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III. *The Kinetics of the Carbon Dioxide-Carbonic Acid Reaction.*

By R. BRINKMAN, R. MARGARIA and F. J. W. ROUGHTON, *from the Physiological Laboratory, Cambridge.*

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Introduction.

In aqueous solutions of Carbon Dioxide, the concentration of dissolved CO_2 as such, is, at equilibrium, far greater than the concentration of carbonic acid, $[\text{H}_2\text{CO}_3]$. On this account solutions of carbon dioxide are found to be only weakly acidic, although H_2CO_3 itself, according to THIEL,* and THIEL and STROHECKER† and later authors, is a fairly strong acid, with a true first ionization constant of about 2×10^{-4} , *i.e.*, $2 \times 10^{-4} [\text{H}_2\text{CO}_3] = [\text{H}^+] [\text{HCO}_3^-]$. The “apparent” first ionization constant of carbonic acid, K_{CO_2} , is, however, given by the equation $K_{\text{CO}_2} (\text{dissolved } [\text{CO}_2] + [\text{H}_2\text{CO}_3]) = [\text{H}^+] [\text{HCO}_3^-]$, and since the dissolved $[\text{CO}_2]$ at equilibrium is found to be of the order of 1000 times greater than the $[\text{H}_2\text{CO}_3]$, the value of K_{CO_2} is correspondingly smaller than 2×10^{-4} , and is given as 3×10^{-7} . MCBAIN‡, THIEL (*loc. cit.*) and others have shown that the reversible reaction $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ is a relatively slow one, and hence that the neutralization of dissolved carbon dioxide by alkali differs from the neutralization of other weak acids in not being instantaneous.

The study of the kinetics of the reaction $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ has recently taken on a new interest, owing to the discovery by physiologists that the red corpuscles of the blood (which contain 30 per cent. by weight of the pigment hæmoglobin) contain a very powerful catalyst of the reaction, the presence of which catalyst is indeed vital for enabling the blood to rid itself of CO_2 sufficiently fast as it travels through the lung. Thus HENRIQUES§ showed that in strong hæmoglobin solutions CO_2 could be shaken off from mixtures of bicarbonate and weak acids far more quickly than from such acid-bicarbonate mixtures alone. This was confirmed by HAWKINS and VAN SLYKE|| who found furthermore that the accelerating effect persisted in solutions of hæmoglobin 20 times more dilute. That the phenomenon is largely, if not entirely,

* ‘Ber. deuts. chem. Ges.,’ vol. 46, pp. 241, 867 (1913).

† ‘Ber. deuts. chem. Ges.,’ vol. 47, pp. 945, 1061 (1914).

‡ ‘J. Chem. Soc.,’ vol. 101, p. 814 (1912).

§ ‘Biochem Z.,’ vol. 200, p. 1 (1928).

|| ‘J. Biol. Chem.,’ vol. 87, p. 265 (1930).

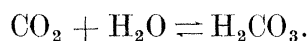
due to a catalyst was shown decisively by the recent work of BRINKMAN and MARGARIA,* confirmed by DIRKEN and MOOK† that acceleration of the reaction was still evident in purified solutions of hæmoglobin diluted to 1 part in 100,000. Finally MELDRUM and ROUGHTON‡ isolated the catalyst from hæmoglobin, with which it had previously been thought to be identical, and obtained it in the form of a solid of which 1 part by weight in 10 million is sufficient to double the rate of the reaction. For this enzyme preparation they have, at the suggestion of Dr. EGGLETON, proposed the name “carbonic anhydrase.”

The detailed study of this catalysis is of obvious interest to the physiologist in working out the mechanism of CO₂-carriage in the blood and of CO₂-elimination in the lung. To the biochemist it must also appeal, not only as a special, but very simple, case of enzyme action well worth investigating for its own intrinsic interest, but also in regard to its relation with the other respiratory enzyme systems, which have been so much studied in recent years. It would, however, be premature to put in hand any comprehensive quantitative investigations of this kind, without having first of all a clear and unequivocal knowledge of the kinetics of the uncatalysed reaction.

In this, however, previous literature is disappointing. The quantitative study of the reaction was begun by THIEL and STROHECKER *loc. cit.* in 1913, and followed up by other workers until 1924, when the beautiful work of FAURHOLT§ appeared. This paper contains full references to the previous work. FAURHOLT concluded that for values of $p_H < 8$, the kinetics of the reaction could be expressed by the equation

$$\frac{d[\text{CO}_2]}{dt} = -k_{\text{CO}_2}[\text{CO}_2] + k_{\text{H}_2\text{CO}_3}[\text{H}_2\text{CO}_3], \quad \dots \dots \dots \text{(I)}$$

i.e. the equation given by the law of mass action as applied to the reversible action



But at $p_H > 8$, a second equation had also to be taken into account, viz. :—

$$\frac{d[\text{CO}_2]}{dt} = -k_{\text{CO}_2 \cdot \text{OH}}[\text{CO}_2][\text{OH}] + k_{\text{HCO}_3}[\text{HCO}_3]. \quad \dots \dots \dots \text{(II)}$$

Between $p_H 8$ and $p_H 10$ both equations are important, but above $p_H 10$ equation II becomes dominant.

Equation II can be obtained either by applying the law of mass action to the reversible reaction $\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^-$, or by supposing that the reaction $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ is catalysed by OH[−] ions, the influence of which only begins to be felt at values of $p_H > 8$.

* ‘J. Physiol.’ vol. 72, p. 6 P (1931).

† ‘J. Physiol.’ vol. 70, p. 373 (1931).

‡ ‘J. Physiol.’ vol. 75, p. 3 P (1932).

§ ‘J. Chem. Phys.’ vol. 21, p. 400 (1924).

FAURHOLT'S method of observation was an indirect one. He mixed together as suddenly as possible in a beaker, a solution of NaHCO_3 (or carbonic acid) with a suitable buffer mixture. The amount of unhydrated CO_2 at any moment was obtained by throwing in an excess of dimethylamine, which was thought to be able to combine instantly with all the CO_2 as such (to form dimethylamine carbamate), but with none of the H_2CO_3 , HCO_3^- or CO_3^{--} present in the solution. The latter constituents were then precipitated immediately afterwards by addition of BaCl_2 . The filtrate and precipitate were then separated and analysed, and thus the $[\text{CO}_2]$ at the instant at which the dimethylamine had been added, was obtained.

In more recent work by BRINKMAN, MOOK and BUYTENDYK* an entirely different technique was used. These authors, by means of a syringe operated by a compressed spring, injected suddenly a small dose of HCl into a solution of NaHCO_3 . Mixture was obtained in about 0.1 second. The subsequent course of the p_{H} of the mixture was registered by a quinhydrone electrode connected up to a thermionic recording device. The results at p_{H} 5.5 to p_{H} 6, could not be fitted by FAURHOLT'S equation I, but required, instead, the equation

$$\frac{d[\text{CO}_2]}{dt} = -k'_{\text{CO}_2}[\text{CO}_2][\text{H}^+] + k'_{\text{H}_2\text{CO}_3}[\text{H}_2\text{CO}_3][\text{H}^+].$$

This equation follows from the law of mass action, if it is assumed that at p_{H} 5.5 to p_{H} 6 the equation $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ is catalysed by hydrogen ions. This possibility had been specially looked for by FAURHOLT, who decided emphatically against it. There is thus complete disagreement between previous authors as regards the mechanism of the reaction in a most important p_{H} range.

One of the essential objectives of the present work was, therefore, to clear up the cause of this discrepancy. The results given below will be found to support the view of the reaction put forward by FAURHOLT, though the numerical values of our velocity constants differ appreciably from his. A special set of experiments brought to light the cause of the difference found by BRINKMAN, MOOK and BUYTENDYK. This turned out to be due to an unsuspected source of error in their technique, the results of which must therefore be set aside.

This experience illustrates once more the danger, well-recognized by physical chemists, of trusting to one type of experimental technique and to a limited variation of the conditions, in elucidating the mechanism of a reaction. In the present work, three independent methods of observation have been used, the influence of hydrogen ion concentration has been studied from p_{H} 1 to p_{H} 13, and the time taken by the various processes has ranged from 30 minutes to 0.04 seconds, *i.e.* a 50,000-fold variation. Special attention has been given to the range p_{H} 6–8, partly because this range is of predominant physiological importance, and partly because the slowness of the reaction under such conditions makes a full investigation much more easy. For the

* 'Biochem J.,' vol. 21, p. 576 (1927).

more rapid processes, of duration 10 seconds and less, the HARTRIDGE-ROUGHTON* method of studying rapid reactions, has, with suitable modifications, proved appropriate. It may be noted here that the formation of CO_2 from bicarbonate will be referred to below as "dehydration," whereas the reverse reaction, *i.e.* the formation of carbonic acid and bicarbonate from CO_2 will be referred to as "hydration."

The general scheme of the remainder of the paper is as follows:—

In section I, the experimental details and precision of the various methods will be described.

In section II the results on hydration and dehydration will be given in detail for the range p_{H} 5·8–8·0.

In section III—the less complete results on dehydration in the range p_{H} 0–6.

In section IV—the hydration of CO_2 at alkaline p_{H} , where FAURHOLT'S second mechanism comes into play.

Whilst in the discussion of results, section V, the results of sections II–IV will be correlated.

SECTION I.

Experimental details.

The three chief methods used for studying the kinetics of the process may be referred to as the "boat" method, the photo-electric method, and DIRKEN and MOOK'S method.

As regards securing accuracy and precision, attention was chiefly given to the boat method, the other methods being mainly used to corroborate the mechanism of the reaction especially in p_{H} ranges where the boat method is inapplicable. The details of each of these will now be described in turn.

(a) *The Boat Method.*—This method is of a simple manometric type, the absorption of CO_2 from a gas phase (for hydration velocity) or the evolution of CO_2 into the gas phase (for dehydration velocity) being recorded by a U-tube pressure gauge connected to the reaction chamber.

The reaction chamber consisted of a glass vessel, capacity 40–50 c.c. and boat-like in shape, B, fig. 1. A rubber cork, through which several leads passed, could be fixed to the central tubular mouth of the vessel. One of these leads was connected to a manometer M, and a second one to a source of gaseous CO_2 for hydration experiments. The

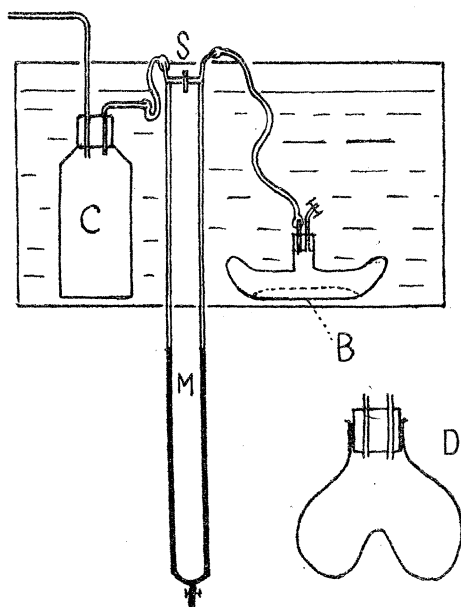


FIG. 1.—Diagram of boat, bath and manometer. D = Transverse Section of boat at centre.

