# Elementary Volumetric Analysis

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# ELEMENTARY
# VOLUMETRIC
# ANALYSIS

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# PREFACE

THIS book is intended for use by students preparing for the practical chemistry papers of the Cambridge Oversea School Certificate and the General Certificate (Ordinary level) examinations. No previous knowledge of the principles or practice of volumetric analysis is assumed. In addition to the basic experiments using acids and alkalis a number of miscellaneous experiments have been included. These experiments are similar to those which are often set in practical examinations; they are meant to encourage students to use their knowledge of analysis and chemistry to solve simple problems.

Specimen results of typical analyses are given. They illustrate the way of writing the results in a clear, concise manner. Solutions to a number of numerical problems are also given in full. The provision of these specimen results and solutions to problems should leave the teacher with more time to devote to the practical work and to help students with their individual difficulties.

A few experiments involving back titrations have been included. Such experiments are not required for the practical examinations, but their inclusion here is justified by the questions and numerical problems which are often set on the theoretical chemistry papers. It is hoped that the students for whom the book has been written will not find any theory, problem or experiment beyond either their need or understanding.

A. A.

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# ELEMENTARY VOLUMETRIC ANALYSIS

## ACIDS AND ALKALIS

### 1. GENERAL

The object of volumetric analysis is to determine the weight of a compound present in a sample of solid or in a solution, e.g. to determine the weight of hydrochloric acid in one litre of dilute acid, to determine the weight of sodium carbonate in some crystals of washing soda, or to find the weight of ammonium chloride in a sample of impure ammonium chloride. In the analysis two aqueous solutions are used, the concentration of one solution is unknown and the concentration of the other must be known. The essential process (called *titration*) consists in running one solution, from a burette, into a fixed volume (usually 10 or 25 c.c.) of the other solution until the two solutions have just reacted completely. For example, hydrochloric acid is added to sodium hydroxide solution until the mixture is just neutral. When this is so the *neutral- or end-point* of the titration has been reached, and the volume of the solution used from the burette is noted.

Volumetric analysis has three advantages:

(*a*) The process can usually be carried out quickly. Most of the experiments described in this book can be completed in one hour or so, and many of the experiments which do not involve weighings require only about half an hour for the practical work.

(*b*) The apparatus needed is simple and inexpensive.

(*c*) The skill and technique necessary to use the apparatus accurately can be acquired readily by a careful and methodical worker.

## 2. EQUIVALENTS OF ACIDS

An acid is a compound which, when dissolved in water, forms hydrogen ions ($H^+$) as the only positively charged ions.

The equivalent of an acid is the number of grams of it which can form 1 g. of hydrogen ions (more accurately, 1·008 g.).

(a) *Hydrochloric acid*

$$HCl \rightarrow H^+ + Cl^-$$
$$(1 + 35.5) \quad 1$$

The equivalent of hydrochloric acid is 36·5.

(b) *Sulphuric acid*

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{--}$$
$$(2 + 32 + 64) \quad 2$$
$$98 \qquad 2$$

The equivalent of sulphuric acid is 49.

(c) *Nitric acid*

$$HNO_3 \rightarrow H^+ + NO_3^-$$
$$(1 + 14 + 48) \quad 1$$

The equivalent of nitric acid is 63.

(d) *Oxalic acid*

$$H_2C_2O_4 \rightarrow 2H^+ + C_2O_4^{--}$$
$$(2 + 24 + 64) \quad 2$$
$$90 \qquad 2$$

The equivalent of anhydrous oxalic acid is 45. The equivalent of the hydrated acid, $H_2C_2O_4 . 2H_2O$, is 63.

