On a New Method for the Determination of Atmospheric Carbon Dioxide, based on the Rate of its Absorption by a Free Surface of a Solution of Caustic Alkali.

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In an appendix to a paper on the static diffusion of gases, communicated to the Society in 1900,* it was shown that when a current of air containing a constant proportion of carbon dioxide is caused to move in a turbulent stream over the free surface of a solution of caustic alkali, the rate of absorption of that gas increases with the velocity of the air-current up to a certain optimal speed, beyond which no further increase in the speed of the current influences the rate of absorption. It was further shown that when the optimal velocity of the air-current has been reached, and the temperature is maintained practically constant, the rate of absorption then varies directly as the partial pressure of the carbon dioxide in the air. In other words, if under the above conditions the rate of absorption per unit of area of the liquid surface is a for a partial pressure of carbon dioxide represented by p, and is a' for a partial pressure of p', then at similar temperatures, $a/p = a'/p'$.

A suggestion was also made that this principle might be found applicable to a determination of the carbon dioxide in air, and that if the method were found to be a practical one it would have the manifest advantage of not requiring any measurement of the air from which the gas was absorbed.

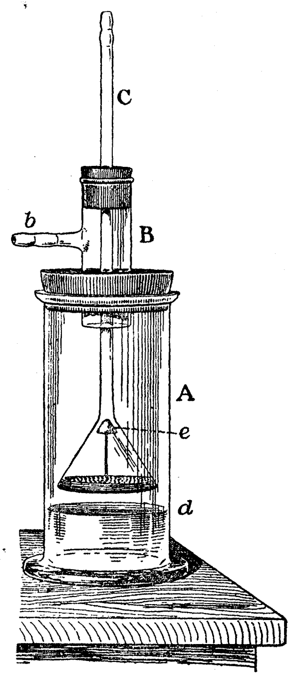
Since the first account of our experiments we have made a more complete investigation of the principles underlying the proposed method, and have succeeded in determining the coefficient of absorption of carbon dioxide under these conditions, and also the manner in which this coefficient is influenced by temperature. When certain precautions are taken, this simplified method of determining atmospheric carbon dioxide gives good results, which in point of accuracy approach those obtained by the more elaborate method with the Reiset's apparatus as described in the preceding paper.

The absorption-apparatus used in the experiments was a slightly modified form of one given at *b*, fig. 8 of 'Phil. Trans.,' B, Vol. 193, p. 284, which is here reproduced with its present modifications.

It consists of a glass cylinder A, about 15·5 cm. long and 6·5 cm. wide, closed with an india-rubber plug with a central perforation, through

* See 'Phil. Trans.,' B, vol. 193, p. 282.

which passes a short wide tube B of 2·5 cm. diameter, opening out into the cylinder below, and having a side tube *b* which can be connected with the aspirator, or the aspirator and meter if measurements of the air are required. The upper part of the tube B is closed with a cork, through which passes a narrower tube C terminating below in a funnel, the width of which is only slightly less than that of the cylinder. The mouth of the funnel is closed with a perforated porcelain disc, which is luted in with paraffin. When air is aspirated through the side tube *b* it enters the apparatus down the narrow tube *c*, and passing through the perforated plate, impinges as a turbulent stream on the surface of the absorbing solution of caustic soda at *d*. In order to distribute the air more completely, a small cone of paraffin *e* is supported on a needle in the position shown in the Figure. The funnel can be adjusted to any desired distance from the surface of the liquid in the cylinder, the ordinary working distance being 1 cm. 100 c.c. of a solution of caustic soda of approximately 4 per cent. concentration are introduced into the cylinder through an india-rubber cap temporarily placed over its mouth, and a similar arrangement at the close of the experiment admits of the liquid being titrated without removal to another vessel.* At the point reached in the cylinder by 100 c.c. of liquid, the area exposed was 32·557 sq. cm.



Hart's method of double titration was used for determining the carbon dioxide absorbed by the alkali ; this has been already fully described.†

In determining the constants of the above apparatus the air-current employed was divided into two parts, one of which passed through the surface absorber, and the other through a Reiset's tower charged with the solution of caustic soda by means of which an independent and accurate determination of the carbon dioxide was obtained. In both cases the volumes of air passed were measured by standardized meters.

