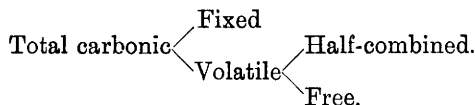


THE ESTIMATION OF CARBONIC ACID IN NATURAL WATERS.

BY CLARENCE A. SEYLER, B.Sc., F.I.C.

(Read at the Meeting, Nov. 3, 1897.)

THE carbonic acid of natural waters may occur in three forms: combined with alkaline earths or alkalis as mono-carbonates, half combined as bicarbonates, and fully-free carbonic acid. Of these the free and half-bound are approximately expelled on boiling, and hence I propose to call them the volatile carbonic acid. This is what is estimated by Pettenkofer's process :



The volatile carbonic acid used to be spoken of as free, but this name must be reserved for that which exists in excess of that necessary to form bicarbonates. The free acid is lost much more readily than the half-bound on exposure to the air.

Pettenkofer's method, though no doubt capable of accurate results with extreme care, is not fitted for the purposes of the busy analyst. It involves the use of many carefully calibrated vessels and frequent standardizing of variable solutions, and even at the best the results are subject to considerable uncertainty. On the assumption that the half-bound acid is equal to the combined, we may estimate the free carbonic acid by subtracting the combined from the volatile, as determined by Pettenkofer's process; but this is inaccurate with small quantities, as well as tedious. We require a rapid and accurate method of estimating the free carbonic acid independently. The proposals of Pettenkofer and Vignon to do so by a direct titration with lime or baryta water, using turmeric or phenolphthalein as an indicator, do not give satisfactory results. Trillich in 1890 appears to have been the first to give a satisfactory process by using sodium hydrate or carbonate, with phenolphthalein as indicator. I have used the process in regular practice since 1892; and in 1894, in the *Chemical News*, vol. lxx., p. 104 *et seq.*, I published the results of a careful examination of the accuracy of the process, together with the results of its application to different classes of water. The method does not seem to have attracted the attention in this country which I believe it deserves, though it is better known in Germany. My object is to direct the attention of analysts to the method, and to supplement my previous

papers with further experience of it. Referring to the journal already cited for details and explanation, I would say that the method depends on the exact neutrality of the bicarbonates, and the alkalinity of the carbonates, whether of the alkalies or alkaline earths, to phenolphthalein. Owing to the difficulty of keeping caustic soda free from carbonic acid, and also on account of its greater delicacy, I use a $\frac{N}{20}$ solution of sodium carbonate. To 100 c.c. of the water a few drops of a neutral alcoholic solution of phenolphthalein are added, and the liquid then titrated (best in a narrow vessel, with continual but not violent stirring) until the occurrence of a faint but permanent pink colour. This gives the free carbonic acid alone.* The combined acid is estimated on the same or a fresh portion of the water by means of methyl orange and $\frac{N}{20}$ acid. The volatile acid is the sum of the two titrations. If the water is neutral to phenolphthalein, it contains only bicarbonates, and no free carbonic acid. If a water is alkaline to the indicator, it can contain no free carbonic acid, and the volatile acid must be less than the fixed. This deficiency can be readily determined by careful titration with $\frac{N}{20}$ hydrochloric acid until the pink just vanishes.

Let m be the number of c.c. of $\frac{N}{20}$ hydrochloric acid required by 100 c.c. of the water, with methyl orange as indicator, p the number of c.c. of $\frac{N}{20}$ sodium carbonate required to produce the pink colour with 100 c.c. of the water, and p' the number of c.c. of acid required to discharge the pink if the water should be alkaline to that indicator. Then—

Free carbonic acid	1·1 p , or 1·1 $(p - 2m')$ parts per 100,000.
Fixed „ „	1·1 m parts per 100,000.
Volatile „ „	1·1 $(m + p)$, or 1·1 $(m - 2p')$ parts per 100,000.
Total „ „	1·1 $(2m + p)$, or 1·1 $(2m - 2p')$ parts per 100,000.

Should the water contain free mineral acid, it will be acid to methyl orange, and can contain only free carbonic acid in addition. If m' be the number of c.c. of sodium carbonate required to destroy the pink with methyl orange, p being, as before, the amount necessary to produce the pink with phenolphthalein, then the free carbonic acid is given by the formula :

$$\text{Free CO}_2 = 1\cdot1 (p - 2m').$$

Thus, in any case we can, by two simple titrations on 100 c.c. of the water, completely determine the amount and condition of the contained carbonic acid in a few minutes. The accuracy of the method has been confirmed in the best of possible ways both by myself and Kippenberger by comparison with Pettenkofer's method and gravimetrically.

