Potentiometric Titration of Acid-Base

Last revised: 2025/02/04

Preparation

Collect the following items

- ❑ One magnetic stir bar (TA distribute)
- ❑ 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

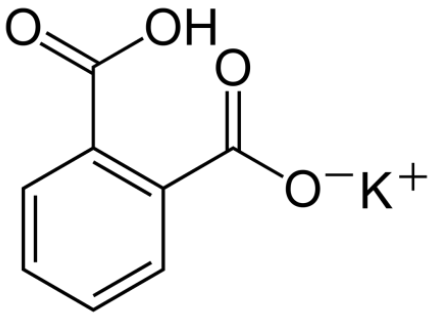
Objective and Principles

- **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 points by titration curves

Standardization of Acid or Base

- Primary standard: substance with high purity and high molar mass
- Secondary standard: standardized acid or base
- Common primary standard base: sodium carbonate (Na_2CO_3)
- Common primary standard acid: potassium hydrogen phthalate (KHP)
- KHP is a monoprotic weak acid with structure



- The neutralization reaction of KHP with NaOH in a **1:1** stoichiometric ratio

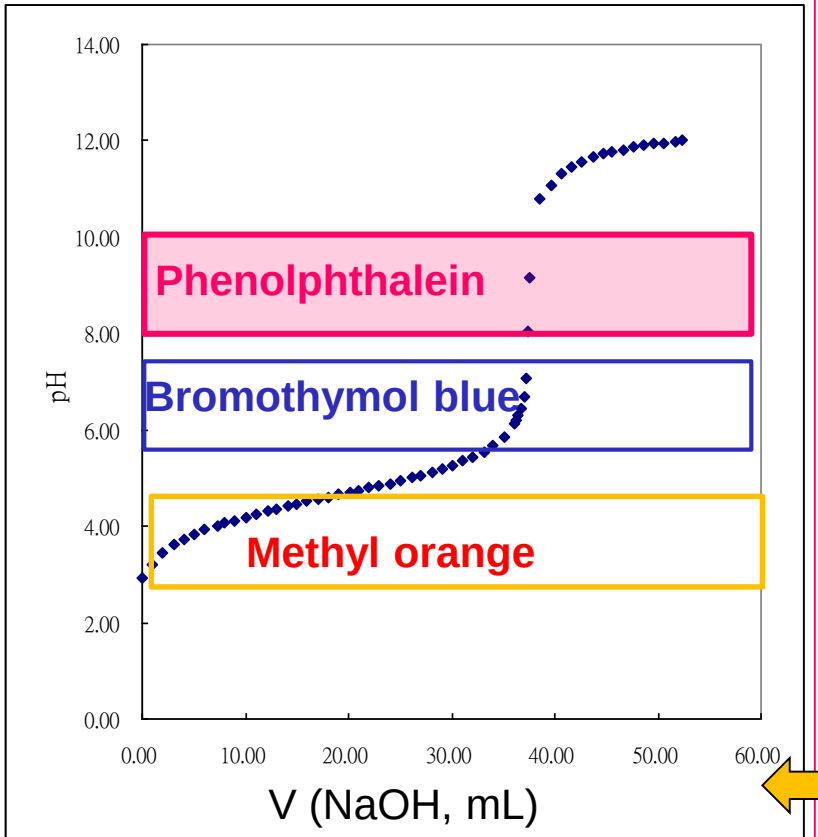
$$HOOCC_6H_4COOK(aq) + NaOH(aq) \rightarrow$$

