Buffer Solutions

Last revised: 2024/10/26

Preparation

Collect the following items

- One 250 mL volumetric flask
- Two 10 mL graduated pipets and one pipet filler
- Four 50 mL beakers
- **Two plastic drop pipets**
- The TA will distribute one stir bar to each group

From your personal equipment

- Two test tubes (clean and dry), one 400 mL beaker
- 10 mL and 50 mL graduated cylinders
- One wash bottle and one 1 L plastic beaker

Objective and Principles

- **Objective:**
  - Prepare HOAc/NaOAc buffer solutions
  - Investigate the factors affecting buffer capacity: **concentration** and **$[A^-]/[HA]$ ratio**

- **Lab techniques:**
  - Operate a pH meter
  - Volumetric flask
  - Graduated pipet

Buffer Solution

- Function: Resisting pH change upon the addition of either acid or base
- Composition:
  - A mixture of weak acid + its conjugate base (e.g. HF/NaF)
  - A mixture of weak base + its conjugate acid (e.g. NH_3/NH_4Cl)
- Acid-base equilibrium:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

Neutralize the added base — *Neutralize the added acid*

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

- Henderson-Hasselbalch equation:

$$[H^+] = \frac{K_a[HA]}{[A^-]} \longrightarrow pH = -\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right)$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Buffer Capacity

- Definition: The amount of OH^- or H^+ (in moles) required to change the pH of buffer solution by 1 unit
- A buffer solution would have a higher buffer capacity when:
  - The total concentration of two components ([HA] + $[A^-]$) is higher
  - The concentration ratio $[A^-]/[HA]$ is closer to 1
- **The most effective buffer range: pK_a ± 1**

When $[A^-] = 10 \times [HA]$, $pH = pK_a + 1$

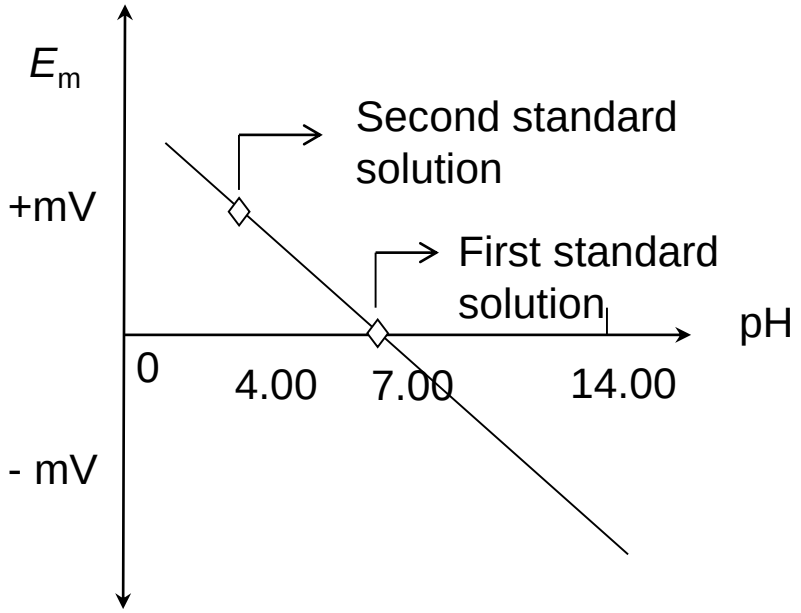
When $[A^-] = [HA]/10$, $pH = pK_a - 1$

Working Principles of pH Meter

A pH meter consists of three parts:

- **pH electrode assembly**
  - Reference electrode (often Ag/AgCl) – potential is fixed
  - Indicator electrode (glass frit) – potential varies with $[H^+]$
- **Voltmeter**: measure the potential difference (E_m) between the two electrodes
- **Thermoprobe**: measure the temperature of solution

Working Principles of pH Meter



- E_m: measured cell potential
- K: constant, determined by the type of electrode used
- R: gas constant
- T: absolute temperature of the solution
- pH: pH value of solution
- n: number of moles of electrons transferred in the reaction
- F: Faraday constant

$$E_m = K - 2.3RT(\mathrm{pH})/nF$$

Reference electrode *Indicator electrode*

$$E_\mathrm{m} = K + mT \times (\mathrm{pH})$$

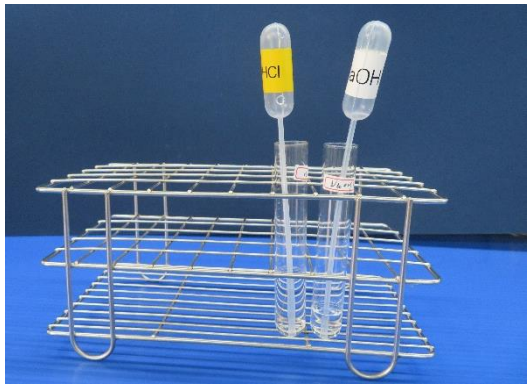
- The pH meter needs to be calibrated in standard solutions (pH 7.00 and pH 4.00)
- After calibration, the measured E_m can be converted to pH

