

XXVIII.—*Apparatus for determining the quantities of Gases existing in Solution in Natural Waters.*

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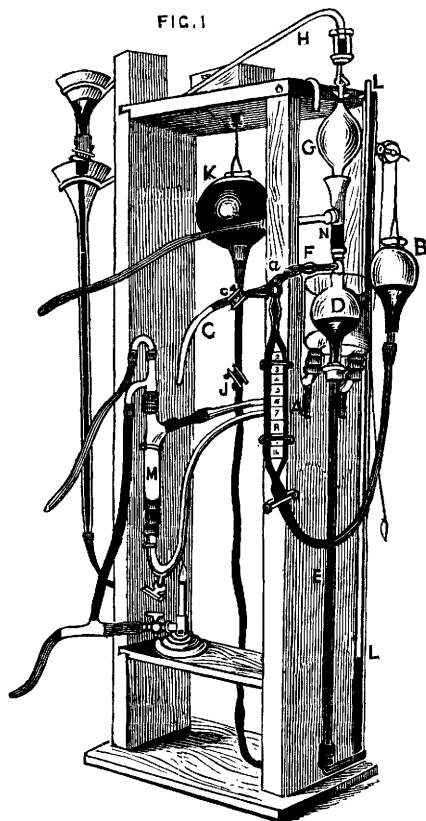
THE object of the following apparatus is to remove the gases existing in solution in natural waters, so as to prevent them, after elimination, from coming in contact with any cold water, which might absorb some of the carbonic anhydride, and thus produce a loss in its estimation. The dissolved oxygen may also be removed from the water at a low temperature, and thus be prevented from acting on any organic or other matter which may be present.

The apparatus consists essentially of three parts:—1. The measuring tube; 2. The flask in which the boiling of the water is carried on; and, 3. The Sprengel's mercurial air-pump to remove the gases after they have been evolved from the water.

The measuring tube consists of a graduated pipette, A (Fig. 1), holding 100 c.c., the lower end of which is connected to a globe, B, by means of a piece of caoutchouc tube sufficiently long to allow the globe to be raised above the level of the top of the pipette. To the upper part of the graduated tube is sealed a piece of narrower glass tube contracted at one point, *a*, and which, above the contraction, is bent at an obtuse angle. Below the contraction another piece of tube is sealed, and this is also narrowed as near to the junction as possible. This lateral tube is joined by means of a caoutchouc

previous one. The tube at the lower part of this second globe should not exceed 1 mm. in internal diameter. A good glass stopcock is sealed to the top of the second globe, and this is connected by means of a joint of india-rubber surrounded with glycerin to the Sprengel's air-pump.

The flask, D, in which the boiling of the water is carried on, consists of a thin glass globe of a capacity of about 150 c.c., with two openings, the lower of which is adapted to a narrow glass tube, E, of about 800 mm. in length, and to the upper opening of the flask a wide tube is joined. A glass stopcock, F, is sealed into the side of this tube, and is connected, by a short piece of caoutchouc bound with wire, to the tube at the top of the measuring tube. The glass tubes within the connector must be in close contact. The upper end of the wide tube is joined to a narrow one, which, by means of a caoutchouc connector, surrounded by mercury, N, is in communication with another globe, G, of nearly the same capacity as the



Woulfe's bottle is filled with water which may be heated by placing a gas flame beneath the metal tube. To the lower end of the long tube, E, is fastened a piece of narrow caoutchouc tube, covered with tape, and long enough to allow the reservoir K to be raised to the level of the upper flask. This reservoir, and also the one in communication with the measuring tube, are suspended by cords, so that they can readily be raised to any required height. Between the tubes E and J, it is convenient to adapt a long perpendicular glass tube L, open at the top, which serves to indicate the pressure within the globes.

In order to use the apparatus, it has to be filled with mercury. For this purpose mercury is poured into the globe, B, and the globe raised until the metal fills the measuring tube and flows out from the narrow tube C. The compression-cock *c* is closed, and mercury is allowed to pass through the stopcock into the boiling flask; when the air has been expelled, the stopcock is shut. Mercury is also poured into the reservoir K so as to expel the air through the stopcock and Sprengel-pump. The Sprengel is then put in action until the connecting tube is filled with mercury, when the stopcock is closed.

