

# THE ESSENTIALS OF VOLUMETRIC ANALYSIS

**John Lambert**

with A. Holderness & F. Sherwood Taylor

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# The Essentials of Volumetric Analysis

JOHN LAMBERT

M SC

*Formerly Senior Chemistry Master at King  
Edward's School, Birmingham*

*in conjunction with*

A. HOLDERNESS

M SC, F R I C

*Sectional Chief Examiner in 'Advanced' Chemistry  
to the Joint Matriculation Board*

*and*

F. SHERWOOD TAYLOR

M A, B Sc, Ph D

*Late Director, Science Museum, London*

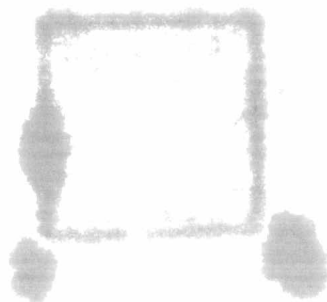


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## Preface

THIS book is intended for use in the preparation of students for the G.C.E. Advanced Level examinations in Practical Chemistry. It is hoped that all the essential experiments are included, and that some help is given to scholarship candidates who often have to work on their own. Wherever it is thought that modern practice can be used to advantage in schools, the modern method is given. A short chapter on adsorption indicators is included.

The exercises given at the end of chapters contain many practical questions taken from scholarship papers and from the practical examinations of the various G.C.E. Boards.

There are many exercises of a more advanced character suitable for scholarship candidates or for students taking the course a second time. Some of these require no preparation on the part of the teacher, but can be worked completely by the student: these are marked with an asterisk so that they can be set in the knowledge that the student can carry on by himself.

We have pleasure in thanking Messrs. John Murray for permission to use experiments from the Science Masters' Book and the Examination Boards for permission to use their questions. The following is a list of these Boards and of the abbreviations used at the end of questions set by them to indicate the source of each particular question :—

Central Welsh Board	.	.	.	(C.W.B.)
University of Durham	.	.	.	(Durham)
University of London	.	.	.	(London)
Joint Matriculation Board	.	.	.	(N.U.J.B.)
Oxford Local	.	.	.	(Oxford)
Oxford and Cambridge	.	.	.	(O. and C.)

We also thank the Examination Syndicates of the Universities of Oxford and Cambridge for permission to use some of their scholarship questions (Schol.), and Messrs. A. S. Langley and A. W. Wellings for proof-reading and for valuable suggestions.

J. L.

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## ✓ CHAPTER I

### INTRODUCTION

As its name implies, volumetric analysis relies on methods involving accurate measurement of volumes of liquids, though one or more weighings may also be needed. Gravimetric analysis involves only weighings. Of the two methods of analysis, gravimetric analysis is the more accurate but volumetric analysis is much more rapidly carried out. Volumetric analysis is, however, by no means inaccurate and the error involved in an analysis carried out by an experienced worker should not exceed 0.2%.

**Standard Solutions. Normality.** In general, a volumetric analysis is carried out by preparing a standard solution of the given material (or using a solution supplied) and determining the volume of it needed to react exactly with a known volume of another solution of accurately known strength, in a chemical reaction for which the equation is known. The course of the reaction is traced by some means, usually by an indicator showing change of colour when the reaction is complete. To take a simple case, the strength of a solution of caustic potash could be determined by adding to it the indicator methyl orange, and then causing the alkali to react with a standard solution of hydrochloric acid slowly added until the solution just becomes orange, the acid being then just in excess. This process of adding one standard solution to another to determine equivalent volumes is called *titration*.

A standard solution is one of which the concentration is known. Any kind of unit of weight or volume may be used, *e.g.*, solutions containing, say, 2 oz. of common salt per gallon or 3 grains of sodium bicarbonate per fluid ounce, are standard solutions, inconvenient though they are for scientific purposes.

For volumetric analysis, the system of working in *normal* solution (or some multiple or submultiple of this strength) is almost universal. A normal solution is a particular kind of standard solution and is defined in the following way :—

A normal solution of a substance is one which contains

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the gram-equivalent weight of the substance in 1 litre of solution.

