Potentiometric Titration of Acid-Base

Last revised: 2024/05/07

Preparation

Note:
Measure 2.5 mL vinegar to titrate

Collect the following items

- One magnetic stir bar (TA distribute)
- One glass funnel
- One 25 mL buret
- One 100 mL volumetric flask
- Two 125 mL Erlenmeyer flasks (check if broken)
- One 5 mL pipet and pipet filler (shared)
- pH 7.00 and pH 4.00 standard buffer solution (shared)

From your personal equipment

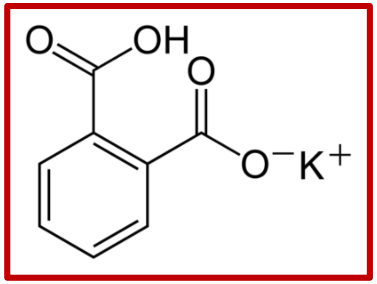
- Two 100 mL beakers
- One wash bottle and one 1 L plastic beaker

Objective and Principles

- **Objective:**
  - To **prepare** and to **standardize** secondary-standard solutions
  - To determine the **equivalence point** and concentration of acetic acid by using the **electric potential method**
  - To determine the dissociation constant of acetic acid, K_a
- **Lab techniques:**
  - Operate a **pH meter**
  - Use of **volumetric flask**, and **graduated pipet**
  - Determine the equivalence point by titration curves

Standardization of Acid or Base

- **Primary standard**: substance with high purity and high molar mass
  - Common base: sodium carbonate (Na_2CO_3)
  - Common acid: potassium hydrogen phthalate (**KHP**)
- **Secondary standard**: standardized acid or base
  - Common base: sodium hydroxide (NaOH)
  - Common acid: hydrogen chloride (HCl)
- KHP is a **monoprotic weak** acid with structure
- The neutralization reaction of KHP with NaOH in a **1:1** stoichiometric ratio



$$HOOCC_6H_4COOK(aq) + NaOH(aq) \rightarrow$$

$$C_6H_4(COO)_2^{2-}(aq) + K^+(aq) + Na^+(aq) + H_2O(l)$$

$$C_{NaOH} \cdot V_{NaOH} = n_{KHP} = \frac{Mass_{KHP}}{204.22}$$

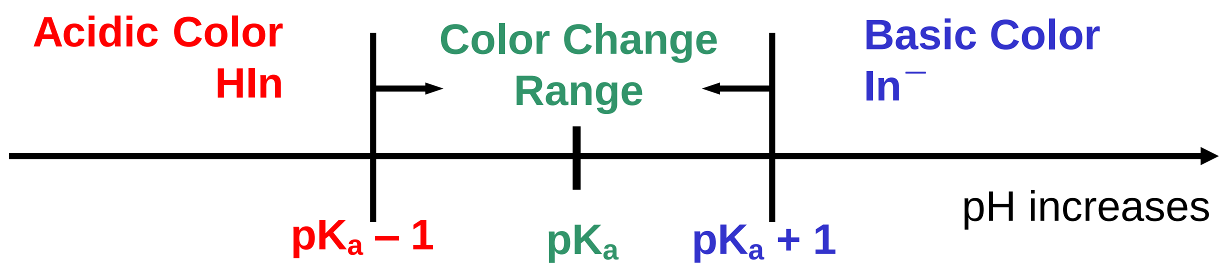
Acid-base Indicator

- Acid-base indicator: a weak organic acid or base
- Weak acid (HIn) and its conjugate base (In^-) with different colors

$$\text{HIn} + H_2O \rightleftharpoons H_3O^+ + In^-$$

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

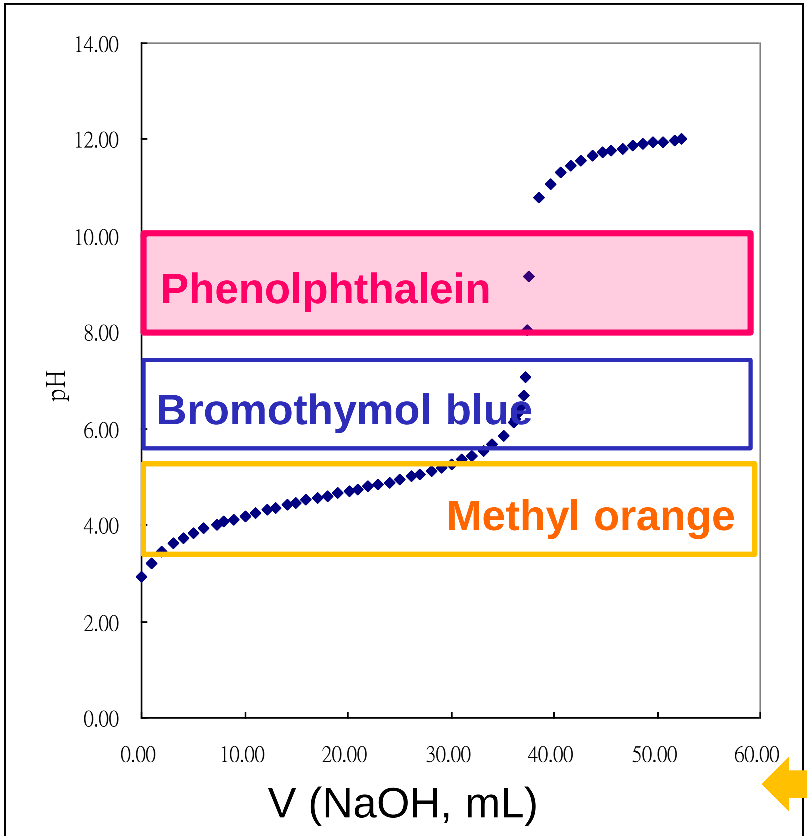
$$pH = pK_a + \log \frac{[In^-]}{[HIn]}$$



