



## **Basics of Titration** (updated June 2019)

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This document covers the technique of acid-base titration. The specific skills relevant to this procedure are:

- proper use of a pipette and a burette
- ability to perform titrations with a high degree of accuracy and precision
- calculations and uncertainty analysis.

## 1 Background Theory

**1.1 A titration** involves measuring the exact volume of a reagent solution (the titrant) that is required to react completely with another reagent in solution; it is an example of volumetric analysis. In this experiment, the analysis involves 2 neutralisation reactions:

- (i) between a solution of a strong acid (HCl) and a solution of a strong base (NaOH)
- (ii) between a solution of a weak acid (acetic acid  $\text{CH}_3\text{COOH}$ ) and a solution of a strong base (NaOH).

### 1.2 Equivalence Point, End Point and Choice of Indicator

An acid-base titration is complete when exactly the right amount of base has been added to react with all of the acid in the solution. This point is referred to as the **equivalence point**.

Often it is not possible to directly observe the equivalence point, and so a chemical (an indicator) is added to the reaction to signal the end of the reaction by a colour change. The indicator is an organic dye which changes colour depending on pH. Usually this colour change is very abrupt, taking place with the addition of only one drop of the titrant. This abrupt colour change is referred to as the **end point**. Each acid-base indicator changes colour over a specific pH range.

The pH of the equivalence point depends on the nature of the acid and base being used in the titration (as the graphs on p. 3 indicate).

A good indicator for a particular reaction is one which gives an end point (colour change) very close to the equivalence point. In the following analysis:

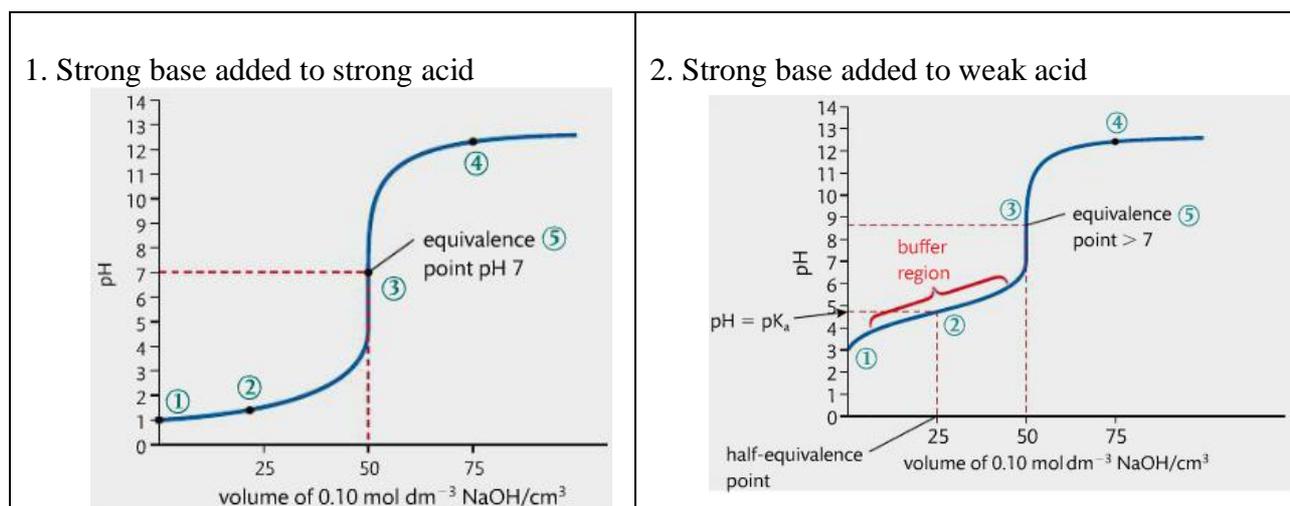
- (i) when NaOH (strong base) is added to HCl (strong acid), the equivalence point occurs at a pH of 7 (as seen in 1.3).
- (ii) when NaOH is added to acetic acid the equivalence point occurs at a pH of approximately 9 (as seen in 1.3).

