[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of Carbonic Acid in Water and the Solubility of Carbon Dioxide in Water and Aqueous Salt Solutions from 0 to 50°

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The cell

$$\text{Pt-H}_2,\ \text{CO}_2 \mid \text{NaHCO}_3(m_1),\ \text{NaCl}(m_2),\ \text{CO}_2(m_3) \mid \text{AgCl-Ag}$$

may be used to determine both the ionization constant of carbonic acid in water and the ionization of this acid in sodium chloride solutions.[2] In order to attain these objectives, it is necessary to measure not only the required electromotive forces but also the solubilities of carbon dioxide in water and in the salt solutions. As a substantial part of this systematic project, we have measured the electromotive force of this cell at various compositions of hydrogen and carbon dioxide at the gas electrode and at electrolyte concentrations suitable for the determination of the ionization constant in water. The measurements have been made at 5° intervals from 0 to 50°. The Henry's law constants of carbon dioxide in water also have been determined through this range of temperature. Further, in preparation for the evaluation of the ionization of carbonic acid in sodium chloride solutions, the Henry's law constants of carbon dioxide in salt solutions of various strengths have also been determined in the range 0 to 50°. The electromotive force measurements at constant sodium chloride and varying sodium bicarbonate concentrations required for the determination of the ionization in sodium chloride solutions will be treated in a subsequent contribution.

The dissociation equilibrium of carbonic acid may be represented by

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

Adopting the usual convention regarding hydrated solutes[3] that for

$$CO_2(\text{aq.}) + H_2O = H_2CO_3(\text{aq.});\ \Delta F = 0 \qquad (1)$$

the ionization constant will be defined by

$$K = \frac{a_{\text{H}}a_{\text{HCO}_3}}{a_{\text{CO}_2}} = \frac{m_{\text{H}}m_{\text{HCO}_3}\gamma_{\text{H}}\gamma_{\text{HCO}_3}}{m_{\text{CO}_2}\gamma_{\text{CO}_2}} \qquad (2)$$

where m_{CO_2} is the total molality of carbon dioxide in the solution. We note that this thermodynamic method cannot be used to determine the equilibrium constant of carbonic acid.[4]

The electromotive force, E, of cell (1) is given by the equation

$$\begin{aligned} E &= E^0 - \frac{RT}{F}\ln m_{\text{H}}m_{\text{Cl}}\gamma_{\text{H}}\gamma_{\text{Cl}} + \frac{RT}{2F}\ln P_{\text{H}_2} \\ &= E^0 - E_c - \frac{RT}{F}\ln m_{\text{H}}m_{\text{Cl}}\gamma_{\text{H}}\gamma_{\text{Cl}} \qquad (3) \end{aligned}$$

where $E_c = (-RT/2F)\ln P_{\text{H}_2}$, E^0 is the standard potential of the cell and the other symbols have their usual significance. The pressure term, E_c, is retained since the results were obtained at various compositions of hydrogen and carbon dioxide and it is desirable to tabulate this term. This differs from the usual method of including the pressure term implicitly by tabulating E at one atmosphere hydrogen pressure. Since the hydrogen ion activity is derived solely from the reaction of carbon dioxide and water, we may substitute m_{H} obtained from equation (2) in equation (3) and obtain by rearranging terms the expression

$$\begin{aligned} -\log K' &\equiv -\left[\log K + \log\frac{\gamma_{\text{H}}\gamma_{\text{Cl}}}{\gamma_{\text{H}}\gamma_{\text{HCO}_3}}\right] \\ &= (E + E_c - E^0)\frac{F}{2.303RT} + \log m_{\text{CO}_2}\gamma_{\text{CO}_2} + \\ &\qquad \log\frac{m_{\text{Cl}}}{m_{\text{HCO}_3}} \qquad (4) \end{aligned}$$

In the subsequent experimental work, the molalities m_{Cl} and m_{HCO_3} were made equal so that the last term vanishes. As a reference state we take γ_{CO_2} to be unity in pure water and express the molality of the carbon dioxide by Henry's law in the form

$$m_{\text{CO}_2} = SP_{\text{CO}_2} \qquad (5)$$

With these simplifications, equation (4) becomes

$$\begin{aligned} -\log K' &= -\left[\log K + \log\frac{\gamma_{\text{H}}\gamma_{\text{Cl}}}{\gamma_{\text{H}}\gamma_{\text{HCO}_3}}\right] \\ &= (E + E_c - E^0)\frac{F}{2.303RT} + \log SP_{\text{CO}_2} \qquad (6) \end{aligned}$$

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(1) This communicaton contains material from a dissertation presented by Raymond Davis, Jr., to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1942.

(2) MacInnes and Belcher (THIS JOURNAL, **55**, 2630 (1933)) have employed a similar cell in which a glass electrode was used instead of a hydrogen electrode.

(3) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1923, p. 297.