The water has next to be measured. To do this, the narrow tube C is passed to the bottom of the bottle containing the water, the reservoir depressed below the level of the extremity of the narrow tube, and the compression-cock *c* gently opened. It is perhaps more advantageous to fully open the compression cock; but, in order to prevent the water from flowing in too rapidly, the passage of the mercury through the caoutchouc-tube into the reservoir is checked. In cases of waters strongly charged with gas, this latter method diminishes the quantity of gas which escapes from the water during its introduction into the measure, and which would, of course, produce an error in the measurement of the liquid. Usually 100 c.c. of water is a convenient quantity to use, but in some cases a much smaller quantity will suffice. When the measurement of the water is completed, the cock *c* is closed and the reservoir B again raised.

A Torricellian vacuum is next produced in the two flasks by lowering the reservoir K until only a small quantity of mercury remains in the lower globe. A compression-cock on the caoutchouc tube J is then closed, and, to avoid any loss which might be occasioned by leakage through the compression-cock, the

reservoir is raised to its original position. The stopcock of the measuring tube is now opened and the water passed into the lower globe, the water in the inverted Woulfe's bottle being maintained as nearly as possible at 50° . The temperature can be kept very nearly constant by means of a thermostat M, placed in the circulating tube; a thermometer, not shown in the figure, being placed in the bath. After a few drops of mercury have been allowed to flow into the flask, the stopcock is turned and the water left for thirty minutes *in vacuo* at 50° . During this time almost the whole of the oxygen which was dissolved in the water will be expelled. This should always be done before raising the temperature to the boiling point, in order to avoid any absorption of the gas by organic matter that the water may contain. To remove the gas from the apparatus, the compression-cock on the long tube J is opened, and the mercury allowed to rise into the flasks. The stopcock is gently opened so as to permit the gas to pass into the Sprengel. When the water has nearly reached the stopcock, the latter is closed, and the reservoir lowered so as once more to produce a vacuum above the water in the globes; the reservoir is again raised and the whole of the gas passed through the Sprengel, the stopcock being turned when the water just reaches it. The reservoir is once more lowered, and the water in the bath heated as far as possible; a piece of rag is placed round the upper flask and a stream of cold water caused to run on to it, the excess of water being collected by the funnel-shaped head of the mercury-joint surrounding the connector N, and escaping through the lateral tube. The water in D rapidly distils into the upper flask, and is prevented from returning to the lower by the narrowness of the connecting tube.

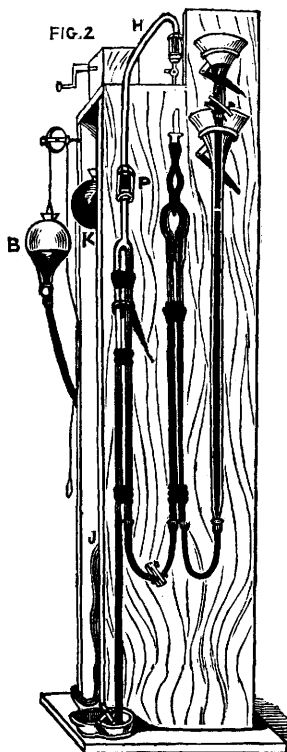
Before commencing the distillation, it is advisable to fill the tube H, above the stopcock, with mercury; this can easily be done by causing the mercury to pass very rapidly through the Sprengel, when some of it rises into the vacuous tube.

When the water has entirely evaporated from the lower flask, mercury is allowed to flow in, and the gas is transferred as before.

As some carbonic anhydride still remains dissolved in the water, the liquid must be again passed into the globe D, by lowering the reservoir K, and the water in the bath heated to boiling and maintained at that temperature for a few minutes.

The remainder of the carbonic anhydride is thus expelled, and is removed by the Sprengel.