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

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

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 equivalence point

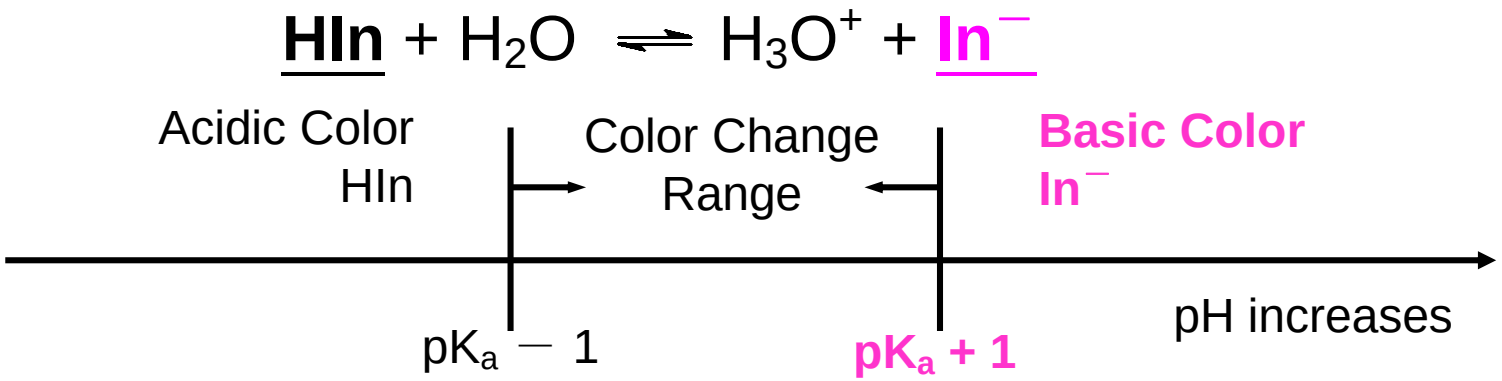


Indicator	Acid form	pH range	Basic form
Methyl orange	Red	3~4	Orange
Bromothymol blue	Yellow	6~7	Blue
Phenol-phthalein	Colorless	8~10	Pink red

Weak acid / strong base titration curve

Acid-base Indicator

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



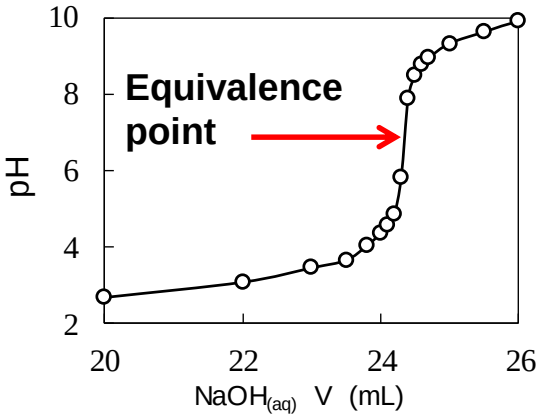
- According to the pH range of the equivalence point, choose the appropriate indicator to match the end-point with the equivalence point
- At the equivalence point, pH of the solution:
  - Strong acid/strong base titration: pH = 7
  - Strong acid/weak base titration: pH < 7
  - **Weak acid/strong base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

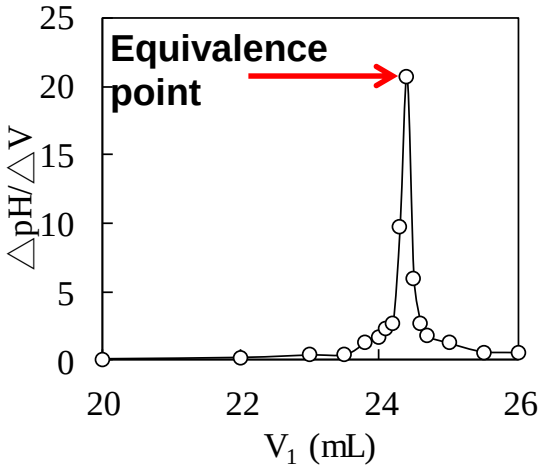
Equivalence Point

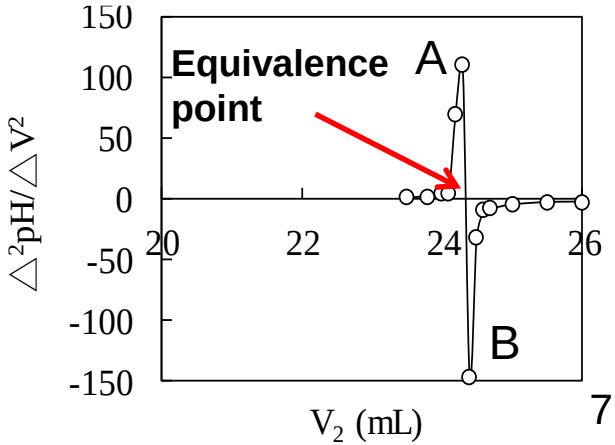
1. **Acid-base titration curve**
   The point on the curve with the maximum slope is the equivalence point