- According to the pH range of the equivalence point, choose the appropriate indicator to match the **end-point** with the **equivalence point**
- At the equivalence point, pH of the solution:
  - Strong acid/weak base titration: pH < 7
  - Weak acid/strong base titration: pH > 7
  - Strong acid/strong base titration: pH = 7

Equivalence Point

- The **pH** of the reacting solution **changes significantly** near the **equivalence point**
- Base on the color change of the acid-base indicator or monitoring the change in pH values to determine the **end-point**



Indicator	Acid form	pH range	Basic form
Methyl orange	Red	4.2~6.0	Orange
Bromothymol blue	Yellow	6.0~7.6	Blue
Phenol-phthalein	Colorless	8.3~10	Pink red

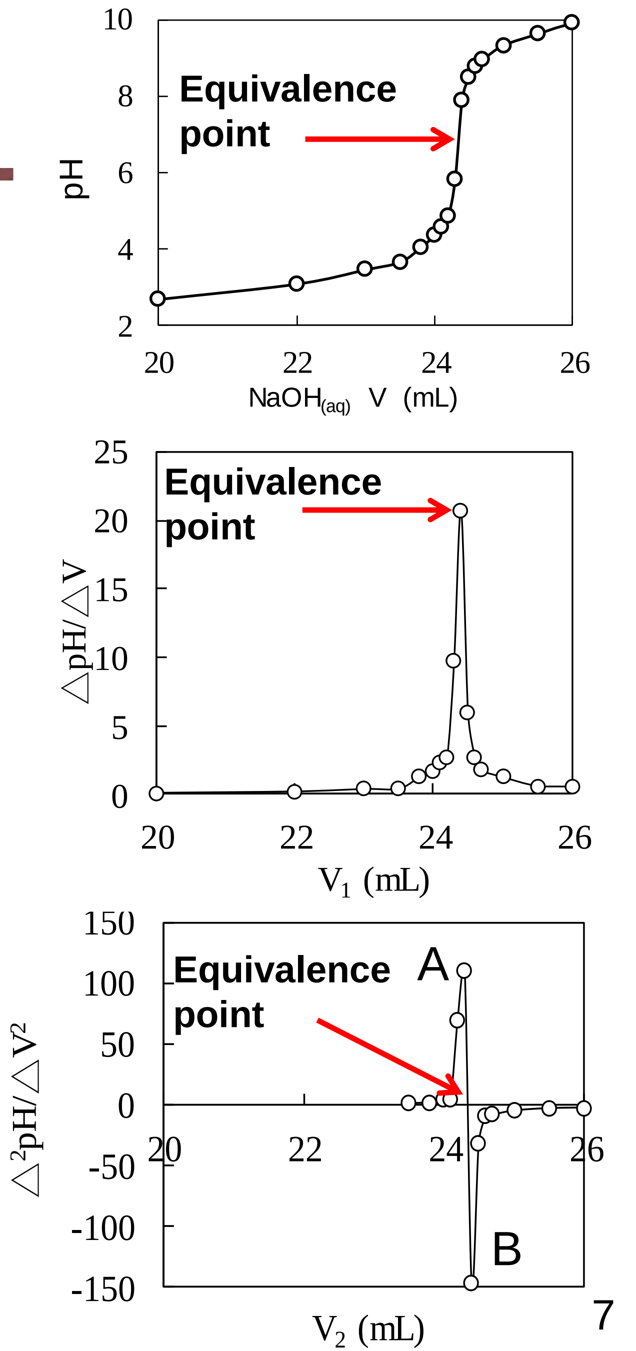
Weak acid / strong base titration curve

Equivalence Point

1. **Acid-base titration curve**
   The point on the curve with the maximum slope is the equivalence point

2. **First derivative of titration curve**
   The maximum point is the equivalence point

3. **Second derivative of the titration curve**
   X-intercept of line A-B is the equivalence point



Dissociation Constant of Weak Acid

- Acid-base neutralization reaction:

