LIII.—On Schützenberger's Process for the Estimation of Dissolved Oxygen in Water.

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THE increased use of Schützenberger's method as a means of determining the amount of dissolved oxygen in water, has led us to make a careful critical examination as to its reliability.

The method has been examined recently by Dupré,* and by Ramsay and Williams (*Chem. Soc. J.*, Trans., 1886, **49**, 751), whose papers may be referred to for a description of the process.

Results not concordant with the same Water.—In the first place, 15 careful experiments made with London tap water, with improved apparatus, showed that with every care the oxygen values found for the same sample varied between 4·55 and 6·50, the mean being 5·57, or a difference of 35 per cent. on the mean value.

The object of the present communication is to indicate the cause and the means adopted to eliminate the source of error attaching to these observations.

High Results when the Titration is performed quickly.—An indication of the nature of the disturbing influence is obtained by varying the conditions under which the experiment is made.

Thus, if instead of adding the hyposulphite solution drop by drop as in the above-mentioned experiments, it be added quickly and nearly the maximum quantity at once, mixing the liquids thoroughly, and finishing the titration drop by drop, a much higher result is obtained than when the addition is made slowly.

The results of four series of estimations by the slow and quick methods alternately, gave the following hyposulphite values:—

	Slow.	Quick.	Slow.	Quick.
	5·30 c.c.	7·05 c.c.	5·50 c.c.	7·45 c.c.
	4·60	7·55	5·65	7·15
	5·25	6·90	5·35	6·60
	5·75	7·15	5·65	7·05
	5·80	7·25	5·80	7·00
Means..	<u>5·34 c.c.</u>	<u>7·18 c.c.</u>	<u>5·59 c.c.</u>	<u>7·05 c.c.</u>

* *The Analyst*, 1885, **10**, 156, or Sutton's *Volumetric Analysis*. 5th Edition.

This indicates a difference of 47 per cent. on the mean of the 20 estimations.

Low Result when the Water has been exposed to Hydrogen.—The cause of these anomalous results was indicated by an experiment in which the water to be analysed, contained in a Winchester quart bottle, was allowed to stand in an atmosphere of hydrogen overnight, estimations being made before and after such exposure. The results obtained show, that whilst the volume of hyposulphite solution needed in the evening was 6·32 c.c., a mean of 10 experiments varying between 5·65 and 6·80, the amount required by the same volume of water after standing overnight in hydrogen was only 4·18 c.c., a mean of four experiments varying between 3·8 and 4·5.

Diffusion the disturbing Influence.—The conclusion was, that when aerated water is introduced into an atmosphere of pure hydrogen, it immediately begins to lose oxygen by diffusion into the hydrogen until an equilibrium is established, a fact hitherto overlooked by the experimenters with this process.

Explanation of the previous Experiments.—This explains the previous observations, viz., that the highest results are obtained when the hyposulphite is added quickly and immediately after the introduction of the water into an atmosphere of hydrogen, because the oxygen is estimated and combined before it has had time to diffuse to any great extent, the slight difference in the time of exposure between a quick and a slow titration being quite sufficient to give a marked loss of oxygen by diffusion during the slower addition of hyposulphite. The variation in the results of the apparently identical experiments first given, being explained by the slightly longer or shorter time taken over each titration, and the consequent greater or less facility for diffusion.

Results less in proportion to the amount of exposure to Hydrogen.—This conclusion, that diffusion is the disturbing influence, is borne out by further experiments easily suggested by the preceding.

Six series of estimations were carried out on the same sample of water, and in each succeeding one a slightly longer time of exposure to hydrogen was given. The figures represent the volumes in c.c. of hyposulphite required for one measure of water.

		Mean of 3 experiments.
Series	I. Titrated immediately and quickly, 6 c.c. of hyposulphite being added at once, the rest carefully drop by drop.....	7.56
„	II. Titrated immediately, but drop by drop	6.18
„	III. Titrated drop by drop, after standing 30 seconds in the hydrogen.....	3.72
„	IV. Titrated as before after standing in a moderate <i>current</i> of hydrogen 1 minute	2.55
„	V. As in IV, but 2 minutes' exposure	1.45
„	VI. As in IV, but 5 minutes' exposure	0.53

It is thus obvious that the result of an oxygen estimation by the present method, depends on the degree of exposure to hydrogen during titration.

Conditions influencing the Amount of Diffusion.—The rapidity and amount of the diffusion of dissolved oxygen depend on (1) the surface area of water exposed to hydrogen, influenced by the size and shape of the vessel and the degree of agitation during titration. (2) The volume of the atmosphere of hydrogen. (3) The time of exposure, up to the point of equilibrium (under the Law of Partial Pressures). (4) The volume of water.

Effect of Size and Shape of Vessel.—If this be the true explanation of the observed differences, it is clear, that if the water be exposed in a shallow layer to a large volume of hydrogen as in Schützenberger's and Dupré's apparatus, diffusion will take place more quickly than if the water be titrated in a small vessel having a limited surface exposure of the liquid. A series of estimations titrated quickly in a small bottle (200 c.c. capacity) gave 13.56, whilst with the same sample of water titrated quickly in a large flask, using the same hyposulphite, the result was only 9.95, both numbers being the mean of five estimations.

