[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The First Ionization Constant of Carbonic Acid, 0 to 38°, from Conductance Measurements

BY THEODORE SHEDLOVSKY AND D. A. MACINNES

Since the appearance of a paper, from this Laboratory, on the ionization of carbonic acid[1] at 25° our attention has been called to two monographs by Kauko,[2] a monograph by Buch and others,[3] and to an abstract of a recent paper by Carlberg.[4] In these publications support is given, by examination of the literature and by new experimental work, to the value 3.5×10^{-7} for the first ionization constant of carbonic acid at 25°. This figure was apparently generally accepted until the appearance of the work by MacInnes and Belcher, who obtained the value of 4.5×10^{-7}. Because of the importance of carbon dioxide in biology, geology and chemistry, an accurate knowledge of its physicochemical constants is of considerable interest.

To test the results of MacInnes and Belcher, who worked with concentration cells without liquid junctions, and glass electrodes, we have redetermined the first ionization constant of carbonic acid from conductance measurements. The two methods are quite independent since they rest on very different fundamental principles. The present work includes measurements in the temperature range from 0 to 38°. From these data the heats of reaction, as well as the thermodynamic mass action constants for the primary ionization of aqueous carbonic acid, have been computed.

The thermodynamic ionization constant K_1 for the reaction $H_2O + CO_2 = H^+ + HCO_3^-$[5] may be computed by means of the familiar equation

$$K_1 = CX^2f^2/(1 - X) \qquad (1)$$

in which C is the concentration, X the degree of ionization and f the mean ion activity coefficient. The degree of ionization may be obtained from conductivity measurements by the relation

$$X = \Lambda_c/\Lambda_\epsilon \qquad (2)$$

Λ_c being the equivalent conductance and Λ_ϵ the equivalent conductance if the carbonic acid were completely dissociated as a monobasic acid. Values of Λ_ϵ may be computed from conductance measurements on "strong" electrolytes by means of the relation

$$\Lambda_{\epsilon H_2CO_3} = \Lambda_{H^+Cl^-} - \Lambda_{K^+Cl^-} + \Lambda_{K^+HCO_3^-} \qquad (3)$$

these Λ values all being at the same ion concentration, CX. For ion concentrations up to 0.001 N Λ_ϵ may also be obtained from the Onsager equation

$$\Lambda_\epsilon = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{CX} \qquad (4)$$

in which Λ_0 is the limiting conductance of carbonic acid, as a monobasic acid, and α and β are theoretical constants dependent upon the temperature, the dielectric constant, and universal constants, and in the case of β also upon the viscosity. Since the value of X depends upon Λ_ϵ, the computation is most easily made by a short series of approximations. For the low ion concentrations involved in the present work the activity coefficient f may be computed with the aid of the Debye–Hückel formula

$$-\log f = A\sqrt{CX} \qquad (5)$$

in which the coefficient A is a function of the temperature, the dielectric constant and universal constants. With K_1 known for one temperature (25°), its value at other temperatures may be determined if the temperature coefficients of Λ and Λ_ϵ are known for a given carbonic acid solution. These coefficients were determined, in the course of the research, from measurements on dilute solutions of carbonic acid, hydrochloric acid, and of potassium chloride and bicarbonate. The principles underlying the computations are as follows. On dividing the expression for the thermodynamic ionization constant K_t at the temperature t by the corresponding expression for the reference temperature (25°) we have

$$\frac{K_t}{K_{25}} = \left[\frac{\Lambda_{ct}/\Lambda_{\epsilon t}}{\Lambda_{c25}/\Lambda_{\epsilon 25}}\right]^2 \frac{C_t f_t^2}{C_{25} f_{25}^2} \times \frac{(1 - \Lambda_{c25}/\Lambda_{\epsilon 25})}{(1 - \Lambda_{ct}/\Lambda_{\epsilon t})} \qquad (6)$$

Of the terms in this equation, the ratio C_t/C_{25} is, for dilute solutions of carbonic acid, equal to the ratio of the densities of water at the two temperatures. By making all the conductance measure-

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(1) MacInnes and Belcher, THIS JOURNAL, **55**, 2630 (1933).