Experiment Tasks

1. Calibrate pH-meter

2. Prepare HOAc and NaOAc solution

3. Measure the volume of one drop of HCl/NaOH



4. Prepare buffer solutions and record their pH values

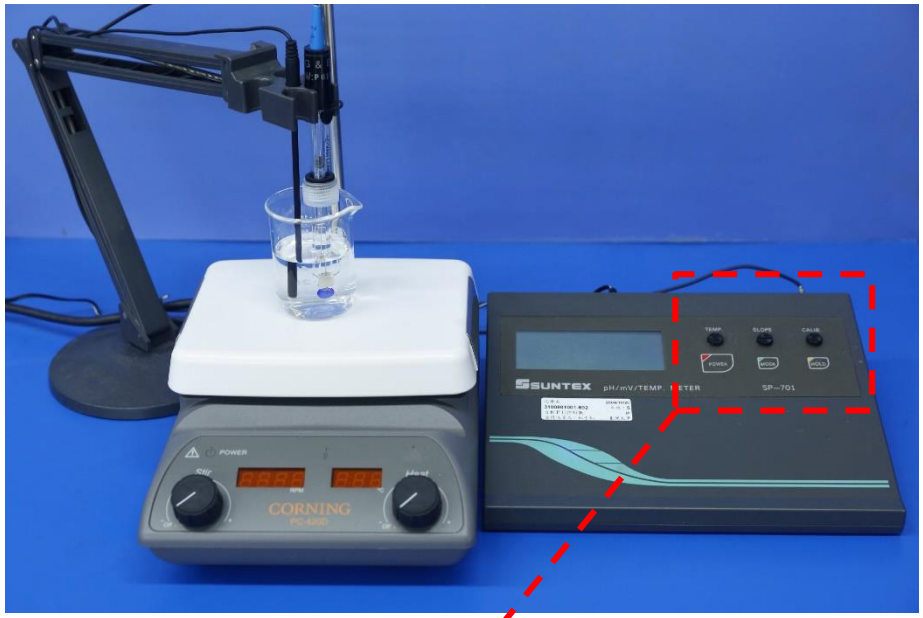
50 mL beaker

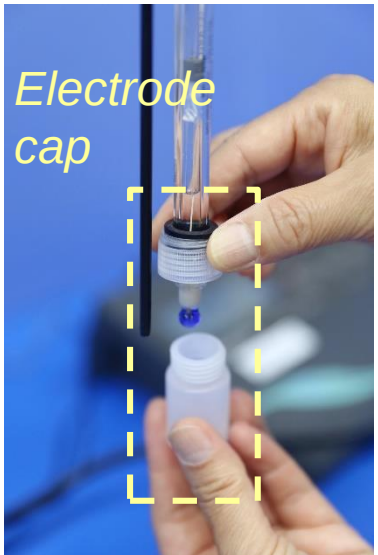
Add 5 drops of HCl(aq)

Add 5 drops of NaOH(aq)

