$E° - RT/5F \ln (H^+)^6(BrO_3^-)$. Taking the degree of dissociation of 0.001 *M* $HBrO_3$ as 0.97,

$$E° = -1.487;\ \Delta F°_{298} = 171550. \qquad (21)$$

$Br(l) + {}^3/_2O_2 + \ominus = BrO_3^-$.—Combining Equation 21 with Equations 9 and 54 of our paper on oxygen and hydrogen compounds, we find

$$\Delta F°_{298} = 1690. \qquad (22)$$

Summary.

The following table gives the free energy of formation of the several forms of elementary bromine and of the bromine compounds which have been considered in this paper:

Substance.	$\Delta F°_{298}$.	Equation.	Substance.	$\Delta F°_{298}$.	Equation.
$Br(l)$	0	..	$HBr(g)$	—12592	13
$Br_2(g)$	755	1, 2	Br^-	—24594	14
$Br(s)$	157	3	Br_3^-	—25267	16
Br_2 (in CCl_4, N = 1)	389	5	Br_5^-	—24400	18
$Br_2(aq)$	977	7	$HBrO(aq)$	—19739	20
$Br(g)$	[22328]	10	BrO_3^-	1690	22

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE POTENTIAL OF THE MERCURY ELECTRODE AGAINST MERCUROUS ION.

BY G. A. LINHART.

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One of the lines of work in progress in this laboratory is the accurate measurement of the electrode potentials of the chemical elements. The present paper deals with the determination of the electrode potential of mercury against Hg_2^{++}.

Ogg[1] has shown, in a qualitative way, that the mercurous ion in a water solution of a mercurous salt, is chiefly in the form of Hg_2^{++}, and to some extent also in the form of Hg^+. But for obvious reasons (notably hydrolysis and oxidation) mercurous nitrate is not a suitable substance for accurate electrochemical measurements. Therefore, for the present investigation, mercurous perchlorate was chosen, because it was shown by Ley[2] that the extent to which this salt hydrolyzes is extremely small, and that the small amount of hydrolysis products thus formed are soluble in water. An almost neutral solution of this salt can be prepared, not by reducing the mercuric salt in solution by means of metallic mercury, but by treating pure mercurous oxide with a water solution of pure perchloric acid. The details of preparation, as well as the method of measurements, are given in the experimental part of this paper. In the

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[1] Ogg, *Z. physik. Chem.*, **27**, 295 (1898).

[2] Ley, *Z. Electrochem.*, **10**, 302 (1904).

table below are given two typical series of a considerable number of e. m. f. measurements obtained from preliminary experiments of concentration cells of mercurous perchlorate in the presence of perchloric acid of the same concentration throughout the cell. The concentration of the perchloric acid was in all cases in large excess as compared with that of the mercurous perchlorate, so that the degree of dissociation of the latter into Hg_2^{++} and ClO_4^- was practically the same in the two half cells. Therefore, the e. m. f. of concentration cells in the ratio of 1 : 2 should be 0.0089 v. This, however, is not the case as is evident from the results given in Table I.

TABLE I.—PRELIMINARY RESULTS AT 25°.

Series No.	Conc. of $HClO_4$.	Conc. of $Hg_2(ClO_4)_2$.		E (volt).
1	0.1035	0.00065	0.0013	0.0093
		0.000325	0.00065	0.0095
		0.0001625	0.000325	0.0097
2	0.0207[1]	0.00065	0.0013	0.0091
		0.000325	0.00065	0.0092
		0.0001625	0.000325	0.0092

The deviations of the e. m. f. values from the theoretical (in this case for a 1 : 2 concentration cell, E = 0.0089 volt) seem to indicate some dissociation of the Hg_2^{++} ions into Hg^+ ions. These deviations were, however, found to be probably due to the method of preparing the perchloric acid, namely, adding the theoretical amount of sulfuric acid to a dilute solution of barium perchlorate. The perchloric acid thus prepared contains a trace of dissolved barium sulfate,[2] in this case it probably contained more sulfate ion than barium ion. It is evident that when this acid is added to two solutions of mercurous perchlorate of different strengths both being extremely dilute, the percentage loss of the mercurous ion from the more dilute solution will be considerably greater than from the more concentrated solution. This phenomenon would account for the regular increase in the e. m. f. in the preliminary results given above. The E_0 calculated from these values would therefore be numerically less than if pure perchloric acid had been used. Many precautions therefore had to be taken in order to obtain accurate results.

The imported perchloric acid used in subsequent experiments proved to be very pure, being prepared presumably by distillation of the acid obtained by heating ammonium perchlorate in the presence of aqua regia.

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[1] In this series the e. m. fs. of the concentration cells were measured also against the hydrogen electrode and the values obtained are given below:

$Hg_2(ClO_4)_2$	0.0013	0.00065	0.000325	0.0001625 *M*.
—E	0.8055	0.7964	0.7872	0.7780 v.