(4) A solution of carbon dioxide in water contains principally carbon dioxide and less than 1% of H_2CO_3 (L. Pusch, *Z. Elektrochem.*, **22**, 206 (1916)). Recently Roughton (THIS JOURNAL, **63**, 2930 (1941)) from kinetic calorimetric measurements of the neutralization of sodium bicarbonate with hydrochloric acid concluded that the ionization constant of carbonic acid is of the order of 2 × 10^{-4} at 0°.

As the ionic concentration decreases, the logarithmic term containing $\gamma_H\gamma_{Cl}/\gamma_H\gamma_{HCO_3}$ approaches zero. Consequently to determine $(-\log K)$, the experimental quantities on the right are extrapolated to infinite dilution of electrolyte. However, this extrapolation is not to pure water but to a solution containing carbon dioxide of molality m_{CO_2}. We have carried out measurements at enough concentrations (pressures) of carbon dioxide to permit the extrapolation to zero concentration of this substance.

In order to determine the ionization, $m_H m_{HCO_3}/m_{CO_2}$, and the activity coefficient product $\gamma_H\gamma_{HCO_3}/\gamma_{CO_2}$, in salt solutions, equation (4) may be rearranged to the suitable form

$$\log \frac{\gamma_H\gamma_{HCO_3}}{\gamma_{CO_2}} = (E - E^0 + E_c)\frac{F}{2.303RT} + \log K + \log \frac{m_{CO_2}m_{Cl}}{m_{HCO_3}} + \log \gamma_H\gamma_{Cl} \quad (7)$$

where $\gamma_H\gamma_{Cl}$ is the activity coefficient of hydrochloric acid at zero concentration in the salt solution under examination. The right side of this equation may be evaluated easily since E is measured, E^0, E_c and K are known, m_{Cl} and m_{HCO_3} are known, and m_{CO_2} may be computed from the Henry's law constants of carbon dioxide in the salt solutions. The data should be extrapolated to zero bicarbonate ion concentration at each fixed concentration of salt.

An important feature of our experimental procedure is that the Henry's law constants have been determined in the same apparatus used for the cell measurements. This method should yield the most consistent kind of results on this important equilibrium.

The Solubility of Carbon Dioxide in Water and Sodium Chloride Solutions from 0 to 50°

Apparatus and Method.—Both the solubility and electromotive force measurements were carried out in the apparatus shown in Fig. 1. For the solubility determinations, carbon dioxide gas was passed first through a preliminary spiral bubbling saturator. Then the gas nearly saturated with water vapor entered the cell, passed through the saturator tube A and finally through the cell B. The solubility was now determined by drawing about 90 cc. of the solution in B into the titrating flask C which contained an excess of a standard barium hydroxide solution. Weight titration of this excess with standard hydrochloric acid yielded the data necessary for the computation of the solubility and Henry's law constants.

For successful determinations of the solubility the following procedure was found necessary. We note that the carbon dioxide–water vapor mixtures entered the cell about 5 mm. below the surface of the liquid and then had a clear passage to the atmosphere through the bent capillary exit tube. By this construction the total pressure inside the cell, $P_{CO_2} + P_{H_2O}$, was equal to the barometric pressure and the capillary tube prevented air from entering the cell. By attaching a small water manometer to one of the electrode stacks, it was found that the pressure in B while passing the gas at the rate of a bubble every two seconds was less than 0.05 mm. of mercury greater than atmospheric. The entire cell was mounted on a motor driven rocker which seemed to keep the surface of the solution constantly agitated, facilitating the attainment of equilibrium. In determining the solubility of gases it is important not to introduce the gas too far under the solution because the additional hydrostatic pressure on the gas bubble tends to dissolve a greater quantity of gas than corresponds to the observed pressure. In the present apparatus the bubbler is so little below the surface that any supersaturation thus caused is entirely negligible. The bubbler seems to agitate the solution and permits at a glance the estimation of the rate at which the gas is passing through the cell.

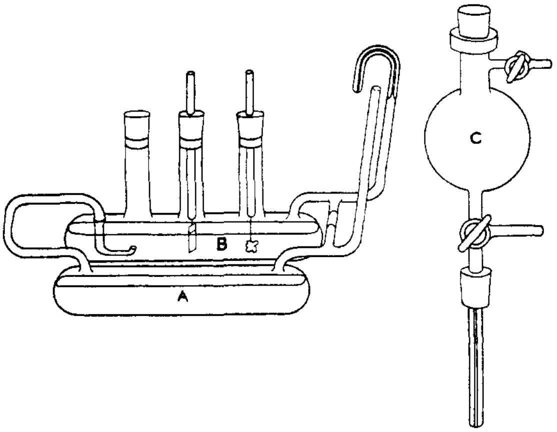

Fig. 1.—Cell and sampling device.

