

R35.4

CHEMISTRY NOTES for D.P.H. CLASS

(1) Volumetric Analysis.

I A.

Volumetric Analysis

In this method quantitative determinations are made by measuring the volumes of solutions of reacting substances which are equivalent to one another. If one of the solutions is of known strength then the concentration of the other solution is simply calculated. The method is capable of a high degree of accuracy provided:-

- (1) the standard solution (see below) is accurately prepared
- (2) the measuring apparatus (burettes, pipettes, etc.) is correctly graduated
- (3) the indicator (see below) is sufficiently sensitive
- (4) the personal technique is good.

Standard Solutions

The standard solution is the key to the method and may be defined as a solution which contains a known amount of a substance in a known volume. Preparing an accurate solution is a task of some difficulty for it needs meticulous care in obtaining pure substances, in weighing, in dissolving and in checking.

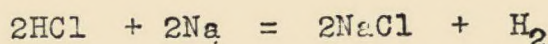
The chief kinds of standard solution are:-

- (1) Normal solutions
- (2) Arbitrary standard solutions.
- (3) Molar solutions.
- (4) Percentage solutions.

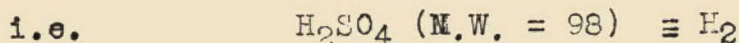
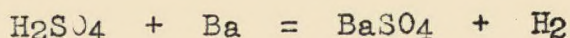
The first two are the ones usually employed in public health chemistry.

The Normal solution is one which contains the gram-equivalent weight of the substance in one litre of the solution. By gram-equivalent weight is meant the amount of the substance equivalent to one gram (actually 1.008 gm.) of replaceable hydrogen.

Consider the following reactions with hydrochloric acid:-



In each case HCl contains one replaceable H or in grams $1 + 35.5 = 36.5$ gms. of HCl yield 1 gram of hydrogen. A normal solution of HCl would therefore contain 36.5 gms., i.e. the M.W. in grams of HCl in 1 litre of solution. With sulphuric acid the case is different because this acid is dibasic:-



or 98 gms. of H_2SO_4 yield 2 grams of hydrogen and hence it is $\frac{98}{2}$ or $\frac{\text{M.W.}}{2}$ grams of sulphuric acid which contain

1 gram of replaceable hydrogen and hence a normal solution of H_2SO_4 contains 49 gms. of the acid in one litre.

With simple organic acids it is the hydrogen of the carboxyl group - COOH which is alone replaceable by metals, so that the number of replaceable hydrogen atoms in an organic acid is the same as the number of carboxyl groups. Note the following:-

Acetic acid								
$CH_3.COOH$	a litre of normal solution contains the M.W. in gms.							
Oxalic acid								
$(COOH)_2.2H_2O$	" " " " " " " "					"	$\frac{M.W.}{2}$	" "
Citric acid								
$C_3H_5O.(COOH)_3.H_2O$	" " " " " " " "					"	$\frac{M.W.}{3}$	" "

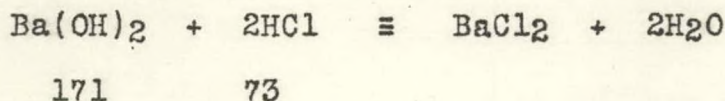
With bases the chemical equivalent is that amount which will neutralize a gram-equivalent of a monobasic acid or in other words that amount which will secure the replacement of one gram of hydrogen in an acid.

Thus:-



Here 40 grams NaOH \equiv 36.5 grams HCl \equiv 1 gram of hydrogen

A normal solution of NaOH contains therefore 40 grams in one litre.



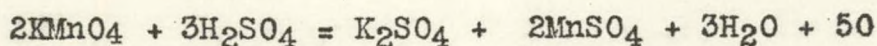
Here 171 grams $Ba(OH)_2 \equiv 73$ grams HCl $\equiv 2$ grams of hydrogen

$$\therefore \frac{171}{2} \text{ grams } Ba(OH)_2 \equiv 1 \text{ gram of hydrogen}$$

A normal solution of $Ba(OH)_2$ contains therefore $\frac{171}{2}$ grams.

Similarly $Na_2CO_3 \equiv 2HCl$, but $NaHCO_3 \equiv 1 HCl$

The nature of the reaction upon which the volumetric analysis is based must always be considered in calculating the strength of a normal solution for this strength may vary according to the conditions under which such reaction takes place. For example potassium permanganate as an oxidising agent behaves differently in acid and in alkaline solution. In acid solution it reacts thus:-

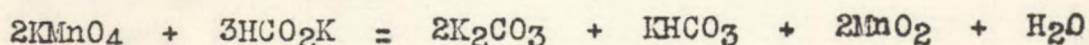


$$\therefore 2KMnO_4 = 5O \equiv 10 H.$$

$$\therefore KMnO_4 = 5 H$$

\therefore a normal solution would contain $\frac{M.W.}{5}$ in grams when used in acid solution.