(2) Y. Kauko, *Ann. Acad. Scientiarum Fennicae*, Series A, **39**, Nos. 1 and 3.

(3) Buch, Harvey, Wattenberg and Gripenberg, "Über das Kohlensäuresystem im Meerwasser," Høst and Sons, Copenhagen, 1932.

(4) J. Carlberg, *Suomen. Chem.*, **7**, B91–92 (1934); *British Chem. Abs.*, **1777** (1934). (The original publication is not available in the U. S. A.)

(5) This reaction consists, of course, of a hydration $H_2O + CO_2 = H_2CO_3$ followed by partial ionization $H_2CO_3 = H^+ + HCO_3^-$.

ments in the same cell small changes with temperature of the cell constant and of concentration tend to cancel out of the ratios $\Lambda_{ct}/\Lambda_{et}$ and $\Lambda_{c25}/\Lambda_{e25}$. From Λ_{25} values at 0.001 N, and the temperature coefficients of the three strong electrolytes mentioned above, Λ_{et} at that ion concentration is obtained for 0, 15 and 38°, using equation (3). From these Λ_{et} values and equation (4), Λ_{0t} for each of these temperatures is found using the appropriate constants α and β. With these figures it is possible to obtain Λ_{et} for any of the temperatures concerned and for any ion concentration, CX, for which equation (4) is valid. However, to compute values of CX at a temperature t it is necessary to know K_t. Since f_t^2 and $(1 - \Lambda_{ct}/\Lambda_{et})$ are both nearly unity for very weak electrolytes, a preliminary value for this constant is found from

$$\frac{K_t}{K_{25}} = \left[\frac{\Lambda_{ct}/\Lambda_{0t}}{\Lambda_{c25}/\Lambda_{025}}\right]^2 \text{ (approximately)} \qquad (7)$$

With this value an estimate of CX is made, using equation (1), from which Λ_{et} and f_t^2 are computed with equations (4) and (5). A more exact evaluation of K_t is then made with equation (6), but, due to the rapid convergence of the functions for this case, it is not necessary to continue the series of approximations any further. In addition to the ionization constants, the heat of the ionization process as a function of the temperature was also obtained from the experimental data.

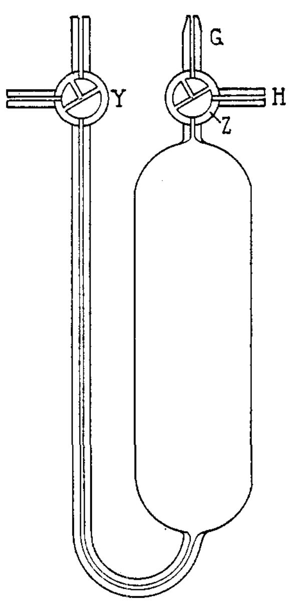

Fig 1.

Experimental

(a) Carbonic Acid Solutions.—The carbon dioxide used in most of our work was pure liquid carbon dioxide, obtained from a commercial source. It was stored in a "siphon type" tank which had been thoroughly rinsed with the gas before filling. Numerous analyses of the gas taken from this tank showed that it was at least 99.97% pure. However, measurements were also made with carbon dioxide from two other sources: gas was generated by the action of phosphoric acid on a saturated solution of purified potassium bicarbonate, and also by the sublimation of solid carbon dioxide. The results of measurements on solutions prepared from the three different sources agreed within the experimental error. Because of the volatility of carbon dioxide, a special technique was necessary for preparing and keeping solutions of definite known composition. For that reason a special conductivity cell was designed in which it was possible to prepare solutions by dissolving measured volumes of the gas in a known volume of water, leaving no residual gas phase. These definite volumes of the gas were obtained by the use of bulbs of the type shown in Fig. 1. The bulbs, which had volumes varying from 20 to 250 cc., were filled in a thermostat at 25° with pure dry carbon dioxide by passing the gas through them until a sample taken from the outlet G proved by analysis to be at least 99.97% pure. For the analysis the apparatus shown in Fig. 2 was used. The gas sample filled the chamber P, which had a volume of about 100 cc. To absorb the gas a 30% solution of potassium hydroxide was then admitted from the cylinder Q through the stopcock K. The capillary tube, T, was calibrated so that the purity of the sample could be read from the length of the residual gas bubble, 4 mm. of gas in the capillary corresponding to 0.01% impurity. The number of moles of carbon dioxide in a bulb of the type shown in Fig. 1 was computed from the accurately known volume, the temperature (25°), and the barometric pressure. The latter was obtained from readings of a recently calibrated barometer, to which the usual corrections were applied.