Record the pH values dropwise

Step 1: Calibration of pH Meter



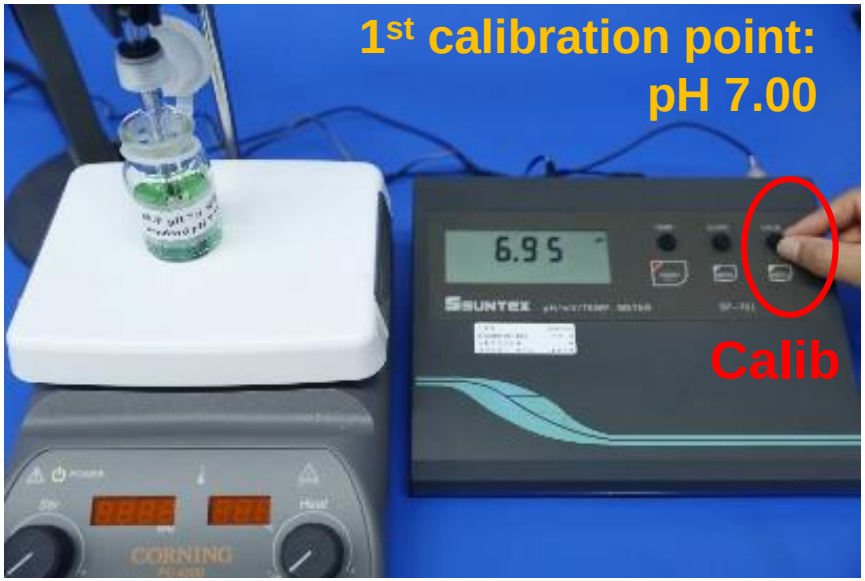


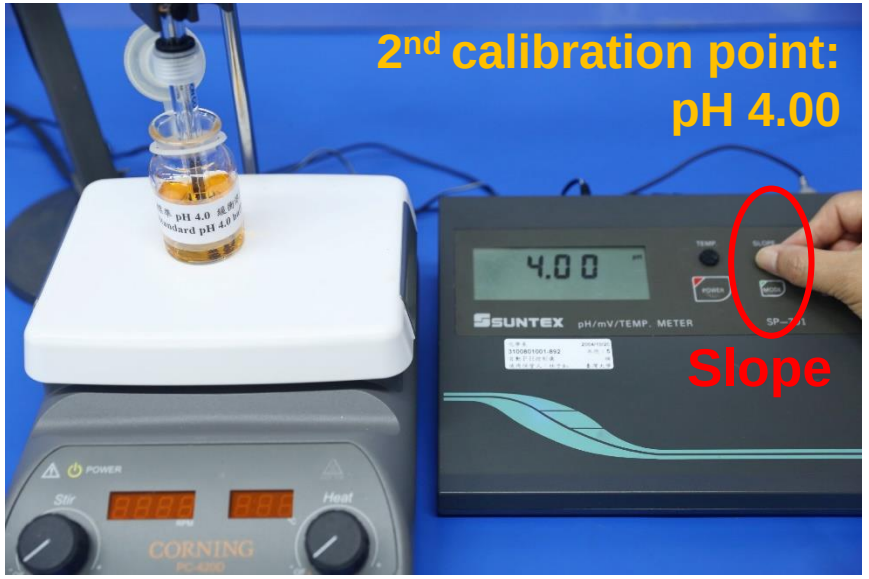
- Press the “POWER” button to turn on the pH meter. Let it warm up for at least 10 min
- Press the “HOLD” button to suspend pH reading
- Remove the electrode cap from by rotating it
- Use a wash bottle to rinse the electrode assembly, then wipe it dry gently with a tissue

✓ Each pH electrode assembly costs NTD 3,000 → Be careful when operate it

Step 1: Calibration of pH Meter

- Press the "MODE" button several times until "Temp" appears on the screen. **Check whether the temperature reading is close to RT**
- Press the "MODE" button again to switch to "pH" function





- Immerse both thermoprobe and pH electrode into **pH 7.00** buffer solution
- Adjust **Calib** knob until '**7.00**' is shown

- Rinse the thermoprobe and pH electrode with DI water
- Switch to **pH 4.00** buffer solution
- Adjust **Slope** knob until '**4.00**' is shown

Step 2: Prepare HOAc & NaOAc Solutions

Odd Group #'s

Prepare 0.050 *M* HOAc

- Measure **0.74 mL** of conc. (17 *M*) HOAc
- Transfer to a 250 mL volumetric flask that contains some DI water
- Dilute to 250 mL
- pH of solution should be ~3

Even Group #'s

Prepare 0.050 *M* NaOAc

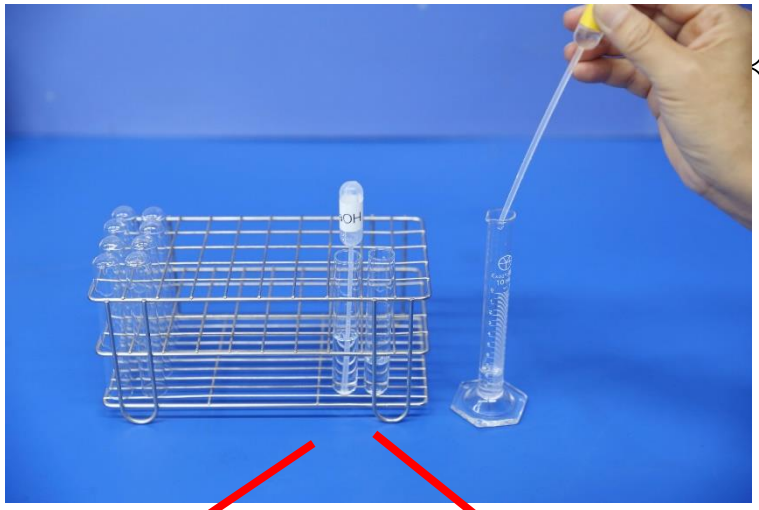
- Measure **1.70 g** of $NaOAc \cdot 3H_2O$, dissolve them in ~ 100 mL DI water in a beaker
- Transfer to a 250 mL volumetric flask (rinse the beaker 2-3 times)
- Dilute to 250 mL
- pH of solution should be ~8

✓ Two groups share one set of HOAc & NaOAc solutions

✓ Transfer the prepared solution into 400 mL beakers (labelled properly)

Step 3: Measure Drop Volumes

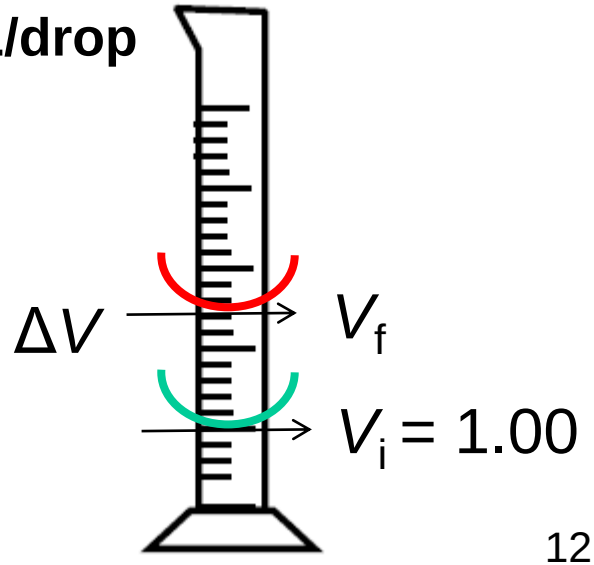
- Measure 5 mL of 1.0 *M* HCl and 1.0 *M* NaOH separately into two dry test tubes
- Use a plastic drop pipet to add 30~50 drops of 1.0 *M* HCl into a 10 mL graduated cylinder; record the volume of solution
- Use another clean plastic drop pipet to add 30~50 drops of 1.0 *M* NaOH into a 10 mL graduated cylinder; record the volume of solution



