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.

NEW HAVEN, CONN. RECEIVED MARCH 13, 1941

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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).

[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).

Elektrisk Kvaelstof A/S, Oslo, was found to contain 99.54 mole% D_2O after distillation in vacuum. The calculation of the mole percentage is based on the density value d^{25}_{25} 1.10764 for pure heavy water.[3,5,6]

A 16-ml. pycnometer of transparent vitreous quartz made by Geyer, Berlin, has a capillary 0.5 mm. in diameter with a small extension near the top. The capillary stem is graduated in millimeters for a length of 5 centimeters. The filling is aided by suction. The ground cap is sealed with mercury during observation. The thermostat used keeps the temperature constant within +0.002°, while the actual temperature is recorded by a thermometer which has a precision of +0.02°.

The density of the sample is determined for the temperature range between 3.8 and 50°. The measurement begins from the region of the density maximum of heavy water.[3,5,7] Tiny portions of the sample are removed successively for the measurement of smaller densities. In the calculation of the density of the sample, its volume is corrected for the thermal expansion of vitreous quartz.[8] All weighings are corrected for the buoyancy of air. The experimental results for 99.54 mole% D_2O are shown in Table I.

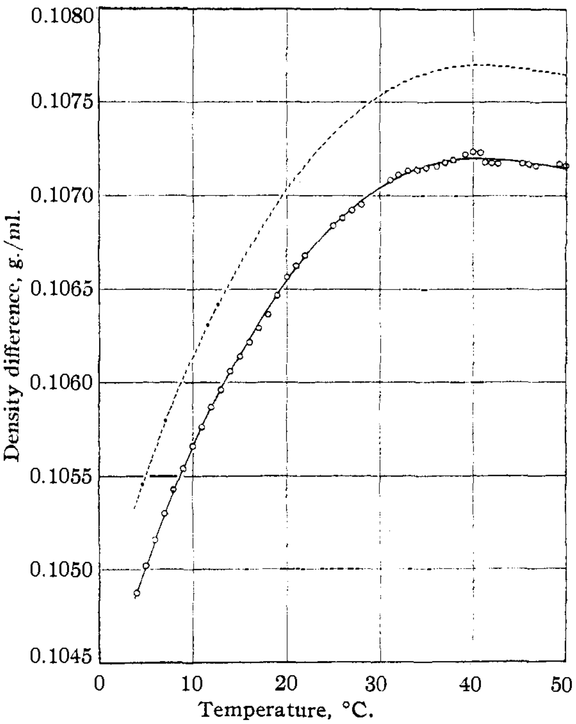

Fig. 1.—Density difference between ordinary and heavy water: ——— $d_{99.54\text{ mol\% }D_2O} - d_{H_2O}$; – – – – $d_{D_2O} - d_{H_2O}$.

TABLE I

MEASUREMENTS ON 99.54 MOLE% D_2O

Temp., °C.	Density, g./ml.	Temp., °C.	Density, g./ml.
4	1.10487	28	1.10322
5	1.10501	29	1.10296
6	1.10513	31.1	1.10242
7	1.10523	32	1.10217
8	1.10530	33	1.10186
9	1.10535	34	1.10154
10	1.10539	35	1.10121
11	1.10540	36.1	1.10084
12	1.10540	37	1.10053
13	1.10537	37.9	1.10022
14	1.10533	39.2	1.09977
15	1.10527	40	1.09948
16	1.10519	40.8	1.09917
17	1.10510	41.3	1.09892
18	1.10499	42	1.09865
19	1.10490	42.7	1.09836
20	1.10480	45.3	1.09729
21	1.10465	46	1.09699
22	1.10448	46.7	1.09668
25	1.10391	49.3	1.09555
26	1.10370	50	1.09523
27	1.10346		

Figure 1 shows the difference between the densities of ordinary water[9] and 99.54 mole % D_2O. The circles represent the experimental points. Their maximum deviation from the smoothed curve is ±0.00004 g./ml. The density differences for 99.54 mole % D_2O are then extrapolated to 100% D_2O, as shown by the dotted curve. Thus, in the order of increasing temperature the density difference at first increases by diminishing amount until it reaches the maximum value 0.10770 g./ml. at 40° and then decreases slowly after 40°.

TABLE II

DENSITY OF HEAVY WATER BELOW 50°

Temp., °C.	d_{H_2O}, g./ml.	d_{D_2O}, g./ml.	$d_{D_2O} - d_{H_2O}$ g./ml.
3.8	1.00000	1.10533	0.10533
5	0.99999	1.10549	.10550
10	.99973	1.10588	.10615
11.2	.99961	1.10589	.10628
15	.99913	1.10577	.10664
20	.99823	1.10527	.10704
25	.99707	1.10440	.10733
30	.99568	1.10321	.10753
35	.99406	1.10172	.10766
38	.99299	1.10068	.10769
39	.99262	1.10032	.10770
40	.99225	1.09995	.10770
41	.99186	1.09956	.10770
42	.99147	1.09917	.10770
43	.99107	1.09876	.10769
45	.99024	1.09792	.10768
50	.98807	1.09572	.10765

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(5) E. Swift, Jr., THIS JOURNAL, **61**, 1293 (1939).