For convenience such an expression as "a normal solution of caustic soda" is usually written concisely as "*N.NaOH*." Double normal (*2N*), semi-normal (*N/2*), decinormal (*N/10*) and centinormal (*N/100*) solutions are also commonly used and have the appropriate multiple or sub-multiple of the concentration of a normal solution.

**Some Normal Solutions.** One litre of a normal solution must, by definition, contain the weight in grams of the solute which is equivalent to one gram \* of replaceable hydrogen. The student should make sure that he understands the following calculations and can apply the principles to similar cases.

\* Or more accurately 1.008 gm. (O = 16.000).

### (1) *Sulphuric Acid.*

$\text{H}_2\text{SO}_4$ ; molecular weight is 98

↑

2 gm. replaceable hydrogen in 98 gm. of acid.

∴ *N.H<sub>2</sub>SO<sub>4</sub>* contains 49 gm. of the acid per litre.

### (2) *Caustic Soda.*

$\text{NaOH} + \text{HCl} = \text{NaCl} + \text{H}_2\text{O}$

↑

40 gm.      1 gm. of replaceable hydrogen.

∴ *N.NaOH* contains 40 gm. of caustic soda per litre.

### (3) *Potassium Permanganate.*

This compound, when reacting in acid solution (p. 38), yields oxygen for oxidation purposes according to the basic equation:—



$$\therefore 2\text{KMnO}_4 \equiv 5[\text{O}]$$

$$\therefore 2\text{KMnO}_4 \equiv 10\text{H}$$

↑

2(39 + 55 + 64)

316 gm.

10 gm. replaceable  
hydrogen.

∴ *N.KMnO<sub>4</sub>* would contain 31.6 gm. of potassium permanganate per litre. Such a solution cannot be used in practice because of limitations imposed by the low solubility of the compound; *N/10 KMnO<sub>4</sub>* solutions, containing 3.16 gm. per litre are usually employed.

### (4) *Silver Nitrate.*



↑

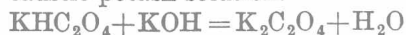
170. gm.

1 gm. of replaceable  
hydrogen.

$\therefore N.\text{AgNO}_3$  contains 170 gm. of silver nitrate per litre. Usually  $N/10 \text{ AgNO}_3$  (17 gm. per litre) is used.

The theoretical justification for the concentration of other normal solutions will be found at appropriate places in the text. It should be noted particularly that the **concentration of a normal solution must be calculated from the equation for the reaction which the compound is to undergo in the analysis to be performed.** This is most important when a compound is capable of reacting in two or more different ways. Consider the following reactions involving acid potassium oxalate :—

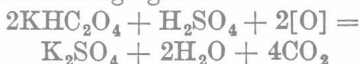
(1) Reaction between potassium hydrogen oxalate and caustic potash solution.



↑  
1 gm. of hydrogen  
to be replaced.

$\therefore N.\text{KHC}_2\text{O}_4$  contains 128 gm.  
per litre.

(2) Reaction between acidified potassium hydrogen oxalate and an oxidising agent.



$\therefore N.\text{KHC}_2\text{O}_4$  contains 64 gm.  
per litre.

Potassium hydrogen oxalate possesses two equivalents each appropriate to a particular reaction; consequently, two solutions of different concentrations may be prepared, each of which is *normal* when considered in relation to its appropriate reaction.

It follows from the definition of normal solutions that they must contain chemically equivalent weights of the compounds per litre of solution and, consequently, that equal volumes of different normal solutions are chemically equivalent to one another, *e.g.*,

25 c.c. of  $N.\text{HCl}$  react exactly with

25 c.c. of  $N.\text{NaOH}$   
or 250 c.c. of  $N/10 \text{ KOH}$   
or 12.5 c.c. of  $2N.\text{Na}_2\text{CO}_3$   
or 50 c.c.  $N/2 \text{ NaOH}$   
or 500 c.c.  $N/20 \text{ AgNO}_3$   
or 2,500 c.c.  $N/100 \text{ KOH}$

