

# **The Properties of Buffers**

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# 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.

# 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 <sub>3</sub> O <sup>+</sup> ], M	[HCOO <sup>-</sup> ], M
Initially	<b>c</b>	<b>0</b>	<b>0</b>
Change	<b>-x</b>	<b>x</b>	<b>x</b>
At equilibrium	<b>c-x</b>	<b>x</b>	<b>x</b>

c = initial conc. of weak acid HA & x is concentration H<sub>3</sub>O<sup>+</sup> or A<sup>-</sup> 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

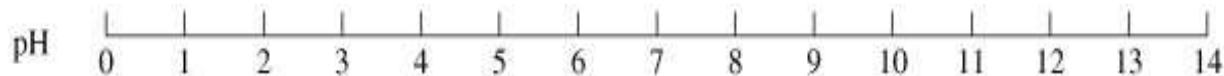
1.00 L water + 0.010 mol  $\text{OH}^-$



1.00 L water



1.00 L water + 0.010 mol  $\text{H}_3\text{O}^+$



### Buffer solution

1.00 L buffer + 0.010 mol  $\text{OH}^-$



1.00 L buffer



1.00 L buffer + 0.010 mol  $\text{H}_3\text{O}^+$



# 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  $\text{H}^+$  or  $\text{OH}^-$  and the buffer components stay the same (pH remains constant)**

# 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



# 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)---

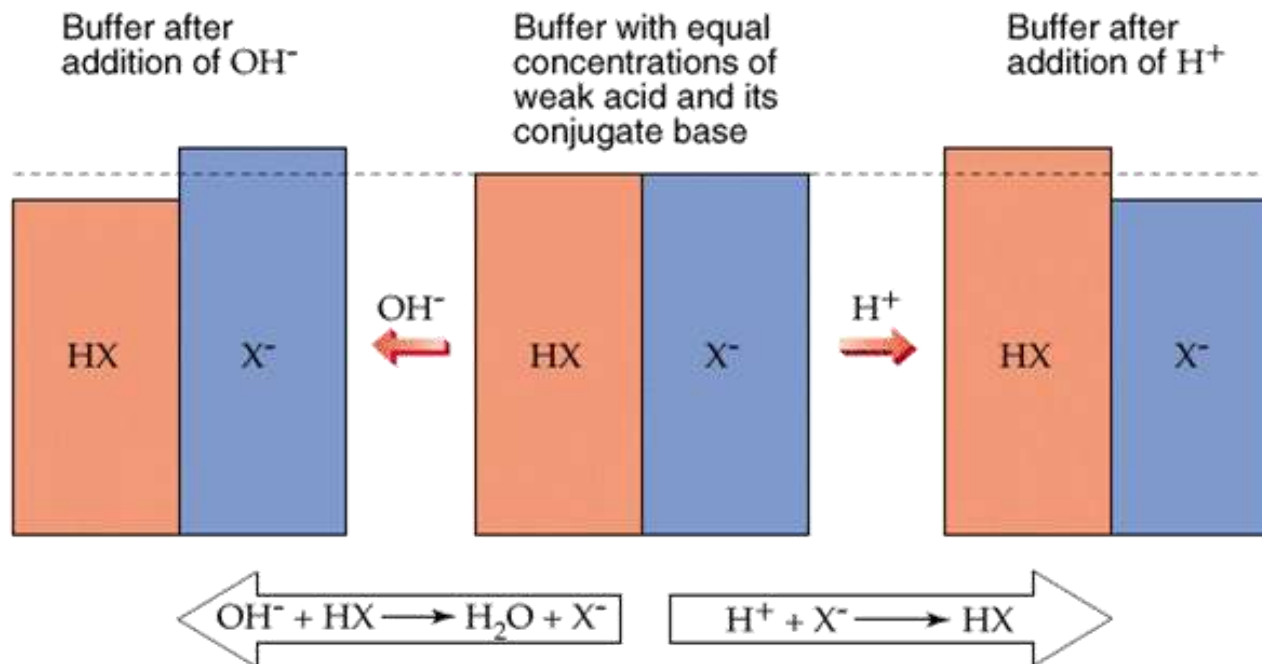
## Henderson-Hasselbalch Equation

Requirements:

