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THE DETERMINATION OF CARBONIC ACID, COMBINED AND FREE, IN SOLUTION, PARTICULARLY IN NATURAL WATERS.[1]

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Owing to the importance, especially in connection with water analysis, of a knowledge of the concentration of carbonic acid, combined and free, in solutions, a great deal of attention has been devoted to methods of de-

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[1] A few days after this paper was originally submitted to the editor, Professor H. N. McCoy transmitted to me two manuscripts sent to him by Mr. C. A. Seyler (of Swansea, England) entitled: "Studies of the Carbonates. II. Hydrolysis of Sodium Carbonate and Bicarbonate, and the Ionization Constants of Carbonic Acid," by C. A. Seyler and P. V. Lloyd, and "Studies of the Carbonates. III. Lithium, Calcium, and Magnesium Carbonates," by C. A. Seyler. After reading these papers I decided to recall my paper, and to delay its publication until I should have corresponded with Mr. Seyler, who has very courteously allowed me to make use of his MSS. I have changed my calculations in order to have them consistent with this most recent determination of the constants; but the resulting slight changes in numerical values have in no wise affected the general argument of the paper. Quite recently Mr. Seyler has forwarded to me a manuscript copy of a third paper "Studies of the Carbonates. IV. The Hydrolysis of Sodium Bicarbonate and the Ionization Constants of Phenolphthalein," in which the suitability of phenolphthalein as an indicator for the titration of carbonates and carbonic acid is discussed in detail. These three papers will, it is expected, be published in the near future in *J. Chem. Soc.*

termination of these constituents; but the question as a whole has hitherto received scant attention, in particular from the theoretical standpoint. It is the purpose of the present paper to discuss the methods of estimating carbonic acid and carbonate from the point of view that the several molecular species with which we are here concerned can co-exist only in definite proportions determined by the known equilibrium constants, and by this means be enabled to judge of the applicability and degree of accuracy of the several methods. This treatment on the basis of fundamental principles enables us, as we shall see, to criticize and coördinate the numerous apparently contradictory statements recorded in the very voluminous literature on this subject; for this conflict is due less to lack of care in the experimental work than to the fact that some essential factor—the importance of which, however, would not be recognized until the theory had been considered—was not adequately controlled. Indeed a large part of the literature would have been unnecessary, and much painstaking experimental work would have been obviated, if it had been generally recognized that we are here dealing with a fairly mobile equilibrium, and consequently that any change in the factors of the equilibrium is followed by a definite predictable change in the concentration of each of the several molecular species present.

In what follows we shall take up first the general question of the equilibrium in aqueous solutions of carbonates, and consider the quantitative relations existing between the concentrations of the several components at equilibrium. Then we shall go on to discuss the several methods in common use for the determination of CO_2, combined and free; and finally present some conclusions which follow from the discussion. In what follows it is to be understood that the only basic radical present is assumed to be soda (or potash) and that no other acidic radical is present, since it is impracticable to take up all possible cases; the presence of other bases, such as lime, magnesia, iron, would introduce certain conditions (*e. g.*, by reason of the limited solubility of their carbonates or oxides), which, however, would merely modify the conclusions in a way which can be readily derived for each particular case. Incidentally it may be remarked that some of the conclusions are of importance with respect to any acidimetric titration in which the highest accuracy is desired, by reason of the presence of some carbon dioxide in the liquids to be titrated consequent upon its presence in the air.

I. The Equilibrium in Solutions of Carbonates.

In any aqueous solution containing carbonates, the following relations hold at equilibrium (provided at least that the total concentration of the solution is not excessive—a limitation which is of no consequence in the present instance), it being premised that symbols, such as $[CO_3^{=}]$, represent the molar concentration of the particular molecular species enclosed within the brackets:

$$[H_2CO_3] = cP \tag{I}$$

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = k_1 \tag{II}$$

$$\frac{[H^+][CO_3^=]}{[HCO_3^-]} = k_2 \tag{III}$$

Equation I expresses the equilibrium between the undissociated dissolved carbonic acid and the partial pressure P of CO_2 in contact with the solution; II and III define, respectively, the first and second ionization constants of carbonic acid in aqueous solution. There is, moreover, the condition that

$$[B^+] + [H^+] = [HCO_3^-] + 2[CO_3^=] + [OH^-],$$

where $[B^+]$ represents the total equivalent concentration of cations present in the solution; in this summation both $[H^+]$ and $[OH^-]$ may usually be neglected, as they are small in comparison with the other quantities.

It may be objected that it is beside the mark to consider equilibrium conditions in connection with titrations; but apart altogether from the circumstance that a knowledge of the equilibrium relations constitutes the best means of predicting what will happen in any case, this objection has very little force in this instance by reason of the relative rapidity of the reactions involved. Two only of the reactions require a measurable interval of time: (1) the diffusion of CO_2 from the air space into and through the solution (the rate of this process depends obviously upon the mode of shaking or stirring, but even in an unstirred liquid contained in an open beaker the process is substantially complete in about ten minutes, as evidenced by the change of electric conductance of water left under such conditions); (2) the rate of neutralization,[1] implying that either the hydration of CO_2 or the ionization of H_2CO_3 proceeds slowly. But in this case again, as McBain remarks,

> "There is no doubt that the reaction proceeds the greater part of the way in a fraction of a minute; but it is sufficiently incomplete to permit of a bright red color repeatedly vanishing within a few minutes after the first apparent attainment of the end point (with phenolphthalein)."[2]

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[1] J. W. McBain, "The Use of Phenolphthalein as an Indicator. The Slow Rate of Neutralization of Carbonic Acid," *J. Chem. Soc.*, 101, 814 (1912), *q. v.*

[2] McBain (*Loc. cit.*) demonstrates conclusively that the fading out of the red color of phenolphthalein in nearly neutral solutions is due to the slow neutralization of the carbonic acid in the solution, for in absence of carbonate the end point is instantaneous and permanent; this is therefore a different phenomenon from the fading in presence of strong alkali. This point is obviously of importance in every titration in which phenolphthalein is used as indicator.

Consequently it is here admissible to make use of the relations deduced for complete equilibrium, especially if in any actual case we take into account the effects to be expected from the slow operation of the above two processes; indeed in the usual titration method for determining free CO_2 it is tacitly assumed that this equilibrium adjusts itself during the titration.

By combination of Equations I, II and III we obtain

$$[HCO_3^-]^2/[CO_3^=] = k_1[H_2CO_3]/k_2 = k_1cP/k_2. \qquad \text{(IV)}$$

It follows, therefore, that, when equilibrium is attained, both the amount of free carbonic acid in solution and the relative proportions of bicarbonate and carbonate ion are determined by the partial pressure of CO_2 in the atmosphere. And it follows, moreover, that a change in P, such as may easily occur when a water is brought from outside into the laboratory, or even in the laboratory from one day to another, will affect all of the quantities, and by amounts which, as we shall see, are not negligible. This is illustrated by experiments recorded by Ellms and Beneker[1] who exposed samples of (*a*) water, (*b*) a solution of calcium bicarbonate, to the air of the laboratory, with the following results, expressed in parts per million:

	(*a*).	(*b*).		
	Free CO_2.	"Free CO_2."	"Half bound."	"Fixed."
Original	0	52.8	109.4	109.4
After 24 hrs.	2.2	7.0	...	...
After 48 hrs.	14.1[2]	1.1	...	...
After 72 hrs.	0.9	0	80.7	84.5

From this one can readily see the possibilities of variation in the amount of free CO_2 in solution—and, consequently, as we shall see, upon the proportion of bicarbonate to carbonate and the degree of alkalinity of the solution—especially when the amount is in excess of that demanded by the equilibrium; for, as was pointed out by McCoy,[3] and since then by others, low results are invariably attained if such solutions, contained in a beaker, are exposed even for four or five minutes.

The values of k_1, k_2 and c depend upon the temperature, and c also depends upon the total concentration of base [B]. For the present purpose it suffices to consider a single temperature, which for convenience has been chosen to be 25°; all calculations in this paper refer to 25°, but a variation of a few degrees away from 25° would make no essential difference in the results. The values of c at 25° for several values of [B] are as follows:[4]

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[1] THIS JOURNAL, **23**, 407 (1901).

[2] On this day a CO_2 generator was being used in the laboratory.

[3] McCoy, *Am. Chem. J.*, **29**, 444 (1903).

[4] On the basis of Bohr's measurements on water and solutions of NaCl (*Ann. Physik*, **68**, 500 (1899)). c decreases with rise of temperature; at 100° it is only 0.011 (Bohr and Bock, *Ibid.*, **44**, 342 (1891)), so that at 100° the concentration of H_2CO_3 would be, ceteris paribus, one-third as great as at 25°.

[B]	0	0.1	0.2	0.3	0.5	1.0
c	0.0338	0.329	0.321	0.314	0.300	0.270

Now the average proportion of CO_2 in the atmosphere is not far from 3 parts per 10,000 (*i. e.*, $P = 0.0003$); but the air of a laboratory will usually contain 4 or 5 parts, and this proportion may range up to 10 or 12, or in especially ill ventilated rooms to still higher values. The concentration of H_2CO_3[1] (*i. e.*, of free CO_2) in any dilute solution in equilibrium at 25° with an atmosphere containing CO_2 at P is, in accordance with Equation I, as follows:

$P \times 10^4$	3	4	5	6	8	10
$[H_2CO_3] \times 10^5$	1.0	1.3	1.7	2.0	2.7	3.3
CO_2, parts per million	0.44	0.59	0.73	0.9	1.2	1.5

Thus the concentration of free CO_2 in any solution in *equilibrium* with laboratory air would be about 1 part per million, or more in certain cases; if the concentration actually present is larger or smaller than corresponds to equilibrium, the solution will tend to give off, or absorb, CO_2, and will actually do so unless due precautions are taken to prevent it.