In alkaline (or neutral) solution however, 2KMnO_4 liberate 3 atoms of available oxygen, i.e.



$$2\text{KMnO}_4 \equiv 30 \equiv 6\text{H}$$

$$\therefore \text{KMnO}_4 \equiv 3\text{H}$$

\therefore a normal solution would contain $\frac{\text{M.W.}}{3}$ in grams when used in alkaline (or neutral) solution.

These known strength solutions are used as normal solutions or as decinormal or centinormal or some other fraction of normal. These are written thus N or 1.0 N, $\frac{\text{N}}{10}$ or 0.1 N, $\frac{\text{N}}{100}$ or 0.01 N.

Arbitrary standard solutions are much used for ease of working. For example in analysing a water for its chlorine content it is more convenient to use the silver nitrate solution in a strength such that 1 c.c. of the AgNO_3 solution = 1.0 ngm. of chlorine as chloride, than to use a normal solution for the calculation would then be somewhat more laborious. The strength required for such a solution can be easily calculated by reference to the equation which expresses the interaction of silver nitrate and a chloride.

Molar solutions are those which contain the molecular weight of the substance in grams dissolved in water to make 1 litre. It is clear from the foregoing that a molar solution may be the same as a normal solution as in the case of HCl, but with sulphuric acid a molar solution is twice as strong as the normal solution and with citric acid three times as strong.

Percentage solutions. The strength of these is obvious. They are rarely used in volumetric analysis, because the use of normal solutions makes the working of analyses and the calculation of the results very much simpler once the underlying principle is understood.

Calculation of results when using normal solutions.

The calculation is simple provided it is always remembered that equivalent volumes are being determined. One volume of N.NaOH will neutralize one volume of N.HCl, but this obviously does not mean that the weights of NaOH and of HCl in the particular volumes chosen are identical, for from the equation



it is clear that 40 grams of NaOH neutralize 36.5 grams of HCl.

$$\text{As } 1000 \text{ c.c. N.NaOH} \equiv 1000 \text{ c.c. N.HCl}$$

$$\text{then } 10,000 \text{ c.c. } 0.1 \text{ N.NaOH} \equiv 1000 \text{ c.c. N.HCl}$$

$$500 \text{ c.c. } 2.0 \text{ N.NaOH} \equiv 1000 \text{ c.c. N.HCl}$$

because 0.1 N.NaOH contains one tenth and 2.0 N.NaOH contains twice the number of grams of alkali as a N solution of NaOH.

Hence we have

$$\begin{array}{l} \text{volume of alkali} \times \text{the normality} \\ \text{of the alkali} \end{array} = \begin{array}{l} \text{volume of acid} \times \text{the} \\ \text{normality of the acid} \end{array}$$

Supposing in a titration 20 c.c. of an acid of unknown normality X requires 35 c.c. of decinormal alkali for neutralization, we then have

$$35 \times 0.1 = 20 \times X$$

$$\therefore X = \frac{35 \times 0.1}{20} = 0.175 \text{ N.}$$

There is no need in such a calculation to bother about atomic weights. These would only be required if there was need to determine the number of grams of HCl in the unknown solution. Here again the calculation is easy for we know that HCl contains one replaceable hydrogen and therefore a N solution contains 36.5 grams in 1 litre and hence a 0.175 N solution contains $36.5 \times 0.175 = 6.39$ grams of HCl in 1 litre.

Methods in Volumetric Analysis.

There are three main types:-

- (1) Acidimetry and Alkalimetry.
- (2) Oxidation and Reduction, for example in the use of potassium permanganate.
- (3) Precipitation, for example the determination of chlorides in water by precipitation with silver nitrate in standard solution.

Methods are either direct or indirect. Examples of the former are the titration of oxalic acid with permanganate or simple acidimetry. Indirect methods would include such a case as the determination of H_2S in a solution: a measured volume of standard iodine known to be in excess of what is required to react with the H_2S is added and when reaction is complete the residual iodine is determined by standard thiosulphate solution. This is called back titration.

Indicators.

In volumetric analysis indicators are required to signal the completion of a reaction. Types of such indicators are:-

- (1) potassium permanganate - here one of the reacting substances in the titration acts as its own indicator.
- (2) potassium chromate - this is added in small amount in the titration of chlorides with silver nitrate, as in water analysis.
- (3) methyl orange, phenol phthalein, litmus and others in the titration of acids and alkalis.

"Rules of Titration" in Acidimetry and Alkalimetry.

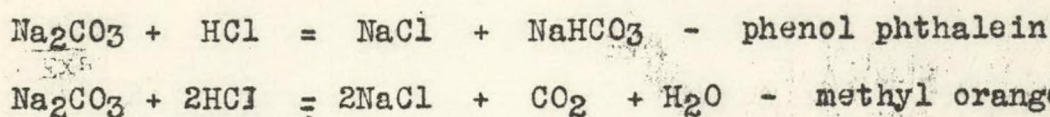
- (1) Strong acid with strong base - any indicator.
- (2) Strong acid with weak base - methyl orange.