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

$$pH = pK_a \pm 1$$

# Preparation of a buffer (3)



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

# 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<sup>-</sup>] = 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<sub>b</sub>/ C<sub>a</sub>)= - 0.75 , then C<sub>b</sub>/C<sub>a</sub> = 10<sup>-0.75</sup>**

**or: C<sub>b</sub>/C<sub>a</sub> = 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.  $m_{AcNa} = ? \text{ g}$**

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

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

**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  $\text{CH}_3\text{COOH}$  and  $V_b$  mL 2.00M  $\text{CH}_3\text{COONa}$  solutions, diluted with deionized  $\text{H}_2\text{O}$ ). \* **See example slide, answers on last slide**

Buffer	Target pH	$C_b/C_a$	$V_a$ (mL) 5.00M $\text{HA}_c$	$V_b$ (mL) 2.00M $\text{A}_c^-$
<b>Example*</b>	<b>4.00</b>	<b>0.178*</b>	<b>1.70*</b>	<b>0.75*</b>
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 3<sup>rd</sup> 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=4.00 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<sub>c</sub> of unknown concentration. Mg observation: two Mg strips add 5-10 drops 0.50M HCl to one strip and then 0.50 M HA<sub>c</sub> to the other.
3. Prepare Buffers Target pH: Target pH, Calculated C<sub>b</sub>/C<sub>a</sub>, Calculated V<sub>a</sub> (to measure & add to 100mL volumetric flask), Calculated V<sub>b</sub> (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<sub>eq</sub>, 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  $\text{CH}_3\text{COOH}$  solution in a 50-mL volumetric flask solution by using 5-mL graduated pipette and adding 5.00mL of 5.0M  $\text{CH}_3\text{COOH}$  into the volumetric flask



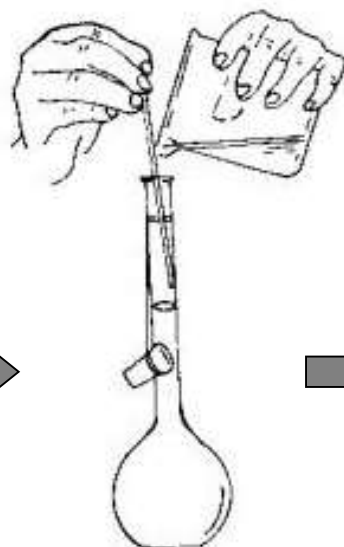
# Procedure

## Part A.1

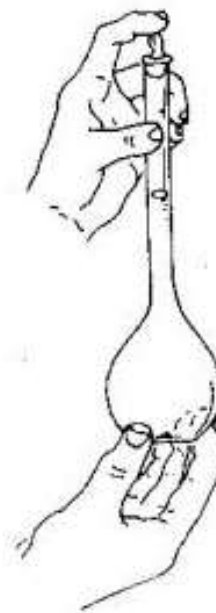
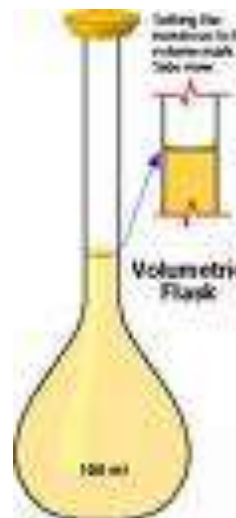
Attention!  
Add drop-wise  
with a pipet!