But even in the small bottle a considerable amount of diffusion had taken place, for by modifying the method of procedure* so as to prevent diffusion, the same water gave 16.6 as compared with 13.56 and 9.95.

The following numbers give the results of this series of observations extended by varying the time of exposure in the large vessel.

* See description of New Method, page 562.

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Series					
I.	II.	III.	IV.	V.	VI.
Small vessel.		Large vessel.			
	Quickly.	Quickly.	1 min.	3 mins.	
—	13·50	10·20	4·20	3·10	—
16·7	13·70	9·90	3·95	2·90	2·7
—	13·60	9·90	4·45	3·00	—
16·5	13·50	9·90	4·20	3·10	2·7
—	13·50	9·85	4·40	3·00	—
16·6	13·56	9·95	4·24	3·02	2·7

In each case, 50 c.c. of water and 10 c.c. of indigo-carmin were used.

- Series I. Maximum result when diffusion is eliminated.
 „ II. Titrated quickly in small bottle.
 „ III. Titrated quickly in large flask.
 „ IV. Titrated after gentle agitation in large flask for 1 minute.
 „ V. Titrated after gentle agitation in large flask for 3 minutes.
 „ VI. Minimum readings* when the diffused oxygen is driven out by a current of hydrogen.

These estimations were repeated the next day with a new and slightly stronger hyposulphite solution, with the following results :—

	I.	II.	III.	IV.	V.	VI.
	Small vessel.		Large vessel.			
		Quickly.	Quickly.	1 min.	5 mins.	
	13·0	10·5	7·4	3·5	2·0	1·9
	13·0	11·0	7·1	3·9	2·0	1·9
Means.....	13·0	10·75	7·25	3·7	2·0	1·9

* The 2·7 c.c. merely represents the combined oxygen in the blue indigo-carmin.

Percentage of Oxygen diffused under various conditions.—It is now easy to calculate the percentage of oxygen thus lost by diffusion. In the first place, it is necessary to subtract from the readings the volume of hyposulphite required for the decolorisation of the indigo-carmin used.

The following numbers show that the percentages of oxygen lost agree very closely in the two series :—

First Series. Diffusible Oxygen $16.6 - 2.7 = 13.9$.

	I.	II.	III.	IV.	V.	
Oxygen diffused =	0	3.04	6.65	12.36	13.58	c.c. Hyposulphite.
Percentage.....	0	22	48	89	97	p.c. of total oxygen.

Second Series. Diffusible Oxygen $13.0 - 1.9 = 11.1$.

	I.	II.	III.	IV.	V.	
Oxygen diffused =	0	2.25	5.75	9.3	11.0	c.c. Hyposulphite.
Percentage.....	0	20	52	84	99	p.c. of total oxygen.

Thus we see, that under favourable circumstances, that is, using a small vessel and titrating quickly with least agitation, 20 per cent. of the oxygen diffuses, whilst in a large vessel such as is recommended to be used, 50 per cent. of the oxygen is lost during the titration. The delay of only one minute causing the loss of 90 per cent., whilst in three minutes practically all the oxygen has left the liquid.

Theoretical Confirmation of amount diffusible.—This result, viz., that it is possible to lose practically all the oxygen by diffusion is confirmed by the following theoretical consideration.

Supposing the 50 c.c. of water and 10 c.c. of indigo-carmin solution to be fully aerated, and that on introduction into the atmosphere of hydrogen, say 1 litre in volume, all the oxygen diffuses into the gas. Then under the law of Dalton and Henry, the amount of oxygen which could be redissolved by the 60 c.c. of water is calculated as follows :—

1000 c.c. of fully aerated water contains (say) 7 c.c. of oxygen, that is, after contact with an atmosphere containing 20 per cent. of oxygen; 60 c.c. therefore will contain 0.42 c.c. of oxygen. 0.42 c.c. oxygen in 1000 c.c. of hydrogen = 0.042 per cent. of oxygen in the hydrogen. 60 c.c. of water dissolve 0.42 c.c. oxygen in a 20 per cent. atmosphere. What volume will be dissolved in a 0.042 per cent. atmosphere?

$$\frac{0.042 \times 0.42}{20} = 0.0008 \text{ c.c. of oxygen, or}$$

$$\frac{0.0008 \times 100}{0.42} = 0.19 \text{ per cent. of the original gas.}$$

And this is the quantity which would remain dissolved in 60 c.c. of fully aerated water, after exposure in 1 litre of hydrogen until perfect absorptiometric equilibrium was established by diffusion. In other words, the possible loss by diffusion under the above conditions is 99·8 per cent.

Even using a quarter of a litre of water, a loss of 99 per cent. is still possible, in the usual apparatus.

Reason for the return of the blue colour.—We are now in a position to understand an observation which the previous experimenters have not failed to note, but which until now has not received a correct explanation. The observation referred to is, that in carrying out the oxygen estimation in the usual manner, the blue colour after having once been destroyed by the hyposulphite almost immediately returns, and if this subsequent coloration be destroyed, the colour will again return, and so on for a long time. The blue colour returns even when the hydrogen used is perfectly freed from all traces of oxygen by passing through the two long tubes filled with beads moistened with the alkaline solution of potassium pyrogallate used in all our experiments.