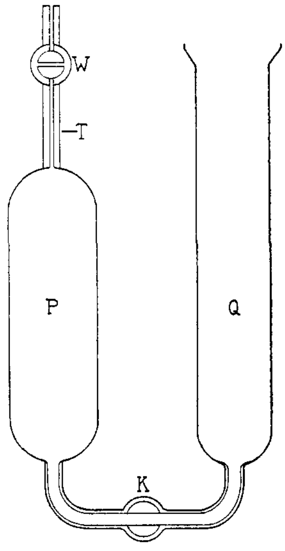

Fig. 2.

The molal volume $\overline{V}$ in liters of carbon dioxide, near atmospheric pressure and at ordinary temperatures, was computed, using the equation

$$\overline{V} = 6.236T/P(1 + aP) \qquad (8)$$

obtained from the data of Cooper and Maass,[6] in which T is the absolute temperature, P the pressure in cm., and $a = [8.88 \times 10^{-5} - 1.09 \times 10^{-6}(T - 273.1)]$. The term is a measure of the deviation in the behavior of carbon dioxide from that of a perfect gas.

The solutions were prepared from accurately known amounts of carbon dioxide by introducing them directly into water in the special conductivity cell shown in Fig. 3. For this purpose it was necessary to have gas-free water ready in the cell, since dissolved air, if not removed, will be "salted out" by the carbon dioxide. The cell was therefore nearly filled with conductivity water and the air was pumped off at C through the three-way stopcock S_1, with the similar stopcock S_2 closed. The cell was then filled completely with conductivity water from the reservoir, V, by turning S_2. The liquid in the cell could be

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(6) Cooper and Maass, *Can. J. Research*, **4**, 283 (1931). See also Beattie and Bridgeman, THIS JOURNAL, **50**, 3133 (1928).

effectively stirred with the floating glass bubble B by turning the apparatus over and over. The glass cross X, fused into the cell, kept the float B from hitting the electrodes, E. To prevent the mercury in the glass tubes M from spilling during this agitation the upper parts of the tubes were filled with paraffin. The stopcocks S_1 and S_2 were lubricated with a grease which had been repeatedly extracted with water, and was shown to have a negligible effect on the conductance of the solutions.

The cell was placed in an oil-filled thermostat and the electrodes E, which were lightly platinized, were connected to the conductivity bridge through the copper wires L. The bridge and thermostat have already been described in a communication from this Laboratory.[7] In no instance was the specific conductance of the water used greater than $3 \times 10^{-7}\ \Omega^{-1}$. Since this conductance has been shown to be due principally to traces of carbon dioxide no solvent correction was necessary.

The actual procedure in making a solution was as follows. With the cell I (Fig. 3) clamped in a horizontal position, and the capillary tube A pointing downward, connection was made to tube G of the gas bulb (Fig. 1), through a ground joint. The capillary passage between the stopcocks Z (Fig. 1) and S_1 (Fig. 3) was evacuated through C, and finally the carbon dioxide was swept from the bulb into the cell by displacing it with pure mercury which entered through the stopcock Y of Fig. 1. The stopcock S_2 was turned momentarily so as to expel a small quantity of solvent into the reservoir V. When all of the gas had been transferred to the cell, the stopcock S_1 was closed, care being taken in this procedure not to introduce any mercury into the cell. The cell was then removed from its support and the solution shaken. As the residual bubble of carbon dioxide was absorbed, more water was admitted from the reservoir V, until finally no gas phase (or a bubble of negligible volume) remained. The solution was next thoroughly mixed with the aid of the glass float B, and placed in the thermostat at 25°. After thermal equilibrium had been established the conductance was measured, and the solution was again mixed until a constant value was obtained. The concentration of the solution was computed by means of equation (8) and the relation

$$C = v/\bar{V} \times W \text{ moles/liter} \qquad (9)$$

where v is the volume of the gas bulb, $\bar{V}$ the molal volume of carbon dioxide, and W the volume (which had been accurately determined) of the cell.