Let us now consider the relative proportions of bicarbonate and carbonate in relation to the partial pressure P of CO_2. The proportion of sodium (or indeed of any univalent base) associated with bicarbonate can be calculated by means of Equation IV if the ratio k_1/k_2 and the degree of ionization of $NaHCO_3(\gamma_1)$ and of $Na_2CO_3(\gamma_2)$ are known. The calculation of k_1/k_2 from the experimental results on which it is based involves γ_1 and γ_2; heretofore, for want of a better method, the assumption has been made that γ_1 and γ_2 are identical with the degree of ionization of sodium acetate and of sodium sulfate, respectively (salts of the same ionic types) an assumption which, however, led to different values of k_1/k_2 at different concentrations of total base.[2] Now Seyler and Lloyd[3] have shown on the basis of McCoy's work, and also of new experiments in more dilute solutions, that a constant value of k_1/k_2 (*viz.*, 7100) is obtained by assigning smaller values to γ_2, as follows:

[Na]	0.05	0.1	0.2	0.3	0.5	1.0
γ_1	0.82	0.78	0.73	0.69	0.64	0.52
γ_2	0.56	0.46	0.37	0.31	0.24	0.14

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[1] In identifying $[H_2CO_3]$ with the total concentration of free CO_2 in solution we are tacitly assuming that all the CO_2—apart from the ionized portion—exists as the hydrated form in solution; this assumption is the best that can be done at present, but introduces no error which is significant in the present connection. This point, and a number of others touched upon in the present paper, have been more fully considered previously (THIS JOURNAL, **37**, 2001 (1915)), *q. v.*

[2] See McCoy, *Am. Chem. J.*, **29**, 437 (1903), or the recalculation of McCoy's results by Johnston (THIS JOURNAL, **37**, 2001 (1915)). Professor Stieglitz pointed out in a letter to me that the true degree of ionization of Na_2CO_3 is in all probability much less than that of Na_2SO_4.

[3] See footnote 1, p. 947.

"These values represent the activity of sodium carbonate (as regards the CO_3 ion) and of sodium bicarbonate in equilibrium with each other and with carbonic acid. Those for γ_1 are founded upon the ionization of sodium acetate calculated from the conductivity. The values for γ_2 are much less than would be expected from analogy with sodium sulfate, even after allowing for the presence of an intermediate ion."[1] And they proceed to show how these values of γ_2 are in harmony with many facts as to the behavior of carbonate solutions and serve to reconcile data hitherto apparently in conflict. We shall, therefore, adopt these values as the best available at the present time for the purpose in hand, and calculate the partial pressure P of CO_2 in equilibrium at 25° with various proportions of bicarbonate and carbonate in a solution 0.1 N with respect to total sodium. If the concentration of sodium as bicarbonate is b, then[2]

$$[HCO_3^-] = b\gamma_1 = 0.78b \text{ and } 2[CO_3^=] = (0.1 - b)\gamma_2 = 0.46(0.1 - b);$$

and from Equations IV and I

$$[HCO_3^-]^2/[CO_3^=] = k_1[H_2CO_3]/k_2 = 7100[H_2CO_3] = 234\ P.$$

Values of P calculated in this way for several values of b are presented in Table I.[3]

TABLE I.—THE PARTIAL PRESSURE OF CO_2 IN EQUILIBRIUM WITH, AND THE ALKALINITY OF, SEVERAL BICARBONATE-CARBONATE SOLUTIONS, 0.1 N WITH RESPECT TO TOTAL SODIUM; TEMPERATURE 25°.

% bicarbonate.	[Na] as $NaHCO_3$. b.	[Na] as Na_2CO_3 $0.1 - b$.	$[HCO_3^-]$ $= b\gamma_1$.	$2[CO_3^=]$ $= (0.1 - b)\gamma_2$.	$P \times 10^4$.	$[OH^-] \times 10^6$.
35	0.035	0.065	0.0273	0.0299	2.14	9.3
40	040	060	0312	0276	3.01	7.5
45	045	055	0351	0253	4.16	6.1
50	050	050	0390	0230	5.65	5.0
55	055	045	0429	0207	7.60	4.1
60	060	040	0468	0184	10.18	3.3
65	065	035	0507	0161	13.65	2.7

This shows the large influence which a change in the proportion of CO_2 in the air, such as may readily take place in a short time in a laboratory, exerts upon the position of the equilibrium carbonate-bicarbonate in solutions 0.1 N with respect to base;[4] the change produced by a given change

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[1] Quoted from the manuscript of Seyler and Lloyd.

[2] The real value of γ_1 and of γ_2 would vary slightly with b by reason of the change in the concentration of $NaHCO_3$ and Na_2CO_3; but neglect of this variation causes no error which is significant in the present connection.

[3] McCoy (*Loc. cit.*) has made a similar calculation.

[4] It is obvious that the above results hold equally for any univalent base, since the degree of ionization of all salts of the same valence type is substantially identical (see, *e. g.*, Noyes and Falk, THIS JOURNAL, 34, 475 (1912)); moreover they would be substantially correct for any base.

in P is inversely proportional approximately to the square root of the total concentration, so that, *e. g.*, in a 1.0 N solution the percentage change would be just about one-third as much as in the 0.1 N solution.[1] The complete establishment of this equilibrium requires some time; thus McCoy,[2] who passed a current of outside air through a solution of (*a*) $NaHCO_3$, (*b*) Na_2CO_3, each 0.1 N with respect to sodium and at 25°, found that the same condition (*viz.*, 40.4% bicarbonate) was reached in either solution in about three days. But though a period of three days is required for the attainment of a state of equilibrium, an interval of a few minutes suffices to bring about a marked change in the proportion of bicarbonate to carbonate (and hence in alkalinity of the solution); this is well illustrated by another experiment of McCoy's, who passed air through a 0.1 N solution originally made up from solid bicarbonate, and examined the rate of change of the proportion, with the following results:

Time in hours	0	0.25	0.67	1.17	2.0	26	48	72
% Na as bicarbonate	95	88	80	76	75	45	43	40

This rate depends, of course, upon the mode of experiment; in any case the above illustration suffices to show that material changes in the proportion may result from exposure of the solution for even a few minutes to an atmosphere other than that with which it is in equilibrium.

From the foregoing it is obvious that most solutions, natural waters especially, which we wish to analyze will have reached substantially the equilibrium state,[3] consequently it is altogether unnecessary to determine the concentration of each of the several constituents, because if two of them are known, the others can be calculated. Moreover the proportion $[HCO_3^-]/[CO_3^=]$ absolutely determines the alkalinity of the solution, and conversely; for by Equation III

$[H^+] = k_2[HCO_3^-]/[CO_3^=] = 4.8 \times 10^{-11}\ [HCO_3^-]/[CO_3^=]$ at 25°[4] and

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[1] The actual percentage of bicarbonate for a given value of P is of course also dependent upon the concentration, as is evident from the form of Equation IV, becoming smaller as the total concentration of base increases.

[2] *Am. Chem. J.*, **29**, 459 (1903). The results indicate that the proportion of CO_2 in the air passed through was about 3.0 parts per 10,000. Likewise one can deduce that the air passed through their carbonate-bicarbonate solutions by Cameron and Briggs (*J. Phys. Chem.*, **5**, 537 (1901)) contained from 5 to 7 parts CO_2 per 10,000 and hence was presumably laboratory air.

[3] For purely scientific purposes there would seem to be little to be gained by determinations of the concentration of the several constituents present in a solution which has not attained substantially to a state of equilibrium.

[4] According to Walker and Cormack (*J. Chem. Soc.*, **77**, 8 (1900)) $k_1 = 3.04 \times 10^{-7}$ at 18°; whence, by means of the van't Hoff formula, on the basis that the heat change accompanying the reaction is 2700 cal., $k_1 = 3.39 \times 10^{-7}$ at 25° (see Lewis and Randall, THIS JOURNAL, **37**, 467 (1915)), and $k_2 = 3.39 \times 10^{-7}/7100$. In strictness the experimental datum 3.04×10^{-7} represents the value at 18° of the expression $[H^+][HCO_3^-]/([H_2CO_3] + [CO_2]s)$; but we do not know what fraction of the total CO_2 in solution

since $[H^+][OH^-] = K_W = 0.8 \times 10^{-14}$ at 25°[1]

$$[OH^-] = 1.7 \times 10^{-4}\ [CO_3^{=}]/[HCO_3^-] \text{ at } 25°. \qquad (IIIa)$$

Alternatively by combination of Equations I, II and III, we obtain:

$$[H^+][HCO_3^-] = k_1 cP = 3.39 \times 10^{-7}\ cP \text{ at } 25° \qquad (V)$$

and

$$[H^+]^2[CO_3^{=}] = k_1 k_2\ cP = 1.66 \times 10^{-17}\ cP \text{ at } 25°. \qquad (VI)$$

Hence, if we know P and the total equivalent amount of CO_2 in the solution, we can determine $[OH^-]$; for example in a carbonate-bicarbonate solution which is 0.1 N with respect to sodium the alkalinity for several values of P is given in the last column of Table I.[2] This emphasizes again the fact that these several quantities are not independent variables; that it suffices to fix two of them only in order to define completely the constitution of the solution.

