Kinetic Studies of Carbonation Reactions Using Radioactive Tracers

D. M. HIMMELBLAU and A. L. BABB
University of Washington, Seattle, Washington

In this study a radioactive tracer technique was used to determine the kinetic reaction rate constants in the CO_2–$NaHCO_3$–Na_2CO_3–H_2O system at temperatures of 32, 50, and 68°F., and at various values of *p*H ranging from 5.6 to 7.6. By operating with this system at chemical equilibrium but at isotopic disequilibrium, it was possible to divorce the influence of the diffusion of CO_2 into and out of the aqueous solution from the kinetic effects of the chemical reaction. Radioactive carbon-14 in the form of CO_2 was analyzed by means of the Bernstein-Ballentine technique in order to measure the rates of reaction.

By this treatment, without using intricate equipment, reaction rate constants were computed from simple, integrated first-order equations. Results showed that values for the forward rate constant of the reaction $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$ agreed well with the values published by previous investigators. On the other hand, the forward rate constants of the reaction $CO_2 + OH^- \rightleftharpoons HCO_3^-$ were about 100 times as large as previously reported values. This difference is believed due to the complete elimination of any mass transfer effects in this study. In addition, values for the rate constants of the reverse reactions were measured for the first time, and the calculated values of the equilibrium constants for the two reactions agreed within 6% on the average with those given by Harned and Owen. The technique used, with its variations, is expected to have numerous applications in the study of the kinetics of heterogeneous systems.

This study is part of a program of investigation into the equilibrium, kinetics, and mass transfer aspects of the system

$$CO_2 - H_2S - Na_2S - Na_2CO_3 - NaHCO_3 - H_2O.$$

The reaction of ultimate interest is

$$NaHS + CO_2 + H_2O \rightleftharpoons H_2S + NaHCO_3 \qquad (1)$$

which is a heterogeneous reaction of gaseous carbon dioxide in a solution of sodium hydrogen sulfide. The over-all process from a chemical engineering viewpoint can be classified as a process of absorption accompanied by chemical reaction. The vapor-liquid equilibrium properties of this system have been presented by Mai and Babb (*1*) together with a discussion of the commercial importance of processes for the absorption of carbon dioxide and the carbonation of sodium sulfide solution.

From a fundamental viewpoint, this system provided an opportunity to inquire into a heterogeneous system of simultaneous absorption and chemical reaction whose features have not yet been investigated, a system where basic information concerning the character and mechanism of the reaction under different environmental conditions could prove of considerable import to kinetic and ionic theory. In addition, the technique utilized, with its variations, was expected to have wide applications in the field of chemical kinetics of heterogeneous reactions.

As a means of studying the kinetics of this carbonation reaction it was convenient to investigate both of the following two-phase reversible reactions, the net result of which is reaction (1):

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \qquad (2)$$

$$H^+ + HS^- \leftrightarrows H_2S \qquad (3)$$

Whichever of these reactions had the slowest rate could be considered to be the controlling reaction. This paper deals with the work accomplished with respect to reaction (2). Results of a study of reaction (3) will appear in a later paper.

The major problem in determining the true thermodynamic reaction rate constant* as opposed to the over-all mass transfer coefficient, is the elimination or separation of diffusion effects from kinetic effects. For years work has been conducted on the reaction of carbon dioxide with water and bicarbonate salts, particularly by Saal (*7*), Faurholt (*8*), Brinkman (*9*), Roughton (*10–14*, *31*), Mills and Urey (*15*), Kiese and Hastings (*16*) and Matsuyama (*32*). Their research, in general, has followed two main trends: one approach is to determine the over-all mass transfer effect in a flow or batch process, and to proceed then to correct this value for the effect of diffusion, arriving at a rate constant presumed to represent solely the kinetic influence; the second approach is to design the experiment so that the diffusion influence is negligible, and by this means to obtain a true kinetic rate constant.

As a description of the first approach, the technique utilized by Pinsent and Roughton (*14*) is among the best. They determined the forward rate constant for the reaction of carbon dioxide and water in the temperature range 0 to 38°C. by measuring manometrically the rate of uptake of carbon dioxide by phosphate buffer solutions, and correcting for the effect of diffusion in each phase. The magnitude of the correction was reported to be 10% or less.

The second approach, that of attempting to eliminate the effects of diffusion, was used by Roughton in his rapid thermal method (*31*) but is more clearly demonstrated by the method of Mills and Urey (*15*) using isotopic oxygen. Carbon dioxide with an O^{18} fraction different from that of natural carbon dioxide was dissolved rapidly in water. Samples of carbon dioxide which were extracted from the solution at periodic intervals had different O^{18} contents due to the exchange among the isotopes of oxygen in the solution of CO_2, HCO_3^-, and $CO_3^=$. As the study was limited to a study of the reaction in the liquid phase, the chemical reactions were at effective equilibrium, and uncertainties due to rates of diffusion and solution were eliminated. The measurement of the O^{18} fraction of each sample was carried out in a mass spectrumeter.

Results of Roughton's most recent work agreed fairly well with those of Mills and Urey below 25°C. as shown in Table 3, and consequently provided a fine basis for testing the results obtained with the apparatus and procedure actually used in this work. Roughton's technique is quite complicated, and involves the collection of a vast amount of data in order to calculate a single value of the reaction rate constant. The method of Mills and Urey is simpler, and a modification of this technique is the basis of the procedure used in this work.

THEORY

The experimental problem, as previously stated, was to eliminate diffusion or mass transfer effects from the kinetic effects in the reaction of carbon dioxide

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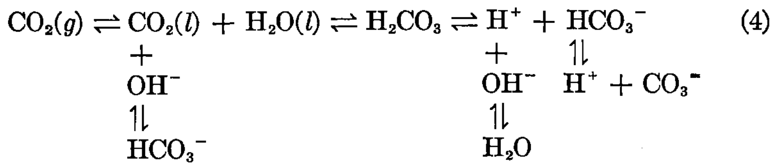
D. M. Himmelblau is at present with the department of chemical engineering, University of Texas, Austin, Texas.

*The true thermodynamic reaction rate constant is defined in terms of activities so that it is independent of concentration and pressure, and for a given solvent, depends only on temperature.

with water or bicarbonate solutions so that only the latter would be measured. Now that radioactive tracers such as carbon-14 and sulfur-35 have become relatively inexpensive, and in view of the substantial progress which has been made in electronic methods of measuring radioactivity, a modification of the Mills and Urey technique provided a practical and effective method of determining the thermodynamic reaction rate constants for the system of interest. The essence of the procedure is to operate with the system at chemical equilibrium but isotopic disequilibrium. With samples taken from a closed reaction vessel at periodic intervals after initially injecting tracer in the form of $NaHC^{14}O_3$ (under controlled conditions of temperature and *p*H), it is possible to follow the rate of reaction (2) by analysis of the percentage of tracer in the solution in the form of $C^{14}O_2$. Mathematical analysis of the problem as outlined below permits the use of a simple first-order integrated rate equation in calculating the reaction rate constant in the forward or reverse direction.

Mathematical Development for Determining Forward Reaction Rate Constants by the Isotopic Exchange Method

In the system of interest the reaction relationships can best be expressed as follows:



$$\begin{array}{llllll}
CO_2(g) \rightleftharpoons & CO_2(l) & + H_2O(l) \rightleftharpoons H_2CO_3 \rightleftharpoons & H^+ & + & HCO_3^- \qquad (4) \\
 & + & & + & & \upharpoonleft\!\downharpoonright \\
 & OH^- & & OH^- & & H^+ + CO_3^{=} \\
 & \upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright & & \\
 & HCO_3^- & & H_2O & &
\end{array}$$

Listing the separate reactions:

$$CO_2(g) \rightleftharpoons CO_2(l) \qquad (5a)$$

$$CO_2(l) + H_2O(l) \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (5b)$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad (5c)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{=} \qquad (5d)$$

$$H^+ + OH^- \rightleftharpoons H_2O \qquad (5e)$$

Other mechanisms for the reactions involved have been proposed but none as yet verified, so the above series must serve the purpose at hand. In addition, carbonate ion is reported to react directly with CO_2, but so slowly that the reaction half-time is of the order of days (15) so this reaction is not included in the discussion.

Reaction (5*a*), a diffusion process, is at equilibrium when liquid samples are taken during an experimental run, and remains so during the remainder of the run, so that this reaction has no net effect on any of the others. Reaction (5*b*) is one for which the forward and reverse reaction rate constants are to be determined. Reactions (5*d*) and (5*e*) are ionic reactions, the rates of which are presumed to be of some high order of magnitude (*17, 18, 33*) so that they instantly come to equilibrium. Reaction (5*c*) is more rapid than (5*b*) but not of ionic speed, and thus the controlling reactions for the system illustrated by reaction (4) above reduce to two reversible, simultaneous reactions (5*b*) and (5*c*). Roughton (*14, 19, 31*) has indicated that reaction (5*c*) becomes influential only if the *p*H is greater than 8, and this point will be considered in greater detail below.