Sampling and Titration.—The bulb of the sampling device was swept with oxygen, stoppered, and, after the stopcocks were closed, the whole device was weighed. The sampler was then fitted into the end electrode stack in such a way that the capillary tube extended to the very bottom of the cell. The cell compartments A and B were each filled with about 100 cc. of the solution in which the solubility of the gas was to be measured and the cell was mounted on the rocker in the thermostat. After passing the gas for some minutes the carbon dioxide line was cut off and the cell was evacuated through the capillary tube. The vacuum line was then closed and the gas line opened, filling the cell completely with carbon dioxide. This procedure was followed since it is very difficult to remove all traces of air. The apparatus was rocked overnight with the gas passing through. We are certain that equilibrium was attained during this time since we had previously observed that electromotive force measurements reached constancy within six to eight hours. The next morning a weighed amount of 0.1 M standard barium hydroxide solution was introduced into the sampler in excess of that required to neutralize the carbon dioxide (20% excess). The sampler was then stoppered and evacuated through the upper stopcock. The vacuum line was attached to the T-stopcock and by just opening this stopcock a small amount of carbon dioxide saturated solution was drawn through the long stem of the sampler as a rinse. Then by proper adjustment of the T-stopcock about 90 cc. of the saturated solution was drawn into the bulb. During this operation the gas was allowed to flow somewhat faster in order to replace the volume of the liquid removed and to assure a constant pressure of carbon dioxide in the gas phase during sampling. Preliminary experiments showed that this procedure was necessary and that it eliminated the error caused by escape of gas from the solution. The sampler was then removed from the cell and the stem was rinsed with water and dried with an air current. The vacuum in the sampler was relieved with oxygen and the entire sampler reweighed. From this weight, the weights of empty sampler and the barium hydroxide solution, the weight of the carbon dioxide solution was computed. After vigorous shaking, the excess of barium hydroxide was determined by weight titration with 0.2 M hydrochloric acid.

Discussion of Errors.—The cylinder carbon dioxide was analyzed by means of an apparatus described by MacInnes and Shedlovsky[5] and illustrated by Fig. 2 of their article. This material was found to be 99.67 ± 0.05% pure carbon dioxide. All subsequent computations were based on this analysis.

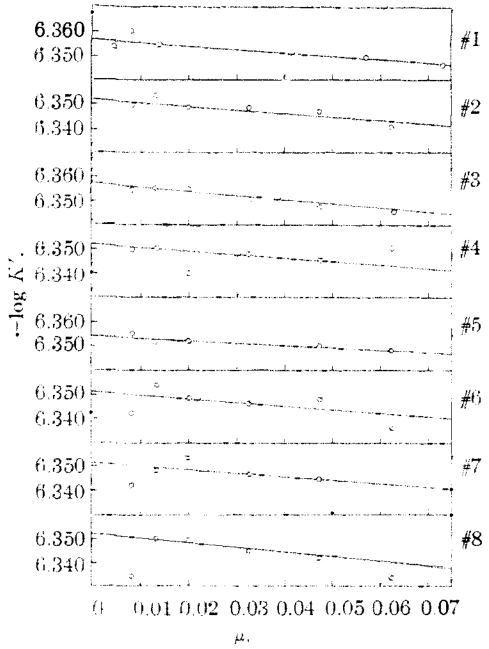

Fig. 2.—Extrapolation of $(-\log K')$ to zero ionic strength at 25°.

Standard solutions of hydrochloric acid (0.2 M) and barium hydroxide (0.1 M) and all sodium chloride solutions were known to within less than 0.1%. Since 90 cc. of unknown samples were titrated, large quantities of these standard solutions (10 g. and upwards) were used and the errors of weighing were negligibly small. The end-points of the titrations in the presence of barium carbonate were sensitive to one drop or approximately 0.05 g. of barium hydroxide solution. At high sodium chloride concentrations, the carbonic acid solution (90 cc.) titrated was approximately 0.01 M and about 10 g. of barium hydroxide solution was required for neutralization. Under these conditions, the titrations would be expected to have a precision of 0.5%. Since more solution was titrated at lower salt concentrations the accuracy in this region was greater than this. At best the reproducibility of this determination of the solubility was of the order of 0.2% while at high temperatures and salt concentrations the average error was approximately 1%.

Experimental Results

The observed Henry's law constants are recorded in Table I. Series A represents the mean of four simultaneous measurements of carbon dioxide in water. In addition, this series comprises single observations of the solubility in 0.2, 0.5, 1, 2, and 3 M sodium chloride solutions. Both of these series covered the entire temperature range. Series B represents the mean of three experiments at each temperature on each salt concentration recorded. Series C: the results of series A and B were plotted on a large scale and all results in doubt redetermined. Most of the first discrepancies occurred at higher concentrations of salt at high temperatures and therefore the results in series C were obtained in this region. They represent the mean of triplicate determinations. The starred values were not given as great a weight as the unstarred values in the final graphical estimation of S.

Large scale plots of $(-\log S)$ *versus* molality of sodium chloride were made. Greater weight was given to the results of series B and C for the salt solutions. For pure water, the values in series A and B agreed closely at all temperatures. The smoothed values of $(-\log S)$ obtained from these graphs are given in Table II.

