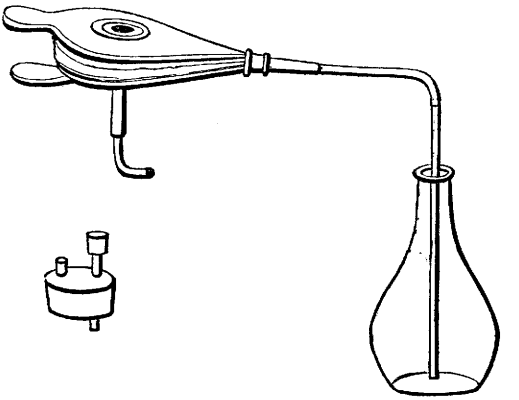
XXIX.—*Volumetric Estimation of Atmospheric Carbonic Acid.*

By Dr. M. Pettenkofer.

To determine the quantity of carbonic acid in the air, from 3 to 3½ litres of air are generally sufficient. A bottle of white glass is selected, containing about that quantity, and its capacity exactly determined, which is best effected by filling it to the brim with water, and ascertaining the quantity of the water by weight or measurement. The cubic content of the bottle is marked upon it with the diamond, and the number of cubic centimeters thus inscribed on a number of bottles used in a series of determinations, may serve to distinguish them one from the other, inasmuch as, even among a large number of bottles, it will rarely happen that two have exactly the same capacity. Each bottle, before being used in the carbonic acid determinations, must be perfectly clean and dry on the inner surface.

To fill a bottle with the air to be examined, that of a room for example, it is best to use a small pair of bellows, which, instead of drawing in the air directly through the valve, inhales it through a tube of the same diameter as the valve, and attached to it. The mouth of the tube is directed successively to all parts of the space from which the air is to be taken. From the bellows the air is

driven through a glass tube, which must not be too narrow, to the bottom of the bottle, this tube being attached by means of a caoutchouc tube to the nozzle. If the volume of air impelled by one movement of the bellows be approximately known, it is easy to calculate how many times the bellows must be worked, in order to ensure that the air in the bottle is completely replaced by that which is to be examined.



The bottle is then closed by a caoutchouc cap, having two tubular openings for the introduction of tubes. In the chemical laboratories of Germany, these caps are now almost exclusively used instead of perforated corks. One opening of the cap is closed with a round glass rod, and the other with a kind of funnel-tube, which enters the vessel to the depth of about two inches. This upper part of the funnel-tube is a wider tube, which can be closed with a cork.

Thirty cubic centimeters of clear lime-water are next introduced into the bottle through the funnel-tube from a pipette graduated for the purpose; the funnel-tube is closed with a cork, and the other opening of the cap with the glass rod; and observations are made of the temperature of the air and the height of the barometer. The volume of air is equal to the capacity of the bottle *minus* the quantity of lime-water introduced (30 cub. cent. are generally sufficient), and may therefore be easily and exactly reduced to 0° C. and 760 mm.

The bottle is now to be held between the two hands in a nearly horizontal position, and the lime-water moved about in it so as to wet the greater part of the surface. When this agitation has been

continued for eight or ten minutes, we may be pretty sure that the absorption is complete, provided always that the lime-water is in excess.

The next operation is the saturation of the free lime with a known quantity of acid. For this purpose, any dilute acid which is not volatile at ordinary temperatures, may be used. I have hitherto used oxalic acid, the employment of which is attended with only one inconvenience, viz., that it often turns mouldy when kept too long. It is best to make the oxalic acid solution of such a degree of dilution that 1 cubic centimeter of it corresponds to 1 milligram of lime (CaO). This degree of dilution is easily attained by placing a quantity of pure crystallized oxalic acid in the exsiccator over sulphuric acid for a few hours, and then dissolving 2·25 grammes of it in a liter of distilled water at 15° C. To ensure accuracy, the strength of the solution should be tested by precipitating the oxalic acid, and the proper quantity of oxalic acid or of water added, if necessary; but if the proportions just mentioned be carefully observed, no correction will be necessary.

With this solution, the quantity of caustic lime in any given sample of lime-water is easily determined. The lime-water for these determinations is prepared by drenching slaked lime several times with water, and rejecting the first decantations in order to get rid of the alkalies which lime generally contains. The accuracy of the process is not however vitiated by a small quantity of alkali in the lime-water, since the oxalates of potash and soda are neutral, and it makes no difference whether a given quantity of oxalic acid is saturated by lime or by an equivalent quantity of potash or soda. The clear lime-water is best kept in bottles of 300 to 400 cubic centimeters' capacity, and having mouths wide enough to admit a pipette capable of withdrawing 30 cubic centimeters of liquid. These bottles are filled as completely as possible, and well corked.

In making an estimation of carbonic acid, the first thing to be done is to determine the strength of the lime-water which is to be used. For this purpose 30 cubic centimeters of the lime-water are introduced by means of a pipette into a flask, whose capacity is about 100 cub. cent., and the normal solution of oxalic acid added from a Mohr's burette, till a drop of the liquid placed upon turmeric paper no longer turns it brown. The exactness of the method depends mainly upon the nicety with which this neutral point can be ascertained. I have found turmeric paper more

delicate for this purpose than any other reagent, reddened litmus paper, for example. To obtain the greatest amount of delicacy, it is not sufficient to immerse a strip of turmeric paper in the liquid, or to touch it with a glass rod dipped in the liquid; an entire drop of the liquid must be let fall on a rather broad strip of the paper by means of a glass rod or tube. The part of the paper not wetted by the drop then absorbs the liquid rapidly round the whole circumference of the drop, and in this manner the alkaline reaction round the drop is greatly intensified. It often happens, indeed, that a drop of liquid thus let fall on the paper exhibits very distinct brown edges, when a strip of paper immersed in the liquid shows no alkaline reaction whatever. As soon as the brown edge round the drop disappears, the liquid is no longer alkaline. The turmeric paper is so delicate, that the addition of four or six drops of lime-water to the neutralized liquid is sufficient to reproduce the alkaline reaction.