* 'Proc. Roy. Soc.,' A, vol. 104, p. 376 (1923); 'Proc. Camb. Phil. Soc.,' vol. 22, p. 426 (1924); *ibid.*, vol. 23, p. 450 (1926).

other limb of the manometer M was connected to a bottle C, which was used to compensate for pressure and temperature changes. The two limbs of M were connected at the top by a cross-piece having a stopcock S in the middle of it. B and C, and the leads therefrom to M were immersed in a well-stirred constant temperature water-bath, B being held in a rocking device which could be shaken violently to and fro by an electric motor. Five minutes' immersion of B in the water-bath was usually sufficient for temperature equilibration. When this was attained, the stopcock S was closed, and the shaker started and kept running till the end of the particular experiment. Readings of the position of the gauge liquid on *one* side of the manometer were taken after shaking had gone on for 15 secs., 30 secs., 1 min., 1·5 mins., 2 mins., 3 mins., 4 mins., etc. These readings could be converted into amounts of CO₂ evolved or absorbed by means of a calibration factor, which was obtained either by calculation from the volume of B and of the tubes connecting it to M, or by noting the difference in level produced by introducing a known amount of gas into B. The two methods gave concordant results. With air, or other difficultly soluble gases, the amount of gas in physical solution in the liquid is negligible in comparison with that in the gas phase, but with CO₂ a correction factor of $1 + \frac{\alpha V_L}{V_G}$ must be applied, V_L and V_G being the volumes of the liquid and gas phases respectively, and α the solubility coefficient. In the present experiment the correction factor ranged from 8 to 17 per cent. The general procedure was thus similar to that used in the Barcroft differential manometer, but with two important modifications. The boat shape of B was chosen so as to make the interchange of CO₂ between the gas phase and the liquid phase in B as rapid as possible. Secondly the original pressure of gas in the system B-M-C was often considerably reduced (to 1/10 atmosphere or less), with the result that the arrangement could be made more sensitive than it would have been had the pressure been atmospheric. The low pressure had furthermore the advantages both of reducing errors caused by temperature fluctuations, and of making it possible to use a manometer tube of wider bore, within which the gauge liquid would flow more readily.

The length of each limb of M was about 60 cm. and the gauge liquid was usually water containing 1 per cent. glycerine (to make it flow more smoothly) coloured blue by a trace of trypan blue.* When large amounts of CO₂ were to be evolved or absorbed, M was replaced by a duplicate containing mercury as the gauge liquid.

For hydration velocity experiments 4 c.c. of a suitable buffer mixture was placed in the boat, the latter corked and fixed in the water-bath. A measured volume of CO₂, at the temperature of the water-bath, was then introduced into the boat via the second lead, and shaking and readings started as soon as possible afterwards.

For dehydration velocity experiments a special boat with two compartments was used. Into one compartment 2 c.c. of sodium bicarbonate solution was placed, into

* Latterly plain distilled water has proved more satisfactory. The gauge liquid was deaerated before introduction into the gauge.

the other 2 c.c. of a suitable buffer mixture. The two compartments were simply made by raising the centre of the bottom of the boat into a ridge, the two valleys on either side of which were more than large enough to accommodate 2 c.c. of separate fluids without their mixing. The boat was then cautiously lowered into its carriage (*i.e.* without allowing any mixing to occur), connected up in the usual way, and in due course shaken. Two to three seconds' shaking was sufficient to mix the fluids in the two compartments completely. Periodically the leads between the boat and the manometer were dried out with a current of warm air, so as to obviate trouble due to condensation of small blocks of water therein.

Precision and Scope of the Method.—The precision of the method may be illustrated by the data given in Table I in which the same dehydration velocity experiment was repeated 5 times.

TABLE I.

Readings in cm. for output of CO_2 from a $\text{NaHCO}_3 - \text{KH}_2\text{PO}_4 - \text{NaKHPO}_4$ mixture.
Temperature : 15.8°C .

Time.	Exp. I.	II.	III.	IV.	V.	Average.	Maximum discrepancy of individual readings from average.
0	66.00	66.00	66.00	66.00	66.00	66.00	—
15	68.25	68.50	68.40	68.40	68.40	68.39	0.14
30	70.20	70.20	70.40	70.25	70.30	70.27	0.13
45	71.58	71.60	71.40	71.75	71.75	71.62	0.22
60	72.70	72.70	73.00	72.30 ?	72.75	72.69	0.39
90	74.41	74.40	74.60	74.50	74.50	74.48	0.12
120	75.60	75.60	75.80	75.60	75.60	75.64	0.16
							Mean 0.193

It will be seen that each individual reading can usually be relied on to within 2 mm. which is accurate enough for the purposes of this and succeeding papers.*

There is no limit to the slowness of the reactions which can be studied by the boat method, indeed in two cases shaking was continued for as long as two hours. As regards rapid reactions, however, the scope is limited by the rate of interchange of CO_2 between the liquid and gas phases, this in turn depending on diffusion, etc. Fig. 2, curve (a) gives the results of shaking, 4 c.c. of dilute HCl saturated with CO_2 : in this experiment there is no chemical reaction and the rate of output of CO_2 into the gas

* In dehydration experiments with the double compartment boat, the reading at 15 seconds is sometimes irregular owing to variations in the time for mixing of the reagents after the beginning of shaking. For this reason the earliest time used in the calculations was 15 seconds rather than at 0 seconds.

phase is only limited by diffusion. Curve (b), CO_2 with excess of 1 N. NaOH; here the chemical reaction takes less than 0.01 second so the rate of uptake of CO_2 is also limited by diffusion.

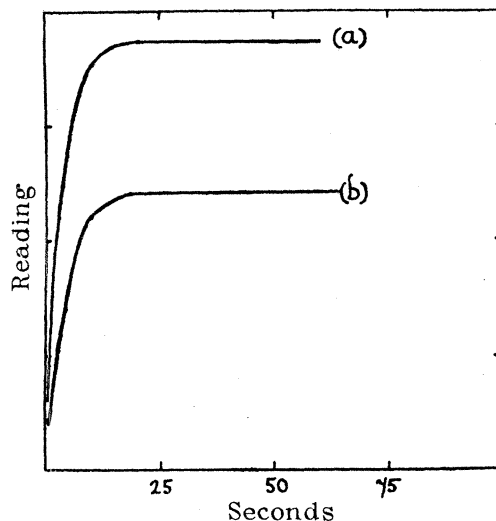


FIG. 2.—Experiments showing limiting effect of diffusion upon the applicability of the boat method to rapid reaction vertical. Reading in cm. on manometer. Horizontal Time in Seconds.

The experiments show that, owing to the slowness of diffusion of CO_2 the processes both appear to take 15–20 seconds instead of being instantaneous. The boat method therefore cannot be used for studying accurately the true chemical reaction velocity of processes which are half completed in less than say 45 seconds.

(b) *The Photo-electric Method.*—In this method suitable p_{H} indicators were added to the reacting mixture, and the p_{H} changes during the course of the reaction were recorded by photo-electric recording of the colour of the solution. From the p_{H} of the solution, the values of $[\text{CO}_2]$, $[\text{H}_2\text{CO}_3]$, $[\text{HCO}_3]$, etc., could be calculated. This technique was applied almost exclusively in conjunction with the Hartridge-Roughton method of measuring rapid velocities, to processes of duration of 10 seconds or less. The application of photo-electric cells to the rapid reaction velocity technique has been studied in detail by MILLIKAN*, and will, it is hoped, be published shortly. Since the methods here adopted were similar to his, no detailed description is necessary. The general procedure was as follows :—

The two solutions to be mixed were made up in separate bottles, and to each was added the same amount of indicator (usually about 0.005 per cent. was suitable). One solution would thus be *e.g.* yellow in colour, and the other *e.g.* red. The two solutions were forced by compressed gas (pressures ranging from $\frac{1}{3}$ atmosphere to 1 atmosphere) through separate leads into the mixing chamber of the Hartridge-Roughton apparatus. Thence the mixed fluid travelled up a vertical observation tube, and finally overflowed into a bucket. The mixing chamber and observation

* Ph.D. thesis Camb. Univ. (1932).

tube (internal bore 0.5 cm.) were mounted in a vertical carriage, which could be moved up and down, so that various parts of the observation tube could be brought into the path of the beam of light illuminating the photo-electric cell. The light was supplied by running off a 6-volt motor battery, the length of the observation tube illuminated by the beam was about 1 mm., and the photo-electric cell was a Serpidex Cu-Cu₂O cell, the current from which was recorded directly by a Moll micro-galvanometer, period $\frac{1}{5}$ second, without any battery drive in the photo-electric circuit.

The usual routine was then as follows. The light was turned on at least 10 minutes in advance, so that it should have time to settle down in intensity. Fluid from the right-hand bottle alone was then driven through the observation tube, and the photo-electric current recorded, = R_1 say; five seconds running of the fluid was usually sufficient. After half a minute (or other definite interval) the left-hand bottle was run alone, = L_1 say. After another half-minute both bottles R and L were run together, reading = B say. Another reading of L was then taken after half a minute = L_2 , and then a final reading of R = R_2 . It will thus be observed that the mean of the two readings R_1 and R_2 , say R , and the mean of the two readings L_1 , L_2 , say L , both correspond in *time* with the reading B. By this procedure, then, errors due to slow drifts in the intensity of the light source, or in the sensitivity of the photo-electric cell and its circuit are greatly cut down.

The values of R , L and B at one position of the observation tube having been determined, the carriage was moved so as to bring another point of the observation tube into the path of the beam of the light, and so on. For each point the value of the expression $(B - R)/(L - R)$ was then calculated. At the end of the experiment, a calibration curve was obtained by running through the observation tube a series of buffer solutions of known p_H , containing the same concentration of indicator. The procedure was exactly the same as before, except that the buffer standard replaced the mixed fluid for the reading B. The values of $(B - R)/(L - R)$ were plotted against p_H , and from the calibration curve so obtained, the p_H of the moving mixed fluid at the various points of the observation tube, determined in the first part of the experiment were read off. The time, corresponding to each point observed, was got in the usual way from the rate of flow of the mixed fluid, the volume of the observation tube per cm., and the distance of the point of observation in cm. from the mixing chamber.

Accuracy.—As a result of many duplicate determinations, it was found that a single value of $(B - R)/(L - R)$ could be depended on to within about 0.8 per cent. This corresponds to an accuracy of about $0.015/p_H$ over the effective p_H range of the indicator.

Indicators so far used.—The following indicators have so far been tried, and all have given satisfactory results:—brom-phenol blue, brom-cresol green, brom-cresol blue, brom-thymol blue, phenol red, and tropoeolin O.

