grant which enabled us to purchase the deuterium oxide used in this work.

Summary

The solubility of carbon dioxide in 99.8% D_2O at 25° has been measured relative to its solubility in H_2O at the same temperature. In terms of the Ostwald coefficient the solubilities are the same within less than 1%. On a molal basis this means that carbon dioxide is 0.902 times as soluble in D_2O as in H_2O.

WILLIAMSTOWN, MASS. RECEIVED JUNE 10, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WILLIAMS COLLEGE]

The First Thermodynamic Ionization Constant of Deuterio-carbonic Acid at 25°[1]

BY JAMES CURRY AND C. L. HAZELTON

Introduction

Since carbon dioxide plays an important role in many physiological processes and the effect of deuterium oxide on living matter has been studied extensively, it is of importance to determine the strength of deuterio-carbonic acid. From the standpoint of chemical theory the strength of this acid is also of interest.

The method used in this work followed that of Korman and La Mer[2] very closely. In this paper it was shown that heavy water studies could be made using a quinhydrone electrode in cells without transference of the type developed by Harned and Ehlers.[3] On account of the cost of deuterium oxide the measurements were limited to a relative determination of the first thermodynamic ionization constants of proto- and deuterio-carbonic acid in dilute solutions. No extrapolation to infinite dilution was attempted.

Measurements were made using the following cells

$$\text{Pt, Q, QH}_2\text{, H}_2\text{CO}_3\text{, KHCO}_3\text{, KCl, AgCl, Ag} \quad \text{(I)}$$

$$\text{Pt, Q, QD}_2\text{, D}_2\text{CO}_3\text{, KDCO}_3\text{, KCl, AgCl, Ag} \quad \text{(II)}$$

As is well known, the potential of cell I is given by

$$E = E_0 - \frac{RT}{F} \ln m_{\text{H}}\, m_{\text{Cl}} - \frac{RT}{F} \ln f_{\text{H}} f_{\text{Cl}} \qquad (1)$$

where the E_0 term includes the standard electrode potential for the quinhydrone and the silver–silver chloride electrodes in H_2O; m is the concentration in molal terms and f is the activity coefficient of the quantities indicated by the subscripts.

The primary dissociation of proto-carbonic acid may be written in the following manner

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

The first thermodynamic ionization constant for proto-carbonic acid is accordingly

$$K_{\text{H}} = \frac{m_{\text{H}}\, m_{\text{HCO}_3}}{m_{\text{CO}_2}} \cdot \frac{f_{\text{H}} f_{\text{HCO}_3}}{f_{\text{CO}_2}} \qquad (2)$$

where m_{CO_2} represents the total concentration ($CO_2 + H_2CO_3$) of dissolved carbon dioxide in molal terms.[4] A similar expression would hold for the thermodynamic ionization constant of deuterio-carbonic acid, K_{D}.

Replacing m_{H} in (1) by its value from (2) we obtain for the e. m. f. of cell I

$$E = E_0 - \frac{RT}{F} \ln \frac{m_{\text{Cl}}\, m_{\text{CO}_2}}{m_{\text{HCO}_3}} - \frac{RT}{F} \ln K_{\text{H}} - \frac{RT}{F} \ln \frac{f_{\text{Cl}} f_{\text{CO}_2}}{f_{\text{HCO}_3}} \qquad (3)$$

In order to determine K_{H} this expression may be put into a somewhat more convenient form. In an aqueous solution, in the region of a partial pressure of 760 mm., carbon dioxide obeys Henry's law so we may say that $m_{\text{CO}_2} = hp_{\text{CO}_2}$ where h is a constant. Using this expression and rearranging (3) we obtain

$$\log K_{\text{H}} = \frac{E_0 - E}{0.0591} - \log \frac{m_{\text{Cl}}}{m_{\text{HCO}_3}} - \log h - \log p_{\text{CO}_2} - \log \frac{f_{\text{Cl}} f_{\text{CO}_2}}{f_{\text{HCO}_3}} \qquad (4)$$

The similar expression which holds for cell II is

$$\log K_{\text{D}} = \frac{E_0' - E}{0.0591} - \log \frac{m_{\text{Cl}}'}{m_{\text{DCO}_3}'} - \log d - \log p_{\text{CO}_2} - \log \frac{f_{\text{Cl}}' f_{\text{CO}_2}'}{f_{\text{DCO}_3}'} \qquad (5)$$

The prime terms refer to the values for D_2O and d corresponds to h except that it refers to the solubility of carbon dioxide in D_2O.

Since carbon dioxide is a neutral molecule its activity will be unaffected by ions in dilute solutions so we may put $f_{\text{CO}_2} = f_{\text{CO}_2}' = 1$.[5] If the

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[1] Based on a thesis presented by C. L. Hazelton to Williams College in 1938, in partial fulfilment of the requirements for the degree of Master of Arts.

