vice and we are also grateful to Dr. J. B. Conant for his valuable suggestions. Dr. W. E. Vaughan and Dr. Ralph D. Thompson have taken part in the early stages of this work.

Summary

Certain brominations and chlorinations have been studied calorimetrically, the following being the results

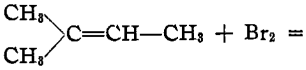
$C_2H_4 + Br_2 = C_2H_4Br_2 - 29{,}058 \pm 300$ cal.

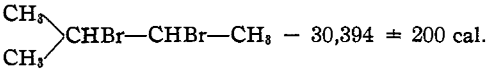
$C_3H_6 + Br_2 = C_3H_6Br_2 - 29{,}412 \pm 200$ cal.

$H_2C{=}CH{-}C_2H_5 + Br_2 = CH_2Br{-}CH_2Br{-}C_2H_5 - 29{,}585 \pm 200$ cal.

trans-$H_3C{-}CH{=}CH{-}CH_3 + Br_2 =$ *i*-$CH_3{-}CHBr{-}CHBr{-}CH_3 - 29{,}075 \pm 200$ cal.

cis-$H_3C{-}CH{=}CH{-}CH_3 + Br_2 =$ *dl*-$CH_3{-}CHBr{-}CHBr{-}CH_3 - 30{,}177 \pm 200$ cal.


$(CH_3)_2C{=}CH{-}CH_3 + Br_2 =$


$(CH_3)_2CHBr{-}CHBr{-}CH_3 - 30{,}394 \pm 200$ cal.

$C_2H_4 + Cl_2 = C_2H_4Cl_2 - 43{,}653 \pm 120$ cal.

All heats of reaction refer to 355°K. and gases at one atmosphere total pressure.

The most notable conclusion to be drawn from these data is that substitution on the ethylenic group results in increased heat evolution on addition of bromine, while previously it was found to decrease the heat of hydrogenation.

It is pointed out that the observed trends give a thermodynamic basis to the so-called Markownikoff rule and to the trend of bromine to replace hydrogen on the most substituted carbon atom of a saturated hydrocarbon. A rule is formulated which makes possible a calculation of quite accurate heats of addition of hydrogen halides and of substitution of bromine.

CAMBRIDGE, MASS. RECEIVED AUGUST 5, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WILLIAMS COLLEGE]

The Solubility of Carbon Dioxide in Deuterium Oxide at 25°[1]

BY JAMES CURRY AND C. L. HAZELTON

In the course of measuring the first ionization constant of deuterio-carbonic acid, it was found necessary to determine the solubility of carbon dioxide in deuterium oxide. This measurement is of interest in itself since, up until the present, no values for the solubility of gases in deuterium oxide have appeared in the literature.

Experimental

Apparatus.—The apparatus used was of the Ostwald type[2] and the measurements were carried out by means of the "dry method." The buret, which was surrounded by a water jacket, had a volume of 10 cc. and was graduated in 0.05 cc. The absorption vessel had a volume of approximately 7 cc. The buret and the absorption vessel were connected by a flexible piece of copper tubing 1.5 meters long and 1 mm. internal diameter. In order to fasten the copper tubing to the glass, short pieces of 7-mm. glass tubing were sealed to the three-way capillary stopcocks which were at the top of the buret and the absorption vessel. The copper tubing was inserted to a depth of about 3 cm. into the glass tubing and the joints were then made fast with picein. In order to minimize breakage the copper tubing was held by a brass clamp at a point near the picein joint at the buret stopcock. This clamp in turn was fastened to the ringstand which held the buret. Another type of brass clamp, acting as a splint, strengthened the other copper–picein–glass joint at the absorption vessel. This mode of connection permitted a vigorous shaking of the absorption vessel but when necessary it was very simple to disconnect the latter.

Materials.—The carbon dioxide came from a commercial tank. It was analyzed by absorption in a potassium hydroxide solution and was found to be 99.8% pure.

The deuterium oxide was from a commercial source and at the beginning of the measurements was 99.9% D_2O. It was purified by distillation from alkaline permanganate, then from phosphoric anhydride and finally carried through a distillation without any reagents in a still especially reserved for this purpose. Before use the deuterium oxide was refluxed in order to remove any dissolved gases. During this operation it was protected from the atmosphere by means of a soda lime–calcium chloride tube. After the solubility measurements were completed the deuterium oxide was used for ionization constant determinations and when these were finished the analysis was 99.1% D_2O.

Measurements.—These were carried out in the usual manner except that a few slight modifications were necessary because the quantities of deuterium oxide used were relatively small and deuterium oxide is hygroscopic. During a measurement the absorption vessel was shaken in a thermostat adjusted to 25.00 ± 0.01°. The absorption vessel contained a short piece of 1-mm. copper wire which moved about during the shaking and thus aided in

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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] Just, *Z. physik. Chem.*, **37**, 342 (1901).

lessening the time required to reach equilibrium. The amount of water in the absorption vessel was obtained from the weight of the dry vessel and the weight of the vessel plus contents at the end of the measurements, allowance being made for the weight of the carbon dioxide present.