This observation is at once an indication and a proof of the correctness of our explanation. The previous experiments would lead us to anticipate that the blue colour *would* return, when we remember the great delicacy of the reagent for gaseous oxygen which we possess in the reduced yellow liquid, a mere trace of oxygen being sufficient to cause the change from yellow to blue.

In the ordinary process, the water to be examined is introduced into a large Woulff's bottle containing a little reduced indigo-carmin, which is quite insufficient to combine with all the dissolved oxygen in the water added. We may divide this dissolved oxygen into three portions in an ordinary estimation: (1) a portion oxidises the reduced indigo, and produces the blue colour; (2) part remains dissolved, and combines with the hyposulphite during the titration; (3) the rest diffuses into the hydrogen. When sufficient hyposulphite has been added to produce the first yellow, the diffused oxygen begins to be reabsorbed by the yellow reduced liquid, with formation of the blue compound.

That there is nothing in the reaction between the hyposulphite and indigo-carmin to cause the return of the blue colour can easily be shown.

No return of the blue colour when free Oxygen is absent.—If the liquid containing indigo-carmin and also the atmosphere above it are perfectly free from uncombined oxygen, and hyposulphite be added until the blue is turned yellow, no return of the blue colour takes place. The experiments showing this were performed in the apparatus

shown in Fig. 1, p. 561, with 50 c.c. of liquid containing various proportions of indigo-carmin. The water was coloured blue, submitted to a current of pure hydrogen for 10 minutes in each case, and then carefully titrated; the following are the results:—

Aerated* water. c.c.	Indigo- carmin. c.c.	Total. c.c.	Hypsulphite required. c.c.
0	50	50	11.6
25	25	50	5.8 [$\frac{1}{2}$ of 11.6]
40	10	50	2.35 [$\frac{1}{5}$ of 11.6]
45	5	50	1.30 [$\frac{1}{10}$ of 11.6]

(1.) The hyposulphite required was proportional to the amount of colouring matter, within experimental error. (2.) In no case was any blue colour developed, or did any change take place in the appearance of the yellow, although the current of hydrogen was in each case continued for 15 minutes after the yellow colour was produced. In the new method (p. 562) of carrying out the estimation, in which diffusion is entirely prevented, the final yellow liquid has often been kept for an hour in a slow current of hydrogen without the least change of colour towards blue.

Proof of the Diffusion of dissolved Oxygen into Hydrogen.—A positive proof that when pure hydrogen comes in contact with aerated water it is contaminated with oxygen, has been obtained as follows:—

A large flask was filled with a fairly strong indigo-carmin solution which was decolorised carefully with hyposulphite. Matters were so arranged that pure hydrogen, freed from all traces of oxygen as before stated, could be passed through aerated water, and thence into the large flask, driving out the sensitive yellow liquid through a tube passing to the bottom of the flask. In this way the hydrogen contaminated with oxygen is imprisoned above a solution which will indicate the presence of oxygen by the formation of a blue colour. This blue colour *was* observed at the surface of the liquid, and after a few minutes it became very intense and unmistakable. Hence the return of the blue colour is proved to be due to the supernatant gas and not to any reaction taking place within the liquid as was supposed by Schützenberger and by Dupré.

Influence of the amount of Indigo-carmin used.—These experiments explain a singular observation made by Schützenberger, namely, that by using a small amount of indigo-carmin only half the dissolved oxygen is estimated, when the first decolorisation of the solution is effected; whilst when a much larger quantity of indigo-carmin is

* The dissolved oxygen contained in this water was entirely lost by diffusion before the liquid was titrated.

employed, *the whole* of the dissolved oxygen is found. The explanation given by him being, that the reaction between reduced indigo and dissolved oxygen is a different one from that taking place between hyposulphite and dissolved oxygen, inasmuch as in the latter reaction, half the oxygen becomes latent as hydroxyl, with subsequent slow liberation of oxygen, whilst in the former no hydroxyl is formed.

His observation, however, will bear another interpretation, namely, if more reduced indigo be present than is sufficient to combine with all the dissolved oxygen contained in the added water, this oxygen is immediately combined by the reduced indigo and its diffusion prevented. Hence *all* the oxygen is obtained. The use of so large a quantity of indigo, however, so disturbs the end-reaction, from the presence of so much of the yellow compound, that "it is difficult to fix the point at which the last trace of blue has been discharged with any degree of accuracy."*

Schützenberger's Ratio 1 : 1.—We will now consider a question on which different experimenters make conflicting statements, namely, the ratio between the first volume of hyposulphite required to give the decolorisation, and the second volume required to give a permanent yellow colour, after all the subsequent returns of colour have been destroyed. Schützenberger† came to the conclusion that for the first decolorisation, "as nearly as possible" half the total volume of hyposulphite is required, and this was afterwards confirmed by Dupré.

Ramsay and Williams' Ratio 3 : 2.—Ramsay and Williams (Trans., 1886, 49, 751), however, did not obtain this ratio, but gave another, namely, 3 : 2. But they found a difficulty in obtaining this ratio in all their experiments, and only gave it as a mean expression of the varying ratios they found. Indeed they add, in speaking of this partition of oxygen into two stages of the process: "but it is difficult to devise an equation which will, in a rational manner, account for this partition of oxygen."