(1) Reaction:

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-:$$

Reaction (5*b*) is in reality composed of two steps

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (5f)$$

and

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (5g)$$

Previous work has been concentrated on the first reaction, and has assumed that the second is of an ionic type and is thus rapid. Moreover, by comparing the results obtained on the basis of this work with those of previous investigators, it was shown that the over-all rate constant for reaction (5*b*) was identical to that for (5*f*). Consequently the mathematical formulation of the rate equation (6*a*) below is based on the initial reactants and final products of reaction (5*b*) since it is quite difficult to measure the activity of carbonic acid in solution. The rate equations for reactions (5*b*), (5*f*), and (5*g*), together with their corresponding equilibrium constants, are as follows:

(5*b*):

$$r_1 = k_F(a_{CO_2})(a_{H_2O}) - k_R(a_{H^+})(a_{HCO_3^-}) \qquad (6a)$$

equilibrium constant:

$$K_b = \frac{k_F}{k_R} = \frac{(a_{H^+})(a_{HCO_3^-})}{(a_{CO_2})(a_{H_2O})} \qquad (6b)$$

(5*f*):

$$r_2 = k_1(a_{CO_2})(a_{H_2O}) - k_2(a_{H_2CO_3}) \qquad (6c)$$

equilibrium constant:

$$K_e = \frac{k_1}{k_2} = \frac{(a_{H_2CO_3})}{(a_{CO_2})(a_{H_2O})} \qquad (6d)$$

(5*g*):

$$r_3 = k_3(a_{H_2CO_3}) - k_4(a_{H^+})(a_{HCO_3^-}) \qquad (6e)$$

equilibrium constant:

$$K_t = \frac{k_3}{k_4} = \frac{(a_{H^+})(a_{HCO_3^-})}{(a_{H_2CO_3})} \qquad (6f)$$

These various equilibrium constants are related in the following way:

K_a = apparent equilibrium constant =

$$\frac{(a_{H^+})(a_{HCO_3^-})}{[(a_{CO_2})(a_{H_2O}) + (a_{H_2CO_3})]} \qquad (6g)$$

K_t = true equilibrium (dissociation) constant =

$$\frac{(a_{H^+})(a_{HCO_3^-})}{(a_{H_2CO_3})} \qquad (6f)$$

$$K_a = \frac{1}{\dfrac{1}{\dfrac{(a_{H^+})(a_{HCO_3^-})}{(a_{CO_2})(a_{H_2O})}} + \dfrac{1}{\dfrac{(a_{H^+})(a_{HCO_3^-})}{(a_{H_2CO_3})}}}$$

$$= \frac{1}{\dfrac{1}{K_b} + \dfrac{1}{K_t}} \qquad (6h)$$

From Equation (6*a*), it is now possible to develop an expression from which k_F and k_R may be determined for reaction (5*b*) from experimental data. Consider the system, consisting of CO_2, H_2O, Na^+, H^+, OH^-, HCO_3^- and a small amount of $CO_3^{=}$, brought to equilibrium, and then a minute amount of tracer in the form of sodium bicarbonate labeled with carbon-14 injected into the reaction vessel. The change of $C^{14}O_2$ concentration in the solution with time is measured.

Parallel equations may be written for this change of activity* of the $C^{12}O_2$ and the $C^{14}O_2$ in the solution with time:

$$r_1 = -\frac{d(a_{C^{12}O_2})}{dt} = +\frac{d(a_{HC^{12}O_3^-})}{dt}$$

$$= k_F(a_{C^{12}O_2})(a_{H_2O}) - k_R(a_{HC^{12}O_3^-})(a_{H^+}) \qquad (7a)$$

$$r_1 = -\frac{d(a_{C^{14}O_2})}{dt} = +\frac{d(a_{HC^{14}O_3^-})}{dt}$$

$$= k_F(a_{C^{14}O_2})(a_{H_2O}) - k_R(a_{HC^{14}O_3^-})(a_{H^+}) \qquad (7b)$$

When tracer is injected into the solution, reaction (7*a*) is at equilibrium, so Equa-

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*The rate of reaction was defined in terms of the change of activity per unit time so that the true thermodynamic rate constants could be measured experimentally. Precise calculation of a rate of reaction in moles/liter/second using these constants would require knowledge of the activity coefficients of all species present in the solution. These may be approximated with sufficient accuracy for engineering purposes from the data of Harned (*3, 6, 20*) and Kielland (*34*).

tion (6*b*) may be used to eliminate k_R from Equation (7*b*) giving

$$r_1 = \frac{-d(a_{C^{14}O_2})}{dt} = k_F(a_{H_2O})$$

$$\left[(a_{C^{14}O_2}) - (a_{C^{12}O_2})\cdot\frac{(a_{HC^{14}O_3^-})}{(a_{HC^{12}O_3^-})}\right] \quad (8)$$

Dividing by $(a_{C^{12}O_2})$ Equation (8) becomes

$$r_1' = -d\,\frac{\dfrac{(a_{C^{14}O_2})}{(a_{C^{12}O_2})}}{dt} = k_F(a_{H_2O})$$

$$\left[\frac{(a_{C^{14}O_2})}{(a_{C^{12}O_2})} - \frac{(a_{HC^{14}O_3^-})}{(a_{HC^{12}O_3^-})}\right] \quad (9)$$

Since this technique is based upon the measurement of the radioactive tracer as a gas which is flashed out of solution and assumed to be representative of the $(a_{C^{14}O_2})/(a_{C^{12}O_2})$ ratio in the solution, it is convenient to eliminate the $(a_{HC^{14}O_3^-})/(a_{HC^{12}O_3^-})$ ratio from Equation (9). This is done by considering the properties of a system not at isotopic equilibrium.

The exchange reactions of molecules or ions containing carbon-14 in the system of interest are known to occur by normal chemical and ionic reactions among the species present. Since the entire system is at chemical equilibrium, but not at isotopic equilibrium, no chemical change takes place. Isotopic equilibrium comes about when the distribution of the C-12 and C-14 isotopes reaches the same ratio among the various molecules and ions which contain the carbon atom in the system. This isotopic equilibrium results in a uniform distribution of the C-12 and C-14 (within one percent) (*21*, *22*). It can be appreciated that the time for the establishment of isotopic equilibrium is much greater than that for chemical equilibrium since the chemical and ionic interchange, forward and reverse, must take place many times before effective isotopic equilibrium is achieved. This isotopic equilibrium may be expressed in the following way:

$$\frac{(a_{HC^{12}O_3^-})_\infty}{(a_{HC^{14}O_3^-})_\infty} = \frac{(a_{C^{12}O_2})_\infty}{(a_{C^{14}O_2})_\infty} \quad (10)$$

where $(a_{HC^{12}O_3^-})_\infty$ and $(a_{HC^{12}O_3^-})_\infty$ are the activities of the $HC^{14}O_3^-$ and the $HC^{12}O_3^-$ respectively at isotopic equilibrium, and similarly $(a_{C^{14}O_2})_\infty$ and $(a_{C^{12}O_2})_\infty$ represent the activities of $C^{14}O_2$ and $C^{12}O_2$ in solution at isotopic equilibrium. These ratios are constants for any given experimental run. The activities of the tracer in the solution, whether as carbon dioxide or bicarbonate ion, change with time after the injection of the tracer, and it is only after a relatively long period of time that they reach the value at isotopic equilibrium.

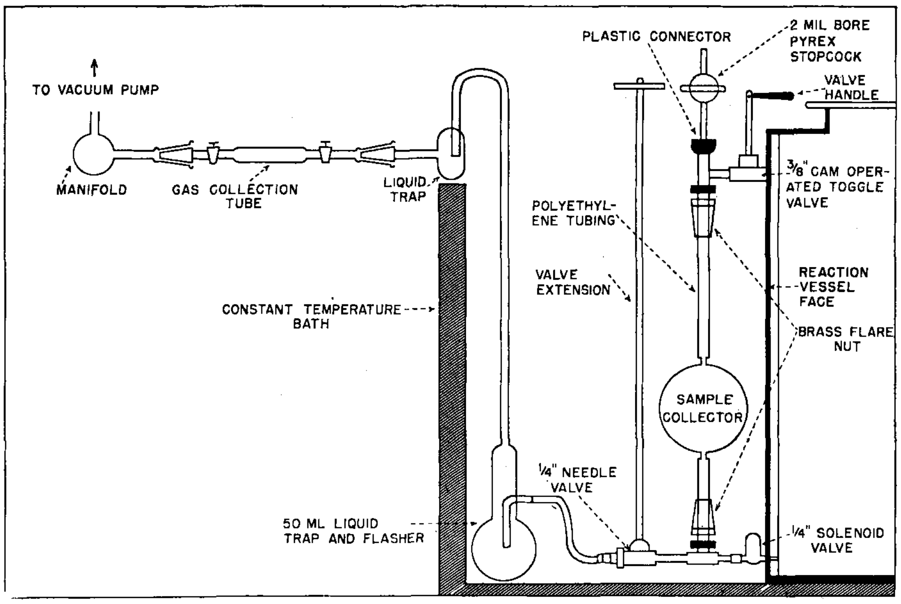

Fig. 1. Schematic diagram of reaction vessel and sampling tubes.