- (3) Weak acid with strong base - phenol phthalein.
- (4) Weak acid with weak base - should never be done.

The principles underlying these rules are dealt with in the notes on hydrogen ion concentration.

Neutrality to Indicators and Equivalence.

It is important to note that neutrality to indicators and equivalence are not necessarily identical. If Na_2CO_3 is titrated with HCl using phenol phthalein as indicator, it is found that the indicator becomes colourless (acid) before all the carbonate has been neutralized to NaCl whereas if methyl orange is used neutrality is not indicated until there has been added an amount of HCl twice that required to signal neutrality with phenol phthalein. The explanation of this is found on considering the equations:-



The reaction proceeds in two stages - the acid carbonate or bicarbonate is first formed and phenol phthalein indicates acidity with sodium bicarbonate. Methyl orange on the other hand still shows alkalinity with the bicarbonate and only changes colour when all the bicarbonate has been decomposed.

(See Hydrogen Ion Concentration)

Other Examples of Volumetric Analysis.

All determinations should, if possible, be done three times and the mean of the results used in the calculation.

1. (A) is a watery solution of NaOH. By means of the decinormal acid provided, using methyl orange as indicator, determine:-
 - (a) the normality of solution (A)
 - (b) the percentage strength
 - (c) the proportion of water which must be added to convert it into a 0.025 N solution.

Pipette 20 c.c. of (A) into a white porcelain dish. Use a 20 c.c. pipette, allow it to drain against the side of the dish and do not blow out its contents. Add a few drops of methyl orange. From a burette run in the standard acid, whilst stirring with a glass rod until there is just apparent a colour change in the indicator. The first titration may be done quickly to obtain an approximate result, but this must be followed by three titrations carefully performed. The mean of these three titrations is used for the calculation.

Calculations.

- (a) Let χ = the normality of (A)

Assume that 18.8 c.c. is the mean of the three titration figures

Then:-

$$\begin{aligned} \chi \times 20 &= 0.1 \times 18.8 \\ \therefore \chi &= 0.094 \text{ N.} \end{aligned}$$

(b) As NaOH is monovalent therefore 1 litre of a Normal solution will contain the gram molecular weight, i.e. 40 grams (Na = 23).

Since 1 litre of a 1.0 N solution contains 40 grams

∴ 1 " " "0.094 N " " 3.76 "

∴ the percentage strength is 0.376%

(c) To find the dilution needed to convert a 0.094 N solution into a 0.025 N solution:-

A 0.094 N solution contains 0.094 x 40 grams per litre

and a 0.025 N " " 0.025 x 40 " " "

∴ $\frac{.025}{.094}$ of a litre of the solution (A) contains the amount of

NaOH in 1 litre of a 0.025 N solution.

Hence $\frac{.025}{.094}$ of a litre of (A) must be diluted to a volume of 1 litre

with water

i.e. the proportion is:-

$$\frac{.025}{.094} : \frac{.094 - .025}{.094}$$

or 25 : 69

∴ The addition of 69 c.c. of water to 25 c.c. of solution (A) will yield a 0.025 N solution.

2. To determine the strength of solution of barium chloride, given standard solutions of Na₂CO₃ and of HCl. This may be done by precipitating the Ba as carbonate by adding a measured quantity of the Na₂CO₃ solution sufficient to provide an excess so as to ensure complete precipitation, filtering off the barium carbonate and then determining the excess of carbonate by titration of the filtrate with the standard acid.



Pipette 20 c.c. of the BaCl₂ solution into a beaker. Add 25 c.c. of the 0.1 N. Na₂CO₃ (experiment must decide whether this does provide excess of Na₂CO₃). Stir, allow to stand some minutes and then filter off the BaCO₃. Wash out the beaker several times with distilled water and pour the washings on to the filter.

Titrate the filtrate with 0.1 N. HCl using methyl orange as indicator.

Supposing 9.4 c.c. is the mean of three titrations. Therefore there is left in the filtrate an amount of alkali equal to the amount of alkali in 9.4 c.c. of 0.1 N. Na₂CO₃.

20 cc fad. solution $\approx 21 \text{ cm}^3$
0.01N thio sulph = 19.



X = Normality of I₂

It req 19 cc 0.01N thio sulph to react with 20 cc NaI.

$$20X \times 20 = 19 \times 0.01$$

$$20X = 19 \times 0.01$$

$$X = \frac{19 \times 0.01}{20} = 0.0095 \text{ N}$$

Calculation:- Let X = the normality of the $BaCl_2$ solution
then 20 c.c. of the $BaCl_2 \equiv 25 - 9.4$ c.c. of 0.1 N. Na_2CO_3
because 9.4 c.c. was the amount of 0.1 N. Na_2CO_3 not used up in
converting the Ba into carbonate.

$$\begin{aligned} \text{Therefore } 20 \times X &= (25 - 9.4) \times 0.1 \\ X &= \frac{(25 - 9.4) \times 0.1}{20} = 0.078 \end{aligned}$$

Hence the $BaCl_2$ solution is 0.078 Normal.