In the experiments of this paper, observations were made at times of about 0.1 second and upwards from the beginning of the reaction. For the results to be serviceable

the time taken by the colour changes of the indicators themselves must be much shorter. Special control experiments with a high-speed mixing apparatus showed that all these indicators completed their colour changes in less than 0.001 second.

(c) DIRKEN and MOOK's *Method*.—This method is a modification of the Hartridge-Roughton rapid reaction method, and consists of measuring the value of the concentration of dissolved CO_2 in the moving fluid, by leading the latter through a small chamber containing gaseous CO_2 connected with a manometer. From the rate of movement of the fluid meniscus in the manometer the rate of exchange of CO_2 between the gas phase and the jet of moving fluid is determined, and since this depends upon the pressure of CO_2 in the gas phase and the concentration of dissolved CO_2 in the liquid, the latter can be obtained with the aid of a calibration curve.

The method has been described by DIRKEN and MOOK, *loc. cit.*, in detail and was repeated by us without any important alteration. We have to thank them warmly for the loan of the necessary apparatus.

The accuracy of the method does not seem to have been fully worked out, and in the time at our disposal the results obtained were extremely rough. They were, however, adequate for the limited purpose to which this method was put, namely, that of testing whether the kinetics of the dehydration reaction in very acid ranges (by mixing NaHCO_3 with excess of HCl) conformed roughly to the same equations as in less acid and neutral ranges.

SECTION II.

Dehydration and hydration in the range p_{H} 6–8.

Dehydration.—For experiments on dehydration velocity 2 c.c. of a buffer mixture p_{H} 5.8–7 were placed in one compartment of the boat, and 2 c.c. of a bicarbonate solution in the other compartment. After 2–5 minutes for temperature equilibration the shaker was started and the output of CO_2 followed by the manometer. Typical results are given in Table I.

(a) *Details of the reagents*.—For the buffer cacodylic acid-sodium cacodylate mixtures of total cacodylate concentration 0.05 M — 0.15 M were used.

The ratio of acid to salt was either 2 : 1, initial p_{H} 5.8, or 1 : 2, initial p_{H} 6.4. There were two reasons for selecting this particular buffer system, (i) it was that used by FAURHOLT, hence the results should be most directly comparable with his, and (ii) it was the most readily available buffer having the salt with a uni-valent anion. Under the latter condition the activity coefficient corrections are much smaller and easier to handle than with the commoner buffer system $\text{H}_2\text{PO}_4^- - \text{HPO}_4^{2-}$, in which the secondary phosphate is divalent.

The sodium bicarbonate solutions ranged from 0.03 M to 0.10 M. Freshly-made NaHCO_3 solution has a p_{H} *circa* 8, but gradually changes on standing to a p_{H} *circa* 9,

since a NaHCO_3 solution can only be in equilibrium with the CO_2 of the atmospheric air, if 10–20 per cent. of it changes into Na_2CO_3 . To get over this difficulty the NaHCO_3 was dissolved not in distilled water, but in a dilute solution of NaOH sufficient to convert 10 per cent. of the bicarbonate into carbonate so that at the outset the solution was nearly in equilibrium. This solution remained stable enough for several days, for titration with HCl to $p_{\text{H}} 8.2$ (using thymol blue as indicator) followed by a second titration to $p_{\text{H}} 3.6$ showed at the end of the series of experiments a ratio of 90.7 per cent. bicarbonate to 9.3 per cent. carbonate. The second of these titrations is of course perfectly easy, but with the first there is a well-known difficulty in getting a good end-point. By adding a trace of carbonic anhydrase to catalyse the reaction $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$, the first titration is much improved. Further details will be given in a later paper.

Temperature.—Most of the experiments were done at $0-0.5^\circ \text{C}$., since this was the staple temperature used by FAURHOLT. The slowness of the reaction at 0°C . is also an advantage, since the boat method can thereby give more accurate results.

Mode of calculation of the Results.—The symbols adopted are as far as possible the same as those used by FAURHOLT. Assume to start with that the reaction takes place entirely in the liquid phase. Let a = total concentration of carbonate radical at the outset.

$$a = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{--}] \text{ at time } t = 0.$$

$$a - x = \text{total concentration of carbonate radical at time } t.$$

then

$$x = [\text{CO}_2] \text{ at time } t.$$

$$a_{\text{H}}, a_{\text{HCO}_3}, a_{\text{CO}_3} = \text{respective activities of } \text{H}^+, \text{HCO}_3^-, \text{ and } \text{CO}_3^{--}.$$

$$f_{\text{H}}, f_{\text{HCO}_3}, f_{\text{CO}_3} \text{ the corresponding activity coefficients.}$$

$$K_{\text{H}_2\text{CO}_3} = \text{true 1st ionization of carbonic acid}$$

$$= \frac{a_{\text{H}} a_{\text{HCO}_3}}{[\text{H}_2\text{CO}_3]}.$$

$$K_{\text{CO}_3} = \text{apparent 1st ionization of carbonic acid}$$

$$= \frac{a_{\text{H}} \cdot a_{\text{HCO}_3}}{([\text{CO}_2] + [\text{H}_2\text{CO}_3])} \text{ at equilibrium.}$$

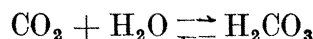
$$K_{\text{HCO}_3} = \text{2nd ionization constant of carbonic acid}$$

$$= \frac{a_{\text{H}} a_{\text{CO}_3}}{a_{\text{HCO}_3}}.$$

$$K_{\text{HCac}} = \text{ionization constant of cacodylic acid}$$

$$= \frac{a_{\text{H}} \cdot a_{\text{Cac}}}{[\text{HCac}]}.$$

Applying the simplest form of the law of mass action to the equation



we have

$$\frac{d[\text{CO}_2]}{dt} = k[\text{H}_2\text{CO}_3] = k'[\text{CO}_2],$$

therefore

$$\frac{dx}{dt} = k[\text{H}_2\text{CO}_3] - k'x.$$

Now

$$\begin{aligned} a - x &= [\text{H}_2\text{CO}_3] + [\text{H}\bar{\text{C}}\text{O}_3] + [\text{C}\bar{\text{O}}_3] \\ &= [\text{H}_2\text{CO}_3] \left(1 + \frac{K_{\text{H}_2\text{CO}_3}}{a_{\text{H}}f_{\text{HCO}_3}} + \frac{K_{\text{H}_2\text{CO}_3}}{a_{\text{H}}f_{\text{HCO}_3}} \frac{K_{\text{HCO}_3}}{a_{\text{H}}f_{\text{CO}_3}} \right), \end{aligned}$$

therefore

$$[\text{H}_2\text{CO}_3] = \frac{a - x}{1 + \frac{K_{\text{H}_2\text{CO}_3}}{a_{\text{H}}f_{\text{HCO}_3}} \left(1 + \frac{K_{\text{HCO}_3}}{a_{\text{H}}f_{\text{CO}_3}} \right)}.$$

Since $K_{\text{HCO}_3} = \text{circa } 3 \times 10^{-11}$ under the conditions of the present experiments $\frac{K_{\text{HCO}_3}}{a_{\text{H}}f_{\text{HCO}_3}}$ is only of the order of 0.001, therefore

$$[\text{H}_2\text{CO}_3] \text{ may be taken } = \frac{a - x}{1 + \frac{K_{\text{H}_2\text{CO}_3}}{a_{\text{H}}f_{\text{HCO}_3}}},$$

therefore

$$\frac{dx}{dt} = \frac{k(a - x)}{1 + \frac{K_{\text{H}_2\text{CO}_3}}{a_{\text{H}}f_{\text{HCO}_3}}} - k'(x).$$

During the early stages of the reaction the back reaction term $-k'x$ can be neglected.

The equation

$$\frac{dx}{dt} = \frac{k(a - x)}{1 + \frac{K_{\text{H}_2\text{CO}_3}}{a_{\text{H}}f_{\text{HCO}_3}}}$$

can be simply integrated over short range of time, $t_1 - t_2$, by assuming that $a_{\text{H}}f_{\text{HCO}_3}$ is constant and equals its average value during $t_1 - t_2$.

The error due to such an approximation is very slight.

We then have

$$\log_e \frac{a - x_1}{a - x_2} = \frac{k(t_2 - t_1)}{1 + \frac{K_{\text{H}_2\text{CO}_3}}{a_{\text{H}}f_{\text{HCO}_3}}}.$$

Since $K_{\text{H}_2\text{CO}_3}$ is of the order of 2×10^{-4} , and $a_{\text{H}}f_{\text{HCO}_3}$ of the order of 10^{-6}

$$\log_e \frac{a - x_1}{a - x_2} \text{ may be taken } = \frac{k(t_2 - t_1) a_{\text{H}}f_{\text{HCO}_3}}{K_{\text{H}_2\text{CO}_3}}.$$

This is equivalent to taking $a - x = [\text{H}\bar{\text{C}}\text{O}_3]$.

*Calculation of $a_{\text{H}} \times f_{\text{H}\bar{\text{C}}\text{O}_3}$.—*We have

$$a_{\text{H}} = \frac{K_{\text{HCac}} [\text{HCac}]}{f_{\bar{\text{Cac}}} [\bar{\text{Cac}}]}.$$

On the DEBYE-HUCKEL theory the bicarbonate ion and the cacodylate ion both being univalent will have the same activity coefficient. This will be assumed to be true, even though the ionic strength of the solutions is above the range calculated in which the DEBYE-HUCKEL equations hold good. If the assumption is incorrect, the absolute values for k will be in error but the relative values of k will be much less affected.

We then have

$$a_{\text{H}} f_{\text{H}\bar{\text{C}}\text{O}_3} = \frac{K_{\text{HCac}} [\text{HCac}]}{[\bar{\text{Cac}}]}.$$

$[\text{HCac}]$ and $[\bar{\text{Cac}}]$ are easily got as follows :—

$[\text{HCac}] + [\bar{\text{Cac}}] = \text{Total cacodylate radical concentration which is known.}$

By the principle of electric neutrality

$[\bar{\text{Cac}}] + [\text{H}\bar{\text{C}}\text{O}_3] = [\text{Na}^+]$ which is known.

$[\text{H}\bar{\text{C}}\text{O}_3] = a - x$, very nearly, under the present conditions.

*Calculation of $a - x$.—*The total amount carbonate radical present in the boat $= a \times V_{\text{L}}$ (the volume of the liquid phase). Subtract from this the total amount of CO_2 in physical solution and in the gas phase, these both being obtained from the gauge reading and the calibration factor. The difference gives the total amount of carbonate radical still present in the liquid phase and this divided by $V_{\text{L}} = a - x$.

Results.—The results are shown in Table II, which gives two pairs of duplicate experiments, one starting at p_{H} 5.8, the other at p_{H} 6.4. Temperature 0°C. in all cases. The values of k are calculated on the assumption that $K_{\text{HCac}} = 10^{-6.29}$, $K_{\text{H}_2\text{CO}_3} = 2 \times 10^{-4}$ [following FAURHOLT]. If the values of these constants are wrong, the absolute, but not the relative, values of k will have to be altered.

