

## A HANDY METHOD OF DETERMINING THE AMOUNT OF CARBONIC ACID IN AIR.

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MANY years ago while making in the laboratory of the late Prof. Carnelley in Dundee, by Pettenkofer's method, a series of Carbonic Acid determinations, in which turmeric paper was used as the indicator, I observed that the last few brown rings made on the paper as the solution approached neutralization showed a tendency to become decolorized in a relatively short space of time, the final ones being seen to vanish even as one looked at them. This at the time—and subsequent observation has confirmed the truth of the conclusion—was ascribed to the  $\text{CO}_2$  of the air rapidly neutralizing the solution of baryta, which getting more and more dilute as the solution of oxalic acid was gradually added, finally reached a degree of dilution that was all but instantly neutralized by the amount of  $\text{CO}_2$  present in an ordinary atmosphere. Even then I came to the conclusion that the phenomenon depended on a principle which might probably be made the basis of a rapid method of estimating the amount of  $\text{CO}_2$  in air generally, but it is only recently that I have had time to adjust the details of the method which I now propose. It will readily be understood that a long series of experiments other than those of which the results are now recorded were carried out before finality was reached on many points of the method. These need not be detailed here, though some of them will be alluded to as occasion arises. It may be stated that the method has been found to give results which approximate to the truth—at least as tested by Pettenkofer's method—much more closely than was at first anticipated.

The special recommendations of the method are, easiness and rapidity of execution, simplicity and inexpensiveness of apparatus, with equal simplicity of the calculations necessary to obtain a definite result.

*Principle of the Method.*

The method depends on the theoretical view that equal quantities of alkali in solution, when they present equal surfaces for absorption and are of equal depth, will be neutralized by the CO<sub>2</sub> in a given atmosphere in equal times: and by implication that surface, depth and strength of solution being constant while other conditions vary, the times necessary for neutralization will be inversely as the amounts of CO<sub>2</sub> present in the atmosphere to which they are exposed. Experiment shows that this is a very close approximation to the truth.

To put the principle in concrete form, it may be said that drops of alkaline solutions which are equal both as regards their diameters and the quantity of solution which they contain, whether of lime water, baryta, or magnesium hydrate, within the limits of strength indicated, if coloured by phenolphthalein, have their colour discharged in times which are practically in the inverse ratio of the amounts of CO<sub>2</sub> present in the several atmospheres to which they are exposed—that is to say, if one atmosphere contains twice as much as another it will decolorize equal-sized spots of these solutions, coloured as indicated, practically in half the time; if it contains three times as much it will decolorize them practically in one-third the time, and so on. If the diameters of the spots are unequal while the quantity of solution in the spots remains constant, the times of decolorization for the same atmosphere are inversely as the square of the diameters of the several spots, that is to say, inversely as their surfaces. This has been found from experimental data to hold good at least within the limits of experimental error.

The method therefore is simply this:—A number of as nearly as possible equal spots of one or other of these solutions, coloured as indicated, is exposed on a white surface to the atmosphere in which it is proposed to estimate the CO<sub>2</sub>, and the time required for complete discharge of their colour noted. The CO<sub>2</sub> present in vols. in 10,000 parts is a function of the strength of the solution used, divided by the time in minutes taken for the discharge of the colour.

Stated generally the formula is:—

$$\frac{s \times f}{x} = \text{vols. of CO}_2 \text{ in 10,000 parts,}$$

where *s* is the strength of the solution stated in particular terms,

*f* is a factor which within the range of experimental error is fairly constant,

*x* is the time of colour discharge in minutes.

*Solutions used, and their strength.*

A solution of lime water, of baryta, or magnesium hydrate—for all these have been used in turn—coloured by the addition of a drop or two of solution of phenolphthalein, and of such strength that 100 c.c. of it has its colour discharged by  $\cdot 5$  to  $2\cdot 5$  c.c. of a solution of oxalic acid, every c.c. of which is equal to 1 mgrm. of  $\text{CO}_2$ , is used for the determinations. This latter solution is made by dissolving  $2\cdot 8636$  grms. of pure crystallized oxalic acid in a litre of distilled water. The strength of the lime water or other alkaline solution may, so far as experiment goes, lie anywhere between the limits indicated, but its equivalent in mgrms. and tenths of a mgrm. of  $\text{CO}_2$  per 100 c.c. of solution must be exactly known—at least where it is intended to find the proportion of  $\text{CO}_2$  in absolute vols. per 10,000 parts of air. If it is only intended to make a comparative estimate, as for example the amount in an internal atmosphere, in terms of the amount in outside air, it is not necessary to know the strength of the solution exactly, but it is still desirable that it should lie within the limits indicated. The strength of the solution should also be to some extent proportioned to the quantity of  $\text{CO}_2$  to be estimated. Thus the  $\text{CO}_2$  in outside air is best determined by a relatively weak solution, and a solution of magnesium hydrate of strength equal to  $\cdot 5$  mgrms. of  $\text{CO}_2$  has been successfully used for this purpose. Stronger solutions take too long time for the discharge of colour and hence afford greater scope for the operation of other disturbing factors. On the other hand a solution of the strength indicated would have its colour discharged too quickly to admit of the correct determination of the time, by the most highly charged atmospheres. For example, spots of a solution equal to  $\cdot 5$  mgrms. of  $\text{CO}_2$  per 100 c.c. of solution, of the average diameter, are decolorized by outside air in about 11 minutes, whereas an atmosphere containing 15 vols. in 10,000 parts would discharge the same spots in something less than  $2\frac{1}{2}$  minutes. A little reflection will show that it is not expedient to reduce the time of exposure below about 10 minutes in any case, because any error in noting the time of discharge becomes relatively larger as the divisor becomes smaller, and the difficulty of accurate observation of the time is proportionately increased as the period of exposure gets shorter. In practice, at least where the same observer both puts out the spots and notes their time of colour discharge, it has been found impossible to estimate the time with greater accuracy than within half a minute. In the case of the more highly charged atmospheres it might be

possible sometimes to come closer, but for most part within half a minute is probably the nearest approximation that could be made by the most careful observer—the time, from the conditions of experiment, really not being capable of more exact determination. But even when the nearest full number of minutes is noted, provided that the number does not fall too low, say below 10, the results will be found sufficiently accurate for most purposes.