In the preparation and measurement of saturated solutions of carbonic acid, which have a concentration of about 0.033 molal, another procedure was adopted. Such solutions were prepared in a rocking apparatus similar to that described by MacInnes and Belcher.[1] Samples saturated at 25° were withdrawn directly into a small conductivity cell of the type described by Jones and Bollinger.[8] This cell, II, had a volume of about 10 cc. and a constant of 0.8052. Samples were also withdrawn for chemical analysis through a long slender capillary tube into calibrated 150-cc. volumetric flasks containing, under an atmosphere of nitrogen, a known excess of standard barium hydroxide solution. The carbonic acid was introduced below the alkali liquid level until the flask was filled just to the graduation mark, when the capillary was withdrawn. The contents of the flasks, containing the insoluble carbonate and an excess of hydroxide, were transferred to a titration vessel in which the liquid was agitated with a stream of nitrogen. Excess alkali was then titrated with standard hydrochloric acid, using phenolphthalein as an indicator. From this analysis the concentration of the carbonic acid solution was obtained with an accuracy of about 0.1%. The standard barium hydroxide solution also contained barium chloride, and was protected from atmospheric carbon dioxide. It was analyzed with standard hydrochloric acid, and also with potassium acid phthalate certified by the Bureau of Standards.

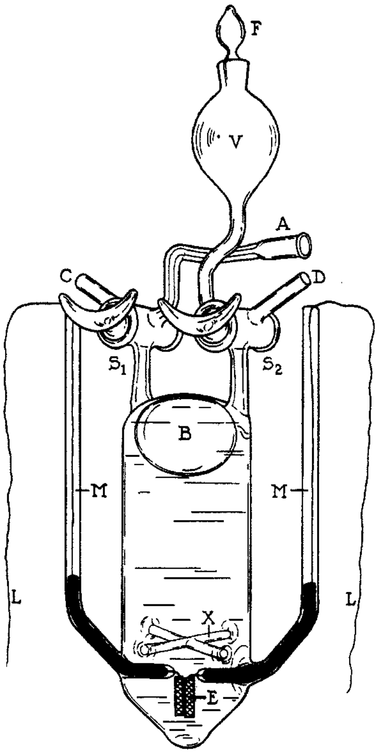

Fig. 3.

To provide a direct comparison between the results of the technique used in preparing the dilute carbonic acid solutions and the results from the chemical analysis, solutions of about 0.02 normal were prepared in cell I by the first method and were subsequently analyzed, after determining their conductances. The samples were displaced from the cell with pure mercury so as not to disturb the concentration by the presence of a gas phase. Concentration values corresponding to the analyses checked those computed from the volumes of gas and solution within 0.2%.

(b) **Potassium Bicarbonate Solutions.**—Pure potassium bicarbonate was prepared by recrystallizing a good grade of the salt from conductivity water saturated with carbon dioxide. The crystals were drained by centrifuging and were dried to constant weight in a desiccator over "dessichlora." A stock solution, about 0.1 molar, was made up accurately by weight and brought to a known pH value (slightly under 7) with carbon dioxide. The

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[7] Shedlovsky, THIS JOURNAL, **52**, 1793 (1930).