The concordance in the values of k is satisfactory, and it will be noted that a variation of 0.6 in initial p_{H} , *i.e.* a 4-fold variation in hydrogen ion concentration, is without effect. The final average value for k , in Table II, *i.e.* 1.75, will only be the true value, if $K_{\text{H}_2\text{CO}_3} = 2 \times 10^{-4}$. The value of $\frac{k}{K_{\text{H}_2\text{CO}_3}}$, *i.e.* 8750, is however independent of the value of $K_{\text{H}_2\text{CO}_3}$, and if future research were to find the value of $K_{\text{H}_2\text{CO}_3}$ exactly, the true value of k could at once be calculated.

Further evidence in favour of the kinetic mechanism so far adopted is given by the effect of a three-fold variation in the concentration both of the cacodylate, and of the bicarbonate. The rate during the first half of the reaction is very nearly three times greater in one case than in the other, as should indeed be nearly so, since the

TABLE II.

Experiment.	I.	I _a .	II.	II _a .
<i>a</i>	0.05 M	0.05 M	0.05 M	0.05 M
Total Na	0.08	0.08	0.105	0.105
Initial HCac	0.05	0.05	0.025	0.025
Initial NaCac	0.025	0.025	0.05	0.05
Initial <i>p</i> _H	5.8	5.8	6.4	6.4
<i>k</i> ₃₀₋₆₀ secs.	1.80	1.78	1.90	1.76
<i>k</i> ₃₀₋₉₀ secs.	1.70	1.74	1.84	1.76
<i>k</i> ₃₀₋₁₂₀ secs.	1.70	1.67	1.79	1.65
Average <i>k</i>	1.73	1.73	1.81	1.72
	1.73		1.76	

effect of the difference in activity coefficients in the two cases is only slight, *i.e.* of the order of 10 per cent.

Effect of temperature.—Comparison of the rate at 0.3° C. with the rate at room temperature (14° C.) gave in one case a ratio of 1 : 3.6, in a second 1 : 3.8, mean 3.7. This gives a temperature coefficient per 10° C., *i.e.* $Q_{10} = 2.6$, agreeing closely with FAURHOLT's value of Q_{10} , *i.e.* 2.7. It should be noted that this Q_{10} is not the Q_{10} of *k* alone, but the Q_{10} of *k* divided by the Q_{10} of $K_{H_2CO_3}$.

Hydration.—For experiments on hydration velocity 4 c.c. of buffer mixture, *p*_H 7–8, were placed in the boat, the latter evacuated and a measured volume of CO₂ gas, 0.7 to 1.0 c.c., introduced. The shaker was then started and readings of CO₂ pressure taken as before.

Details of the reagents.—For the buffer mixture M/15 phosphate buffer *p*_H 6.8–8.0 was used. Activity corrections here do not enter into the forward reaction, so there is no longer objection to the use of phosphate. The buffer range of cacodylic acid-sodium cacodylate was not suitable in the present instance. FAURHOLT also used M/15 phosphate buffer. The CO₂ was drawn from a compressed gas cylinder, containing 99.5 per cent. CO₂ by analysis. The measured volume of CO₂ was brought to the same temperature as the water-bath before being let into the boat. Shaking would therefore be started directly afterwards.

Temperature.—Most of the experiments were again done at 0–0.5° C., but a few were also done at room temperature.

Mode of calculation.—Let $a - x$ = total concentration of carbonate radical as before.

Then according to the law of mass action $\frac{d(a-x)}{dt} = k' [CO_2]$ neglecting the back reaction. Let P_0 = pressure of CO₂ in gas phase (mm. Hg) at $t = 0$.

P = pressure of CO_2 in gas phase (mm. Hg) at t .

$[\text{CO}_2 \text{ in solution}]$ at time $t = \frac{760}{P} \times \frac{\alpha (\text{solubility coefficient})}{22.4}$ mols/litre.

V_G = volume of gas phase.

V_L = volume of liquid phase.

Then

$$x = \frac{(P_0 - P) V_G}{760 \times 22.4} + \frac{(P_0 - P) \alpha V_L}{760 \times 22.4} \text{ mols/litre}$$

$$= \frac{P_0 - P}{760 \times 22.4} \left(\frac{V_G}{V_L} + \alpha \right),$$

therefore

$$\frac{d(a - x)}{dt} = -\frac{dx}{dt} = -\left(\frac{V_G}{V_L} + \alpha \right) \frac{1}{760 \times 22.4} \frac{dP}{dt} = k_1 [\text{CO}_2 \text{ in solution}] = \frac{k' P \alpha}{760 \times 22.4},$$

therefore

$$-\frac{dP}{dt} = \frac{k' P \alpha}{\left(\frac{V_G}{V_L} + \alpha \right)}.$$

Integrating

$$\log_e \frac{P_1}{P_2} = \frac{k' \alpha}{\frac{V_G}{V_L} + \alpha} \times (t_2 - t_1).$$

From this equation the value of k' can thus readily be calculated.

Results.—The results of a typical experiment are shown in fig. 3: when plotted

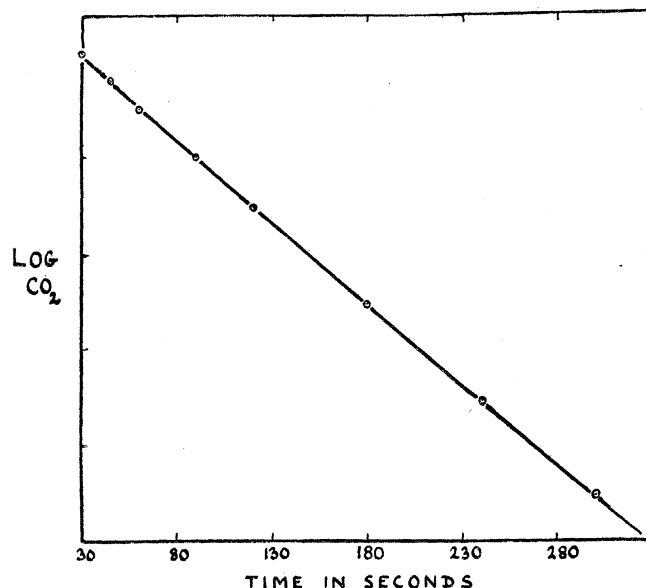


FIG. 3.—Rate of hydration of CO_2 at p_H 7.5 Vertical. Logarithm of CO_2 pressure in gas phase Horizontal. Time in Seconds.

logarithmically the points fall well upon a straight line, in accordance with the uni-molecular velocity equation just given.

In Table III the results at 0° C. with various phosphate buffers are summarized.

TABLE III.

Total phosphate conc. M/15 in all experiments.

Experiment.	I.	II.	III.	IV.	V.	VI.
$[\text{HPO}_4]/[\text{H}_2\text{PO}_4]$	3·6/0·4	3·4/0·6	2·6/1·4	2·6/1·4	2/2	2/2
k'_{30-60} secs.	0·00108	—	0·00278	0·00314	0·00258	0·00269
k'_{60-90} secs.	0·00305	0·00305	0·00233	0·00247	0·00231	0·00238
k'_{90-120} secs.	0·00328	—	0·00315	0·00263	0·00231	—
$k'_{120-180}$ secs.	0·00317	0·00333	0·00268	0·00268	0·00251	—
$k'_{180-240}$ secs.	0·00282	—	—	0·00268	—	—
$k'_{240-360}$ secs.	0·00280	0·0302	0·00251	0·00262	—	—
$k'_{360-480}$ secs.	—	0·0302	0·00247	0·00237	—	—
$k'_{480-600}$ secs.	—	0·0268	—	—	—	—
Average	0·00277	0·00302	0·00265	0·00264	0·00243	0·00254
General average = 0·00268.						

At the most acid p_{H} , viz., 6·8, the back reaction soon becomes important, so that values of k' are only calculated for the earliest stages. There is again no appreciable effect of p_{H} on k' .

Varying concentration of CO_2 .—The reaction velocity equation was further tested by varying the initial concentration of CO_2 . The values of k' obtained from the rate of uptake of CO_2 by 0·2 M phosphate buffer p_{H} 7·6, temperature 16·9° C., at three widely different initial CO_2 pressures were as follows :—

Initial pressure of CO_2	k' .
20 mm. Hg	0·0167
380 mm. Hg	0·0197
1100 mm. Hg	0·0171
Average	0·0184

The effect of temperature.—Since k' at 16·9° C. = 0·0184, and k' at 0·5° C. = 0·00268, Q_{10} , the temperature coefficient per 10° C. = 3·2.

This may be compared with FAURHOLT'S Q_{10} = 3·3.

Relation between dehydration velocity constant k , the hydration velocity constant k' and the equilibrium constant of the reaction.

A further test of the mechanism of the reaction and of the correctness of the velocity constants is obtained by comparing the ratio of the velocity constants with the equilibrium constant of the reaction.

At equilibrium $k [\text{H}_2\text{CO}_3] = k' [\text{CO}_2]$.

Therefore

$$\frac{k}{k'} = \frac{[\text{CO}_2]}{[\text{H}_2\text{CO}_3]}.$$

Also $[\text{H}^+][\text{HCO}_3^-] = K_{\text{H}_2\text{CO}_3}$, $[\text{H}_2\text{CO}_3] = K_{\text{CO}_2}([\text{CO}_2] + [\text{H}_2\text{CO}_3])$
 $= K_{\text{CO}_2}[\text{CO}_2]$ nearly enough since at equilibrium $[\text{CO}_2]$ is of the order of 1000 times greater than $[\text{H}_2\text{CO}_3]$.

Therefore

$$\frac{[\text{CO}_2]}{[\text{H}_2\text{CO}_3]} \text{ at equilibrium} = \frac{K_{\text{H}_2\text{CO}_3}}{K_{\text{CO}_2}}.$$

Therefore

$$\frac{k}{k'} = \frac{K_{\text{H}_2\text{CO}_3}}{K_{\text{CO}_2}}.$$

From page 76

$$\frac{k}{K_{\text{H}_2\text{CO}_3}} \text{ at } 0^\circ \text{ C.} = 8750.$$

Making use of the temperature coefficient given on p. 77.

$$\text{At } 18^\circ \text{ C. } \frac{k}{K_{\text{H}_2\text{CO}_3}} = 53000.$$

$$\text{At } 18^\circ \text{ C. } k' = 0.196,$$

therefore

$$K_{\text{CO}_2} \text{ should} = \frac{0.196}{53000} \text{ i.e. } 3.7 \times 10^{-7}.$$

The direct value of K_{CO_2} .—This is not quite certain. The chief method has been that of electrical conductivity and the results of earlier workers, collated and criticized by KENDALL,* give values ranging from 3×10^{-7} to 3.8×10^{-7} . KENDALL's own careful measurements give a value of 3.12×10^{-7} at 18° C. and his results seem very

* 'J. Amer. Chem. Soc.,' vol. 38, p. 1480 (1916).

concordant. In a later paper, however, WILKE* reports experimental difficulties not mentioned by KENDALL.