The solubility data can be expressed as a function of the absolute temperature by

$$-\log S = -\frac{A^*}{T} + D^* - C^*T \qquad (8)$$

consistent with the free energy equation

$$\begin{aligned}(-\Delta F^0) &= 2.3026\ RT \log S \\ &= A' - D'T + C'T^2 \qquad (9)\end{aligned}$$

where

$$\begin{aligned}A' &= 2.3026\ RA^* \\ B' &= 2.3026\ RB^* \\ C' &= 2.3026\ RC^* \qquad (10)\end{aligned}$$

ΔF^0 is the free energy of solution of carbon dioxide

$$CO_2(\text{gas, 1 atm.}) = CO_2(\text{solution}, m_{CO_2}, m_{NaCl}) \qquad (11)$$

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[5] Shedlovsky and MacInnes, THIS JOURNAL, **57**, 1705 (1935).

TABLE I

HENRY'S LAW CONSTANTS FOR CARBON DIOXIDE IN WATER AND SODIUM CHLORIDE SOLUTIONS; $S = m_{CO_2}/P_{CO_2}$

t	Series	Water	0.2 *M* NaCl	0.5 *M* NaCl	1 *M* NaCl	2 *M* NaCl	3 *M* NaCl
0	A	0.07726	0.07256	0.06708	0.05869	0.04608	0.03695
	B	.07676	.....	.06642	.05895	.04597	.03718
5	A	.06402	.06099	.05593	.04932	.03910	.03166
10	A	.05359	.05096	.04714	.04160	.03339	.02716
	B	.05367	.....	......	.04156	......	.02729
15	A	.04554	.04330	.04009	.03550	.02886	.02381
20	A	.03923	.03725	.03450	.03085	.02504	.02071
	B	.03928	.....	......	......	......	.02086
25	A	.03438	.03278	.03054	.02707	.02223	.01810*
	B	.03458	.....	.03036	.02668*	.02227	.01844
	C	.....	.....	......	.02734	.02242	.01847
30	A	.03026	.02861	.02674	.02407	.01971	.01658
	B	.03021	.....	.02588*	.02418	.01927*	.01688*
	C	.....	.....	......	......	.01965	.01655
35	A	.02678	.02553	.02388	.02108*	.01763	.01488
	C	.....	.....	......	.02167	.01778	.01488
40	A	.02407	.02289	.02141	.01913	.01566	......
	B	.02407	.....	.02188*	.01922	.01629*	.01372*
	C	.....	.....	......	......	.01575	.01344
45	A	.02192	.02084	.01955	.01752	.01492	.01212
	C	.....	.....	......	.01743	.01441	.01216
50	A	.01982	.01897	.01753	.01597	.01317	.01093
	B	.01969	.....	.01765	.01559*	.01330	.01145*
	C	.....	.....	......	......	.01317	.01099

TABLE II

SMOOTHED VALUES OF (− LOG S). DEVIATIONS (OBS. − CALCD.)[a]

	Water	0.2 *M*	0.5 *M*	1 *M*	2 *M*	3 *M*
0	1.1144(+4)	1.1383(+2)	1.1738(0)	1.2313(−4)	1.3365(−8)	1.4290(−24)
5	1.1938(−10)	1.2167(−14)	1.2510(−18)	1.3065(+17)	1.4077(−14)	1.4980(−8)
10	1.2695(−5)	1.2920(−5)	1.3259(−3)	1.3800(−4)	1.4768(+4)	1.5642(+17)
15	1.3412(+13)	1.3638(+20)	1.3970(+25)	1.4482(−20)	1.5422(+27)	1.6255(+29)
20	1.4063(+15)	1.4285(+25)	1.4605(+8)	1.5110(+28)	1.6012(+25)	1.6822(+29)
25	1.4635(−16)	1.4842(+16)	1.5152(−18)	1.5645(−14)	1.6530(−9)	1.7323(−8)
30	1.5209(+1)	1.5410(−1)	1.5712(−3)	1.6191(−2)	1.7055(−1)	1.7820(−12)
35	1.5722(0)	1.5917(−3)	1.6210(−9)	1.6668(−20)	1.7508(−31)	1.8280(−27)
40	1.6200(+5)	1.6393(+2)	1.6678(−5)	1.7140(−7)	1.7982(−7)	1.8733(−21)
45	1.6593(−36)	1.6797(−27)	1.7092(−19)	1.7564(−5)	1.8404(−4)	1.9168(−8)
50	1.7053(+26)	1.7241(+22)	1.7523(+22)	1.7972(+15)	1.8815(+18)	1.9602(+21)

[a] Numbers in parentheses represent deviations in fourth decimal place of (− log S).

In this terminology, the heat content, heat capacity and entropy of the process are

$$\Delta H^0 = -A' + C'T^2 \qquad (12)$$

$$\Delta C_p{}^0 = 2C'T \qquad (13)$$

$$\Delta S^0 = D' + 2C'T \qquad (14)$$

Table III contains the parameters of equation (8) obtained from the data by the method of least squares

The deviations of the observed results from those calculated by equation (8) are given in parentheses immediately following the values. The maximum deviation is 0.0036 and the average deviation is 0.0015 in log S which corresponds to 0.8 and 0.3% in S. Equations (12), (13) and (14) should yield good estimates of the derived thermodynamic quantities, ΔH^0, $\Delta C_p{}^0$ and ΔS^0.