1.0 *M* NaOH 1.0 *M* HCl

$V_{avg,\ HCl}$ = _____ **mL/drop**

$V_{avg,\ NaOH}$ = _____ **mL/drop**



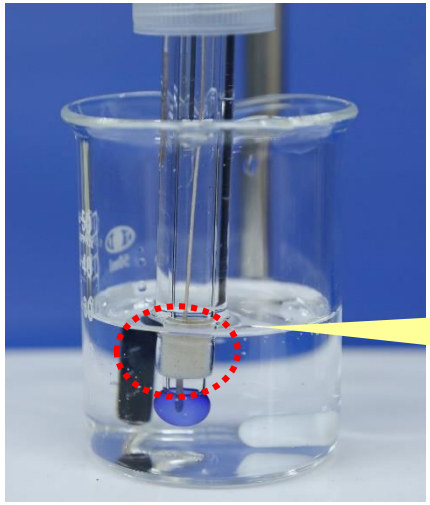
Step 4: Preparing Test Solutions

- Use 10 mL graduate pipets to measure volume accurately for HOAc and NaOAc solutions
- Make two copies of each test solution in 50 mL beakers (for adding acid and base, respectively)
- Perform the measurements in the sequence of **(a), (b)**, (c), (d), then **(e)**

Test solution	0.050 *M* HOAc (mL)	0.050 *M* NaOAc (mL)	DI water (mL)
(a)	**15**	**15**	**0**
(b)	**5**	**5**	**20**
(c)	30	0	0
(d)	0	30	0
(e)	**0**	**0**	**30**

Step 5: Measuring pH Changes

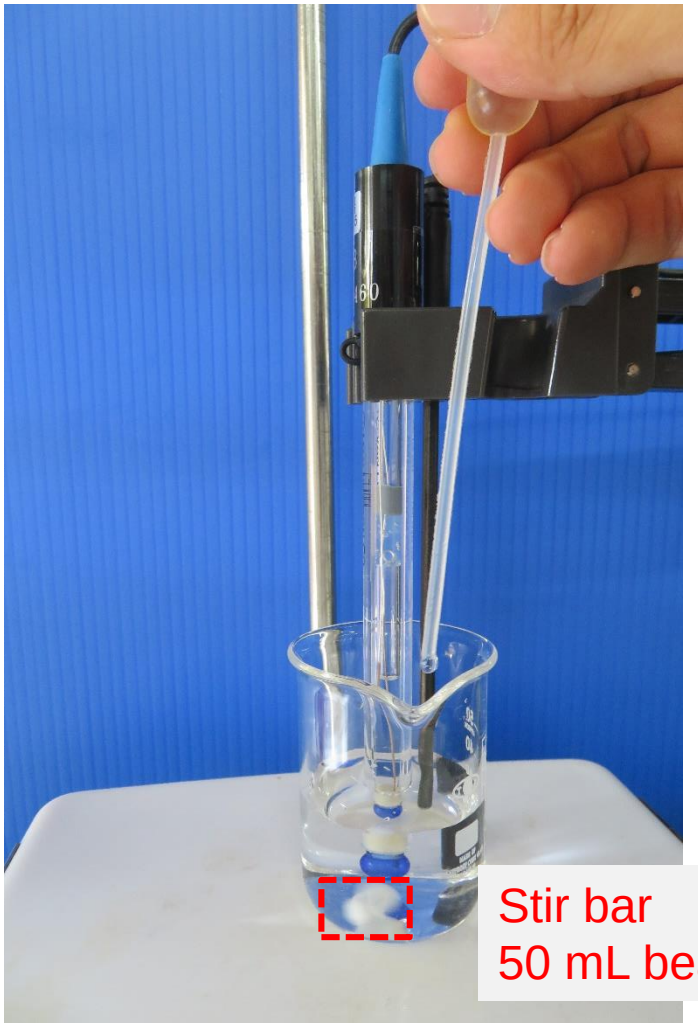
Stir bar
50 mL beaker



Salt bridge

- Both the thermoprobe and the pH electrode should be fixed on the holder and immersed in the test solution (the salt bridge of pH electrode should be fully immersed)
- Adjust the position of beaker and the pH electrode so that the stir bar does not collide with the electrode assembly
- Use plastic drop pipets to add HCl or NaOH into the test solution, record the solution pH dropwise
- When changing between solutions: press the “HOLD” botton on the pH meter, rinse both the electrode and the thermoprobe with DI water, then wipe dry with a tissue paper