The presence of ferrous salts in quantity requires a modification of the process, and in the case of highly-mineralized waters, such as the Hunyadi Janos water, some interfering factor remains to be explained ; but such cases are rare. I give some examples of Kippenberger's careful comparisons of the methods, which show that the process may lay claim not only to practical, but to scientific, accuracy :

* If much free CO_2 is present, the experiment must be repeated, running in nearly the right amount at once.

Free CO ₂ .	Combined.	Sum.	Pettenkofer.	Gravimetric.
2.10	5.05	7.15	7.35	7.24
2.09	11.90	13.99	13.85	13.78
1.43	9.25	10.68	10.7	10.63
2.00	6.60	8.60	8.55	8.33
11.35	6.77	18.12	18.12	
5.67	3.38	9.05	9.06	

The formulæ in the case of waters alkaline to phenolphthalein have not been verified in this way, and must therefore be accepted with caution.

As the method depends for its accuracy on the exact neutrality of the bicarbonates to phenolphthalein, which has recently been challenged by Küster (*Zeit. f. Anorg. Chem.*, B. XIII., s. 127, October, 1896), I thought it necessary to repeat his experiments. Küster affirms that the neutrality of sodium bicarbonate is only approximate, this salt being slightly alkaline to the indicator. He states that on titrating a solution of sodium carbonate with an acid, the pink to phenolphthalein does not vanish exactly at half the quantity required with methyl orange, but much later, 2 per cent. more acid (reckoned on the methyl orange titration) being required. Although a loss of CO₂ during the titration of a $\frac{N}{2}$ solution in an Erlenmeyer flask would account for this phenomenon, he states that this cannot be the cause, since by "a somewhat careful working one can see no trace of carbonic acid being evolved from the solution," and he expresses his conviction that the explanation is a totally different one, lying in theoretical considerations which he elaborates at considerable length. This is certainly most unconvincing, and contrary to all my experience. In my experiments the carbonate was prepared in different ways: twice recrystallized and dissolved without ignition, ignited at a dull red heat, and also dried at 150° C. The carbonate was dissolved in well-boiled water, generally neutralized together with the solution of the indicator by means of a few drops of $\frac{N}{100}$ baryta, and made up to 100 c.c. The acid was added from a verified burette with a long capillary spit reaching nearly to the bottom of the tall narrow cylinder in which the liquid was titrated with continual stirring by a circular glass rod, which was never lifted above the surface of the liquid. In this way the formation of bubbles and loss of carbonic acid was as far as possible prevented.

The carbonate was also dissolved in enough water to make the solution $\frac{N}{2}$, and titrated by the same apparatus without further dilution, as also in an Erlenmeyer flask with the ordinary burette as carefully as possible. The following table gives the results:

Methyl Orange.	Methyl Orange $\times \frac{1}{2}$.	Phenolphthalein.	Difference per Cent.	Remarks.
28.55	14.27	14.32	+ .17	Soda twice recrystallized. Vol. 100 c.c.
28.57	14.28	14.27	- .03	
25.80	12.90	12.95	+ .19	
25.85	12.92	13.00	+ .27	Ordinary soda ignited in muffle. Diluted.
39.05	19.52	19.45	- .18	
22.85	11.42	11.60	+ .70	Twice recrystallized. Dried at 150° C.
28.55	14.27	15.20	+ 3.26	" " " " Not diluted.
				" " Ordinary titration.

It is thus shown that, with proper precautions to avoid loss of carbonic acid, the pink of the phenolphthalein vanishes exactly at half the quantity required with

methyl orange within the limit of experimental error—that is, under 0.2 per cent. on the carbonate present. It is also shown that by working without dilution and other precautions, loss of carbonic acid of from 1 to 3 per cent. can easily occur, so that Küster's results are fully explained, and the neutrality of sodium bicarbonate vindicated.