To express this in terms of grams per litre:-

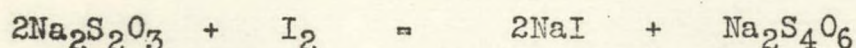
Barium is divalent and therefore a normal solution would contain the M.W. grams in one litre. This M.W. works out at

$$208.29 \frac{Ba}{2} = 137.37 \quad Cl = 35.467.$$

Therefore 1 litre of normal $BaCl_2$ contains $\frac{208.29}{2} = 104.145$ gms.
and 1 litre of 0.078 N. $BaCl_2$ contains 104.145×0.078 gms.
= 8.123 gms.

3. Solution C contains 1.27 grams of a sample of iodine per litre. Given 0.01 N sodium thiosulphate ($Na_2S_2O_3$) determine the percentage purity of the iodine.

The reaction between iodine and sodium thiosulphate is frequently used in volumetric analysis thus:-



The iodine is converted into colourless sodium iodide. The end point is determined by means of starch which in the presence of free iodine gives a blue colour due to iodide of starch.

Into a small flask pipette say 20 c.c. of the iodine solution. From a burette add the thiosulphate slowly until only a faint iodine colour remains. Then add a few drops of starch solution when a blue colour appears. (Note that the end point is sharpest when the addition of starch is delayed till nearly the end of the titration). Continue adding the thiosulphate drop by drop, mixing between each addition, until the blue colour disappears. Repeat three times and take the mean of the determinations.

Calculation.

Let X = normality of the iodine solution and assume that 19.0 c.c. of the thiosulphate are used in the titration of 20 c.c. of the iodine solution.

$$\begin{aligned} \text{Thus:-} \quad X \times 20 &= 19.0 \times 0.01 \\ \therefore X &= 0.0095 \text{ N} \end{aligned}$$

Now 1 litre of a Normal solution of iodine (A.W. = 127) contains
127.0 gms. of iodine

∴ 1 litre of solution C contains $127 \times .0095$ gms. = 1.2065 gms.

From this figure taken in conjunction with the fact that 1.27 grams of the particular sample of iodine was present in a litre of solution C, it is clear that the iodine was impure and its percentage purity can thus be calculated.

1 litre contains 1.2065 gms iodine
1.2700

$$\begin{array}{r} 1.2065 \text{ gms iodine} \\ \times 100.00 \\ \hline 120.65 \\ 1143 \\ \hline 12065 \end{array}$$

~~13.8 cm H₂O~~ = ~~13.8 cm NaOH x N~~

13.8 cm H₂O 0.1N = 25 cm NaOH x N.

$$25x = 13.8 \times 0.1$$

$$x = \frac{13.8 \times 0.1}{25}$$

$$= \underline{\underline{0.0552 N}}$$

$$\begin{array}{r} .0552 \\ 25 \overline{) 1.38} \\ \underline{125} \\ 130 \\ \underline{125} \\ 50 \end{array}$$

Practical Exercises.(1) Estimate the CO₂ content of the Laboratory Air [Pettenkoffer's Process].

(a) Fill the flask provided with water - inserting stopper. Measure the volume of water used and thus determine the volume of the bottle, which is the volume of air to be used in the analysis.

(b) Take 100 cc.s of Ba(OH)₂ solution, and divide it into two portions of 50 cc.s each. Quickly add one portion to the flask [thus displacing 50 cc.s of air], re-stopper and place the jar aside for one hour, occasionally rolling it gently to ensure absorption of CO₂.

22.1 Meanwhile estimate the alkalinity of the other 50 cc.s of Ba(OH)₂, by titration with a standard oxalic acid solution [1 cc. = 0.5 cc. of CO₂ at N.T.P.], using phenolphthalein as indicator. 22.5 cc
18.5 cc

(c) At the end of the hour, titrate the unneutralized Ba(OH)₂ in the flask with oxalic acid solution and phenolphthalein. It is permissible to perform the titration in the jar itself.

(d) Note the temperature and barometric pressure of the laboratory air.

(e) Calculate the percentage of CO₂ in the air. 750 mm
Temp 21°C 70°F

Example.

(a) Suppose the volume of air in the flask as measured was 3050 cc.s. After deducting 50 cc.s, the volume occupied by the Ba(OH)₂, the volume of air is 3000 cc.s at the temperature and pressure of the laboratory, which, for example, may be 15°C and 740 mms. respectively. Hence at N.T.P. the volume of the 3000 cc.s of air will be:-

$$3000 \times \frac{273}{288} \times \frac{740}{760} = 2768 \text{ cc.s at N.T.P.}$$

(b) Suppose 50 cc.s of Ba(OH)₂ solution required 24 cc.s of standard oxalic acid solution, and that the Ba(OH)₂ solution in the flask at the end of one hour required 20 cc.s of oxalic acid solution:-

Then 24-20 = 4 cc.s of standard oxalic acid solution is equivalent to the CO₂ in 2768 cc.s of air.