But for our present purpose it is better to consider the relation between the alkalinity of the solution and the concentration of free CO_2 (which, it will be recalled, determines the proportion of bicarbonate to carbonate); for knowledge of this relation, which is readily derived, is essential to the understanding of any titration process in which carbonic acid in any form is present. By combining the condition $[B^+] + [H^+] = [HCO_3^-] + 2[CO_3^{=}] + [OH^-]$, where $[B^+]$ is the total equivalent concentration of ionized base, with Equations II, III and the relation $[H^+][OH^-] = K_W$, we obtain

$$([B^+] + [H^+])[H^+]^2 - (k_1[H_2CO_3] + K_W)[H^+] - 2k_1k_2[H_2CO_3] = 0$$

whence

$$[H_2CO_3] = \frac{([B^+] + [H^+])\ [H^+]^2 - K_W[H^+]}{k_1[H^+] + 2k_1k_2} = \frac{([B^+] + [H^+])\ [H^+]^2 - 8 \times 10^{-15}[H^+]}{3.4 \times 10^{-7}\ [H^+] + 3.3 \times 10^{-17}} \text{ at } 25°.$$

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exists as H_2CO_3, except that it is probably more than one-half. This point is more fully considered in a previous paper (THIS JOURNAL, **37**, 2001 (1915)); in the present paper it is presumed that all the uncombined CO_2 in solution exists as H_2CO_3.

[1] This is undoubtedly the most accurate value now available (see Lewis and Randall, THIS JOURNAL, 36, 1979 (1914)). Neglect of the contact potentials is of itself sufficient to account for the higher value given by Frary and Nietz (THIS JOURNAL, **37**, 2263 (1915)); their use of this higher value in interpreting their further experiments is however perfectly justified.

[2] For similar calculations for solutions of carbonates of calcium and magnesium see Johnston, THIS JOURNAL, **37**, 2012, 2016 (1915); Johnston and Williamson, *Ibid.*, **38**, 975 (1916); cf. also Auerbach and Pick, "Die Alkalinität wässeriger Lösungen kohlensaurer Salze," *Arbeiten kais. Gesundheitsamt*, **38**, 243 (1911); in their equations, however, as in those of Frary and Nietz (THIS JOURNAL, **37**, 2268 (1915)), the assumption is implicit that the solution neither gains nor loses CO_2, which would require that the experiments be carried out in closed vessels completely filled with liquid, and consequently some of their conclusions do not necessarily hold for all cases.

This formula[1] allows us to calculate values of $[H_2CO_3]$ for any value of $[B^+]$ and $[H^+]$—in other words to calculate the concentration of free CO_2 (and hence the ratio of bicarbonate to carbonate) in a solution of any total concentration at the end point registered by any indicator. A series of such calculations have been carried out, the results of which are presented in Table II, to which it may here be remarked that indicators which change color at values of $[H^+]$ greater than 10^{-6} are—as is obvious from the table—insensitive towards ordinary amounts of CO_2, and that the higher concentrations of H_2CO_3 are unlikely to occur in ordinary practice, since even 10 parts CO_2 per million would require a partial pressure in the atmosphere of about 0.007 (*i. e.*, 70 parts in 10,000) to prevent the solution from losing any CO_2.

By means of this table, in conjunction with a table of indicator constants,[2] one is enabled to choose an indicator and to conduct any titration of a carbonate solution so that the error from the free CO_2 still in solution at end point shall not exceed a certain limit. As an example, if the untitrated CO_2 must be less than 1 part per million, and the total concentration of base at the end point is 0.001, one must choose an indicator at a concentration such that the color change takes place when $[H^+]$ is between 10^{-8} and 10^{-9}—*e. g.*, phenolphthalein at the proper concentration.[3] To this question we shall revert when we take up the several methods; but before doing so, we shall consider a few other general points, affecting all of the methods, which follow directly from the various principles which we have discussed.

The illustrations presented in the preceding pages demonstrate the futility of attempting to determine the real proportions of free CO_2, or of carbonate and bicarbonate, in any solution, unless special precautions be taken to ensure that no change can take place during the manipulations, from the collection or preparation of the sample onwards. It is

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[1] An analogous formula has been given by Prideaux (*Proc. Roy. Soc.*, (*A*) **91**, 535 (1915)) who has used it to calculate the acidity of carbonate solutions for several values of $[H_2CO_3]$ and [B].

[2] The most complete tables are given in papers by Sörensen (*Biochem. Z.*, **21**, 131 (1909); **22**, 353 (1909); **24**, 381 (1910)). For some data, and references to others, see A. A. Noyes "Quantitative Application of the Theory of Indicators to Volumetric Analysis," THIS JOURNAL, **32**, 815 (1910); see also Walpole, *Biochem. J.*, **8**, 628 (1914); Lubs and Clark, *J. Wash. Acad.*, **5**, 609 (1915). A very good discussion of indicators and their properties will be found in "Die Theorie der alkalimetrischen und azidimetrischen Titrierungen," by N. Bjerrum (*Ahrens' Sammlung*, **21**, Heft 1–3 (1914)); it should be consulted by all who are interested in the definitive accuracy of titration methods. In this pamphlet, which was brought to my attention by Dr. R. C. Wells after the present paper was completed, Bjerrum also takes up some of the problems considered in the following pages.

[3] On this point see Rosenstein, "The Ionization Constant of Phenolphthalein and the Effect upon it of Neutral Salts," THIS JOURNAL, **34**, 117 (1912).

TABLE II.—THE CONCENTRATION OF FREE CO_2, EXPRESSED IN (*a*) MOLES PER LITER (*b*) PARTS PER MILLION, WHICH WOULD BE IN EQUILIBRIUM WITH THE HYDROGEN-ION CONCENTRATION $[H^+]$ AT THE TOTAL EQUIVALENT ION-CONCENTRATION OF BASE $[B^+]$.

		$[H^+]$						
$[B^+]$.		10^{-12}.	10^{-11}.	10^{-10}.	10^{-9}.	10^{-8}.	10^{-7}.	10^{-6}.
0	*a*	....	....	...	...	...	5.8×10^{-9}	2.9×10^{-6}
	b	....	....	...	...	...	0.00025	0.13
0.0001	*a*	....	....	3.0×10^{-9}	3.5×10^{-7}	2.9×10^{-6}	2.9×10^{-5}	2.9×10^{-4}
	b	....	....	0.00013	0.015	0.13	1.3	13
0.001	*a*	....	5.5×10^{-10}	1.4×10^{-7}	3.7×10^{-6}	2.9×10^{-5}	2.9×10^{-4}	2.9×10^{-3}
	b	....	0.000024	0.0062	0.16	1.3	13	130
0.01	*a*	6.0×10^{-11}	2.5×10^{-8}	1.5×10^{-6}	3.7×10^{-5}	2.9×10^{-4}	2.9×10^{-3}	2.9×10^{-2}
	b	0.0000026	0.0011	0.066	1.6	13	130	1300
0.1	*a*	2.8×10^{-9}	2.7×10^{-7}	1.5×10^{-5}	3.7×10^{-4}	2.9×10^{-3}	2.9×10^{-2}	2.9×10^{-1}
	b	0.00012	0.012	0.66	16	130	1300	13000
1.0	*a*	3.0×10^{-8}	2.7×10^{-6}	1.5×10^{-4}	3.7×10^{-3}	2.9×10^{-2}	2.9×10^{-1}	2.9
	b	0.0013	0.12	6.6	160	1300	13000	130000

to be borne in mind that any titration (or other) method of analysis of a solution containing combined CO_2 can yield information only as to the total amount of the particular constituent present up to the end of the titration—an amount which bears no necessary relation to that originally present unless the solution be preserved in bottles absolutely filled and tightly sealed and all the manipulations be carried out expeditiously. Likewise any solution to be used as a standard—*e. g.*, a solution of Na_2CO_3 for the determination of free CO_2—must either be freshly prepared or kept in a vessel arranged so that the solution withdrawn is automatically replaced by mercury or some other immiscible liquid in which CO_2 is not soluble; and any manipulations with such a solution must be performed as quickly as possible, and in such a way that the gas space in contact with it is kept small. The necessity of precautions of this kind has been discovered in practice; for instance by Lunge,[1] also by Tillmanns and Heublein[2] who recommend that a preliminary titration be made and that then the exact titration, which must be carried out in a closed flask containing as little air as is compatible with the manipulations, be made rapidly by adding nearly the right amount, shaking and then bringing to the end point. Rapid titration is advisable for another reason—namely, that addition of any solution to a solution containing combined CO_2 of itself changes the state of equilibrium, the adjustment of which condition is, as we have seen, not instantaneous; errors due to this source can be minimized by rapid titration, and by the addition of a salt with a common ion,[3] which is effective because it sets back the ionization of the carbonates and in this way reduces the rate of the reaction $CO_3^= + H_2CO_3 = 2HCO_3^-$.

The necessity of these precautions has been emphasized here because the standard text-books of quantitative analysis pay little or no attention to them. Neglect of them, even in work otherwise very carefully done, is responsible for glaring inconsistencies in published analyses; but it would be invidious to single out an instance from so many.

We shall now proceed to the discussion of particular applications and illustrations of the general principles we have outlined. To discuss all of the possible cases is, of course, impracticable; so I have taken up only those methods which are in common use and, for the sake of simplicity, have considered that the only bases present are alkali metals.

II. Estimation of the Total Base in Alkalies Containing Carbonate.

When an alkali containing carbonate is titrated with acid, and methyl

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[1] See *postea*, p. 964.

[2] Tillmanns and Heublein, *Z. Nahr. Genussm.*, 20, 617 (1910).