Electrometric methods have also been used, but these, as pointed out by STADIE and HAWES† involve an uncertainty in the value of $K_{\text{H}_2\text{CO}_3}$, owing to ignorance of (i) the absolute H^+ ion activity of the reference solution against which the p_{H} of the carbonic acid solution has to be measured, and (ii) the value of the liquid junction potentials. STADIE and HAWES' data suggest a value of 3.8×10^{-7} at 18°C .

On the whole, considering the slight uncertainty in the direct value of K_{CO_2} , and the influence of possible experimental errors in the values of k' and $\frac{k}{K_{\text{H}_2\text{CO}_3}}$,‡ the agreement between the direct and indirect value of K_{CO_2} is not unsatisfactory.

Photo-electric data.—The values of k and k' by the boat method are both appreciably higher than those given by FAURHOLT. It seemed conceivable that this might in some way be caused by the rapid agitation of the gas/liquid interface in our experiments. A few experiments were therefore done in the p_{H} 6–8 range using the all-fluid phase rapid reaction method, the progress of the change being recorded by following the p_{H} of the moving fluid by indicators, using the photo-electric method of estimation. In certain of these experiments the conditions, as regards concentration of reagents, were very similar to those obtaining in BRINKMAN and MARGARIA'S work (*loc. cit.*) upon the rate of hydration and dehydration in very thin films of NaHCO_3 adhering to an antimony electrode, by means of which the p_{H} changes were followed. BRINKMAN and MARGARIA'S experiments lead to anomalous values of the velocity constants of the reaction, hence it was desirable to check them under conditions as similar as possible by an alternative method.

The experiments were of two types :—

[A] *Experiments without foreign buffers.*

(i) *Dehydration.*—A solution of 0.02 M NaHCO_3 was rapidly mixed with 0.001 M HCl. The H^+ ions first combine with HCO_3^- ions to form H_2CO_3 , and the mixture gets gradually alkaline as the H_2CO_3 changes into CO_2 .

(ii) *Hydration.*—A solution of CO_2 was mixed with a solution of NaHCO_3 containing 10–20 per cent. carbonate. The H_2CO_3 present in the CO_2 first of all reacts with the carbonate to make bicarbonate, further H_2CO_3 is formed by hydration of CO_2 so that the p_{H} gradually gets more acid.

Mode of calculation.—Here it is necessary to take into account the buffer effect of the indicator itself. In the dilute solutions used below the activity corrections are only of the order of 10 per cent. and have been neglected. By the usual principles

* 'Z. anorg. Chem.,' vol. 119, p. 365 (1921).

† 'J. Biol. Chem.,' vol. 77, p. 241 (1928).

‡ In this case there is further possibility of error owing to the uncertainty of the assumptions that (i) $f_{\text{Ca}^{++}} = f_{\text{HCO}_3^-}$, and (ii) $K_{\text{HCac}} = 10^{-6.29}$, as mentioned on p. 76.

it can be shown that the rate of change of $[\text{CO}_2]$ is related to the rate of change of $[\text{H}^+]$ by the equation:—

$$\frac{d[\text{CO}_2]}{dt} = -\frac{dh}{dt} \left\{ \frac{\left(1 + \frac{K\omega}{h^2} + 2 \frac{[\text{HCO}_3^-]}{h^2} K_{\text{HCO}_3} + \frac{I\lambda}{(h+\lambda)^2}\right) \left(\frac{h}{K_{\text{H}_2\text{CO}_3}} + 1 + K_{\text{HCO}_3}\right)}{\left(1 + 2 \frac{K_{\text{HCO}_3}}{h^2}\right)} - [\text{HCO}_3^-] \left(\frac{1}{K_{\text{H}_2\text{CO}_3}} - \frac{K_{\text{HCO}_3}}{h^2}\right) \right\},$$

where

I = total concentration of indicator.

λ = ionization constant of indicator treated as a weak acid.

In the range p_{H} 7–8.

$$\frac{h}{K_{\text{H}_2\text{CO}_3}} < \frac{1}{2000}, \quad \frac{K_{\text{HCO}_3}}{h} < \frac{1}{200}.$$

If $[\text{HCO}_3^-] > 0.01$

$$\frac{d[\text{CO}_2]}{dt} = -\frac{dh}{dt} \left(\frac{I\lambda}{(h+\lambda)^2} + \left(\frac{1}{K_{\text{H}_2\text{CO}_3}} + \frac{K_{\text{HCO}_3}}{h^2} \right) [\text{HCO}_3^-] \right) \text{ to within 1 per cent.}$$

= according to the mechanism of the reaction

$$\frac{kh[\text{HCO}_3^-]}{K_{\text{H}_2\text{CO}_3}} - k'[\text{CO}_2].$$

Hence from the relation between h and t , k and k' are calculable.

The results are shown in Table IV.

TABLE IV.— λ for Brom-thymol-blue = 1×10^{-7} , $K_{\text{H}_2\text{CO}_3}$ taken = 2×10^{-4} ,
 $K_{\text{HCO}_3} = 6 \times 10^{-11}$.

Reagents.	Tem- perature.	Time in seconds.	p_{H} .	Velocity constant.
(i) Dehydration. 0.02M NaHCO_3 mixed with 0.00097M HCl. Indicator = 0.004 per cent. brom-thymol-blue	15° C.	$\left\{ \begin{array}{l} 0.044 \\ 0.103 \\ 0.530 \end{array} \right.$	$\left\{ \begin{array}{l} 7.19 \\ 7.24 \\ 7.40 \end{array} \right.$	$\left\{ \begin{array}{l} 11.0 (\pm 30 \text{ per} \\ \text{cent.}) \end{array} \right.$
(ii) Hydration— (a) 0.02M NaHCO_3 mixed with 0.0455M CO_2 . Indicator = 0.004 per cent. brom-thymol-blue	15° C.	$\left\{ \begin{array}{l} 0.536 \\ 0.652 \\ 0.780 \\ 1.020 \\ 1.260 \end{array} \right.$	$\left\{ \begin{array}{l} 8.37 \\ 8.20 \\ 7.80 \\ 7.06 \\ 6.26 \end{array} \right.$	$\left\{ \begin{array}{l} 0.0177 \\ 0.0221 \\ \text{Back reaction too} \\ \text{fast for calcula-} \\ \text{tion to be accurate} \end{array} \right.$
(b) 0.04m NaHCO_3 mixed with 0.0455 M CO_2 . Indicator = 0.004 per cent. brom-thymol-blue	16° C.	$\left\{ \begin{array}{l} 1.12 \\ 1.45 \\ 1.82 \end{array} \right.$	$\left\{ \begin{array}{l} 8.28 \\ 7.90 \\ 7.33 \end{array} \right.$	$\left\{ \begin{array}{l} 0.02 \\ 0.018 \end{array} \right.$

In the dehydration velocity experiment, the change of p_H available for calculation of the velocity constant was unfortunately very small, hence the wide margin of error (± 30 per cent.) in the velocity constant. The results are on the average a little (10–20 per cent.) higher than those of the boat method, but the disagreement is not outside experimental error and is in the opposite direction to the discrepancy with FAURHOLT's results. There is no indication that the discrepancy between FAURHOLT's values and the boat values is caused by the gas/liquid interface in the latter method.

BRINKMAN and MARGARIA's antimony electrode results give values of k and k' only about 1/10 of those given in Table IV, and furthermore the shape of their p_H /time curve is quite at variance with the theoretical formula developed above. A possible explanation of the discrepancy is as follows.

The antimony electrode records the p_H of the fluid in its immediate neighbourhood. A solution of $\text{CO}_2 - \text{H}_2\text{CO}_3 - \text{NaHCO}_3$ total molality 0.01 M is very badly buffered as regards *quick* p_H changes in the range p_H 6–8, since for these only the system $\text{H}_2\text{CO}_3 - \text{NaHCO}_3$ (rather than the whole system $\text{CO}_2 - \text{H}_2\text{CO}_3 - \text{NaHCO}_3$) can function as a buffer, and the effective range for this system is about p_H 2.6 – p_H 4.6 (*i.e.*, 1 p_H unit on either side of the p_H of H_2CO_3). The antimony electrode is therefore in contact with a very poorly buffered fluid, from the point of view of these experiments. p_H electrodes in general give bad results in poorly buffered solutions, and in this case there is especially the possibility that the electrode in virtue of the chemical reaction, which it must engage in with the fluid in its neighbourhood in order to record p_H , may itself modify the p_H of that fluid. Thus it may be that a correction term ought to be applied for the "buffer effect of the electrode itself" analogous to the buffer effect of the indicator in Table IV, and that in absence of such correction unduly low values of the velocity constants would be obtained owing to the slowing down by the electrode of the p_H changes in its immediate neighbourhood.

(B) *Experiments with phosphate buffers.*

For dehydration a solution of NaHCO_3 was mixed with $\text{KH}_2\text{PO}_4 - \text{NaKHPO}_4$ buffer (p_H *circa* 6), and the increase of p_H followed, whilst for hydration a solution of CO_2 was mixed with another $\text{KH}_2\text{PO}_4 - \text{NaKHPO}_4$ mixture p_H *circa* 6 and the decrease of p_H followed. The calculation is much simpler than in the experiments with foreign buffers, A.

The photo-electric readings give the p_H value and hence the ratio $\frac{\text{H}_2\bar{\text{P}}\text{O}_4}{\text{H}\bar{\text{P}}\text{O}_4}$. Since

in dehydration the reaction $\text{H}\bar{\text{C}}\text{O}_3 + \text{H}_2\bar{\text{P}}\text{O}_4 \rightarrow \text{H}_2\text{CO}_3 + \text{H}\bar{\text{P}}\text{O}_4$ proceeds from left to right, whilst in hydration the reaction proceeds from right to left in either case.

$\Delta \text{H}\bar{\text{C}}\text{O}_3$, the change in $\text{H}\bar{\text{C}}\text{O}_3$ concentration = $\Delta \text{H}_2\bar{\text{P}}\text{O}_4$. Thus from the initial concentrations at $t = 0$, and the concentration of $\text{H}_2\bar{\text{P}}\text{O}_4$ and $\text{H}\bar{\text{P}}\text{O}_4$ at t , the concentrations of $\text{H}\bar{\text{C}}\text{O}_3$ and CO_2 at t can be calculated. The velocity constants k , k' can then be obtained by formulæ similar to those used in the boat experiments.

The following results were obtained in two preliminary experiments.

(i) *Dehydration experiment*.—A 0.0285 M KH_2PO_4 /0.0015 M NaKHPO_4 buffer mixture was mixed with 0.03 M NaHCO_3 , indicator 0.004 per cent. brom-cresol purple. Time range 0–2 secs., temp., 17.5. Average value of $k = 8.5$. This value of k agrees closely (to within less than 5 per cent.) with the value from the boat experiment.

(ii) *Hydration experiment*.—0.0190 M CO_2 solution mixed with 0.007 M KH_2PO_4 /0.018 M NaKHPO_4 indicator 0.004 per cent. phenol red.

