode tip **carefully** with a tissue.



Calibrating a Digital pH Meter

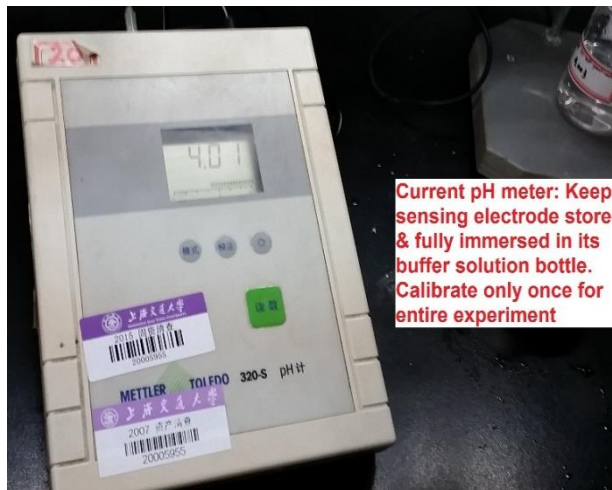
4. Immerse the electrode in pH 4.003 buffer. Swirl the solution to fully saturate the electrode with buffer.



Calibrating a Digital pH Meter



5. Press the “校准” “RESET” button again. After the reading is stable, the meter will return to the Measure screen and a tiny boxed A appears at the top left hand side of the display. The box may blink and disappear between, indicating that calibration is complete.



Calibrating a Digital pH Meter



6. Remove the solution from the pH 4.003 buffer and rinse the electrode with de-ionized water. Dry the electrode tip **carefully** with a tissue. **Safe and label the used buffer solution for collection by TA at end of lab.**

pH measurement

- *Now the meter is ready to use for measuring the pH of any solution.*
- Immerse the electrode in the pH unknown solution and swirl.
- Press “测量” “MEASURE” button, after the reading is stable, record pH.
- A tiny boxed “A” or “A/” or “/” appears at the top left hand side of the display. The box may blink and disappear between, indicating that calibration is complete.



BUFFERS

CH17: p707-713 VC210 textbook (12th ed.)

Conclude

Buffer sample #1 with designed pH = 4.15 will take less no. of drops of HCl than sample #4 with designed pH = 5.35 before the pH starts to drop significantly, indicating the approach of Buffer Capacity Point. Because buffer Sample #1 is made of lesser volume of conjugate base (1mL) than Sample # 5 (4mL). So, it will take lesser amount of HCl to neutralize the lesser amount of conjugate base.