$CuSeO_3 \cdot 2NH_3$, $CuSeO_3 \cdot 3NH_3$ and $CuSeO_3 \cdot 4NH_3$ have been prepared, identified, and their ranges of stability determined.

3. Evidence has been given for the existence of a new hydrated ammonate having the general formula $CuSeO_3 \cdot 3NH_3 \cdot xH_2O$.

4. The work of Boutzaureanu has been checked and the existence of $CuSeO_3 \cdot NH_3 \cdot H_2O$ substantiated.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE ACTIVITY COEFFICIENTS OF CESIUM CHLORIDE AND HYDROXIDE IN AQUEOUS SOLUTION[1]

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The present investigation comprises the evaluation of the activity coefficients at 25° of cesium chloride and hydroxide from measurements of the cells

$$Ag \mid AgCl \mid CsCl(m) \mid Cs_xHg \mid CsCl(0.1) \mid AgCl \mid Ag \qquad \text{(Type I)}$$

and

$$H_2 \mid CsOH(m) \mid Cs_xHg \mid CsOH(0.05) \mid H_2 \qquad \text{(Type II)}$$

Experimental

Cells.—Cells of the type developed by MacInnes and Beattie,[2] Harned,[3] Knoble[4] and Åkerlöf[5] were used. A vacuum technique was always employed and all solutions were boiled *in vacuo* before introduction into the cells. Each cell had a capacity of 100 cc. They were carefully dried before each measurement so as to avoid the waste of solution accompanying the usual method of rinsing.

Electrodes.—Silver–silver chloride electrodes of the kind referred to as Type II in a recent investigation by Harned[6] were used. The hydrogen electrodes were of platinized platinum foil 0.7 by 3 cm. in size. The cesium amalgams were made either by electrolysis of the chloride in a vessel containing a porous cup which served to separate the anode and cathode solutions, or by the electrolysis of cesium hydroxide. Some of the measurements of the cells containing cesium chloride were made with a 0.01% amalgam, while others were obtained by employing a 0.1% amalgam. Both strengths yielded good consistent results, although the potentiometer readings were somewhat difficult to obtain with the 0.01% amalgam. On the other hand, it is important to note that although the 0.1% amalgam gave satisfactory results in the hydroxide solutions, the more dilute amalgam did not.

Cesium Chloride.—This was obtained from the mineral pollucite, $H_2O \cdot 2Cs_2O \cdot 2Al_2$-

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[1] Constructed from part of the thesis presented by O. E. Schupp, Jr., to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy, **1930**.

[2] MacInnes and Beattie, THIS JOURNAL, **42**, 1117 (1920).

[3] Harned, *ibid.*, **47**, 676 (1925).

[4] Knoble, *ibid.*, **45**, 70 (1923).

[5] Åkerlöf, *ibid.*, **48**, 1160 (1926).

[6] Harned, *ibid.*, **51**, 417 (1929).

$O_3 \cdot 9SiO_2$, by slightly modifying the methods of Godeffroy[7] and Wells,[8] so as to obtain readily the pure chloride. The finely ground mineral was treated with strong hydrochloric acid and evaporated to small volume on a hot-plate. This strongly acid solution was somewhat diluted, filtered and poured into three to four times its volume of boiling ammonium hydroxide solution in order to precipitate the aluminum. By adding the acid solution to the ammonium hydroxide instead of the reverse process, the precipitate could be very rapidly filtered onto a large Büchner funnel and readily washed with boiling water. The solution was then evaporated to small volume, the ammonium salts removed by nitric acid and the alkali salts converted to the chloride by repeatedly evaporating with hydrochloric acid. This mixture of cesium and other alkali metal chlorides was concentrated and the strongly acid solution treated with antimony trichloride to precipitate the insoluble double salt, $3CsCl–2SbCl_3$. This salt was hydrolyzed with several changes of water, giving an acid solution containing the cesium chloride together with a little antimony trichloride, but almost free from other alkali salts. Hydrogen sulfide was used to remove the last of the antimony and the solutions evaporated to dryness to obtain the very nearly pure cesium chloride.

