In Table IV are shown the results obtained for the ionic ratios calculated from the data of other investigators. A comparison of either of the ratios involving magnesium is hardly justifiable, since the methods of analysis are open to criticism in the light of Epperson's work. For the Ca/Cl, however, several workers, with samples from widely scattered sources, obtained values agreeing with those found by the authors.

Conclusions

1. A study of the methods of analysis for calcium and magnesium in sea water has been made. The gravimetric calcium oxalate method and Epperson's modification of the magnesium ammonium phosphate method are the most accurate. Because of the large quantities of interfering ions, three precipitations are necessary for both the calcium and magnesium determinations.
2. The constancy of composition of the waters of the North and Northeast Pacific with reference to the calcium and magnesium ions and the chlorinity has been demonstrated.
3. The ratio for calcium chlorinity is 0.02150, for magnesium chlorinity 0.06694 and for calcium–magnesium 0.3212. The amounts of calcium and magnesium per kilo of sea water may be very closely estimated by multiplying the chlorinity by these factors.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

THE DISSOCIATION CONSTANT OF WATER FROM AN EQUILIBRIUM INVOLVING MERCURIC OXIDE AND MERCUROUS BROMIDE[1]

BY ROY F. NEWTON AND M. G. BOLINGER

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Introduction

The dissociation constant of water has usually been determined by one of three methods: by measurement of the conductivity of water, by determining the hydrolysis of salt solutions, or by finding the e.m.f. of cells. Possibly the best determination by conductivity measurements is that of Kohlrausch and Heydweiller[2] on the conductivity of water. It is rather difficult to estimate the magnitude of the uncertainty of their result, but their method of extrapolation from their best water to the conductivity of pure water would seem to introduce an uncertainty of 5% or more in

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[1] From a thesis submitted by M. G. Bolinger to the Graduate School of Purdue University in partial fulfilment of the requirements for the Degree of Master of Science.

[2] Kohlrausch and Heydweiller, *Z. physik. Chem.*, **14**, 330 (1894); *Ann. Physik*, [4] **28**, 503 (1909).

the dissociation constant. Lewis and Randall[3] by calculation from the e.m.fs. of cells, obtain a value differing by about 3% from that of Kohlrausch and Heydweiller. Lewis and Randall[3] state that the measurements by hydrolysis involve uncertainties of 10 to 20% in the assumptions alone.

The values obtained by e.m.f. measurements may be in error by 2 to 3% due to uncertainties in correction for liquid junction potentials. It would seem desirable to check the dissociation constant of water by an e.m.f. method which does not involve liquid junction potentials. A determination of the equilibrium between Hg(l), HgO(s), Br^-, Hg_2Br_2(s), and OH^- according to the reaction

$$^1/_2\,HgO(s) + {}^1/_2\,Hg(l) + {}^1/_2\,H_2O(l) + Br^- = {}^1/_2\,Hg_2Br_2(s) + OH^-$$

has been carried out in order to make possible the employment of the existing measurements of the potential of the mercury–mercuric oxide electrode[4] and of the potential of the mercury–mercurous bromide electrode[5] in the calculation of the dissociation constant of water.

Preparation of Materials

Mercury was washed in a column of nitric acid and distilled under reduced pressure in a slow current of air.

Mercurous bromide was prepared by adding potassium bromide in slight excess to a solution of mercurous nitrate which had been prepared from C. P. nitric acid and the purified mercury. The precipitate was washed three or four times by decantation, filtered and dried at 105°. The product was free from acid and soluble bromides. It was stored in dark bottles and kept away from strong light.

Mercuric oxide was prepared by heating a good C. P. product until small globules of mercury appeared. T. F. Buehrer in an unpublished investigation has shown that such mercuric oxide gives the same e.m.f. in a mercury–mercuric oxide half cell as that obtained by Ming Chow.

Potassium bromide was purified by three recrystallizations. The potassium bromide solutions were standardized by Volhard's method against silver nitrate, which had been checked against standard sodium chloride.

The sulfuric acid used for titrating the hydroxide in the equilibrium mixtures was standardized against sodium carbonate.