*Quantity of solution in a 'drop' or 'spot,' and variations in the diameter of the 'spots.'*

As regards the size of the drops it may be stated that the two 50 c.c. stoppered burettes with which the determinations were made both gave us nearly as possible 22 drops per c.c. (one drop = .045 c.c.) when discharging at the ordinary rate at which the spots are made. This is therefore considered the standard drop. There is no doubt considerable variation in burettes in this respect, but from an investigation which has been made on my behalf in regard to this point it would appear that there is likely to be no difficulty in procuring burettes of similar calibre to those which I used. It may be remarked that small deviations from the quantity indicated may be safely discounted, as drops of larger size on falling the same distance as smaller drops spread out to spots of larger diameter than the smaller, thus tending towards compensatory adjustment as regards their depth. As will be readily understood it is really the depth of the spot which is the important dimension from our present point of view. A drop of the standard size if it falls about  $\frac{1}{2}$  inch gives a spot about 9 mm. in diameter. The tabulated results which accompany this paper, unless where otherwise stated, were made from the observation of spots of that diameter. Where the spots vary in diameter their times of discharge as before indicated are inversely as the square of their diameters, so that it is comparatively easy to reduce the time results obtained from the observation of spots of abnormal size to the time results of normal-sized spots. If we have spots say of 8, 9, and 10 mm. diameter respectively, but containing the same quantity of liquid, their times of discharge for the same atmosphere will be as the reciprocals of the squares of these numbers, or as  $\frac{1}{64}$ ,  $\frac{1}{81}$ ,  $\frac{1}{100}$ .

The following rule may be given for the reduction of the time of spots of abnormal diameter to the time of spots of normal diameter. If the spot is 8 mm. in diameter multiply the time by  $\frac{9}{64}$ ; if 10 mm.

diameter multiply by  $\frac{100}{81}$  to reduce their time to that of spots of 9 mm. diameter.

In practice, however, it has been found possible in the majority of instances to get over any difficulty arising from differences in the size of the spots, by carefully selecting spots of the particular size required and discounting all those of abnormal size. It has frequently been observed—more particularly as it appears in the case of outside determinations—that owing probably to variations of atmospheric moisture the surface tension of the drops varied from day to day. They would sometimes stand up like beads for several consecutive days together, at other times they flattened out to a greater or less degree. Still even here it was nearly always possible, either by gently tapping the edge of the plate on which they were exposed, or by careful selection, to get spots of the required diameter. It was further found that the plate had always to be free from adherent moisture, otherwise the spots ran, and were consequently of no use for the purpose of estimation. The slightest trace of grease on the surface of the plate is equally fatal to a successful result.

*How to prepare and keep the working solution.*

A solution may be prepared by diluting a saturated<sup>1</sup> solution of lime water about 50 times, say 20 c.c. up to a litre, with distilled water that has been boiled for some time and cooled to the exclusion of air, and then adding phenolphthalein solution till the maximum degree of coloration is attained. This solution is then standardized against a solution of oxalic acid, every c.c. of which corresponds to one mgr. of carbonic acid. To do this 100 c.c. of the coloured solution is placed in a porcelain basin and the oxalic acid run in drop by drop with constant stirring till complete decolorization is obtained. The process should be repeated till coincident results are obtained or the average of several determinations may be taken as the working strength of the solution. A very convenient solution may also be prepared by burning so much magnesium ribbon and allowing the resulting magnesia to drop into a flask of water which has been boiled for some time and allowed to cool with exclusion of air. This solution coloured

<sup>1</sup> Lime water of the shops is very variable in strength. I found it to vary so that 25 c.c. of solution ranged from 16.5 to 26.1 c.c. of oxalic acid, 1 c.c. of which was equal to one milligramme  $\text{CO}_2$ . Normal strength is about 20 c.c. for distilled water and pure lime at ordinary temperatures.

with phenolphthalein forms a convenient working solution and after standing for a few days with occasional shaking is found to be just about the required strength. It must of course be kept closely stoppered. It was at first hoped in this way to obtain a solution of constant strength, but results show that this cannot be depended on with certainty. It has therefore to be always standardized against the oxalic acid solution. Solutions of magnesium hydrate in strength from .5 to 2.5 mgr. of carbonic acid per 100 c.c. have been made and used in this investigation.

The only apparatus required is a stoppered burette and a white glazed stoneware plate.

The burette is washed out with some of the solution and is then filled from the remainder. To the open end of the burette is fitted a small U-tube containing soda-lime to prevent the entrance of carbonic acid. For additional protection the distal end of this tube when the apparatus is not in use may be closed with a tight-fitting rubber stopper. Thus protected the solution is maintained of the same strength for a considerable time, and a single burette full of solution is good for a large number of determinations.

#### *Technique of method.*

To make a determination, the rubber stopper is removed from the distal end of the protecting U-tube. The few drops of solution in the beak of the burette are then run out, because the carbonic acid of the air having had access to this portion of the solution has reduced its strength. Then, holding the beak of the burette about  $\frac{1}{2}$  inch above the plate, its long axis as nearly vertical as possible, the operator gradually turns the stopper and allows the solution to fall, but not too quickly, in drops from the burette while he at the same time gradually moves it over the surface of the plate. Ten or a dozen spots will usually suffice. They take less than as many seconds to put out. The number of minutes from the time the last spot is put out onwards to complete decolorization of all the spots has now to be noted. The slight difference in their exposure periods, arising from the fact of the spots being not simultaneously but successively made, is, as will be inferred from what has already been said, of no consequence and is accordingly discounted. Immediately after recording the time of commencement of the period of exposure of the spots, the observer proceeds to note whether any material difference in the diameter of the spots exists; and if there be any decided difference he may as alternative measures, either (1) expunge the extremes,

that is to say those that vary most from the average 9 millimetre diameter—this facilitates observation of the normally-sized spot; or (2) he notes separately the time for 8 millimetre spots, for 9 and 10 millimetre spots respectively, and calculates out the result separately for each set according to the process of reduction already stated. Observation of the normally-sized spots and of either the 8 or the 10 millimetre spots, not both, will usually be found as much as one can conveniently attend to. Where two results have been calculated out from the discharge periods of different-sized spots, they have generally been found to show a remarkable coincidence. The process by expunging the abnormal-sized spots is, however, the one to be recommended in the first instance. (3) At first from 40 to 60 spots were put out and the time of discharge, as they became decolorized in batches, noted. The average time per spot was then calculated out and taken as the mean time of discharge. This method was mostly used for outside air, the time for inside atmospheres of any intensity as regards their charge of CO<sub>2</sub> being often too short, and the time for the various spot groups often falling too closely together, to admit of accurate observation.