On the other hand, the activities of the $C^{12}O_2$ and the $HC^{12}O_3^-$ do not change at any time during the experimental run, and so the initial values are the same as the final values. Thus Equation (10) can be rewritten as

$$\frac{(a_{HC^{12}O_3^-})}{(a_{HC^{14}O_3^-})_\infty} = \frac{(a_{C^{12}O_2})}{(a_{C^{14}O_2})_\infty} \quad (10a)$$

Equations (9) and (10) may be expressed in terms of concentrations since the activity terms in these relations consist of ratios permitting cancellation of the activity coefficients:

$$-d\,\frac{\dfrac{[C^{14}O_2]}{[C^{12}O_2]}}{dt} = k_F(a_{H_2O})$$

$$\left(\frac{[C^{14}O_2]}{[C^{12}O_2]} - \frac{[HC^{14}O_3^-]}{[HC^{12}O_3^-]}\right) \quad (9a)$$

and

$$\frac{[HC^{12}O_3^-]}{[HC^{14}O_3^-]_\infty} = \frac{[C^{12}O_2]}{[C^{14}O_2]_\infty} \quad (10b)$$

Noting that the C-14 content of the solution is constant and equal to the initial amount of tracer injected into the reaction vessel, one observes that a material balance for the tracer gives

$$\begin{aligned}[C^{14}O_2]_o + [HC^{14}O_3^-]_o &= [C^{14}O_2] + [HC^{14}O_3^-] \\ &= [C^{14}O_2]_\infty + [HC^{14}O_3^-]_\infty \quad (11)\end{aligned}$$

where the subscript *o* signifies initial concentration.

Now, by eliminating $[HC^{14}O_3^-)_\infty$ between Equations (10*b*) and (11) one obtains

$$\left(\frac{[C^{14}O_2]}{[C^{12}O_2]} - \frac{[HC^{14}O_3^-]}{[HC^{12}O_3^-]}\right) = \frac{([C^{14}O_2] - [C^{14}O_2]_\infty)([HC^{12}O_3^-] + [C^{12}O_2])}{([C^{12}O_2][HC^{12}O_3^-])} \quad (12)$$

Finally, by substituting Equation (12) into Equation (9*a*), one obtains the derived rate equation for this reaction.

$$r_1' = -d\,\frac{\dfrac{[C^{14}O_2]}{[C^{12}O_2]}}{dt} = k_F(a_{H_2O}) \quad (13)$$

$$\left(\frac{[C^{14}O_2]}{[C^{12}O_2]} - \frac{[C^{14}O_2]_\infty}{[C^{12}O_2]}\right)\left(1 + \frac{[C^{12}O_2]}{[HC^{12}O_3^-]}\right)$$

Equation (13) may be simplified to

$$r_1' = -\frac{dR}{dt} = k_F(a_{H_2O})(R - R_\infty)$$

$$\left(1 + \frac{[C^{12}O_2]}{[HC^{12}O_3^-]}\right) \quad (13a)$$

where $R = [C^{14}O_2]/[C^{12}O_2]$ and $R_\infty = [C^{14}O_2]_\infty/[C^{12}O_2]$.

(2) Reaction:

$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$

The rate equation for reaction (5*c*) is

$$r_4 = k_f(a_{CO_2})(a_{OH^-}) - k_r(a_{HCO_3^-}) \quad (14a)$$

which has the equilibrium constant

$$K_* = \frac{k_f}{k_r} = \frac{(a_{HCO_3^-})}{(a_{CO_2})(a_{OH^-})} \quad (14b)$$

Again parallel equations may be written for the change of activity of the $C^{12}O_2$ and the $C^{14}O_2$ in the solution with time:

$$r_4 = -\frac{d(a_{C^{12}O_2})}{dt} = k_f(a_{C^{12}O_2})(a_{OH^-}) - k_r(a_{HC^{12}O_3^-})$$

$$r_4 = -\frac{d(a_{C^{14}O_2})}{dt} \quad (15b)$$

$$= k_f(a_{C^{14}O_2})(a_{OH^-}) - k_r(a_{HC^{14}O_3^-})$$

Since Equation (15*a*) is at chemical equilibrium, k_r can be eliminated from Equation (15*b*) by the use of Equation (14*b*) to give Equation (16) after division by $(a_{C^{12}O_2})$

$$r_4' = -d\,\frac{\dfrac{(a_{C^{14}O_2})}{(a_{C^{12}O_2})}}{dt} = k_f(a_{OH^-}) \left[\frac{(a_{C^{14}O_2})}{(a_{C^{12}O_2})} - \frac{(a_{HC^{14}O_3^-})}{(a_{HC^{12}O_3^-})}\right] \qquad (16)$$

Making the same transformation on Equation (16) as previously accomplished from Equations (9) through (13), including the introduction of concentration units, one obtains

$$r_4' = -\frac{dR}{dt} = k_f(a_{OH^-})(R - R_\infty)\left(1 + \frac{[C^{12}O_2]}{[HC^{12}O_3^-]}\right) \qquad (17)$$

(3) Rate Equation for the Simultaneous Reactions

Since reactions (5*b*) and (5*c*) are simultaneous reactions, the over-all rate r_5' is given by the sum of the rates represented by Equations (13) and (17)

$$r_5' = r_1' + r_4' = -\frac{dR}{dt}$$

$$= (k_F(a_{H_2O}) + k_f(a_{OH^-}))(R - R_\infty)\left(1 + \frac{[C^{12}O_2]}{[HC^{12}O_3^-]}\right) \qquad (18)$$

Equation (18) may be integrated to give

$$-\ln(R_\infty - R) = (k_F(a_{H_2O}) + k_f(a_{OH^-}))\left(1 + \frac{[C^{12}O_2]}{[HC^{12}O_3^-]}\right)(t) + C \qquad (19)$$

Normally the constant

$$[C^{12}O_2]/[HC^{12}O_3^-]$$

is measured by chemical analysis but it is possible, by making use of Equations (10*a*) and (11) and by measuring the initial amount of tracer injected into the solution, to determine this ratio in another way. The added amount of tracer is so small in terms of the added C-12, that its influence on any relations involving C-12 may be ignored. From Equations (10*a*) and (11)

$$\left(1 + \frac{[C^{12}O_2]}{[HC^{12}O_3^-]}\right) = \left(1 + \frac{[C^{14}O_2]_\infty}{[HC^{14}O_3^-]_\infty}\right) = \left(1 + \frac{[C^{14}O_2]_\infty}{[HC^{14}O_3^-]_o + [C^{14}O_2]_o - [C^{14}O_2]_\infty}\right) \qquad (20)$$

If the $[C^{14}O_2]_o = 0$, i.e., no substantial amount of C-14 is present as CO_2 in the injected tracer, then a simple relationship develops from Equation (20). Moreover, the fact that the tracer solution contains some $CO_3^=$ as C-14 is unimportant since on reaching the reaction solution the $C^{14}O_3^=$ is instantly converted into $HC^{14}O_3^-$ by reaction (5*d*), and consequently the net result is the same as if $HC^{14}O_3^-$ alone had been added to the reaction vessel. Thus Equation (20) becomes

$$\left(1 + \frac{[C^{12}O_2]}{[HC^{12}O_3^-]}\right) = \left(\frac{[HC^{14}O_3^-]_o}{[HC^{12}O_3^-]} \times \frac{[C^{12}O_2]}{[C^{14}O_2]_\infty}\right) = \left(\frac{R^*}{R_\infty}\right) \qquad (21)$$

where

$$R^* = \frac{[HC^{14}O_3^-]_o}{[HC^{12}O_3^-]}.$$

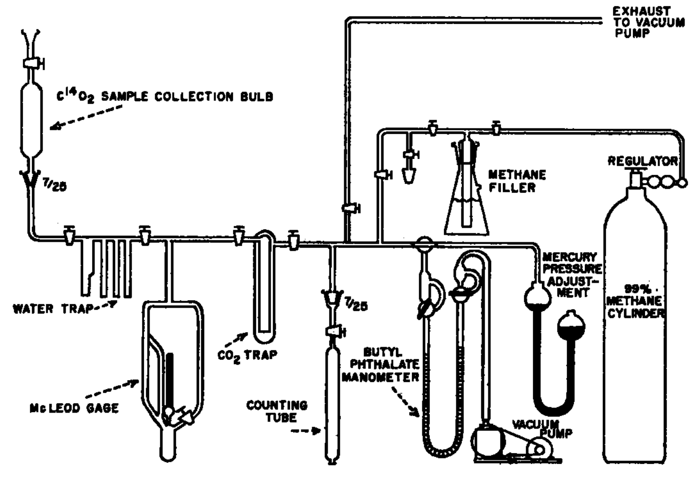

Fig. 2. Schematic diagram of Bernstein-Ballentine transfer apparatus.