Time range 0–10 secs. Temp., 17.5. Average value of $k' = 0.026$.*

Recent work suggests that the precision of these methods can be increased two- or three-fold, and their application to the kinetics of the reaction, when catalysed by carbonic anhydrase, should open up an interesting field. Hitherto enzyme reactions have been studied usually with a time scale of minutes; but in the present investigation it should be feasible to substitute one of thousandths of a second, and hence to study the effect of far higher concentrations of enzyme than have been tried before.

SECTION III.

Dehydration in the acid range p_{H} 0–6.

Dehydration velocity in range p_{H} 3–5.—Three experiments were carried out in this range. In all of them 0.02N NaHCO_3 was mixed in the rapid reaction apparatus with 0.01 M HCl . In the first two experiments 0.004 per cent. brom-phenol blue was used as indicator, whilst in the third 0.004 per cent. brom-cresol green. These indicator concentrations are only of the order of $\frac{\text{M}}{10000}$, and can be neglected, since the $[\text{HCO}_3^-]$ is of the order of 0.01 M, and the $\text{H}_2\text{CO}_3 - \text{NaHCO}_3$ acts as a good buffer as regards *quick* processes in the present p_{H} range.

The amount of carbonate present in the bicarbonate solution (10–20 per cent.) was not controlled. As will be evident from the mode of calculation below, it is not necessary to know it in calculating k , but a knowledge of it would have given us an independent method of obtaining $K_{\text{H}_2\text{CO}_3}$ from the data, so it is a pity that exact determination of it was omitted.

Mode of calculation.—

$$\left. \begin{aligned} \text{Let } a &= [\text{Cl}^-] \\ b &= [\text{Na}^+] \\ h &= [\text{H}^+] \end{aligned} \right\} \text{ in mixed fluid.}$$

* This value of k' is about 30 per cent. higher than the boat value, but the experiment was only partially successful, since there was some uncertainty about the exact strength of the CO_2 solution which may have been as much as 20 per cent. too low. If so, the calculated value of k' would have to be reduced. On the whole these two experiments, as far as they go, are also confirmatory of the previous conclusions.

By the principle of electric neutrality

$$2[\bar{\text{CO}}_3] + [\text{HCO}_3] + [\bar{\text{Cl}}] + [\text{OH}] = [\text{Na}^+] + [\text{H}^+].$$

In this p_{H} range $[\bar{\text{CO}}_3]$ and $[\text{OH}]$ are negligible.

Therefore

$$[\text{HCO}_3] = h + b - a.$$

Therefore

$$[\text{H}_2\text{CO}_3] = h \frac{(h + b - a)}{K_{\text{H}_2\text{CO}_3}}$$

neglecting activity corrections which are only of the order of 10 per cent.

Therefore

$$\begin{aligned} [\text{CO}_2] &= \text{Total CO}_2 - [\text{HCO}_3] - [\text{H}_2\text{CO}_3] \\ &= \text{Constant} - (h + b - a) \left(1 + \frac{h}{K_{\text{H}_2\text{CO}_3}}\right). \end{aligned}$$

Therefore

$$\frac{d[\text{CO}_2]}{dt} = -\frac{d}{dt} \left\{ (h + b - a) \left(1 + \frac{h}{K_{\text{H}_2\text{CO}_3}}\right) \right\}.$$

But according to the mechanism of the reaction

$$\frac{d[\text{CO}_2]}{dt} = \frac{k(h)(h + b - a)}{K_{\text{H}_2\text{CO}_3}} - \text{back reaction (which only amounts to 0.3 per cent. in this } p_{\text{H}} \text{ range)}.$$

Therefore

$$-\frac{d}{dt} \left\{ (h + b - a) \left(1 + \frac{h}{K_{\text{H}_2\text{CO}_3}}\right) \right\} = kh \left(\frac{h + b - a}{K_{\text{H}_2\text{CO}_3}} \right).$$

Whence

$$\frac{dh}{dt} \left\{ 1 + \frac{2h}{K_{\text{H}_2\text{CO}_3}} + \frac{b - a}{K_{\text{H}_2\text{CO}_3}} \right\} = kh \left(\frac{h + b - a}{K_{\text{H}_2\text{CO}_3}} \right).$$

Integrating between t_1 and t_2 .

$$k(t_1 - t_2) = \left(1 + \frac{K_{\text{H}_2\text{CO}_3}}{b - a}\right) \log_e \frac{h_1}{h_2} + \left(1 - \frac{K_{\text{H}_2\text{CO}_3}}{b - a}\right) \log_e \frac{h_1 + b - a}{h_2 + b - a}.$$

Of the two terms on the right-hand side of this equation the second one is only of the order of 4 per cent. of the first. Also $\frac{K_{\text{H}_2\text{CO}_3}}{b - a}$ is only about 0.04.

Therefore the absolute value of k should be calculable from the slope of the line relating p_{H} to time without the necessity of knowing $K_{\text{H}_2\text{CO}_3}$ very accurately.

Results.—Fig. 4 gives the plot of p_{H} against t for the second and third of the experiments, the first one being only a preliminary trial of the method; in both the points

fall on or near a straight line. It may be noted that in the brom-cresol green experiment the p_H range was very wide, viz., 3.6 to 5.0.

For the brom-phenol blue experiment the calculated value of $k = 9.0$ temp. 15°C .

For the brom-cresol green experiment the calculated value of $k = 10.0$ temp. 15°C .

Average	9.5
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From the boat experiments taking k at $0^\circ \text{C} = 1.75$, $Q_{10} = 2.6$, $K_{\text{H}_2\text{CO}_3} = 2 \times 10^{-4}$, k at 15°C should equal 7.5.

If, however, $K_{\text{H}_2\text{CO}_3}$ was taken as 2.4×10^{-4} instead of 2×10^{-4} , then k at 15°C would equal 9.5 in the boat method.

That 2×10^{-4} may actually be rather too low a value for $K_{\text{H}_2\text{CO}_3}$ is suggested by the lines of fig. 4. These, when extrapolated back to the vertical axis, give the p_H of the fluid the instant after mixture. From this, together with the relative

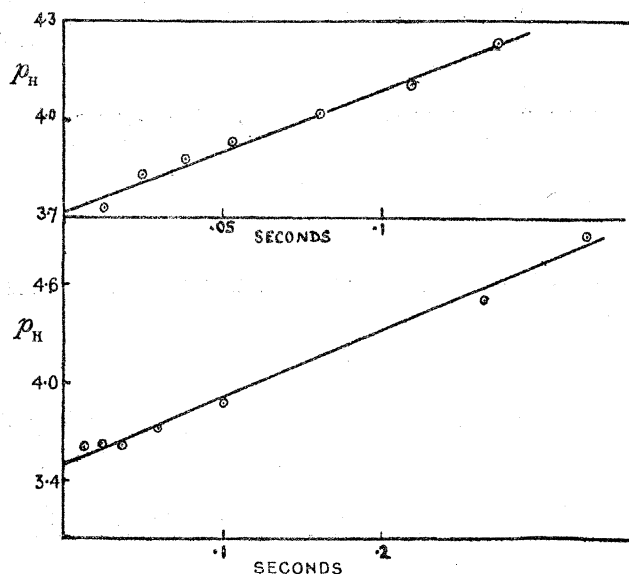


FIG. 4.—Rate of dehydration of carbonic acid in range p_H 3-5.

deliveries of the two fluids, the value of $K_{\text{H}_2\text{CO}_3}$ could be directly calculated if the carbonate content of the bicarbonate solution were known.

Assuming carbonate content negligible, values of 2×10^{-4} and 2.8×10^{-4} , mean 2.4×10^{-4} are obtained for $K_{\text{H}_2\text{CO}_3}$. With a finite carbonate content, a higher value of $K_{\text{H}_2\text{CO}_3}$ would result.

A series of experiments, like the two given in fig. 4, with varying ratios of NaHCO_3 and HCl , together with an accurate knowledge of the carbonate content of the bicarbonate, would probably be the most accurate way of determining the value of $K_{\text{H}_2\text{CO}_3}$.

From the value of $K_{\text{H}_2\text{CO}_3}$ at different temperatures, the "true" heat of ionization

could be calculated by the Van't Hoff Isochore, and from this, together with the "apparent" heat of ionization as calculated from the effect of temperature on K_{CO_2} , the heat of the reaction $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$ could be obtained.

Dehydration velocity in the extremely acid range p_{H} 0-2.

Method and mode of calculation.—Deaërated NaHCO_3 solutions (0·02 M to 0·04 M) were mixed with deaërated HCl solutions (0·04 M to 0·5 M) in DIRKEN and MOOK'S apparatus, and the progress of the reaction was followed by their method.

In all four of the experiments given in Table V, the concentration of HCl was greater than the concentration of NaHCO_3 .

TABLE V.

Reagents.	p_{H} .	Time.	Temp.	k .	k at 15° C.
0·0239 M NaHCO_3 0·0405 $\overset{+}{\text{M}}$ HCl	1·8	0·104	20	13·8	9·0
0·0415 M NaHCO_3 0·048 $\overset{+}{\text{M}}$ HCl	2·2	0·07	15·5	13·3	12·7
0·0416 M NaHCO_3 0·240 $\overset{+}{\text{M}}$ HCl	0·70	0·07	15·5	15·8	15·0
0·0415 M NaHCO_3 0·481 $\overset{+}{\text{M}}$ HCl	0·35	0·07	16	16·7	15·1
				Average	12·9

Therefore $[\text{HCO}_3^-]$ must at once have been converted into $[\text{H}_2\text{CO}_3]$ almost completely (*i.e.*, to an extent of 97 per cent. even in the least favourable case).

Therefore $[\text{H}_2\text{CO}_3]$, at time 0, = $[\text{Na}^+]$ in mixed fluid.

$$[\text{H}_2\text{CO}_3], \text{ at } t, = [\text{Na}^+] - [\text{CO}_2] \text{ at } t.$$

Therefore

$$\frac{d[\text{CO}_2]}{dt} = k[\text{H}_2\text{CO}_3] = k([\text{Na}^+] - [\text{CO}_2]).$$

Integrating

$$\log_e \frac{[\text{Na}^+]}{[\text{Na}^+] - [\text{CO}_2]} = k(t - t_0).$$

In this equation $[\text{Na}]^+$ was known from the concentration of NaHCO_3 used and the relative deliveries of the two fluids to the mixing chamber, $t - t_0$ was calculated from the dimensions of the apparatus and the rate of flow and $[\text{CO}_2]$ at time t was obtained by DIRKEN and MOOK's technique. Hence the value of k could be calculated.

Results.—The speed of the reaction being very high, readings were usually taken at the shortest time measurable in the apparatus, which under our conditions of work was 0.07 seconds.

Owing probably to lack of experience and practice the readings in each experiment showed usually a wide variation, and the value of k given in each is the best average of several observations.