  $HA(aq) + OH^-(aq) \rightarrow H_2O(l) + A^-(aq)$

- Dissociation of weak acid

  $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

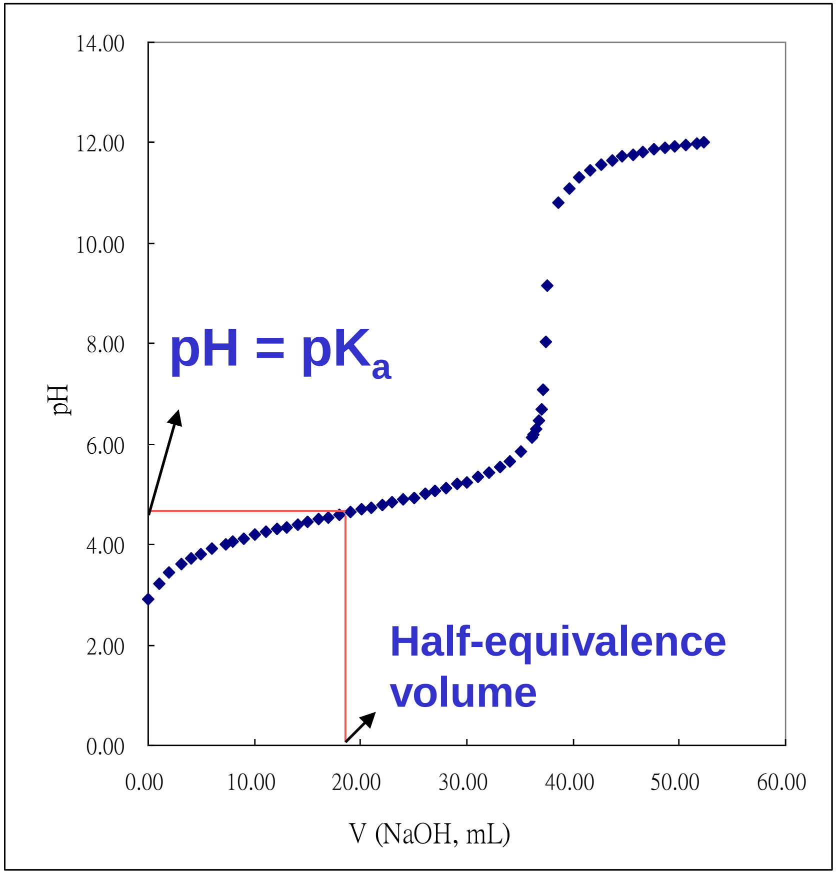
$$K_a = \frac{[\cancel{A^-}][H_3O^+]}{[\cancel{HA}]}$$

- **At half-equivalence point**

  $[HA] = [A^-]$; $[H_3O^+] = K_a$

  $pH = pK_a$

Weak acid – strong base titration curve



Dissociation Constant of Weak Acid

For example:

Equivalence volume = 37.50 mL

- Half-equivalence volume = 18.75 mL

  V = 18.00 mL, pH = 4.60

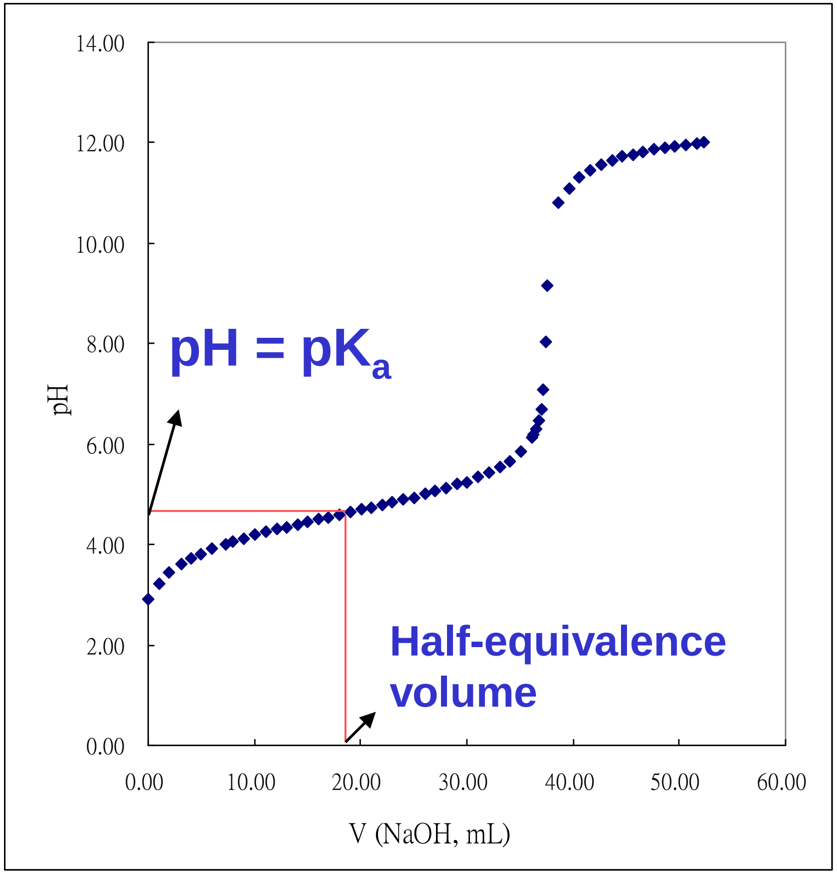
  V = 19.10 mL, pH = 4.65

- pH of the half-equivalence point = 4.63

$$K_a = \frac{\cancel{[A^-]}[H_3O^+]}{\cancel{[HA]}}$$

- pK_a = pH = 4.63, $K_a = 2.3 \times 10^{-5}$

Weak acid – strong base titration curve



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

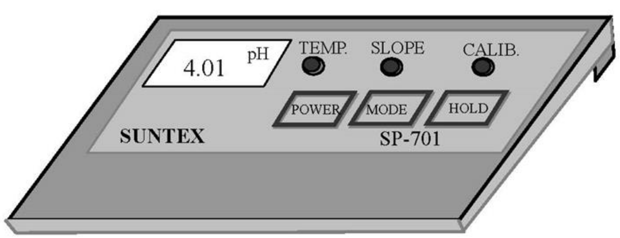
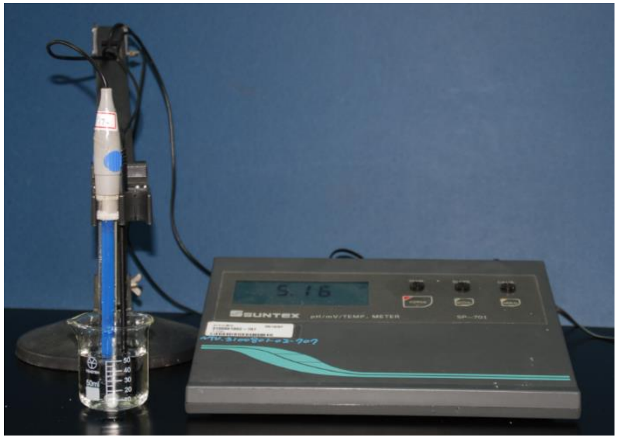
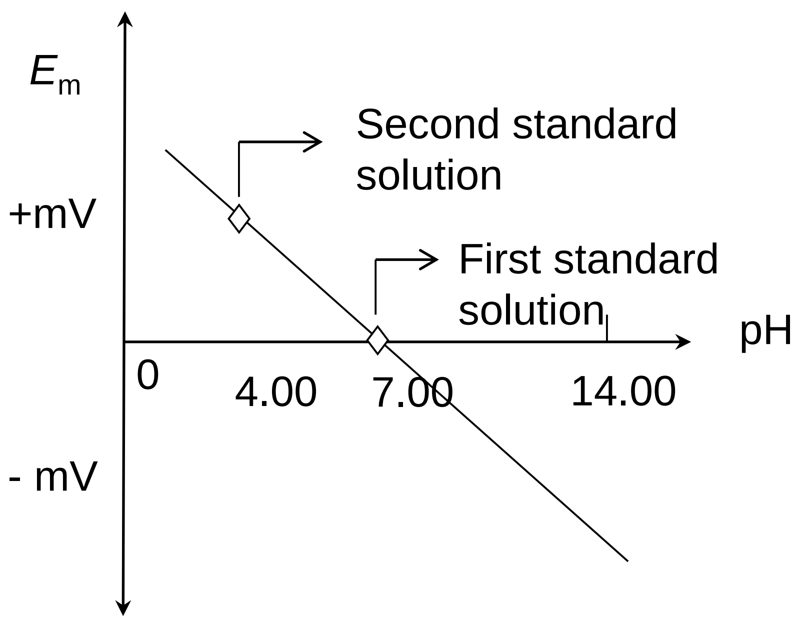


Fig. T16-1 pH meter in lab (SUNTEX SP-701)



Working Principles of pH Meter



$$E_m = \underbrace{K}_{\text{Reference electrode}} - \underbrace{2.3RT(pH)/nF}_{\text{Indicator electrode}}$$

$$E_m = K + mT \times (pH)$$

- 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

- 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

Experiment Tasks

1. Prepare NaOH(aq)
2. Standardize NaOH(aq)
3. Calibrate pH-meter
4. Titrate vinegar with NaOH(aq)

Step 1: Prepare 0.1 M NaOH Solution

- Measure 10 mL of 1 M NaOH to a 100 mL volumetric flask that **contains some DI water**
- Dilute to 100 mL

- Stopper and invert the volumetric flask several times to mix thoroughly
- Transfer to a 100 mL beaker (label properly)

- Rinse buret twice with **5 mL** NaOH(aq)
- Fill the buret
- Read initial volume of buret (V_i) to 0.01 mL