[3] This course also is recommended by Lunge. Such an addition will at the same time have a slight effect on the relative proportion of base associated with carbonate and bicarbonate.

orange as indicator,[1] there is some uncertainty as to when the end point is reached because there is a gradual reddening as the true end point is approached. Küster[2] showed how this difficulty can be overcome, and demonstrated by careful experimental work that his method of determining the end point yields reproducible and accurate results. A false impression prevails quite commonly that CO_2 is without effect upon methyl orange; but, as a matter of fact, a current of CO_2 will change the color of this indicator to a reddish yellow and this shade persists for a long time if the solution is preserved in a closed flask or in such a way as to prevent loss of CO_2. This color change is, of course, due to the presence of H^+. During the titration of carbonate solutions the concentration of H^+ is so small as not to begin to affect methyl orange until the titration is very nearly complete, *i. e.*, until the concentration of HCO_3^- and $CO_3^=$ are very small. As the last portions of acid are added, the concentration of H^+ increases very slowly until, when the amount of acid just equivalent to the soda has been added, it is practically the same as in a solution of CO_2 in water and consequently the colors in the two cases are identical; a further drop of acid now produces a sudden increase in $[H^+]$, and consequently a sudden color change. Accurate and definite results can, therefore, be obtained by titrating until the solution is of the same shade as a comparison solution made by passing CO_2 into water containing the same proportion of methyl orange. The accuracy of the results obtained by the use of such a comparison shade is attested by the work of Küster[3] who made up two solutions—one of NaOH which proved to be altogether free from CO_2,[4] a second of Na_2CO_3 which contained no appreciable quantity of either hydroxide or bicarbonate—and titrated various mixtures of the two with the following results:

Cc. taken.		Cc. 0.5 *N* acid.	
NaOH.	Na_2CO_3.	Used.	Calc.
15	30	66.65	66.66
15	20	57.28	57.28
15	10	47.95	47.91
15	5	43.31	43.22
15	2	40.41	40.41
15	..	38.54[5]	38.53

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[1] This is sometimes called the Hehner method, sometimes (especially in German) the Lunge method; according to Lunge himself (*Chem. Tech. Untersuchungsmethoden*, 1, 838 (1904)) he was the first to publish it in 1885.

[2] F. W. Küster, "Kritische Studien zur volumetrischen Bestimmung von Alkalikarbonaten, sowie über das Verhalten von Phenolphthalein und Methylorange als Indikatoren," *Z. anorg. Chem.*, 13, 127 (1897), *q. v.*

[3] *Loc. cit.*, p. 147.

[4] Incidentally it may be remarked that the presence of small quantities of CO_2 in solutions of alkali hydroxide will not necessarily be detected merely by addition of barium chloride, as Küster (*Loc. cit.*, p. 134) remarked; for a small quantity of $BaCO_3$ will not precipitate when the concentration of NaOH is high.

[5] No comparison at all was necessary in this case. Each datum is the mean of three concordant titrations.

By means of this simple precaution, then, the results are accurate; if it is neglected, the uncertainty may be as much as 0.5% of the total amount of base actually present.

Ellms,[1] presumably in an endeavor to obviate this uncertainty, used lacmoid, phenacetoline, or erythrosine as indicators in a series of titrations, but found that the color change occurs when only 98–99% of the base actually present has been neutralized. This result could now be predicted from the constants of these indicators, all of which change color at too small a concentration of H^+ for the purpose in hand; it may be possible to select another indicator somewhat more suitable for this purpose than methyl orange, although it is to be expected that no indicator will yield any more accurate results except a similar comparison method be used.[2]

III. Estimation of the Free Alkali in Liquids Containing Carbonates.

Küster[3] observed relatively large differences between the results of titrations of alkali containing carbonate carried out according to the procedures recommended in various text-books; in order to ascertain which of these methods yields correct results he made a careful comparison of them. To this end he made a series of analyses of an alkali solution (*A*) about 2 *N*, precipitating with a 10% solution of $BaCl_2$ and titrating back with acid and phenolphthalein until the solution was colorless; his results are as follows, each figure being the mean of three separate titrations which did not differ among themselves by more than 0.05 cc.:

Procedure.	Cc. 0.5*N* acid used.	Percentage of total Na as carbonate.
10 cc. *A* titrated directly, with methyl orange to normal color	42.49	..
I. 20 cc. *A* + 20 cc. $BaCl_2$; filtered; 20 cc. filtrate (= 10 cc. *A*) titrated	33.61	20.9
II. 20 cc. *A* + 50 cc. H_2O + 20 cc. $BaCl_2$ + 10 cc. H_2O; filtered; 50 cc. filtrate (= 10 cc. *A*) titrated	33.90	20.2
III. 20 cc. *A* + 150 cc. H_2O + 20 cc. $BaCl_2$ + 10 cc. H_2O, filtered; 100 cc. filtrate (= 10 cc. *A*) titrated	34.01	20.0
IV. 20 cc. *A* + 15 cc. H_2O + 20 cc. $BaCl_2$ + 10 cc. H_2O; 100 cc. liquid (not filtered) titrated	34.39	19.1
V. 10 cc. *A* + 50 cc. hot H_2O + 10 cc. $BaCl_2$; filtered and ppt. well washed; total filtrate titrated	34.50	18.8
VI. 10 cc. *A* + 100 cc. H_2O + 10 cc. $BaCl_2$; allowed to stand, titrated without being filtered	34.72	18.3
VII. 10 cc. *A* titrated directly, with phenolphthalein until colorless	38.58	18.4

The low result—corresponding to too great an apparent percentage of carbonate—of Procedures I–IV, Küster attributes to absorption of alkali

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[1] J. W. Ellms, THIS JOURNAL, **21**, 359 (1899).

[2] See also Norton and Knowles, THIS JOURNAL, **38**, 877 (1916).

[3] *Z. anorg. Chem.*, **13**, 127 (1897).

by filter paper and precipitate and to absorption of CO_2 by the solution in the course of the manipulations. That the results obtained by Procedure VI are correct he shows by similar titration of known mixtures of (*a*) a solution of NaOH entirely free from CO_2 with (*b*) a freshly prepared solution of Na_2CO_3 which contained no appreciable quantity of either hydroxide or bicarbonate:

Cc. taken.			Cc. 0.5*N* acid.	
NaOH.	Na_2CO_3.	$BaCl_2$.	Used.	Calculated.
15	30	30	38.51	38.53
15	20	20	38.52	
15	10	10	38.54	
15	5	10	38.53	
15	2	10	38.52	
15	..	10	38.55	

From this it is obvious that this method, which, since filtration is omitted, is at the same time the simplest to carry out, yields correct results for the free alkali, which are independent of the proportion of carbonate present in the solution. On the other hand, it is claimed by Bruhns[1] that the precipitated $BaCO_3$ is attacked to a slight extent by the acid used to titrate the excess of hydroxide, with consequent small errors in the results; to obviate which he filters off the precipitate in a special funnel arranged so that the filtrate does not come in contact with the air. There is little question that such a source of error is quite possible; yet by allowing the precipitate to settle completely and then by careful manipulation during the titration it should be easily practicable to render this error negligible, as indeed it appears to be in Küster's work. Again,[2] Sörensen and Andersen made a series of very carefully controlled experiments in which, however, they allowed only ten minutes for the settling of the precipitate and titrated to the same pink color as a comparison solution containing $BaCO_3$ and the same amount of phenolphthalein; and found that this method yields slightly too high results for the alkalinity,[3] but accurate

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[1] G. Bruhns, *Z. anal. Chem.*, **45**, 473 (1906). As a partial protection against the air he uses a layer of benzene. A film of ether was used for this purpose by Stransky (*Chem. Ztg.*, **9**, 100 (1908)).

[2] S. P. L. Sörensen and A. C. Andersen, *Z. anal. Chem.*, **47**, 279 (1908).

[3] This they attribute to the formation of a small quantity of $Ba(HCO_3)_2$. If too much hydroxide is present, some basic carbonate is, according to the authors, precipitated in cold solution; solutions containing bicarbonate obviously should not be heated. But these difficulties can be surmounted by addition of substantially the equivalent amount of acid or NaOH respectively before the heating and subsequent precipitation by means of $BaCl_2$. Sörensen and Andersen prove, therein confirming Guth (*Gesundheitsingenieur*, **31**, 737 (1908)), that the assertion of Le Blanc and Novotny (*Z. anorg. Chem.*, **51**, 181 (1906); repeated *Ibid.*, **53**, 344 (1907)) to the effect that addition of $BaCl_2$ to a 0.1 *N* solution of Na_2CO_3 results in a slightly acid solution, is untrue so long as the sodium carbonate is free from bicarbonate. The greater part

results if the precipitation is carried out in hot solution, provided that the original solution was mainly carbonate. Nevertheless, in the opinion of the writer, this conclusion, though applicable to this particular procedure, does not hold if several hours be allowed to elapse between precipitation and titration and particularly if titration with acid is continued until the solution is colorless; for from the theory of the method (developed in the next section) it follows that we must titrate in such a way as to determine the total amount of OH^- present in the solution after the precipitate of $BaCO_3$ has separated out, and hence must continue until the indicator has ceased to show pink.

The seventh method—direct titration with acid and phenolphthalein as indicator—is not to be recommended. For, as was shown by Küster, and also independently by Lunge,[1] the result depends greatly on what one chooses as the point at which the solution is considered to have become colorless;[2] it may well be 4% too high, though this amount is diminished in presence of sodium chloride.[3] On the other hand Seyler[4] found, as the result of a series of careful titrations, that this error is due chiefly to a loss of CO_2; and Tillmanns and Heublein[5] showed directly that in such titrations the solution loses CO_2,[6] and on carrying out titrations in closed flasks observed sharper end points and were able to obtain good results. Nevertheless this method could yield correct results only if titration were continued until a certain shade was reached, but, since this proper depth of shade is not invariable but depends upon the concentration and constitution of the solution,[7] this course would be impracticable if the highest accuracy is desired.

of this confusion is directly due to a failure to recognize that there is *equilibrium* between the several molecular species.