The quantity of oxalic used gives directly the amount of lime in the lime-water, inasmuch as a cubic centimeter of the oxalic acid solution saturates exactly one milligram of lime. Of the lime-water used in my experiments, 30 cubic centimeters required from 34 to 38 cub. cent. of the oxalic acid solution, within which limits the strength of the lime-water prepared as above described will generally fall. In a well corked bottle containing but a small quantity of air, the strength of the lime-water does not vary perceptibly in the course of several days. Even when a bottle holding about 300 cubic centimeters is half empty, samples taken at intervals of 24 hours scarcely exhibit any difference if the bottle is well corked.

Lastly, to find how much lime has been saturated by the carbonic acid contained in the air, the lime-water in the bottle in which it has been shaken up with the air, is neutralised with the solution of oxalic acid. To avoid overstepping the point of neutralisation, small strips of turmeric paper are used, fastened by a small clamp at the end of a stick, which is of such thickness as to pass readily through one of the apertures of the caoutchouc cap, and long enough to reach the bottom of the bottle. As soon as an immersed strip of turmeric paper is no longer distinctly browned, it is necessary, after each addition of acid, to take out a small portion of the liquid with a glass tube, and let a drop of it fall upon the turmeric paper; the remaining portion is then returned to the bottle. The gradual addition of the oxalic acid is continued till the drops no longer exhibit any alkaline reaction. As small

quantities of the lime-water adhere to the sides of the bottle, it is necessary, after each addition of acid, especially towards the end of the operation, to agitate the liquid in the bottle in the same manner as at the beginning of the process, to promote the absorption of the carbonic acid.

If the quantity of carbonic acid in the air is so great that only a small quantity (from 2 to 4 cub. cent.) of oxalic acid is required to saturate the lime, the experiment must be repeated, and about 45 cub. cent. of lime-water, instead of 30, introduced into the bottle at the beginning of the process, in order that at least 10 or 15 milligrams of lime may be left in excess; because an aqueous solution which is but very slightly alkaline, absorbs carbonic acid but slowly, and sometimes imperfectly. In all cases it is advisable to fill two bottles with the same air, and examine the air in both. When once the quantity of oxalic acid required for the first bottle is known, the saturation of the liquid in the second may be performed with greater accuracy.

The method here described is as exact as any others which are in use, and possesses the advantage of being very quickly performed, so that it enables us to determine the amount of carbonic acid in the air at any given time and from any particular part of a given space. The determination of the carbonic acid in the air by weighing, for which a considerable volume of air must be drawn in by an aspirator, and deprived of its water and carbonic acid, gives only the medium quantity of carbonic acid in the air during a considerable interval of time; and, according to my experience, is not well adapted to researches on ventilation in inhabited apartments. But by the method just described, when every thing is well prepared and a proper number of dry bottles and caoutchouc caps are at hand, samples of air may be collected and examined at intervals as short as may be desired. After a little practice, an experiment (not reckoning the time required for the subsequent calculations) may be made in 20 minutes.

It was important to ascertain, whether, when the proportion of carbonic acid in the air is small, a volume of air not exceeding $3\frac{1}{2}$ liters is sufficient to ensure a due degree of accuracy. I therefore made two comparative experiments, in which bottles were used containing 3 and 15 liters. The results obtained with the air of a dwelling-room were as follows:

(*a*.) Contents of the bottle 3425 cub. cent.
Temperature of the air, 18° C.
Barometer, 718 mm.

The air was shaken up with 30 cub. cent. of lime-water containing 35·7 milligrams of lime.

After the absorption of the carbonic acid, the lime-water still required for its saturation 31 cub. cent. of oxalic acid. Consequently 4·7 milligrams of lime were saturated by CO_2, which corresponds to 3·7 milligr. CO_2, or 1·861, cub. cent. CO_2 at 0° C. and 760 mm. Bar.; and on reducing the volume of air in the bottle, after deducting 30 cub. cent. for the lime-water, to the normal pressure and temperature, the amount of carbonic acid in the air is found to be 0·061 per cent.

(*b*.) Capacity of bottle, 15115 cub. cent. Temperature, height of barometer, and strength of lime-water the same as in experiment *a*. Into the bottle were introduced 130 cub. cent. of lime-water containing 154·7 milligr. of lime. After absorption of carbonic acid, 133 cub. cent. of the oxalic acid solution were required to saturate the lime, so that 21·7 milligr. of lime had been saturated by the carbonic acid. This gives 17·1 milligr. or 8·601 cub. cent. of CO_2 at 0° and 760 mm. Hence the quantity of carbonic acid in the air was 0·064 per cent.

Hence it appears that a volume of air not exceeding 3 liters is sufficient to determine by this method the amount of carbonic acid in the air, with all the exactness that can be required.

Finally, I will observe that this method of estimating the carbonic acid in the air presupposes the same condition as all other methods given for the purpose, viz., that the air contains no other acid than carbonic acid.