Since 1 cc. standard oxalic acid solution = 0.5 cc.s CO₂

∴ 4 cc.s. " " " " = 2.0 cc.s CO₂

∴ Percentage of CO₂ in the air is:-

$$\frac{2}{2768} \times 100 = 0.072 \text{ per cent.}$$

II. Of the waters (A) and (B), one is supposed to contain poisonous metals, and the other has been chlorinated on account of sewage pollution. Test for poisonous metals, and if found, estimate the amount of metal present.

Test for free chlorine as follows:-

Put 100 cc.s of the water into a Nessler glass and add 1 cc. of Ortho-tolidine solution. Mix and allow to stand at least five minutes. Small amounts of free chlorine give a yellow and larger amounts an orange colour.

Make a quantitative estimation by comparing the colour obtained with those of the standards provided. The standards are mixtures (100 cc.s) of CuSO₄ and K₂Cr₂O₇, the colours of which match those of varying amounts of chlorine when treated with ortho-tolidine.

It required 22.7cc to neutralize 50cc Ba(OH)_2

1.00 = 0.55

10

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- I. (A) is a solution of NaOH in water. By means of the decinormal HCl provided, using methyl orange as indicator, determine:-
- (a) the normality of solution (A)
 - (b) the percentage strength
 - (c) the proportion of water which must be added to (A) to convert it into a 0.025 N, solution.

What differences (if any) would there be in your answers to (a), (b) and (c) if (A) were a solution of Na_2CO_3 and you had obtained the same titration figures?

Would there be any differences if (A) had been NaHCO_3 ?

Supposing the decinormal acid had been sulphuric acid, would there have been any difference in the titration figures?

2. Estimate the strength of the given solution (B) of barium chloride. A.W. of Ba = 137.
(Precipitate the Ba solution, say 20 c.c., with excess of the S.S. of sodium carbonate, say 25 c.c. Filter off the Ba carbonate and titrate excess of sodium carbonate).
3. Solution (C) contains 1.27 grams of iodine per litre. Given 0.01 N sodium thiosulphate, determine the percentage purity of the iodine.

$$25 \text{) } \begin{array}{r} 1.25 \\ \underline{1.25} \\ 0.06 \end{array} \quad 17.5$$

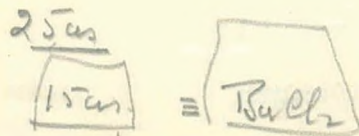
23.4
23.4
24.5

$$\frac{7.5 \times 0.1}{20}$$

$$20 \text{) } \begin{array}{r} .75 \\ \underline{.0375} \end{array} \text{ N.}$$

71.6

23.8



10 cm. 0.1N. Na_2CO_3

25 cm. Solution C \equiv 23.5 cm. 0.07N. This.

Let x = Normality of C

$$25x = 23.5 \times 0.07$$

$$x = \frac{23.5 \times 0.07}{25} = 25 \text{) } \begin{array}{r} .0094 \\ \underline{.275} \\ 225 \\ \underline{100} \end{array}$$

$$x = 0.0094 \text{ N.}$$

Solution C is 0.0094 N.

$$\begin{array}{r} 127 \\ \underline{.0094} \\ 508 \\ \underline{1143} \\ 1.1928 \end{array}$$

1 liter of N. Solution contains 127 gms.

1 " " 0.0094 N " " $127 \times 0.0094 = \underline{1.194}$ gms.

$$\frac{1.194}{1.270} \times 100 = \text{ \% Purity}$$

Practical III

1. Compare the pH of (i) tap water, (ii) distilled water, (iii) boiled distilled water, (iv) cold boiled distilled water after expired air has been blown through it.
2. Given 0.1 N HCl and acetic acid, make dilutions of 10 cc. each from 0.1 to 0.0001 N and compare the pH of the corresponding dilutions of the two acids, as accurately as you can.

Approximately:-

0.1 N HCl = pH 1.0
0.01 N HCl = pH 2.0

0.1 N acetic = pH 2.87
0.01 N acetic = pH 3.37

3. Similarly, compare the titrable acidity of the corresponding dilutions. (Use 10 cc.)
4. Put up two series of 6 tubes each containing 10 cc. of 0.1 N acid, HCl in one series and acetic acid in the other. Add 0.2 cc. N NaOH to the first pair of tubes, 0.4 cc. N alkali to the second pair and so on. Compare the pH of each series and draw a curve to show the course of events.
5. Compare the pH of the 'neutral' solutions of sodium chloride, sodium cyanide and ammonium chloride. Explain your findings. (Phenol Red)

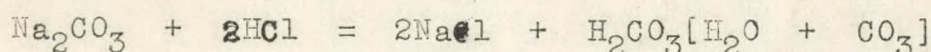
Thymol Blue	1.2 - 2.8
Bromo-phenol Blue	2.8 - 4.6
Methyl Red	4.2 - 6.3
Bromo-cresol Green	3.6 - 5.2
Bromo-cresol Purple	5.2 - 6.8
Bromo-thymol Blue	6.0 - 7.6
Phenol Red	6.8 - 8.4
Cresol Red	7.2 - 8.8
Thymol Blue	8.0 - 9.6

D.P.H.