[1] G. Lunge, *Z. angew. Chem.*, 10, 41 (1897).

[2] This is the same phenomenon as is discussed at length in Section V.

[3] This was also observed by Lunge and Lohhöfer, *Z. angew. Chem.*, **14**, 1125 (1901). The reason for this action is that the added salt sets back the ionization of the carbonate and bicarbonate, and hence diminishes the speed of readjustment of the equilibrium. For this reason, too, titration with a solution of $KHSO_4$, as suggested by Cameron (*Am. Chem. J.*, **23**, 471 (1900)) will, other things being equal, yield closer results than titration with a simple acid.

[4] C. A. Seyler, *Analyst*, **22**, 314 (1897).

[5] Tillmanns and Heublein, *Z. angew. Chem.*, **24**, 874 (1911).

[6] Absorption of CO_2 by the solution may occur in certain cases, particularly in natural waters which have been diluted with distilled water—a procedure which may well yield misleading results with respect to the composition and properties of the undiluted water; for instance, the alkalinity of the diluted water is not a direct measure of that of the undiluted water.

[7] This deduction is confirmed by the experimental work recorded by Seyler in "Studies of the Carbonates IV" (see note, p. 947). Correct results could of course be attained by suitable calibration of the method, as Seyler proposes; but it seems simpler to follow the procedure recommended by Küster.

IV. Estimation of Both Carbonate and Bicarbonate.

The method most commonly used for this determination—*viz.*, to titrate until phenolphthalein is colorless, to add methyl orange and continue the titration until the color change is observed—is not to be recommended where any accuracy is desired. For, as we have seen, the uncertainty as to the proper end point with phenolphthalein in presence of carbonates is such that there may be an error of 5% in this portion of the titration—an error which may cause a very large percentage error in the proportion of bicarbonate since the latter is obtained by difference. According to Tillmanns and Heublein,[1] somewhat better results can be obtained either by titrating in a closed flask, or by proceeding as follows: Determine the amount of acid required to bring about the color change with methyl orange as indicator, then to a separate portion of the solution add this amount of acid and titrate back with NaOH, until phenolphthalein just shows a pink color.

But, for reasons already given, none of these methods, as ordinarily carried out, is trustworthy; moreover they are unnecessary since there is an equally simple procedure which is reliable. The total alkali is determined as before by titration with methyl orange to the "normal" color of a comparison solution.[2] In order to ascertain the proportion of bicarbonate,[3] one adds the solution to a known excess of standard alkali, previously mixed with excess of barium chloride, sets aside until the precipitate has settled, and, without filtering, titrates, using phenolphthalein, until the solution is colorless; the alkali used up corresponds to the bicarbonate present. The following figures, due to Küster, attest the accuracy of this method; for the difference in the amount of acid used is proportional to the added amount of a mixed carbonate-bicarbonate solution:

Cc. taken.		Cc. 0.5*N* acid.	
NaOH.	$\left\{\begin{array}{l}Na_2CO_3,\\NaHCO_3\end{array}\right.$	Used.	Difference.
15	..	38.53	.....
15	5	37.92	$0.61 = 5 \times 0.122$
15	10	37.30	$1.23 = 10 \times 0.123$
15	30	34.80	$3.73 = 30 \times 0.124$

That this method should yield accurate results follows also from a consideration of the theory of the method. Besides the reaction:

$$Na_2CO_3 + BaCl_2 = \mathbf{BaCO_3} + 2NaCl,$$

or better,

$$CO_3^{=} + Ba^{++} = \mathbf{BaCO_3},$$

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[1] Tillmanns and Heublein, *Z. anorg. Chem.*, **24**, 874 (1911).

[2] See Section II.

[3] Compare Section III. Confirmatory evidence of the accuracy of this procedure is offered by McCoy (*Am. Chem. J.*, **29**, 444 (1903)). Care must be taken that no free CO_2 is lost during the manipulations.

which is accompanied by no change in the alkalinity[1] of the solution, there are the two reactions

$$2NaHCO_3 + BaCl_2 + Ba(OH)_2 = 2\mathbf{BaCO_3} + 2NaCl + H_2O, \quad (I)$$

or better,

$$HCO_3^- + OH^- + Ba^{++} = \mathbf{BaCO_3} + H_2O,$$

$$H_2CO_3 + Ba(OH)_2 = \mathbf{BaCO_3} + 2H_2O, \quad (II)$$

whence it follows that one equivalent of OH^- disappears for each equivalent of HCO_3^- taken out of solution (as $\mathbf{BaCO_3}$) and for each equivalent of free H_2CO_3 present originally. When the precipitation is complete—*i. e.*, before the excess of alkali has been titrated back—the following equilibrium equations[2] hold:

$$[Ba^{++}][CO_3^{=}] = K_B = 7 \times 10^{-9} \quad (a)$$

$$[H^+][CO_3^{=}] = k_2[HCO_3^-] = 4.8 \times 10^{-11}[HCO_3^-] \quad (b)$$

whence we obtain

$$[HCO_3^-] = \frac{K_W K_B}{k_2[OH^-][Ba^{++}]} = \frac{10^{-12}}{[OH^-][Ba^{++}]}.$$

Consequently, the greater the concentrations of $[OH^-]$ and $[Ba^{++}]$ are at this point, the smaller will be the concentration of residual bicarbonate, *i. e.*, of bicarbonate which will remain untitrated. In other words, the error of this method can be made as small as we please by having excess of both $[OH^-]$ and $[Ba^{++}]$ present when precipitation is complete.

As an illustration let us make an approximate calculation of a titration recorded by McCoy:[3]

9.94 cc. of a carbonate-bicarbonate solution, 0.1 *N* with respect to sodium, was run into 7.49 cc. 0.1 *N* $Ba(OH)_2$ and 2 cc. 0.5 *N* $BaCl_2$ and the residual free alkali required 0.70 cc. 0.1 *N* HCl. The total barium present initially was 0.00175/2 mols; that used up, which is equivalent to the total sodium, was 0.000994/2 mols; so that the total barium present in the 20 cc. at the end was 0.00076/2 mols., and therefore $[Ba^{++}] = 0.019$.[4] The OH^- remaining (that is, before the titration with acid) was equivalent to 0.70 cc. 0.1 *N* acid, and therefore $[OH^-] = 0.0035$. By substitution of these values in the above expression, we find that

$$[HCO_3^-] = \frac{10^{-12}}{1.9 \times 10^{-2} \times 3.5 \times 10^{-3}} = 10^{-8}$$

consequently the HCO_3^- remaining untitrated is negligible—in other words the method yields correct results.

This method then, when carried out as outlined above, yields correct results for the proportion of bicarbonate to carbonate present in the solution at the time of analysis, provided that the only metals present

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[1] This of course refers only to the carbonate which is present as such in the solution, and does not imply that there is no change in alkalinity when $BaCl_2$ is added to an actual solution of alkali carbonate.

[2] (*a*) is the solubility product constant of barium carbonate at 16° (Johnston, THIS JOURNAL, **37**, 2019 (1915)); (*b*) is Equation III of the present paper.

[3] *Am. Chem. J.*, **29**, 448 (1903).

[4] For the sake of simplicity we assume here that ionization is complete.

are those with soluble hydroxides; otherwise, a correction must be made for the equivalent alkalinity of the insoluble hydroxide or "basic salt" precipitated upon addition of the baryta. This correction, which is discussed in the text-books, is necessary in many cases, since most natural waters contain magnesia and some contain iron; its application always detracts from the accuracy of the method because one cannot ensure that some part of the insoluble base is not precipitated as an indefinite "basic salt." In any case it is to be borne in mind that a reliable method of analysis yields useful results only if due precautions in preparing (or sampling) and preserving the solution have been taken. As an illustration of some of these points let us take up a practical case and the directions which have been given for it.

The Evaluation of Solid Sodium Bicarbonate.—The procedure recommended by Lunge[1] is as follows:

> "A 5 g. sample of bicarbonate, contained in a 1000 cc. beaker, is dissolved in about 100 cc. of distilled water, previously boiled out and cooled to 15 or 20°; the process of solution may be hastened by breaking up the large particles by means of a glass rod, but all stirring or violent motion of the liquid must be avoided. These precautions are absolutely necessary to the attainment of trustworthy results, since otherwise the bicarbonate solution loses carbonic acid very readily. The temperature of the water must be between 15° and 20°; for if it is colder dissolution is too slow, while if it is warmer the danger of loss of carbonic acid is greater. In this solution the double quantity (10 g.) of pure NaCl is now dissolved, the solution is cooled to nearly 0°; phenolphthalein is added and the buret containing the acid so arranged that its tip dips into the solution. It is now titrated with 1 N HCl until the red color has just disappeared ($= a$ cc. acid); methyl orange is added and the titration continued until the color changes ($= b$ cc. acid); $2a$ represents the Na_2CO_3, $b - a$ the $NaHCO_3$."

The precautions emphasized by Lunge are in accordance with, and could have been predicted from, the principles discussed in this paper. Retention by the solution of all the CO_2, which is essential if reliable results are to be attained, is favored by low temperature and by the avoidance of any stirring, produced either by intention or by the dropping in of the acid during the titration. It is also essential that the change bicarbonate to carbonate, which will always tend to proceed unless the CO_2 pressure has the appropriate value (a condition which in practice is altogether exceptional) be slowed up as much as possible; this change, which is an ionic reaction according to the scheme $2HCO_3^- = CO_3^= + CO_2 + H_2O$, can be slowed up by diminishing the concentration of HCO_3^- in the solution, and this is accomplished by the addition of a large amount of sodium chloride, which sets back the ionization of the carbonate. Lunge's interpretation of the end points is, as we have seen, not absolutely correct; nevertheless it is ample for the practical evaluation of sodium bicarbonate as carried out according to the above directions.