[2] The solubility of barium sulfate in the presence of perchloric acid is apparently quite appreciable, as on addition of either SO_4^{--} or Ba^{++} a slight precipitate of $BaSO_4$ was observed.

Experimental.

Apparatus.—The hydrogen electrode used is of the type developed in this laboratory, and will be described in a subsequent paper by Prof. G. N. Lewis and Dr. R. L. Sebastian. For the other half cell see Fig. 1.

The cells and separatory funnels previously used in the preliminary experiments were subsequently kept in a cleaning mixture, consisting of fairly pure sulfuric acid saturated with chromic acid, for several weeks, then thoroughly washed, steamed, rinsed with conductivity water,[1] and finally dried in an oven and cooled in a desiccator. The rubber stoppers were boiled in dilute alkali, thoroughly washed and dried. Pure mercury was then introduced into each cell to a depth of about half an inch in order to prevent the solution from coming in contact with the platinum wire beneath the mercury in case of accidental tipping of the cell. The end of the separatory funnel, containing the same solution as the corresponding cell, when inserted into the cell, was almost in contact with the surface of the mercury in order to facilitate the renewal of the solution near the mercury surface.

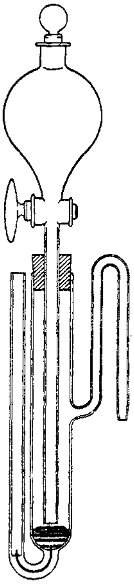

Fig. 1

Preparation of Substances.—Starting with pure mercury (twice distilled), pure sodium hydroxide and pure water, pure mercurous oxide was obtained. This was then treated with pure perchloric acid, the excess mercurous oxide filtered out and the solution of mercurous perchlorate thus obtained was shaken with pure mercury and allowed to stand for several days in order that the dispersed mercury could settle out. The solutions were then analyzed[2] and diluted with conductivity water to the desired concentration in specially resistant glass vessels, and then diluted with equal volumes of perchloric acid. These solutions thus prepared were immediately transferred to the cells, treated as described above, and the e. m. f. of each measured against the hydrogen electrode. The acid with which the solutions of the mercurous perchlorate were diluted was exactly twice as concentrated as

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[1] Distilled water was redistilled with alkaline permanganate. This kind of water was used in all operations.

[2] 100 cc. of this solution gave, on analysis, 0.2500 g. of mercurous chloride, corresponding to 0.005308 *M* mercurous perchlorate. This solution was diluted and used in the experiments with 0.0118 *M* and 0.0059 *M* $HClO_4$. The stock solution used for the other experiments was 0.00550 *M*. Hydrochloric acid was used in the precipitations of the mercurous chloride, giving concordant results with those obtained when sodium chloride was used. Moreover, the filtrate from the sodium chloride precipitations reacted neutral towards litmus paper, showing that there was no excess acid in the mercurous perchlorate, although the original solution of the mercurous perchlorate was slightly acid due to slight hydrolysis.

the acid used in the hydrogen electrode cell and in the connecting vessel forming the liquid junction, so that the concentration of the perchloric acid was the same throughout the cell.

Electromotive Force Measurements.—In the first column of Table II is given the number of the series of the e. m. f. measurements; in the second, the concentrations of the perchloric acid in mols per liter of solution; in the third, the concentrations of the mercurous perchlorate in mols per liter of solution; in the fourth and fifth, the observed e. m. fs. of these solutions measured in duplicate against the hydrogen electrode; and in the sixth, the average difference in e. m. f. for a two-fold concentration ratio of the mercurous perchlorate half cells. It may be stated here that the direct measurement of the e. m. fs. of the concentration cells agreed in every case within 0.1 mv. with the differences given in the sixth column.

TABLE II.

Series No.	Conc. of $HClO_4$.	Conc. of $Hg_2(ClO_4)_2$.	—E.		ΔE (volt).
1	0.0817	0.002750	0.7777	0.7777	0.0089
		0.001375	0.7688	0.7688	
2	0.0817	0.000550	0.7569	0.7568	0.0089
		0.000275	0.7480	0.7479	
3	0.0236	0.000550	0.7920	0.7920	0.0089
		0.000275	0.7831	0.7832	
4(*a*)	0.0118	0.0001062	0.7890	0.7889	0.0091
		0.0000531	0.7802	0.7795	
4(*b*)[1]	0.0118	0.0001062	0.7890	0.7889	0.0087
		0.0000531	0.7802	0.7803	
4(*c*)	0.0118	0.0001062	0.7889	0.7889	0.0090
		0.0000531	0.7798	0.7800	
5(*a*)	0.0059	0.0001062	0.8057	0.8055	0.0089
		0.0000531	0.7970	0.7964	
5(*b*)	0.0059	0.0001062	0.8062	0.8061	0.0089
		0.0000531	0.7973	0.7973	
				Av.,	0.0089

Discussion of Results.—No appreciable change in the e. m. f. of Series 1 and 2 (limit of error being 0.05 mv.) could be observed either at the end of one hour or on renewing the solutions near the mercury surface by means of the separatory funnel. In the remaining series, where the concentrations of the perchloric acid were considerably more dilute, the maximum variation in e. m. f. on renewal of the solution was 0.2 mv.,

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[1] (*b*) and (*c*) denote, respectively, the first and second renewals of the solutions near the mercury surface by means of the separatory funnels.

the limit of error being 0.1 mv. in Series 3 and 4 and 0.2 mv. in Series 5. The same maximum variations were observed also after the cells remained in the thermostat for 30 minutes.