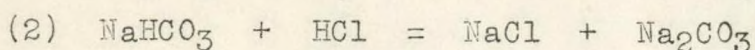
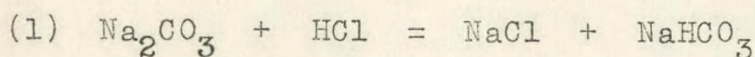
Practical IV

1. Determine the amounts of sodium carbonate and of bicarbonate in the given solution (A). Given N/10 acid and indicators. Use 20 c.c.
2. Titrate 20 c.c. of the NH_4OH solution (B) with N/10 HCl in the presence of methyl orange; then titrate another 20 c.c. in the presence of phenol phthalein. Titrate 20 c.c. of the acetic acid solution (C) with N/10 NaOH in the presence of phenol phthalein; then titrate another 20 c.c. in the presence of methyl orange. Observe the differences in the titrations and try to explain these differences.
3. Given 0.1N HCl and 0.1N acetic acid, make dilutions of 100 c.c. each from 0.1N to 0.001N and compare their titrable acidity using phenol phthalein and methyl orange in separate titrations for each. (Do each titration in duplicate using 20 c.c.). This experiment shows that to obtain accuracy a suitable indicator must be chosen.

1. The neutralisation of sodium carbonate by hydrochloric acid may be represented by the following equation.



Actually, however, the neutralisation takes place in two stages, the carbonate first being converted quantitatively into bicarbonate, the latter forming sodium chloride on the addition of a further quantity of acid. The neutralisation process may be represented by the following two equations, therefore



It will be seen then that exactly twice as much acid is required to convert the carbonate into chloride as is required to convert it into bicarbonate. If therefore we could stop the addition of acid at the point when all the carbonate had been converted into bicarbonate we should get a titration figure equal to half the amount of acid required for complete neutralisation. In actual practice it is found that the indicator phenol phthalein, which changes colour from pink to colourless at about pH 8.3, satisfactorily marks the end point of equation (1). This is due to the fact that even a weak solution of the base, sodium carbonate, gives a solution more alkaline than pH 8.3 and therefore turns phenol phthalein red, whereas a concentrated solution of sodium bicarbonate is not as alkaline as this and hence in bicarbonate solutions phenol phthalein is colourless.

If then a sodium carbonate solution be neutralised with hydrochloric acid using phenol phthalein as indicator we shall get a titration value of only half that which would be obtained in the presence of methyl orange. [This indicator changes colour about pH 4.0]

By making use of these two indicators it is not only possible to neutralise the carbonate in two definite stages, represented by equations (1) and (2), but it is also possible to determine the amounts of carbonate and bicarbonate present in a mixture of these two substances.

Determination of carbonate in a carbonate-bicarbonate mixture.

Take 20 c.c. of the mixture, add a drop or two of phenol phthalein. As carbonate is present the colour turns pink. Run in N/10 HCl from a burette till the pink colour is just discharged. At this point all the carbonate has been converted into bicarbonate, as equation (1), and therefore the total carbonate present will be equivalent to twice this value.

Suppose using phenol phthalein as indicator

20 c.c. of mixture required 9 c.c. of N/10 HCl

Then " " " = 9 x 2 c.c. N/10 Na₂CO₃

∴ Normality of carbonate in mixture = $\frac{9 \times 2 \times 0.1}{20} = 0.09$

The equivalent weight of Na₂CO₃ = $\frac{1}{2}$ M.W. = $\frac{23 \times 2 + 12 + 16 \times 3}{2}$
= $\frac{106}{2} = 53$

Determination of bicarbonate in a carbonate-bicarbonate mixture.

This determination should be carried out in two ways.

(a) Continue with the sample already neutralised to the phenol phthalein end point. As this indicator is now colourless a second indicator, such as methyl orange, may be added and the titration continued to the end point of the latter.

Suppose a further quantity of 21 c.c. of N/10 HCl is required to reach the methyl orange end point.

Then this titration figure represents the neutralisation of all the original bicarbonate and of half the original carbonate of the solution, for by the previous titration, using phenol phthalein as indicator, the carbonate has been converted into bicarbonate.