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

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

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

- **At half-equivalence point**

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

  therefore, **pH = pK_a**

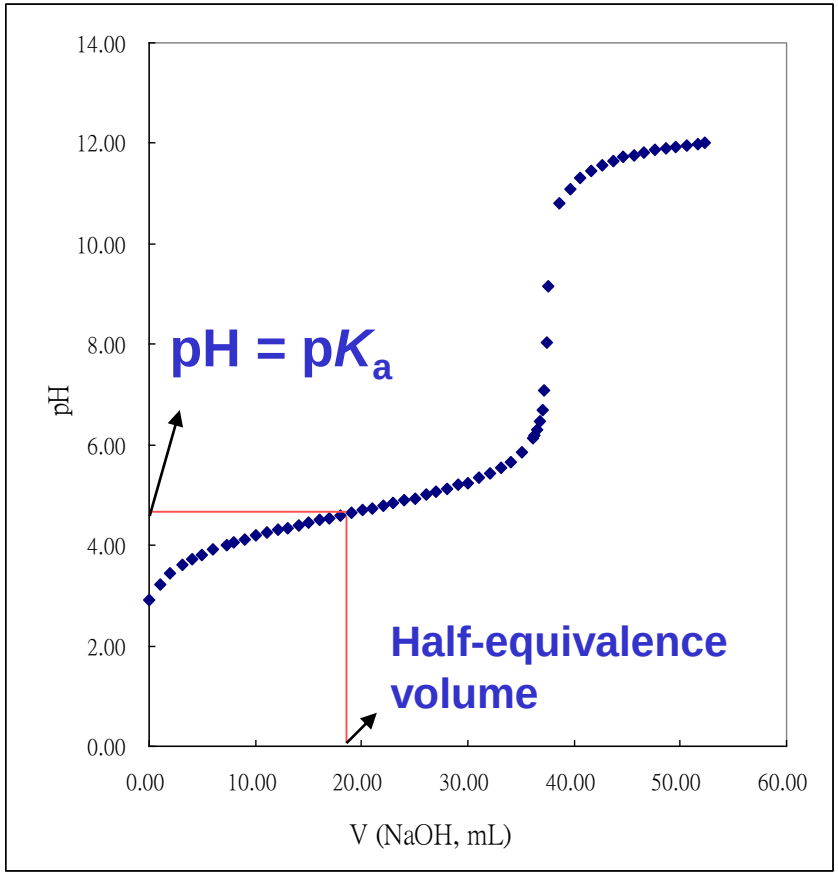
For example

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

Weak acid – strong base titration curve

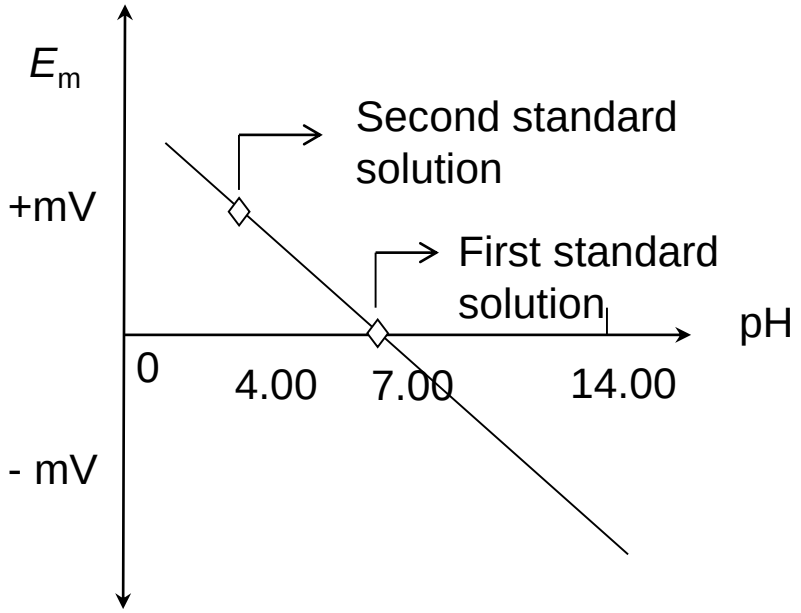


Working Principles of pH Meter

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

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

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

Reference electrode *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

Experiment Tasks



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

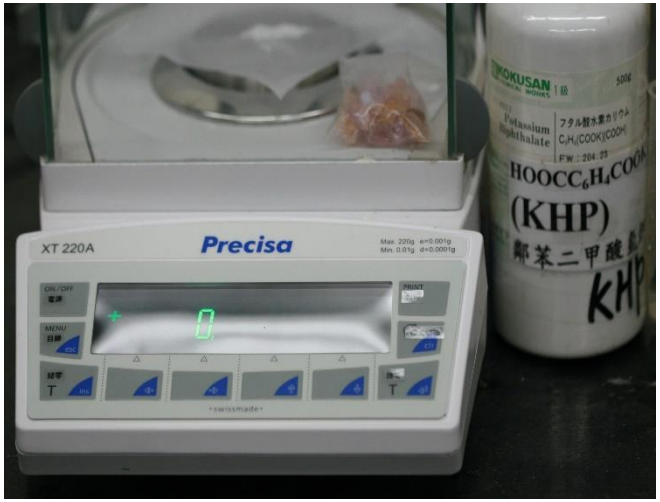
Step 1: Prepare 0.1 *M* NaOH Solution

- Measure 10 mL of 1 *M* NaOH
- Transfer 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 small portion of NaOH(aq)
- Fill the buret
- Read initial volume of buret (V_i) to 0.01 mL