For further purification, a concentrated solution of the practically pure chloride was heated with an equivalent weight of iodine and chlorine bubbled into the solution until precipitation of the $CsCl_2I$ ceased. Recrystallization yielded a salt free from other alkali metals, and it was then decomposed into pure cesium chloride by heating. Chloride analyses on the final product calculated to CsCl varied from 99.85 to 100.06% on different samples of salt.

The cesium chloride prepared as described above was used directly, or was converted to the hydroxide. The chloride and hydroxide used in the measurements were recovered in the form of the chloride in the following manner. The solutions were evaporated to dryness on the hot-plate, making certain that an excess of hydrochloric acid was present when hydroxide had been used. This residue was taken up with water and hydrogen sulfide bubbled into the solution to precipitate any dissolved silver, mercury, etc., and the solution filtered and again evaporated. At this point the solution was sometimes evaporated to dryness, the solid scraped out, ground in a mortar, ignited and used for further experiments. At other times the solution was taken nearly to dryness, and the greater part of the salt remaining in solution precipitated as a fine, crystalline product by the addition of considerable 95% alcohol. The material thus obtained was dried in the oven, and then ignited as in the previous case, to obtain the salt ready for use.

Cesium Hydroxide.—Dilute cesium hydroxide—0.1 and 0.05 molal—was prepared by treating a weighed portion of cesium acid sulfate with just enough half normal barium hydroxide solution to react completely, keeping the solutions at all times out of contact with carbon dioxide. The solution thus prepared was filtered through asbestos, carefully tested for sulfate and barium ions, and either sulfuric acid or barium hydroxide added when necessary. This solution was again filtered, analyzed and diluted with boiled distilled water to the desired concentration.

The cesium acid sulfate was obtained by treating the cesium chloride with sulfuric acid, evaporating until all excess sulfuric acid was removed and the acid sulfate slightly decomposed. The salt thus obtained was dissolved in a minimum of hot water and precipitated by the addition of a very considerable quantity of alcohol. This yielded a material which could be dried in the oven, readily ground and mixed and titrated for acid content. From this single analysis, and the assumption that the salt was a mixture of pure cesium acid sulfate and normal cesium sulfate, the amount of barium hydroxide solution required to react with the sulfate in a given amount of salt was calculated, and

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[7] Godeffroy, *Ber.*, **7**, 375 (1874).

[8] Wells, *Am. Chem. J.*, **26**, 265 (1901).

the two quantities of materials allowed to react. The assumption was evidently correct, for tests of the solutions thus obtained showed only faint traces of either barium or sulfate ions.

The more concentrated cesium hydroxide solution was prepared in a similar way. A hot barium hydroxide solution of about 1.5 molal concentration was prepared and analyzed as accurately as possible. To a weighed amount of this solution an equivalent amount of cesium acid sulfate was added and the two allowed to react. After allowing the barium sulfate to settle, the clear hydroxide solution was siphoned off through an asbestos filter into a second flask, where it was treated with additional barium hydroxide or sulfuric acid until the solution was practically free from an excess of either sulfate or barium ions. This solution was filtered through asbestos as before, analyzed and diluted with boiled distilled water to make solutions of the desired concentrations.

TABLE I

THE ACTIVITY COEFFICIENTS OF CESIUM CHLORIDE SOLUTIONS

1 Molality of CsCl	2 Normality of CsCl	3 E	4 No. cells	5 Max. diff.	6 Hückel	7 Obsd.	8 Harned	9 Diff., mv.
0.001	0.001	....	.	...	0.966	..	..	...
.01	.00997	....	.	...	.899	..	..	...
.02	.01993	....	.	...	.864	..	..	...
.05	.04975	−0.03201	2	±0.03	.803	0.802	0.799	0.07
.10	.09931	.00000	.	...	(.747)	(.747)	.748	.00
.20	.1978	.03111	5	.16	.685	.685	.688	.00
.50	.4885	.07110	5	.32	.598	.596	.601	.18
.70	.6784	.08568	2	.00	.568	.566	.571	.18
1.0	.9578	.10134	5	.07	(.537)	(.537)	.537	.00
1.5	1.4078	.11925	2	.01	.507	.507	.505	.00
2.0	1.8405	.13228	2	.02	.488	.491	.486	.32
2.5	2.2538	.14214	2	.16	(.476)	(.476)	.475	.11
3.0	2.6511	.15020	1	...	.467	.464	.470	.33

For Hückel's equation, $A = 0.52$; $B = 0.0160$. For Harned's equation, $\alpha = 0.063$; $\beta = 0.333$; $\alpha' = 0.400$.