As regards the utility of determining the carbonic acid in water, I would make the following observations: The interpretation of the results of water analysis, especially of the organic matter and nitrogen compounds, depends entirely on the origin of the supply—whether upland surface, mixed water from cultivated ground, deep or shallow well, the calcareous and pervious nature of the strata, etc. Now, the nature and amount of the carbonic acid is highly characteristic of waters from these different sources. In upland surface waters both the free and combined carbonic acid are characteristically low. In mixed water from cultivated land the free carbonic acid is low, and the combined generally moderate, while free carbonic acid over 0.5 per 100,000 is usually characteristic of water of underground origin. Its amount is, as a rule, greater in deep wells than in springs, and closely related to the porosity of the strata. Much fixed carbonic acid is also indicative of ground water, and related to the calcareous nature of the strata—a fact of importance in regard to the degree of nitrification. Many cases will occur to the experienced analyst in which these determinations will guide him in that most difficult task—the interpretation of the results of water analysis. Especially valuable in this connection is a determination of the free oxygen, which can now be rapidly and accurately made by the iodometric method of Ludwig Winkler. The amount of free oxygen is often distinctly correlated to the amount of free carbonic acid, varying in the opposite direction. Independently of these considerations, the carbonic acid is of importance in regard to the hardness of the water and the possibility of softening it, the free carbonic acid being as important in Clark's process as the combined and half-bound. Again, as regards the action on lead, the amounts of free and combined carbonic acid are, I believe, the chief factors.

Finally, I would draw attention to the not infrequent presence in natural waters of such as are alkaline to phenolphthalein, and therefore contain less carbonic acid than is required to form bicarbonates. The usual idea that a water which is strongly alkaline after boiling must contain alkaline carbonates is incorrect; the carbonates of lime and magnesia, especially the latter, are soluble as such in water, and exhibit an alkaline reaction with phenolphthalein. These alkaline waters are usually surface waters, or those containing magnesium carbonate, which have been exposed to the atmosphere. Sea-water is a typical example. I first met with this curious fact of the alkalinity of sea-water in the neighbourhood of Swansea, and my friend, Mr. J. E. Clennell, has had the kindness to test it for me at various points in the Atlantic, both north and south of the equator, with the result that the water was always alkaline to this indicator (strongly in the open sea, faintly near land), and therefore always devoid of free carbonic acid.

I had the opportunity of investigating a case of a fresh water of this kind in a reservoir supplied by a stream fed by springs, and considered this of sufficient interest to examine more closely. The streams entering and leaving, and the water of the

reservoir itself, were examined at intervals of a week, the temperature of the air and water and the degree of saturation with oxygen being also followed. This is of interest in connection with the fact previously observed by me, that water may be, and frequently is in Nature, supersaturated with oxygen to a very considerable extent; that is, may contain much more oxygen than is theoretically possible according to its coefficient of solubility at the temperature, even when exposing a large surface to the air. The temperature of the air was practically the same as that of the water at all depths. The stream entering contained a fair amount of free carbonic acid, and was generally nearly saturated with oxygen at the temperature of the air or water. In spite of this, on the first two occasions the water at the surface of the reservoir was alkaline to phenolphthalein and devoid of free carbonic acid. At the same time it was supersaturated with oxygen, the amount corresponding to a temperature some 5 degrees below that of the water. The water of the stream flowing out always contained a trace of free carbonic acid, and was practically saturated with oxygen at the temperature of the air and water.

On the following week the water of the surface had become acid to the indicator, containing about 0.4 parts per 100,000 of free carbonic acid, and was now deficient in oxygen, being saturated with the gas at about 5 degrees above the atmospheric temperature.

A week later the water had again become alkaline to phenolphthalein, and had reverted to a condition of supersaturation with oxygen to the extent of 7 degrees. A sample from a depth of 10 feet below the surface, however, contained at the same time as much as 0.7 parts of free carbonic acid, and was deficient in oxygen, being saturated at no less than 15 degrees above the temperature of the water, which was the same at that depth as at the surface. At the same time the distribution of chlorine and of combined carbonic acid was quite uniform, showing that the diffusion of gases must be much slower than that of salts in solution. The combined carbonic acid of the reservoir was considerably higher than that of the stream supplying it.

DISCUSSION.