Schützenberger's ratio 1 : 1 is exactly what we find‡ when working according to the conditions of his experiments, namely, using a large vessel and a small amount of indigo. Ramsay and Williams' ratio (3 : 2) can easily be explained by the use in their experiments of a smaller titration vessel.

Infinite range of ratios possible.—It is evident from the following considerations that this ratio is susceptible of an infinite range of variation.

* Dupré, *loc. cit.*

† *Fermentation*, by P. Schützenberger.

‡ See III, percentages of oxygen diffused under various conditions, p. 556.

Apparatus adopted.—Fig. 1 shows the apparatus adopted by us for carrying out the estimation.

FIG. 1.

It consists essentially (1) of an apparatus for the continuous generation and purification of hydrogen, by the action of dilute sulphuric acid on zinc; (2) a 200 c.c. wide-mouthed bottle fitted with three burettes with glass taps, inlet and outlet tubes for a current of hydrogen, and an outlet tube for the titrated liquid; (3) Winchester stock-bottles of hyposulphite, indigo (not shown), and water, communicating with their respective burettes by glass syphons.

The hydrogen generated in A passes through two wash-bottles containing caustic potash, thence through two Emmerling's tubes filled with glass beads moistened with an alkaline solution of potassium pyrogallate, an arrangement being made whereby the beads may be re-moistened with fresh pyrogallate from the bottles beneath, the liquid being forced up by hydrogen pressure.

Pure hydrogen is supplied continuously (1) to the stock-bottle of hyposulphite, (2) to the hyposulphite burette, and (3) to the titration bottle.

The New Method.—A sample of water is examined as follows:—

(1.) 20 c.c. of the water is introduced into the small bottle and about 3 c.c. of indigo solution added.

(2.) A moderate current of hydrogen is passed through the blue liquid by a very fine jet for three minutes to free both water and supernatant gas from free oxygen.

(3.) Hyposulphite is now carefully added, during the flow of hydrogen, until the change from blue to yellow occurs, taking care not to overstep this point.

(4.) A further measured quantity of hyposulphite is now added (say 10 c.c.) sufficient to combine with all the dissolved oxygen in the volume of water, 50—100 c.c., proposed to be used in the estimation.

(5.) The important point now is, that the water is run in from a burette by a capillary tube passing *beneath the surface of the liquid* to the bottom of the vessel. Thus we introduce the water into a liquid which will *at once* combine the free oxygen and thus prevent its diffusion on coming in contact with the hydrogen, the reduced indigo acting as an indicator for the complete oxidation of the hyposulphite. The liquid is kept in constant motion during the addition of the water, which is shut off the moment a permanent blue colour appears.

(6.) The blue is decolorised by a further slight addition of hyposulphite. The volume of water used and the total hyposulphite, minus the first addition, are noted and the estimation repeated for confirmation.

When the water contains very little oxygen the second addition of hyposulphite may be omitted, the reduced indigo-carmin being sufficient to take up all the dissolved oxygen. In this case, care must be taken that the oxygen added should require not more than half the hyposulphite first added to decolorise the indigo-carmin.

Standardisation of the Hyposulphite.—In order to complete the estimation it is necessary to know the strength of the hyposulphite solution employed. This has entailed a very considerable amount of labour, inasmuch as of the two methods hitherto adopted for this purpose the first was found to be fundamentally wrong, and the second to depend on erroneous data.

FIG. 2.

The first method involves the use of a standard solution of ammonio-cupric sulphate, the second the use of distilled water saturated with air at a known temperature and pressure, using Bunsen's coefficients of absorption to obtain its oxygen value.

Re-determination of the Oxygen-value of aerated distilled water.—The importance of the accuracy of the data employed for the calculation of the oxygen value of distilled water saturated with air, induced us to make independent estimations by boiling out the gases *in vacuo* and subsequently measuring the volume of oxygen.

For this purpose we devised and constructed the apparatus shown in Fig. 2.

At the outset it will easily be understood that an essential in apparatus designed for the boiling out of dissolved gases *in vacuo* is, that there should be no possibility of atmospheric air gaining access to the vacuous interior. India-rubber joints freely exposed to air are inadmissible, because air is capable of diffusing through even thick india-rubber. To secure freedom from such leakage, the apparatus was constructed entirely of glass, with the exception of two tight india-rubber joints which were between glass surfaces and water luted. The glass taps, also, are all submerged in water.

It was found necessary to place an air trap, as shown, beneath C and E to intercept air which was found to leak through the thick india-rubber tubing connecting the mercury reservoir R with the mercury-pump, even though the joints were securely wired. Fig. 3 sufficiently explains how the air was intercepted in A. The apparatus

FIG. 3.

is first completely exhausted of air as follows: About 200 c.c. of distilled water is pumped through the side tube F, into the large bolt-head. The lamp beneath A is lit, and the apparatus exhausted by the air-pump, the water meanwhile boiling and aiding in the expulsion of the air.

To complete the exhaustion the mercury-pump is used.

The three-way tap beneath B is turned to communicate with the mercury reservoir R, mercury rises in B, and, by a suitable turn of the three-way tap, is allowed to flow into the U-tubes, the tap is closed, and thus all communication with the air is shut off.

The boiling is continued, the vapour carrying all the remaining air into D and E, whence it is forced out through the capillary barometer tube and trough T by raising R, and suitably opening the taps beneath C and E. On lowering R a vacuum is produced in E and D, and the last traces of air collected and driven out as before.

