formation of ketene. A chain mechanism, which accounts for the pressure dependence of the reaction, has been proposed.

Diacetyl also promotes the decompositions of diethyl ether, acetaldehyde, and ethyl alcohol, as well as the polymerization of ethylene.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of HCO_3^- from 0 to 50°

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The cell

$$H_2 \mid Na_2CO_3(m_1),\ NaHCO_3\ (m_2),\ NaCl\ (m_3) \mid AgCl - Ag$$

has been employed by MacInnes and Belcher[2] to determine the ionization constant of HCO_3^- at 25 and 38°. These measurements have been extended by us to include the range from 0 to 50° and sufficient measurements obtained at intermediate temperatures to determine the entropy, heat content and heat capacity of the ionization reaction.

Experimental Technique and Observed Electromotive Forces

An important feature of this investigation is the use of a stationary cell connected to an enclosed gas pumping system. By this device, the hydrogen circulates through the cell unidirectionally, flowing through a saturator, then over the hydrogen electrode, and finally out of the cell back into the gas pump. This is effected by a suitable set of electrically controlled valves.[3] By means of this enclosed gas system, it is possible to sample the gas for analysis at any time, or if possible determine its composition by thermal analysis. Therefore, a cell of this kind is very well adapted for measurements in which small quantities of gas (300 cc.) are available, when the composition of the gas is required or when the solvent itself is highly volatile. In the latter case, only a short hydrogen saturation device is required.

The behavior of the cells was quite satisfactory. It was possible to change the temperature from 25 to 50° or from 25 to 0° and then back to 25° and reproduce the readings to within 0.1 mv. Two complete series of results were obtained. Of these, the second was the more consistent. We attribute this to the improvement in technique acquired as a result of experience. Duplicate measurements were made at each concentration and the recorded observations represent the mean of these results.

The solutions were made by introducing one-half an equivalent of a standard hydrochloric acid solution to a standard sodium carbonate solution whereby the carbonate, acid carbonate and chloride were present in nearly a 1:1:1 ratio. The acid was added very carefully drop by drop in order to avoid loss of carbon dioxide by local action. The concentrations of electrolytes were known to be within 0.1%. No correction was necessary for the very small partial pressure of carbon dioxide over these solutions.[4]

Since the final values of the ionization constant were evaluated from our second series of results, only these have been recorded in Table I. The first series of results, however, were fairly good and will be shown on the figures. The accuracy of these measurements is estimated to be about 0.1 mv. Some results were obtained at lower ionic strengths but it was found that when the chloride concentration was below 0.003, or the total ionic strength below 0.018, less consistent results were obtained. This concords with our previous experience with cells of this type.

Calculation of Ionization Constant.—By combining the equation of the cell

$$E = E^0 - RT/F \ln m_{H}m_{Cl}\gamma_{H}\gamma_{Cl} \quad (1)$$

with the thermodynamic equation for the reaction namely

$$HCO_3^- \rightleftarrows H^+ + CO_3^{--}$$

$$K_{2A} = \frac{m_{H}m_{CO_3}\gamma_{H}\gamma_{CO_3}}{m_{HCO_3}\gamma_{HCO_3}} \quad (2)$$

we obtain

$$(E - E^0)k + \log \frac{m_{HCO_3}m_{Cl}}{m_{CO_3}} + \log \frac{\gamma_{HCO_3}\gamma_{Cl}}{\gamma_{CO_3}} = - \log K'_{2A} = - \log K_{2A}]_{\mu = 0} \quad (3)$$

E^0 is the standard potential of the cell: $H_2 | HCl (m) | AgCl - Ag$, $k = F/2.3026\ RT$, and m_{HCO_3}, γ_{HCO_3}, etc., are the molalities and activity coefficients of the ionic species designated by subscripts. K_2' is an apparent ionization constant which equals the true ionization constant at zero ionic strength.

Two methods of extrapolation have been employed. The first method, employed by MacInnes and Belcher, is to combine the term con-

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[1] This communication contains part of the material of a dissertation presented by Samuel R. Scholes, Jr., to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1940.

[2] MacInnes and Belcher, THIS JOURNAL, **55**, 2630 (1933); **57**, 1683 (1935).

[3] A complete description of the apparatus is contained in the Dissertation to which reference has been made.[1]

[4] Walker, Bray and Johnston, THIS JOURNAL, **49**, 1935 (1927).