Examples will now be given of the different methods of recording the period of discharge of the spots.

(1) Spots 9 millimetres in diameter of a solution of lime water equal to 1·5 milligrammes of carbonic acid per 100 c.c. of solution, required a uniform period of 17 minutes to discharge their colour in a certain atmosphere. This according to the scheme of calculation which was afterwards worked out gave 6·08 vols. of carbonic acid per 10,000. A determination by Pettenkofer's method, made as nearly as possible simultaneously, gave 6·3 vols.

(2) Spots of 9 millimetres diameter of a solution of magnesium hydrate which was equal to 2·5 milligrammes of carbonic acid per 100 c.c. required 17 minutes, while spots of 8 millimetres diameter required 21 minutes.

The 9 millimetre spots took 17 minutes, and gave by calculation 10·12 vols. of CO<sub>2</sub>.

” 8 ” ” ” 21 ” ” ” ” ” 10·37 ” ”

Pettenkofer's method gave 10·06 vols.

(3) In determining the carbonic acid in outside air on one occasion 50 spots of a solution of lime water equal to 2·1 milligrammes of CO<sub>2</sub> per 100 c.c. were put out and gave the following results as regards time of discharge:—

4 spots required	34 minutes	34 × 4 =	136,
11 ” ”	38 ”	38 × 11 =	418,
18 ” ”	40 ”	40 × 18 =	720,
5 ” ”	45 ”	45 × 5 =	225,
12 ” ”	53 ”	53 × 12 =	636,
		50	2135,

$\frac{2135}{50} = 42\cdot7$  minutes as average time of discharge.

This according to the method of reduction would be equivalent to 3·67 vols. of CO<sub>2</sub> in 10,000.

*Determination of Factor for Reduction of Results.*

For the purpose of determining what relation obtained between the strength of solution and the time of exposure on the one side and the value of CO<sub>2</sub> in parts per 10,000 on the other, a large number of determinations both in outside air (21) and in indoor atmospheres (77) were, as far as the essential differences in the methods allowed, simultaneously made by this method and by Pettenkofer's method, and the results as obtained by the latter method were taken as the basis for determining the relation subsisting between these three functions according to the formula :

$$\frac{\text{Strength of Solution (in milligrammes of CO}_2 \text{ per 100 c.c.)}^{(1)} \times \text{Constant}^{(2)}}{\text{Time of Colour discharge in minutes}^{(3)}} = \text{vols. of CO}_2^{(4)} \text{ in 10,000 parts.}$$

That is to say, in a given case (1), (3), and (4) being known, it was required to find (2), the constant factor.

*Example.* A solution of lime water equal to 1·5 mm. of CO<sub>2</sub> in 10,000 requires 17 minutes to decolorize in an atmosphere which was shown by Pettenkofer's method to contain 6·3 vols. of CO<sub>2</sub> in 10,000. Find the factor or constant (2) in this case :

$$\text{Here} \quad \frac{1\cdot5 \times \text{factor}^{(2)}}{17} = 6\cdot3.$$

$$\text{Whence} \quad \text{factor}^{(2)} = \frac{6\cdot3 \times 17}{1\cdot5} = 71\cdot4.$$

In this way the factor was obtained in every case throughout the 21 outside cases and also throughout the 77 cases of inside atmosphere, and the corresponding factors are tabulated in the accompanying tables.

The average factor in the case of

21 determinations in outside air was found to be 74·6 for unreduced Pettenkofer results and 80·5 when reduced to normal temperature and pressure ;

57 determinations in ordinary inside atmospheres was found to be 68·8 for unreduced and 73·9 for reduced results ;

20 determinations in highly vitiated inside atmospheres was found to be 70·5 for unreduced and 78·8 for reduced.



The probable explanation of these differences will be considered later. The first factor (74·6) was provisionally used for the reductions of outside air generally, and the second (68·8) for ordinary inside atmospheres.

When the results in the case of inside atmospheres are thrown into groups according to the amount of carbonic acid present, some little difference in the factors was shown to obtain, probably pointing to some divergence from the strict proportional ratio from atmospheres of less to atmospheres of greater intensity as regards the amount of CO<sub>2</sub> present.

Again, solutions of lime water, baryta, and magnesium hydrate of various strengths, within the limits indicated, were used for the determinations, and on calculating out the average factor for each substance no grounds have been obtained for preferring the solution of one substance to that of another, as very little difference in the average factors was disclosed. What difference does obtain in the case of one of the solutions may be ascribed to some little deviation of the strength of the solution from that actually recorded against it.

Thus lime water used in 4 different strengths gave as the average of 30 determinations in ordinary inside air 68·81 ;

baryta used in one strength gave as the average of 10 determinations 70·59 ;

magnesium hydrate used in 4 different strengths gave as the average of 17 determinations 68·3.

It may be concluded therefore that 68·8 is a sufficiently approximate factor for the reduction of ordinary inside atmospheres and 74·6 for outside air. It should be stated, however, that some difference in these figures may be expected to arise as the result of personal equation, but this is not likely to be great.

Before going on to cite a few examples it may be well to give a general formula to facilitate the calculation of results. This formula is

$$\frac{s \times c}{x} = \text{CO}_2 \text{ in vols. in 10,000 parts,}$$

where  $s$  = the strength of solution in mgrs. of carbonic acid per 100 c.c. of solution,

$c$  = the constant—74·6 for outside air ; 68·8 for ordinary inside atmospheres.

$x$  = the number of minutes required for discharge of colour.

Examples—first, when solutions of different alkalis have been used.