The basicity of an acid is the number of hydrogen ions ($H^+$) that can be formed from one molecule of the acid.

| | | |
|---|---|---|
| Hydrochloric acid | $HCl \rightarrow H^+ + Cl^-$ | Monobasic |
| Nitric acid | $HNO_3 \rightarrow H^+ + NO_3^-$ | Monobasic |
| Sulphuric acid | $H_2SO_4 \rightarrow 2H^+ + SO_4^{--}$ | Dibasic |
| Phosphoric acid | $H_3PO_4 \rightarrow 3H^+ + PO_4^{---}$ | Tribasic |

A simpler method of calculating the equivalent of an acid is to use the formula

$$\text{Equivalent of an acid} = \frac{\text{Molecular Weight}}{\text{Basicity}}.$$

The proof of the formula is as follows:

Consider an acid of molecular weight $M$, basicity $B$ and equivalent $E$. Therefore

1 molecule of the acid contains $B$ atoms of ionizable hydrogen,

i.e. $M$ grams of the acid contain $B$ grams of ionizable hydrogen,

i.e. $\dfrac{M}{B}$ grams of the acid contain 1 gram of ionizable hydrogen.

From the definition of the equivalent of an acid it follows that

$E$ grams of acid contain 1 gram of ionizable hydrogen.

Therefore $$E = \frac{M}{B}$$

$$\text{Equivalent} = \frac{\text{Molecular Weight}}{\text{Basicity}}.$$

*Q.E.D.*

The table below shows how the equivalents of the common acids are calculated from this formula:

| Acid | Formula | Molecular Weight | Basicity | Equivalent |
|---|---|---|---|---|
| Hydrochloric | $HCl$ | 36·5 | 1 | 36·5 |
| Sulphuric | $H_2SO_4$ | 98 | 2 | 49 |
| Nitric | $HNO_3$ | 63 | 1 | 63 |
| Oxalic | $H_2C_2O_4$ | 90 | 2 | 45 |
| Hydrated oxalic | $H_2C_2O_4 . 2H_2O$ | 126 | 2 | 63 |
| Acetic | $H_4C_2O_2$ or $CH_3COOH$ | 60 | 1 | 60 |

## 3. EQUIVALENTS OF BASES AND CARBONATES

A base is a compound which contains oxide ($O^{--}$) or hydroxyl ($OH^-$) ions and reacts with an acid to form a salt and water only.

An alkali is a compound which, when dissolved in water, forms hydroxyl ions as the only negatively charged ions.

| Chemical name | Common name | Formula | | Ions |
|---|---|---|---|---|
| Sodium hydroxide | Caustic soda | $NaOH$ | $\rightarrow Na^+$ | $+ OH^-$ |
| Potassium hydroxide | Caustic potash | $KOH$ | $\rightarrow K^+$ | $+ OH^-$ |
| Calcium hydroxide | Slaked lime | $Ca(OH)_2$ | $\rightarrow Ca^{++}$ | $+ 2OH^-$ |
| Ammonium hydroxide | Ammonia solution | $NH_4OH$ | $\rightleftharpoons NH_4^+$ | $+ OH^-$ |

The equivalent of a base or carbonate is the number of grams of it which will neutralise the equivalent weight of an acid.

(a) *Sodium hydroxide*

$$NaOH \;+\; HCl \;\rightarrow\; NaCl \;+\; H_2O$$
$$(23+16+1) \quad (1+35\cdot5)$$
$$40 \qquad\qquad 36\cdot5$$

This equation shows that 40 grams of sodium hydroxide neutralise $36\cdot5$ grams, i.e. the equivalent weight, of hydrochloric acid.

The equivalent of sodium hydroxide is *40*.

(b) *Potassium hydroxide*

$$KOH \;+\; HNO_3 \;\rightarrow\; KNO_3 \;+\; H_2O$$
$$(39+16+1) \quad (1+14+48)$$
$$56 \qquad\qquad 63$$

56 grams of potassium hydroxide neutralise 63 grams, i.e. the equivalent weight, of nitric acid.

The equivalent of potassium hydroxide is *56*.