The PRESIDENT having invited discussion,

Dr. RIDEAL said he was sorry Mr. Seyler seemed to think that his paper in the *Chemical News* had not been read or appreciated. At the time of the publication of that paper he (Dr. Rideal) had taken note of it, and a student working in his laboratory at the time had repeated the work, and obtained satisfactory results. This mixed titration with methyl orange and phenolphthalein had proved useful to him in the examination of sewage-contaminated waters, in which the increased amount of carbonic acid was a measure of the amount of organic matter present in solution; it also threw a good deal of light on the variations in the chief constituents of sewage undergoing bacteriological treatment. Mr. Adeney, of Dublin, had some two years previously published a long monograph, in which the subject of the gases in water—viz., carbonic acid and oxygen—was dealt with at some length. Mr. Adeney had calculated the ratio of the oxygen to the carbonic acid much in the same way as Mr. Seyler had done in the case of the reservoir waters referred to in the

paper, and had drawn very important conclusions from his results. Mr. Adeney's task, however, had been a very laborious one, inasmuch as he had pumped out all the gases and analysed them by the ordinary methods of gas analysis, whereas the methods of estimating the dissolved oxygen and carbonic acid used by Mr. Seyler afforded a quick and ready means of arriving at the ratio between the two, and the conclusions were just as valuable as those obtained by the more laborious method. He might mention that only the previous day he had had to examine a mixture of caustic soda, sodium carbonate, and sodium silicate, and had got out his results by titrating with normal acid (using phenolphthalein as a first indicator, and finishing off the titration with methyl orange), calculating the total alkalinity in the two forms of sodium hydrate and sodium carbonate, and then determining the silica in another portion gravimetrically, calculating the percentage of sodium silicate, and deducting that from the alkalinity as sodium carbonate, thus getting the three determinations required. It had occurred to him, when Mr. Seyler was mentioning some of the methods he had been examining, that the discrepancy between the methyl orange titration and the amount of carbonic acid actually present might be due to the presence of sodium silicate in the mineral waters investigated.

Mr. BERTRAM BLOUNT inquired whether he was right in understanding that when the author said that sea-water was alkaline to phenolphthalein he meant that when neutral phenolphthalein was added a pink colour was obtained. If so, he thought that was a very interesting fact. It seemed to him that the practice of quoting analytical methods by the names of their authors rather than according to the principles upon which they were based was to be deprecated. It was almost impossible to carry in one's mind the multitude of names which it was thus rendered necessary to remember. The method, for instance, used in this investigation for the determination of oxygen was perfectly unfamiliar to him by the name of its author, though he gathered that it was of a similar nature to one (devised at an earlier period by Dr. Thresh) depending on the use of nitrous acid as a carrier for oxygen, which possessed the advantage that the danger of oxygen escaping during the process of titration into the neutral atmosphere above the water being titrated was removed. The time occupied was also much shortened. Unless some process of this kind were used, he did not think that oxygen determinations in water could be looked upon as possessing much real value.

Mr. ALLEN inquired whether the author had any actual evidence of the existence of bicarbonate of calcium. For his own part, he was very sceptical on this point. It was interesting theoretically, and no doubt convenient in practice, to make use of the expression "half-combined carbonic acid," but he had grave doubts as to the existence of such a body as bicarbonate of calcium. Some years ago a series of experiments had been made under his supervision, in which an attempt was made to demonstrate the existence of bicarbonate of calcium, but all that was arrived at was the fact that the proportion of carbonic acid requisite to keep the calcium carbonate in solution varied according to the extent to which the liquid was diluted. He raised this question from a theoretical point of view: it did not affect the practical accuracy of the results. He could fully endorse what Mr. Seyler had said as to the impracticability of precipitating the whole of the carbonate of calcium or carbonate of mag-

nesium in water by boiling. The amount which remained in solution was, however, very erratic.

Mr. HEHNER desired to reiterate Mr. Allen's remarks, which in fact comprised all that he himself wished to say. He also had made experiments with a view to ascertaining whether a neutral solution at ordinary temperatures could contain bicarbonate of calcium in the ordinary chemical sense, and had also failed to establish the existence of this body. He thought it might be probable, however, that at some temperature lower than the ordinary such a substance would exist. He did not himself quite see the object of going into the differentiation of the "half-combined" and fully-combined carbonic acid. With regard to the subject of dissolved oxygen, the diagram exhibited was exceedingly interesting. Might not the supersaturation with oxygen be due to algæ, which decomposed the carbonic acid and apparently liberated oxygen under the influence of light, since the phenomenon occurred near the surface.