The absence of any consistent departure of the e. m. f. for a two-fold concentration ratio from the theoretical value, 0.0089 v. is evidence that there is no appreciable dissociation of the Hg_2^{++} ion into Hg^+ ion even with 0.00005 molal mercurous perchlorate in 0.006 molal perchloric acid.

Calculation of the E. M. Fs. in Hypothetical Molal Concentration of the Reacting Substances.—The reaction taking place at the electrodes may be represented by the following equations:

$$H_2 + 2\oplus = 2H^+ \qquad (1)$$

$$Hg_2^{++} + 2\ominus = 2Hg \qquad (2)$$

Whence,

$$E_o = E_{obs.} + 0.02957 \log \frac{(H^+)^2}{(Hg_2^{++})[H_2]}, \qquad (3)$$

or

$$E_o = E_{obs.} + 0.02957 \log \frac{\gamma_1^2(HClO_4)^2}{\gamma_2(Hg_2[ClO_4]_2)[H_2]}, \qquad (4)$$

where γ_1 denotes the corrected degree of dissociation of $HClO_4$ and γ_2 that of $Hg_2(ClO_4)_2$.

Concerning the activity of bivalent ions[1] in solutions of uni-bivalent salts, little information is at present at hand, especially when the uni-bivalent salt, as in the present case, is mixed with a uni-univalent electrolyte. It has been pointed out by Adams and Rosenstein[2] that in a mixture of a bi-univalent salt and a uni-univalent salt, with the same anion, the degree of dissociation (as measured by conductivity) of the former is equal approximately to the square of that of the latter. If we assume provisionally that this is true also of the corrected degree of dissociation, Equation 4 becomes,

$$E_o = E_{obs.} + 0.02957 \log \frac{(HClO_4)^2}{(Hg_2[ClO_4]_2)[H_2]}. \qquad (5)^3$$

If this assumption, which is tested in Table III, were correct, identical values of E_o would be obtained. As might have been expected, the assumption fails in the most concentrated solutions, but in the three more dilute solutions E_o is nearly constant, and the average value (0.7926 v.) may be taken as the normal electrode potential of mercury against Hg_2^{++} at hypothetical molal concentration.

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[1] Lewis and Lacey, THIS JOURNAL, 36, 804 (1914).

[2] Linhart, *Ibid.*, 38, 1272 (1916).

[2] The corrections for the barometric pressure of the hydrogen gas amounted to +0.5 mv. in all but the last series of Table III, for which it was +0.6 mv.

TABLE III.

Series No.	$HClO_4$.	$Hg_2(ClO_4)_2$.	$E_{obs.}$[1]	E_0 (volt).
1	0.0817	0.002750	0.77770	0.78960
		0.001375	0.76880	0.78960
			Av.,	0.78960
2	0.0817	0.000550	0.75685	0.78945
		0.000275	0.74795	0.78945
			Av.,	0.78945
3	0.0236	0.000550	0.79200	0.79270
		0.000275	0.78315	0.79275
			Av.,	0.79273
4	0.0118	0.0001062	0.78893	0.79293
		0.0000531	0.78000	0.79290
			Av.,	0.79292
5	0.0059	0.0001062	0.80588	0.79220
		0.0000531	0.79700	0.79220
			Av.,	0.79220
Average of Series 3, 4, and 5				0.7926

Conclusions.

(1) The fair agreement of the E_0 values, with the exception of those with 0.0817 *M* $HClO_4$, seem to justify the adoption for dilute solutions of the rule, proposed by Adams and Rosenstein with reference to the degree of dissociation of bi-univalent salts.

(2) The best value for the potential of the mercurous electrode is —0.7928 v. (av. of Series 3 and 4).

(3) From the e. m. f. measurements of concentration cells no regular deviations from the theoretical value were observed, from which it may be concluded that there is no appreciable dissociation, of Hg_2^{++} into Hg^+ even in very dilute solutions with reference both to the perchloric acid (0.0059 *M*) and to the mercurous perchlorate (0.0000531 *M*).

Finally, I wish to express my indebtedness, for many helpful suggestions, to Professor G. N. Lewis and Doctor E. Q. Adams.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ARIZONA.]

THE VANADATES OF BERYLLIUM.

BY PAUL H. M.-P. BRINTON.

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In the course of a general study of vanadates Berzelius[2] prepared what he describes as a yellow, neutral, difficultly soluble, and pulverulent

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[1] Averages of $E_{obs.}$ of Table II.

[2] *Pogg. Ann.*, **22**, 58 (1831).