The Activity Coefficient of Cesium Chloride.—Table I contains the electromotive forces, E, of cells of Type I. These are the mean of the number of measurements given in Col. 4. Column 5 shows the maximum variation of the readings from the mean. Column 6 contains the activity coefficients computed by Hückel's equation[9]

$$\log \gamma = -\frac{0.354\sqrt{2c}}{1 + A\sqrt{2c}} + B(2c) - \log(1 + 0.036m) \qquad (1)$$

The constants A and B given in the table were obtained by the usual method from the electromotive forces of the 0.1, 1 and 2.5 molal cells. Column 7 contains the activity coefficient computed from the reference value of 0.747 at 0.1 M obtained from Hückel's equation by the well-known equation for the cell, namely

$$E = 0.1183 \log \frac{\gamma m}{0.747 \times 0.1} \qquad (2)$$

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[9] Hückel, *Phys. Z.*, **26**, 123 (1925).

Further, since we desire the vapor pressures of the solutions for further studies, and since Hückel's equation is complicated for this calculation, we include values computed by Harned's[10] equation

$$\log \gamma = -\beta m^{\alpha'} + \alpha m \qquad (3)$$

The constants β, α' and α are given at the bottom of the table. It is clear that in the concentration range of 0.05 to 3 M this equation holds satisfactorily.

The agreement between the observed values and those computed by Hückel's equation is very good as evidenced by the differences in mvs. given in Col. 9. That the activity coefficient of cesium chloride falls in the expected place in respect to the other chlorides is shown by Fig. 1, where the results are plotted along with those obtained by Harned for potassium, sodium and lithium chlorides,[11] and by Randall and Young for hydrochloric acid.[12]

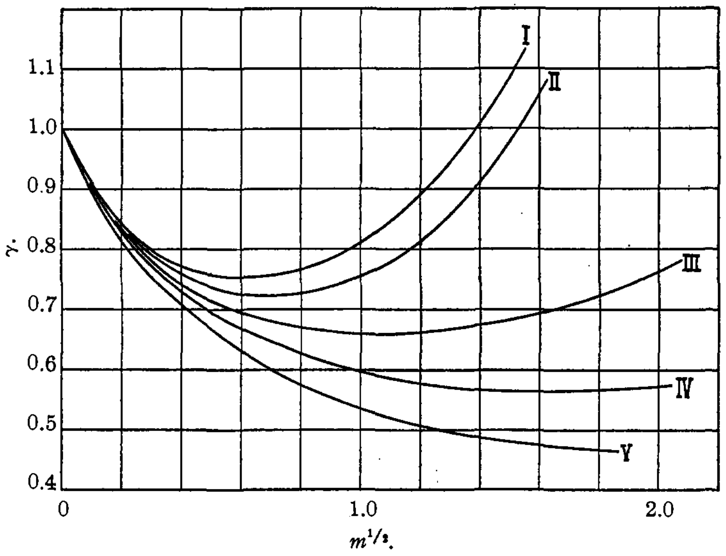

Fig. 1.—The activity coefficients of the alkali chlorides: I, HCl; II, LiCl; III, NaCl; IV, KCl; V, CsCl.

The Activity Coefficient of Cesium Hydroxide in Aqueous Solution.—The electromotive forces of cells of Type II are related to the activity coefficients according to the equation

$$E = 0.1183 \log \frac{\gamma_{CsOH(m_1)}}{\sqrt{a_{H_2O(m_1)}}} \cdot \frac{\sqrt{a_{H_2O(m_0)}}}{\gamma_{CsOH(m_0)}} \times \frac{m_1}{m_0} \qquad (4)$$

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[10] Harned, This Journal, **42,** 1080 (1920).

[11] Harned, *ibid.*, **51,** 416 (1929).

[12] Randall and Young, *ibid.*, **50,** 989 (1928).