Step 5: Measuring pH Changes



Obtain 1.0 *M* HCl with a drop pipet

↓

Add one drop into soln. (a)

↓

Mix thoroughly
and record pH values

↓

Repeat adding acid for 5 times

↓

Prepare another part of soln. (a)

↓

Obtain 1.0 *M* NaOH with a drop pipet

↓

Record pH values after adding each drop (5 drops in total)

↓

Repeat the same procedures with soln. (b)(c)(d)(e)

Clean-Up and Check-Out

- Immerse the pH electrode in DI water (use a 100 mL beaker)
- Switch off the pH meter (keep the power cord plugged in)
- Salt solutions resulted from acid-base neutralization can be disposed into the sink
- Return the magnetic stir bar to TA
- Clean up the lab bench and check personal equipment inventory (have an associate TA sign the check list)

- This is a **Full Report** experiment:
  - Member A: **Have the lab notes and results checked by the TA, and hand in the report next week.**
  - Member B: **Hand in prelab to the TA**

- Groups on duty shall stay and help clean up the lab

Example of Data Table

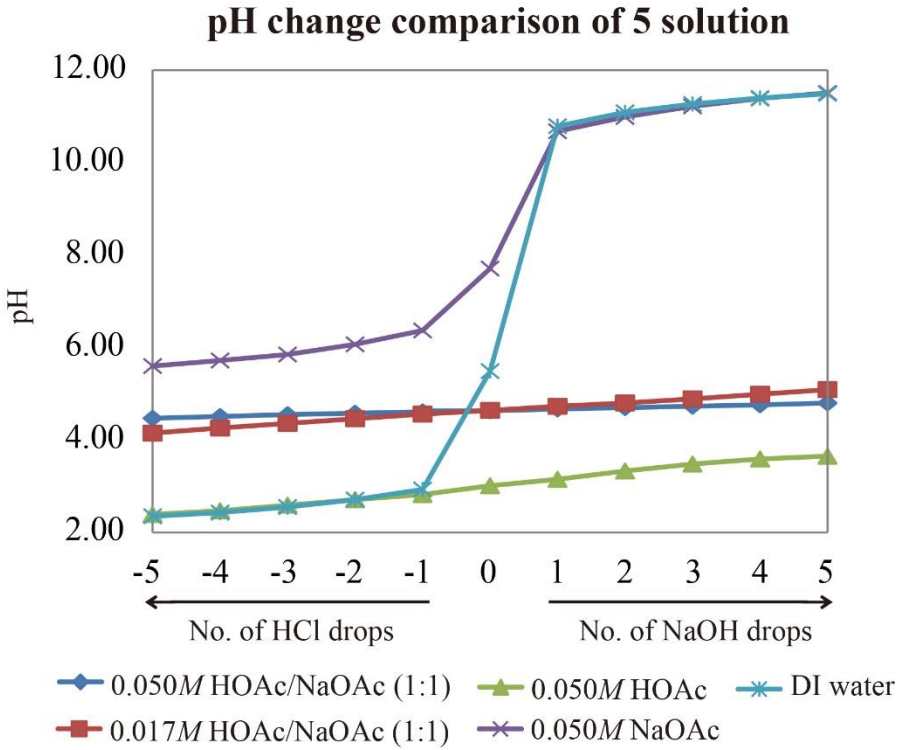
Table 1

	No. of drop	c	d	c	d	e
		0.050 M HOAc/NaOAc	0.017 M HOAc/NaOAc	0.050 *M* HOAc	0.050 *M* NaOAc	DI water
Add NaOH(aq)	**5**	4.80	5.09	3.65	11.51	11.49
	4	4.76	4.99	3.59	11.39	11.40
	3	4.73	4.89	3.48	11.22	11.27
	2	4.70	4.80	3.33	10.93	11.09
	1	4.67	4.73	3.15	10.78	10.79
Avg. pH of acid and base	**0**	**4.65**	**4.64**	**3.00**	**7.71**	**5.49**
Add HCl(aq)	**-1**	4.61	4.56	2.82	6.37	3.01
	-2	4.58	4.46	2.71	6.07	2.71
	-3	4.55	4.36	2.59	5.85	2.55
	-4	4.51	4.26	2.47	5.72	2.43
	-5	4.47	4.15	2.39	5.60	2.35

Plot pH vs. # Drops of Acid/Base

- Use ‘x-y scattering plot’ function in MS Excel (or similar software); use lines to connect adjacent data points
- Plot all five dataset in a same figure (with appropriate axis labels and legends)
- The data table and figure should be included in the full lab report

