changes which accompany dilution to take place before the solution is made up to volume. Solvent is now added to bring the solution to the calibration mark. The last few drops may be added with a dropper. The stoppered flask is repeatedly inverted to obtain uniform mixing—at least 15 inversions, more if the solution is viscous.

Volumetric flasks should never be placed on a flame or hot plate to dissolve a difficult solute. This can cause permanent changes in the volume of the flask. If a solute is difficult to dissolve, carry out the dissolution in a beaker or flask and then quantitatively transfer the solution to the volumetric flask and bring to the final volume. Ultrasonic bath cleaners can be used to dissolve solutes in volumetric flasks.

Prepare the solution at some temperature **-** usually room temperature. The volume of the solution and consequently the concentration of the solution is dependent on the coefficient of expansion of the solution. (If all volumes are measured in glass equipment, then it is the difference between the coefficient for the solution and the coefficient for glass that is significant.) Around room temperature the coefficient of expansion for dilute aqueous solutions is about 0.024%/$^o$C. A change of 4$^o$C, therefore, corresponds to a change in concentration of about 1 ppt.

### Burets

The calibration lines on a 50 ml. buret are at 0.10 ml. intervals. To obtain maximum precision, volumes are estimated to 0.01 ml. The calibrations on the 10 ml. micro-burets are at 0.020 ml. intervals and volumes are estimated to 0.002 ml.

When using a 50 ml buret, the standard deviation of a single buret reading is assumed to be ± 0.02 ml. The two readings required in measuring the volume of reagent transferred introduces an uncertainty of $[(0.02)^2 + (0.02)^2]^{1/2} = 0.03$ ml. Thus, volume less than 20 ml, even under ideal conditions, may have an uncertainty greater than 1 ppt. Most operators prefer to work in the 40 ml. range.

### Use of a buret to carry out a titration

Teflon stopcocks are commonly used in burets. The Teflon stopcock requires no lubricant.

All stopcock burets are designed to be operated with the left hand so that the right hand is free to agitate the reaction mixture. With the scale of the buret facing the operator, the handle of the stopcock is on the operator's right. With the base of the left hand to the left of the buret, the thumb and first two fingers encircle the buret to control the handle of the plug, the last two fingers against the left of the tip. This braced position of the hand leads to maximum control of the stopcock. It also makes it possible to keep constant pull on the plug into a secure position in the seat. This is essential with glass stopcocks to avoid leakage. If initially the position of the left hand seems awkward, make a sensible effort to develop skill.

To fill the 50 ml buret rinse three times with 3–4 ml portions of the liquid to be used. Use a buret funnel so this liquid can be directed to flow over the entire interior surface. Do this in the buret stand to prevent any titrant which may spill from running down to your hand. Allow time for each portion to drain from the buret before the next is added. Fill the buret, including the tip, and replace the buret funnel with a buret cap. Never leave the buret funnel in the buret during a titration since it may add a drop of titrant during the titration.

#### *Caution*

If titrant is spilled on the outside of the buret, it must be cleaned up and the waste neutralized and disposed of in a proper manner.

## EXPERIMENT 2

## Determination of percentage purity of ammonium chloride

**Ammonium chloride** ($NH_4Cl$) is a white water-soluble crystalline salt of ammonia. The aqueous ammonium chloride solution is mildly acidic. Ammonium chloride is used as expectorant, diuretic and systemic acidifier.

### Experimental overview

It contains not less than 99.0% and not more than 100.5% of $NH_4Cl$, calculated with reference to the dried substance.

The assay is based on indirect acid–base titration. An aqueous solution of the substance is treated with neutralized formaldehyde solution. This results in the liberation of hydrochloric acid equivalent to ammonium chloride. This is then titrated with a standard solution of sodium hydroxide using phenolphthalein as an indicator yielding pink color at the endpoint.

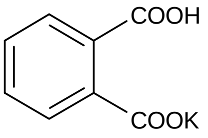
$$\begin{aligned} 4NH_4Cl + 4H_2O &\longrightarrow 4\,NH_4OH + 4\,HCl \\ 4NH_4OH + 6\,HCHO &\longrightarrow (CH_2)_6N_4 + 10H_2O \\ &\quad\;\; \text{(Hexamine)} \\ 4HCl + 4NaOH &\longrightarrow 4\,NaCl + 4H_2O \end{aligned}$$

### Reagents required

1. Potassium hydrogen phthalate
2. 0.1 M NaOH solution**.** Dissolve 4.2 g of sodium hydroxide in sufficient carbon dioxide free water to produce 1000 ml to produce 0.1 M solution.
   **Note:** NaOH is not a primary standard due to its hydroscopic nature.
3. Phenolphthalein indicator.

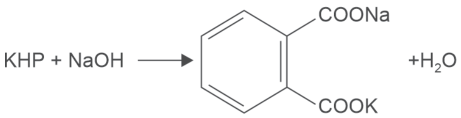
### Procedure

1. **Standardization of 0.1 M sodium hydroxide solution:**
   (i) Weigh accurately about 0.5 g of potassium hydrogen phthalate (KHP), previously powdered and dried at 120ºC for 2 hours, and dissolve in 75 ml of carbon dioxide free water.



Potassium acid phthalate
Molar mass 204.23 g/mol

   (ii) Add 0.1 ml of phenolphthalein solution and titrate with sodium hydroxide solution until a permanent pink color is produced.



Sodium potassium phthalate

carbonate to a beaker and add about 100 ml of distilled water to dissolve it completely. Add 2 drops of methyl orange indicator. Titrate the carbonate solution with the given dilute sulfuric acid until the color of solution just changes from yellow to orange. Repeat the titration twice.