(1) Spots of normal size of a solution of lime water equal to 1·5 milligrammes of carbonic acid per 100 c.c., in a certain atmosphere took 9 minutes to decolorize. What was the amount of CO<sub>2</sub> in vols. per 10,000 present?

$$\text{Calculation} \quad \frac{1.5 \times 68.8}{9} = 11.47 \text{ vols. CO}_2 \text{ in 10,000.}$$

By Pettenkofer's method the same atmosphere gave 11·56 vols.

(2) Spots of normal size of a solution of magnesium hydrate equal to ·5 milligrammes of CO<sub>2</sub> per 100 c.c. required 3½ minutes to decolorize in a certain atmosphere. What was the amount of CO<sub>2</sub> per 10,000 present?

$$\text{Calculation} \quad \frac{.5 \times 68.8}{3.5} = 9.83 \text{ vols.}$$

By Pettenkofer's method this was found to be 9·66 vols.

(3) Normal-sized spots of a solution of baryta equal to 1·7 milligrammes of CO<sub>2</sub> in 100 c.c. of solution required 18 minutes for complete decolorization. What was the content of CO<sub>2</sub> in parts per 10,000 vols. of the atmosphere under examination?

$$\text{Calculation} \quad \frac{1.7 \times 68.8}{18} = 6.5 \text{ vols. CO}_2.$$

Pettenkofer's method gave 6·52 vols.

The following two examples will suffice for spots of abnormal size:—

(1) Spots of 8 millimetres diameter of a solution of magnesium hydrate equal to 1·8 milligrammes of CO<sub>2</sub> in 100 c.c. required 34 minutes to decolorize. What was the content of CO<sub>2</sub> in parts per 10,000 in the atmosphere under examination?

$$\text{Calculation} \quad \frac{1.8 \times 68.8}{\frac{8}{4} \times 34} = 4.61 \text{ vols.}$$

By Pettenkofer's method this was equal to 4·43 vols.

(2) Spots of 10 millimetres diameter of a solution of magnesium hydrate equal to 2·5 milligrammes of CO<sub>2</sub> per 100 c.c. required 17 minutes to decolorize. What was the content of the atmosphere as regards CO<sub>2</sub> in parts per 10,000?

$$\text{Calculation} \quad \frac{2.5 \times 68.8}{\frac{10}{1} \times 17} = 8.195 \text{ vols.}$$

By Pettenkofer's method this was equal to 8·14 vols.

In the appended tables the rough rule of simply increasing by  $\frac{1}{4}$ th the observed time for 10 mm. spots and of decreasing by  $\frac{1}{5}$ th the observed time for 8 mm. spots to obtain the time for 9 mm. spots was the one followed. Hence some little discrepancy will be found between the above results and those there given. The procedure now indicated is probably sufficiently accurate for practical purposes and is certainly much simpler.

So much for inside atmospheres; an example will now be given in the case of outside air:—

*Example.* Spots of a solution of magnesium hydrate equal to .5 milligrammes of CO<sub>2</sub> in 100 c.c. required 12 minutes to decolorize. What was the volume of CO<sub>2</sub> in the air?

$$\text{Calculation} \quad \frac{.5 \times 74.6}{12} = 3.11 \text{ vols.}$$

By Pettenkofer's method this was found to be 3.08 vols.

The difference of factor employed for outside air should be noted.

Where the observer is not in a position to determine the strength of his working solution by standardizing it against oxalic acid of known strength, he may still make comparative determinations of the amount of carbonic acid in one atmosphere in terms of that in another, *e.g.* of one inside atmosphere in terms of that in another inside atmosphere, or of an inside atmosphere in terms of that in external air; but in comparing outside air with an inside atmosphere the difference in the factors for reducing these two groups should not be forgotten, and the average amount of carbonic acid in outside air should be taken with some approach to accuracy. It appears to be necessary to insist that this is not always, or even frequently, 4 parts, but usually about 3.4 parts in 10,000, as determined by Pettenkofer's method. Of 23 determinations made in Elgin the average was 3.45 vols.

*Example.* Spots of a solution of indefinite strength gave for outside air 39 minutes; for an internal atmosphere 14 minutes for colour discharge. What was the probable amount of carbonic acid in 10,000 parts in the latter atmosphere?

$$\text{Calculation} \quad \frac{39 \times 68.8 \times 3.45}{14 \times 74.6} = 8.86 \text{ vols.}$$

Pettenkofer's method gave 9.35 vols.

Again, the content of outside air as regards CO<sub>2</sub> being known both in terms of this method and of Pettenkofer's method, the content of any other atmosphere of which the discharge period for the same solution is known, can be calculated from the data indicated.

*Example.* Outside air containing 3.08 vols. in 10,000 parts according to Pettenkofer's method required 12 minutes to decolorize normal-sized spots. What would be the volume of CO<sub>2</sub> in an atmosphere which decolorized the spots in 3½ minutes?

$$\text{Calculation} \quad \frac{12 \times 68.8 \times 3.08}{3.5 \times 74.6} = 9.74 \text{ vols.}$$

Pettenkofer's method gave 9.66 vols.

It hardly needs to be stated that the results by this method of

procedure are not calculated to attain the same degree of accuracy as those that are directly deduced from the ascertained strength of the solution and the exposure period for the given atmosphere.

One application to which the present method lends itself with marked facility may be mentioned, and that is for indicating when the limits of healthy ventilation are being exceeded. For instance it may be asked how by this method could it be shown when the limit of 9 vols. per 10,000 was being reached or exceeded in a given case? This in practice simply amounts to determining the number of minutes that will be required by an atmosphere containing 9 vols. of CO<sub>2</sub> to discharge spots of a solution of given strength. This may be found from the formula:

$$\frac{s \times 68.8}{x} = 9.$$

If the strength of the solution be taken at, say, 2 mgrms. of CO<sub>2</sub> per 100 c.c. then

$$\frac{2 \times 68.8}{x} = 9, \text{ whence } x = 15.3 \text{ minutes.}$$

If then, spots of normal size, of a solution of the strength indicated, take 15 or any less number of minutes to discharge, the limit of 9 vols. in 10,000 is being exceeded. Similarly, the time for any other limit, the strength of solution being known, may be determined. But if the strength of the solution is not known, then the time taken by outside air becomes the standard; and of this an average of a considerable number of determinations should be taken and used as the working value. Say that it takes  $y$  minutes for 3.4 vols. per 10,000 in external air, what will be the relation between  $x$  and  $y$  when the result is 9 vols. of CO<sub>2</sub> in 10,000?

$$\text{Calculation} \quad \frac{y \times 68.8 \times 3.4}{x \times 74.6} = 9.$$

$$\text{Whence} \quad x = \frac{y}{2.8} \text{ nearly.}$$

That is to say, the limit of 9 vols. is being exceeded when the time taken by outside air is more than 2.8 times as great as the time taken by the atmosphere under examination.