Figure 1



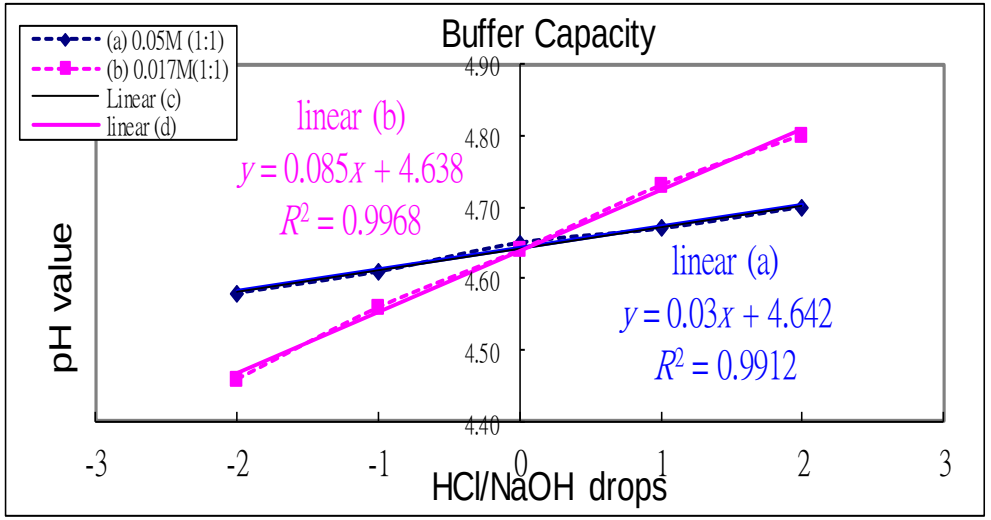
Calculating Buffer Capacity

- For solutions (a) and (b), use the central 5 points in the dataset (see example Table 2)
- Use *linear regression analysis* to obtain the **slope** and **R^2 value**
- The data table and figure should be included in the full lab report

Table 2

No.	a	b
Drops	0.050 *M* HOAc/NaOAc	0.017 *M* HOAc/NaOAc
-2	4.58	4.46
-1	4.61	4.56
0	**4.65**	**4.64**
1	4.67	4.73
2	4.70	4.80

Figure 2



Calculating Buffer Capacity

$$\text{Buffer Capacity (meq/L} \cdot \text{pH)} = \frac{1}{\text{slope}}(\text{drop/pH}) \times V_{\text{drop}}(\text{mL/drop}) \times C_{\text{M}}(\text{eq/L}) \times \frac{1000\ (\text{mL/L})}{30\ \text{mL}}$$

$(V_{\text{avg. of HCl}} + V_{\text{avg. of NaOH}}) / 2$

0.050 *M* (1:1): 22 meq/L·pH

0.017 *M* (1:1): 7.8 meq/L·pH

Table 2

No.	a	b
Drops	0.050 *M* HOAc/NaOAc	0.017 *M* HOAc/NaOAc
-2	4.58	4.46
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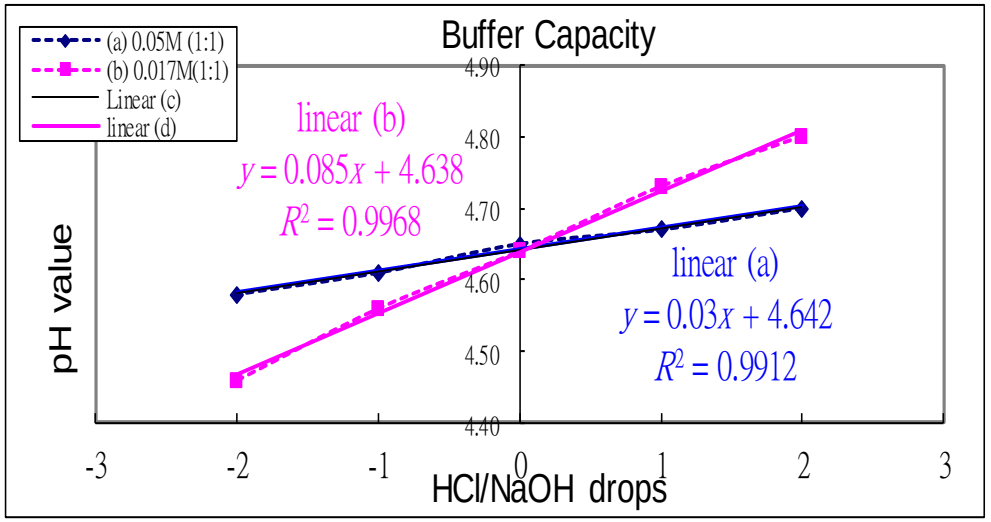
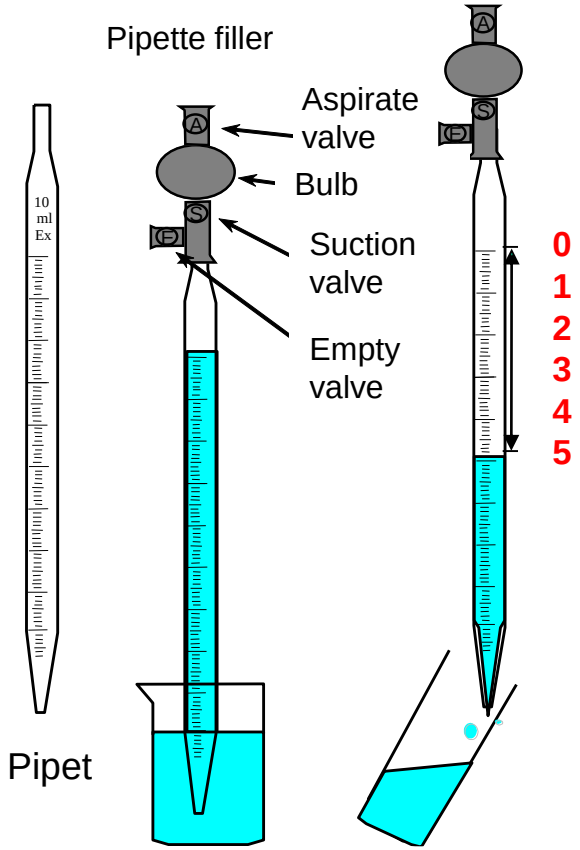
Figure 2