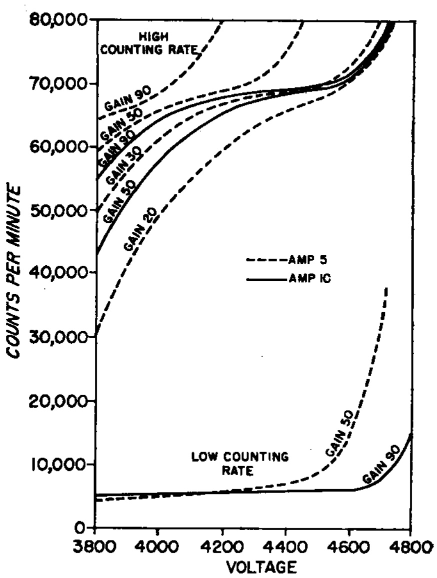

Fig. 3. Counting curves in the plateau region.

The final integrated equation is now

$$-\ln(R_\infty - R) = ((k_F)(a_{H_2O}) + (k_f)(a_{OH^-}))\left(\frac{R^*}{R_\infty}\right)(t) + C \qquad (22)$$

where R_∞, R, and R^* can be readily determined experimentally.

By plotting $-\ln(R_\infty - R)$ vs. t for any experimental run one can determine $[k_F(a_{H_2O}) + k_f(a_{OH^-})]$ from the slope of the line so obtained. In order to determine k_F or k_f separately, the data from several runs at various values of pH can be plotted vs. the a_{OH^-}, and the slope of the line so developed represents k_f while the intercept of the line is $k_F(a_{H_2O})$.

Reaction Rate Constants for the Reverse Reactions

Reaction rate constants for the reverse reactions may be computed by combining the forward reaction rate data with the proper equilibrium constant. For example, for reaction (5*b*):

$$k_R = \frac{k_F}{K_b} \qquad (23)$$

and for reaction (5*c*):

$$k_r = \frac{k_f}{K_*} \qquad (24)$$

These reactions may be used to check the reverse reaction-rate constants computed from data obtained for the computation of the forward rate constants.

(1) Reaction:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

In a manner similar to that outlined

TABLE 1. EXPERIMENTAL RESULTS

Run No.	Temp.	pH	[NaHCO$_3$]	[CO$_2$] [HCO$_3^-$]	Slope Eqs. (32a) & (32b)	[OH$^-$] × 10^8	γOH$^-$*	(aOH$^-$) × 10^8	$[k_F(a_{H_2O})+k_f(a_{OH^-})]$	$\left[\frac{\gamma_{H^+}\gamma_{HCO_3^-}}{\gamma_{CO_2}a_{H_2O}}\right]$**	[H$^+$] × 10	γH$^+$*	$\left[k_R[H^+]+\frac{k_r}{\gamma_{H^+}}\right]$
7	0°C.(32°F.)	5.53	0.01	9.73	0.0218	0.047	0.90	0.042	0.00203	0.881	29.3	0.91	0.0224
9		6.59	0.10	0.605	0.00408	0.687	0.76	0.522	0.00254	0.598	2.58	0.83	0.00257
10		6.55	0.10	0.631	0.00403	0.429	0.76	0.326	0.00247	0.598	2.80	0.83	0.00261
11		7.23	0.50	0.094	0.00610	3.76	0.67	2.50	0.00557	0.425	0.586	0.79	0.00123
12		6.93	0.20	0.227	0.00432	1.74	0.71	1.23	0.00353	0.519	1.16	0.81	0.00154
13		7.13	0.20	0.144	0.00533	2.75	0.71	1.95	0.00465	0.519	0.736	0.81	0.00129
14		7.48	0.50	0.053	0.00866	6.60	0.67	4.39	0.00823	0.425	0.333	0.79	0.00104
15	10°C.(59°F.)	6.70	0.10	0.357	0.0138	2.29	0.76	1.74	0.00995	0.595	2.00	0.83	0.00598
16		7.04	0.20	0.14	0.018	5.55	0.71	3.94	0.0158	0.516	0.906	0.81	0.00382
17		6.43	0.041	0.788	0.0146	1.09	0.82	0.090	0.00818	0.705	3.74	0.85	0.00913
19		6.92	0.10	0.200	0.0151	3.63	0.76	3.10	0.0126	0.555	1.20	0.83	0.00454
20	20°C.(68°F.)	6.78	0.10	0.237	0.0338	6.64	0.76	5.04	0.0274	0.592	1.66	0.83	0.0111
21		6.13	0.0285	1.39	0.0411	1.21	0.85	1.02	0.0172	0.780	7.39	0.88	0.0306
22		6.80	0.10	0.208	0.0338	5.19	0.76	3.94	0.0280	0.592	1.59	0.83	0.00982

Note: All concentrations in moles/liter. Activity coefficients from Kielland expressed on molar basis; those of Harned on molal basis.
*From Kielland (*34*).
**From Harned (*3, 6, 20*).

in the previous section, a relation for the reverse reaction rate constant k_R in Equation (5b) may be developed. Using Equation (6b) to eliminate k_F from Equation (7b) one obtains

$$r_1 = -\frac{d(a_{C^{14}O_2})}{dt}$$

$$= (k_R)(K_b)(a_{C^{14}O_2})(a_{H_2O}) - (k_R)(a_{H^+})(a_{HCO_3^-}) \quad (25)$$

Following a development similar to that for Equations (9a) and (13), Equation (25) becomes

$$r_1' = -\frac{dR}{dt} = (k_R)(K_b)(a_{H_2O})$$

$$(R - R_\infty)\left(1 + \frac{[C^{12}O_2]}{[HC^{12}O_3^-]}\right) \quad (26)$$

(2) Reaction: $CO_2 + OH^- \rightleftharpoons HCO_3^-$

Proceeding as before, by eliminating k_f from Equation (15b) one can show that

$$r_4' = -\frac{dR}{dt} = (k_r)(K_*)(a_{OH^-})$$

$$(R - R_\infty)\left(1 + \frac{[C^{12}O_2]}{[HC^{12}O_3^-]}\right) \quad (27)$$

(3) Rate Equation for the Simultaneous Reactions

Adding the rates given by Equations (26) and (27), one obtains the over-all rate r_5':

$$r_5' = -\frac{dR}{dt}$$

$$= [k_R(K_b)(a_{H_2O}) + k_r(K_*)(a_{OH^-})]$$

$$(R - R_\infty)\left(1 + \frac{[C^{12}O_2]}{[HC^{12}O_3^-]}\right) \quad (28)$$

Substituting for K_b and K_* from Equations (6b) and (14b), respectively, and integrating this differential equation gives an equation similar to Equation (19).

$$-\ln(R_\infty - R)$$

$$= (k_R[H^+] + k_r/\gamma_{H^+})\left(\frac{\gamma_{H^+}\gamma_{HCO_3^-}}{\gamma_{CO_2}(a_{H_2O})}\right)$$

$$(a_{H_2O})\left(1 + \frac{[HC^{12}O_3^-]}{[C^{12}O_2]}\right)(t) + C' \quad (29)$$

In conformity with Equation (21), which transforms the quantity

$$\left(1 + \frac{[C^{12}O_2]}{[HC^{12}O_3^-]}\right)$$

into combinations of tracer ratios, it can be shown that:

$$\frac{[C^{12}O_2]}{[HC^{12}O_3^-]} = \frac{R^*}{R_\infty} - 1 \quad (29a)$$

so that

$$\left(1 + \frac{[HC^{12}O_3^-]}{[C^{12}O_2]}\right) = \left[1 + \frac{1}{\frac{R^*}{R_\infty} - 1}\right]$$

$$= \left[\frac{1}{1 - \frac{R_\infty}{R^*}}\right] \quad (30)$$

The final integrated equation is now

$$-\ln(R_\infty - R)$$

$$= \left((k_R)[H^+] + \frac{k_r}{\gamma_{H^+}}\right)(t)\left[\frac{1}{1 - \frac{R_{00}}{R^*}}\right]$$

$$\left(\frac{\gamma_{H^+}\gamma_{HCO_3^-}}{\gamma_{CO_2}a_{H_2O}}\right)(a_{H_2O}) + C' \quad (31)$$

where all the terms are the same as in the previous discussion.