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[1] G. Lunge, "*Chemisch-technische Untersuchungsmethoden,*" 5te Auflage, I, p. 477.

V. Determination of Free Carbonic Acid in Solution.

The method most generally used appears to be that proposed first by Trillich (but also referred to as the Seyler[1] method); namely, to titrate with a freshly prepared solution of sodium carbonate (0.02 or 0.05 *N*) with phenolphthalein as indicator until a permanent pink color is developed. In practice it has been found[2] that certain precautions must be observed, and that in any case the method does not always yield accurate results; for instance, the result is generally too low unless the total concentration of carbonate present at the end point is small—a condition which implies that the aggregate equivalent concentration of free CO_2, carbonate and bicarbonate present in the liquid under investigation was below a certain limit. We shall now consider the theory underlying this method in order to elucidate the reason for this apparently anomalous behavior and to ascertain if it be possible to obviate these disadvantages.

In this titration the reaction is

$$H_2CO_3 + Na_2CO_3 = 2NaHCO_3$$

or better,

$$H_2CO_3 + CO_3^{=} \rightleftarrows 2HCO_3^{-}.$$

It is, therefore, the equilibrium which forms the subject of this paper; and it is worth noting that, in the ordinary interpretation of the results of this method, there is the tacit assumption that this equilibrium adjusts itself practically instantaneously. The relation between the several concentrations at equilibrium is given by Equation IV, *viz.*,

$$[HCO_3^-]^2/[CO_3^=] = 7100[H_2CO_3] = 7100cP.$$

Now $[H_2CO_3]$ is at equilibrium determined, in accordance with Equation I, by the partial pressure of CO_2 in the atmosphere in contact with the solution; and for a given total concentration of carbonate, as we have seen, both $[HCO_3^-]$ and $[CO_3^=]$ are fixed if the alkalinity of the solution (*i. e.*, $[H^+]$ or $[OH^-]$) is fixed, as it is in fact at the end point as registered by an indicator. But, as Equation IV shows, the two quantities $[H^+]$ and P are not independent variables; if we choose a value of P, we thereby fix $[H^+]$, provided that equilibrium obtains, and conversely. Consequently, unless the value of P prevailing at the time of titration corresponds to that of $[H^+]$ registered by the indicator, the end point will tend to be uncertain and the result of the titration incorrect; and it is obvious that these two quantities can have corresponding values only exceptionally, for, unless by the adoption of some special procedure to control P, its value in actual titrations is accidental and may vary from

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[1] C. A. Seyler, *Chem. News*, **70**, 104 (1894); *Analyst*, **22**, 312 (1897).

[2] First, apparently, by Paul, Ohlmüller, Heise and Auerbach (*Arb. Gesundheitsamt*, **23**, 333 (1906)); independently, since then, by several others. F. Guth (*Gesundheitsingenieur*, **31**, 737 (1908)) gives a large number of references to the literature up to that time; he too observed that this method is not exact, but considered it good enough in practice.

one hour to another. An example may serve to bring out this point. When phenolphthalein just turns pink, $[H^+]$ the concentration of hydrogen ion in the solution is, according to the work of Rosenstein,[1] about 10^{-9}. Consequently if we conduct a titration with phenolphthalein, the conditions for equilibrium at the end point between $[HCO_3^-]$, $[CO_3^=]$ and the partial pressure P of CO_2 in the air-space above the liquid are, from Equations V and VI $[HCO_3^-] = 12.6\ P$, $[CO_3^=] = 0.685\ P$, whence $[B^+] = [HCO_3^-] + 2[CO_3^=] = 14\ P$. In other words, under the conditions specified, the total equivalent aggregate concentrations of carbonate and bicarbonate at the end point must for equilibrium be $14\ P$, or about 14×0.0005 or 0.007 under laboratory conditions. If $[B^+]$ at the end point is less than 0.007, CO_2 will tend to be absorbed continuously by the solution and thus to cause a repeated fading out of the color until the total alkali added reaches this limiting value; if $[B^+]$ is greater than 0.007, the results will tend to be low, apart altogether from the circumstance that the solution will tend to lose CO_2 to the air space above it. Now it is obvious that the smaller this air space is, the less CO_2 must be transferred to bring the two phases into equilibrium and consequently the smaller the error; this is the theoretical basis for the procedure recommended by Tillmanns and Heublein,[2] namely, to titrate rapidly in a closed flask containing as little air-space as is compatible with the manipulations.

Now if the equivalent concentration of CO_2, either free or combined, was such that at the end point $[B^+]$ is greater than the limiting value (the magnitude of which depends upon the H^+ concentration actually registered by the indicator) then some fraction of the free CO_2 will be "covered up"—an effect which has been noted by serveral investigators. But by a suitable choice of indicator one is enabled, in theory at least, to conduct the titration of any solution so that the error from this source shall not exceed a certain limit; the information required is given in Table II in conjunction with a table of indicator constants. As an example, if the untitrated CO_2 is to be less than 1 part per million, and the total concentration of base at the end point is 0.001,[3] one must choose an indicator which changes when $[H^+]$ is between 10^{-8} and 10^{-9}—*e. g.*, phenolphthalein

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[1] Rosenstein, THIS JOURNAL, 34, 1117 (1912), *q. v.* The value of $[H^+]$ at the end point varies with the amount of indicator added, the concentration of salt present at the end point, and the depth of color fixed upon as denoting the end point.

[2] Tillmanns and Heublein, *Z. Nahr. Genussm.*, 20, 617 (1910). The apparent accuracy of the determinations of free CO_2 by titration recorded in this paper is due to the circumstance that the authors happened to choose the particular concentration of phenolphthalein which admits of correct results with solutions of the concentration which they investigated.

[3] This implies that the free CO_2 originally present did not exceed 0.0005 N or about 22 parts per million, or a smaller amount if any carbonate was present originally in the solution.

used under appropriate conditions.[1] It is obvious, therefore, that the use of a single indicator under specified conditions cannot yield correct results in general; that with increasing concentration of either carbonate or indicator the amount of free CO_2 left untitrated increases rapidly. Similar conclusions have also been reached by Auerbach.[2]

These conclusions are in harmony with the careful experimental work of Noll,[3] who made a large number of titrations of the free CO_2 in distilled water in various solutions of bicarbonates of sodium, calcium, and magnesium and in natural waters, using various concentrations of phenolphthalein, and compared the results with those of control experiments made by the Pettenkofer method. Table III illustrates his results; in each case he took 200 cc. of the solution, added 0.5 cc. of a solution of the given dilution of phenolphthalein in 96% alcohol, and titrated until a faint permanent pink color was obtained.

TABLE III.—THE VARIATION OF THE AMOUNT OF "FREE CO_2," AS ESTIMATED BY TITRATION WITH Na_2CO_3 SOLUTION, WITH THE AMOUNT OF INDICATOR; ACCORDING TO THE EXPERIMENTS OF NOLL.

	"Free CO_2" (mg. per l.).	
Dilution of phenolphthalein solution.[4] 1 g. phth. to *x* g. 96% EtOH.	In Hamburg water stated to contain about 13.6 mg. CO_2 per l.	In 0.0112 *N* $NaHCO_3$ stated to contain about 11.7 mg. CO_2 per l.
2000	16.5	26.4
1500	14.85	...
1000	13.2	15.4
800	12.1	13.2
600	11.0	11.55
400	9.35	8.25
200	7.7	3.85
100	6.6	(very faint pink)
50	5.5	(faint pink)
30	3.85	(red)

Noll's conclusions follow:

> "The determination of free carbonic acid in waters by the Trillich method yields reliable results if the waters contain no bicarbonate and if the content of free CO_2 is not so high that an appreciable concentration of bicarbonate is present at the end point. If on the other hand the waters contain any considerable amount of bicarbonate, the results will be incorrect unless the proper strength of phenolphthalein solution is chosen; the results for CO_2 may be too high as well as too low, since bicarbonate solutions which appear acid when tested by small amounts of indicator may appear to be alkaline when a larger concentration of indicator is used."

In a later paper[5] Noll investigates the use of rosolic acid as an indi-

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[1] For a discussion of this see Rosenstein, THIS JOURNAL, **34**, 1117 (1912).

[2] Auerbach, *Z. angew. Chem.*, **25**, 1722 (1912).

[3] Noll, *Z. angew. Chem.*, **25**, 998 (1912); see also Morgulis and Fuller, "Can Carbon Dioxide in Sea Water be Directly Determined by Titration," *J. Biol. Chem.*, **24**, 31 (1916).

[4] 0.5 cc. to 200 cc. liquid taken in each titration.

[5] Noll, *Z. angew. Chem.*, **26**, 85 (1913).

cator in this titration, and finds, in agreement with Tillmanns and Heublein,[1] that the results so obtained are incorrect; this could, indeed, be inferred from Table II and the known constant of this indicator. Indeed, as was pointed out above, while in any specified case one indicator may yield more nearly correct results than another, no indicator will be satisfactory over the whole range of concentrations; and the choice of a suitable indicator and of the proper end point can be made only if the total CO_2 content is known in advance. It has also been proposed to titrate with NaOH or $Ca(OH)_2$; but the choice of end point is open to the same uncertainty, and the results are unreliable—a conclusion which has also been confirmed by experience. This method is obviously altogether inapplicable to waters which contain some free acid other than carbonic acid, *e. g.*, to waters carrying a salt, such as $FeSO_4$, which is readily hydrolyzed.