The first series of experiments, of which the results are given in the following Table, was undertaken for testing still further the accuracy of the above

* Care must be taken not to wet the sides of the cylinder above the level of the liquid.

† See 'Phil. Trans.,' B, vol. 193 (1900), p. 289; also 'Roy. Soc. Proc.,' this vol., p. 35.

Table I.—Showing the Relation of the Surface-absorption of Carbon Dioxide by a 4 per cent. NaHO Solution to the Partial Pressure of that Gas in the Air-Stream when the Velocity of the Air-Current exceeds the Optimum for Maximal Absorption.

N.B.—The experiment which is taken as unity for the ratios of absorptions and of partial pressure is one in which the CO_2 content is practically that of normal air.

1.	2.	3. Rate of flow of air-current through absorption apparatus.		4.	5.	6.	7.	8. Ratios.	
No. of experiment.	Mean temperature, Centigrade.	Litres per hour.	Mean linear velocity in metres per hour.	CO_2 in vols. per 10,000 of dry air determined by Reiset's apparatus.	Partial pressure of CO_2 in moist air in terms of $\frac{1}{10000}$ atmosphere.	CO_2 absorbed per hour by 32·557 sq. cm. of surface of NaOH (in cubic centimetres of CO_2 at N. T. P.).	CO_2 in cubic centimetres absorbed by 1 sq. cm. of surface per hour for one part in 10,000 of CO_2.	(*a*) Of partial pressures of CO_2.	(*b*) Of rates of absorption of CO_2.
1	14°·1	192·9	328	0·040	0·039	0·076	0·0583	0·012	0·013
2	12°·3	187·2	319	0·189	0·186	0·324	0·0526	0·056	0·058
3	14°·4	163·1	278	0·568	0·558	0·982	0·0531	0·168	0·177
4	14°·8	146·2	249	1·080	1·062	1·870	0·0531	0·320	0·337
5	12°·4	162·3	276	1·152	1·135	1·984	0·0553	0·342	0·357
6	11°·2	167·3	285	3·216	3·174	5·252	0·0501	0·958	0·946
7	13°·6	140·1	238	3·364	3·313	5·547	0·0506	1·000	1·000
8	15°·3	156·0	266	4·588	4·511	7·725	0·0517	1·361	1·392
9	13°·8	164·1	279	4·893	4·817	8·329	0·0522	1·453	1·501
10	13°·5	155·3	264	6·759	6·656	11·276	0·0512	2·009	2·032
11	13°·2	143·7	245	7·653	7·540	12·492	0·0501	2·275	2·250
12	13°·7	155·3	264	8·547	8·416	13·863	0·0498	2·540	2·499
13	13°·7	167·1	284	12·532	12·341	20·873	0·0511	3·724	3·763
14	15°·2	156·8	267	17·949	17·645	30·905	0·0528	5·325	5·571

proposition that under the conditions postulated, the rate of surface-absorption of carbon dioxide is proportional to the partial pressure of that gas in the moving air-current.

A preliminary series of experiments, which need not be quoted here, had already established the fact that with this special form of apparatus, and with amounts of carbon dioxide not exceeding about 14 parts per 10,000 of air, a velocity of current of about 150 litres per hour was sufficient to ensure a maximum rate of absorption. With the funnel adjusted to a distance of 1 cm. from the surface of the liquid, this corresponds to an average forward movement in the turbulent air-stream of about 260 metres per hour.

In those cases where it was required to employ air containing less than the normal amount of carbon dioxide, part of the air was previously passed through a tower containing soda-lime, the necessary admixture with ordinary air being made on emergence from the tower before it was divided between the two forms of apparatus. When, on the other hand, air richer in carbon dioxide than ordinary air was required, the air stream was passed through a tower containing fragments of marble, on which there dropped a graduated flow of one-tenth normal hydrochloric acid.

In the last two columns of the above Table are given side by side the ratios of the partial pressures of the carbon dioxide in the air employed, and the ratios of the rates of absorption by the surface of the alkaline solution. It will be seen that these series of values are practically identical, thus clearly showing the direct relation between the partial pressures and the rates of absorption.