Step 2: Standardize NaOH Solution

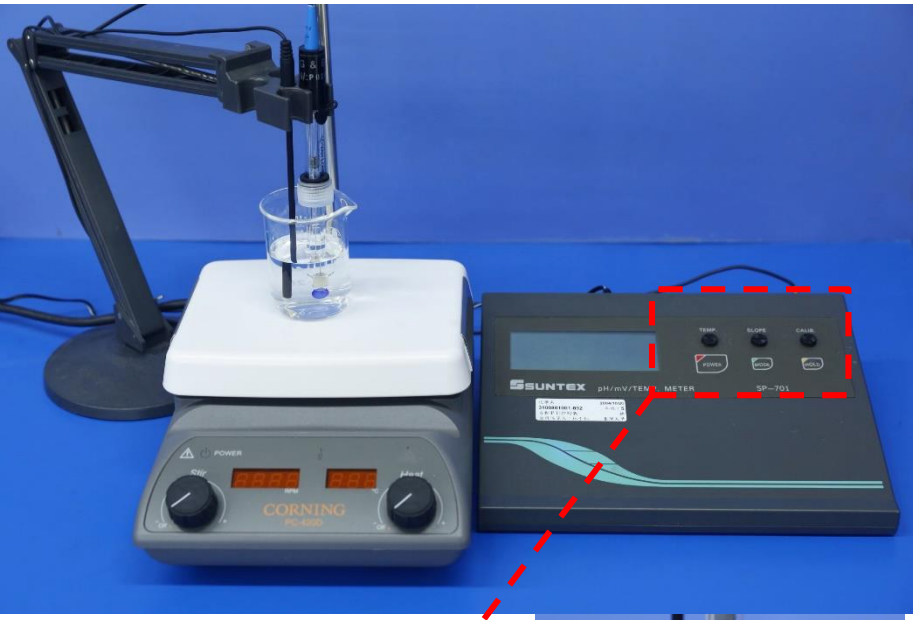


1. Dissolve with 50 mL DI water
2. Add 2 d of phenolphthalein
3. Titrate with 0.1 M NaOH

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

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

Step 3: Calibration of pH Meter

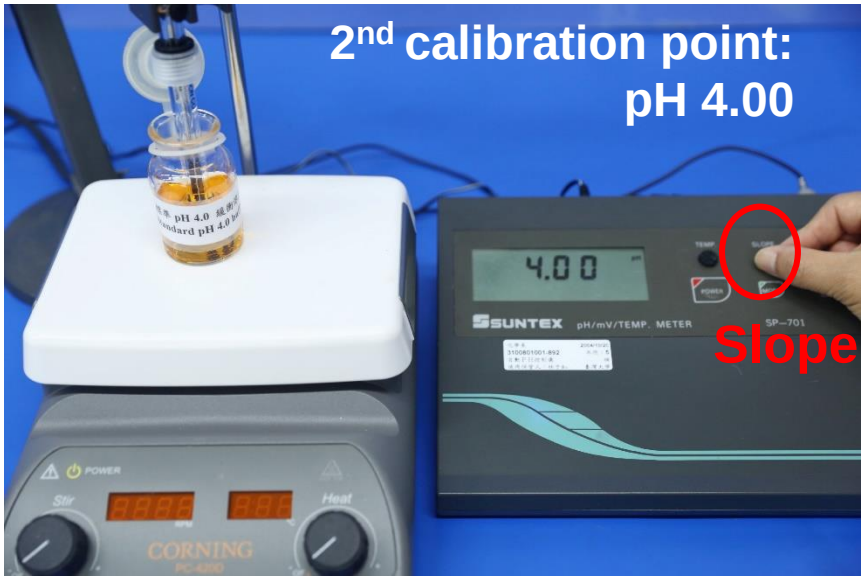


- Press the “POWER” button to turn on the pH meter. Let it warm up for at least 10 min
- Press the “HOLD” button to suspend pH reading
- Remove the electrode cap by rotating it
- Use a wash bottle to rinse the electrode assembly, then wipe it dry gently with a tissue

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

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

- Immerse the pH electrode in DI water (use a 100 mL beaker) or place electrode in plastic-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
- Dispose of the unused NaOH(aq) into indicated bottle
- 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:
  - **Have the lab notes and results checked by the TA, and hand in the report next week**
- Groups on duty shall stay and help clean up the lab

Example of Data Sheet

Round to two decimal places

$V_{titrant} = V_{read} - V_i$

E.g.: 9.30 – 9.30 = 0.00

11.30 – 9.30 = 2.00

Mark half- equivalence point

Mark equivalence point