Step 2: Standardize NaOH Solution

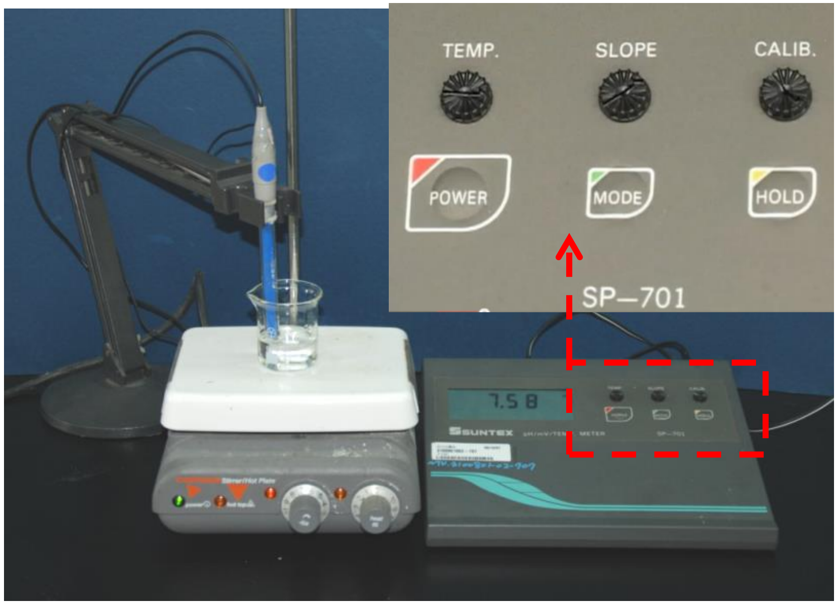
1. Dissolve with 50 mL DI water
2. Add 2 d of phenolphthalein
3. Titrate with 0.1 M NaOH

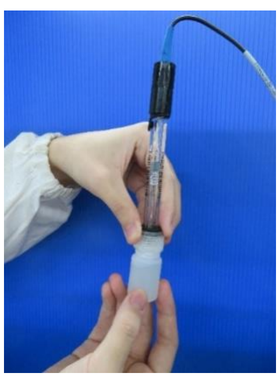
- Measure ca. **0.2~0.22 g** KHP with analytical balance
- Record accurate weight
- Place into a 125 mL Erlenmeyer flask

✓ KHP dissolves slowly

- Titrate the solution to appear pink and persist for 30 s
- Record V_i and V_f (to 0.01 mL)
- Carry out a duplicate test
- Calculate average concentration of NaOH

Step 3: Calibration of pH Meter





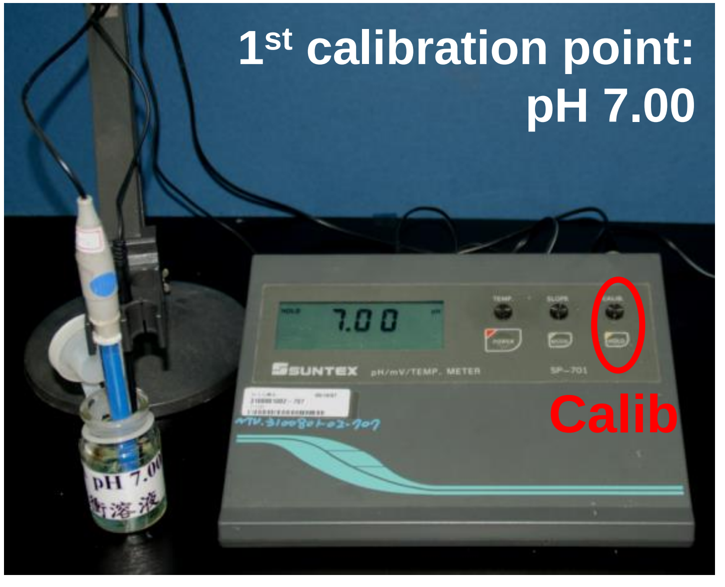
- Press the **"POWER"** button to turn on the pH meter. Let it **warm up** for at least **10 min**
- Press the **"HOLD"** button to suspend pH reading
- Remove the electrode cap by rotating it
- Use a wash bottle to rinse the electrode assembly, then wipe it dry gently with a tissue

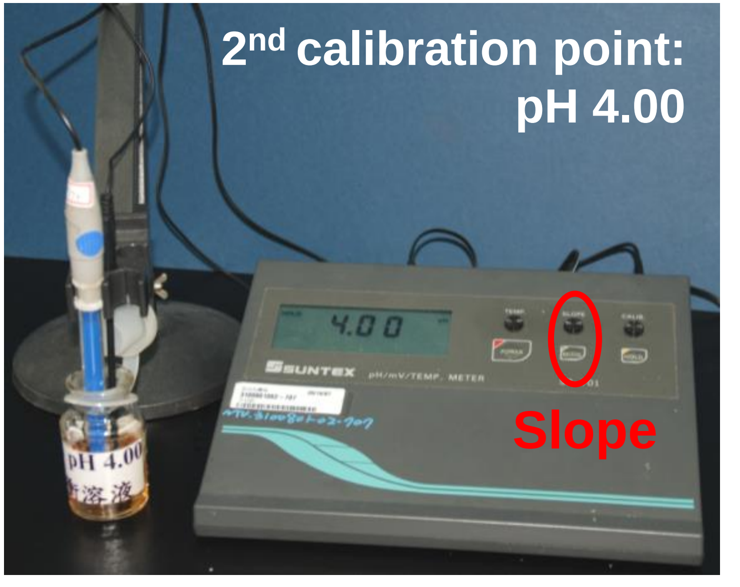
✓ Remove electrode cap and operate with care