Altogether, then, titration methods, as ordinarily carried out, are of very little use as a means of accurately determining small quantities of free CO_2 in solution; such a method might, perhaps, be used, by reason of its convenience and rapidity, in cases where it is necessary to make comparative determinations on a long series of very similar waters; but it would then be advisable to calibrate the method by applying it to known solutions, as has been suggested by Auerbach[2] and carried out very recently by Winkler.[3]

Free CO_2 in solution can be determined by boiling the liquid, or by aspirating a current of air through it. and absorbing the CO_2 set free by either means, but only if it exists entirely in uncombined form. If some of it exists in combined form, the results of such a procedure have no very definite meaning; for as the free CO_2 is removed, the equilibrium between HCO_3^-, $CO_3^=$ and CO_2 tends to reëstablish itself and more CO_2 is regenerated. Consequently the results will always be too high, and be higher the longer the boiling or aspiration process is continued; if the latter is conducted rapidly, the weight of CO_2 absorbed will be an approximate measure of the aggregate amount existing in the solution as free CO_2 and as bicarbonate. Indeed by aspirating a stream of air absolutely free from CO_2 through a carbonate solution for a long enough time, one can—theoretically at least—drive out absolutely all the carbonate, and be left with a solution containing only hydroxide. Similar remarks apply to the process of "raining" the solution (*i. e.*, letting it fall in small drops through the air), a procedure employed by Tillmanns and Heublein as a means of causing the solution to lose CO_2 rapidly. Obviously, therefore, it is not generally admissible to use this or an analogous procedure

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[1] Tillmanns and Heublein, *Z. Nahr. Genussm.*, 20, 617 (1910).

[2] F. Auerbach, *Z. angew. Chem.*, **25**, 1722 (1912).

[3] L. W. Winkler, *Z. anal. Chem.*, **53**, 746 (1914).

for this purpose, as Classen does,[1] unless very approximate results will suffice; indeed, in special cases the result may be absolutely erroneous. For instance, Hillebrand,[2] in analyzing a mineral water containing mainly the radicals SO_4, Zn, Ca, CO_3 (in the order of their abundance), found that *all* the CO_2 was expelled on simply boiling the water, although it was neutral to litmus, and that simultaneously ZnO was precipitated; this loss of CO_2, which must occur to some extent with several other metallic radicals, notably with iron and under certain circumstances with magnesium, is determined by the solubility-product constants of $Zn(OH)_2$ and $ZnCO_3$.[3] Incidentally, a determination of total solids by evaporation would, as Hillebrand notes, involve a very serious error in addition to those usually encountered.

Forbes and Pratt[4] made a comparison of this method with titration methods, and found that their aspiration method yielded higher results, which they believed to be correct; for practical work, however, they favored the Lunge, Trillich or Seyler method (*i. e.*, titration with a solution of Na_2CO_3) by reason of its convenience. But, as we have seen, neither of these methods is to be recommended where accuracy is desired; this matters the less because the information desired can be obtained in other ways.

If accurate results are required, they can be secured by employing the method described recently by Swanson and Hulett.[5] The principle of this method is to introduce a given volume of the liquid into an evacuated vessel of known volume, to shake until equilibrium between the CO_2 in both phases has been attained,[6] and then to determine the proportion of CO_2 in the vapor phase—a determination which is simple, rapid and accurate.[7] By combining this result with the appropriate solubility of CO_2 we can derive directly the concentration of free CO_2 in the liquid as at the end of the experiment; whence by taking into account the relative

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[1] Classen, "*Ausgewählte Methoden der Analytischen Chemie,*" **2**, 189 (1903).

[2] W. F. Hillebrand, *Am. J. Sci.*, **43**, 418 (1892).

[3] For the analogous case with magnesium see Johnston, THIS JOURNAL, **37**, 2015 (1915).

[4] F. B. Forbes and G. H. Pratt, "The Determination of Carbonic Acid in Drinking Water," THIS JOURNAL, **25**, 742 (1903). These authors give many good practical hints, especially in connection with the method discussed in Section IV *supra.*

[5] Swanson and Hulett, THIS JOURNAL, **37**, 2490 (1915). The ideal method would be, as Swanson and Hulett point out, to prepare and know the composition of the gas phase which would be in equilibrium with the solution; but this would hardly be a practical analytical method.

[6] If no appreciable amount of carbonate (as distinct from bicarbonate) is present after shaking, the attainment of this equilibrium would require only a few minutes; if otherwise, time must be allowed for the readjustment of the equilibrium between HCO_3^-, $CO_3^=$ and CO_2 in solution, for the position of equilibrium is shifted by the loss of CO_2 to the vapor space.

[7] J. Walker, *J. Chem. Soc.*, **77**, 1110 (1900); cf. A. G. Woodman, THIS JOURNAL, **25**, 150 (1903).

volumes of the liquid and vapor phase we can readily calculate the original concentration of free CO_2, provided either that no appreciable proportion of $CO_3^=$ was present at the end of the experiment or that the volume of the vapor phase was very small as compared with that of the liquid. In practice the latter condition would usually not be fulfilled, but the former would, since one would be unlikely to employ this method unless the amount of free CO_2 is considerable (and hence, $CO_3^=$ small); yet with the above data and a knowledge of the amount of base equivalent to the combined CO_2 the calculation of the original proportions of carbonate, bicarbonate and free CO_2 can be performed in all cases, though it may be somewhat troublesome.[1]

It must, of course, always be borne in mind that this analysis only tells us the quantity of free CO_2 present in the liquid at the time of analysis, a quantity which bears no necessary relation to the amount originally present, unless due precautions have been taken in collecting and preserving the sample. The same remark applies to all of the determinations discussed in this paper.

VI. Estimation of Total CO_2, Free and Combined.

The best procedure appears to be that recommended and described fully by Treadwell.[2] The principle of this method is to expel the carbon dioxide first by reducing the pressure over the liquid and finally by adding acid and heating until the expulsion is complete; the volume of gas thus set free is read off. This method possesses two great advantages: that there is no doubt as to the interpretation of the results (which cannot be said of all the methods proposed); and that the determination may readily be made in a short time at the source of the water, so that errors due to loss of CO_2 are reduced to a minimum. Equally good results are also obtained by absorbing the expelled CO_2 in suitable tubes, and weighing it; the use of this method, which obviously can only be carried out in a laboratory, is indicated whenever the total amount of CO_2 is small.

Mention should also be made of the Winkler method,[3] because it has been used extensively; he expels the CO_2 by generating hydrogen from zinc and hydrochloric acid within the solution, absorbs it in caustic potash and determines the increase in weight. But in a quite recent paper[4] he himself notes that there are sources of error—namely, that the CO_2 is not completely expelled, and that some water passes over and is absorbed—

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[1] The mode of calculation is analogous to that employed in computing the solubility of calcite in water for various partial pressures of CO_2 (see THIS JOURNAL, **37**, 2011 (1915)).

[2] Treadwell, "Analytical Chemistry," 1st ed., Vol. **2**, p. 309 (1906). It is a modification of the original Petterson method.

[3] L. W. Winkler, *Z. anal. Chem.*, **42**, 735 (1903).

[4] *Ibid.*, **52**, 421 (1913); cf. Casares and de Rubies, *C. A.*, **7**, 3377 (1913).

to obviate which he recommends that the apparatus be calibrated by working with known similar solutions under the same conditions. But, apart from this disadvantage, this method is inconvenient in the field, and hence is not well adapted to the determination of the total CO_2 in natural waters. Titration methods have also been used, but they need not be discussed further here, for they are substantially identical with those already discussed.

VII. General Conclusions.

In the foregoing pages we have reviewed the most important methods for the determination of the various constituents of a solution containing alkali carbonates; some of these methods yield accurate results, while others do not. If due precautions are taken, accurate determinations of the total base equivalent to the combined CO_2 and of the *total* CO_2 are readily made; but the results of all estimations of the amount of free CO_2, of bicarbonate (half-bound CO_2), or of carbonate (bound CO_2) must be scrutinized carefully, as they may be very much in error. The reasons for this are in the main two: (1) That in such solutions there is equilibrium between CO_2 (which in turn is determined by the proportion of CO_2 in the air), HCO_3^- and $CO_3^=$ and the base B^+, the state of which is altered—and altered fairly rapidly—by any change in the concentration of any of these constituents; consequently any attempt to estimate the proportion of one of these constituents cannot prove successful unless it is practicable to slow up the readjustment of this equilibrium to such an extent that the change in concentration of the constituent during the time required for the analysis is inappreciable; (2) that a comparatively slight change in the concentration of hydrogen ion corresponds to a much larger change in the concentrations of CO_2 free and combined, and that the concentration of H^+ at the *proper* end point of the titration (*i. e.*, for correct results) is not an invariable quantity, but depends upon the constitution of the solution being analyzed; consequently the result obtained depends in a marked degree upon the indicator adopted and upon the end point chosen. Indeed, as we have seen, no single indicator and no arbitrary end point can yield satisfactory results over the whole range of possible concentrations.