[2] Korman and La Mer, THIS JOURNAL, **58**, 1396 (1936).

[3] Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

[4] For a discussion of this expression see MacInnes and Belcher, *ibid.*, **55**, 2630 (1933).

[5] This statement is not absolutely true due to the salting-out effect of the electrolytes on the carbon dioxide. The influence of this factor will be considered later.

molal concentration of potassium chloride is about the same as that of potassium bicarbonate, then in dilute solutions, since they are both uni-univalent electrolytes, their respective activity coefficients will be practically equal, so in (4) and (5) the last logarithmic term on the right-hand side will be almost zero and consequently may be neglected. This will be true for both the H_2O and D_2O solutions. Even if these terms do not vanish completely they should be the same in H_2O and D_2O solutions of the same molal concentrations since the dielectric constant of H_2O is nearly identical with that of D_2O. Therefore, in order to determine the ratio of ionization constants it is only necessary to determine K_H and K_D at one and the same ionic strength. The measurements should be carried out in dilute solutions which have been made up so that m_{Cl} and m_{HCO_3} (or m'_{Cl} and m'_{DCO_3}) are about equal. A discussion of the remaining quantities in equations (4) and (5) will be given later.

Experimental

Materials.—The carbon dioxide was obtained from a commercial tank and was 99.8% pure. The deuterium oxide was purified as previously described[6] and at the end of the measurements was 99.1% D_2O. Eastman Kodak Co. quinhydrone was used without further purification. The potassium bicarbonate was purified by the method of MacInnes and Belcher[4] (p. 2633) and the potassium chloride was recrystallized twice from distilled water and dried at 120°. A semi-micro balance was used in making up the D_2O solutions.

Electrodes.—The silver–silver chloride electrodes were prepared by the method of Brown.[7] Pairs showing a potential difference of not more than 0.05 mv. were used in each experiment. The platinum electrodes were of the spiral type and were kept in cleaning solution when not in use. They agreed with each other better than 0.05 mv. Before insertion into the cells, both types of electrodes were well rinsed with the appropriate solution. This required about 1.6 cc. per electrode.

Cells.—Two identical cells (A and B) were used and all measurements were carried out in duplicate. Each cell was shaped like the letter H. The two side arms had an inside diameter of 8 mm. and a length of 8 cm. and were of course closed at the bottom. The top of each arm was widened out so that it would take a no. 2 rubber stopper. The two side arms of a cell were connected by means of a stopcock which had a 1.5-mm. bore. The connection tubes were sealed in just where the side arms started to widen out and the stopcocks were greased only at the top and bottom. Each rubber stopper carried an electrode, an inlet tube for the introduction of carbon dioxide and an outlet tube. The total amount of solution needed for each cell was about 6 cc. The cells were immersed in a thermostat adjusted to 25.00 ± 0.01°.

Before the carbon dioxide entered the cell it was saturated with water vapor by allowing it to bubble through a trap immersed in the thermostat and filled with the appropriate water. After bubbling through the cell solution the carbon dioxide escaped into the air through a tube which dipped just under the surface of some paraffin oil.[8] Thus the pressure of carbon dioxide over the solution was essentially equal to the atmospheric pressure minus the vapor pressure of water in the cell. The gas connections were arranged so that the pressure was the same in all four compartments. It should be pointed out that carbon dioxide was bubbled through both the quinhydrone and the silver–silver chloride electrode compartments. This was done in order to eliminate the possibility of any liquid junction potential.

Experimental Procedure.—Measurements were made with a Leeds and Northrup type K potentiometer and a type R galvanometer. The standard cell was checked against one calibrated by the Bureau of Standards. Measurements were made first with H_2O and then with D_2O. Reproducible results were obtained without resorting to a vacuum technique to remove oxygen. In making measurements the appropriate solution was first saturated with carbon dioxide and then part of it was put in cell A and part in cell B. Quinhydrone was then added, the stoppers inserted tightly and carbon dioxide bubbled through the cells with the stopcocks closed. A gentle flow of gas was maintained except when e. m. f. measurements were actually being made. Equilibrium was established in about thirty minutes and the potential of any one cell remained constant within 0.2 mv. for a period of two to three hours. After equilibrium was established the e. m. f. values were the same whether or not the stopcocks were open.

Results and Discussions

In order to test the method, apparatus and materials the thermodynamic ionization constant for acetic acid in H_2O was determined using the above method except that acetic acid and potassium acetate were used instead of carbon dioxide and potassium bicarbonate. At an ionic strength of 0.06132 the ionization constant was found to be 1.75×10^{-5}, which is in good agreement with the value in the literature.[9]

Table I lists our experimental data and the calculated results.