TABLE III

LEAST SQUARED CONSTANTS OF EQUATIONS (8) TO (14); m = MOLALITY OF NaCl

m	*A**	*D**	*C**
0.0	2385.73	14.0184	0.0152642
.2	2347.16	13.8090	.0149259
.5	2309.60	13.6316	.0146492
1.0	2195.84	12.9875	.0136050
2.0	1912.43	11.2968	.0108268
3.0	1622.96	9.5253	.0078770

The solubility of carbon dioxide in water has been repeatedly measured. The majority of these results are expressed in terms of the Bunsen or Ostwald coefficients.[6] These were converted to S by the use of suitable equations. At 25° the values[7] of S were found to range between 0.0337 and 0.03420. The results of Bohr are the only ones which include a sufficient number of results suitable for interpolation at 5° intervals from 0 to 50°. From an analytical equation expressing his data values at these temperatures were computed and were found to agree with the present results with an average deviation of 0.0011 in $(-\log S)$. Since Bohr's measurements were made by shaking carbon dioxide in a known volume of water and reading the volume of the gas, a method quite different from ours, the agreement is very satisfactory.

Markham and Kobe[7] have determined the solubility of carbon dioxide in sodium chloride solutions at 0, 25 and 40°. Their results agree well with ours at 0° but at 25 and 40° the discrepancies between the two series are large. We offer no explanation of this. Further, our value of S in water at 25° is 0.4% to 2% higher than the values derived from the data of previous investigators,[7] indicating that under the conditions of our experiments, somewhat greater saturation was obtained.

Electromotive Force Data

All the electromotive force measurements were made by cells of the type shown in Fig. 1 with electrodes in the positions indicated. In using a rocking cell, the question arises whether an electrode which merely oscillates up and down in respect to the solution gives the same electromotive force as the usual type of hydrogen electrode in which the gas bubbles over the platinum. This matter was tested by placing two electrodes in the cell, one over the bubbler and one in the central stack. Measurements showed that the electromotive forces of these two electrodes against the same silver chloride electrode agreed to within ±0.02 mv.

An analyzed mixture of hydrogen and carbon dioxide contained in a cylinder was passed through the cells continuously during the electromotive force measurements. This cylinder was filled from a hydrogen cylinder and a carbon dioxide cylinder by means of a three-way connecting unit constructed of copper and brass parts. Before the cylinder was filled, it was first rinsed four or five times by filling with carbon dioxide gas to several atmospheres and then evacuating. After the hydrogen and carbon dioxide were introduced, mixing was facilitated by heating the cylinder on a hot plate for several hours. This procedure was required in order to obtain accurate results within a reasonable time. The mixed gases were analyzed by an Orsat apparatus with an accurately calibrated buret. The analyses were reproducible to within 0.1% which corresponds to an error in $\log K'$ of 0.0011. Enough gas for one series of measurements was available if the cylinder was filled to 150 lb. pressure at the beginning of the experiment.

The salt solutions were prepared by weighing sodium bicarbonate and sodium chloride into water. Sodium chloride, dried at 350°, was found to be 99.98% pure. The sodium bicarbonate was analyzed by heating to 800° in an atmosphere of carbon dioxide in platinum crucibles under which conditions it should be completely converted to carbonate. Check analyses indicated that the bicarbonate used was 99.91% pure. This factor was taken into account in computing concentrations.

Platinum foil electrodes and silver chloride electrodes prepared from silver oxide[8] were employed. The cells were filled with the mixed gases by the vacuum technique described in the solubility measurements. Usually the cells were operated overnight before the first measurement was made. Upon changing the temperature, two to four hours were required to obtain constant readings of the electromotive forces. All series of observations were started at 25° and the temperature was varied from 0 to 25°, or from 25 to 50°. In every series the temperature was finally readjusted to 25° and the electromotive force was found to agree with the initial reading to within ±0.1 mv. regardless of whether the return was from the high or low temperature.

All the electromotive force and analytical data necessary for the calculation of the ionization

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(6) Consult "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 260. See also the comprehensive survey of the subject by Markham and Kobe, *Chem. Rev.*, **28**, 519 (1941).

(7) From the data of Findlay and Creighton, *J. Chem. Soc.*, **97**, 536 (1910); Findlay and Shen, *ibid.*, **101**, 1459 (1912); Findlay and Howell, *ibid.*, **105**, 291 (1914); **107**, 282 (1915); Findlay and Williams, *ibid.*, **103**, 636 (1913); Just, *J. physik. Chem.*, **37**, 342 (1911); Kunerth, *Phys. Rev.*, **19**, 522 (1922); Geffcken, *J. physik. Chem.*, **49**, 257 (1904); Markham and Kobe, *Chem. Rev.*, **28**, 519 (1941); Shedlovsky and MacInnes, THIS JOURNAL, **57**, 1705 (1935); C. Bohr, *Ann. Physik*, **68**, 500 (1899).