Experimental

Samples were made by adding 100 ml. of a solution of potassium bromide to 1–20 g. each of mercuric oxide, mercurous bromide and mercury, in well-stoppered pyrex Erlenmeyer flasks. Some flasks had ground glass stoppers and some were stoppered with thoroughly cleaned rubber stoppers. No differences occurred which could be attributed to the stoppers. The flasks were agitated in a thermostat kept at 25.00 ± 0.02°. At intervals

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[3] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 487.

[4] (a) Brönsted, *Z. physik. Chem.*, **65**, 84, 744 (1909), and (b) Ming Chow, THIS JOURNAL, **42**, 488 (1920).

[5] Gerke and Geddes, *J. Phys. Chem.*, **31**, 886 (1927).

of from twenty-four to seventy-two hours the suspended solids were allowed to settle, samples were pipetted off from the clear supernatant liquid and the flasks were reagitated. The weight ratio of mercuric oxide to mercurous bromide in the samples varied from 8:1 to 1:4.

The hydroxide concentration was determined by titration with standard sulfuric acid, using phenolphthalein as indicator. The bromide concentration was determined by adding an excess of silver nitrate solution and back titrating with standard thiocyanate solution, according to Volhard's method.

In most of the samples a solution of 0.088 or 0.099 *N* potassium bromide with no potassium hydroxide was used in making up the mixtures. In two of the mixtures a solution of potassium hydroxide and potassium bromide having approximately twice the equilibrium concentration of hydroxide was added to the mixture of mercuric oxide, mercurous bromide and mercury. In these cases just a trace of mercurous bromide had been added, and the hydroxide concentration of the solutions remained high; but upon adding 1 g. of mercurous bromide and agitating the solutions, the hydroxide concentration decreased to about the same value as that of the other samples.

The concentration ratios of hydroxide to bromide were first calculated and the activity ratios were then found by multiplying the concentration ratios by the ratio of the activity coefficients of the hydroxide and bromide ions in solutions of the same total ionic strength.[6] Our weighted mean activity ratio at equilibrium is 0.204, which is the equilibrium constant for the reaction

$$^1/_2\,HgO(s) + {}^1/_2\,Hg(l) + {}^1/_2\,H_2O(l) + Br^- = {}^1/_2\,Hg_2Br_2(s) + OH^- \qquad (1)$$

Substituting in the equation $\Delta F^\circ_{298} = -1365 \log K$, we obtain for the above reaction, $\Delta F^\circ_{298} = 943$ calories.

Brönsted[4a] found for the cell Hg, HgO(s), OH^-, H_2, Pt: $E^\circ = -0.9268$ volt, which, converted to the new international volt, is -0.9265 volt. Ming Chow[4b] and also Buehrer (in an unpublished investigation) have found $E^\circ = -0.9264$ volt, from which we find, for the reaction

$$^1/_2\,Hg(s) + {}^1/_2\,H_2O(l) = {}^1/_2\,HgO(s) + {}^1/_2\,H_2 \qquad (2)$$

$\Delta F^\circ_{298} = 21{,}375$ calories.

Gerke and Geddes[5] found for the cell H_2, H^+, Br^-, $Hg_2Br_2(s)$, Hg(l) $E^\circ = 0.1396$ volt, from which we obtain for the reaction

$$^1/_2\,H_2 + {}^1/_2\,Hg_2Br_2(s) = H^+ + Br^- + Hg(l) \qquad (3)$$

$\Delta F^\circ_{298} = -3221$ calories.

Adding Equations 1, 2 and 3, and adding the free energy changes, we find

$$H_2O(l) = H^+ + OH^-;\ \Delta F^\circ_{298} = 19{,}097 \text{ calories}$$

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[6] Lewis and Randall, Ref. 3, p. 382.

Substituting this value in the expression $\Delta F^\circ_{298} = -1365 \log K$, we find $K_w = 1.02 \times 10^{-14}$ at 25°, as compared to 1.005×10^{-14} by Lewis and Randall, and 1.04×10^{-14} by Kohlrausch and Heydweiller.