**Phenolphthalein** is chosen as the indicator because:

- the colour change occurs over the pH range 8.3 – 10, and although this is slightly higher than the equivalence point for the HCl titration, the volume of base added to change the pH from 7 to 8.3 is miniscule; and
- the end-point is very clear as the colour change is from colourless to pink – good for beginning titrations.

### 1.3 Titration curves

In each case,  $0.1 \text{ mol L}^{-1}$  (or  $0.1\text{M}$  or  $\text{mol dm}^{-3}$ ) base is being added to  $50 \text{ mL}$  of  $0.1 \text{ mol L}^{-1}$  ( $0.1\text{M}$  or  $\text{mol dm}^{-3}$ ) acid.



## 2 Rationale for procedures used in titration

Titration is a procedure which a skilled practitioner can perform with a high degree of both precision and accuracy. For a simple acid-base titration such as that in the accompanying experiment, experimental error is approximately 0.2%. When the recommended protocols are performed carefully, this level of accuracy can be achieved consistently.

The rinsing protocols ensure that the solutions being measured are the same as those supplied, neither contaminated nor diluted. In the hands of a competent titrator, correct pipette transfer method, correct use and reading of the burette, and timely recognition of the end-point, ensure that volumes measured are both precise and accurate.

### Rinsing protocols

- Flasks are rinsed with DI water only
- Burette and pipette must be rinsed first with DI water, then with the appropriate solution.
- Both pipette and burette should be rinsed 3 times with DI water, then 3 times with the solution they will be used for. Small volumes (a few mL) should be used for each rinse.

### 3 Pipette preparation and use

**Safety Note:** Do not attempt to attach the pipette filler to a pipette until the teacher has demonstrated the correct procedure.

A pipette is used to measure and deliver an accurately-known volume of solution. The desired solution is drawn up into the pipette with a pipette filler. (Do NOT pipette by mouth.) Hold the pipette **near the top** and gently insert it into the bottom of the pipette filler. Moistening the top end of the pipette with a little water may make it easier to insert.



Holding the pipette near the bulb may cause it to break, causing severe injury to the hand.



Holding the pipette near the top is more secure and less likely to cause breakage and serious injury.

When drawing liquid up into the pipette, always ensure that the tip is well below the liquid surface, in order to avoid sucking air and possibly contaminating the filler.

**The pipette must be rinsed thoroughly** before it is used to measure and transfer the desired solution. First it is rinsed internally with distilled water (3 small rinses). Then it must be rinsed 3 times with the solution to be pipetted, as follows:

Transfer about 20mL of distilled water into a clean dry beaker and, using a pipette filler, draw a small amount (5mL) of water into the pipette. Remove the filler, then hold the pipette in a horizontal position, and roll it so that the rinse liquid contacts all parts of the internal walls of the pipette. Discard the rinse liquid. Repeat another 2 times with water, then 3 times with the solution to be pipetted.

**Measuring and transferring a sample:** Make sure that the flask to receive the pipetted liquid is close at hand (do not attempt to carry a filled pipette more than a few centimeters).

To fill the pipette, draw the solution up a centimeter or two above the mark using the pipette filler, and then wipe the lower part of the outside of the pipette with a clean tissue (to remove any droplets of solution adhering to the outside walls).

Ensure that the calibration mark is held at eye level, (you may have to bend your knees) and carefully release some solution (into a waste beaker) until the bottom of the meniscus just touches the mark. Touch the tip of the pipette against the wall of the waste beaker to remove any adhering drop.

Insert the tip of the pipette well inside the titration flask, remove the filler, and allow the solution to drain with the pipette held vertically. Then touch the tip of the pipette against the side of the flask at the liquid/air interface for 10 seconds to complete the draining. Do not blow any residue from the pipette.

#### 4 Burette preparation and use

**Safety Note:** Steps should be taken to avoid filling the burette above eye level. Different laboratories employ a range of methods to ensure this, including lowering the burette in the stand, or standing on a step to reach.