[8] Jones and Bollinger, *ibid.*, **53**, 411 (1931).

conductances at 25° of a series of dilute solutions were determined. The necessary solvent correction was made by a method already described for the quite analogous case of the hydrolyzable salt, sodium acetate.[9]

(c) **Temperature Coefficients.**—The ionization constants at temperatures other than 25° were obtained from measurements of temperature coefficients of solutions of hydrochloric acid, potassium bicarbonate, and potassium chloride, each at a concentration of 0.001 normal, and of saturated solutions of carbonic acid. The conductivity cell II was filled with a solution and its conductance measured at 25°, then at another temperature (0, 15 or 38°) in another thermostat, and again at 25°. This procedure was adopted to detect any possible change in the solution during this process, but in no case was the difference between the two measurements at 25° greater than ±0.05%. Since each solution was measured at the various temperatures in the same cell, changes in cell constant, as well as changes in concentration, with temperature canceled out in the equivalent conductance *ratios* required in the subsequent computations.

Results

The conductance data obtained for solutions of potassium bicarbonate at 25° are given in Table I. The limiting conductance, $\Lambda_0 = 118.00$, was obtained by extrapolating graphically from a linear plot of $\Lambda_0' = (\Lambda + \beta\sqrt{C})/(1 - \alpha\sqrt{C})$ against the concentration C.[10] In this equation α and β are the theoretical Onsager constants and have values of 0.2274 and 59.79, respectively, at 25°. The conductance equation for dilute solutions of potassium bicarbonate is, accordingly

$$\frac{\Lambda + 59.79\sqrt{C}}{1 - 0.2274\sqrt{C}} = 118.00 + 76.0\,C$$

A comparison between the experimental values and those computed from this equation also appears in Table I.

TABLE I

THE EQUIVALENT CONDUCTANCE OF POTASSIUM BICARBONATE AT 25°

$C \times 10^3$	$\sqrt{C}$	Λ obs.	Λ computed
0	0	....	118.00
0.8773	0.02962	115.55	115.51
1.8312	.04279	114.48	114.43
4.4866	.06698	112.50	112.54
10.571	.10282	109.83	109.87
19.639	.14014	107.27	107.30

The limiting equivalent conductance of carbonic acid at 25°, $\Lambda_0 = 394.2$, as a monobasic acid was obtained by combining the Λ_0 value of potassium bicarbonate with those of hydrochloric acid and potassium chloride. The latter constants were taken from the work of Shedlovsky.[11] Substituting this value in equation (4) gives

$$\Lambda_\epsilon = 394.2 - 149.4\sqrt{CX} \qquad (4')$$

for carbonic acid at 25°.

The conductance data obtained for carbonic acid solutions at 25° are listed in columns 1 and 2 of Table II. The corresponding values of Λ_ϵ, of the ionization function, $K_1' = CX^2/(1-X)$, and of the thermodynamic ionization constant, $K_1 = K_1'f^2$, appear in the following three columns. The source of the gas and the measurements for which the concentration was determined by chemical analysis are indicated in the last column of the table.[12] The average value for the thermodynamic ionization constant, $K_{25} = 4.310 \times 10^{-7}$ is probably correct within 0.1% although, as might be expected, the experimental error is greater for the lower concentrations.

TABLE II

EQUIVALENT CONDUCTANCES AND FIRST IONIZATION CONSTANT VALUES FOR CARBONIC ACID AT 25°

Concn. $C \times 10^3$	Λ_c	Λ_ϵ	$K_1' \times 10^7$	$K_1 \times 10^7$	Source of CO_2
1.867	5.854	393.4	4.316	4.265	Solid
1.869	5.977	393.4	4.379	4.325	Tank
1.881	5.941	393.4	4.354	4.300	Tank
1.918	5.877	393.4	4.345	4.291	$KHCO_3 + H_3PO_4$
5.093	3.632	393.2	4.385	4.315	$KHCO_3 + H_3PO_4$
5.096	3.642	393.2	4.413	4.342	Tank
5.101	3.623	393.2	4.416	4.345	Tank
5.112	3.617	393.2	4.367	4.297	Tank
5.125	3.595	393.2	4.324	4.256	Tank
10.572	2.521	393.0	4.397	4.295	Tank
10.877	2.493	393.0	4.404	4.320	Tank
10.890	2.490	393.0	4.400	4.316	$KHCO_3 + H_3PO_4$
10.985	2.476	393.0	4.388	4.304	Tank
21.40	1.780	392.7	4.417	4.317	Tank concn. detd. by chem. analysis
21.78	1.763	392.7	4.409	4.309	
32.20	1.453	392.6	4.418	4.306	
32.24	1.452	392.6	4.429	4.317	
32.47	1.449	392.6	4.437	4.325	
32.73	1.439	392.6	4.415	4.303	
32.73	1.439	392.6	4.415	4.303	
			Average	4.310 ± 0.004	