Each ml of 0.5 M $H_2SO_4$ solution = 0.05299 g or 52.99 mg of $Na_2CO_3$

2. **Determination of sodium carbonate:** Weigh accurately about 0.5 g, dissolve in 20 ml of water, and titrate with 0.5 M sulfuric acid solution, using bromophenol blue solution as indicator till yellow color appears **(endpoint: blue to yellow)**.

### Observation and calculation

1. **Standardization of sulfuric acid:** The standardization of sulfuric acid is based on the reaction of sulfuric acid with sodium carbonate:

$$H_2SO_4 + Na_2CO_3 \longrightarrow H_2CO_3 + Na_2CO_3$$

$$\text{Molarity of sulfuric acid} = \frac{\text{Weight of } Na_2CO_3 \text{ (g)}}{106 \times \text{Vol. of } H_2SO_4 \text{ consumed (in litre)}}$$

106 is the molecular weight of anhydrous $Na_2CO_3$.

2. **Determination of sodium carbonate:** From the equation:

$$1 \text{ mole of } Na_2CO_3 = 1 \text{ mole of } H_2SO_4$$

Molecular weight of $Na_2CO_3.10H_2O$ = 286

1000 ml of 0.5 M $H_2SO_4$ solution contain $\frac{1}{2}H_2SO_4$ equivalent to $\frac{1}{2}Na_2CO_3.10H_2O$

Each ml of 0.5 M sulfuric acid solution is equivalent to 0.143 g of $Na_2CO_3.10H_2O$

| *S. No.* | *Weight of sodium carbonate sample taken* | *Vol. of $H_2SO_4$ consumed* | *Average vol of $H_2SO_4$ consumed* |
|---|---|---|---|
| 1 | 0.5 g | ml | 'M' ml |
| 2 | 0.5 g | ml | |

$$\text{Percentage purity} = \frac{\text{Burette reading} \times 0.143 \times \text{Molarity (cal)} \times 100}{0.5 \times 0.5 \text{ (given molarity)}}$$

### Result

The percentage purity of the sample was found to be … %.

### Judge yourself

1. What is common name for sodium carbonate?
2. How the equivalent weight of sodium carbonate is calculated?
3. What is the pH range for methyl orange and methyl red indicator?
4. What is the meaning of "weighing by difference"?
5. Suggest one method other than using acid–base indicator to detect the endpoint of an acid–alkali titration.
6. How anhydrous sodium carbonate is prepared?

### Procedure

### A. Standardization of 0.1 M HCl solutions

1. Dry primary standard-grade sodium carbonate for 1 hour at 110°C and cool it in a desiccator. Bring to constant weight. Weigh approximately containing enough $Na_2CO_3$ to react with ~25 ml of 0.1 M HCl and place each in a 250 ml flask. Add 25 ml of distilled water, swirl the flask to dissolve the solid and add 3 drops of methyl red indicator solution. Titrate one rapidly to a pink color to find an approximate endpoint. The stoichiometry of the reaction is shown here:

$$2HCl + Na_2CO_3 \longrightarrow CO_2 + 2NaCl$$

2. Titrate carefully other samples to the pink color endpoint. During each titration, you should periodically tilt and rotate the flask to wash all liquid from the walls into the bulk solution using deionized water from a plastic squeeze bottle. When very near the end, you should deliver less than 1 drop of titrant at a time.
3. Calculate the mean HCl molarity.

$$\text{Molarity of HCl} = \frac{\text{Wt. of } Na_2CO_3\,(g) \times 2}{\text{Mol. wt. of } Na_2CO_3 \times \text{Volume of HCl (in litre)}}$$

### B. Preparation and standardization of 0.1 M NaOH solution

All NaOH solutions come with impurities and contamination the make each NaOH solution imprecise unless calibrated. Calibrated NaOH solutions have limited shelf-life even when protected against atmospheric carbon dioxide. Furthermore, store your solution only in a plastic bottle and insure that the cap is free of solution between uses.

1. Place (using a volumetric pipette) 25.00 ml of your dilute HCl solution into a 250 ml Erlenmeyer flask. Add 2–3 drops of phenolphthalein indicator solution, and titrate to an endpoint with the NaOH solution. The endpoint is the first appearance of faint pink color that persists for 15 seconds (The color will slowly fade as $CO_2$ from the air dissolves in the solution.)
2. Make two more replicate determinations of 25.00 ml of NaOH solution using the standardized HCl solution. Calculate the average molarity with the formula, $M_1V_1$ (HCl) = $M_2V_2$ (NaOH).

### C. Volumetric determination of carbonate and bicarbonate

1. Store Solid unknown in a desiccator to keep dry; however, do not heat the sample. Even mild heating at 50°–100°C converts $NaHCO_3$ to $Na_2CO_3$. Accurately, weigh 2.0 to 2.5 g of unknown into a clean 250 ml volumetric flask. A funnel may be used to aid transfer of sample to the volumetric flask. Rinse the funnel repeatedly with small portions of freshly boiled and cooled water to dissolve and transfer the sample to the flask. Remove the funnel, mix well, and dilute to the mark. This is your unknown solution.
2. Pipette a 25.00 ml aliquot of the unknown solution into a 250 ml Erlenmeyer flask, add 3 drops of bromocresol green indicator solution and titrate rapidly (to a green endpoint) using your standardized HCl solution (from above). Then, repeat in triplicate this procedure carefully with 25.00 ml samples of unknown solution. Record the average titre value '**M**' ml. This volume will give us total alkalinity.
3. Pipette a 25.00 ml aliquot of the unknown solution and 50.00 ml of your standardized NaOH solution into a 250 ml flask. Swirl thoroughly and add using a graduated cylinder 10 ml of 10% w/w $BaCl_2$ solution. Swirl again to precipitate $BaCO_3$, add 2 drops of phenolphthalein