✓ Each pH electrode assembly costs NTD 3000

Step 3: 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

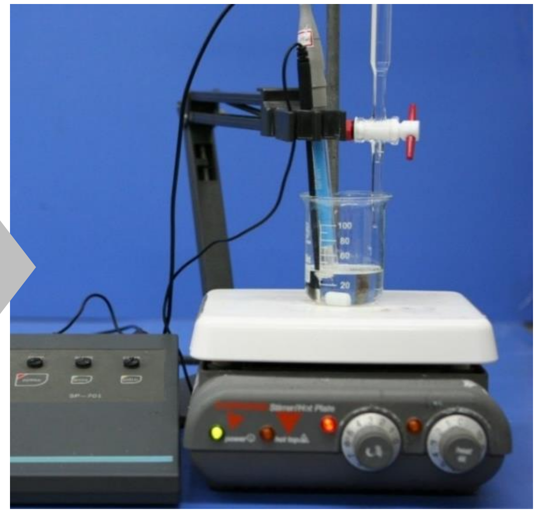


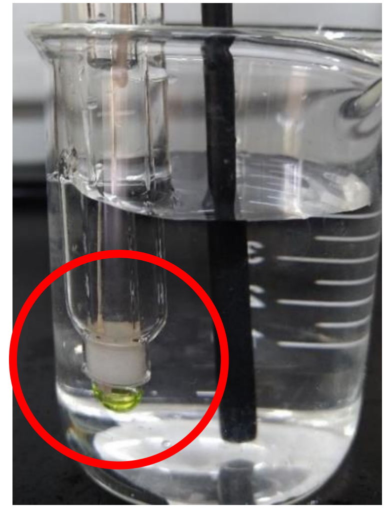


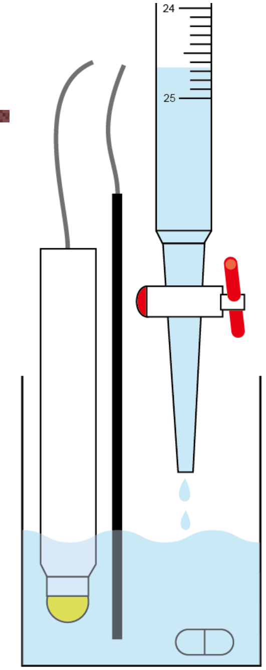
- Immerse both thermoprobe and pH electrode into **pH 7.00** buffer solution
- Adjust **Calib** knob until '**7.00**' is shown

- 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 4: Titration of Vinegar







- Transfer **2.5 mL** vinegar into a 100 mL beaker
- Record the **brand** and **concentration** of vinegar
- Add 40 mL of DI water
- Add 2 d. of phenolphthalein
- Place stirring bar, the electrode, and thermoprobe in solution
- Titrate with standardized 0.1 M NaOH and **record V_i, V_f**, and **pH value** after each addition
  - At pH < **5.5**: add ~ 1 mL of NaOH
  - At pH **5.5~10**: add ~ **0.2 mL** NaOH
  - At pH 10~11: add ~ 1 mL NaOH
- Observe and record the change in **color** of solution during titration

Clean-Up and Check-Out

- Place the pH electrode in **electrode-cap filled with 3 M KCl**
- 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 (<u>have an associate TA sign the check list</u>)
- Groups on duty shall stay and help clean up the lab
- This is a **Full Report** experiment:
  - **Have the lab notes and results checked by the TA, and hand in the report next week.**

Data Analysis of Report

1. **Average standardized concentration of NaOH**
2. **Experimental data**
3. **3 plots**
4. **3 equivalence points**

In Excel

$$C_{NaOH} \cdot V_{NaOH} = \frac{Mass_{KHP}}{204.22}$$

$$C_{NaOH}V_{NaOH} = C_{HOAc}V_2$$

5. **The molar concentration of acetic acid in vinegar (C_{HOAc})**
6. **Mass percent concentration**

- Compare with labels (assume density is same as water)

For example:

$C_M = 0.737\ M$

$$\frac{0.737\, {}^{mol}\!/_{L} \times 60.0\, {}^{g}\!/_{mol}}{1000\, {}^{mL}\!/_{L} \times 1.0\, {}^{g}\!/_{mL}} \times 100\% = 4.4\%$$

7. ***K_a* of acetic acid**

- Compare with theoretical value

Example of Data Sheet

Set data to two decimal places

$V_{titrant} = V_{read} – V_i$

0.35 – 0.35 = 0.00

1.35 – 0.35 = 1.00

Mark half- equivalence point

V_{ead} (mL)	$V_{titrant}$ (mL)	pH
0.35	0.00	2.94
1.35	1.00	3.34
2.35	2.00	3.60
3.35	3.00	3.78
4.35	4.00	3.92
5.35	5.00	4.03
6.35	6.00	4.13
7.35	7.00	4.22
8.35	8.00	4.31
9.35	9.00	4.39
10.35	10.00	4.47
11.35	11.00	4.54
12.35	12.00	4.62
13.35	13.00	4.70
14.35	14.00	4.78
15.35	15.00	4.86