A burette is used when we are not sure of the exact volume of solution that will be required for reaction. The volume delivered by a burette can be measured to a high degree of accuracy and precision. A burette must be prepared properly before use.

**To prepare a burette:** Firstly, it is rinsed thoroughly (3 small rinses) with distilled water, to remove any contaminants that may react with the titrant. Use your wash bottle to add about 5 mL of water to the burette. Hold the burette horizontally and rotate/roll it so that the water contacts all parts of the internal wall, and then discard the rinse liquid. It must then be rinsed 3 times with the titrant by pouring 15 - 20 mL of solution into a clean dry beaker, and using a funnel to transfer a few millilitres into the burette for each of 3 rinses. This rinsing ensures that there is no residual water to dilute the titrant when the burette is filled.

**To fill the burette:** Procedure may vary, depending on the steps taken to keep the funnel below eye level.

Clamp the burette vertically. Place a waste beaker under the tap, place a clean dry funnel in the top, and open the tap briefly as you pour solution in. This will allow some of the solution to run out of the burette, to flush any air bubbles from the tap. Close the tap and fill the burette to near (below) the 0 mark. **Remove the funnel.**

Record the initial burette reading (to 2 decimal places) before titration, and the final burette reading at the end of the titration. There is no need to fill the burette exactly to the zero mark; the volume of solution delivered is calculated by subtracting the initial reading from the final reading.

## 5 Performing a titration

To use the burette tap in the traditional way, the fingers of the left hand should wrap around the burette from behind (away from the operator), with the thumb in front (towards the operator). In order to mix the reactants, the right hand should swirl the flask as titrant is added.

In the early stages of the titration, titrant can be run into the flask in a continuous stream. The indicator will change colour locally, but in the early stages, the colour will quickly revert to the initial colour on mixing. Periodically, rinse down the walls of the beaker with small volumes of distilled water; this is particularly important close to the end point.

As the indicator colour change becomes a little more persistent, switch to adding single drops. When approaching the end point, add only PART of a drop of titrant at a time. Do this by carefully opening the tap until a small droplet (eg about half a drop) forms and hangs on the tip of the burette; then rinse this partial drop into the flask with water from the wash bottle. The end-point is reached when the desired indicator colour persists for 10 seconds after mixing.

Once the end point is reached, the burette should be read to TWO decimal places of a millilitre (you must estimate the second decimal place value).

When reading the burette:

- use a burette reader card to increase visibility of the meniscus
- ensure that your eyes are level with the meniscus,
- remember that the zero mark is at the top (the scale values increase DOWN the burette).

## 6 Experiment

### Finding the molarity of a solution of acetic acid given a standard solution of HCl

#### 6.1 Aim

- (i) to standardise a solution of NaOH by titrating it with a standard solution of hydrochloric acid (HCl)
- (ii) to use the standardised NaOH to find the molarity of a solution of acetic acid.

#### 6.2 Risk Assessment

The titration operation involved in this competition is not inherently high risk; however, precautions should be employed to minimise the low level of risk still further.

*All participants should wear a lab. coat and safety glasses, and suitable footwear.*

#### Apparatus

By far the highest risk is in the improper use of **pipette fillers**, as, if the pipette is inserted while held by the stem far from the filler, the pipette may break and cause serious injury to the hands. **It is essential that all students be thoroughly taught the correct way to use a pipette filler** (see Section 4).

When filling **burettes**, the top of the burette should be below the level of your eyes in order to avoid accidentally spilling solution onto your face and eyes. A lab step can be used, or the burette can be lowered and kept below eye level while being filled.

**Pasteur pipettes** can potentially cause injury to another person if waved through the air. This should never happen. Serious injury would occur only if an eye was struck, and safety glasses should prevent this.

It is possible that any other of the glass apparatus may break and cause minor cuts. Clamping a burette too tightly may cause it to snap. Apparatus dropped on the floor will break, and minor cuts are possible.