In the same way that $k_F(a_{H_2O})$ and k_F could be computed by plotting $-\ln(R_\infty - R)$ vs. t for a given experimental run, so may k_R and k_r/γ_{H^+} be determined if

$$\left(\frac{\gamma_{H^+}\gamma_{HCO_3^-}}{\gamma_{CO_2}a_{H_2O}}\right)(a_{H_2O})$$

is known.

Evaluation of Activity Coefficients

In order to determine the individual values of k_F, k_f, k_R, and k_r from Equations (19) and (33), or (22) and (35), it is apparent that the values:

$$a_{OH^-},\quad a_{H_2O},\quad \gamma_{H^+},$$

$$(\gamma_{H^+}\gamma_{HCO_3^-}/\gamma_{CO_2}a_{H_2O}),$$

$$(\gamma_{H^+}\gamma_{OH^-}/a_{H_2O})$$

must be evaluated at the conditions of each experimental run so that true thermodynamic rate constants may be computed. Other investigators have either worked in dilute solutions, hoping to avoid activity effects (*15*), or have carried out their experiments in successively less concentrated solutions, and extrapolated their results to infinite dilution (*31*), to eliminate activity effects. This latter procedure was not found to be feasible in this study. Consequently, the activity factors of Kielland (*34*) for γ_{H^+} and γ_{OH^-}, which have an error of about 5% when translated into mean ionic activity coefficients, were utilized. The a_{OH^-} could then be computed from

$$a_{OH^-} = \frac{K_w(a_{H_2O})}{(a_{H^+})} = [OH^-](\gamma_{OH^-})$$

In general, the a_{H_2O} was considered to be 1, which is not strictly true, but no better approximation was available.

There are no data directly available from the literature for the activity coefficient products

$$\left(\frac{\gamma_{H^+}\gamma_{HCO_3^-}}{\gamma_{CO_2}a_{H_2O}}\right)$$

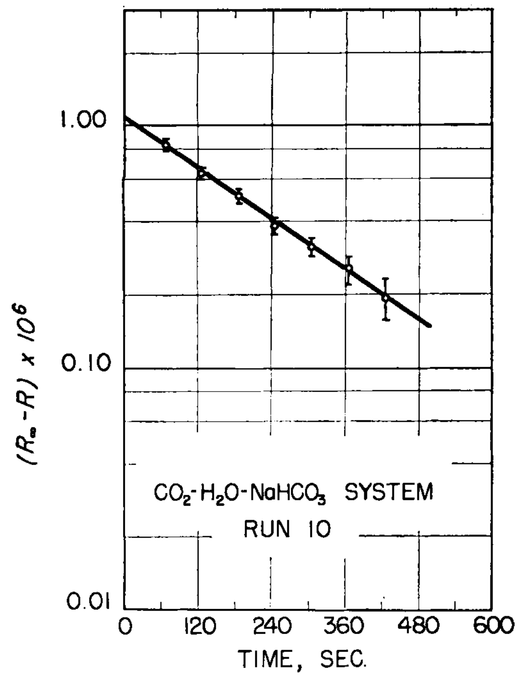

Fig. 4. Experimental rate data at 32°F. and $pH = 6.55$.

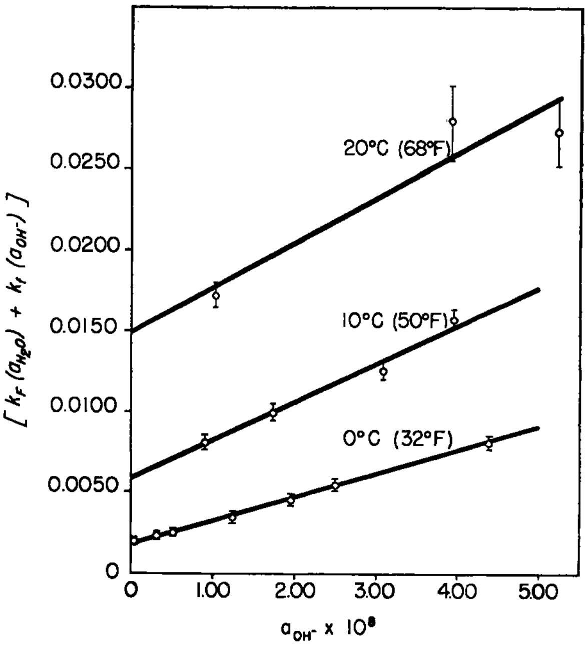

Fig. 5. Correlation of forward reaction rate data with hydroxyl ion activity.

and

$$\left(\frac{\gamma_{H^+}\gamma_{OH^-}}{a_{H_2O}}\right).$$

However, Harned and his co-workers (*3–6, 20*) have collected data which permit a calculation of these values in various concentrations of NaCl solution. Harned also has carried out some work in solutions of NaCl with $NaHCO_3$ concentrations up to .05 molar which showed that the HCO_3^- ion and the Cl^- ion could be considered to have identical activity effects (*35, 36*). A review of the activity coefficients calculated by Kielland indicated that the $\gamma_{HCO_3^-}$ and the γ_{Cl} are quite similar up to .10 molar solutions. It seemed sound, therefore, to say that the HCO_3^- ion and the Cl^- are approximately equivalent in ionic effects up to .50 molar, without introducing too great an error into the calculation of the ionic activity products required in the rate equations. Based on this assumption, it was possible to use the values tabulated by Harned and his co-workers to evaluate the quantity

$$\left(\frac{\gamma_{H^+}\gamma_{HCO_3^-}}{\gamma_{CO_2}a_{H_2O}}\right)$$

in Equation (29). Although the data of Harned are reported on a molal basis, the error involved in not converting the activity coefficient products to a molar basis was negligible compared to the errors inherent in extending Harned's data to this system.

EXPERIMENTAL METHOD

The experimental method used to determine the forward-and-reverse reaction constants from Equations (19) and (29) involved: (1) the equilibration of a solution of known ionic strength at a given pH and temperature in a stainless steel reaction vessel; (2) the injection of a sodium bicarbonate solution labelled with carbon-14 into the reaction vessel; (3) the withdrawal of liquid samples from the reaction vessel at various times after the injection of the tracer; (4) the release of carbon dioxide gas from the samples by flashing into evacuated sample bulbs; and (5) the transfer of the gas sample to a proportional counting tube for the determination of the $C^{14}O_2/C^{12}O_2$ ratio. A brief description of the apparatus used in the above steps will be given in the following sections, but complete details are available in the original thesis (*2*).

Reaction Tank and Sampling Apparatus

A schematic diagram of the reaction vessel and sampling tubes is shown in Figure 1. The reaction tank was made of 316 stainless steel and had a solution capacity of 4 gal. The eight sample collectors shown in Figure 1 were connected to outlets at the top of the reaction tank through $\frac{3}{8}$ in. toggle valves which were connected together so that they might be opened and closed simultaneously. At the bottom of the reaction tank the sample collectors were connected to outlets through $\frac{1}{4}$ in. solenoid valves which could also be opened and closed simultaneously.

The lid for the reaction vessel was machined to accommodate pH and conductivity electrodes, a stirrer, a thermometer well, and a connection to an 80-cm. Hg manometer. This lid was bolted to the vessel and a pressure seal obtained with a $6\frac{3}{4}$ in. "0" ring.

At the beginning of the experiment, after decontamination of the reaction vessel and allied apparatus from the previous run, sodium bicarbonate of proper normality was poured into the reaction tank until only about $\frac{1}{4}$ in. of free space remained over the liquid. The reaction vessel lid was attached, and CO_2 was introduced at the desired pressure into the system. After the gas and liquid phases had reached equilibrium, the gas collection tubes and liquid traps (Figure 1) were evacuated, and then 1 to 2 g. of tracer solution (0.1 to 1.0 mc./g.) were injected into the reaction vessel through a gate valve and rubber diaphragm with a hypodermic syringe. After a mixing time of 20 sec., the upper and lower valves leading to the sample collection tubes were opened, allowing the mercury in them to be replaced with solution from the reaction vessel. After 30 sec. both sets of valves were closed. This technique permitted collection of a liquid-phase sample only, and eliminated the problems involved in flashing CO_2 out of a liquid-gas system.