Several of the quantities in equations (4) and (5) require further discussion. E_0 was obtained from Harned and Wright's[10] data for the quin-

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(6) Curry and Hazelton, THIS JOURNAL, **60**, 2771 (1938).

(7) A. S. Brown, *ibid.*, **56**, 646 (1934).

(8) With this technique it is conceivable that the cell solution became supersaturated with carbon dioxide. If such an effect did occur it must have been small because, as will be pointed out later, our value for K_H agrees well with careful measurements made by other workers. Even if supersaturation did occur it should be practically the same in H_2O and D_2O and accordingly have no appreciable effect on K_H/K_D.

(9) See for example reference (3), page 1355.

(10) Harned and Wright, *ibid.*, **55**, 4849 (1933).

TABLE I

FIRST THERMODYNAMIC IONIZATION CONSTANTS OF PROTO- AND DEUTERIO-CARBONIC ACID AT 25°

$E_0 = -0.4775$, $\log h = -4.3533$; $E_0 = -0.5119$, $\log d = -4.3987$

P_{CO_2}, mm	Molality		E			pK	$K \times 10^7$
	KCl	Bicarbonate	Cell A	Cell B	Av.		
			H_2O				
711.8	0.02580	0.02122	0.0182	0.0176	0.0179	6.354	4.43
719.7	.02612	.02224	.0183	.0182	.01825	6.338	4.59
719.3	.02546	.01229	.0323	.0318	.03205	6.351	4.46
718.3	.03054	.02351	.0202	.0203	.02025	6.347	4.50
							4.50 ± 0.05
			>99.1% D_2O				
716.4	.02608	.02530	.0206	.0206	.0206	6.775	1.68
725.0	.03161	.02431	.0265	.0263	.0264	6.783	1.63
718.5	.02393	.01959	.0256	.0255	.02555	6.766	1.72
							1.68 ± 0.02

$K_H/K_D = 2.68$

hydrone electrode and the silver–silver chloride electrode. The term E_0' is made up of the standard electrode potential of quinhydrone in D_2O and the standard electrode potential for the silver–silver chloride electrode in D_2O. The quinhydrone potential was obtained from the work of La Mer and Korman,[11] and is equal to -0.7341 v. The standard electrode potential of the silver–silver chloride electrode should be the same in D_2O as in H_2O since there is no theoretical reason for thinking that f_{Cl} and f'_{Cl} differ, provided the molal concentrations of the chloride ions are the same in the two kinds of water.

The terms h and d are the Henry's law constants for the molal solubility of carbon dioxide in H_2O and D_2O when the partial pressure of this gas is expressed in mm., and these, or rather their logarithms, have been calculated from some previous work done by us.[6] In very exact work the salting out effect of the electrolytes on the carbon dioxide should be considered but this often is neglected. At the ionic strengths we used, if this correction were made the values of K_H and K_D recorded above would have to be increased by about 0.7%. This correction would certainly be practically the same for both kinds of water and accordingly would not affect the K_H/K_D ratio given above.

No account has been taken of the secondary dissociation of carbonic acid. This is allowable since it is very small ($K_{II} = 7 \times 10^{-11}$) compared to the first dissociation. It also should be pointed out that the solution actually used for cell II was made up using $KHCO_3$ but exchange must take place very rapidly and at the concentrations used the equilibrium point should be far over on the $KDCO_3$ side.

In order to establish the reliability of our measurements it is necessary to compare our values for K_H with those recorded in the literature. Up until a few years ago it was thought that K_H was equal to 3.5×10^{-7} at 25°. Recently, however, MacInnes and associates redetermined K_H using two methods; with a glass electrode[4] they found K_H equaled 4.5×10^{-7}, and by conductivity methods[12] to be 4.3×10^{-7}.

Our value of 4.5×10^{-7} agrees very well with that of MacInnes and Belcher at the same ionic strength. Of course we used a potentiometric method also but ours differed considerably from theirs in respect to details.

The heavy water used in determining the above K_H/K_D ratio was at least 99.1% D_2O. To a first approximation the curve $K_H/K_D - N_{D_2O}$ is linear and this would mean that for 100% D_2O the ratio would be greater but certainly not more than 1% higher. Since this is less than the precision of our measurements this correction will not be applied.

It is of interest to compare our results with those of other workers. Rule and La Mer,[13] making very careful measurements on five acids, found that the K_H/K_D ratio increases as the strength of the acid decreases. This is in accordance with the prediction of Lewis and Schutz and the theory of Halpern.[14] From the Rule–La Mer data one might expect for carbonic acid a ratio of 3.6.

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[11] La Mer and Korman, THIS JOURNAL, **57**, 1511 (1935). See also ref. (2).