(8) Harned, THIS JOURNAL, **51**, 416 (1929), Type (2) electrodes.

TABLE IV

Electromotive Forces of the Cells: Pt–H_2, CO_2 | $NaHCO_3$ (m_1), NaCl (m_2), CO_2 (m_3) | AgCl–Ag; $m_1 = m_2$; $m_3 = SP_{CO_2}$; P_B, barometric pressure in mm., is given in parentheses immediately following E_t. Gas composition in % by volume.

Series (1). % CO_2 = 77.80; % H_2 = 22.20

Cell number	1	2	3	4	5	6
$m_1 = m_2$	0.10385	0.03687	0.02859	0.007177	0.003951	0.002182
E_{25} (762.6)	.67106	.67192	.67209	.67243	.67271	.67236
E_{30} (762.7)	.67740	.67769	.67829	.67864	.67917	.67865
E_{35} (763.1)	.68335	.68403	.68458	.68498	.68546	.68492
E_{40} (763.5)	.68958	.69043	.69087	.69124	.69174	.69124
E_{45} (762.3)	.69653	.69719	.69752	.69792	.69833	.69784
E_{50} (762.0)	.70275	.70351	.70386	.70428	.70460	.70418

Series (2). % CO_2 = 85.40; % H_2 = 14.60

The concentrations of electrolytes, m_1 and m_2, given in the second row are those employed through series (2) to (8).

Cell number	1	2	3	4	5	6
$m_1 = m_2$	0.03137	0.02360	0.01646	0.01005	0.006684	0.004271
E_{25} (762.6)	.66382	.66423	.66427	.66433	.66460	.66438
E_0 (760.2)	.63309	.63404	.63415	.63445	.63417	.63472
E_5 (760.7)	.63928	.64004	.64022	.63997	.64040	.64033
E_{10} (763.1)	.64542	.64599	.64617	.64606	.64629	.64597

Series (3). % CO_2 = 54.48; % H_2 = 45.42

E_{25} (758.5)	0.69025	0.69034	0.69050	0.69046	0.69079	0.69075
E_{30} (758.7)	.69964	.69674	.69695	.69693	.69725	.69723
E_{35} (759.4)	.70334	.70341	.70367	.70366	.70391	.70370
E_{40} (758.8)	.71012	.71024	.71052	.71050	.71085	.71039
E_{45} (758.5)	.71682	.71702	.71749	.71746	.71758	.71732
E_{50} (758.5)	.72357	.72381	.72413	.72411	.72422	.72388

Series (4). % CO_2 = 23.07; % H_2 = 76.93

E_{25} (754.4)	0.71953	0.71917	0.71933	0.71886	0.71948	0.71944
E_0 (755.3)	.68459	.68461	.68479	.68499	.68481	.68480
E_5 (760.0)	.69138	.69140	.69152	.68935	.69119	.69145
E_{10} (760.8)	.69816	.69835	.69839	.69557	.69785	.69820
E_{15} (761.5)	.70535	.70527	.70552	.70628	.70582	.70557
E_{20} (762.5)	.71264	.71235	.71261	.71313	.71265	.71265

Series (5). % CO_2 = 49.51; % H_2 = 50.49

E_{25} (752.7)	0.69436	0.69449	0.69350	0.69459	0.69455	0.69475
E_{30} (752.3)	.70096	.70110	.70006	.70110	.70112	.70096
E_{35} (752.8)	.70780	.70783	.70708	.70790	.70785	.70764
E_{40} (756.1)	.71454	.71443	.71384	.71472	.71459	.71443
E_{45} (756.8)	.72138	.72131	.72069	.72141	.72142	.72110
E_{50} (758.7)	.72821	.72817	.72774	.72840	.72824	.72820

Series (6). % CO_2 = 34.67; % H_2 = 65.33

E_{25} (757.2)	0.70596	0.70672	0.70659	0.70668	0.70707	0.70638
E_{20} (755.5)	.69907	.69991	.69972	.69987	.70053	.69975
E_{15} (754.0)	.69211	.69317	.69310	.69316	.69387	.69324
E_{10} (753.0)	.68489	.68646	.68620	.68637	.68720	.68676
E_0 (751.4)	.67049	.67283	.67276	.67291	.67374	.67315
E_{30} (751.0)	.71269	.71355	.71346	.71364	.71381	.71357

Series (7). % CO_2 = 17.78; % H_2 = 82.22

E_{25} (751.8)	0.72571	0.72666	0.72684	0.72722	0.72689	0.72654
E_{30} (752.2)	.73301	.73358	.73385	.73408	.73390	.73352
E_{35} (753.4)	.74064	.74087	.74107	.74137	.74130	.74108
E_{40} (754.1)	.74796	.74821	.74850	.74858	.74859	.74848