V_{ead} (mL)	$V_{titrant}$ (mL)	pH
16.35	16.00	4.95
17.35	17.00	5.05
18.35	18.00	5.17
19.35	19.00	5.30
20.35	20.00	5.47
20.55	20.20	5.51
20.75	20.40	5.56
20.95	20.60	5.60
21.15	20.80	5.66
21.35	21.00	5.72
21.55	21.20	5.79
21.75	21.40	5.85
21.95	21.60	5.93
22.15	21.80	6.04
22.35	22.00	6.17
22.55	22.20	6.33
22.75	22.40	6.57
22.95	22.60	6.86
23.15	22.80	8.35
23.35	23.00	9.20
23.55	23.20	9.80
23.75	23.40	10.21
24.75	24.40	11.09

Mark equivalence point

Example of Data Analysis

$$V_1 = \frac{0.00 + 1.00}{2} = 0.50$$

$$V_2 = \frac{0.50 + 1.50}{2} = 1.00$$

$$\Delta pH/\Delta V = \frac{3.34-2.94}{1.00-0.00} = 0.40$$

$$\Delta(\Delta pH/\Delta V)/\Delta V_1 = \frac{0.26-0.40}{1.50-0.50} = -0.14$$

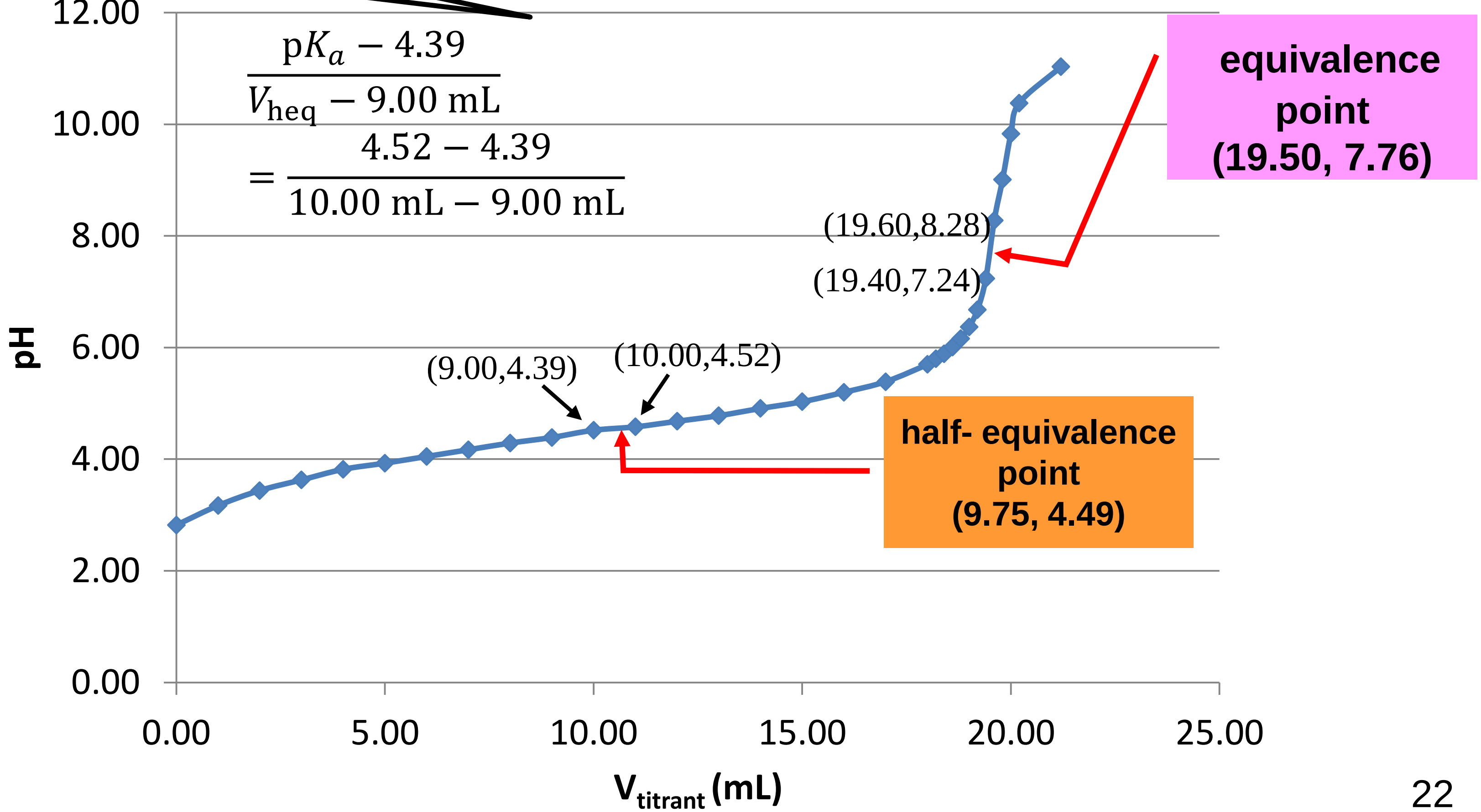
Titration curve		First derivative		Second derivative	
V_{NaOH}	pH	V_1	$\Delta pH/\Delta V$	V_2	$\Delta(\Delta pH/\Delta V)/\Delta V_1$
0.00	2.94	0.50	0.40	1.00	-0.14
1.00	3.34	1.50	0.26	2.00	-0.08
2.00	3.60	2.50	0.18	3.00	-0.04
……	……	……	……	……	……
22.40	6.57	22.50	1.45	22.60	30.00
22.60	6.86	22.70	7.45	22.80	-16.00
22.80	8.35	22.90	4.25	23.00	-6.25
23.00	9.20	23.10	3.00	23.20	-4.75