#### Solutions

Acid and base solutions provided are approx.  $0.1 \text{ mol L}^{-1}$ . This is too dilute to cause skin damage if spilled on the skin. If spilled on clothing and not rinsed off, it may eventually cause holes to form in the cloth. Any spills on skin or clothing should be rinsed off immediately. If any is splashed on the eyes (which should be prevented by safety glasses), it would sting but there would be no lasting damage if rinsed away rapidly. If any of the solutions were to enter the mouth (unlikely if pipette fillers are used), the taste would be unpleasant, but again no tissue damage would occur. The mouth should be rinsed, and if solutions were swallowed, copious water should be drunk.

### 6.3 Apparatus – per group of 3

- 1 x 500 mL bottle each of approx.
  - 0.1 mol L<sup>-1</sup> HCl,
  - 0.1 mol L<sup>-1</sup> NaOH and
  - 0.1 mol L<sup>-1</sup> CH<sub>3</sub>COOH
- 1 x bottle phenolphthalein
- 3 x Pasteur pipettes
- 3 x wash bottles and supply of DI water
- 3 x 20 or 25 mL bulb pipettes
- 3 x 50 mL burettes, retort stands and clamps
- 6 x 250 mL conical flasks
- 9 x 100 or 250 mL beakers
- 3 x pipette fillers
- 3 x funnels for filling burettes
- 3 x white sheets of paper/tiles
- 3 x burette reading cards

### 6.4 Experimental Procedure

Distilled/deionised water should be used from a wash bottle only and should not be wasted. Good accuracy requires careful measurement of samples, along with care and patience in the titrations. It is important that you assess your results as you proceed. If your titration volumes for a particular analysis vary significantly, then your technique is faulty. For each analysis, a moderately competent student should be able to obtain titration volumes that agree within 1% (about 0.2 mL in this instance) and this should be your target. If necessary and if time permits, you may perform extra titrations in an attempt to improve precision, discarding the less satisfactory results.

#### (i) Standardisation of Hydrochloric Acid

1. Rinse a 20 or 25 mL bulb pipette with distilled water (3 small rinses) and then 3 times with small volumes of HCl solution. (See Section 3 *Pipette* above).
2. Rinse two 100mL or 250mL conical flasks with distilled water (3 small rinses). Pipette 20 or 25mL of the HCl solution into each flask. (See Section 3 *Pipette* above). Then add three drops of phenolphthalein indicator to each flask.
3. Prepare the burette by rinsing it first with distilled water (3 small rinses), and then with NaOH solution (3 small rinses). (See Section 4 *Burette* above). Make sure that all internal walls of the burette are rinsed with NaOH. Discard the rinse liquid.
4. Fill the burette with NaOH, ensuring there are no air bubbles remaining in the tip. Record the initial reading of the burette (to two decimal places) in the *Results Sheet* (Section 7). Run the base out of the burette into the conical flask containing the acid, mixing the contents of the flask by swirling with your free hand. The indicator will turn pink locally, but will revert to colourless on mixing. When the pink colour becomes more persistent you are approaching the end point. Wash the inside walls of the flask with small volumes of distilled water from your washbottle to ensure that no unreacted acid or base is adhering. When the end point (a pale pink that persists for 10 seconds before fading) has been reached, stop adding NaOH and record the final burette reading in your *Results Sheet* (Section 7).

5. Repeat the titration using the second flask of acid. This time, add the NaOH rapidly until the volume added is about 0.5 - 1.0mL less than the expected end point (determined in the first run), then add the NaOH one drop at a time, and finally only part of a drop at a time. After each addition, wash the sides of the flask down with distilled water to ensure that there is no base on the walls of the flask. Remember the change in colour takes place with the addition of only one drop or less of the titrant. It is very important to add the NaOH slowly close to the end point so that the precise volume of NaOH can be determined.
6. Do a further 2 titrations by repeating steps 2, 4 and 5 above, refilling the burette as necessary.
7. Select the titres that are in agreement with each other (ideally within 1% - varying by only about 0.2mL), and calculate the average titre.
8. Calculate the molarity of the NaOH (for assistance with calculations see Section 8).