Series (8). % CO_2 = 67.55; % H_2 = 32.45

E_{25} (751.4)	0.67959	0.68033	0.68053	0.68077	0.68079	0.67975
E_0 (755.5)	.64746	.64800	.64880	.64930	.64913	.64690
E_{10} (755.3)	.65987	.66097	.66133	.66178	.66166	.65984
E_{15} (753.8)	.66608	.66713	.66727	.66783	.66783	.66602

constant are contained in Table IV. The values of the standard electromotive force, E^0, of Harned and Ehlers[9] were used. From the gas composition, the barometric pressure and the vapor pressure of water, the partial pressures of the gas in the cell, P_{H_2}, P_{CO_2} and P_{H_2O} may be computed. From P_{H_2}, E_c in equation (6) may be evaluated and, from the Henry's law constants and P_{CO_2}, the last term in equation (6) computed. All these data are necessary for the evaluation of $(-\log K')$ by this equation.

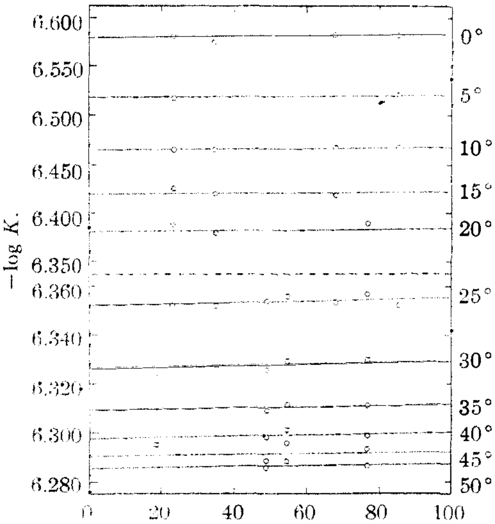

Fig. 3.—Extrapolation of $(-\log K)$ to zero per cent. carbon dioxide.

Evaluation of the Ionization Constant and Derived Thermodynamic Functions

In Fig. 2, $(-\log K')$ at 25° is plotted against the ionic strength. These extrapolated values of $(-\log K)$ are not for pure water but for a solvent containing water and SP_{CO_2} moles per liter of carbon dioxide. That the presence of carbon dioxide makes no appreciable difference is shown by Fig. 3 where the values of $(-\log K)$ at all temperatures are plotted against the percentage of carbon dioxide in the gas mixture. Table V contains these observed extrapolated values of $(-\log K)$.

These results can be expressed within the experimental accuracy by the equation[10]

$$\log K = -(A^*/T) + D^* - C^*T \qquad (15)$$

TABLE V

OBSERVED AND CALCULATED VALUES OF (− LOG K) AND K

t	$-\log K$ (obs.)	$\Delta \times 10^{4a}$	$K \times 10^7$ (calcd.)
0	6.5787	14	2.647
5	6.5170	− 1	3.040
10	6.4640	− 7	3.430
15	6.4187	−13	3.802
20	6.3809	−14	4.147
25	6.3519	5	4.452
30	6.3268	− 2	4.710
35	6.3094	8	4.914
40	6.2978	18	5.058
45	6.2902	11	5.139
50	6.2851	−22	5.161

[a] Observed minus calculated values of $(-\log K)$.

It follows from this relation that the free energy, heat content, heat capacity of ionization, the temperature, T_θ, at which the ionization constant is a maximum and the value of the ionization constant at T_θ are given by

$$\Delta F^0 = A' - D'T + C'T^2 \qquad (16)$$
$$\Delta H_i^0 = A' - C'T^2 \qquad (17)$$
$$\Delta C_{p_i}^0 = -2C'T \qquad (18)$$
$$\Delta S_i^0 = D' - 2C'T \qquad (19)$$
$$T_\theta = \sqrt{A^*/C^*} \qquad (20)$$
$$\log K_\theta = D^* - 2\sqrt{C^*A^*} \qquad (21)$$

where $A' = 2.3026\ RA^*$; $D' = 2.3026\ RD^*$; and $C' = 2.3026\ RC^*$. The numerical values of these quantities evaluated by the method of least squares are: $A^* = 3404.71$; $D^* = 14.8435$; $C^* = 0.032786$; $A' = 15{,}576.6$; $D' = 67.9093$; $C' = 0.149992$.

The third column in Table V contains the deviations of the observed values of $(-\log K)$ from those calculated by equation (15). In the last column values of K computed by this equation are listed.

In Table VI, the results obtained by us are compared with the values of Shedlovsky and MacInnes[11] derived from conductance measurements and by MacInnes and Belcher[12] from cells without liquid junction containing a glass electrode. We note that although good agreement with the conductance data is obtained at 0°, there is an increasing deviation as the temperature rises so that at 38° the difference is 4%.

TABLE VI

COMPARISON WITH THE RECENT DETERMINATIONS

t	$K \times 10^{7a}$	$K \times 10^{7b}$	$K \times 10^{7c}$	ΔH_i^a	ΔH_i^b
0	2.647	2.613	..	4390	4484
15	3.802	3.722	..	3127	2952
25	4.452	4.310	4.54	2248	2075
38	5.007	4.817	4.91	1060	1109

[a] Present investigation. [b] Shedlovsky and MacInnes. [c] MacInnes and Belcher.