Since the activity of water is proportional to its vapor pressure, we may write

$$E + 0.05915 \log \frac{p_{H_2O(m_1)}}{p_{H_2O(m_0)}} = 0.1183 \log \frac{\gamma_{CsOH(m_1)}}{\gamma_{CsOH(m_0)}} \qquad (5)$$

We are interested in computing both γ_{CsOH}, and γ'_{CsOH}, or γ_{CsOH}/a_{H_2O}. For the former, we must use Equation 5 and for the latter Equation 4, which may be written

$$E = 0.1183 \log \frac{\gamma'_{CsOH(m_1)}}{\gamma'_{CsOH(m_0)}} \times \frac{m_1}{m_0} \qquad (4a)$$

Table II contains the observed electromotive forces, E, and the values of γ' computed by Hückel's equation and from the observed electromotive forces by Equation 4a. Column 2 contains measurements of the density of cesium hydroxide solutions. Since the electromotive force values were difficult to obtain, a curve was drawn through the observed values and the more consistent values given in Col. 5 were read off this plot. Column 6 gives the number of measurements of each cell, and Col. 7 the deviation (±) from the mean. The 0.05, 0.5402 and 1.3205 molal cells were used to evaluate the constants in Hückel's equation which are given at the bottom of the table. Column 8 contains the values of γ' computed by Hückel's equation, Col. 9 the values of γ' calculated by Equation 4a by employing 0.831 as the reference value at 0.05 *M*, and Column 10 similar values computed from the results in Column 5.

TABLE II

THE VALUE OF γ' FOR CESIUM HYDROXIDE IN AQUEOUS SOLUTION

1 Molality of CsOH	2 Density of CsOH	3 Normality of CsOH	4 E meas.	5 E curve	6 No. of cells	7 Max. diff., mv.	8 γ' Hückel	9 γ' Obs.	10 γ' Curve
0.01016	0.99838	0.01013	−0.07638	−0.0775	2	±0.18	0.905	0.925	0.905
.02044	.99969	.02037	.04306	.0433	2	.00	.876	.879	.876
.02550	1.00033	.02541	.03246	.0325	2	.19	.865	.866	.865
.05	1.00343	.04980	.00000	.0000	.	...	(.831)	(.831)	(.831)
.09065	1.0087	.09021	+ .02888	+ .0289	2	.02	.800	.804	.804
.1	1.0100	.09951	....	.0336	.	...	.795	...	.799
.232	1.0270	.2303	.07379	.0742	2	.01	.759	.753	.759
.38	1.0458	.3731	....	...	.	...	.750	...	...
.5402	1.0659	.5326	.11676	.1172	2	.20	(.753)	.747	(.753)
.8902	1.1099	.8715	.14421	.1448	2	.00	.782	.773	.782
1.0	1.1238	.9774	....	.1517	.	...	.795	...	.796
1.3205	1.1626	1.2817	.16865	.16865	2	.04	(.8385)	.8385	(.8385)

Constants for Hückel's equation: $A = 0.94$; $B = 0.0663$.

There remains the calculation of γ according to Equation 5, which necessitates a knowledge of vapor pressures of the solutions. The method employed to determine the corrections to the electromotive forces, ΔE, corresponding to the second member on the left of Equation 5 was the same as that used by Harned.[13] The constants, α, β and α' of Equation 3

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[13] Harned, THIS JOURNAL, 47, 676 (1925).

were evaluated and the logarithms of the vapor pressure ratios were computed by the equation

$$\ln \frac{p_0}{p} = \frac{m}{55.5}\left[2 + 2.303\alpha m - \frac{4.605\ \alpha'\beta}{\alpha' + 1}\ m^{\alpha'}\right] \qquad (6)$$

From the values of p thus obtained, ΔE was evaluated. Table III contains the results. Column 2 contains the corrections, ΔE, Col. 3, the corrected electromotive forces obtained by subtracting ΔE from the corresponding values of E given in Col. 5, Table II. Column 4 contains the values of γ computed by Hückel's equation, Col. 5 the values of γ