TABLE III

DATA FOR COMPUTING Λ_ϵ FOR CARBONIC ACID AT VARIOUS TEMPERATURES

	Λ for C = 0.001				H_2CO_3	
t	HCl	$KHCO_3$	KCl	A	Λ_0	$\alpha\Lambda_0 + \beta$
0°	263.6	62.2	80.4	0.483	248.0	83.2
15°	358.9	92.9	119.0	.495	336.7	121.1
25°	421.2	115.3	146.9	.506	394.2	149.4
38°	498.7	146.4	185.0	.527	466.1	190.3

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(9) MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932).

(10) Shedlovsky, *ibid.*, **54**, 1405 (1932).

(11) Shedlovsky, *ibid.*, **54**, 1411 (1932).

(12) In the case of the saturated carbonic acid solutions it was possible to obtain Henry's law constant for carbon dioxide at 25° from the concentration values and the corresponding barometer readings. The result obtained was 0.03372 ± 0.00005 mole, per liter, per atmosphere.

The equivalent conductances of completely dissociated carbonic acid, Λ_e, at other temperatures than 25° were obtained from measurements (Table III) on conductances of hydrochloric acid, potassium chloride and potassium bicarbonate solutions, each at 0.001 normal. The values of Λ_0 and of the factor $(\alpha\Lambda_0 + \beta)$ of equation (4) for carbonic acid, used in computing Λ_e at the various temperatures, are listed in the last two columns of the table. Column 5 contains the Debye–Hückel coefficients A of equation (5), used in obtaining the activity coefficients, f.

The quantities required for computing the first ionization constant K_1 at the various temperatures are given in the first five columns of Table IV. It includes the conductance values for a carbonic acid solution which was 0.03275 normal at 25°. Values of K_1 are listed in column 6, and the pK_1 values (*i. e.*, $-\log K_1$) in column 7. A plot of these pK_1 values, indicated by black circles, against the reciprocal of the corresponding absolute temperatures is given in Fig. 4. This plot also includes pK_1 values obtained from the results of other workers.[13] The curve through our experimental points is not linear, as would have been the case if the change in heat content, ΔH, for the reaction $CO_2 + H_2O = H^+ + HCO_3^-$ were independent of the temperature. The heat quantity ΔH may be obtained from the thermodynamic equation