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.**

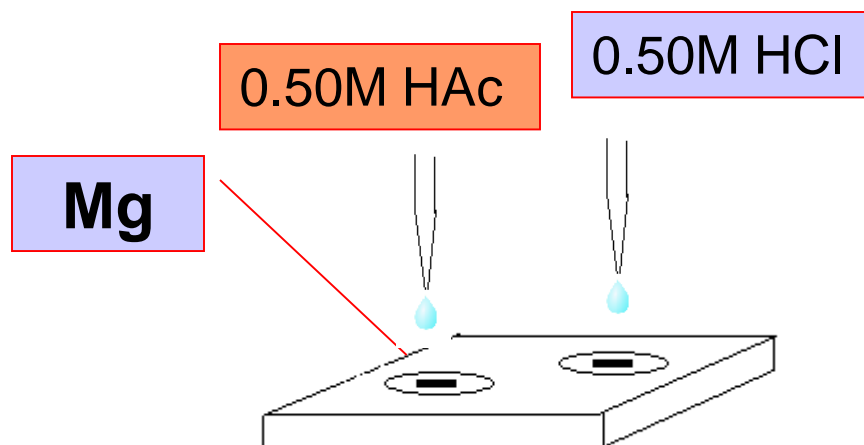


# PROCEDURE-- Part A.3

- ***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  $\text{CH}_3\text{COOH}$  and  $V_b$  mL 2.00M  $\text{CH}_3\text{COONa}$  solutions, diluted with deionized  $\text{H}_2\text{O}$ .

Buffer	Target pH	$V_a$ (mL) 5.00M $\text{HA}_c$	$V_b$ (mL) 2.00M $\text{A}_c^-$
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  $\text{HA}_c$ ) & 2.00  $V_b$  (mmole  $\text{A}_c^-$ )

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

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:

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

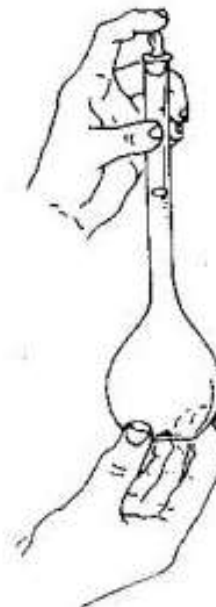
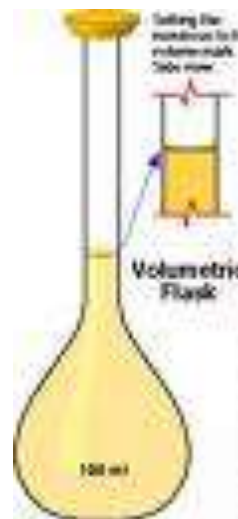
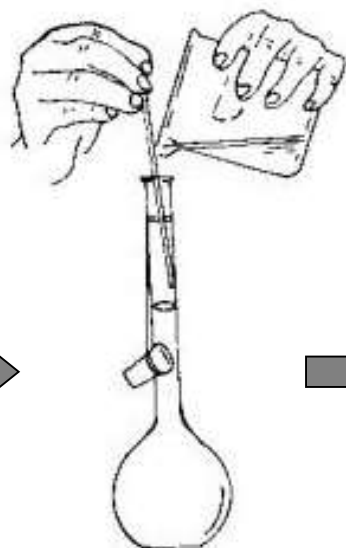
$$\bullet \text{Similarly: } 2.00 \text{ M} \times V_b = 100 \text{ mL} \times 0.015\text{M}, \quad V_b = 0.75 \text{ mL}$$