The values of k , though rough, agree to within 50 per cent.* with those obtained earlier in this paper at hydrogen ion concentrations 1,000–1,000,000 times less acid.

Accordingly it seemed worth quoting them as additional cumulative evidence in support of the conclusion that the dehydration velocity is *not* catalysed by hydrogen ions.

BRINKMAN, BUYTENDYK and MOOK's experiments.†

From Table V it follows that even in experiments in which HCl is mixed with excess of NaHCO_3 , mixture must be finished in at most 0.01 second for kinetic calculations to be valid. Otherwise, during the early stages of the mixing process appreciable amounts of dissolved CO_2 would form locally at places, where the HCl concentration was high, and this CO_2 would later hydrate back slowly to H_2CO_3 . Such a process could not be treated quantitatively.

This simple deduction was confirmed experimentally by following, with indicators, the change of p_{H} after mixture of HCl with excess of NaHCO_3 (i) when the mixing took 0.1–1.0 seconds (ii) when mixing took 0.002 seconds (in the Hartridge-Roughton apparatus). In (i) the p_{H} went quickly to a rather alkaline value and then returned slowly to a more acid end-point, whereas in (ii) with just the same solutions the p_{H} began by being rather acid just after mixture, and then rose slowly to its final end-point. Only in the latter would kinetic calculations be valid, as is indeed shown in Experiment I of Table IV, which is a particular example of such condition and gives a value of k of the right order.

In the method of BRINKMAN, MOOK and BUYTENDYK, mixture unfortunately took about 0.1 second. Hence their results and conclusions as to the mechanism of the reaction must be set aside as invalid.

* No allowance has been made in Table V for the carbonate content of the bicarbonate. The proper values for k should probably be 10–20 per cent. higher than those given in the table.

† 'Biochem. J.', vol. 21, p. 576 (1927).

SECTION IV.

Hydration velocity in alkaline range.

In the Introduction it was mentioned that, according to FAURHOLT, above p_H 10 the hydration velocity follows another equation, viz. :

$$\frac{d[\text{CO}_2]}{dt} = k_{\text{CO}_2 \cdot \text{OH}} [\text{CO}_2] [\text{OH}^-] - k_{\text{HCO}_3^-} [\text{HCO}_3^-]$$

and that in the range p_H 8–10 this equation together with that previously tested, namely,

$$\frac{d[\text{CO}_2]}{dt} = k' [\text{CO}_2] - k [\text{H}_2\text{CO}_3]$$

both operate.

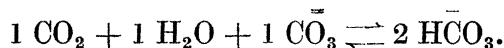
Some experiments to test FAURHOLT's alkaline equation have been made both with the boat method and the photo-electric method, the total p_H range covered being p_H 10–12·5—a more extensive range than that available by FAURHOLT's methods.

(i) *Boat experiments.*—These were in principle just the same as the boat hydration experiments in the range p_H 6–8, but instead of phosphate buffers Na_2CO_3 – NaHCO_3 mixtures of p_H 10–11 were used. Two different buffer mixtures were prepared by dissolving a known weight of NaHCO_3 in a solution of NaOH of known strength, the whole being kept adequately free from the CO_2 of the air.

The strength of the Na_2CO_3 – NaHCO_3 solution was about 0·10 M in total carbonate molality, *i.e.*, about the same as that used by FAURHOLT, the volume placed into the boat was 5 c.c., and the amount of CO_2 introduced into the boat was about 3 c.c. The conditions were thus similar to those of FAURHOLT, but the method has a considerable advantage over his, in that much lower concentrations of dissolved CO_2 are feasible and hence that time intervals of up to 3 minutes can be used instead of intervals of only 10–20 seconds.

Mode of calculation of results.—Since the present reaction involves OH^- ions, activity corrections must be taken into account. The method of calculation now to be given may not be rigorous, but at any rate follows just the same lines as FAURHOLT followed in this case. Our numerical results should therefore be directly comparable with his.

Stoichiometrically the uptake of CO_2 by NaHCO_3 – Na_2CO_3 solutions is expressed by the equation



Therefore

$$\begin{aligned} [\text{CO}_3^{--}] \text{ at time 0} - [\text{CO}_3^{--}] \text{ at } t &= \frac{1}{2} [\text{HCO}_3^-] \text{ at } t - \frac{1}{2} [\text{HCO}_3^-] \text{ at time 0} \\ &= \text{CO}_2 \text{ which has disappeared from gas phase} + \text{liquid} \\ &\quad \text{phase of boat.} \end{aligned}$$

$$= \frac{P_0 - P}{760 \times 22 \cdot 4} \left[\frac{V_G}{V_L} + \alpha \right] v, \text{ p. 78.}$$

Using the same symbols as on pp. 78 and 89, the equation

$$-\frac{d[\text{CO}_2]}{dt} = k_{\text{CO}_2, \text{OH}} [\text{CO}_2] [\text{OH}^-] \text{ [Back reactions being neglected]}$$

becomes

$$\frac{dP}{dt} = -k_{\text{CO}_2, \text{OH}} P \frac{\alpha}{\frac{V_G}{V_L} + \alpha} \times \text{mean} [\text{OH}^-],$$

which when integrated gives

$$\log_e \frac{P_1}{P_2} = k_{\text{CO}_2, \text{OH}} \frac{\alpha}{\left(\frac{V_G}{V_L} + \alpha\right)} \times (t_2 - t_1) \times \text{mean value of } [\text{OH}^-] \text{ over range } t_2 - t_1,$$

whence

$$k_{\text{CO}_2, \text{OH}} [\text{mean value of OH}^-] = \frac{1}{t_1 - t_2} \left(\frac{V_G}{V_L} + \alpha \right) \log_e \frac{P_1}{P_2}.$$

This equation is only strictly correct if the velocity of the other reaction of hydration, viz., $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$, is negligible in comparison with the velocity of the reaction $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$. If this is not so allowance can be made by means of the following complete formula which holds for *both* reactions proceeding concurrently.

$$k_{\text{CO}_2, \text{OH}} [\text{mean value of OH}^-] + k' = \frac{1}{t_1 - t_2} \left(\frac{V_G}{V_L} + \alpha \right) \log_e \frac{P_1}{P_2}.$$

This was necessary for the results given in Table VI, the correction factor amounting to 5–20 per cent.

In the calculations k' was taken = 0.0027 at 0° C., 0.02 at 16° C.

V_G , V_L were given by the dimensions of the apparatus and the amount of liquid introduced.

α was taken = the value for pure water less 2.5 per cent., this being the extent by which α is reduced for a NaCl solution of the same molality.

P_1 , P_2 were obtained from the gauge readings.

The mean value of (OH^-) over the interval $t_2 - t_1$ was got as follows :—

- (i) The p_H of the solution placed in the boat was measured at the start by means of the hydrogen electrode. Readings were constant to 1 millivolt for a period of 5 minutes or more. This gives p_H at time 0.
- (ii) Since the uptake of CO_2 by the solution was not very large during the course of the experiment, there was but little change in the ionic strength of the

solution. It was therefore felt justifiable to calculate the p_H at time $\frac{t_1 + t_2}{2}$, i.e., the mean p_H over the interval $t_2 - t_1$ by means of the equation.

$$p_H \text{ at time } 0 - p_H \text{ at } t = \frac{t_1 + t_2}{2} = \log_{10} \frac{[\bar{\text{CO}}_3] \text{ at } t = 0}{[\bar{\text{HCO}}_3] \text{ at } t = 0} - \log_{10} \frac{[\bar{\text{CO}}_3] \text{ at } t = \frac{t_1 + t_2}{2}}{[\bar{\text{HCO}}_3] \text{ at } t = \frac{t_1 + t_2}{2}},$$

$[\bar{\text{CO}}_3]$, $[\bar{\text{HCO}}_3]$ at $t = 0$ were given by the quantities of NaHCO_3 and NaOH used in making up the solution.

$[\bar{\text{CO}}_3]$, $[\bar{\text{HCO}}_3]$ at $t = \frac{t_1 + t_2}{2}$ were calculated therefrom, with the knowledge of CO_2 taken up between $t = 0$ and $t = \frac{t_1 + t_2}{2}$ as given by the gauge readings.

- (iii) p_{OH} at $\frac{t_1 + t_2}{2}$ was assumed $= 14.85 - p_H$ at 0°C .
 $= 14.27 - p_H$ at 18°C .

in concordance with the values used by FAURHOLT.

- (iv) $[\text{OH}^-] = \frac{10^{-p_{\text{OH}}}}{f_{\text{OH}^-}},$

f_{OH^-} was taken $= 0.75$ in agreement not only with the formula used by FAURHOLT,* but also with the data given by LEWIS and RANDALL† for solutions of this ionic strength.

The values obtained in three experiments are shown in Table VI.

TABLE VI.

Experiment.	I.	II.	III.
Initial ($\bar{\text{HCO}}_3$) molality . .	0.036	0.073	0.036
Initial ($\bar{\text{CO}}_3$) molality . . .	0.067	0.034	0.067
Electrometric p_H	10.54	10.01	10.41
Temperature	0.5°C .	0.5°C .	16°C .
$k' \text{ CO}_2\text{OH}$ 15-45 secs. . .	770	1020	1430
45-90 secs.	770	850	1600
90-180 secs.	790	800	1950
Average	780	890	1660
	840		

The electrometric p_H 's in Table VI check to within $0.09 p_H$ with the values of FAURHOLT in the Tables VIII and IX of his 1925 paper, *loc. cit.*, so that the calculated values of $k'_{\text{CO}_2\text{OH}}$ ought to agree to within 20 per cent. with his values. This is so

* 'J. Chem. Phys.,' vol. 22, p. 1 (1925).

† "Thermodynamics" (New York, 1923).

at room temperature, for FAURHOLT's value at 18° C. was 1740, but not at 0° C., for here FAURHOLT's value was 400.

(ii) *Photo-electric experiments*.—Solutions of CO_2 [0·018–0·045 M] were mixed in the rapid apparatus with solutions of NaOH [0·04–0·06 M] and the p_{H} changes followed photo-electrically by use of 0·01 per cent. tropoeolin 0 as indicator. This indicator gives a suitable colour change from yellow to red, and its accuracy at high alkalinities has been checked by MCBAIN, LAING, and CLERK,* who have shown that it gives results correct to within 0·07 p_{H} over the range p_{H} 12·74–12·15. The present experiments fall within this range.

Mode of calculation of results.

Let

$$a = \text{initial } [\text{CO}_2]$$

$$b = \text{initial } [\text{Na}^+]$$

$$x = [\text{OH}^-].$$

Then

$$b = x + 2 [\text{CO}_3^{--}].$$

Therefore

$$[\text{CO}_3^{--}] = \frac{b - x}{2}.$$

Therefore

$$[\text{CO}_2] \text{ at } t = a - \frac{b - x}{2}.$$

So

$$-\frac{d[\text{CO}_2]}{dt} = k_{\text{CO}_2\text{OH}} [\text{CO}_2] [\text{OH}^-]$$

becomes

$$-\frac{1}{2} \frac{dx}{dt} = k_{\text{CO}_2\text{OH}} \left(a - \frac{b - x}{2} \right) x.$$

Integrating

$$\log_e \left[\frac{x}{2a - b + x} \right]_{t_2}^{t_1} = \left[k_{\text{CO}_2\text{OH}} (2a - b) t \right]_{t_2}^{t_1}.$$

Results.—The results of two experiments are shown in Table VII.