$$d(\ln K_1) = (\Delta H/RT^2)dT \qquad (10)$$

or its equivalent form

$$d(pK_1)/d(1/T) = \Delta H/R \qquad (10')$$

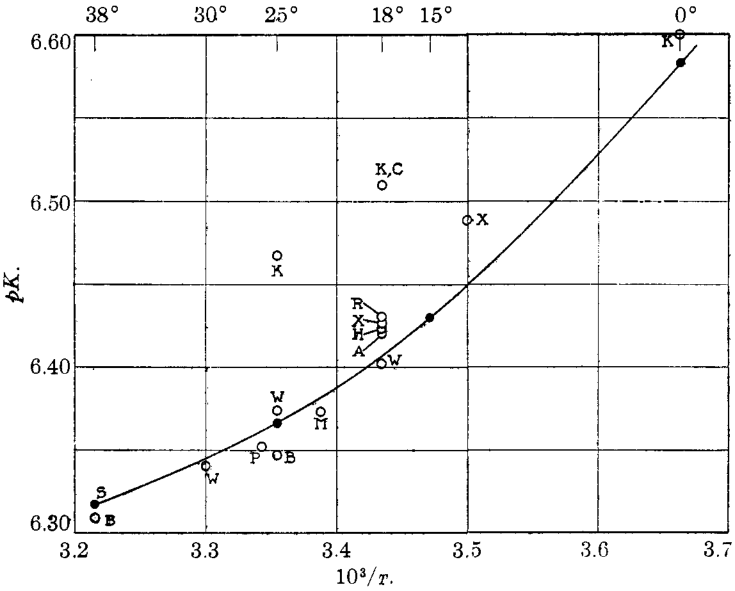

Fig. 4.—Primary ionization constant of carbonic acid: A, Stadie and Hawes, *J. Biol. Chem.*, **77**, 265 (1928); **B**, MacInnes and Belcher, THIS JOURNAL, **55**, 2630 (1933); **57**, 1683 (1935); C, Walker and Cormack, *J. Chem. Soc.*, **77**, 5 (1900); H, Hasselbalch, *Biochem. Z.*, **30**, 317 (1910); **78**, 112 (1916–1917); K, Kendall, THIS JOURNAL, **38**, 1480 (1916); M, Michaelis and Rona, *Biochem. Z.*, **67**, 182 (1914); P, Wilson, Orcutt and Peterson, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 356 (1932); R, Brinkman, Margaria and Roughton, *Proc. Roy. Soc.* (London), **A232**, 95, (1933); S, Hastings and Sendroy, *J. Biol. Chem.*, **65**, 445 (1925); W, Wilke, *Z. anorg. Chem.*, **119**, 365 (1921); X, Knox, *Wied. Ann.*, **54**, 44 (1895).

in which R is the gas constant and T is the absolute temperature.

As can be readily seen from equation (10′) values of ΔH can be obtained from the slope at any desired point of the curve given in Fig. 4. The heat ΔH thus obtained was found to vary nearly but not quite in a linear manner with the temperature and could therefore be expressed by the equation

$$\Delta H = \Delta H_0 + AT + BT^2 \qquad (11)$$

in which ΔH_0, A and B are constants. Substituting equation (11) in equation (10) and performing the integration there results

$$R \ln K_1 = -\Delta H_0 + A \ln T + BT + D \qquad (12)$$

The constants in this equation were determined from the experimental values of K_1 at the various temperatures and the following numerical equations were obtained

$$\Delta H = 78{,}011 - 427.6\,T + 0.5799\,T^2 \qquad (11')$$

$$pK_1 = (17{,}052/T) + 215.21 \log T - 0.12675\,T - 545.560 \qquad (12')$$

Columns 7 and 8 in Table IV give the observed pK_1 values and those computed from equation (12′). An examination of equation (11′) shows

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(13) Some of these pK_1 values have been corrected as indicated below: (a) P and M, for the pH scale, $E_0 = 0.3376$ to $E_0 = 0.3358$ at 25° (see "Cold Spring Harbor Symposia on Quantitative Biology," Long Island Biological Association, **1**, 190 (1933)); (b) B, at 25° for Henry's law constant given in this paper; (c) S, $pK = 6.33$ changed to 6.316 (private communication from Dr. Sendroy); (d) the values W have been recomputed, using our figures for Λ_0 at the various temperatures, since Wilke's estimates of this factor were not derived from actual measurements but from computations based on a rough generalization by Walden. In his paper, Wilke presents two series of measurements on the conductance of carbonic acid solutions: one series was obtained with a cell having platinized platinum electrodes, and another using a large cell with large gold-plated copper electrodes. The latter gave lower conductance values which the author preferred because they were in closer agreement with Kendall's measurements. However, we consider them less trustworthy than the former, since such electrodes may produce relatively large errors. See Jones and Christian, THIS JOURNAL, **57**, 272 (1935).