TABLE I

OBSERVED ELECTROMOTIVE FORCES AT 760 MM. HYDROGEN PRESSURE

μ	0.01975	0.02810	0.02917	0.05792	0.08318	0.11176	0.13130	0.16246
$m_1 = m_3$	.003940	.005606	.005821	.011556	.01660	.02230	.02620	.03241
m_2	.003956	.005628	.005843	.011602	.01666	.02239	.02630	.03254
t, °C.				E				
0	0.93582	0.92678	0.92594	0.90764	0.89818	0.88530	0.88993	0.8790
5	.94218	.93311	.93226	.91356	.90399	.89098	.89562	.8843
10	.94836	.93900	.93825	.91935	.90976	.89640	.90119	.8897
15	.95456	.94507	.94432	.92514	.91528	.90192	.90678	.8952
20	.96072	.95109	.95041	.93101	.92101	.90737	.91241	.9007
25	.96680	.95746	.95647	.93700	.92693	.91302	.91808	.9062
30	...	...	.96262	.94281	.93276	.91866	.92358	.9115
35	...	...	.96846	.94878	.93841	.92537	.92941	.9173
40	...	...	.97434	.95467	.94412	.93009	.93514	.9229
45	...	...	.98026	.96055	.95011	.93582	.94102	.9286
50	...	...	.98598	.96652	.95608	.94187	.94685	.9344

taining the activity coefficients with the term on the right and plot the function $(E^0 - E)k + \log m_{HCO_3}m_{Cl}/m_{CO_3}$ against the square root of the ionic strength and determine its value $(-\log K_2)$ at zero ionic strength. The second method involves replacing the activity coefficient term by the expression

$$\log \frac{\gamma_{HCO_3}\gamma_{Cl}}{\gamma_{CO_3}} = \frac{2u\sqrt{\mu}}{1 + A\sqrt{2\mu}} \tag{4}$$

derived from the Debye and Hückel theory. Equation (3) then becomes

$$(E - E^0)k + \log \frac{m_{HCO_3}m_{Cl}}{m_{CO_3}} + \frac{2u\sqrt{\mu}}{1 + A\sqrt{2\mu}} = -\log K'_{2A} = -\log K_{2A} + f(\mu) \tag{5}$$

A plot of the left side of this equation against μ should approach linearity in the dilute solutions and afford a satisfactory extrapolation. The third term on the left was evaluated by letting A equal unity which corresponds to a mean distance of approach of the ions of approximately 4 Å. With this value of A, a suitable extrapolation was effected since $f(\mu)$ was reduced to a small value.

In order to evaluate the second term on the left of this equation, it is necessary to correct for hydrolysis, or for the reaction

$$CO_3^{--} + H_2O \rightleftarrows HCO_3^- + OH^-$$

The thermodynamic constants for this reaction may be written

$$K_h = \frac{K_w}{K_{2A}} = \frac{m_{HCO_3}m_{OH}\gamma_{HCO_3}\gamma_{OH}}{m_{CO_3}\gamma_{CO_3}a_{H_2O}} \tag{6}$$

where K_h is the ratio of the ionization constant of water to that of HCO_3^-. From this relation, we obtain

$$\frac{K_w}{K_{2A}} \frac{\gamma_{CO_3}}{\gamma_{OH}\gamma_{HCO_3}} = \frac{x(m_2 + x)}{(m_1 - x)} \tag{7}$$

where x is the molality of the hydroxyl ion, and m_1 and m_2 are the stoichiometrical molalities of the carbonate and bicarbonate in the cell. The activity coefficient function was assumed to be given by

$$\log \frac{\gamma_{CO_3}}{\gamma_{OH}\gamma_{HCO_3}} = -\frac{2u\sqrt{\mu}}{1 + A\sqrt{2\mu}} \tag{8}$$

where A was again assigned the value of unity. An examination of this procedure indicates that it is necessary to recalculate the ionic strength at each temperature, since the ratios of concentrations used in the first approximation of the ionic strength have been altered by hydrolysis. This, in turn, required a recalculation of the right-hand member of equation (8). The change caused by this computation is quite small compared to that in the extrapolation function caused by the hydrolysis correction of the ratio of the molalities.

MacInnes and Belcher make the hydrolysis correction by a different method and obtain values which are very nearly the same as ours. Since the hydrolysis correction increases as the ionic strength decreases, an element of uncertainty is always present in the extrapolation. In Table II, typical calculations of these functions are given at the lowest and highest temperatures measured which correspond to the smallest and largest hydrolysis correction. It is to be noted that the correction at 50° is many times that at 0°. Indeed, at 0° the maximum correction at the lowest concentration used corresponds to about 0.6 mv. whereas at 50° it corresponds to more than 6 mv.