(*c*) *Ammonium hydroxide*

$$NH_4OH \quad + \quad HCl \rightarrow NH_4Cl + H_2O$$
$$(14+4+16+1) \quad 36 \cdot 5$$
$$35 \qquad\qquad 36 \cdot 5$$

The equivalent of ammonium hydroxide is *35*.

(*d*) *Sodium carbonate*

$$Na_2CO_3 \quad + \quad H_2SO_4 \rightarrow Na_2SO_4 + CO_2 + H_2O$$
$$(46+12+48) \qquad 98$$
$$106 \qquad\qquad 98$$
$$53 \qquad\qquad 49$$

53 grams of sodium carbonate neutralise 49 grams, i.e. the equivalent weight, of sulphuric acid.

The equivalent of sodium carbonate is *53*.

Similarly, the equivalent of potassium carbonate is *69*, and the equivalent of washing soda crystals,

$$Na_2CO_3 \cdot 10H_2O,$$

is *143*.

(*e*) *Sodium bicarbonate*

$$NaHCO_3 \quad + \quad HCl \rightarrow NaCl + CO_2 + H_2O$$
$$(23+1+12+48) \quad 36 \cdot 5$$
$$84 \qquad\qquad 36 \cdot 5$$

The equivalent of sodium bicarbonate is *84*.
Similarly, the equivalent of potassium bicarbonate is *100*.

(*f*) *Calcium carbonate*

$$CaCO_3 \quad + \quad 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$$
$$(40+12+48) \qquad 2 \times 63$$
$$100 \qquad\qquad 2 \times 63$$
$$50 \qquad\qquad 63$$

The equivalent of calcium carbonate is *50*.

(g) *Calcium hydroxide*

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$$
$$(40+32+2) \quad 2 \times 36 \cdot 5$$
$$74 \qquad 2 \times 36 \cdot 5$$
$$37 \qquad 36 \cdot 5$$

The equivalent of calcium hydroxide is *37*.

## 4. STANDARD, NORMAL AND MOLAR SOLUTIONS

**A standard solution is one which contains a known weight of a solute in a given volume of solution.**

**A normal solution is one which contains one gram-equivalent of a solute in one litre of solution.**

**A molar solution is one which contains one formula weight (mole) of a solute in one litre of solution.**

Hence, a solution which contains 9·473 grams of sodium hydroxide in 426·5 c.c. of solution is a standard solution. A solution which contains 40 grams (i.e. the gram-equivalent) of sodium hydroxide in one litre of solution is a normal solution. Note very carefully that in these two definitions it is the volume of SOLUTION that is important and not the volume of water used to make the solution.

Normal or molar solutions ($N$ or $M$ solutions) are often too concentrated for use in ordinary volumetric analysis and it is usual to prepare and use more dilute solutions. A *decinormal* (usually called an $N/10$ or $0·1N$) solution is one which contains one-tenth of a gram-equivalent of a solute in one litre of solution. A decimolar ($M/10$ or $0·1M$) solution contains one-tenth of a mole of a solute in one litre of solution. Similarly,

A $2N$ solution contains two gram-equivalents per litre of solution, i.e. it is twice as concentrated as an $N$ solution.

A $0.5M$ solution contains half a mole per litre of solution, i.e. it is half as concentrated as an $M$ solution.

$$\text{Molarity} = \frac{\textbf{Concentration in grams per litre}}{\textbf{Mole (or formula weight)}}$$

$$\text{Normality} = \frac{\textbf{Concentration in grams per litre}}{\textbf{Equivalent weight}}$$

It should now be clear that

1 litre of $N$ hydrochloric acid contains 36·5 grams acid;

1 litre of $M$ sulphuric acid contains 98 grams acid;

1 litre of $N/2$ or $0.5N$ sodium hydroxide contains 20 grams alkali;

1 litre of $N/10$, $0.1N$, $M/10$ or $0.1M$ hydrochloric acid contains 3·65 grams acid;

$M/20$ or $0.1N$ sodium carbonate solution contains 5·3 grams per litre, and so on.