T12.2 – Measuring (Graduated) Pipet

Deliver 5 mL solution – Method 1

- Clean a 10 mL pipet and rinse it twice with small amount of the liquid to be transferred
- Press valve **A** of the pipet filler and simultaneously squeeze the bulb to expel air from it, then insert the top of pipet gently into the pipet filler
- Bring the pipet tip below the liquid surface, press valve **S** to draw liquid to the 0.00 mL marking
- Wipe off any excess liquid near the pipet tip
- Use the other hand to hold the new container. Maintain the pipet in a vertical position and let its tip touch the inner wall of the container. Press valve **E** to drain the liquid to the 5.00 mL marking
- Do not force out any liquid remaining at the tip
- Wash the pipet thoroughly after use

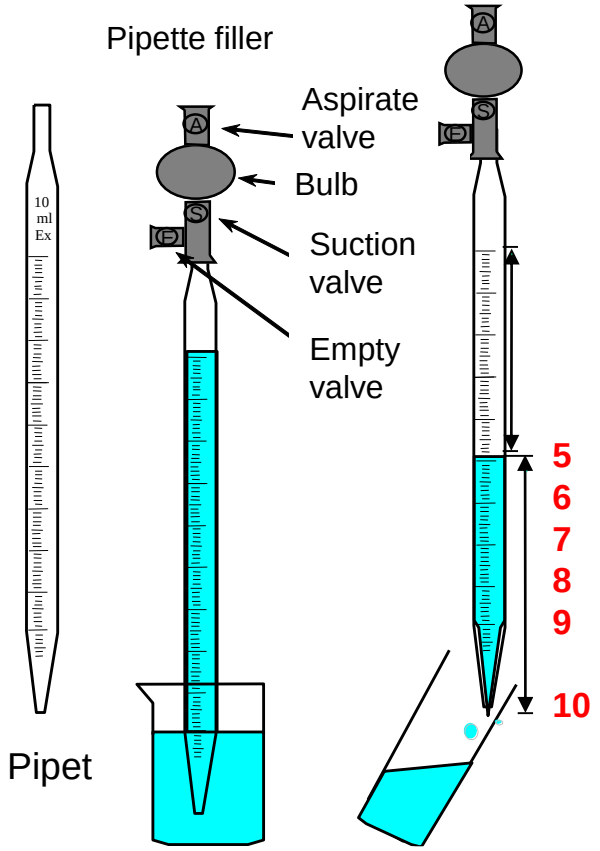


T12 Video (YouTube link)

T12.3 – Measuring (Graduated) Pipet

Deliver 5 mL solution – Method 2

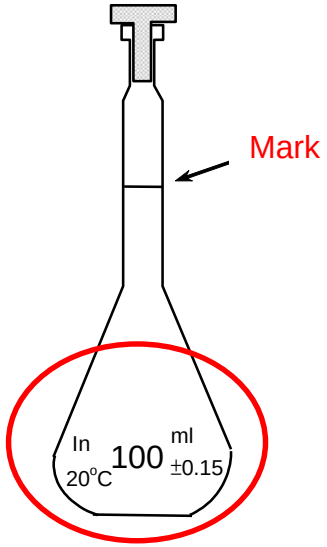
- Clean a 10 mL pipet and rinse it twice with small amount of the liquid to be transferred
- Press valve **A** of the pipet filler and simultaneously squeeze the bulb to expel air from it, then insert the top of pipet gently into the pipet filler
- Bring the pipet tip below the liquid surface, press valve **S** to draw liquid until it rises above the 5.00 mL marking
- Remove the pipet filler and quicky use an index finger to close the top of pipet. Use the finger to adjust the liquid level to the 5.00 mL marking
- Wipe off any excess liquid near the pipet tip
- Use the other hand to hold the new container. Maintain the pipet in a vertical position and let its tip touch the inner wall of the container. Release the index finger so that liquid is transferred
- Do not force out any liquid remaining at the tip
- Wash the pipet thoroughly after use



T12 Video (YouTube link)