At the proper time interval for each sample: (a) the valve to the gas collection receiver was opened, (b) the air pressure inlet was opened at the same time to drive the liquid sample out of the collection bulb, and (c) the liquid ran into the first trap where the CO_2 flashed out into the gas tube receiver, which was then shut off from the trap. The gas samples thus obtained were then transferred to the counting tubes as described below. Two or three liquid samples were saved for titration to determine the amount of $C^{12}O_2$ and $HC^{14}O_3^-$ in the solution as required by Equations (19) or (29).

Transfer of Carbon Dioxide Samples to Counting Tubes

The radioactive carbon dioxide gas collected in the collection tubes was transferred to a proportional counting tube by means of the Bernstein-Ballentine transfer apparatus shown schematically in Figure 2. Details of the construction and use of this apparatus may be found in the literature (*2, 24, 25*). In order to measure accurately without a cathotometer the low pressures of carbon dioxide encountered, both a McLeod gauge and a butyl phthalate manometer were employed.

Proportional Counting Technique

Techniques of gas-phase analysis of C-14 are briefly described by Glastock (*25*). Among the various possible methods which might be utilized, proportional counting was selected because it is generally conceded to be more reliable and accurate than Geiger or ionization chamber counting (*25*). Among the methods of proportional counting available were those of Bernstein-Ballentine (*24*), Freedman and Anderson (*26*), Bradley, Holloway, and McFarlane (*27*), and Arrol and Glastock (*28*). The method of Bernstein and Ballentine was selected because of its simplicity and reliability, and also because the counting tubes and shield could be purchased commercially at a reasonable cost.

Bernstein and Ballentine found that for a given activity of radioactive C-14 the observed counting rate did not vary significantly with gas composition as long as the partial pressure of the carbon dioxide in the gas mixture used was under 100 mm. Hg. The lower the pressure of the carbon dioxide, the more extended the counting plateau became, and so a partial pressure of about 20 mm. CO_2 was chosen as being most desirable. In this work, various combinations of voltages and amplification factors were tried out to determine under what conditions the best counting plateau could be obtained with the equipment used. Sample curves are shown in Figure 3. A counting voltage of 4,350 v. was fixed as the operating voltage. Under these conditions the slope of the counting plateau was 0.8%/100 v. for a range of 400 v. (beginning at about 4,200 v.) at counting rates of 6,000 counts/min., and 1.2%/100 v. for rates 10 times as great.

The electronic equipment used in all analyses of radioactive samples is fully described elsewhere (*2*).

(1) *Calibration of Counting Tubes.* Calibration of the absolute counting rate was not required in this work since ratios of tracer quantities were used in the calculations, but was carried out as a check on the accuracy and reliability of the electronic equipment. This calibration also permitted the use of counting tubes of slightly different characteristics for counting gas samples from the same experimental run. A calibration curve was prepared for each tube by plotting the counts per minute vs. the millimoles of $C^{14}O_2$. The tubes had quite similar characteristics, and the slopes of the calibration curves agreed within 3%. The maximum deviation of any of the points from the least square slope was 3% for one tube and 2% for the other. No significant changes in the tube calibrations were noted over an eighteen-month period.

From calculations based on the mass spectrometer analysis of the C-14: C-12 ratio in the standard (N.B.S.) used for the calibrations, it was concluded that the counting tubes were counting at least 98% of all the disintegrations present, the same as reported by Bernstein-Ballentine in their work (*24*).

(2) *Procedure Used in Counting.* The counting tube, filled with the sample last counted, was again counted before refilling to determine if there was any variation in the counting rate from the rate formerly observed. No change was ever found, even over a period of six months, except in one instance when air leaked into the proportional tube. If no change was found, the counter was pumped out for 10 min. in the Bernstein-Ballentine apparatus, filled with 99% methane, and then a background count was taken. No difference in background was found to exist between a tube filled solely with methane and one filled with 20 mm. of $C^{12}O_2$ plus methane at one atmosphere. Finally, the methane was pumped out, and the tube was filled with a sample containing $C^{14}O_2$ and $C^{12}O_2$ from a new experimental run (plus methane). The filled tube was then transferred to the

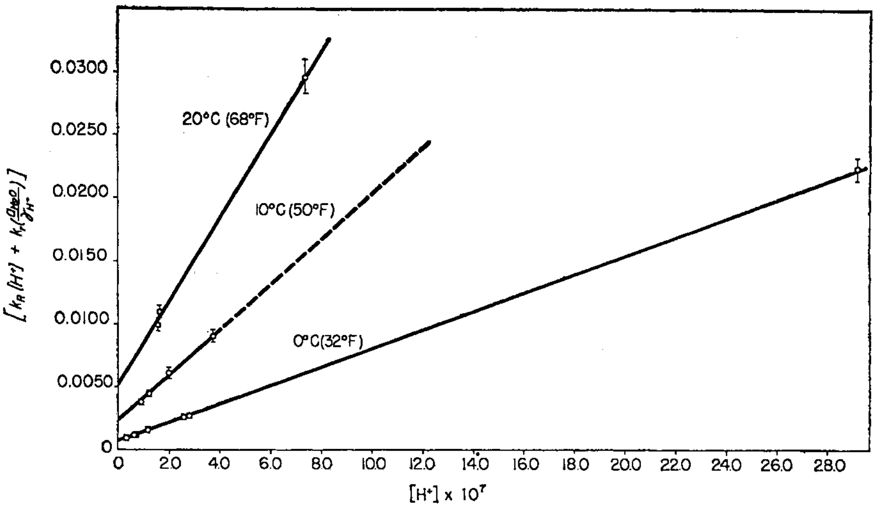

Fig. 6. Correlation of reverse reaction rate data with hydrogen ion concentration.

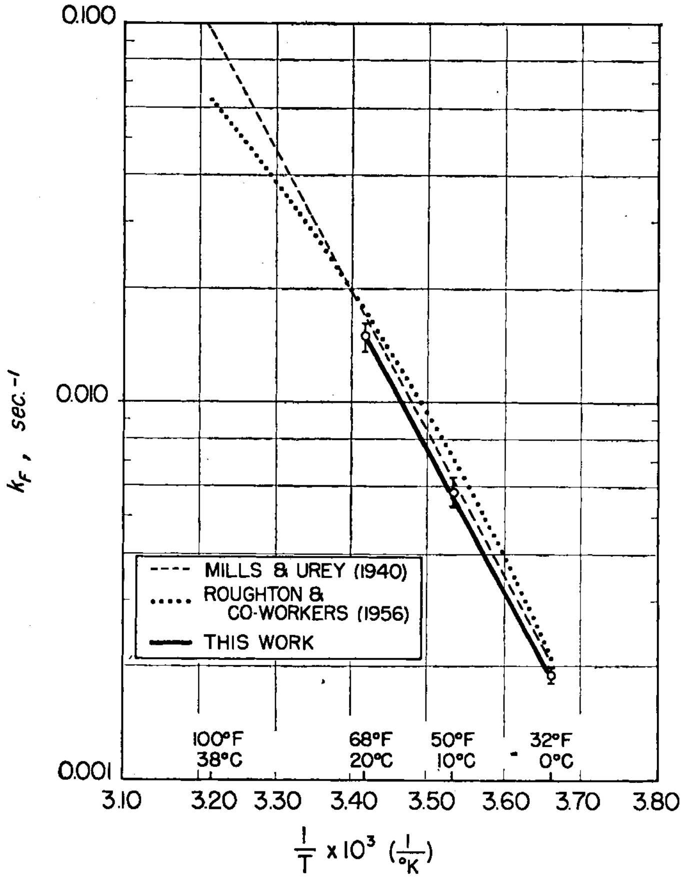

Fig. 7. Temperature dependence of the forward rate constant for the reaction:
$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$