A few words may here be said on the form of mercurial pump (Fig. 2) used for this apparatus. This is slightly modified from the invaluable instrument for which chemists and physicists are so deeply indebted to Dr. H. Sprengel, and described by him a few years ago*. A piece of thick glass tube about 8 feet in length, and 1 mm. internal diameter, is bent at a distance of 3 feet from one of its ends. The bend is made as sharp as possible, and the tubes are firmly bound together with copper wire at two points. To the top of the bend a piece of straight tube is sealed and connected by a joint, P, surrounded by glycerin, with the tube communicating with the apparatus. The end of the longer limb of the pump is curved so as to act as a delivery tube, the shorter one communicating with the tube supplying the mercury by means of a piece of caoutchouc tube covered with tape. By this arrangement the pump is perfectly movable, being merely held in the perpendicular position by a support at the upper part, the lower end resting on the bottom of the mercurial trough. The pump is also provided with an apparatus for removing any air entangled or dissolved in the mercury, which will soon be fully described by Dr. Sprengel, by whom it was kindly suggested. This form of pump has been found to work very satisfactorily, the best exhaustion measured being $\frac{516}{1000}$ th of the original volume of air in the receiver. This, however, is much inferior to that obtained by Dr. Sprengel with his original apparatus, which amounted to $\frac{1.300}{1000}$ th. By means of a pump of this form, Dr. Frankland and Mr. Lockyer, in their experiments on the spectra of gases, have rarefied perfectly dry oxygen, nitrogen, and hydrogen, to such an extent,



* Journ. Chem. Soc., vol. xviii (N.S., vol. iii), p. 9.

that they possessed a resistance to the spark of the induction coil equal to that of the atmosphere; and since then a tube has been prepared containing a residue of air of a resistance seventy-five times as great as that of moist air, at the ordinary pressure and temperature.

By careful management, only very small quantities of liquid water pass over with the gas, there being usually only sufficient to moisten the sides of the receiver, a quantity which would not produce any appreciable loss of carbonic anhydride.

The gas evolved at 50° may be analysed either separately, or first mixed with that given off on distillation. It was hoped that, by removing the gas at two different temperatures, a separation might be effected between the gases dissolved and those combined; but it appears that the dihydric calcic dicarbonate is slowly decomposed even at 50°. Small quantities of oxygen and nitrogen are also invariably found in the gases evolved on distillation: and in an experiment made with a solution of carbonic anhydride in distilled water, only a portion of the gas, amounting, however, to nearly $\frac{1}{2}$ ths, escaped from the solution at 50° in 30 minutes. It has been found very difficult to decompose the dihydric calcic dicarbonate by boiling the water: even after the temperature had been maintained at 105°—108°, for two or three hours it was found that the whole of the carbonic anhydride had not been evolved. It may, however, be presumed that the carbonate will not remain undecomposed when the water is evaporated to dryness.

The following results have been obtained in the determination of the gases in 100 volumes of Grand Junction water, as drawn from the cistern at the Royal College of Chemistry:—

I.			
	Evolved at 50°.	Evolved on distillation.	Total.
Nitrogen.....	1·391	0·007	1·398
Oxygen	0·609	0·011	0·620
Carbonic anhydride	0·420	3·877	4·297
	<hr/> 2·420	<hr/> 3·895	<hr/> 6·315

II.

	Evolved at 50°.	Evolved on dis- tillation.	Total.
Nitrogen.....	1·396	0·002	1·398
Oxygen	0·606	0·013	0·619
Carbonic anhydride	0·499	3·681	4·180
	<u>2·501</u>	<u>3·696</u>	<u>6·197</u>

Determination of gases in rain that fell on July 28, 1869,
between 10 a.m. and noon:—

I.

	Evolved at 50°.	Evolved on dis- tillation.	Total.
Nitrogen.....	1·348	0·033	1·381
Oxygen	0·671	0·014	0·685
Carbonic anhydride	0·045	0·071	0·116
	<u>2·064</u>	<u>0·118</u>	<u>2·182</u>

II.

	Evolved at 50°.	Evolved on boiling (not distilled).	Total.
Nitrogen.....	1·344	0·039	1·383
Oxygen	0·651	0·010	0·661
Carbonic anhydride	0·065	0·090	0·155
	<u>2·060</u>	<u>0·139</u>	<u>2·199</u>

These experiments were conducted at the Royal College of
Chemistry.