(6) The density values of pure heavy water given by different authors differ considerably from one another, *e. g.*, P. W. Selwood, H. S. Taylor, J. A. Hipple, Jr., and W. Bleakney [*ibid.*, **57**, 642 (1935)] gave d^{25}_{25} 1.10790. However, H. L. Johnston [*ibid.*, **61**, 878 (1939)] gave d^{25}_{25} 1.10763.

(7) T. L. Chang and J. Y. Chien, *J. Chinese Chem. Soc.*, **8**, No. 1, (1941).

(8) "Int. Crit. Tables," Vol. IV, 1928, p. 21.

(9) "Int. Crit. Tables," Vol. III, 1928, p. 24.

Table II gives the density differences between ordinary and heavy water for some even temperatures between the freezing point of heavy water and 50°, including a value at its density maximum and some in the neighborhood of the maximum difference. The density values of heavy water given in the third column agree with those of Stokland, Ronaess and Tronstad within ±0.00007 g./ml. in the temperature range of their measurement.

Furthermore, the ratio of the densities of ordinary and heavy water, namely, d_{D_2O}/d_{H_2O}, also increases by diminishing amount with increasing temperature. Since the ratio becomes 1 at 370°, it must also pass through a maximum. This maximum ratio lies, however, beyond the temperature range of this investigation.

Summary

The density of heavy water is measured with a quartz pycnometer between its freezing point and 50°. The differences between the densities of ordinary and heavy water show a maximum at 40°.

KUNMING, CHINA RECEIVED MARCH 22, 1941

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Elimination of Liquid Junction Potentials. III. Comparison of the Silver–Silver Chloride and Silver–Silver Bromide Electrodes at 25°

BY BENTON BROOKS OWEN AND EDWARD J. KING

As a further test of a method proposed[1,2] for eliminating liquid junction potentials by extrapolation, the standard potentials of the silver–silver chloride and silver–silver bromide electrodes were compared by means of the cell

$$\text{Ag-AgBr}\left|\begin{matrix}\text{KBr}(x)m\\ \text{KNO}_3(1-x)m\end{matrix}\right|\begin{matrix}\text{KCl}(x)m\\ \text{KNO}_3(1-x)m\end{matrix}\left|\text{AgCl-Ag}\right.$$

The electromotive force of this cell may be expressed by the equation

$$E = E^0 - k \log a_{\text{Cl}}/a_{\text{Br}} \pm E_j \qquad (1)$$

where $k = 0.00019844\ T$, and E_j is the unknown liquid junction potential. Keeping m constant, and varying x so that $m_{\text{Br}} = m_{\text{Cl}}$, this equation may be written

$$E = E^0 - k \log \gamma_{\text{Cl}}/\gamma_{\text{Br}} \pm E_j \qquad (2)$$

In the limit, when $x = 0$, E_j must also be zero. Furthermore the term containing the activity coefficient ratio assumes thermodynamic significance under this condition, and should vary linearly with the ionic strength in dilute solutions. Consequently a value of $E_{x=0}$, obtained by extrapolation against x at constant m, differs from E^0 only by the term $[k \log \gamma_{\text{Cl}}/\gamma_{\text{Br}}]_{x=0}$ which is proportional to m. E^0 is determined by extrapolation of $E_{x=0}$ against m.

Materials and Technique.—The stock solutions of potassium chloride and nitrate were prepared from the purified salts described in the first paper in this series.[1] The potassium bromide was some of sample B used by Owen and Foering,[3] and their materials were also used in the preparation of the electrodes. The experimental procedure was similar to that outlined previously,[1] but the cells were rebuilt to eliminate the intermediate "salt bridge" of potassium nitrate. All measurements were made in duplicate. The average difference between duplicate cell readings was 0.03 m. v., and the maximum was 0.07 m. v. The electromotive forces would remain constant within these limits for a day or more.

Experimental Results and Discussion

The observed electromotive forces for $m = 0.05$ and 0.03 at 25° are plotted in Fig. 1. Each circle represents the average reading of duplicate cells. The total variation of E with x is so small that the scale of the plot is large enough to permit reading off E to 0.01 m. v. A table of data is therefore omitted. The values of $E_{x=0}$ obtained by extrapolation are 0.15128 at $m = 0.05$, and 0.15117 at $m = 0.03$. Upon the assumption that $E_{x=0}$ varies linearly[1,2] with m, these results lead to $E^0 = 0.15100$. Since E^0 for the cell is the difference between the standard potentials of the silver–silver bromide and silver–silver chloride electrodes, it may be computed from the values obtained for these electrodes from cells without liquid junctions. The standard potential of the

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[1] Owen, THIS JOURNAL, **60**, 2229 (1938).

[2] Owen and Brinkley, *ibid.*, **60**, 2233 (1938).

[3] Owen and Foering, *ibid.*, **58**, 1575 (1936).