20 c.c. of mixture = 21 c.c. 0.1N HCl to neutralise solution from the phenol phthalein to the methyl orange end point

∴ 21 c.c. 0.1N HCl = all original bicarbonate + $\frac{1}{2}$ (original carbonate) of 20 c.c. mixture

∴ bicarbonate of 20 c.c. mixture = 21-9 = 12 c.c. 0.1N HCl

∴ normality of bicarbonate = $\frac{12 \times 0.1}{20} = 0.06$

As the acid of bicarbonates, viz. H.HCO₃, has only one replaceable H. its equivalent weight equals its molecular weight.

∴ Equivalent weight of NaHCO₃ = 23 + 1 + 12 + 48 = 84 g.

∴ 1 litre of N.NaHCO₃ solution contains 84 g.

and 1 " " 0.06N. " " 84 X 0.06 g.

∴ 100 " " " " " $\frac{84 \times 0.06}{10} = 0.504$ g.

(b) Alternatively the bicarbonate may be estimated by taking a fresh 20 c.c. quantity of the mixture and titrating this straight away to the methyl orange end point and deducting from this value twice that obtained by the previous phenol phthalein titration.

Students should try both these methods.

14.5 cc Perm
25 cc oxal
.1N Oxalate

Practical II.

1. Estimation of Free Oxalic Acid $\begin{matrix} \text{COOH} \\ | \\ \text{COOH} \end{matrix} \cdot 2\text{H}_2\text{O}$ and Potassium Oxalate $\begin{matrix} \text{COOK} \\ | \\ \text{COOK} \end{matrix} \cdot \text{H}_2\text{O}$ in a solution.

Calculate the amounts of each in grams per litre.

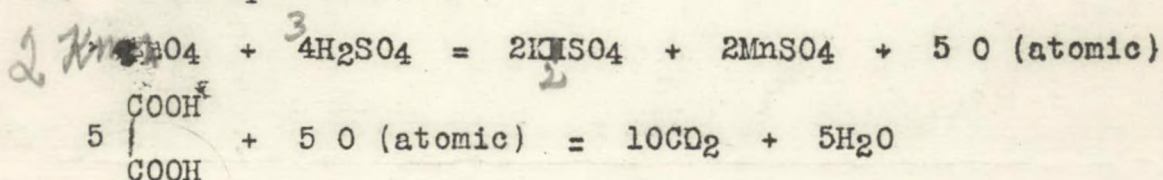
You are given N/10 KMnO_4 , N/10 NaOH , and conc. H_2SO_4

Method. Determine:-

(i) The normality of the total oxalate radicle $\begin{matrix} \text{COO-} \\ | \\ \text{COO-} \end{matrix}$, that is free oxalic acid plus K- oxalate.

This is performed by titrating a volume of the solution with N/10 KMnO_4 in the presence of strong H_2SO_4 .

The H_2SO_4 converts the K-oxalate into its equivalent of free oxalic acid, which along with the free oxalic acid originally in the solution is to be oxidised by the KMnO_4 ; obviously then, the total oxalate radicle in the solution is estimated by the KMnO_4 titration



For example. Suppose 20 cc. of solution after adding H_2SO_4 required 25 cc. of 0.1N KMnO_4 . The normality of total oxalate radicle (X) is then found by the equation:-

$$20 \times X = 25 \times 0.1$$

$$X = \frac{25 \times 0.1}{20}$$

$$= .125 \text{ N}$$

(ii) Determine the normality of the free oxalic acid.

Another volume of the solution is titrated by N/10 NaOH , using phenol phthalein as indicator.

This is an ordinary acid-base reaction. The NaOH reacts only with free oxalic acid, not at all with K-oxalate.



For example. Suppose 20 cc. of solution was neutralised by 15 cc. of N/10 NaOH , the normality of the free oxalic acid is then found by the equation:-

$$20 \times X = 15 \times 0.1$$

$$X = 0.075 \text{ N}$$

(iii) Since the normality of total oxalate is known from (i), and that of free oxalic acid from (ii), the normality of K-oxalate is equal to $\underline{[(i) - (ii)]} = .125 - .075 = 0.050 \text{ N}$

Practical Procedure to Question 1.

(i) Determination of normality of total oxalate radicle.

Into a conical flask pipette accurately 20.c.c. of solution.

Add approximately 5 c.c. of conc. H_2SO_4 (not HCl nor HNO_3) *because they react with $KMnO_4$*

Support the flask on a tripod, and heat the flask to nearly boiling over a Bunsen burner.

Run in N/10 $KMnO_4$ from a burette, shaking after each addition until a permanent pink colour is obtained. Keep the solution

over a small flame throughout the titration.

Observe the amount of N/10 $KMnO_4$ used.

Repeat at least twice and average the readings.

Calculate the normality of total oxalate radicle.

(ii) Determination of normality of free oxalic acid.

Into a conical flask or dish pipette 20 c.c. of solution.

Add a few drops of phenol phthalein.