Equilibrium was established in about ten minutes. The vessel was then allowed to stand for fifty minutes in contact with the carbon dioxide and was then shaken for a few minutes. No additional absorption was ever noted.

Results

In order to test the apparatus, measurements were also made on the solubility of carbon dioxide in ordinary water. The experiments were carried out in exactly the same way except that H_2O was used in place of D_2O. Thus if any errors were present while one kind of water was being used they also would be present during the measurements with the other kind of water. The experimental data and the calculated results are given in the table.

SOLUBILITY OF CARBON DIOXIDE IN H_2O AND D_2O AT 25°

The total volume of the absorption vessel was 6.811 cc. except in the first experiment with H_2O, where it was 8.868 cc.

	Buret		Abs. vessel			
Atm. pres., mm.	t, °C.	Change in vol., cc.	Par. pres. of CO_2 mm.	Wt. of water, g.	Ostwald coef. λ	
			H_2O			
749.4	21.6	7.64	722.9	4.7374	0.816	
754.0	21.2	6.12	728.2	2.2735	.822	
747.5	21.8	6.12	721.5	2.4543	.834	
735.5	21.3	5.90	709.3	3.3496	.813	
				Av.	0.821	± 0.007
			D_2O			
741.2	20.8	6.11	718.6	2.6003	0.817	
743.7	21.0	5.90	720.4	3.9476	.818	
749.9	21.4	5.92	726.6	3.8461	.817	
732.8	21.2	6.00	709.7	3.5729	.831	
735.9	23.0	5.94	712.6	4.0429	.823	
754.5	21.3	5.88	731.2	3.9585	.810	
				Av.	0.819	± 0.005

There is no general agreement as to the best method for expressing the solubility of gases in liquids. We have chosen the Ostwald coefficient, λ, *i. e.*, the volume of gas (measured at experimental conditions) absorbed by unit volume of liquid, because it is often used in theoretical discussions.

In order to determine the partial pressure of the carbon dioxide in the absorbing vessel it was necessary to know the vapor pressures of the two waters at 25°. For deuterium oxide the value 20.7 mm. was used.[3]

As mentioned previously, the composition of the deuterium oxide changed slightly during the experiment. The average composition was taken as 99.8% D_2O. Thus in calculating the above results $d^{25}{}_4$ was taken as 1.1042. In the calculations correction was made for the slight amount of impurities in the carbon dioxide.

Discussion

Shedlovsky and MacInnes[4] have made the most recent determination of the solubility of carbon dioxide in H_2O. The value they obtained was 0.03372 mole per liter per atmosphere. In terms of the Ostwald coefficient this corresponds to $\lambda = 0.825$. Our value agrees with theirs well within our experimental error, which is less than 1%, so we can conclude that our results are fairly reliable. It should be pointed out that the precision obtainable in solubility measurements is largely determined by the quantities of water used. With the present high cost of D_2O it is necessary to make some sacrifice in precision.

Thus, from our data, it is apparent that the values for the Ostwald coefficient for carbon dioxide in H_2O and D_2O are the same within less than 1%. Consequently on a molal basis (moles/1000 g. of water) carbon dioxide is less soluble in D_2O than in H_2O, the respective solubilities being 0.0304 and 0.0337 molal when the partial pressure of carbon dioxide is one atmosphere.

This result is about what one would expect from theory. It has been known for a long time that there usually is at least a qualitative relationship between solubility of a gas and surface tension of the solvent. Uhlig[5] has been one of the latest to attempt a quantitative expression. Early workers reported a difference of about 7% in the surface tension of the two kinds of waters but this result has not been substantiated. Jones and Ray[6] found that the surface tensions were the same within 0.054%. Thus one would expect no great difference in the solubility of a gas, such as carbon dioxide, in the two waters, particularly since, in addition, the values for the dielectric constants are the same within 1%.[7]

We are indebted to the Class of 1900 Fund for a

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(3) Wahl and Urey, *J. Chem. Phys.*, **3**, 411 (1935).

(4) Shedlovsky and MacInnes, THIS JOURNAL, **57**, 1708 (1935). For a summary of the literature see Morgan and Pyne, *J. Phys. Chem.*, **34**, 1578 (1930).

(5) Uhlig, *J. Phys. Chem.*, **41**, 1215 (1937).

(6) Jones and Ray, *J. Chem. Phys.*, **5**, 505 (1937). See also Lachs and Minkow, *Nature*, **136**, 186 (1935).

(7) Lewis, Olsen and Maroney, THIS JOURNAL, **55**, 4731 (1933).

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

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

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

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.