#### *Physics of the method.*

It need hardly be said that it was naturally anticipated that in consequence of the freer movements of the air, outside determinations

would show a much quicker rate of discharge than those in internal atmospheres. That this was not the case is, and remains, the paradox of the investigation. There cannot be a doubt however that as regards the discharge of colour the conditions in the two sets of atmospheres are quite dissimilar. Inside, where the movements of the air are necessarily at a minimum, it will be seen, if the spots are closely watched, that as the period of exposure advances, the colour moves in from the edge—and presumably also from the surface—of the spot, so as eventually to show a colourless margin all round it. This colourless margin broadens as time goes on, till finally, just before complete neutralization, a minute point of colour, often, to the last, of the same general intensity of colour as the original spot, is left at its centre. The final vanishing of this point of colour in the case of internal atmospheres gives a very definite and precise end-reaction. In the case of outside air, on the other hand, except on all but the calmest days, this marginal process of colour discharge is not observed. In consequence of the relatively greater movement of the air, the general mixing of the different layers of the spots causes the colour to be maintained of a uniform though gradually fading tint throughout the spot up to the moment of complete colour discharge. The end-reaction for this reason is in this case very much less definite and precise. But it must not be inferred that this fact has in any way led to a general overstating of the time of discharge. Rather the reverse was the case: for I found there was a general tendency on my part to consider the reaction as complete when just the faintest perceptible trace of colour remained. For the reasons just given I am strongly inclined to believe that the difference in the rate of discharge in the two cases is intimately related to the different physical conditions that obtain. These I now proceed to discuss.

In the case of internal atmospheres, three elemental processes appear to be involved in bringing about the discharge of colour. These are (1) Solution of the carbonic acid in the surface layers of the spot, (2) Neutralization of the alkali by the carbonic acid so dissolved, (3) Diffusion of the carbonic acid subsequently dissolved into the deeper layers of the spot, with further neutralization of the alkali in these layers. Conceiving the spot, as made up of a series of concentric shells we may picture the process of colour discharge somewhat as follows: A quantity of carbonic acid proportional to what exists in the atmosphere immediately in contact with the spot is dissolved in its surface layer, and proceeds to neutralize the alkali in it, which done, the surface layer

dissolves a similar quantity of carbonic acid from the atmosphere, which thereafter passes on by diffusion into the second layer and there neutralizes the alkali. It is succeeded in the surface layer by a further proportional quantity of carbonic acid, which also passes on by diffusion to the deeper layers as they are successively neutralized, to be succeeded by another in the surface layer and so on. In this way we may conceive the spot gradually invaded by a series of waves of carbonic acid, starting from and taking up their intensity of change from the quantity of carbonic acid present in the atmosphere, the first wave always neutralizing the alkali, the next passing on into its place by diffusion, and proceeding to neutralize another layer of alkali, and so on till the whole is neutralized and the total colour discharged. If these several changes could be supposed to go on simultaneously, continuously, and *pari passu*—not successively as described—we should I think have a fairly complete picture of what takes place in a spot. Of these three processes the general time rate of discharge is no doubt determined by the rate of solution of the carbonic acid and the rate of neutralization of the alkali conjointly,—the one rate necessarily being a function of the other. The rate of diffusion very evidently depends on and is limited by the rate of neutralization, as the carbonic acid cannot possibly diffuse through a layer of alkali, that is to say, the alkali must first be neutralized before the carbonic acid can pass on. For this reason the diffusion in a spot must take place at a slower rate than it would in water or any simple neutral solution. But it is evident that it must, at least within the limits of experiment, have always been sufficient to keep a proportional quantity of carbonic acid in contact with the particular layer of the spot in which neutralization was taking place.

It will also be apparent on this view of the physics of the method of colour discharge that an excess of carbonic acid must exist in the surface layers of a spot at and before the moment of complete discharge. That this is the case may be demonstrated by shaking the plate on which the spots are exposed just as they are nearing their final stage, when the discharge of the remaining colour will be seen to be perceptibly accelerated by the coloured area still remaining being brought into contact with the carbonic acid dissolved in the colourless surface layers.

In the case of outside determinations on the other hand (1) solution and (2) neutralization are confined to a hypothetical surface layer, and the effect of this surface solution and neutralization is immediately distributed through the liquid of the spots by (3) convection currents,

arising from the movement of the liquid of the spot, such movement being impressed on it by the movements of the air with which it is in contact. In consequence of the mixing of the different layers of the spots, the repeated fractional bleachings that take place in the surface layer have their general effect distributed through the total liquid of the spot, thus leading finally by imperceptible degrees to total bleaching of the same. The liquid of the spot is, as it were, rotated by the movements indicated. Coming in contact with the air in the surface layer, it absorbs a quantity of carbonic acid proportional to the amount present in the air, its alkali is neutralized, when it is forthwith carried off to be succeeded by another portion of the liquid of the spot which is similarly affected. This again is succeeded by another and another portion of the liquid with the same result till finally the colour of the spot is entirely discharged. This process, it will be seen, is very different from that described as probably obtaining in the case of spots exposed to internal atmospheres. Whether this movement of the liquid in thus limiting the action of the carbonic acid to the surface layer of the spot has any effect in retarding the general rate of solution of the carbonic acid—and as a consequence the general rate of neutralization of the alkali also—may be left an open question, but it certainly strikes one as probable that the process of mixing of the liquid of the various layers of the spot must take some time for its accomplishment, and hence naturally lead to a general increase in the length of time required for colour discharge. In any case if the rationale of the various changes that take place in the spots is on the lines just indicated, it will be very evident that a different rate of discharge in the two cases is extremely probable.