Mark equivalence point

Example of Titration Curve

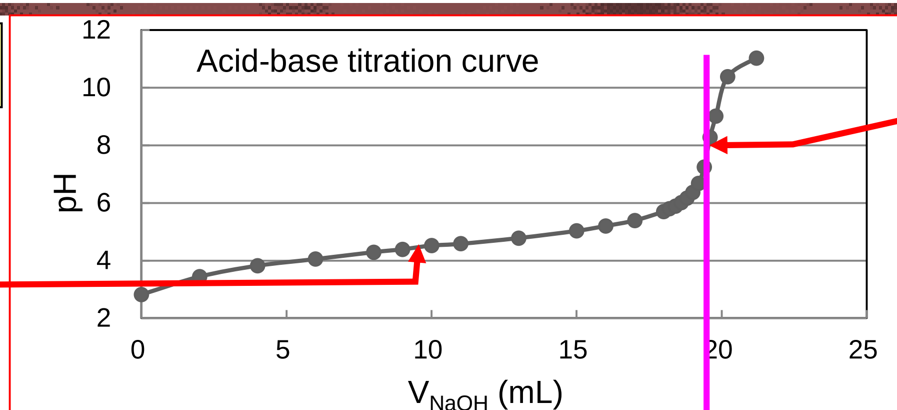
Mark
1. **equivalence point**
2. **half- equivalence point**

$$V_{\mathrm{eq}} = \frac{19.60\ \mathrm{mL} + 19.40\ \mathrm{mL}}{2} = 19.50\ \mathrm{mL}$$



Example of Figures

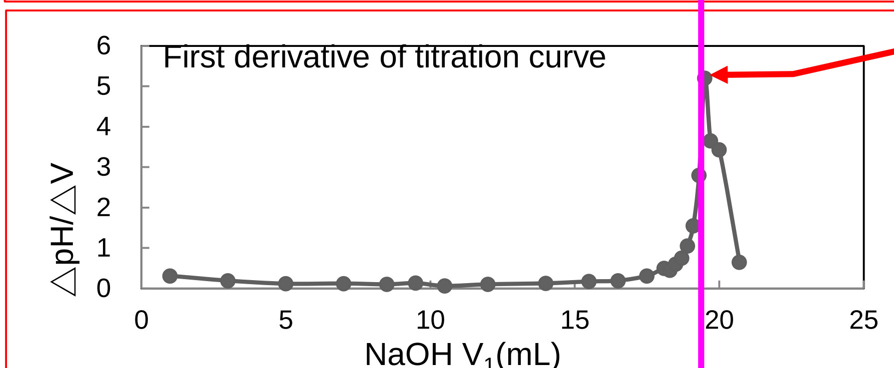
Figure 1



Mark half- equivalence point in fig. 1

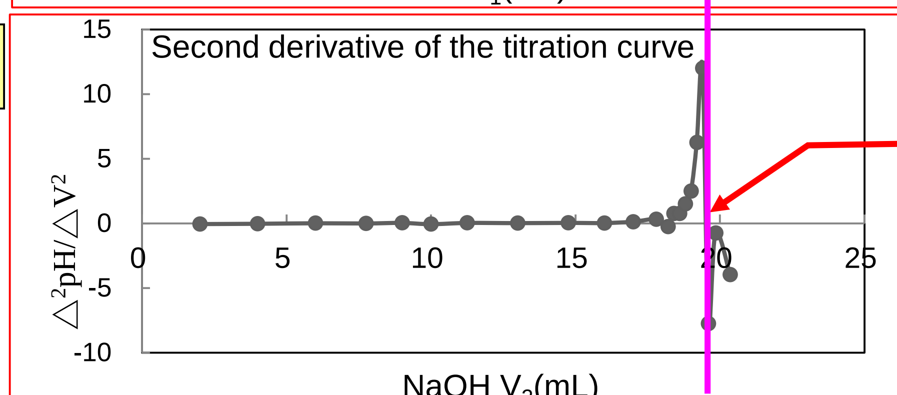
Mark equivalence point in 3 figures

Figure 2



Mark equivalence point in 3 figures

Figure 3



Mark equivalence point in 3 figures