The values given in the seventh column were obtained by dividing the number of cubic centimetres of carbon dioxide (measured at N. T. P.) absorbed per square centimetre of liquid surface per hour by the number of volumes of carbon dioxide contained in 10,000 volumes of dry air. The results represent the coefficient of absorption of carbon dioxide, stated in the form of cubic centimetres per square centimetre per hour, corresponding to a uniform partial pressure of 1/10000 of an atmosphere. Had there been an *exact* correspondence between partial pressure and rate of absorption in all these experiments, this coefficient would have been a constant. The variations which occur are largely due to differences of temperature ranging from 11°·2 to 15°·3 C.

In order to investigate the influence of temperature on the rate of surface-absorption of carbon dioxide by soda-solutions, a separate series of experiments was undertaken, in which the absorption cylinder was immersed in

water, the temperature of which was observed at frequent intervals.* Six experiments of this nature were made between 13°·7 and 23°·7 C., ordinary air being used, of which the content of carbon dioxide was independently observed with the Reiset's apparatus.

Table II.—Showing the Influence of Temperature on the Coefficient of Absorption of CO_2 by the Surface of a 4 per cent. NaOH Solution.

Temperature.	Coefficient of absorption of CO_2 per square centimetre of liquid surface per hour, for 1 vol. of CO_2 in 10,000 vols. of air (dry).
13°·7	0·0519
15°·3	0·0537
15°·7	0·0537
19°·5	0·0583
21°·8	0·0623
23°·7	0·0635

On plotting out these results, it may be seen that within the experimental limits the coefficient of absorption varies directly with the temperature, and that an increase of temperature of 1° C. corresponds to an increase of 0·0018 in the absorption coefficient. Hence the value of this coefficient for any temperature $t°$ within the above limits will be represented by $0·0356 + t° \, 0·0018$, 0·0356 being the coefficient of absorption at 0° C., as determined by extra polation.

Assuming now that the relation of the partial pressures to absorptions is of the simple nature already postulated, then the volume of carbon dioxide contained in 10,000 volumes of dry air should be given by the formula

$$\frac{A}{0·0356 + t° \times 0·00118},$$

where A represents the carbon dioxide absorbed per square centimetre of surface per hour, at temperature $t°$, from an air-stream which is drawn over the absorbing liquid at a sufficient rate to ensure the limit of maximal absorption being reached; A being stated in terms of cubic centimetres at normal temperature and pressure.

With the knowledge thus gained we are now in a position to compare the estimations of carbon dioxide made by means of the method of surface-absorption with those made with the Reiset's apparatus.

* In order to avoid evaporation and consequent cooling of the absorbing solution, the stream of air was previously saturated with moisture before being passed into the absorption apparatus.

In Table III we have taken the results obtained with the surface-absorption method as given in Table I, in which very variable amounts of carbon dioxide were present in the air-stream, and have calculated the amount present in volumes per 10,000 by means of the formula $\frac{A}{0{\cdot}0356 + t^\circ \times 0{\cdot}00118}$. Alongside these results we have given the amount of carbon dioxide found by an independent determination with the Reiset's apparatus.

Table III.—CO_2 in Parts per 10,000 of Dry Air.

No. of experiment.	By Reiset's apparatus.	By surface absorption with NaHO solution. $\frac{A}{0{\cdot}0356 + t^\circ \times 0{\cdot}00118}$.	Difference.
1	0·04	0·04	0·00
2	0·19	0·19	0·00
3	0·56	0·57	+0·01
4	1·08	1·08	0·00
5	1·15	1·21	+0·06
6	3·21	3·30	+0·09
7	3·36	3·30	−0·06
8	4·58	4·41	−0·17
9	4·89	4·93	+0·04
10	6·75	6·72	−0·03
11	7·65	7·50	−0·15
12	8·54	8·23	−0·31
13	12·53	12·40	−0·13
14	17·94	17·74	−0·20

A further comparative test of the two methods was made with ordinary air, and gave the following results :—

Table IV.—CO_2 in Parts per 10,000 of Dry Air.

No. of experiment.	Tempera-rure.	By Reiset's apparatus.	By surface absorption with NaHO. $\frac{A}{0{\cdot}0356 + t^\circ \times 0{\cdot}00118}$.	Difference.
1	15°·3	3·29	3·29	0·00
2	15°·7	3·33	3·32	−0·01
3	21°·8	3·05	3·10	+0·05
4	23°·7	3·15	3·16	+0·01

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