It is also convenient to note that if  $V_1$  c.c. of a solution of normality  $N_1$  is equivalent to  $V_2$  c.c. of a solution of normality  $N_2$  then

$$V_1 N_1 = V_2 N_2$$

For example 10 c.c.  $1.08 N \equiv 10.8 \text{ c.c. } N.$

## INSTRUMENTS OF VOLUMETRIC ANALYSIS

The course of a volumetric analysis is usually the following :—  
A standard solution of the material to be analysed is made up by weighing in a *weighing bottle* an appropriate quantity of the material,



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making it up to 250 c.c.<sup>1</sup> of aqueous solution in a *measuring flask*, transferring 25 c.c.<sup>1</sup> of this solution to a conical flask by means of a *pipette* and titrating it with a standard (often decinormal) solution of some reagent from a *burette*, using a suitable indicator. Each of these measuring instruments and the manner of its use will now be considered. A measuring cylinder may occasionally be used but only for very approximate work.

**Weighing Bottle.** This consists of a cylindrical glass vessel with an accurately ground stopper (Fig. 1), in which the materials can be weighed out of contact with the open atmosphere. The weighing bottle is usually heated in a steam oven before use to ensure dryness and is then allowed to cool in a desiccator. It should be handled in a dry cloth to avoid contamination with grease from the fingers. It may be used in one of two

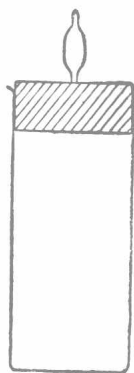


FIG. 1.

ways. The first method is to weigh the bottle empty, powder the material given in a clean dry mortar and then weigh out an amount of material exactly against counterpoising weights. This has the disadvantage of being tedious and exposing the material to the atmosphere while adjustments of amount are being made. A spatula of horn or stainless metal is used to transfer the material. The second method is to weigh the bottle containing an amount of the material known to be roughly suitable for the purpose in hand, to transfer the material to a measuring flask as described in the next paragraph and weigh the bottle containing a trace of residual material, after which the actual weight transferred to the measuring flask can be obtained by difference.

The second method is much quicker and is preferable except where solutions of an exact normality are being prepared directly: the first method is then essential.

The degree of accuracy necessary in the weighings will be considered later (p. 9).

**Measuring Flask.** Measuring flasks of 250 c.c. capacity are usually employed (Fig. 2) because the amount of solution used in a single titration is usually 25 c.c. and several such titrations may be carried out by drawing from the 250 c.c. of solution prepared. Measuring flasks of 100 c.c., 200 c.c., 500 c.c., 1,000 c.c. and 2,000 c.c. are also in frequent use.

It should be noted that a measuring flask is made to *contain* a volume of liquid and will not *deliver* that volume, because some liquid is inevitably retained as a film on the sides of the flask. Measuring flasks are usually graduated at 15° C. and should only be used at temperatures close to this.

<sup>1</sup> It is also convenient to make 100 c.c. of solution and to take 20 c.c. portions.

When a solution is to be made up the measuring-flask should first be well rinsed with several small quantities of the solvent (usually distilled water) that is to be used. This removes any traces of impurities. A small beaker should be similarly rinsed and the material transferred to it carefully from the weighing bottle. The solvent is then added from a wash-bottle down the sides of the beaker so that there is no splashing. Gentle stirring with a glass rod will hasten the process of solution, but the rod should not be removed from the beaker unless all solution is first washed from its surface into the beaker. (If the solvent is used hot, the solution must finally be cooled to room temperature. The solution must

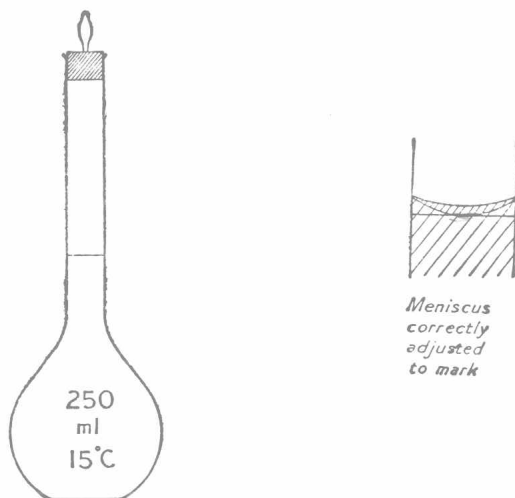


FIG. 2.