**(ii) Finding the molarity of acetic acid**

Repeat steps 1, 2, 4 and 5, 6 and 7 substituting acetic acid for HCl.

## 7 Results Sheet

### For HCl and NaOH

Titration number	Burette Readings (record to 2 dec. places)		Volume delivered V <sub>2</sub> -V <sub>1</sub> (mL)
	Initial V <sub>1</sub> (mL)	Final V <sub>2</sub> (mL)	
1			
2			
3			
4			
			<b>Average:</b>

### For acetic acid and NaOH

Titration number	Burette Readings		Volume delivered V <sub>2</sub> -V <sub>1</sub> (mL)
	Initial V <sub>1</sub> (mL)	Final V <sub>2</sub> (mL)	
1			
2			
3			
4			
			<b>Average:</b>

**Note:** The averages should be recorded to 3 decimal places (i.e. one more digit than the correct number of significant figures).

## 8 Calculations

### 1. Standardisation of NaOH

$$\text{Molarity of NaOH} = \frac{(\text{molarity of HCl}) \times (\text{volume of HCl})}{(\text{volume of NaOH})}$$

### 2. CH<sub>3</sub>COOH

$$\text{Molarity of acetic acid} = \frac{(\text{molarity of NaOH}) \times (\text{volume of NaOH})}{(\text{volume of acetic acid})}$$

### 3. Check Formula – only valid if the same pipette was used for both sets of titrations

$$\text{Molarity of acetic acid} = \frac{(\text{molarity of HCl}) \times (\text{volume of NaOH to neutralise acetic acid})}{(\text{volume of NaOH to neutralise HCl})}$$

## Appendix 1: Sources of Random and Systematic Error in Titrations

### Systematic Errors

Source of error	Steps to reduce error
Inaccuracy of <b>volumetric glassware</b>	Careful calibration of pipette, burette and volumetric flask (if using). This may not be possible in the school lab.
	Use A grade volumetric apparatus – cost may be prohibitive for schools
	Use large volumes e.g 20 or 25 mL pipette, to reduce relative error
	Do 2 sets of titrations (standardisation followed by analysis of an unknown as in the accompanying procedure); errors due to lack of calibration will ‘cancel out’ to a large extent providing the same volumetric glassware is used throughout.
<b>Endpoint detection</b> when using an indicator, resulting from the fact that end point and equivalence point may not be at the same pH, and because colour change can be slow to develop.	Complete 2 sets as above, being careful to titrate to a consistent endpoint colour for each titration.
<b>Inaccuracy of molarity of standard solution</b>	Use a primary standard (e.g AR grade potassium hydrogen phthalate for an acid, or AR grade anhydrous sodium carbonate for a base). If possible, ensure that balance and volumetric flask are correctly calibrated.

**Random Errors:** In general, random errors can be reduced by ensuring that standard laboratory protocols are followed carefully. By their very nature, random errors cannot be eliminated completely, but their effect can be reduced by performing replicates. Successive titres should agree to within 1% of each other (0.2 mL for a 20 mL titre).

Source of error	Steps to reduce error
Misjudgement of indicator colour	Add titrant slowly when colour change starts to become more persistent around added drops, swirl flask contents constantly. Perform at least 4 replicate titrations, aiming for concordance.
Inconsistency in reading burette	Lighting for start and finish points should be the same; avoid parallax error; place a burette reading card behind the meniscus.
Contamination or dilution of solutions	Flasks should be rinsed with DI water only. Pipette and burette should be rinsed 3 times with DI water, then 3 times with the solution they will measure and transfer.
Amount of indicator	This should be consistent across all titrations; 3 drops is usual.
Dirty volumetric glassware – reaction with reactants; not draining properly.	Ensure that all glassware is properly cleaned and rinsed before beginning any analysis. Check that liquid does not cling to inside walls.
Air bubble in burette tip	Begin filling with the tap slightly open to flush out air before closing tap.
Failure to remove funnel	Remove funnel

## Appendix 2: Worked example of uncertainty analysis for a single titration

(as per Syllabus Chemistry 2019 v1.3 Unit 1 Topic 3 requirements)

20.00 mL of 0.1000 mol L<sup>-1</sup> HCl was neutralised by NaOH of unknown concentration. Use the data below to find the concentration of NaOH, including the associated uncertainty.