When a few minutes' boiling, producing a rush of vapour from C to D, gives no gas on condensing the contents of D and E into the capillary barometer tube, the exhaustion is perfect, and the apparatus ready for the introduction of the water to be examined.

The Winchester quart bottle filled with water is placed so that F passes to the bottom, the tap is opened, and the water rushes in with an immediate escape of part of the gases previously held in solution. When about 2 litres of water have run in, the tap is closed and the heating continued; the gas meanwhile being given off with brisk effervescence, finds its way into the cold chamber E, whence it is driven over and collected in G, a gas tube filled with mercury.

After several exhaustions of E, the water in A boils at a low temperature, and the vapours soon drive all the remaining gas forward into the cool chamber D, where the water condenses and the gas passes forward into E and is driven over as before.

A little practice is necessary to obtain the gas free from water, but this can be accomplished with a little care.

With impure waters, the last portions of gas consist of almost pure carbonic acid, the last traces of which are only expelled on prolonged boiling *in vacuo*. Hence, with distilled water, the exhaustion is perfected much more easily than with waters containing a considerable amount of carbonic acid.

When the gases are completely extracted, it is only necessary to fill up the Winchester quart bottle and measure the volume of water taken for analysis—generally from 1500—2000 c.c.—and to proceed with the analysis of the gases.

The gas tube is removed from the mercury trough T, by introducing a large crucible beneath it. It is transferred to the apparatus shown in Fig. 4, which is a modification of Frankland's gas apparatus, the important point being that the two measurements which require great accuracy are made in the narrow part of the tube G, thus diminishing the experimental error of each reading, namely, (1) nitrogen at the upper part, the wider part at the top being made of sufficient capacity to hold nearly all the nitrogen, (2) nitrogen and

FIG. 4.

oxygen at the lower part. The carbonic acid measurement is made on the lower and wider part of the gas tube.

The tube G joins the collecting tube by a "sealed" tap* and a ground conical joint fitting into a cup and luted by mercury.

The carbonic acid was absorbed by a 20 per cent. solution of caustic potash, the gas being allowed to stand in the absorption-tube, with its sides wet with the reagent, for half an hour. The oxygen was absorbed by introducing pyrogallie acid to the strong

* Cetti's patent, avoiding all chance of leakage.

potash solution—the absorption being allowed three-quarters of an hour.

The piece A slides along the side of the table, and by its means the gas can be adjusted to the centimetre marks on G with the greatest nicety.

The pressure, above or below that of the atmosphere—taken at each observation—is read off on the tube P marked in millimetres. The thermometer is also read each time a gas measurement is made, and the apparatus allowed to gain the temperature of the gas-room by standing untouched for a quarter of an hour before each observation. The readings are made by a telescope at the near end of the table, where the gas is also adjusted by moving A backwards or forwards.

Method of Aeration.—Before giving the results of the estimations made with distilled water saturated with air, it is necessary to describe the method of aeration.

Freshly distilled water adjusted to the required temperature was aerated by vigorous agitation in two Winchester quart bottles half full of water, the air being renewed five or six times by emptying the contents of one bottle into the other and again dividing into two portions, which were repeatedly agitated with fresh air.

When aerated, one bottle was filled and allowed to stand, stoppered, for half an hour, to an hour to get rid of minute air-bubbles. Then the gases were extracted and analysed, as before described, the barometer having been read to obtain the pressure at which the water was aerated.

The results are calculated from the following formula:—

$$\frac{v_{1, 2, 3} \times [P \pm d \pm c - t]mm \times 273000}{[pa - t_a]mm \times T \times V} = x_{1, 2, 3},$$

where v = volume of gas measured.

P = atmospheric pressure when measured.

d = difference in level of mercury in the two limbs.

c = correction to be applied to adjust the graduation.

t = tension of aqueous vapour at T .

pa = atmospheric pressure when the water is aerated.

t_a = tension of aqueous vapour at temperature of aeration.

T = absolute temperature when gas was measured.

V = volume of water used.

The results are thus found in cubic centimetres of gas, measured at 0° C. and 760 mm. bar. dissolved by 1000 c.c. of water aerated at t° C. with a dry pressure of 760 mm.

The barometer readings need not be reduced to zero, as this correction would act in two ways counteracting each other.

The above formula is not applicable to a sample of water taken for analysis, in which the actual volume of gas present is required to be found. In this case, 760 must be substituted for $[pa - ta]$ mm. It was thought best to fix, with as great accuracy as possible, the values at 10°, 15°, 20°, and 25°, by means of several determinations at each temperature, and from these values to calculate the remaining ones.

The following are the numbers obtained. They indicate close agreement between the several experiments at each temperature, and also throughout in the ratio between the oxygen and total oxygen plus nitrogen, a ratio always between 33 and 34 per cent., and evidently not a function of the temperature, as some observers claim it to be.*

They show a wide discrepancy from Bunsen's numbers, but agree well with Dittmar's determinations.†

*Determinations of Dissolved Gases in fully Aerated Distilled Water.
Temperature 10° C. Pressure 760 mm. (dry).*

	Nitrogen.	Diff. from mean.	Oxygen.	Diff. from mean.	Total gas.	Percentage of oxygen.
(1)	15.45	-0.02	7.84	-0.03	23.29	33.69
(2)	15.53	+0.05	7.85	-0.02	23.38	33.58
(3)	15.56	+0.09	7.85	-0.02	23.41	33.54
(4)	15.43	-0.04	7.92	+0.05	23.35	33.94
(5)	15.38	-0.09	7.90	+0.03	23.28	33.96
Mean values..	15.47	—	7.87	—	23.34	33.74

Temperature 15° C. Pressure 760 mm. (dry).