Run in N/10 NaOH from a burette until a pink colour is obtained.

Observe the amount of N/10 NaOH used.

Repeat at least twice and average the readings.

Calculate the normality of the free oxalic acid.

(iii) Calculate the strength in grams per litre of free oxalic acid and K-oxalate from the molecular formulae given.

2. Estimate the 'Volume Strength' of the H₂O₂ solution.

The 'Volume Strength' is the volume of oxygen yielded by one volume of H₂O₂ solution.

e.g. if 5 c.c. of H₂O₂ solution yield 45 c.c. of oxygen,

$$\text{V.S.} = \frac{45}{5} = 9$$

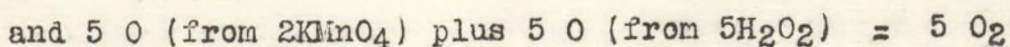
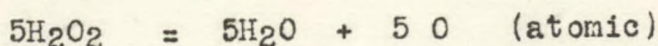
if 2 litres " " " " 10 litres of oxygen,

$$\text{V.S.} = \frac{10}{2} = 5$$

You are given N/10 KMnO₄, and dilute H₂SO₄.

Method.

(i) This is an oxidation reaction: but in this case during the reaction, atomic oxygen is provided by KMnO₄ which combines with atomic oxygen from the H₂O₂, to yield molecular (gaseous) oxygen. Actually one half of the oxygen yielded comes from the KMnO₄, and the other half from the H₂O₂ as shown by the equation:



(ii) Determine the normality of the H₂O₂ solution.

This is performed by titrating a volume of the H₂O₂ (usually 5 c.c.) suitably diluted with distilled water, in the presence of H₂SO₄ (Not HCl, nor HNO₃).

For example: Suppose 5 c.c. of H₂O₂ solution required 40 c.c. of N/10 KMnO₄

$$\text{Then } 5 \times X = 40 \times 0.1$$

$$\therefore X \text{ (normality of H}_2\text{O}_2\text{)} = \frac{40 \times 0.1}{5}$$

$$= 0.8 \text{ N}$$

(iii) The volume strength can be estimated from the normality by using the following facts:-

A normal solution of oxygen is one in which 1 litre of solution contains 8 grams of oxygen (which is equivalent to 1 H atom)

∴ A normal solution of H₂O₂ is one in which 1 litre yields 8 grams of oxygen (which is equivalent to 1 H atom).

1 litre normal solution of H₂O₂ contains 8 gms
1 litre of 0.8 N. H₂O₂ contains 8 gms = 1 gm. of O
32 gms oxygen N.F. occupies 22.4 vol. of O₂
∴ 0.64 gms oxy occurs

22.4 x 0.8 = 18.08
18.08 x 0.64 = 11.67
11.67 x 0.64 = 7.47

5.66
1.64
2.424
3.336
3.336
11.67
7.47

The molecular weight of all gases at N.T.P. occupy 22.4 litres

∴ 32 gms. of oxygen ($O_2 = 2 \times 16$) at " " 22.4 "

∴ 8 " " " " " 5.6 "

that is 1 litre of 1 N oxygen solution contains 5.6 litres Oxygen

that is 1 litre of 1 N H_2O_2 solution yields 5.6 "

∴ 1 litre of 0.8 N (i.e. normality found) yields
5.6 x 0.8 litres

= 4.48 litres

Since 1 litre of this H_2O_2 solution would yield 4.48 litres

∴ its volume strength is $\frac{4.48}{1} = 4.48$

Note The strength of the H_2O_2 solution in grams per litre may be determined from the normality, e.g.

Since $H_2O_2 = H_2O + O$

∴ 16 gms. of oxygen are yielded by 34 gms. of H_2O_2

∴ 8 " " " " " " 17 gms. of H_2O_2

i.e. 1 litre of 1 N H_2O_2 solution contains 17 gms. H_2O_2

∴ 1 " " 0.8N H_2O_2 " " 17 x 0.8 gms. H_2O_2

Practical Procedure to Question 2.

To a conical flask add approximately 100 c.c. distilled H₂O

Pipette accurately 5 c.c. H₂O₂ solution into the water.

Add roughly 30 c.c. of dilute H₂SO₄.

Do not heat the flask. (Compare with oxalates)

Run in N/10 KMnO₄ from burette with continual shaking till a permanent pink colour is obtained.

The solution becomes hot during the titration.

Observe the burette reading.

Perform at least two more titrations and average the readings.

Calculate the normality and volume strength.

5 cc. H₂O₂ req. 6 cc KMnO₄

3. Solution (C) contains 2.48 gms. of a sample of sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, per litre

Determine the percentage purity of the sodium thiosulphate by means of the 0.01 N iodine solution.

The method and practical procedure are the same as those detailed for determining the percentage purity of a sample of iodine by means of standard sodium thiosulphate solution.

(See Practical I, Question 3).

Na = 23, S = 32, O = 16, H = 1

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