I should also be inclined to think that movement of the liquid of the spot rather than movement of the air over it—if it were possible to dissociate the two in fact—is really the important element in the case. The movement of the air containing carbonic acid can hardly be conceived as sensibly affecting the solution of the carbonic acid in the liquid of the spot, provided that air containing the same constant quantity of carbonic acid is always in contact with it: whereas the constant movement of the liquid in which this solution takes place, or the continued replacement of one portion of the liquid which has been momentarily in contact with the air by another portion, may have an important bearing on the quantity of carbonic acid dissolved. Neutralization of the alkali, depending as it does entirely on the quantity of carbonic acid dissolved, would necessarily vary with the rate of solution.

Experiments are in progress which have for their object the finding of specific answers to some of the points just raised.

*A uniform factor suggested.*

It is well known as a matter of fact that, notwithstanding the possibility of numerous individual errors arising from a variety of causes—which need not be detailed here—Pettenkofer's method gives results which are on the whole too high. This may be illustrated by a reference to the results obtained for external air. The careful experiments of Reiset and others on the Continent, and those of J. S. and E. S. Haldane<sup>1</sup> in this country by the gravimetric method, give an average for outside air of just under 3 vols. in 10,000.

Pettenkofer's method gives an average of 3·5 vols. 3·45 was found by me as an average of the determinations in Elgin by Pettenkofer's method. Dr Angus Smith's average for the air of Scotland generally was 3·36 vols. It is very evident that Pettenkofer's method cannot be put in competition with any carefully executed determination by a gravimetric method. Hence it must be concluded that Pettenkofer's method gives results which are about ·5 vols. too high. For this reason the factors we have deduced for this method ought, doubtless, to be proportionally reduced. If the factor 74·6 for outside air is reduced in the ratio indicated, it will be found to give 63·9 as the corresponding factor. The average all over for ordinary internal atmospheres is 68·8. In specially vitiated atmospheres it was 70·5. These latter factors would also be subject to some reduction for the average error of Pettenkofer's method. As all these variations of the reducing factor practically fall within the limits of estimational error of the individual analyses, I think on the score of practical expediency the factor 68·8 should be used all over, and I am further of opinion that no great loss of precision is likely to result in consequence. Only in cases where special accuracy is desirable, as in reducing the averages of large numbers of determinations, ought special factors to be used.

Something may be said as to how far the results obtained by the present method and by Pettenkofer's method are capable of comparison. They are not strictly comparable. This method estimates the amount of carbonic acid over the whole period of exposure of the spots, and the results as determined by it may be taken as giving the average amount of carbonic acid during that period. Pettenkofer's method on the other

<sup>1</sup> *This Journal*, vol. II. p. 421, 1902.



hand gives the amount of carbonic acid at the moment of collection of the specimen. Generally speaking the sample for estimation by Pettenkofer's method was taken some time during the exposure of the spots. This of course would rarely, if ever, be coincident with the mean period of the spots, and especially when it is considered that the determinations were made in atmospheres which were for the most part undergoing rapid increase as regards their carbonic acid, some discrepancy between the results as obtained by the two methods might reasonably be expected. The discrepancy was certainly greater when the interval between the determinations by the two methods was greatest. Again, the determinations were not always carried out under similarity of conditions as regards place. The following example will show what is meant. A determination at 9.10 a.m. in the laboratory by the spots at the height of the working bench gave 3.65 vols. A sample taken at the same time at the height of the collecting jar above the floor gave by Pettenkofer's method 6.42 vols. Two hours later the spots gave 5.7 vols. at the height above the floor at which the sample for Pettenkofer's method was taken. Here there was distinctly indicated the existence of a stratum of air highly charged with carbonic acid extending along the floor, but which evidently did not reach to the level of the working bench and had not been dispelled—at least to any great extent—two hours later. Hence arose the discrepancy of the results at the two levels and by the two methods.

On the whole it may be said that the method now described gives more reliable results than could have been anticipated on theoretical grounds, and though it is not propounded as a method of scientific precision, I am disposed to think it will be found useful and sufficiently exact for most purposes. Its very evident simplicity as regards apparatus, manipulation, and the subsequent calculation of results, strongly recommend it. It is believed from the ease with which the necessary apparatus can be carried from place to place, and the results worked out on the spot, that it will be found of much service for the informal sampling of air as regards its content of carbonic acid, and of indicating where other methods, if thought necessary, may be brought in to clinch the result. In the hands of an intelligent factory manager or schoolmaster I believe it will be found capable of producing results of the greatest value from a hygienic point of view.

Determination of CO<sub>2</sub> in Air

TABLE I. Ordinary Internal Atmospheres.