It should also be clear that 36·5 grams of hydrochloric acid (or the gram-equivalent of any solute) will make

|     |                                               |
|-----|-----------------------------------------------|
|     | 1 litre of $N$ solution,                      |
| or  | 2 litres of $N/2$ or $0.5N$ solution,         |
| or  | 0·5 litre of $2N$ solution,                   |
| or  | 10 litres of $N/10$ or $0.1N$ solution,       |
| or  | $x$ litres of $N/x$ solution.                 |

These examples illustrate the truth of the following relationship:

Volume × Normality = a constant (for a given weight of solute)

If a solution of known normality or molarity is diluted:

**(Normality × Volume) = (Normality × Volume)** and
**(Molarity × Volume) = (Molarity × Volume)**
  of original solution      of diluted solution

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Students familiar with the Boyles' Law equation $P_1V_1 = P_2V_2$ should have little difficulty in using this normality-volume or molarity-volume equation.

We can now deduce a formula connecting the volumes and normalities of solutions of acids and bases which just neutralise one another.

1 litre of $N$ acid solution contains one gram-equivalent of acid.

1 litre of $N$ alkali solution contains one gram-equivalent of the base.

Since one gram-equivalent of a base neutralises one gram-equivalent of an acid, then 1 litre of $N$ acid will neutralise 1 litre of $N$ base or carbonate.

Also, 1 litre of $N/10$ acid will neutralise 1 litre of $N/10$ base, and

1 litre of $N/100$ acid will neutralise 1 litre of $N/100$ base and so on.

Further,      1 litre of $N$ acid will neutralise
               1 litre of $N$ base,

or          2 litres of $N/2$ base,

or          0·5 litre of $2N$ base,

or          10 litres of $N/10$ base, and so on,

because all these solutions contain one gram-equivalent of the base.

This example illustrates the truth of the following relationship:

$$\textbf{(Volume} \times \textbf{Normality)} = \textbf{(Volume} \times \textbf{Normality)}$$
$$\textbf{of acid} \qquad\qquad\qquad \textbf{of base}$$

i.e. $\dfrac{\text{Volume of acid}}{\text{Volume of base}} = \dfrac{\text{Normality of base}}{\text{Normality of acid}}$

(for solutions which just neutralise one another).

This relationship is most important and it will be used in most of the calculations.

WORKED EXAMPLES

The following worked examples illustrate the use of the principles outlined above.

*Example* 1. What is the normality of a solution of sulphuric acid which contains 9·8 grams of the pure acid in 500 c.c. of solution?

$$\text{The equivalent of sulphuric acid} = \frac{\text{Molecular weight}}{\text{Basicity}}$$
$$= \frac{98}{2} = 49.$$

49 grams of pure acid in 1,000 c.c. solution is an $N$ solution.

∴ 9·8 grams of pure acid in 1,000 c.c. solution is a $\frac{9·8}{49}$ $N$ solution.

9·8 grams of pure acid in 500 c.c. solution is a

$$\frac{9·8 \times 1000}{49 \times 500} \ N \text{ solution} = 0·4N.$$

The normality of the acid is *0·4N*.

*Example* 2. How many c.c. of $0·127N$ sodium hydroxide are required to prepare 10 litres of $N/10$ sodium hydroxide?

Using the formula $\dfrac{\text{First volume}}{\text{Second volume}} = \dfrac{\text{Second normality}}{\text{First normality}}$

we have, $\dfrac{\text{First volume}}{10 \text{ litres}} = \dfrac{0·1}{0·127}$

i.e. $\text{First volume} = 10 \times \dfrac{0·1}{0·127} \text{ litres}$
$$= 7·874 \text{ litres}.$$

The volume of sodium hydroxide required is *7874 c.c.*

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