In Fig. 1, plots of $-\log K'_{2A}$, uncorrected and corrected for hydrolysis against μ at 0, 25 and 50° are shown. The solid lines represent the curves

TABLE II

EXTRAPOLATION FUNCTIONS SHOWING HYDROLYSIS CORRECTION[a]

	0°			50°		
μ[b]	$-\log K_{2A} - 10$	$10^4 x$	$-\log K_{2A} - 10$ (cor.)	$-\log K_{2A} - 10$	$10^4 x$	$-\log K_{2A} - 10$ (cor.)
0.01975	0.6166	0.366	0.6247	....	...	....
.02810	.6207	.353	.6261	....	...	....
.02917	.6235	.347	.6286	0.1023	5.018	0.1751
.05792	.6241	.320	.6268	.1409	4.93	.1774
.08318	.6319	.300	.6343	.1630	4.77	.1871
.11176	.6272	.300	.6305	.1685	4.65	.1891
.1313	.6262	.300	.6276	.1716	4.61	.1912

[a] The required values of K_w were taken from the determinations of Harned and Hamer, THIS JOURNAL, 55, 2194 (1933). Values of E^0 used are those of Harned and Ehlers, *ibid.*, 55, 2179 (1933). [b] Stoichiometric: $\mu = m_2 + m_3 + 3m_1$.

employed for the extrapolation while the dashed curves are plots of the function without the hydrolysis correction. The diameters of the circles correspond to 0.2 mv. The crosses are the results computed from our first series of measurements and are seen to be less consistent than the final series of results. The extrapolation at the lower temperatures is more certain than at high temperatures, since the hydrolysis correction is less and since the results at the lower ionic strengths (< 0.03) are more reliable. This is indicated by the most dilute result at 25° which is 0.6 mv. lower than the straight line employed for the extrapolation. At all temperatures, the results fall on straight lines between 0.03 and 0.15 μ, as required by theory.

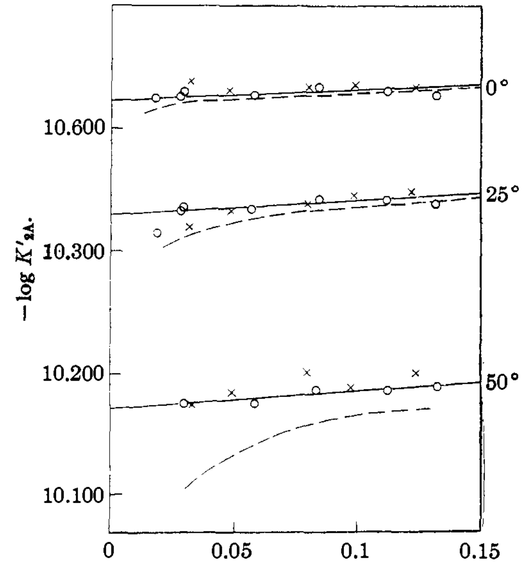

Fig. 1.—Extrapolations at 0, 25 and 50°: ×, first series; ○, second series; – –, uncorrected for hydrolysis.

In Fig. 2, we have plotted the function ($-\log K'_{2A}$) at 25° computed from all the results obtained by MacInnes and Belcher and by us. Although the experimental values from the different sources check each other, we note that at concentrations below 0.03 to 0.05 μ the points fall below the theoretical curve. We have rejected these results as probably erroneous in the estimation of the ionization constant. MacInnes and Belcher found that if $(E - E^0)\, k + \log m_{HCO_3}m_{Cl}/m_{CO_3}$ was plotted against $\mu^{1/2}$ the results in dilute solution fall on a straight line which they used for the extrapolation. Since the slope of this line was less than one-half of that required by theory, we seriously doubt the correctness of this extrapolation. Their value of $-\log K_{2A}$ is 10.251 as compared with 10.329 obtained by the extrapolation in Fig. 2.

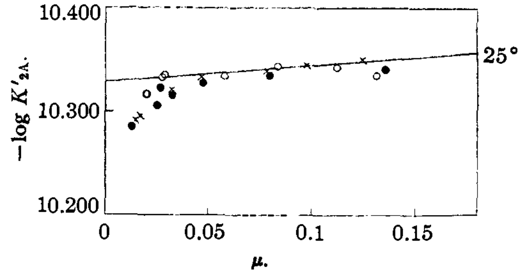

Fig. 2.—Extrapolation at 25°: ●, MacInnes and Belcher ×, first series; ○, second series.

TABLE III

IONIZATION CONSTANTS

	$K_{2A} \times 10^{11}$	$-\log K_{2A}$	Δ[a]
0	2.36	10.625	+0.002
5	2.77	10.557	− .003
10	3.24	10.490	− .001
15	3.71	10.430	.000
20	4.20	10.377	.000
25	4.69	10.329	+ .001
30	5.13	10.290	− .002
35	5.62	10.250	+ .002
40	6.03	10.220	+ .001
45	6.38	10.195	− .001
50	6.73	10.172	− .001

[a] Δ = [log K_{2A} (obsd.) − log K_{2A} (calcd.)].