The least satisfactory method in general is the titration method for free CO_2 as ordinarily carried out, for the results cannot be interpreted unless the constitution of the solution is already known. This method might, of course, yield satisfactory comparative—though somewhat empirical—results when applied to a long series of very similar waters, as in the daily testing of a water supply. The free CO_2 is readily determined by a gasometric method, provided that the concentration of combined CO_2 is very small; if it should prove necessary to determine free CO_2 directly in a solution containing a material amount of combined

CO_2, one can achieve any desired accuracy in the result by observing the precautions discussed in the text. The most common method of estimating the relative proportions of bicarbonate and carbonate—*viz.*, to titrate first with phenolphthalein, subsequently with methyl orange—also yields only approximate results; these amounts can, however, be determined with sufficient accuracy in many cases by following the procedure recommended by Küster and discussed in the text.

On the other hand it is doubtful if it is worth while making the latter determinations, especially in natural waters, for the following reasons: In the first place, we are dealing with an equilibrium capable of fairly rapid readjustment, and so any change in the proportion of one constituent affects—in many cases, very markedly—the proportions of the others; consequently any method, even if it is in itself reliable, will not yield information as to the true proportions originally present in the solution unless due precautions are observed to prevent any alteration in the solution previous to the analysis—and that such precautions have in many cases not been taken is evident if one glances at any collection of water analyses. In the second place, since we are dealing with an equilibrium, there is no point in actually determining all of these constituents, because if we determine a certain number of them, we can calculate the concentration of each of the others; in other words, we can obtain just as much useful information—*i. e.*, information which we can interpret—from this smaller number of determinations. For we are justified in inferring that natural waters have had time to attain substantial equilibrium in respect to these components under the prevailing conditions. This, of course, does not imply that they are necessarily in equilibrium in a water as it issues from a spring, for such water is encountering rapidly changing conditions; on the other hand it is hard to see what useful conclusions we can draw from determinations of the concentration of, for instance, carbonate or bicarbonate present under such circumstances.

In general, then, it suffices to determine (*a*) the total base equivalent to the combined carbonate, (*b*) the total CO_2, free and combined, both of which are easy, reliable and unaffected by the presence of alkaline earths or of iron; for with a knowledge of these one is enabled to calculate the concentration of (*c*) carbonate, (*d*) bicarbonate, (*e*) hydrogen ion, which is a measure of the degree of acidity (or alkalinity) of the water. Alternatively one may in certain cases prefer, instead of (*b*), to determine either the proportion of bicarbonate to carbonate—a determination which can, subject to certain conditions, be made accurately—or the alkalinity directly by means of indicators in conjunction with a series of comparison solutions; for, when the respective ionizations (which depend upon the concentration of total base, $[B^+]$) are taken into account, these two quantities are related to one another by Equation III or III*a* and to the other quantities by the other appropriate equations. Which procedure one chooses depends upon individual preferences as regards manipulation and computation, and upon what one is chiefly interested in ascertaining; which brings up the question as to which of these several quantities has the greatest practical utility in each case. But it is to be observed that for all scientific, as well as for many technical purposes, we wish to know the equilibrium, so we would choose the most convenient and most accurate way under the circumstances of ascertaining the concentrations of the factors.

Let us consider, for example, the suitability of a water for use in a boiler, insofar as it is affected by the presence of CO_2 combined and free. For the sake of simplicity we shall suppose that the only base combined with the carbonic acid is lime. The total amount of calcium carbonate present is limited[1] by the total concentration of CO_2; though it need not correspond quantitatively to the latter—in other words, the water may not be saturated with respect to calcium carbonate, in which case a definite proportion of the free CO_2 will be "aggressive," a question to which we shall revert presently. However this may be, the CO_2 will be expelled very soon after the water enters the boiler, and we shall have in the boiler a saturated solution which deposits $CaCO_3$ as the water is evaporated. This precipitation within the boiler can be minimized by reducing the content of carbonate before the water enters the boiler; this can be accomplished by blowing air through the water and adding an amount of alkali[2] (soda or slaked lime) equivalent to the bicarbonate present *at the time of addition*. This amount has usually been taken to be equivalent to the difference between the phenolphthalein and methyl orange end points; but this is, as we have seen, a somewhat uncertain procedure which tends to lead one to add more alkali than is requisite, and any excess of alkali is undesirable because it leads to foaming within the boiler. Consequently one should determine the concentration of bicarbonate by the accurate method, or at least calibrate by means of this method the procedure which is employed. The final amount of calcium carbonate will always correspond to its solubility under ordinary atmospheric conditions, *i. e.*, about 60 parts per million; it will not be diminished substantially by any permissible residual concentration of alkali, but can be materially decreased if the precipitation is carried out at elevated tempera-

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[1] In presence of calcium sulfate it will of course always be smaller by an amount readily calculable; but this we are not taking into consideration here.

[2] Calcium sulfate is got rid of by the addition of the equivalent quantity of Na_2CO_3. The equilibrium $CaSO_4 + Na_2CO_3 \rightleftarrows Na_2SO_4 + CaCO_3$ proceeds further to the right (1) the greater the solubility of $CaSO_4$ (2) the smaller the solubility of $CaCO_3$; consequently the process should be carried out so far as practicable at a low temperature and after the CO_2 has been removed.

ture, since both the solubility of CO_2 and the solubility-product constant of $CaCO_3$ decrease with increase of temperature.

Let us now take up the case of a water which contains CO_2 in excess of the amount required to keep all the lime in solution. It had been observed that certain waters attack concrete, dissolving out $CaCO_3$, or iron pipes and by doing so cause trouble in the water supply;[1] this was attributed to what was called the "aggressive" CO_2, which by many was assumed to be identical with the total free CO_2. But when the endeavor was made to prevent this action by removing all of the free CO_2, other difficulties were encountered which remained unaccountable until in 1912, Tillmanns and Heublein, having learned that the solubility of $CaCO_3$ depends upon the partial pressure of CO_2 in the adjacent air, deduced that the "aggressive" CO_2 was that amount of the free CO_2 in excess of what was required to keep the $CaCO_3$ (or other insoluble carbonate) in solution. Accordingly, they made up a series of solutions containing $CaCO_3$ and free CO_2, left them in contact with pieces of marble for 10 days or more, and finally determined the concentrations of bound and free CO_2; in effect, therefore, they made determinations of the solubility of $CaCO_3$ in water containing various proportions of CO_2. The results when plotted are in general agreement with those of Schloesing, though, since the temperature of experiment is indefinite, it is useless to calculate any definite constant from them; this was, indeed, done roughly by Auerbach[2] who gave a better smoothed out curve, and a simple geometrical construction, by means of which the concentration of "aggressive" CO_2 may be read by inspection from the solubility curve. This amount can also be calculated readily from the equations given in a previous paper,[3] if lime is substantially the only base present; otherwise, since the solubility-product constants of the various carbonates are different, these curves and equations are not applicable, and it would be better to determine directly by experiment the concentration of aggressive CO_2. This concentration cannot be ascertained from experiments with any indicator, because the degree of alkalinity at which we begin to have aggressive CO_2 is not an invariant quantity—in other words, the alkalinity of saturated solutions of carbonates is not constant, but depends upon the total base in solution. If now, in an attempt to remove this aggressive CO_2 (by blowing air through the water, or otherwise) too much CO_2 is removed we are left with a supersaturated solution of carbonates which will slowly be deposited—a process which reproduces free CO_2 which again can act aggressively and cause trouble. Similar remarks apply to the process for the removal of iron by

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[1] References are given by Tillmanns and Heublein, *Gesundheitsingenieur*, **35**, 669 (1912); also by Tillmanns, *J. Gasbeleuchtung*, **56**, 370 (1913).

[2] Auerbach, *Gesundheitsingenieur*, **35**, 809 (1912).

[3] J. Johnston, THIS JOURNAL, **37**, 2011 (1915).

blowing air through the water; and the redissolving of iron by treated water has been an occasional source of trouble.[1]

These instances have been discussed at some length because they illustrate the point that by considering that there is a mobile equilibrium and applying the appropriate quantitative relations we are enabled to coördinate and account very readily for things which otherwise are isolated and inexplicable facts. The application of these principles to other specific cases may be made in the same way, though in some cases experimental work on the constants involved may be required before the complete quantitative solution of the problem can be given.

Summary.

Within any solution containing carbonate there is a readily attained equilibrium between the carbonate ion $CO_3^{=}$, the bicarbonate ion HCO_3^-, and the carbonic acid H_2CO_3, and in turn between the carbonic acid and the partial pressure of carbon dioxide above the solution; consequently these molecular species can coëxist only in definite proportions determined by the several equilibrium constants. An examination from this standpoint of the most commonly used titration methods for the estimation of the combined and free CO_2 in solution leads to the conclusion that many of these procedures do not yield definite results—a conclusion which is corroborated by all of the careful comparative experimental work bearing on these methods. In principle the only absolutely reliable methods are those for the total base combined with the carbonic acid and for the *total* CO_2 present in solution; in practice they yield accurate results provided that due attention is paid to the conditions discussed, or referred to, in the paper. But these two determinations suffice in general to characterize the solution with respect to either its content of free CO_2, the proportion of carbonate to bicarbonate, or the degree of alkalinity or acidity; for, since we are dealing with an equilibrium capable of fairly rapid readjustment, we are justified in applying the equilibrium constants to calculate the above quantities in the great majority of those cases in which a knowledge of them is of real importance.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON.]

THE COMPLETE SOLUBILITY CURVE OF CALCIUM CARBONATE.

BY JOHN JOHNSTON AND E. D. WILLIAMSON.

Received February 24, 1916.

Since the publication of a previous paper[2] dealing with the solubility-

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[1] For references see Tillmanns and Heublein, *Gesundheitsingenieur*, 35, 609 (1912); or Tillmanns, *J. Gasbeleuchtung*, 56, 370 (1913).

[2] Johnston, THIS JOURNAL, 37, 2001 (1915), *q. v.;* hereinafter referred to as *Loc. cit.*