also, of course, remain unchanged by heat.) When the solute is completely dissolved the glass rod should be placed in a funnel which rests in the neck of the measuring flask and the solution poured down it from the beaker into the flask. The entire interior surface of the beaker should then be washed several times with the solvent and the washings transferred to the flask down the rod which will also be washed by them. (If the material is being weighed by difference, the weighing bottle should now be weighed again. If not, the weighing bottle should be washed out with solvent in the same way as the beaker and the washings added to the contents of the flask.) The measuring flask is then filled with the solvent from a wash-bottle until the bottom level of the meniscus is at the mark (Fig. 2). A pipette should be used to add the last drop or two. (When deciding whether the level is correctly adjusted,

lower the eye until the mark is at your eye-level and so avoid error due to parallax.) The flask should then be stoppered and **shaken vigorously** for some few minutes to make the solution uniform.<sup>1</sup>

If time is an important factor the solution can be made uniform more quickly by pouring it into a large dry flask in which it can easily be swirled round for a short time. **It is essential that the solution should be of uniform concentration throughout.** Whenever the words "shake well" appear in the text they mean this essential process of making the solution uniform.

**Pipette.** The pipette (Fig. 3) is designed to *deliver* a certain volume of liquid. When filled to the mark it contains more than this volume, a little of the liquid being retained after delivery as a film on the sides of the pipette and in the tip. The actual volume *delivered* from the pipette should be constant, and it is therefore important to observe certain conditions when using the pipette so that the small volume of liquid retained in it is constant.

The pipette is filled above the mark by sucking <sup>2</sup> solution into it and this liquid is allowed to drain away. This process of filling and allowing the liquid to run away should be repeated to ensure that the pipette contains nothing but the solution which is to be measured. The pipette is then filled above the mark and the liquid is retained by pressing the forefinger on the open end of the stem. The pipette is then raised so that the mark is at eye-level and by controlled release of the finger from the stem, the liquid is allowed to fall slowly until the bottom level of the meniscus is at the mark. The tip of the pipette is then placed inside a conical flask

which should be dry or should contain only distilled water. By removing the finger from the stem, the liquid may be delivered from the pipette into the flask. A 25 c.c. pipette should deliver its contents in not less than 20 secs.<sup>3</sup> and a drainage time of about 15 secs. should be allowed with the point of the pipette touching the side of the vessel. A little liquid will be retained in



FIG. 3.

<sup>1</sup> After shaking, the solution will be *below* the mark. This is because some of the solution is retained as a film on the stopper and neck of the flask. The total volume is still, however, 250 c.c. and 25 c.c. taken from it will be accurately one-tenth. Do not be tempted to make the solution up to the mark again. This proceeding makes the volume 250 c.c. plus an unknown added volume.

<sup>2</sup> A vacuum bottle or a burette should always be used for poisonous solutions. If a liquid is taken into the mouth it should be spat out at once and the mouth washed out.

<sup>3</sup> If delivery is more rapid than this, the volume delivered is not constant. A pipette which delivers too rapidly should have its extreme tip heated very gently in a flame, when the hole will close slightly.

the tip; no attempt should be made to expel it as the pipette will already have *delivered* 25 c.c. of liquid which is now available for titration with a standard solution from a burette, using a suitable indicator. The greatest difference between deliveries from a 25 c.c. pipette should not exceed 0.025 c.c.