TABLE III

THE ACTIVITY COEFFICIENT OF CESIUM HYDROXIDE IN AQUEOUS SOLUTION

Molality of CsOH	ΔE	$E_{\text{corr.}}$, curve	γ Hückel	$\gamma_{\text{obs.}}$, measured	γ Harned
0.01016	....	−0.0775	0.905	0.925	..
.02044	....	.0433	.876	.879	..
.0255	....	.0325	.865	.866	..
.05	−0.00000	.00000	(.831)	(.831)	(0.831)
.09065	− .00003	.0289	.800	.804	.803
.1	.00004	.0336	.795	..	.798
.232	.00016	.0740	.757	.753	.762
.38	.00029	...	.746	..	.749
.5402	.00044	.1168	(.747)	.740	(.748)
.8902	.00078	.1440	.770	.761	.769
1.0	.00090	.1508	.781	..	.780
1.3205	.00125	.1674	(.818)	.818	(.819)

Constants for Hückel's equation: $A = 0.97$; $B = 0.0604$.
Constants for Harned's equation: $\alpha = 0.152$; $\beta = 0.260$; $\alpha' = 0.362$.

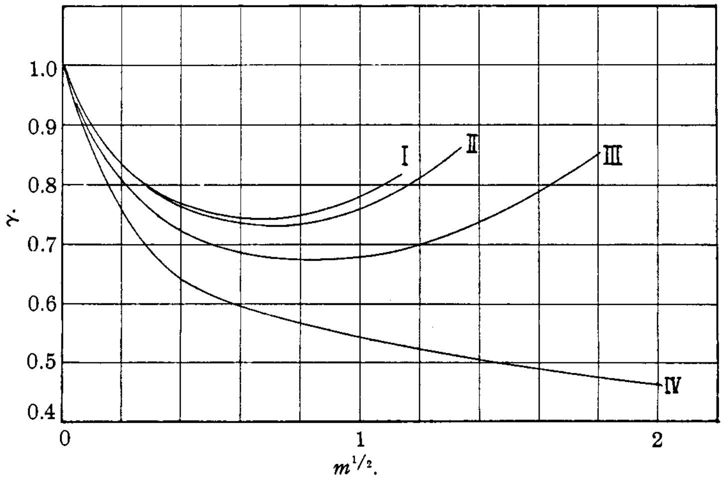

Fig. 2.—The activity coefficients of the alkali hydroxides. I, CsOH; II, KOH; III, NaOH; IV, LiOH.

computed from the observed electromotive forces by employing the reference value of 0.831 at 0.05402 molal concentration. Column 6 contains the values of γ computed by Harned's equation. The constants A, B, α, β and α' are given at the bottom of the table.

In Fig. 2 the activity coefficients of the alkali hydroxides have been plotted against $m^{1/2}$. The activity coefficient of cesium hydroxide lies somewhat higher at all concentrations but close to that of potassium hydroxide. The general rule that the hydroxides show the reverse distribution to the chlorides is verified.

Summary

1. The activity coefficients of cesium chloride and hydroxide in aqueous solution at 25° have been obtained by measurements of the cells,

$$Ag/AgCl/CsCl(m)/Cs_xHg/CsCl(m_0)/AgCl/Ag, \text{ and}$$
$$H_2/CsOH(m)/Cs_xHg/CsOH(m_0)/H_2$$

respectively.

2. The constants of Hückel's equation have been obtained from these results.

3. The constants of Harned's equation have been computed. From these, the vapor pressures of the chloride solutions may be calculated. The vapor pressures of the hydroxide solutions have been computed.

4. Both the chloride and hydroxide activity coefficients are of the expected order of magnitude, and conform with the distribution of the same quantities in the cases of the other alkali chloride and hydroxide solutions

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[Contribution from the Sterling Chemistry Laboratory of Yale University]

THE ACTIVITY COEFFICIENT AND DISSOCIATION OF WATER IN CESIUM CHLORIDE SOLUTIONS[1]

By Herbert S. Harned and Orion E. Schupp, Jr.

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In a series of studies, values for the variation of the dissociation and the ionic activity coefficient of water in some uniunivalent halide solutions were computed from measurements of three types of cells without liquid junction.[2]

In the present communication these same quantities have been determined in cesium chloride solutions. Further, a somewhat different method

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[1] Constructed from part of the thesis presented by O. E. Schupp, Jr., to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy, 1930.

[2] (a) Harned, This Journal, **47**, 930 (1925); (b) Harned and Swindells, *ibid.*, **48**, 126 (1926); (c) Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).