	Nitrogen.	Diff. from mean.	Oxygen.	Diff. from mean.	Total gas.	Percentage of oxygen.
(1)	13.81	-0.02	7.11	+0.02	20.92	33.97
(2)	13.86	+0.03	7.07	-0.02	20.93	33.76
Mean values..	13.83	—	7.09	—	20.92	33.86

Temperature 20° C. Pressure 760 mm. (dry).

	Nitrogen.	Diff. from mean.	Oxygen.	Diff. from mean.	Total gas.	Percentage of oxygen.
(1)	12.74	-0.02	6.42	-0.02	19.16	33.52
(2)	12.73	-0.03	6.44	—	19.17	33.60
(3)	12.75	-0.01	6.45	+0.01	19.20	33.62
(4)	12.81	+0.05	6.45	+0.01	19.26	33.46
Mean values..	12.76	—	6.44	—	19.20	33.55

* Winkler (*Ber.*, 1888, 2851). † "Challenger" Reports, vol. i, Pt. I, p. 160.

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Temperature 25° C. Pressure 760 mm. (dry).

	Nitrogen.	Diff. from mean.	Oxygen.	Diff. from mean.	Total gas.	Percentage of oxygen.
(1).....	11·81	+ 0·03	5·94	+ 0·03	17·75	33·46
(2).....	11·76	- 0·02	5·88	- 0·03	17·64	33·34
Mean values..	11·78	—	5·91	—	17·69	33·40

From these results, the following table has been constructed, giving the oxygen values for fully aerated distilled water for each half-degree between 5° C. and 30° C., and for an *observed** pressure of 760 mm. —

Oxygen Dissolved by Distilled Water. 5—30° C.

Temp. C.	c.c. Oxygen N.T.P. per litre Aq.	Diff. for 0·5° C.	Temp. C.	c.c. Oxygen N.T.P. per litre Aq.	Diff. for 0·5° C.
5·0°	8·68	0·10	18·0°	6·54	0·07
5·5	8·58	0·09	18·5	6·47	0·07
6·0	8·49	0·09	19·0	6·40	0·06
6·5	8·40	0·09	19·5	6·34	0·06
7·0	8·31	0·09	20·0	6·28	0·06
7·5	8·22	0·09	20·5	6·22	0·06
8·0	8·13	0·09	21·0	6·16	0·06
8·5	8·04	0·09	21·5	6·10	0·06
9·0	7·95	0·09	22·0	6·04	0·05
9·5	7·86	0·09	22·5	5·99	0·05
10·0	7·77	0·08	23·0	5·94	0·05
10·5	7·68	0·08	23·5	5·89	0·05
11·0	7·60	0·08	24·0	5·84	0·04
11·5	7·52	0·08	24·5	5·80	0·04
12·0	7·44	0·08	25·0	5·76	0·04
12·5	7·36	0·08	25·5	5·72	0·04
13·0	7·28	0·08	26·0	5·68	0·04
13·5	7·20	0·08	26·5	5·64	0·04
14·0	7·12	0·08	27·0	5·60	0·03
14·5	7·04	0·08	27·5	5·57	0·03
15·0	6·96	0·07	28·0	5·54	0·03
15·5	6·89	0·07	28·5	5·51	0·03
16·0	6·82	0·07	29·0	5·48	0·03
16·5	6·75	0·07	29·5	5·45	0·03
17·0	6·68	0·07	30·0	5·43	0·02
17·5	6·61				

* In this table the results are not calculated for aeration at a *dry* pressure of 760 mm., but for an *observed* barometric pressure of 760 mm. When the observed pressure is *below* 760 mm. $\frac{1}{8}$ th the value must be *subtracted* for every 10 mm. diff. The same value must be *added* when the pressure is *above* 760 mm.

The following numbers show the variation from Bunsen's figures (hitherto used for the standardisation of the hyposulphite), and the close agreement with Dittmar's determinations:—

Oxygen.				Nitrogen.			
	Found.	Dittmar.	Bunsen.		Found.	Dittmar.	Bunsen.
10° C. ..	7·87	8·00	6·79	10° C. ..	15·47	15·35	12·70
15 	7·09	7·20	6·25	15 ..	13·83	13·95	11·67
20 	6·44	6·53	5·93	20 ..	12·76	12·79	11·08
25 	5·94	5·97	—	25 ..	11·81	11·82	—

From this comparison, we have no hesitation in adopting the values we have obtained, for the standardisation of the hyposulphite solution by aerated distilled water. This method has the advantage of being a titration carried out under almost the same conditions as the examination of a sample of water.

Indigo Standardisation.—When once the hyposulphite has been carefully standardised by distilled water, this rather troublesome aeration may be avoided by finding the oxygen-value of the indigo-carmin solution. This solution remaining constant may be used for the subsequent standardisation of the hyposulphite.