**Burette.** The burette is illustrated in Fig. 4. Burettes employed in volumetric analysis usually have a capacity of 50 c.c. and are graduated in c.c. and  $1/10$  c.c. A glass-stoppered<sup>1</sup> burette is to be preferred and the stopper should turn smoothly. (If it sticks, the socket and stopper should be dried and a *very thin* smear of vaseline placed on the stopper. If too much is used, the vaseline may black the hole in the stopper. A rubber band may be used to prevent the stopper from sliding out of the socket.) The burette is first washed out with the solution it is to contain, the washings being allowed to run away *through the jet* so as to wash this part also. A second washing is desirable to ensure complete elimination of impurities. It is then filled up to the region of the zero mark with the solution and *the jet is filled* by opening the tap for a second or two. Time is then allowed for drainage down the sides of the burette, after which with the surface of the liquid at eye-level, the reading of the *bottom level* of the meniscus is taken. A white sheet of paper held behind the liquid at an angle of 45 degrees will help to define the meniscus and a good approximation to the second decimal place may be obtained. The titration is then completed and the new reading taken, after which the volume of liquid delivered is found by difference.

As a titration must be accurate to one drop of reagent and the volume of it needed is at first only very approximately known, it is almost always a saving of time to carry out a rough titration first in the following way, after which accurate titration can be quickly performed. To the solution and indicator in the conical flask, add the solution from the burette 1 c.c. *at a time*, until excess is present as shown by the change in the indicator. Suppose that the indicator changes between the 23rd and 24th c.c. added. Then it is clear that in subsequent titrations 23 c.c. of solution can be safely added from the burette, after which adjustment to the accurate end-point must be made drop by drop, but the greatest possible addition at this

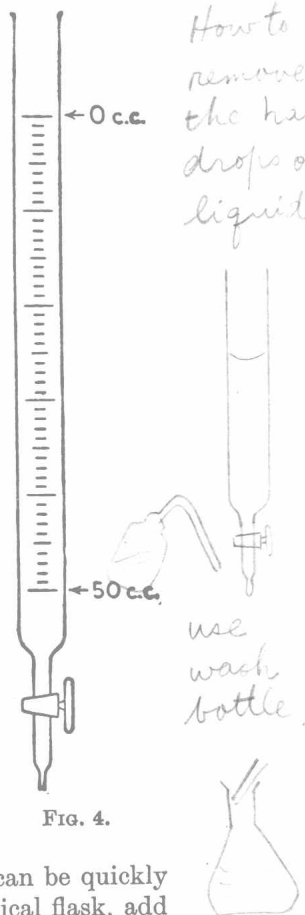


FIG. 4.

<sup>1</sup> A Mohr burette is quite satisfactory for most purposes, but it should not be used with iodine solutions. The rubber connection is attacked by iodine.

slow rate can only be 1 c.c. and will probably be much less. It is usually quicker to carry out a deliberately approximate titration first, although with some indicators a fairly accurate first titration is possible because the indicator shows signs of the arrival of the end-point. In the second and subsequent titrations, the flask should be shaken at intervals and the reagent should be added in quantities of not more than about 5 c.c. because the large local excess of reagent which may result is apt to induce undesirable variants of the main reaction.

A burette (including the tap) should always be well washed out after use. If an alkaline solution has been in the burette, about 10 c.c. of dilute acid should be run into the burette after running out the alkali, and the burette then well washed out with water.

### SOURCES OF ERROR

The following are the chief sources of error in volumetric analysis.

**Solution not Homogeneous.** This is a frequent source of error. After the solution has been made up to the mark, it is essential either to shake very well or to pour the solution into a large flask and swirl.

**Inaccuracy of Instruments Used.** Measuring flasks, burettes and pipettes of reasonable price are necessarily manufactured by mass-production methods and inaccuracies are certain to arise. An experienced analyst can calibrate his apparatus and so practically eliminate errors from this source. Actually the least accurate of the instruments is the burette for the following reasons:—

(1) An error of a drop may arise in the titration because this is the least amount that can be added. The volume of a drop from an ordinary school burette may be about 0.04 c.c., but the error may be reduced by averaging three close titrations.

(2) The burette may drain irregularly. For this reason, burettes should be treated at intervals with a cleaning mixture (such as 10% chromic acid in sulphuric acid) to remove grease.

(3) The second decimal place in the readings can only be obtained approximately.