[12] Shedlovsky and MacInnes, *ibid.*, **57**, 1705 (1935).

[13] Rule and La Mer, *ibid.*, **60**, 1974 (1938).

[14] Lewis and Schutz, *ibid.*, **56**, 1913 (1934); Halpern, *J. Chem. Phys.*, **3**, 456 (1935).

Our value, 2.68, is 25% smaller, and this difference is much greater than our experimental error which is about 2%. However, it should be remembered that carbonic acid is a peculiar acid in that the proton (or deuteron) must come exclusively from the water. Thus the hydration equilibrium plays an important role and it probably will not be the same in H_2O and D_2O. This factor may account for the difference mentioned above.

We are indebted to the Class of 1900 Fund for a grant which enabled us to purchase the deuterium oxide used in this work.

Summary

The ratio of the first thermodynamic ionization constants of proto- and deuterio-carbonic acid has been determined potentiometrically using a cell without transference in which the electrodes were quinhydrone and silver–silver chloride. Using 99.1% D_2O the ratio, K_H/K_D, has been found to be 2.68 at 25°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Conductivities of Concentrated Mixtures of the Nitrates of Some Uni-, Di-, and Trivalent Cations in Aqueous Solution

BY PIERRE VAN RYSSELBERGHE AND GOON LEE

As a further step in our investigation of the conductivity of concentrated mixtures of strong electrolytes[1] we have studied a number of nitrates of uni-, di-, and trivalent cations at different total concentrations ranging from 1 to 5 *N*. All possible types of binary mixtures have been included: two univalent cations, one uni- and one divalent cation, two divalent cations, one uni- and one trivalent cation, one di- and one trivalent cation, two trivalent cations. The method was essentially the same as in our previous work. The conductivities of the pure salts were found to be in close agreement with the existing standard data (I. C. T.; L. B. R.), except in three cases [$LiNO_3$, $Mg(NO_3)_2$, $Cr(NO_3)_3$] for which the standard data seem to be somewhat in error. Moreover, some conductivities of pure salts are reported here for the first time. Others have been obtained for the first time at 25°. The results are recorded in Table I in which we give the conductivities of twenty types of mixtures arranged in series corresponding to the same total equivalent concentration. We represent by x and $1-x$ the fractions of the total equivalent concentration corresponding to salts 1 and 2, salt 1 being the first in the title of the series. For each solution we give the specific and the equivalent conductivity and the difference $\Delta\Lambda$ between the measured conductivity and that calculated from the simple, uncorrected mixture rule:

$$\Lambda = x\Lambda_1 + (1 - x)\Lambda_2$$

Two series of mixtures (19 and 20) contain nitric acid as one of the components, the maximum amount of nitric acid present being in both cases half the total normality.

TABLE I

CONDUCTIVITIES OF CONCENTRATED MIXTURES AT 25°

Composition x	$1-x$	Specific conductivity	Equivalent conductivity Measured	Calculated	$-\Delta\Lambda$
	1.1	1 *N* mixtures of $KNO_3 + NaNO_3$			
1	0	0.09254	92.54		
$^3/_4$	$^1/_4$	.08798	87.98	88.37	0.39
$^1/_2$	$^1/_2$	.08324	83.24	84.19	.85
$^1/_4$	$^3/_4$	.07973	79.73	80.02	.29
0	1	.07585	75.85		
	1.2	2 *N* mixtures of $KNO_3 + NaNO_3$			
1	0	0.15848	79.24		
$^3/_4$	$^1/_4$	.14993	74.97	75.20	0.23
$^1/_2$	$^1/_2$	.14104	70.52	71.17	.65
$^1/_4$	$^3/_4$	.13383	66.92	67.12	.20
0	1	.12617	63.09		
	1.3	3 *N* mixtures of $KNO_3 + NaNO_3$			
1	0	0.21042	70.16		
$^3/_4$	$^1/_4$	.19996	65.99	66.00	0.01
$^1/_2$	$^1/_2$	.18413	61.38	61.85	.48
$^1/_4$	$^3/_4$	.17222	57.41	57.72	.31
0	1	.16075	53.58		
	2	5 *N* mixtures of $NaNO_3 + LiNO_3$			
1	0	0.19815	39.65		
$^3/_4$	$^1/_4$	.18944	37.89	38.28	0.39
$^1/_2$	$^1/_2$	.18167	36.42	36.72	.30
$^1/_4$	$^3/_4$	.17511	35.02	35.27	.25
0	1	.16910	33.82		

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[1] Van Rysselberghe and Nutting, THIS JOURNAL, **56**, 1435 (1934); **59**, 333 (1937); Van Rysselberghe, Grinnell and Carlson, *ibid.*, **59**, 336 (1937).