It is only necessary to take a suitable quantity of indigo solution, diluted with water if necessary, free it from all dissolved oxygen by a current of pure hydrogen continued for five minutes, then carefully decolorise with hyposulphite, the value of which has been carefully found by using aerated distilled water. The hyposulphite solution slowly loses strength even when kept in hydrogen, and should be standardised daily when required to be used.

Copper Method of Standardisation.—We are now in a position to examine the method of standardisation by the use of ammoniacal cupric sulphate. This consists in titrating a standard solution of cupric sulphate containing in 1 litre, 4·462 grams of the hydrated salt precipitated and re-dissolved in ammonia, adding the hyposulphite in an atmosphere of hydrogen until the blue ammoniacal liquid is rendered colourless. 10 c.c. of such a solution are equivalent to 1 c.c. of oxygen, N.T.P.

The method was tested by applying the oxygen-value thus found for the hyposulphite to the examination of fully aerated distilled water at 10°, 15°, and 20°. The results thus found for distilled water are so far removed from the actual values found by extracting the gases *in vacuo*, that we may safely reject this method of standard-

isation as inaccurate. The following are the details of this comparison :—

Titration of the Copper Solution.

20 c.c. copper solution =	39.40	or	19.70	} Mean 19.76 c.c. hypo- sulphite = 1 c.c. oxygen N.T.P.
	39.55		19.77	
	39.55		19.77	
	39.65		19.82	
	39.50		19.75	

Examination of the Distilled Water.

Distilled water.	Hypo.	c.c. Oxygen found.	Means.	Another series gave	True value.
10° C... 1000 c.c. =	114.6	5.79	} 5.71	} 5.67	} 7.77
	112.9 ÷ 19.76 =	5.71			
	111.1	5.62			
15° C... 1000 c.c. =	100.4	5.08	} 5.02	} 5.09	} 6.97
	99.5 ÷ 19.76 =	5.03			
	98.1	4.96			
20° C... 1000 c.c. =	92.6	4.68	} 4.62	} 4.65	} 6.28
	89.8 ÷ 19.76 =	4.54			
	92.2	4.66			

The probable causes of the failure of the copper method of standardisation are not far to seek.

In the first place, the copper solution is alkaline, and this, as we shall show, exerts a disturbing influence. In the second place, the reaction occurring when free oxygen is estimated in water, is probably not so simple as has been supposed. The *nascent* sulphite formed no doubt taking up a portion of the free oxygen with formation of sulphate, whilst in the case of the combined oxygen in the cupric solution, this latter reaction does not take place.

Thus the oxygen taking part in reaction (2) is *lost* where the hyposulphite solution is standardised by a method in which this latter reaction is unrecognised.

Comparison of the New Method with the Volume of Gas found.—We next proceed to apply the volumetric process as thus modified to the examination of samples of water from different sources, and to com-

pare the results with the absolute volume of gas obtained by boiling out the same water *in vacuo*.

The following formula is applicable to the volumetric process $\frac{d \times hs \times Od}{s \times hd} = x$ c.c. oxygen per litre of water, where d and s = the volumes of distilled water and sample respectively used and hd and hs = hyposulphite required for distilled water, and sample respectively, and Od the volume of dissolved oxygen (N.T.P) contained in 1 litre of the distilled water used.

The following are the results of this comparison made on five different samples of London tap water collected on five different days. In each case a Winchester quart bottle was filled with the water as drawn from the tap. Three estimations were made by the improved method, and then about 1700 c.c. of the remaining water taken for the gasometric estimation.

London Tap Waters.

	(1.)	(2.)	(3.)	(4.)	(5.)
	c.c.	c.c.	c.c.	c.c.	c.c.
Nitrogen.....	13·22	13·95	13·36	13·43	13·49
Oxygen	5·15	5·91	5·38	6·31	5·80
Carbonic acid	7·98	9·29	6·70	7·35	8·11
Total gas.....	26·35	29·15	25·44	27·09	27·40
Oxygen by the new volumetric method .	5·52	6·13	5·64	6·41	6·24
Gas obtained	5·15	5·91	5·38	6·31	5·80
Difference	0·37	0·22	0·26	0·10	0·44

Mean difference 0·28 c.c. oxygen per litre of water.

The oxygen values obtained by the two methods show close agreement, considering the possible experimental error in so complex a comparison. The mean difference being only 0·28 c.c. of oxygen per litre of water, showing that the method gives good results with ordinary drinking waters.

The next series of comparisons were made on Thames water collected just below the bridge at Richmond. These, like the tap waters, show that the method is applicable to tolerably pure river water.

The following are the details of the estimations:—

Thames at Richmond.

	(1.)	(2.)	(3.)	(4.)
Nitrogen	17·14	16·74	13·75	13·11
Oxygen	8·37	8·00	5·24	6·06
Carbonic acid	7·35	7·18	7·38	7·95
Total gas	32·86	31·92	26·37	27·12
Oxygen by the new method	8·95	8·98	5·87	6·13
Gas obtained	8·37	8·00	5·24	6·06
Difference	0·58	0·98	0·63	0·07

Mean difference, 0·56 c.c. of oxygen per litre of water.