Pipette volume  $V_{\text{HCl}} = 20.00 \pm 0.03$  mL (uncertainty will vary with pipette used)

Molarity of HCl = 0.1000 mol L<sup>-1</sup>

Initial burette reading  $V_1 = 2.22 \pm 0.02$  mL (with 0.1 mL graduations, it is possible to read to +/- 0.02 mL with practice)

Final burette reading  $V_2 = 20.79 \pm 0.02$  mL

$$V_{\text{NaOH}} = V_2 - V_1 = 18.57 \text{ mL}$$

The uncertainty in volume NaOH is given by **adding uncertainties**.

$$\text{Thus } V_{\text{NaOH}} = 18.57 \pm 0.04 \text{ mL}$$

Because the calculation of  $M_{\text{NaOH}}$  requires multiplication and division, we must **add the % uncertainties** of the measurements involved.

$$\% \text{ uncertainty in } V_{\text{HCl}} = \frac{0.03}{20.00} \times 100 = 0.2\% \text{ (% uncertainty given to 1 sig. fig.)}$$

$$\% \text{ uncertainty in } V_{\text{NaOH}} = \frac{0.04}{18.57} \times 100 = 0.2\%$$

Assuming that the molarity of HCl is taken as exactly 0.1000 mol L<sup>-1</sup> with 0 uncertainty:

$$\text{Overall \% uncertainty in } M_{\text{NaOH}} = 0.2\% + 0.2\% = 0.4\%$$

$$M_{\text{NaOH}} = \frac{M_{\text{HCl}} \times V_{\text{HCl}}}{V_{\text{NaOH}}}$$

$$M_{\text{NaOH}} = \frac{0.1000 \text{ mol L}^{-1} \times 20.00 \text{ mL}}{18.57 \text{ mL}}$$

$$M_{\text{NaOH}} = 0.1077 \text{ mol L}^{-1} \pm 0.4\%$$

$$M_{\text{NaOH}} = 0.1077 \pm 0.0004 \text{ mol L}^{-1}$$

Note that all raw data used was given to 4 significant figures, and that the answer is also given to 4 significant figures. The absolute uncertainty indicates that the final digit only is in doubt.

### Appendix 3: Worked example of uncertainty analysis for replicate titrations

As is usually the case, **replicate titrations of the same pair of solutions were carried out.** The titres were as follows:

$$18.61 \quad 18.53 \quad 18.55 \quad 18.59 \rightarrow \text{mean} (\bar{x}) = 18.570 \text{ mL} = V_{\text{NaOH}}$$

In this case the **sample deviation** for the average titre is calculated as follows:

$$\text{Sample deviation} = \sqrt{\frac{\sum(x - \bar{x})^2}{(n - 1)}}$$

$$s \text{ or } s_{n-1} = \sqrt{\frac{(0.02)^2 + (0.02)^2 + (0.04)^2 + (0.04)^2}{4 - 1}}$$

$$s \text{ or } s_{n-1} = 0.04 \text{ (to 1 sig fig)}$$

$$\text{Thus \% uncertainty for the average titre} = \frac{0.04}{18.57} \times 100 = 0.2\%$$

$$\% \text{ uncertainty in } M_{\text{NaOH}} = 0.2\% + 0.2\% = 0.4\% \text{ (sum of uncertainties in } V_{\text{NaOH}} \text{ and } V_{\text{HCl}})$$

$$M_{\text{NaOH}} = 0.1077 \pm 0.0004 \text{ mol L}^{-1}$$

Note that the degree of precision in the actual titres will influence the magnitude of uncertainty; greater precision will give reduced uncertainty.