The probable error in using the burette is about 1 part in 500, and this is usually the greatest error an experienced analyst will encounter. The other instruments are generally more accurate, provided that they are consistently used as previously described in the text.

**Errors in Weighing.** As the error in using the burette is about 1 part in 500, there is no point in weighing out material extremely accurately. If one gm. or more is being weighed, a mistake of one unit in the third decimal place will introduce an error of one part

in 1,000, which is much less than the burette error. Thus a weighing of one gm. or more of material should not be carried beyond the third decimal place.

**Impurity of Materials.** It is obvious that if analyses are based on solutions made up from impure chemicals, the results will be unreliable. There has, however, been a remarkable improvement in recent years in the quality of analytical reagents, and chemicals of analytical<sup>1</sup> reagent quality are now so pure that the errors they introduce, compared with those from other sources, are almost always negligible.

Errors may arise from the action of light, atmospheric carbon dioxide, dust particles or oxygen on standard solutions. These may be minimised by the use of coloured glass bottles, tightly fitting stoppers, soda-lime tubes to absorb carbon dioxide and in other ways. If a solution is kept for a long time, it should be standardised at frequent intervals.

### **Inaccuracy in the End-point Recorded.**

If too much indicator is added to the solution to be titrated, a certain amount of the reagent added will be needed to cause the colour change to take place. It is often helpful to perform a "blank" experiment to ascertain the volume of reagent necessary to affect the indicator which has been added to a volume of water approximately equal to the final volume of solution likely to be obtained in the actual titration. Furthermore, where a change in colour indicates the end-point of a reaction, practice is often necessary before the change can be clearly recognised. It is sometimes useful to have on the bench for comparison a flask containing a few drops of the unchanged indicator added to water, so that any alteration in colour can be easily observed.

<sup>1</sup> These chemicals (A.R. quality) should always be used. Moisture is nearly always present to the extent of 0.2 to 0.5% in any powder not specially dried. This impurity can usually be removed by storing the substance before use for a few hours in a desiccator.

## CHAPTER II

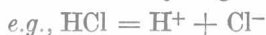
### INDICATORS

**Ionisation.** The aqueous solutions of some substances will readily conduct an electric current and decomposition occurs as a result. These substances are termed electrolytes, and acids, alkalis, and the majority of salts belong to this class. Thus a solution of hydrochloric acid in water conducts an electric current and is decomposed into hydrogen (which is evolved at the negative pole or cathode) and chlorine (at the anode or positive pole). This is explained by assuming that ions are present in the liquid before any current is passed through it. These ions are electrically charged atoms or groups of atoms, ions of metals or metallic groups being positively charged and ions of non-metals and non-metallic groups being negatively charged. The amount of charge is directly proportional to the valency of the atom or group. Since the majority of the volumetric processes depend upon the interaction of ions we shall often represent a substance, not by its usual formula, but by its ionic formula. This indicates the ions furnished by that substance when dissolved in water. Thus :—

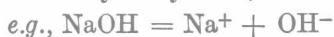


The plus sign between them merely indicates that the ions are present in the same solution in those proportions. It does not imply any chemical bond between the ions. They are free to move anywhere in the solution. When an electric current is passed, however, the negative ions or anions move to the positive pole and the positive ions or cations to the negative pole ; and the phenomenon of electrolysis is observed.

**Definitions.** An *acid* is a substance which contains hydrogen and when dissolved in water furnishes hydrogen ions,



A *base* is a substance which will react with hydrogen ions to give a salt and water only. The alkalis are substances which when dissolved in water furnish hydroxyl ions,



*Neutralisation* is a reaction between an acid and a base producing a salt and water only, *e.g.*,



It will be clearly seen that, since the common salt produced is in the form of ions of sodium and chlorine, neutralisation consists essentially of the action between hydrogen ions and hydroxyl ions to form molecules of water which are undissociated. (See p. 12.)



**Weak and Strong Electrolytes.** According to Arrhenius the ions are furnished by a reversible reaction in which an undissociated molecule splits up into ions to an extent which varies considerably from substance to substance and according to the dilution of the solution. The greater the dilution the greater the dissociation.