A further comparison was made with very impure Thames water collected at Crossness, opposite the southern outfall for London sewage, 12 miles below London Bridge.

These in like manner indicate that the method gives good results even with an impure water of this character.

The following are the details of the analyses :—

Thames, opposite Southern Sewage Outfall.

	(1.)	(2.)	(3.)	(4.)	(5.)	(6.)
Nitrogen	17·08	17·58	17·60	17·46	15·96	16·96
Oxygen	2·51	0·59	0·13	1·06	4·36	4·68
Carbonic acid	14·00	15·29	15·77	14·51	26·18	15·13
Total gas	33·59	33·46	33·50	33·03	46·50	36·77
Oxygen by the new method	3·01	0·99	0·34	1·65	5·18	5·94
Gas obtained	2·51	0·59	0·13	1·06	4·36	4·68
Difference	0·50	0·40	0·21	0·59	0·82	1·26

Mean difference, 0·63 c.c. of oxygen per litre of water.

In sample (5) the low nitrogen is explained by the abnormally high carbonic acid.

The process thus applied to waters of such varied character, and containing such widely different amounts of oxygen, with a mean

difference of only 0.5 c.c. from the value obtained by extracting and measuring the gases, shows that, although perfect accuracy cannot be guaranteed for the process thus improved, yet the results obtained are not far removed from the truth, and certainly give very valuable indications as to the oxymetric condition of samples of water submitted to its operation. Perhaps no other volumetric process satisfies so well the conditions of so difficult a problem as the estimation of dissolved oxygen in water.

In investigations on the action of micro-organisms in the purification or putrefaction of impure waters, it is hoped the process will give valuable aid.

Influence of Acidity and Alkalinity.—Although the method is applicable to pure and impure waters, and even to brackish waters, this is not the case if the water contains even small quantities either of free acid or alkali. Thus, if $\frac{1}{10000}$ th part of sulphuric acid be added to pure water, not only is the oxygen value obtained a different one, but the whole reaction is disturbed. The volume of hyposulphite required for the first decolorisation is greater; this only producing a light, straw-yellow, instead of the fine deep-yellow of a normal titration. The delicacy of the reaction is altogether destroyed, a much larger volume of water than usual only slowly producing a light-blue colour, instead of the distinct coloration produced by even half a cubic centimetre of pure water in a normal titration. Oxalic acid has a similar action. The same proportion of ammonia has an entirely opposite effect. The oxygen value is raised instead of lowered, and the delicacy of the reaction is not impaired, although the colour reaction is very much modified. The results compare as follows:—

	Pure water.	$\frac{1}{10000}$ part of sulphuric acid.	$\frac{1}{10000}$ part of ammonia.
100 c.c. =	28.5	17.3	35.5
	28.7	17.3	36.1
	28.9	—	—
	29.0	17.3	35.8
	28.1	—	—
	Mean 28.6		

Sodium bicarbonate has no effect.

Of course, when other substances than oxygen, which decompose hyposulphite, are present in the water, the accuracy of the method is proportionately disturbed.

Delicacy of the Reaction.—With pure water, the change of colour is a very highly sensitive reaction and the most delicate test for the presence of free oxygen we possess, one part of oxygen in two million parts of water being sufficient to bring about a distinct change of colour.

If a quantity of the reduced yellow liquid be sealed up in a vessel containing pure hydrogen, it retains its yellow colour and its power of turning blue when opened and exposed to air, even after many days.

The blue compound obtained by exposing the titrated liquid to air is likewise permanent in pure hydrogen, but it is a curious fact that it slowly fades and turns to yellow on further exposure to air. This is no doubt due to the presence of sulphite, as a crystal of sodium sulphite dropped into a solution of the untitrated indigo-carmines causes the same slow fading of colour, and gives subsequently the same yellow liquid.

This is in strict accordance with the observations made on the action of atmospheric oxygen in the fading of colour in dye-stuffs (*Chem. News*, **39**, 313).

Diffusion of Oxygen through India-rubber.—The delicacy of this reaction may be employed to show the rapid diffusion of atmospheric air through india-rubber tubing. The experiment is made as follows :—

FIG. 5.

100 c.c. of water and 3 c.c. of indigo-carmines are freed from oxygen and decolorised in the usual way. The liquid is then forced out by hydrogen pressure on opening A.

When the liquid has flowed through B, C, D, E for a few seconds the pinchcock A is closed.

The liquid is seen to be yellow at F, B, and D, and is allowed to remain in the india-rubber tube C for five minutes. If now A be carefully opened so as to allow the former contents of C to be seen in the glass tube D, it will at once be observed that whilst the liquid in F, B, and D had remained unchanged, that in C had turned quite blue from the absorption of atmospheric oxygen diffused through the india-rubber. Even one minute's exposure is sufficient to give an indication.

This experiment has a practical bearing on the construction of the apparatus as figured in Dupre's paper and in Sutton's book, in which the hyposulphite solution is made to pass through several feet of india-rubber tubing before reaching the titration vessel, its strength, of course, diminishing with the time of remaining in contact with the india-rubber.

In the form adopted by us, the hyposulphite is conveyed from the stock bottle to the titration vessel by a *glass* syphon, and only sufficient india-rubber used to accommodate a pinchcock and to make one other connection necessary for the free motion of the titration vessel.