V_{read} (mL)	$V_{titrant}$ (mL)	pH	Color
9.30	0.00	2.82	Colorless
11.30	2.00	3.44	Colorless
13.30	4.00	3.82	Colorless
15.30	6.00	4.05	Colorless
17.30	8.00	4.29	Colorless
18.30	9.00	4.39	Colorless
19.30	10.00	4.52	Colorless
20.30	11.00	4.58	Colorless
22.30	13.00	4.78	Colorless
24.30	15.00	5.03	Colorless
25.30	16.00	5.20	Colorless
26.30	17.00	5.39	Colorless
27.30	18.00	5.70	Colorless
27.50	18.20	5.80	Colorless
27.70	18.40	5.89	Colorless
27.90	18.60	6.01	Colorless
28.10	18.80	6.16	Colorless
28.30	19.00	6.37	Colorless
28.50	19.20	6.68	Colorless
28.70	19.40	7.24	Pink
28.90	19.60	8.28	Pink
29.10	19.80	9.01	Pink
29.50	20.20	10.38	Pink
30.50	21.20	11.03	Pink

Example of Data Analysis

Table 1

$$V_1 = \frac{(17.00 + 18.00)}{2} = 17.50$$

$$V_2 = \frac{(17.50 + 18.10)}{2} = 17.80$$

		First derivative		Second derivative	
V_{NaOH}	pH	V_1	$\Delta pH/\Delta V$	V_2	$\Delta(\Delta pH/\Delta V)/\Delta V_1$
17.00	5.39	17.50	0.31	17.80	0.32
18.00	5.70	18.10	0.50	18.20	-0.25
18.20	5.80	18.30	0.45	18.40	0.75
18.40	5.89	18.50	0.60	18.60	0.75
18.60	6.01	18.70	0.75	18.80	1.50
18.80	6.16	18.90	1.05	19.00	2.50
19.00	6.37	19.10	1.55	19.20	6.25
19.20	6.68	19.30	2.80	19.40	12.00
19.40	7.24	19.50	5.20	19.60	-7.75
19.60	8.28	19.70	3.65	19.85	-0.75
19.80	9.01	20.00	3.43	20.35	-3.96
17.00	5.39	17.50	0.31	17.80	0.32