TABLE IV

THERMODYNAMIC CONSTANTS FOR THE FIRST IONIZATION OF CARBONIC ACID

t	C	Λ_c	Λ_e	f^2	$K_1 \times 10^7$	pK_1 Obsd.	pK_1 Computed	ΔH, cal.
0°	0.03284	0.7040	247.2	0.9785	2.613	6.5830	6.5839	4484
15°	.03282	1.1410	335.4	.9764	3.722	6.4293	6.4300	2952
25°	.03275	1.4401	392.6	.9746	4.310	6.3655	6.3654	2075
38°	.03262	1.8040	464.0	.9731	4.817	7.3173	6.3173	1109

that ΔH assumes a value of zero at 58.1°. Consequently, pK_1 would be expected to pass through a minimum (6.293) and K_1 to reach a maximum (5.09×10^{-7}) at that temperature. Such behavior is in accord with similar results on all other weak acids, so far as they have been studied.[14]

In the last column of Table IV are listed values for ΔH in calories, computed from equation (11′). The value at 25° ($\Delta H = 2075$ calories) is in excellent agreement with that derived from e. m. f. measurements at 18 and 38° by Stadie and Hawes,[15] and also by Cullen, Keeler and Robinson,[16] both giving $\Delta H = 2050$ calories. Direct calorimetric measurements by Thomsen[17] at room temperature, probably 15–16°, gave 2800 calories in reasonable agreement with our value of 2952 at 15°.

Summary

New measurements have been made at 25° on the conductances of solutions of carbonic acid and of potassium bicarbonate. The relative conductances at 0, 15, 25 and 38° of saturated carbonic acid solution and of potassium bicarbonate, potassium chloride and hydrochloric acid at 0.001 normal have also been determined. From these data the thermodynamic dissociation constant of carbonic acid as a monobasic acid has been obtained for the temperatures given. These values have been used in obtaining equations by means of which the ionization constant K_1 and the heat ΔH of the reaction $H_2O + CO_2 = H^+ + HCO_3^-$ are expressed as functions of the temperature. The values of the constant K_1 are 4.31×10^{-7} at 25° and 4.82×10^{-7} at 38°, in reasonable agreement with the corresponding values 4.5×10^{-7} and 4.9×10^{-7} obtained by MacInnes and Belcher at these temperatures.

NEW YORK, N. Y. RECEIVED JUNE 6, 1935

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[14] Harned and Embree, THIS JOURNAL, **56**, 1050 (1934).

[15] Stadie and Hawes, *J. Biol. Chem.*, **77**, 241 (1928).

[16] Cullen, Keeler and Robinson, *ibid.*, **66**, 301 (1925).

[17] Thomsen, "Thermochemische Untersuchungen," Leipzig, 1882.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Photolysis of Dry Ozone at λλ 208, 254, 280 and 313 mμ. II. Reaction Kinetics

BY LAWRENCE JOSEPH HEIDT

Recent data from this Laboratory[1] on the photolysis of dry ozone, largely at λ 208 mμ, gave quantum yields, ϕ, referred to ozone as large as 6.7. This strongly suggested a chain mechanism; but the decrease in ϕ with p_{O_3}/p_{O_2} was not so great as that given by Beretta and Schumacher[2] at λ 313 mμ, nor was ϕ independent of the light intensity. Further interpretation of the data was therefore postponed until a check was made upon the work at λ 313 mμ and until the influences of concentrations and wave length upon quantum yields were more fully established. Such data are presented here.

The experimental procedure, precautions, and corrections were the same as previously followed.[1] At λ 313 mμ an inverted U type quartz mercury arc lamp[3] was used as a light source. The trap at the top of the inverted U was omitted. Instead, the U was tilted so that the plane containing it made an angle of approximately 15° with the plane containing the plungers. The plunger connected to the upper positive electrode was seated; the other was slightly unseated. The luminous column was contained in a quartz tube 4 mm. inside diameter and 7 mm. o. d. The arc length was 60 mm. The lamp was operated on a 110-v. storage battery source at from 2 to 4 amp. It was as intense, constant and durable for slit illumination as its higher voltage type predecessor.[3]

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[1] Heidt and Forbes, THIS JOURNAL, **56**, 2365 (1934).

[2] Beretta and Schumacher, *Z. physik. Chem.*, **17B**, 417 (1932).

[3] Forbes and Heidt, THIS JOURNAL, **53**, 4349 (1931).