**•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

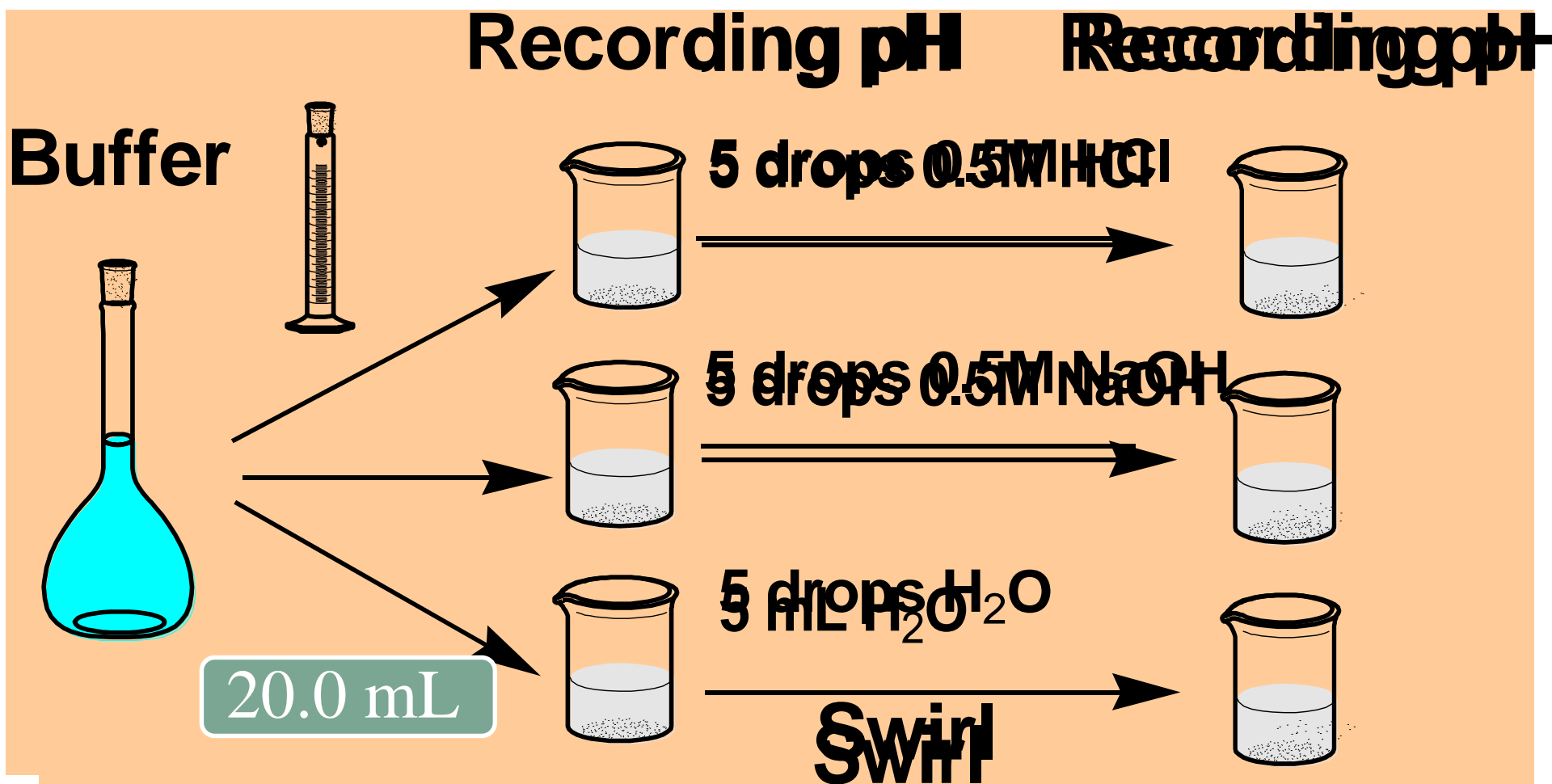
Dilute the solution to  
100.00mL

Invert  
>20 times



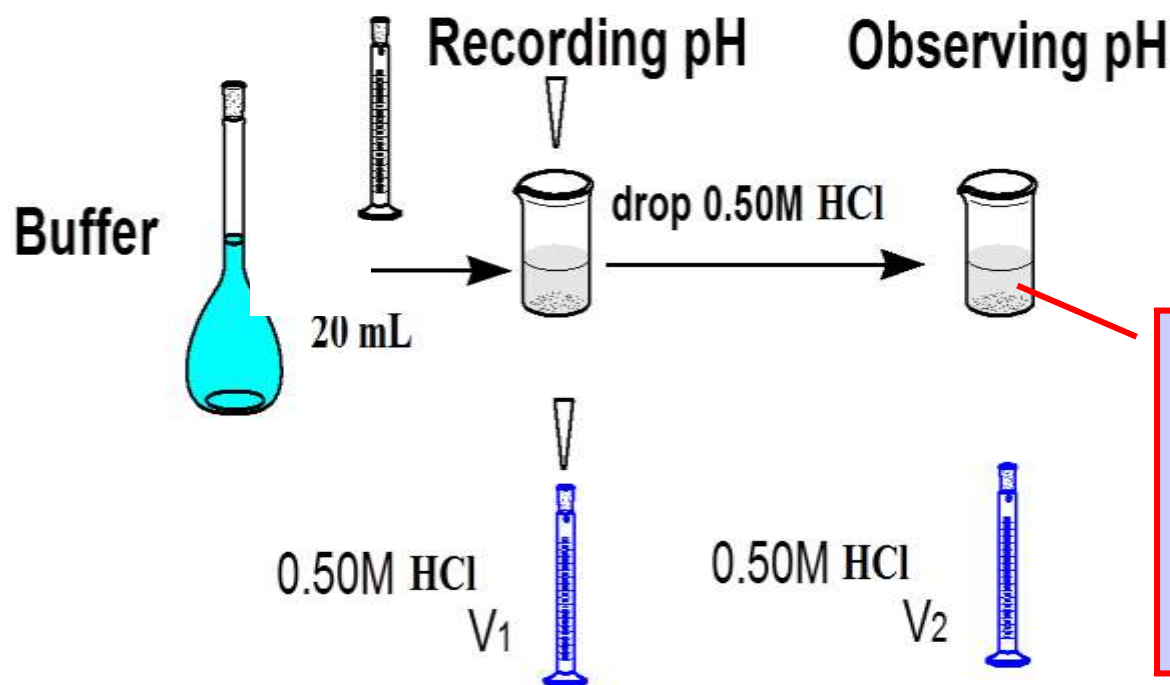


# Procedure Part C: Properties of Buffer



# PROCEDURE--- Part D.

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



Until the pH drops sharply [with addition of NaOH, pH rises sharply above 7.0]

# 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  $K_{eq} = e^{-\Delta G^\circ/RT}$  but:  $\Delta G^\circ$  &  $R$  constants,*

*then:  $T_1 \ln K_{eq1} = T_2 \ln K_{eq2}$*

Knowing  $T_1 = 298 \text{ K}$  &  $K_{eq1} = 1.8 \times 10^{-5}$

Then calculate  $K_{eq2}$  at measured lab average  $T_2$



## 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

$\Delta G^\circ$  [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 before removing the electrode probe.
3. Remove the electrode probe 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 probe electrode with buffer.



# Calibrating a Digital pH Meter



5. Press the “校准” “RESET” button again. After the reading is stable (decimal dot & vertical line stop blinking), the meter will return to the “Measure” screen and a tiny boxed “[A]” appears at the top left hand side of the display (also the dot & vertical bar stops blinking). The box may blink and disappear between, indicating that calibration is complete and pH should be 4.00. Do not press “measure” again.





# Calibrating a Digital pH Meter



**8. Rinse the electrode with distilled water and wipe softly with clean tissue. Immerse the electrode properly into the sample bottle to measure its pH by following the next step.**

6. Before removing the electrode from the buffer solution (of pH 4.003) and in a separate small beaker, prepare a sample to measure its unknown pH. If the sample is not ready within 10-15 minutes then you must **follow the next step.**