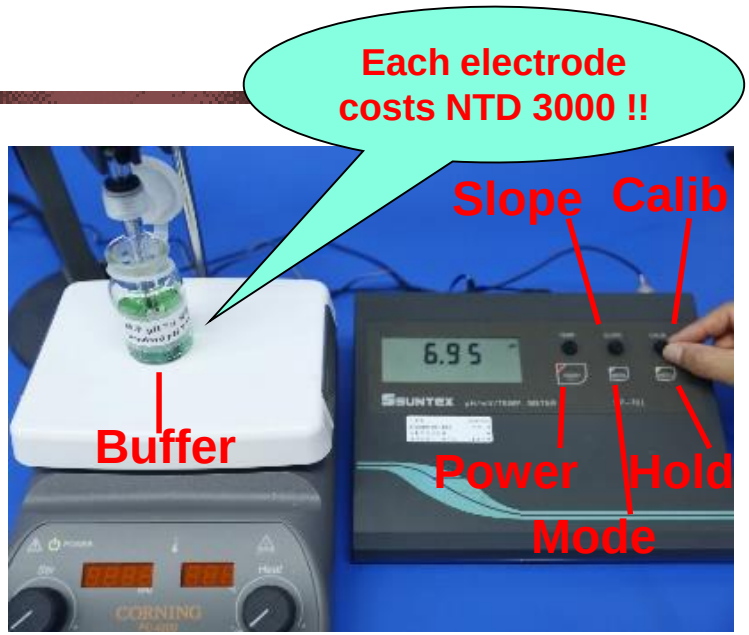
T13 – Volumetric Flask

- Clean the volumetric flask thoroughly, then rinse it with a small amount of solvent
- Using a funnel, transfer the solution to be diluted into the volumetric flask
- Fill solvent into the flask until about half full, swirl the flask to let the solution mix
- Add more solvent so that the liquid level approaches (but does not exceed) the inscribed mark
- Use a dropper pipet to add solvent slowly, so that the liquid level matches the inscribed mark
- Install the stopper cap (hold with a finger), invert the flask several times to ensure thorough mixing
- Pour the solution into a beaker for later use (do not store solution in the flask)
- Wash the volumetric flask immediately after use and let it air dry (do not put flask on a hot plate or in an oven)



T13 Video (YouTube link)

T16.1 – pH Meter



Preparation and calibraion:

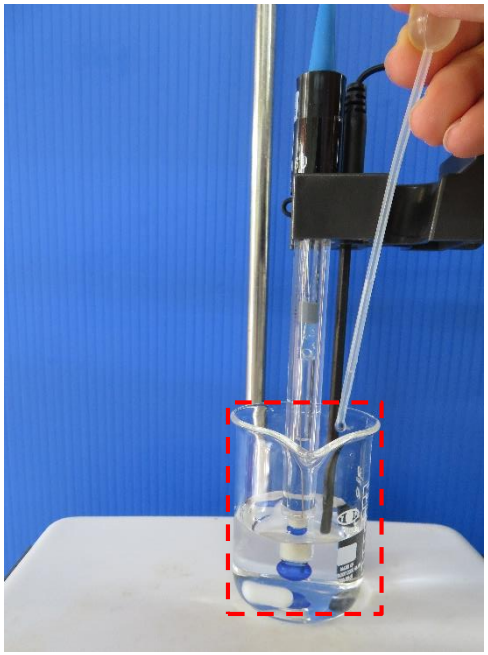
- Press the "POWER" button to turn on the pH meter. Let it warm up for at least 10 min
- Press the "MODE" button several times until "Temp" appears on the screen. Check whether the temperature reading is close to RT
- Press the "MODE" button again to switch to "pH" function
- Press the "HOLD" button to suspend pH reading
- Rotate the electrode cap (3 M KCl) to remove it
- Use a wash bottle with DI water to rinse the electrode, then gently dry it with a tissue paper
- Immerse both the electrode and the thermoprobe into the pH 7.00 buffer solution
- Press "HOLD" again to unfreeze the reading. Adjust the "Calib" knob until 7.00 is shown
- Press "HOLD" to suspend pH reading. Remove the electrode and the thermoprobe, rinse them with DI water then immerse them into the pH 4.00 buffer solution
- Press "HOLD" again to unfreeze the reading. Adjust the "Slope" knob until 4.00 is shown

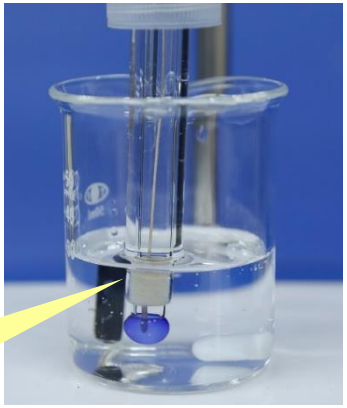
T16 Video (YouTube link)

T16.2 – pH Meter

Measuring pH:

- Use a beaker to hold the solution to be tested. Add a magnetic stir bar and place the beaker atop a stirrer
- When changing between solutions: press the “HOLD” botton on the pH meter, rinse both the electrode and the thermoprobe with DI water, then wipe dry with a tissue paper
- The *salt bridge* at the bottom of electrode should stay below the liquid level, however avoid hitting the electrode with stir bar
- Immerse the electrode in clean DI water when not in use
- For long-term storage, put the electrode back into the 3 M KCl solution in the electrode cap





T16 Video (YouTube link)