TABLE I

COMPOSITION OF SOLUTIONS IN EQUILIBRIUM WITH MERCURIC OXIDE AND MERCUROUS BROMIDE

Weight ratio HgO/Hg_2Br_2	Time of shaking, hours	Concn. of hydroxide, mole/liter	Concn. of bromide mole/liter	Concn. ratio	Activity ratio
1:4	0	.....	.....	0	0
	81	0.01297	0.0710	0.1827	0.187
	170	.01316	.0693	.1899	.195
1:2	0	.....	.....	.190	...
	23	.01412	.0710	.1989	.203
	70	.01305	.0682	.1913	.196
	132	.01283	.0654	.1962	.200
1:1	0	.....	.....	0	0
	26	.01402	.06975	.2010	.206
	146	.01392	.0698	.1994	.204
	298	.01370	.0689	.1988	.204
1:1	0	.....	.....	.19	...
	23	.00904	.0467	.1936	.197
	70	.00901	.04605	.1956	.199
	132	.00891	.0450	.1980	.202
1:1	0	.....	.....	.18	...
	24	.01384	.0704	.1966	.202
	80	.01383	.0703	.1967	.202
	136	.01343	.0705	.1905	.196
2:1	0	.....	.....	0	0
	26	.01415	.0703	.2013	.206
	142	.01389	.0699	.1987	.204
	226	.01363	.0700	.1947	.200
	340	.01353	.0699	.1935	.199
2:1	0	.....	.....	.24	...
	38	.01873	.09025	.2075	.213
	86	.01836	.08995	.2041	.209
	143	.01735	.0902	.1923	.197
2:1	0	.....	.....	*ca* 0.4	...
	189	.02019	.0924	.2185	.223
	249	.01926	.0911	.2114	.216
6:1	0	.....	.....	*ca* 0.4	...
	123	.01856	.09065	.2047	.210
	214	.01903	.0895	.2126	.218
	274	.01817	.0896	.2028	.208
8:1	0	.....	.....	0	0
	72	.01316	.0647	.2034	.209
	118	.01325	.0645	.2054	.211
				Mean activity ratio	.204

T. Fischer and H. von Wartenberg[7] report evidence of compound formation between HgO and Hg_2Br_2 in contact with water at 180°. The fact that under our experimental conditions the hydroxide–bromide ratio was independent of large changes in the mercuric oxide–mercurous bromide ratio indicates that we were obtaining the equilibrium with respect to the mercuric oxide and mercurous bromide, and not with respect to some compound of the two.

About three months after the experimental work had been completed, a new solid phase was observed in some of our mixtures. It is purplish-red and can very readily be distinguished from the mercuric oxide present. The compound has appeared in only a few of our samples. The formation of the compound is well illustrated by sample Number 4, which was made up April 4, 1928. Within twenty-four hours the hydroxide–bromide ratio became 0.20 and remained there for five days or more. During the following September the formation of the new compound was observed. By May, 1929, no mercurous bromide was visible in the mixture, and the hydroxide-bromide ratio had risen to 0.34. Solutions in equilibrium with mercuric oxide and the compound will undoubtedly show a higher hydroxide–bromide ratio than those in equilibrium with mercuric oxide and mercurous bromide, or those in equilibrium with the compound and mercurous bromide. The measurement of the two equilibria with the compound would serve as a valuable check on our measurements with mercuric oxide and mercurous bromide, but thus far we have been unable to prepare sufficient of the compound to carry out such measurements, nor to obtain it in sufficiently pure state to establish its composition.

Summary

The equilibrium constant for the reaction

$$^1/_2\ HgO(s) + {}^1/_2\ Hg(l) + {}^1/_2\ H_2O(l) + Br^- = {}^1/_2\ Hg_2Br_2(s) + OH^-$$

has been measured, and found to be 0.204 at 25°.

The dissociation constant of water at 25° has been calculated from the above equilibrium constant and the electrode potentials of the mercury–mercurous bromide–bromide ion electrode, and of the mercury–mercuric oxide–hydroxide ion electrode, reported by other authors. The dissociation constant is found to be 1.02×10^{-14} as compared to 1.04×10^{-14} by Kohlrausch and Heydweiller, and 1.005×10^{-14} by Lewis and Randall.

The occurrence of compound formation between mercuric oxide and mercurous bromide, reported by Fischer and von Wartenberg, has been confirmed. The composition and chemical properties of the compound have not as yet been studied.

LAFAYETTE, INDIANA

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[7] Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," **1923,** Vol. IV, p. 876; *Chem.-Ztg.*, **29,** 308 (1905).