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[9] Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932); **55** 3179, (1933).

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

[11] Shedlovsky and MacInnes, THIS JOURNAL, **57**, 1705 (1935). They compare their results with earlier values.

[12] MacInnes and Belcher, *ibid.*, **55**, 2630 (1933); **57**, 1683 (1935).

MacInnes and Belcher's values agree somewhat more closely but not really satisfactorily. However, in spite of these differences, these conductance and electromotive force values are in much better agreement than the earlier values[13] which range between far greater limits. The heat content data check fairly well when we take into account that they were derived by differentiation. Direct calorimetric measurements have been made recently by Pitzer[14] who reported $\Delta H_{\mathrm{i}}^0 = 1843 \pm 60$ cal. at 25°.

Summary

1. The solubility of carbon dioxide in water and aqueous sodium chloride solutions from 0 to 50° has been measured by analyzing the solution contained in cells which were employed for the electromotive force measurements and with the conditions identical in both cases.

2. The logarithms of the Henry's law constants computed from these measurements were expressed by quadratic equations and the constants for these equations were found by the method of least squares.

3. The first dissociation constant of carbonic acid from 0 to 50° was measured by means of cells without liquid junction.

4. The logarithms of the dissociation constants were expressed by a least squared equation. The thermodynamic quantities for the dissociation were calculated from this equation.

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[13] Kauko and Elo, *Z. physik. Chem.*, **A184**, 211 (1939), for example, obtained 2.33 × 10^{-7} and 3.46 × 10^{-7} at 0° and 25°, respectively.

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

NOTES

Derivatives of 2-Bromo-3-methylpentanoic Acid

BY CHARLES D. HURD AND F. W. CASHION

In the course of another investigation, 2-bromo-3-methylpentanoyl bromide and several of its derivatives have been prepared.

To a mixture of 25 g. of 3-methylpentanoic acid[1] with 3 g. of red phosphorus in a 200-cc. three-neck flask fitted with a condenser, mercury seal stirrer, and separatory funnel, 30 g. of bromine was added slowly with stirring. The flask was then placed on a water-bath at 95° and about 30 g. of bromine added with stirring until no further absorption took place. The product was distilled at 23 mm. pressure and the fraction boiling between 92 and 102° collected. Redistilled, a yield of 30 g., or 54% of colorless 2-bromo-3-methylpentanoyl bromide, boiling at 98–100° under 23 mm. pressure and fuming in air, was obtained. It was analyzed for bromine by fusion with sodium peroxide.

Anal. Calcd. for $C_6H_{10}OBr_2$: Br, 62.0. Found: Br, 63.1.

2-Bromo-3-methylpentanamide.—A well-stirred mixture of 1 g. of the acid bromide in 10 cc. of concentrated ammonium hydroxide was filtered and the solid amide crystallized from 2 cc. of a 25% aqueous alcohol; yield, 0.3 g. of a white crystalline substance, m. p. 104° and slightly soluble in water.

Anal. Calcd. for $C_6H_{12}ONBr$: Br, 41.2. Found: Br, 40.7.

2-Bromo-3-methylpentananilide.—One gram of the acid bromide was mixed with 1 g. of aniline. Considerable heat was evolved. After trituration with 10 cc. of water and decantation, the remaining solid was crystallized twice from 4-cc. portions of a 60% aqueous alcohol; yield, 0.5 g. of a white, crystalline, water-soluble compound of m. p. 84°.

Anal. Calcd. for $C_{12}H_{16}ONBr$: Br, 29.6. Found: Br, 30.3.

2-Bromo-3-methylpentane-*p*-toluidide.—A similar procedure to the above with 1 g. of *p*-toluidine yielded 0.6 g. of the white, water-insoluble *p*-toluidide, m. p. 105°.

Anal. Calcd. for $C_{13}H_{18}ONBr$: Br, 28.1. Found: Br, 28.8.

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[1] "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1931, Vol. 11, p. 76.

2,2,2-Trifluoroethyl Iodide

BY HENRY GILMAN AND R. G. JONES

2,2,2-Trifluoroethyl iodide has been prepared by the reaction of hydrogen iodide with 2,2,2-trifluorodiazoethane[1a] in toluene solution at −75°. Although the reaction was violent at the low temperature used, a 77% yield of trifluoroethyl iodide was obtained.

$$CF_3CHN_2 + HI \longrightarrow CF_3CH_2I + N_2$$

The reaction of red phosphorus and iodine with trifluoroethanol[1b] produced large quantities of hydrogen iodide, but gave only very small yields of the 2,2,2-trifluoroethyl iodide.

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[1] (a) Gilman and Jones, THIS JOURNAL, **65**, 1458 (1943); (b) Gilman and Jones, *ibid.*, **65**, (1943).