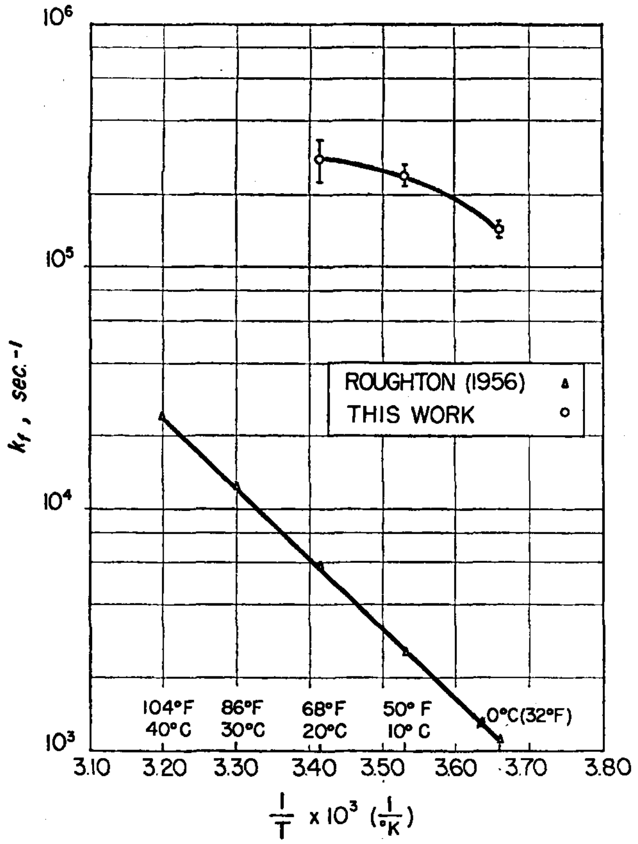

Fig. 8. Temperature dependence of the forward rate constant for the reaction: $CO_2 + OH^- \rightleftharpoons HCO_3^-$

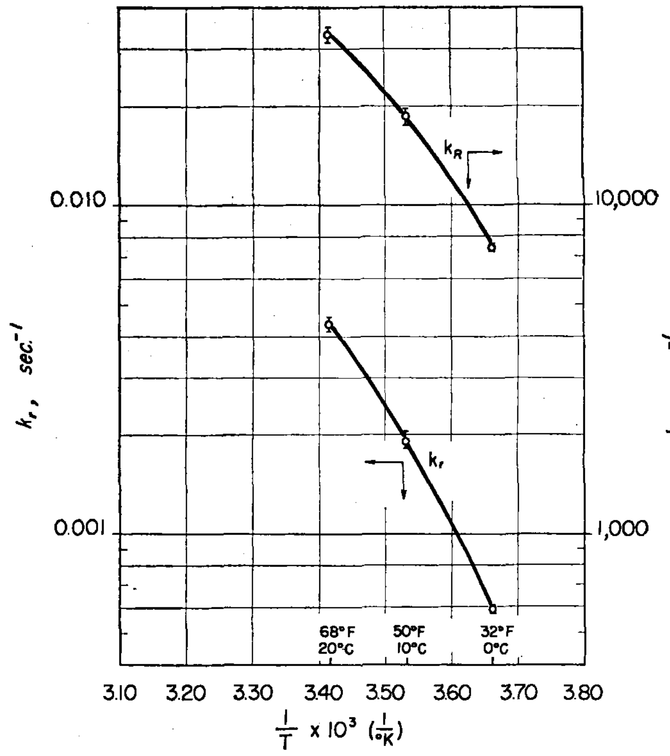

Fig. 9. The temperature dependence of the reverse reaction rate constants:

k_R for $CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$
k_r for $CO_2 + OH^- \rightleftharpoons HCO_3^-$

tube shield where it was connected to the counting apparatus.

Enough counts were taken to insure that the statistical error was below one half of one percent. This meant that 200,000-300,000 counts were required, amounting to 10 min. to 2 hr. counting time at the counting rates normally employed. Net counting rates ranged from 50,000 to 1,000 counts/min. The background, which averaged about 145 counts/min., was the same as noted by Bernstein and Ballentine (*24*). Counting was not continuous for any one sample, but broken up into 10, 20, or 30-min. periods so that any nonreproducibility of the counting rate could be readily detected.

RESULTS AND DISCUSSION

Sufficient data were obtained for each run to determine the values in the integrated forward-and-reverse reaction rate equations, and also to provide for verification of pH and ionic concentrations. The results of one run and the approximate error involved for each value of $(R_\infty - R)$ are shown in Figure 4. The slope of this line is determined from Equation (19) by

$$\text{slope} = \frac{\ln (R_\infty - R_2) - \ln (R_\infty - R_1)}{t_1 - t_2}$$
$$= (k_F(a_{H_2O}) + k_f(a_{OH^-}))\left(1 + \frac{[CO_2]}{[HCO_3^-]}\right) \quad (32a)$$

and from Equation (29) by

$$\text{slope} = \left(k_R[H^+] + \frac{k_r}{\gamma_{H^+}}\right) \quad (32b)$$
$$\cdot\left(1 + \frac{[HCO_3^-]}{[CO_2]}\right)\left(\frac{\gamma_{H^+}\gamma_{HCO_3^-}}{\gamma_{CO_2}a_{H_2O}}\right)(a_{H_2O})$$

The actual determination of slope was accomplished by a least-square method using variable weighting factors based on the concepts outlined by Bennett and Franklin (*30*). The weighting factors chosen were inversely proportional to the error involved in the measurement of $(R_\infty - R)$, i.e., the greater the error of $(R_\infty - R)$, the less the assigned weight. This determination was originally carried out with a desk calculator, but was later programmed for the IBM 650 computer with a great saving in time over the initial hand computer calculations.

Once the slope shown by Equation (32) had been calculated by the least-square method, the constant

$$\left(1 + \frac{[CO_2]}{[HCO_3^-]}\right) \text{ or } \left(1 + \frac{[HCO_3^-]}{[CO_2]}\right)$$

was determined in three ways:

(a) from pH readings on the pH meter

(b) from R^*/R_∞ [see Equations (21) and (30)]

(c) from titration data on samples taken from the reaction vessel

The value determined by method (c) was actually used; the others served as

Table 2. Forward and Reverse Reaction Rate Constants

Reactions: $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$		0°	10°	20°C.
k_F (sec.$^{-1}$)	$(\times 10^3)$	1.89 ± 7%	5.82 ± 10%	14.9 ± 10%
k_R (sec.$^{-1}$)	$(\times 10^{-4})$	0.74 ± 1%	1.85 ± 5%	3.32 ± 5%
$K_b = \frac{k_F}{k_R}$	$(\times 10^7)$	2.56	3.15	4.49
K_b $(\times 10^7)$	(data of Harned)	2.65	3.43	4.14
Reaction: $CO_2 + OH^- \rightleftharpoons HCO_3^-$				
k_f (sec.$^{-1}$)	$(\times 10^{-5})$	1.44 ± 5%	2.41 ± 10%	2.77 ± 20%
k_r (sec.$^{-1}$)	$(\times 10^3)$	0.591 ± 5%	1.93 ± 5%	4.35 ± 5%
$K_* = \frac{k_f}{k_r}$	$(\times 10^{-7})$	24.4	12.5	6.37
K_* $(\times 10^{-7})$	(data of Harned)	23.3	11.4	6.09

TABLE 3. COMPARISON OF VALUES OF k_F AND k_f WITH THOSE OF OTHER INVESTIGATORS

		k_F(sec.$^{-1}$) Reaction: $H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^-$					k_f(sec.$^{-1}$) Reaction: $CO_2 + OH^- \rightleftharpoons HCO_3^-$		
Investigator	Lit. Cited	0°C.	10°C.	20°C.	25°C.	38°C.	0°C.	10°C.	20°C.
Faurholt (1924)	(*8*)	.0030*					840*		
Roughton & Booth (1938)	(*10*)	.0021 .0027*							
Mills & Urey (1940).	(*15*)	.00205 ± 3% .0027*	.0059†	.0160 ± 6%	.0275	.10			
Pinsent & Roughton 1950).	(*14*)	.00205 ± 2%			.0337	.11	1050 ± 5%	2300 ± 15%	
Pinsent, Pearson & Roughton (1956).	(*31*)	.00205	.0065†	.0164	.0257	.0620	1095 ± 7%	2250 ± 5%	5900 ± 8%
This work		.00189 ± 7%	.00582 ± 10%	.0149 ± 10%			1.44×10^5 ± 5%	2.41×10^5 ± 10%	2.77×10^5 ± 20%

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*In buffered solution
†Interpolated value

checks. Then the expressions $[k_f(a_{H_2O}) + k_f(a_{OH^-})]$ and $[k_R[H^+] + k_r/\gamma_{H^+}]$ were calculated. These results are shown in Table 1.

In computing these expressions, the $(a_{H_2O}) = 1$, and the activity coefficient product $(\gamma_{H^+}\gamma_{HCO_3^-}/\gamma_{CO_2}a_{H_2O})$ were secured from the data of Harned (*6*). Plotting these two expressions vs. (a_{OH^-}) and $[H^+]$ respectively as shown in Figures 5 and 6 obtained linear functions as expected from Equations (19) and (29), and the individual values k_F, k_f, k_R, and k_r/γ_{H^+} could be found from the slopes and the intercepts of the least-square lines at each temperature. Using an average value of γ_{H^+} for each temperature introduced an error of less than 3%, and permitted the easy calculation of k_r. The values obtained for the forward and reverse reaction rate constants at 0, 10, and 20°C. are shown in Table 2. The reverse reaction rate constants in Table 2 and Figure 9 are reported for the first time.