Strong electrolytes<sup>1</sup> are dissociated to a considerable extent even in fairly concentrated solution, whereas weak electrolytes are only slightly dissociated. The following table shows how the dissociation varies for a few weak electrolytes and also how the dilution affects the degree of dissociation.

TEMPERATURE 18° C. DEGREE OF DISSOCIATION

	<i>N</i> /10.	<i>N</i> /100.	<i>N</i> /1000.
Ammonium hydroxide . . . . .	0.0133	0.0415	0.125
Acetic acid . . . . .	0.0133	0.0415	0.125
Boric acid . . . . .	0.00007	0.00024	0.0007

Thus in *N*/10 acetic acid 1.33% of the weight of the acetic acid consists of hydrogen ions and acetate ions.

**Dissociation Constant.** Consider an electrolyte AB which ionises when in solution.



According to the Law of Mass Action, when equilibrium has been attained.

$$\frac{(\text{Conc. of A}^+) (\text{Conc. of B}^-)}{(\text{Conc. of unionised AB})} = \text{a constant.}$$

where the concentrations are expressed in gram-ions and gram-molecules per litre of solution respectively. The equation is often expressed thus :—

$$\frac{[\text{A}^+] [\text{B}^-]}{[\text{AB}]} = K \text{ (the equilibrium constant).}$$

The equilibrium constant in this case is termed the dissociation

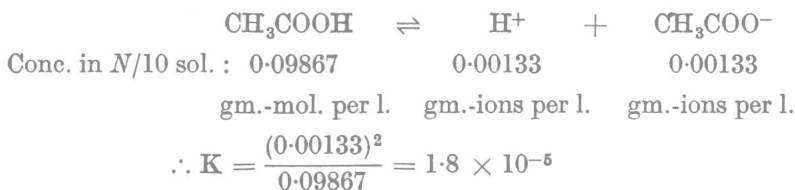
<sup>1</sup> Strong electrolytes are now believed to be completely dissociated even in concentrated solution, and it is because their mobility (*i.e.*, the free movement of the ions) is restricted in concentrated solution that they appear to be to some extent undissociated.



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constant of the electrolyte. This can be calculated from the above table thus :—

*Dissociation Constant for Acetic Acid.*



**Ionic Product of Water.** We have seen that neutralisation consists of the formation of molecules of undissociated water by the chemical union of hydrogen ions and hydroxyl ions.



Like other ionic reactions this is to some extent reversible.

It is true that pure water is practically a non-conductor of electricity, but from conductivity experiments it can be shown that pure water does contain minute quantities of both hydrogen ions and hydroxyl ions. Then:



represents the equilibrium between the ions and undissociated water, and the dissociation constant  $K$  would be represented by

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = K$$

The amount of the ions is so small, however, that  $[\text{H}_2\text{O}]$  can be considered to be constant without serious error and the expression  $[\text{H}^+][\text{OH}^-]$  is therefore also constant and is termed the ionic product of water. The value of this product at  $25^\circ \text{C}$ . is very nearly  $10^{-14}$ , and since the ions are present in equal amounts (1 gm.-mol. of water gives 1 gm.-ion of hydrogen and 1 gm.-ion of hydroxyl ion) it follows that pure water contains a concentration of hydrogen ion of  $10^{-7}$  gm. per litre.

$$[\text{H}^+][\text{OH}^-] = 10^{-14} \text{ (at } 25^\circ \text{C.)}$$

Concentrations are expressed in gm.-ions per litre thus :—

$$[\text{H}^+] = 10^{-7} \text{ gm.-ions per litre or } 10^{-7} \text{ gm. of hydrogen ions per litre.}$$

$$[\text{OH}^-] = 10^{-7} \text{ gm.-ions per litre or } 17 \times 10^{-7} \text{ gm. of hydroxyl ions per litre.}$$

Although this ionic product is exceptionally small it is of great importance because it is this constant which is used to trace the alteration of the hydrogen ion concentration which takes place during neutralisation.