Average Factor for Reduction, 68.8.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
Date	Time	Place	Capacity of Room	Time taken by "Spots" $\frac{x}{P}$	CO <sub>2</sub> in vola. per 10,000 By "Spots" $\frac{S \times 68.8}{x}$	By Pettenkofer $\frac{P}{P}$	Pettenkofer reduced to 760 mm. and 0° C.	Calculated factor $\frac{S \times f = P}{x}$	Strength of solution in milligrammes of CO <sub>2</sub> per 100 c.c. = S	Remarks
Sept. '04 16th	8 p.m.	Dining Room	3200 ft.	Minutes 17	6.08	6.8	6.82	71.40	CaH <sub>2</sub> O <sub>2</sub> = 1.5	4 persons present. 3 gas-jets for 1 hour.
	9 "	"	"	11	9.38	9.27	10.06	67.98	"	
	9.56 "	"	"	9	11.47	11.56	12.57	69.86	"	
	7.30 "	"	"	12.	8.60	8.07	8.52	64.56	"	
	8.30 "	"	"	10	10.30	10.79	11.45	71.93	"	
19th 20th	8.10 "	"	"	14	9.09	9.01	9.64	68.72	CaH <sub>2</sub> O <sub>2</sub> = 1.85	Ventilation in the interval.
	8.14 "	"	"	14	9.09	9.35	10.11	70.76	"	
21st	9.30 "	"	"	13 for 10 m. 21½	7.83	6.97	7.57	60.29	"	2 persons present for 9 hrs. Window open, door ajar. Simultaneously determined by solutions of CaH <sub>2</sub> O <sub>2</sub> and MgH <sub>2</sub> O <sub>2</sub> of strengths indicated.
	8.30 a.m.	Bedroom	2400	9.92	5.92	5.32	5.63	61.83	"	
22nd	8.40 p.m.	Dining Room	3200	9	10.70	9.66	10.50	62.10	CaH <sub>2</sub> O <sub>2</sub> = 1.4	2 persons for 9 hrs. Window open, door ajar.
	"	"	"	3½	9.83	"	"	67.62	MgH <sub>2</sub> O <sub>2</sub> = .5	
	10.15 "	"	"	7½	12.84	12.58	13.59	67.40	CaH <sub>2</sub> O <sub>2</sub> = 1.4	
	8.40 a.m.	Bedroom	2400	18	5.35	5.69	6.02	73.16	"	
	7.30 p.m.	Dining Room	3200	11	8.75	9.06	9.65	71.19	"	
23rd	8.30 "	"	"	9	10.70	10.71	11.47	68.85	"	2 persons for 9 hrs. Window open, door shut.
	10.15 "	"	"	9½	10.14	10.20	10.95	69.22	"	
	8.45 a.m.	Bedroom	2400	17	5.67	5.75	6.04	69.82	"	
	7.21 p.m. S.	Dining Room	3200	14	6.88	7.67	8.19	76.70	"	
	7.45 "	"	"	"	"	"	"	"	"	
24th	8.30 "	Laboratory	870	10	9.63	8.92	9.55	63.72	"	2 persons for 9 hrs. Window open, door ajar. Strong wind blowing in at window.
	9.12 "	Bedroom	2400	12	8.03	8.24	8.75	70.63	"	
	8.25 a.m.	Laboratory	870	19	5.07	4.84	5.09	65.69	"	
	7.38 p.m.	"	"	15	6.42	6.29	6.60	67.40	"	

25th	2.30 p.m.	Laboratory	870	15	8.26	7.82	8.36	65.17	} Distilling water all day. Gas lighted in the inter- val. Moist atmosphere. Temp. latterly 68° Fah. 2 persons present for 9 hrs. Door and window open.
	5.40 "	"	"	14	8.84	8.50	9.25	66.11	
	6.45 "	"	"	9	13.76	14.62	16.02	73.10	
	7.25 "	"	"	8	15.48	Not det.	—	—	
26th	8.30 a.m.	Bedroom	2400	26	4.76	4.60	4.91	66.44	
	7.20 p.m.	Dining Room	3200	15	8.26	8.38	8.96	69.83	
	8.30 "	"	"	14	8.84	8.50	9.13	66.11	
	9 "	Laboratory	870	15½	7.99	7.82	8.36	67.33	
27th	4.30 "	"	"	34 for 8 m.	4.66	4.43	4.72	72.50	
28th	9.10 a.m.	"	"	3.65	6.42	6.42	6.72	"	
	11.10 "	"	Spots on Bench Pk. Height of jar above floor	18	5.72	5.11	5.44	66.43	
	3.20 p.m.	Consulting Room	1750	19½	5.29	5.11	5.44	66.43	
	7.15 "	Dining Room	3200	8	12.90	13.09	13.95	69.81	
	9.15 "	"	"	7	14.74	14.61	15.71	68.18	
29th	8.15 "	"	"	10	10.32	9.69	10.32	64.60	
	8.30 "	"	"	"	"	"	"	74.28	
	8.45 "	"	"	11½	8.97	8.23	8.38	71.06	
30th	4 "	"	"	33	3.14	3.23	3.38	70.66	
	10 "	Consulting Room	1750	8	12.9	13.25	14.10	65.78	
	7 "	Dining Room	3200	11½	8.97	8.58	9.10	70.68	
Oct. 1st	7.50 "	"	"	9	11.47	11.78	12.38	71.88	
2nd	6.35 "	"	"	20	6.88	7.18	7.67	73.88	
3rd	9 "	"	"	15	9.19	9.85	10.63	79.88	
4th	9.20 "	"	"	18	7.64	6.97	7.50	62.73	
5th	9.15 "	"	"	13½	8.66	8.10	8.65	64.80	
6th	8.20 "	"	"	16	7.31	7.65	8.29	72.00	
7th	2.45 "	"	"	35 for 8 m.	4.18	4.5	4.82	74.11	
8th	"	"	"	15	7.80	8.34	9.08	73.59	
10th	"	"	"	25	4.68	4.79	5.16	70.44	
	7.40 "	"	"	12	9.75	10.06	10.83	71.01	
	8.55 "	"	"	8½	13.76	14.28	15.36	69.03	
11th	9.40 "	"	"	18	6.50	6.52	7.02	69.03	
12th	7 "	"	"	15	7.80	8.15	8.79	71.91	
	9.5 "	"	"	13 for 8 m.	11.24	11.05	11.98	67.60	
	10.2 "	"	"	17	10.12	10.35	11.27	70.38	
17th	7 "	"	"	20	8.6	8.14	8.86	65.12	
	"	"	"	17 for 10 m.	8.1	69.19	68.41	69.19	
19th	6.50 "	"	"	21 for 8 m.	10.37	10.06	10.86	67.58	
	"	"	"	"	"	"	"	"	
	"	"	"	"	"	"	"	"	

TABLE III. Results in Specially Vitiated Atmospheres.