Ionization Constants and Derived Thermodynamic Functions.—Table III contains the values of K_{2A} and $-\log K_{2A}$ at the temperatures designated. In the last column are the deviations between the observed results and those calculated by an equation which expresses the standard free energy as a quadratic function of the absolute temperature.[5] The numerical equations for $\log K_{2A}$ and the standard thermodynamic functions, derived by the method of least squares are

$$\log K_{2A} = \frac{-2902.39}{T} + 6.4980 - 0.02379T \quad (9)$$

$$\Delta F^0 = 13278.55 - 29.7286T + 0.10884T^2 \quad (10)$$

$$\Delta H^0 = 13278.55 - 0.10884T^2 \quad (11)$$

$$\Delta C_p^0 = -0.21768T \quad (12)$$

$$\Delta S^0 = 29.7286 - 0.21768T \quad (13)$$

The values of the heat content, heat capacity and entropy at 25° are 3600 cal., -65 cal. deg.$^{-1}$ and -35.16 cal. deg.$^{-1}$, respectively. The value ΔH^0 agrees with the recent calorimetric result (3500 ± 100) of Pitzer within the error of experiment. Our result also confirms Pitzer's[6] value of -35.2 for the standard entropy, ΔS^0.

The maximum value of the ionization constant is found to occur at 349.3° Å. and the value of $-\log K_{2A}$ is 10.121 at this temperature.

The following values have been reported for K_{2A} at 25°: McCoy,[7] 6×10^{-11}; (recalculated by Stieglitz, 5.4×10^{-11}); Seyler and Lloyd,[8] 4.3×10^{-11}; Hastings and Sendroy,[9] 5.51×10^{-11}; MacInnes and Belcher, 5.61×10^{-11}; this measurement, 4.69×10^{-11}. At 38°, Hastings and Sendroy obtained 6.03×10^{-11}; MacInnes and Belcher 6.25×10^{-11}, which are somewhat higher than 5.86×10^{-11} obtained by us at this temperature by equation (9).

We take this opportunity to express our thanks to Dr. Gösta Åkerlöf who supervised the construction and design of the apparatus.

Summary

1. By means of an enclosed gas electrode system, the ionization constant of HCO_3^- has been determined at 5° intervals from 0 to 50°.

2. Equations have been derived from these results by means of which the standard heat content, heat capacity, and entropy of the ionization reaction may be computed. The standard heat content found is in good agreement with that derived from calorimetric measurements.

3. Our values of the ionization constant at 25° and 38° are lower than that obtained by recent investigators. This is due to our consistent use of the limiting theoretical equations in making the extrapolations.

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[5] Harned and Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

[6] Pitzer, THIS JOURNAL, **59**, 2365 (1937).

[7] McCoy, *Am. Chem. J.*, **29**, 437 (1903).

[8] Seyler and Lloyd, *J. Chem. Soc.*, **111**, 138 (1917).

[9] Hastings and Sendroy, *J. Biol. Chem.*, **65**, 445 (1925).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NATIONAL SOUTHWESTERN ASSOCIATED UNIVERSITY, KUNMING, CHINA]

Maximum Difference between Densities of Ordinary and Heavy Water

BY TSING-LIEN CHANG AND JEN-YUAN CHIEN

Farkas[1] calculated the density of heavy water below 40° from the dilatation data of Lewis and Macdonald[2] and inferred that the differences between the densities of ordinary and heavy water shows a maximum at 25°. By repeating the experiment with quartz pycnometers between 10 and 27°, Stokland, Ronaess and Tronstad[3] concluded that such a maximum cannot exist below 30°. As the density difference found by them increases by a diminishing amount with increasing temperature, it tends indeed to pass through a maximum at a temperature higher than their investigated range. Since ordinary and heavy water have equal density at 370°,[4] a maximum difference in density necessarily exists.

In the present investigation measurements on the dilatation of heavy water are extended to 50°. It is thereby found that the maximum of density difference between ordinary and heavy water lies at 40°.

Experimental

A sample of heavy water obtained from Norsk Hydro-

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[1] A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge, 1935, p. 172.

[2] G. N. Lewis and R. T. Macdonald, THIS JOURNAL, **55**, 3057 (1933).

[3] K. Stokland, E. Ronaess and L. Tronstad, *Trans. Faraday Soc.*, **35**, 312 (1939).

[4] E. H. Riesenfeld and T. L. Chang, *Z. physik. Chem.*, **B30**, 61 (1935).