TABLE VII.

Reagents.	Time Interval.	Temperature.	Average value of $k_{\text{CO}_2\text{OH}}$
$\left. \begin{array}{l} 0\cdot0423 \text{ M NaOH} \\ 0\cdot0173 \text{ M CO}_2 \end{array} \right\} \begin{array}{l} + 0\cdot01 \text{ per cent.} \\ \text{Tropoeolin 0} \end{array}$	0–0·091 secs.	15·5° C.	2300 (2000)
$\left. \begin{array}{l} 0\cdot062 \text{ M NaOH} \\ 0\cdot045 \text{ M CO}_2 \end{array} \right\} \begin{array}{l} + 0\cdot01 \text{ per cent.} \\ \text{Tropoeolin 0} \end{array}$	0–0·046 secs.	18° C.	2600 (2300)

* 'J. Gen. Physiol.', vol. 12, p. 698 (1929).

Readings were taken at three different times within each interval. Individual values of $k_{\text{CO}_2\text{OH}}$ were fairly satisfactorily concordant, except that the first one, *i.e.*, that calculated for the interval 0 to the earliest time, tended to be a good bit higher than the average. This may in past have been caused by the use of a somewhat inefficient mixer in these experiments.

The bracketed values in Table VII are those obtained when the first irregular reading is omitted. The mean of these at 16° C. is 2000 (assuming $Q_{10} = 2$), and this value agrees to within 16 per cent. with that found at 16° C. by the boat method. This is not unsatisfactory in view of the experimental errors of each method, and of the theoretical uncertainties in the computation of the velocity constants owing to activity considerations.

SECTION V.

Discussion of results.

The results of Sections II–IV show that from $p_{\text{H}} 0 - p_{\text{H}} 8$ the velocity of the reversible carbon dioxide \rightleftharpoons carbonic acid reaction is, within rather wide limits of experimental error, expressible by the equation

$$\frac{d[\text{CO}_2]}{dt} = k[\text{H}_2\text{CO}_3] - k'[\text{CO}_2],$$

the values of k , k' being independent of p_{H} , and that above $p_{\text{H}} 8$ the second equation

$$\frac{d[\text{CO}_2]}{dt} = k_{\text{HCO}_3}[\text{HCO}_3] - k_{\text{CO}_2\text{OH}}[\text{OH}][\text{CO}_2],$$

comes into play, becoming predominant above $p_{\text{H}} 10$.

FAURHOLT's general view of the reaction is thus confirmed, and the only point of disagreement with him lies in the numerical values of the velocity constants. In Table VIII, the best values of the present paper are compared with the best values of FAURHOLT.

TABLE VIII.

	0° C.		18° C.	
	FAURHOLT.	Present Paper.	FAURHOLT.	Present Paper.
k	1.16	1.70	7.1	$\left. \begin{matrix} 10.4 \text{ } b \\ 11.8 \text{ } p \end{matrix} \right\} 11.1 \text{ } a$
k'	0.0013	0.0026	0.011	$\left. \begin{matrix} 0.021 \text{ } b \\ 0.026 \text{ } p \end{matrix} \right\} 0.024 \text{ } a$
$k_{\text{CO}_2\text{OH}}$	405	840	1740	$\left. \begin{matrix} 1800 \text{ } b \\ 2300 \text{ } p \end{matrix} \right\} 2050 \text{ } a$

b = results by boat method.

p = results by photo-electric method.

a = average.

The present values at 0° C. are all much higher than FAURHOLT's value. There is the same tendency at 18° C., except for $k_{\text{CO}_2\text{OH}}$, in which the disagreement is not outside experimental error.

We have at present no definite explanation for this discrepancy, but the following points should be borne in mind.

(i) FAURHOLT's method of determination of $[\text{CO}_2]$ on the one hand, and of $[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ on the other hand, is a very indirect one.

It was only tested by him in one control experiment on a pure solution of carbonic acid, at unstated temperature.

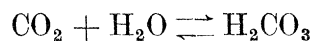
He found about 99·5 per cent. CO_2 , about 0·5 per cent. $([\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}])$. The expected figures were about 99·85 per cent. CO_2 , and 0·15 per cent. $([\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}])$. It would have been far more satisfactory if he had done similar controls upon equilibrated CO_2 -bicarbonate mixtures, in which the concentrations of $[\text{CO}_2]$, and of $([\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}])$ were much more nearly equal than in the extreme case of carbonic acid solution. Such mixtures would have resembled much more closely those with which he had to deal in his main experiments and hence would have given more conclusive controls.

(ii) In his dehydration experiments, FAURHOLT does not mention how he avoided or controlled the presence of carbonate in his NaHCO_3 solution. Omission here would tend to give too low values of k .

(iii) The boat method of the present paper is a very direct one, and it is hard to see where it can have gone astray, unless conditions at the gas/liquid interface are responsible. Against this is the fact that the precise and repeatable results of the boat method are approximately confirmed by the rougher, but all-fluid, photo-electric method. Results by the latter are from 10–20 per cent. *higher* instead of lower than those by the boat method. We feel therefore for the present inclined to put more trust in our own numerical values for the velocity constants than in FAURHOLT's, but we much hope that in the future it may be possible to analyse the discrepancy more thoroughly.

Summary.

1. Manometric and photo-electric methods are described for measuring the speed both of the forward and backward reactions of the reversible process



The manometric method is available for slow reactions taking more than 45 seconds for half-completion whereas the photo-electric method (involving HARTRIDGE and ROUGHTON's rapid reaction velocity technique) is available down to 0·01 seconds.

2. Of these the manometric method was developed to considerable precision. The photo-electric method was used mainly for confirmatory purposes and for dealing

especially with the reaction in ranges inaccessible to the manometric method. A few rough experiments were also made at very acid p_H 's by DIRKEN and MOOK's method.

3. The kinetic results confirm the view of FAURHOLT, namely, that

(i) in the range p_H 0 — p_H 8, the equation

$$\frac{d[\text{CO}_2]}{dt} = k[\text{H}_2\text{CO}_3] - k'[\text{CO}_2],$$

corresponding to the mechanism $1 \text{ mol CO}_2 + 1 \text{ mol H}_2\text{O} \rightleftharpoons 1 \text{ mol H}_2\text{CO}_3$, holds good.

The values of k and k' are independent of p_H in this range. Their ratio agrees fairly well with the equilibrium constant of the reaction.

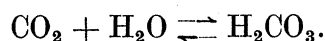
(ii) whilst from p_H 10–13 the equation

$$\frac{d[\text{CO}_2]}{dt} = k_{\text{HCO}_3^-}[\text{HCO}_3^-] - k_{\text{CO}_2, \text{OH}^-}[\text{CO}_2][\text{OH}^-]$$

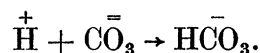
becomes predominant. Between p_H 8 and 10 both equations must be taken into account.

4. The velocity constants calculated from the manometric results by these equations are consistent, and agree fairly well with those given by the rougher photo-electric method, which tend, however, to be somewhat higher. The best values for the velocity constants are distinctly higher than the best values of FAURHOLT. The origin of this discrepancy is discussed.

5. It is shown that existing data give no index of the heat of the reaction



6. A new value is found for the heat of the reaction



7. Some errors in previous work are detected and discussed.

APPENDIX.

Note upon the heat of the reaction $\text{H}^+ + \text{CO}_3^{--} \rightarrow \text{HCO}_3^-$.

The value of the heat of this reaction was wanted on several occasions during the course of this research, notably for calculating by the Van't Hoff isochore the effect of temperature upon K_{HCO_3} . No directly measured value, however, was found in the physico-chemical tables consulted, and in view of the discrepancy between the indirect values calculated from (i) the difference between the heat of neutralization of HCO_3^- , and of HCl by NaOH (THOMSEN), *i.e.*, 4200 cal., (ii) the effect of temperature

on K_{HCO_3} , *i.e.*, 5400 cal. (WALKER, BRAY, and JOHNSTON),* we thought it advisable to make a new and direct determination. The heat of the reaction was therefore measured with ROUGHTON's† rapid thermos-thermocouple method,† by mixing together HCl with more than twice its equivalent of Na_2CO_3 . One thermo-junction was placed in the observation tube about 12 cm. from the mixing chamber, whilst the other was placed in constant-temperature water in a thermos-flask. The thermo-electric currents were measured by the Moll micro-galvanometer.

In Table IX, L, R, B represent the readings of the galvanometer where fluid was running from bottle L alone, bottle R alone, and both bottles together.

In Experiment I

$$L = 0.37 \text{ M HCl}$$

$$R = 0.75 \text{ M NaOH}$$

and $B - \frac{L+R}{2}$ is proportional to the heat of the reaction $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$.

In Experiment II

$$L = 0.37 \text{ M HCl}$$

$$R = 0.75 \text{ M Na}_2\text{CO}_3$$

and $B - \frac{L+R}{2}$ is proportional to the heat of the reaction $\text{H}^+ + \text{CO}_3^{--} \rightarrow \text{HCO}_3^-$.

TABLE IX.—Galvo readings in mm. deflection.

	L.	R.	B.	R.	L.	$B - \frac{R+L}{2}$
I	237	243.5	151	243.3	237	89.2
	236	242.5	150.5	242.2	235.5	88.6
						Average 88.9
II	236.5	250.5	219.3	251.0	236.5	24.33
	235.2	249.2	218.0	250.0	235.0	24.35
						Average 24.34

Therefore

$$\frac{\text{Heat of reaction } \text{H}^+ + \text{CO}_3^{--} \rightarrow \text{HCO}_3^-}{\text{Heat of reaction } \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}} = \frac{24.34}{88.9}.$$

Since

$$\text{Heat of reaction } \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} = 13,700 \text{ calories.}$$

* 'J. Amer. Chem. Soc.', vol. 49, p. 1235 (1927).

† 'Proc. Roy. Soc., A.', vol. 126, p. 439 (1927).

Therefore

Heat of reaction $\bar{\text{H}}^+ + \bar{\text{CO}}_3 \rightarrow \bar{\text{HCO}}_3 = 3750$ calories at room temperature.

This value is somewhat lower than THOMSEN'S figure (4200 cal.) and a great deal lower than the figure of WALKER, BRAY, and JOHNSTON (5360 cal.).

A discrepancy in the opposite sense occurs for the heat of the first ionization of carbonic acid $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \bar{\text{H}}^+ + \bar{\text{HCO}}_3$.

This is discussed by STADIE and HAWES (*loc. cit.*), who give reasons for doubting the possibility of calculating accurately the heat of ionization from electrometric measurements of the ionization constant at different temperatures.