7. Remove the electrode from the buffer solution (pH 4.003) and rinse its probe with de-ionized water. Dry the electrode tip **carefully** with a tissue. **Save and label the used buffer solution (pH 4.003) for collection by TA at end of lab.**

# pH measurement

- *Now the meter is ready to use for measuring the pH of any solution.*
- **Rinse the electrode with distilled water, wipe with clean tissue**
- Immerse the electrode into the prepared sample to measure its unknown pH and swirl.
- Press “测量” “MEASURE” button, after the reading is stable (when the decimal dot & the vertical bar stops blinking), record the 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 measurement is complete. Do not hit “MEASURE” again, proceed in measuring the next pH sample, make sure you rinse and wipe correctly with distilled water between each measurement.



# AVOID DAMAGE TO THE pH METER

- Remember you calibrated with buffer pH=4.003
- Follow the calibration and measurements instructions carefully.
- When you measure the pH with 5 drops of 0.5M HCl, or with 5 drops of 0.5M NaOH, do not exceed the number of drops. If it is exceeded, then the pH may go down to 2 or up to 12. This means you are abusing the electrode and it will take overnight saturation with distilled water to re-establish the sensitivity of the buffer pH range.

# **BUFFERS**

**CH17: p707-713 VC210 textbook (12<sup>th</sup> ed.)**

## **Conclude**

Buffer sample #1 with designed  $\text{pH} = 4.15$  will take less no. of drops of  $\text{HCl}$  than sample #4 with designed  $\text{pH} = 5.35$  before the  $\text{pH}$  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  $\text{HCl}$  to neutralize the lesser amount of conjugate base.