Date	Place	Time of start	Strength of solution in milligrammes CO <sub>2</sub> per 100 c.c.	Time of Spots		Carbonic acid vols. in 10,000.				Remarks	
				First (Normal 9 mm.)	Last (Normal 8 mm.)	First	Last	Average	Unreduced		Pettenkofer
1905 Jan. 12th	Consulting Room 1750 ft.	Shut up at 4.50 p.m. 6.10 p.m.	Ca H <sub>2</sub> O <sub>2</sub> 4.1	Minutes 8	Minutes 9	35.26	39.67	37.47	37.80	42.92	Two gas brackets. Damper down. Gas stove.
		8 "	"	7	10	40.29	35.70	37.99	37.06	42.02	
14th	Dining Room 3200 ft.	5.20 "	"	23	29	12.26	12.31	12.29	13.86	14.98	
"	Drawing Room 3200 ft.	8.30 "	"	12	16	23.51	22.31	22.92	21.17	22.89	17 children, 4 adults. 3 gas-jets for 2 hrs. Pk. sample taken as spots nearly exhausted.
15th	Consulting Room 1750 ft.	Shut up at 4.50 p.m. Spots. 5.39 p.m. Pk. 5.43 "	"	15 for 10 m.	22	15.23	16.23	15.73	14.75	16.25	Two gas-jets. Gas fire. Damper partially down.
16th	"	Shut up at 7.5 p.m. S. 7.59 p.m. Pk. 8.4 "	"	18 for 10 m.	22	15.67	16.23	15.95	16.25	17.64	As before.
		S. 8.50 "	"	20	25	14.11	14.28	14.20	15.75	17.10	Very windy night.
		Pk. 8.53 "	"	11	15	22.52	20.40	21.46	23.82	25.95	5 adults. 4 gas-jets for 1 hr.
17th	Drawing Room 3200 ft.	S. 8.58 " Pk. 9.5 "	3.6								
18th	Consulting Room 1750 ft.	Shut up at 7.15 p.m. S. 8.9 p.m. Pk. 8.16 "	"	9½ for 8 m.	(14)	32.99	(Ratio 29.86)	32.99	33.08	37.30	As above. Damper completely down. Spots abnormally small.
		S. 8.48 " Pk. 9 "	"	7½ for 8 m.	(10)	41.8	(Ratio 46.06)	41.8	44.89	51.19	

19th	Consulting Room 1750 ft.	Shut up at 7.30 p.m. S. 8.19 p.m. Pk. 8.23 "	3-6	7	10	35-38	31-35	33-36	36-08	40	
		S. 9.9½ "	"	6½	9	38-1	34-83	36-47	43-36	48-99	
		Pk. 9.21 "	"								
21st	"	Shut up at 7.57 p.m. S. 8.54 p.m. Pk. 8.59 "	"	10	13	24-77	24-11	24-44	23-43	25-77	
		S. 9.50 "	"	6	7½	41-80	41-95	41-88	40-36	45-29	
		Pk. 9.59 "	"								
22nd	"	Shut up at 7 p.m. S. 7.50 p.m. Pk. 7.54 "	5-1	8½ for 10 m.	10½ for 9 m.	33-44	33-41	33-3	30-92	34-35	Large spots.
		S. 8.35 "	"	9	11	38-99	40-37	39-68	38-54	43-23	Spots usual size.
		Pk. 8.38 "	"								
		S. 9.13 "	"	7½ for 10 m.	8½	37-5	41-28	39-39	42-46	47-86	Spots large.
		Pk. 9.16 "	"								
25th	"	Shut up at 6.57 p.m. S. 7.50 p.m. Pk. 7.54 "	"	11	(16½)	31-90	---	31-90	35-08	38-98	Small spots.
		S. 8.36 "	"	9	12	38-99	37-01	38-00	37-38	41-86	Spots of ordinary size.
		Pk. 8.38 "	"								
		S. 9.29 "	"	7 for 10 m.	10	40-60	44-41	42-51	43-38	49-29	Large spots.
		Pk. 9.33 "	"								

TABLE II. External Air.

Average Factor for Reduction, 74.6.

Date	Time	x = Time of exposure	S = Strength of solution in milligrammes of CO <sub>2</sub> per 100 c.c.	Carbonic acid in parts per 10,000			Remarks
				By "Spots" $\frac{S \times f}{x}$	By Pettenkofer unreduced	Pettenkofer reduced to 760 mm. and 0°C.	
Sept. 1904		Minutes					
17th	—	32.8	CaH <sub>2</sub> O <sub>2</sub> = 1.5	3.41	3.23	3.50	
18th	—	32.2		3.48	3.07	3.30	
19th	9.15 a.m.	46	CaH <sub>2</sub> O <sub>2</sub> = 2.2	3.57	3.40	3.61	
	12.10 p.m.	37.7	CaH <sub>2</sub> O <sub>2</sub> = 1.85	3.66	3.10	3.37	
20th	12.45 "	40	" "	3.45	3.12	3.52	
	4.30 "	39	" "	3.54	3.57	3.84	
21st	11.50 a.m.	29.6	CaH <sub>2</sub> O <sub>2</sub> = 1.4	3.53	3.40	3.78	
	3 p.m.	29.4		3.55	3.07	3.36	
22nd	9.30 a.m.	11½	MgH <sub>2</sub> O <sub>2</sub> = .5	3.25	3.36	3.56	
	4.30 p.m.	34½	CaH <sub>2</sub> O <sub>2</sub> = 1.4	3.03	3.21	3.42	
23rd	1.15 "	12	MgH <sub>2</sub> O <sub>2</sub> = .5	3.11	3.08	3.36	
	2.50 "	34	CaH <sub>2</sub> O <sub>2</sub> = 1.4	3.08	2.92	3.18	
24th	12.30 "				3.60	3.85	} Period of low barometric pressure.
	2.20 "				4.16	4.43	
	3.15 "	34½		3.03	3.40	3.61	
27th	9.10 a.m.	53 for 8	CaH <sub>2</sub> O <sub>2</sub> = 1.8	3.17	3.69	3.92	
28th	12.25 p.m.	26 for 10	" "	4.13	3.91	4.21	
29th	2.30 "	29 for 10	" "	3.70	3.55	3.80	
30th	12.30 "	22 for 10	CaH <sub>2</sub> O <sub>2</sub> = 1.5	4.05	3.64	3.94	
Oct. 1st	12.30 "	34	" "	3.29	3.07	3.27	
3rd	11.45 a.m.	65 for 8	MgH <sub>2</sub> O <sub>2</sub> = 2	2.87	3.64	3.93	} Period of low barometric pressure.
4th	2.30 p.m.	60 for 8	" "	3.11	3.83	4.13	
5th	12 m.	38 for 8	BaH <sub>2</sub> O <sub>2</sub> = 1.7	4.16	4.43	4.82	