Mark equivalence point

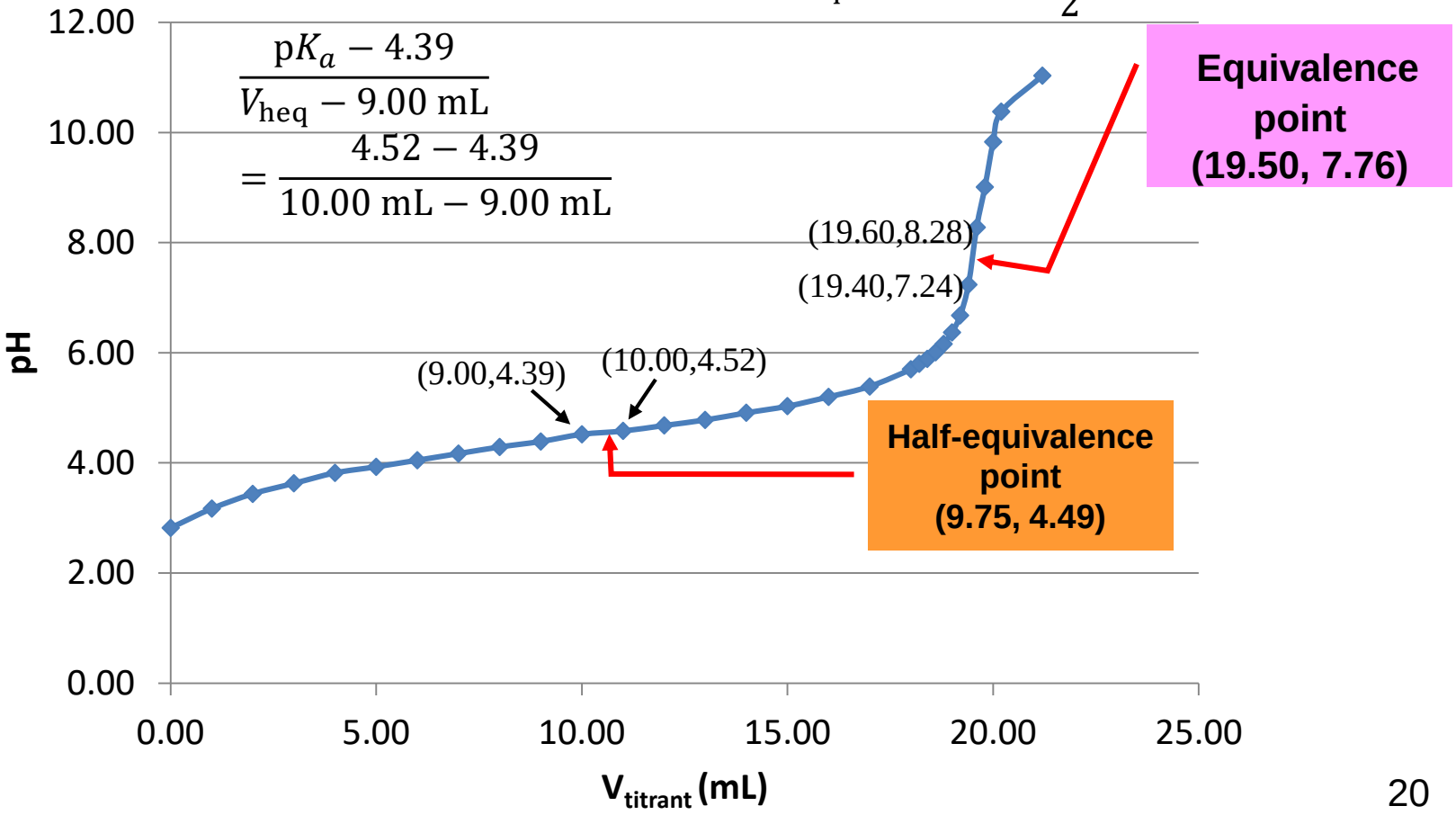
Example of Titration Curve

Figure 1. Titration curve

Mark
1. **Equivalence point**
2. **Half-equivalence point**

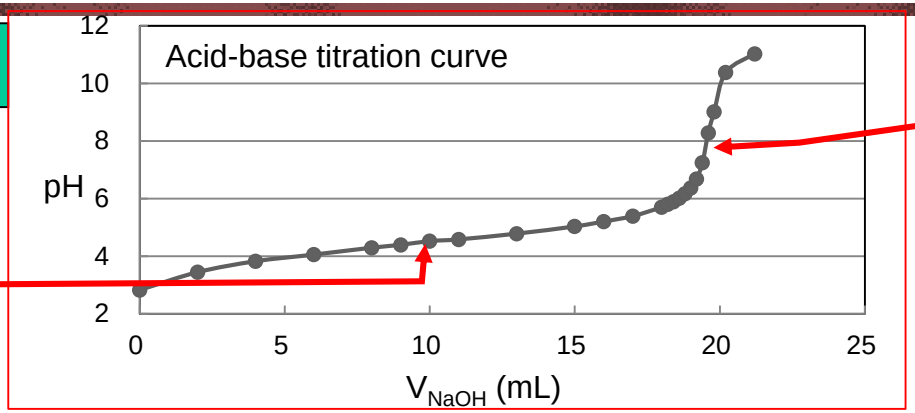
$$V_{\text{eq}} = \frac{19.60\ \text{mL} + 19.40\ \text{mL}}{2} = 19.50\ \text{mL}$$