Mr. A. C. CHAPMAN remarked that Mr. Allen and Mr. Hehner might equally extend their scepticism to the existence of calcium bisulphite, the evidence for the existence of both compounds being of an analogous character. In regard to the bicarbonate, the experimental results which had been obtained were not by any means conclusive as to its existence. A point incidentally referred to by the author, which was of some importance in connection with water analysis, and more especially so in the case of water containing a large proportion of alkaline chlorides, was the marked solubility of magnesium carbonate. In the analysis, for example, of London tertiary waters, which often contained a good deal of common salt, it was usual in the estimation of the alkaline carbonates to find considerable quantities of magnesium carbonate dissolved. The author's method would, of course, not apply to those waters (which, however, were not very numerous) in which organic acids of a peaty character were present.

Mr. RICHMOND said he remembered reading a paper in which it was shown that if a water saturated with oxygen at say 10° C. was cautiously raised to 15° C. without shaking or agitation, it would retain practically the whole of the oxygen, and be supersaturated. It had occurred to him on seeing Mr. Seyler's diagram that probably the water would be subjected to a good deal of agitation while running into the reservoir, and would absorb oxygen; this agitation would cease after the water had finished flowing into the reservoir, and a rise in temperature might conceivably take place unaccompanied by any diminution in the proportion of dissolved oxygen.

The PRESIDENT said that the interesting nature of the discussion in itself constituted a vote of thanks to Mr. Seyler, whom he would ask to kindly make such reply as was necessary.

Mr. SEYLER, referring to Dr. Rideal's remarks, said that he had read Mr. Adeney's paper with much interest, but the apparatus required was too expensive, and the operations too lengthy for ordinary use. He had given some examples of the application of the titrimetric method to sewage in his papers in the *Chemical News*, but confessed to some disappointment with the results in this case, as there were several interfering factors. Phenolphthalein was so much affected by ammonia that he was afraid the presence of this body in sewage might affect the results. This

difficulty might possibly be overcome by using tropæolin 000, which behaved exactly like phenolphthalein, but as far as he knew was not affected by ammonia. He had found large quantities of butyrates in sewage, and these were alkaline to methyl orange almost to the same extent as carbonates. It was quite true that the presence of silicates was a disturbing factor. In this connection it was of interest that Kippenberger had shown silicic acid to be alkaline to methyl orange—slightly, it was true, but distinctly. He (Mr. Seyler), however, thought that the difficulty was not of practical importance. With regard to the question raised by Mr. Blount as to Ludwig Winkler's method, he thought it was sometimes useful to refer to methods by their authors' names. In this method the source of inaccuracy mentioned by Mr. Blount was avoided, as in the process devised by Dr. Thresh, the oxygen carrier being, however, manganese hydrate instead of nitric oxide. The only objection to the method was the fact that sewage often absorbed iodine; but this could probably be avoided by titrating separately and deducting the iodine absorbed in this way. With regard to the scepticism which had been expressed as to the existence of calcium bicarbonate, he thought that the experiments on which such scepticism was based must have been very inconclusive. He thought that there could be no better proof of the existence of calcium bicarbonate than the figures which he had written down—the agreement would be impossible if calcium bicarbonate did not exist in the waters. Shortly before coming to town he had prepared a solution of calcium bicarbonate in the following way. He took a fairly strong solution of carbonic acid in water, and added lime-water until he got an indication of a precipitate of calcium carbonate, when he stopped the addition of lime-water, and filtered the solution (which was slightly alkaline to phenolphthalein owing to the solubility of calcium monocarbonate in water), and determined the volatile carbonic acid by Pettenkofer's method. Titration with methyl orange gave 20·7 milligrammes of carbonic acid per 100 c.c. Deducting the slight alkalinity (0·4 c.c.) for the monocarbonate present, there remained 20·3 as the amount of "half-combined" carbonic acid. Pettenkofer's method gave volatile carbonic acid 19·97. Thus, in a solution of calcium carbonate in carbonic acid neutral (like other bicarbonates) to phenolphthalein the volatile carbonic acid was shown to be approximately equal to the fixed, thus proving in his (the speaker's) opinion that the solution contained practically calcium bicarbonate. Very probably the solution on standing for some time would decompose, possibly into sesquicarbonate of calcium and free carbonic acid. There was no evidence of any abundance of algæ in the water supersaturated with oxygen. He thought that probably the explanation suggested by Mr. Richmond was the correct one. He would like to mention that the alkalinity of sea-water was enormously increased by the action of plant-life (marine algæ, etc.), which took up the "half-combined" carbonic acid, leaving magnesium monocarbonate in solution.