Accuracy of Data and Results

The statistical error and coincidence losses in the gas-phase counting were less than 0.5%. The reproducibility of sample counting was governed primarily by the reliability of the high voltage supply which was ±1% of the output voltage. An over-all estimate of the error involved in the value of R_f for each sample must also include the cumulative experimental error in handling the gas samples in the Bernstein-Ballentine apparatus, and amounts to about 3%. The value of the constant

$$\frac{[CO_2]}{[HCO_3^-]}$$

as determined by titration methods was usually known within 4% which permitted the values of the constants

$$\left(1 + \frac{[CO_2]}{[HCO_3^-]}\right)$$

and

$$\left(1 + \frac{[HCO_3^-]}{[CO_2]}\right)$$

to be still more reliable. The activity coefficients of Kielland introduced an error of approximately 5% into the calculation of the rate constants, while the activity coefficient products secured from the data of Harned were good to at least 1%. The error limits shown in Table 2 were computed by the standard technique for determining confidence limits (for 9 chances out of 10) as described in Bennett and Franklin (*29*). The higher errors at 10 and 20°C. are primarily due to the lesser number of runs carried out at these temperatures as compared with 0°C.

Comparison of Results with Those of Other Investigators

The calculated values of the forward rate constants are compared with those reported by previous investigators in Table 3 and in Figures 7 and 8. It will be noted that the values of k_F are slightly lower than those reported by Roughton, and Mills and Urey. Although the range of error involved might explain this deviation, it is believed that previous investigators' values for k_F are slightly high for the reasons to be discussed shortly. The values of k_f appear to be of a different order of magnitude from the previously reported values of Faurholt and Roughton. These workers noted no effect of reaction (5*c*) $(CO_2 + OH^- \rightleftharpoons HCO_3^-)$ below a *p*H of 8 while in this study the influence of this reaction was recorded as low as a *p*H of 6. At a *p*H of 7.5, it was found to provide a greater effect on the value of $[k_F(a_{H_2O}) + k_f(a_{OH^-})]$ than reaction (5*b*) $(CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+)$.

Dividing the forward reaction rate constant by the reverse reaction rate constant as shown in Table 2 made possible the computing of the equilibrium constants for reactions (5*b*) and (5*c*). These values agreed well with the generally accepted equilibrium constants for this system determined by Harned and his co-workers.

Mills and Urey set up three simultaneous differential equations for the exchange of O^{18} as a function rate of the hydration of CO_2 which were valid in the *p*H range where only hydration occurred (they assumed the dissociation of H_2CO_3 was rapid). Based on the work of Faurholt, which was the only investigation completed at that time on the reaction of CO_2 and OH^-, they assumed that the hydration of CO_2 was the sole reaction in their system below a *p*H of 8. After a number of simplifying assumptions were made, it was possible to solve their differential equations in terms of rate constants and other constants which could be determined experimentally. A review of the published results at 0°C. (*15*) shows a linear decrease of $k_F(a_{H_2O})$ from .0021 to .00093 with increasing

$$\frac{[HCO_3^-]}{[CO_2]}$$

ratio for values of this ratio from 0 to 11.2. In effect, this is the same as a *p*H range of about 4 to 8, or an OH^- range of about $.001 \times 10^{-8}$ to 10×10^{-8} in the solutions actually used. They felt this deviation from the value of k_F in acid solution was due to experimental error, but it seems more probable, in view of the value of k_f discovered in this work, that their assumption that only the hydration reaction was functioning was slightly in error. As the *p*H or $(OH^-]$ increased, a correction should have been made for the effect of the $CO_2 + OH^- \rightleftharpoons HCO_3^-$ reaction. The values of Mills and Urey for k_F in acid solutions (*p*H less than 5) would be valid if activity corrections had been applied. Since the ionic strengths of their acid solutions varied from .01 to .36, not enough data are published in their paper to re-evaluate k_F with proper corrections for activity coefficients.

Roughton and his co-workers have published several articles with values for k_F showing close agreement with those of Mills and Urey (below 25°C.). A careful perusal of their "boat" technique (*14*) indicates that $.04M$ to $.15M$ $K_2HPO_4 - KH_2PO_4$ solutions (*p*H of about 7 to 8) were used to establish the values of k_F. The value of k_F was actually determined by extrapolating to zero concentration of buffer and correcting for reaction (5*c*) by a small amount, about −4% at 15°C. Utilizing the results of the present work convinces one that this correction was not large enough, although the magnitude of the proper correction is not quite certain in view of the lack of information about the theoretical pH in infinitely dilute buffer solutions containing CO_2 and HCO_3^-. Furthermore, the technique of measuring the change of k_F with change of concentration of buffer introduces an additional variable since the pH of the solution is varying as this extrapolation is carried out.

An examination of the values of k_f in Table 3 discloses such large differences between the reported results in this study and those of Roughton that the question arises immediately whether the same phenomena are being measured. A possible explanation of this difference lies in unsuspected mass transfer effects entering into both the rapid thermal and "boat" techniques. In any system in which a chemical reaction takes place, unless the constituents are intimately mixed at the start of the reaction, the reactants must move into the points of reaction, and the products move away from these points. Consequently, as the rate constant increases for a given reaction under a given set of experimental conditions, a point will be reached where the actual rate of reaction is more rapid than the speed of movement of the reactants together and/or the speed of movement of the products away. Then the controlling process for the over-all reaction (which is what is actually measured) becomes a function of the mass transfer aspects of the system. Matsuyama (*32*), for example, indicates that for contact times of less than 5/1000 of a second, complete uniform distribution of reactants may not take place, although a reproducible degree of mixing may be achieved.

SUMMARY

Values for the forward and reverse reaction rate constants for the reactions $CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$ and $CO_2 + OH^- \rightleftharpoons HCO_3^-$ have been determined at 32, 50, and 68°F. and in a pH range of 5.6 to 7.6 by use of a radioactive tracer technique. Since measurements were taken at physical and chemical equilibrium, the problem of segregating kinetic from mass transfer effects has been eliminated. Results for the forward rate constants for the reaction $CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$ were 8% lower than those of previous investigators, which is believed due to improper correction for the reaction $CO_2 + OH^- \rightleftharpoons HCO_3^-$. The forward rate constants for this reaction were found to be about 100 times greater than the previously published values. Calculated values for the equilibrium constants for these two reactions agreed within 6% on the average with those given by Harned and Owen.

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NOTATION

a = activity of component indicated by subscript

C, C' = constants of integration

k_1 = forward reaction rate constant for the reaction $CO_2 + H_2O \rightleftharpoons H_2CO_3$, sec.$^{-1}$

k_2 = reverse reaction rate constant for the reaction $CO_2 + H_2O \rightleftharpoons H_2CO_3$, sec.$^{-1}$

k_3 = forward reaction rate constant for the reaction $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$, sec.$^{-1}$

k_4 = reverse reaction rate constant for the reaction $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$, sec.$^{-1}$

k_f = forward reaction rate constant for the reaction $CO_2 + OH^- \rightleftharpoons HCO_3^-$ sec.$^{-1}$

k_F = forward reaction rate constant for the reaction $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$, sec.$^{-1}$

k_r = reverse reaction rate constant for the reaction $CO_2 + OH^- \rightleftharpoons HCO_3^-$, sec.$^{-1}$

k_R = reverse reaction rate constant for the reaction $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$, sec.$^{-1}$

K_a = apparent equilibrium constant for reaction $CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$

K_b = equilibrium constant for reaction $CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$

K_c = equilibrium constant for reaction $CO_2 + H_2O \rightleftharpoons H_2CO_3$

K_t = true equilibrium constant for reaction $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

K_* = equilibrium constant for reaction $CO_2 + OH^- \rightleftharpoons HCO_3^-$

K_w = ionization constant for water $(H^+ + OH^- \rightleftharpoons H_2O)$

r = reaction rate, change of activity per unit time

R = ratio of C-14 to C-12 in counting gas at any time t

R_∞ = ratio of C-14 to C-12 in counting gas at isotopic equilibrium $(t = \infty)$

R_0 = ratio of C-14 to C-12 in counting gas at $t = 0$

R^* = ratio of concentration of tracer injected as bicarbonate C-14 at $t = 0$ to concentration of bicarbonate in form of C-12

t = time, sec.

Subscripts

o = initial

∞ = at infinite time

Greek Letters

γ = activity coefficient of component indicated by subscript

μ = total ionic strength

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