$$\frac{\text{p}K_a - 4.39}{V_{\text{heq}} - 9.00\ \text{mL}} = \frac{4.52 - 4.39}{10.00\ \text{mL} - 9.00\ \text{mL}}$$



Examples of Figures

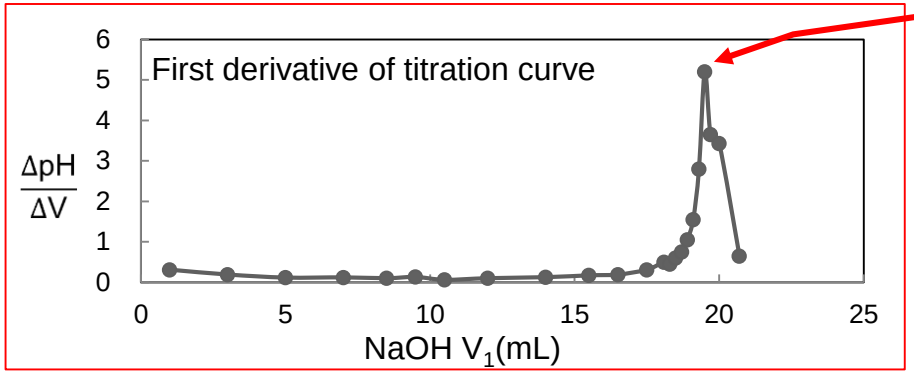
Figure 1



Equivalence point

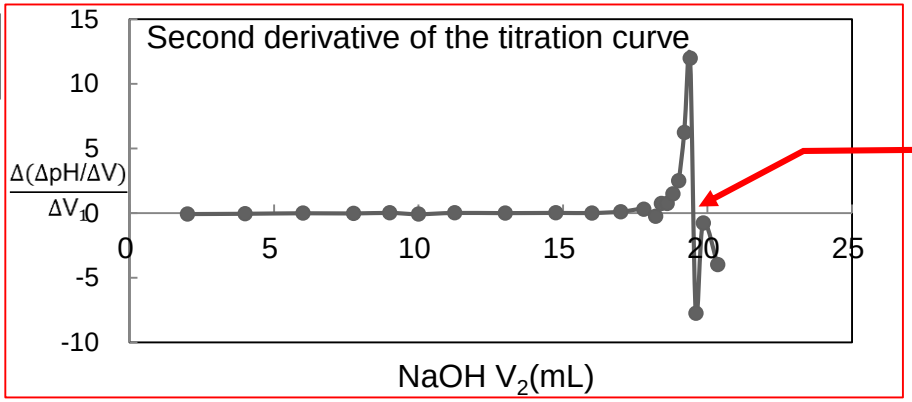
Mark half-equivalence point in Fig. 1

Figure 2



Equivalence point

Figure 3



Equivalence point

Data Analysis of Report

- Calculate **average standardized concentration of NaOH**
- Tabulate the **experimental data**, give **3 plots**, and indicate **3 equivalence points** in Excel
- Calculate **the molar concentration of acetic acid in vinegar (C_M)**

$$C_1V_1 = C_MV_2$$

- Calculate the **mass percent concentration** and compare with labels (assume density of the vinegar is 1.00 g/cm^3)

For example:

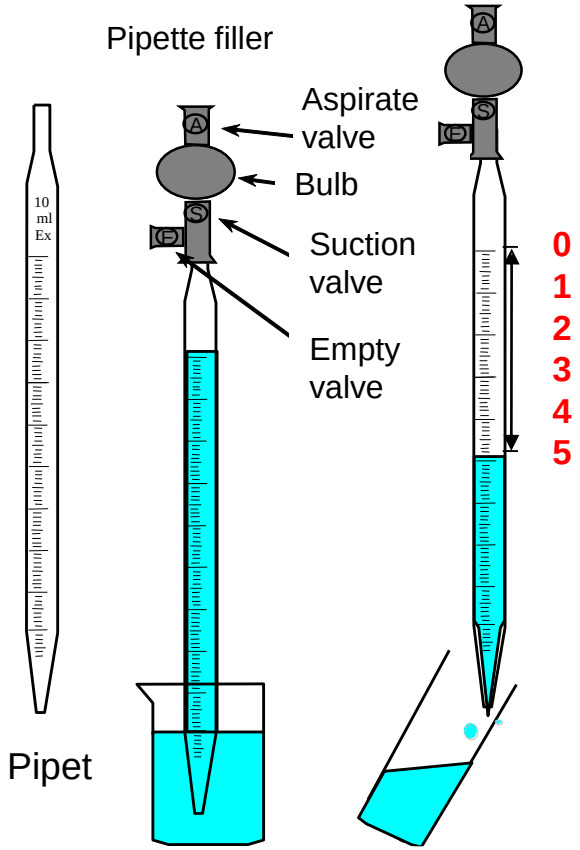
$$C_M = 0.737\ M \Rightarrow \frac{0.737\ {}^{\text{mol}}/_{\text{L}} \times 60.0\ {}^{\text{g}}/_{\text{mol}}}{1000\ {}^{\text{mL}}/_{\text{L}} \times 1.00\ {}^{\text{g}}/_{\text{mL}}} \times 100\% = 4.42\%$$

- Determine **K_a of acetic acid** from the half-equivalence point

T12.2 – Measuring (Graduated) Pipet

Deliver 5.00 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

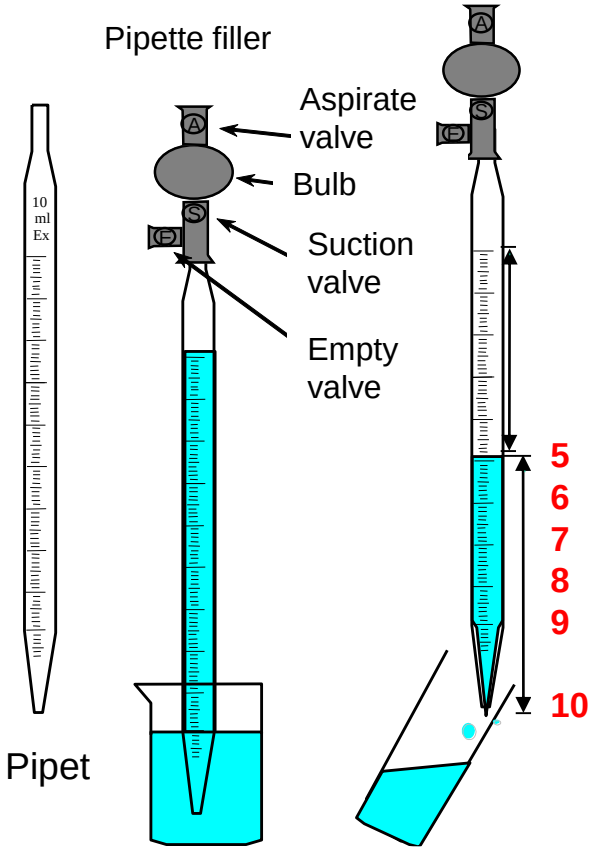


T12 Video (YouTube link)

T12.3 – Measuring (Graduated) Pipet

Deliver 5.00 mL solution – Method 2

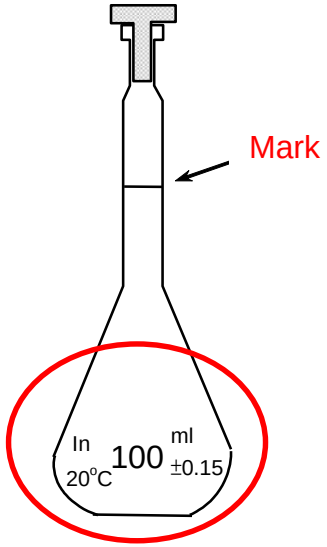
- Clean a 10 mL pipet and rinse it twice with small amount of the liquid to be transferred
- Press valv
- e **A** of the pipet filler and simultaneously squeeze the bulb to expel air from it, then insert the top of pipet gently into the pipet filler
- Bring the pipet tip below the liquid surface, press 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



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)