diameters. Both the treatment of Gronwall, La Mer and Sandved and that of Bjerrum lead to the same conclusion, namely, that deviations from the Debye–Hückel limiting slope are to be expected in solutions of lower dielectric constant even in very dilute solutions and the smaller the average ion diameter the greater the positive deviation from the limiting slope.

By applying the results of Bjerrum's calculations a value of 2.5 Å. is obtained for the average ion diameter in the potassium perchlorate–ammonium nitrate mixtures in ethyl alcohol. This appears to be a reasonable value. Moreover, taking different points on the curve, the average diameters obtained are fairly constant.

Summary

The solubilities of potassium chloride, potassium perchlorate and barium nitrate in the presence of other salts in ethyl alcohol have been measured and the results compared with those predicted by the inter-ionic attraction theory.

While the solubility results in ethyl alcohol show marked deviations from those predicted on the basis of the original Debye–Hückel approximation, they seem to be, qualitatively at least, in agreement with the inter-ionic attraction theory as developed by Gronwall, La Mer and Sandved or by Bjerrum.

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[Contribution from the Chemical Laboratory of the University of California]

THE FREE ENERGY OF STANNOUS HYDROXYL CHLORIDE AND THE ACTIVITY COEFFICIENT OF STANNOUS CHLORIDE AND STANNOUS ION

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The hydrolysis product of stannous ion is the basic stannous hydroxyl chloride $SnOHCl\cdot H_2O$, which is a stable white insoluble solid.[1] The determination of the equilibrium of the hydrolysis reaction

$$Sn^{++} + Cl^- + 2H_2O(l) = SnOHCl\cdot H_2O(s) + H^+;\ K_m = m(H^+)/m(Sn^{++})m(Cl^-) \quad (1)$$

enables us, by combination with the known free energies of the other substances occuring in Equation 1, to determine the free energy of the solid hydrolysis product. Furthermore, from the rather unusual way in which the activity coefficients of H^+ and Cl^- occur in the expression for the equilibrium constant, the individual activity coefficient of the stannous ion

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[1] The simplest formula of the basic salt is used. The amount of hydration is uncertain. See (a) Proust, *J. Phys.*, **61**, 338 (1804); *Ann. chim.*, **28**, 213 (1798); (b) Davy, *Trans. Roy. Soc.* (London), **102A**, 169 (1912); (c) Ditte, *Compt. rend.*, **94**, 792, 1114 (1882): *Ann. chim.*, [5] **27**, 145 (1882); *Compt. rend.*, **97**, 42 (1883).

is obtained by means of assumptions which are less uncertain than those usually employed.

The Solubility of Stannous Hydroxyl Chloride in Aqueous Hydrochloric Acid at 25°.—The stannous hydroxyl chloride was prepared in two ways. (1) In the first series of experiments an approximately 0.5 *M* solution of stannous chloride was prepared by dissolving C. P. $SnCl_2 \cdot 2H_2O$ in conductivity water with the addition of just enough C. P. hydrochloric acid (0.006–0.008 *M*) to give a clear solution. Pure metallic tin was then added. The air was displaced and the solution agitated by a stream of pure nitrogen which was bubbled through. The solution was then added, in the absence of air, to a large volume of air-free conductivity water. The precipitate formed was washed several times by decantation with air-free water. The suspension of the solid in water was used for the solubility experiments. (2) In the remaining experiments the stock solution of acid stannous chloride was precipitated by adding an air-free solution of sodium chloride and hydroxide, the chloride being in large excess. The precipitate was washed free from sodium ion by decantation, as before. On analysis our salt corresponded to the formula $SnOHCl \cdot (1.00 \pm 0.01)H_2O$.

A portion of the paste containing about 10 g. of the solid phase was transferred, in the absence of air, to a 250-ml. pyrex distilling flask body which had been swept free of air by nitrogen. Dilute air-free hydrochloric acid

TABLE I

$Sn^{++} + Cl^- + 2H_2O(l) = SnOHCl \cdot H_2O(s) + H^+ (25°)$

Expt.	Days rotated	Sn^{++}	Cl	H^+	Log K_m	$\mu^{1/2}$	Ratio $HCl/SnCl_2$	1/3Log K_m	Log $\gamma(SnCl_2)$ + const.
1	4	0.02968	0.14020	0.08124	1.289	0.411	2.23	0.430	0.3511
2	6	.03045	.14074	.07985	1.270	.412	2.62	.423	.3449
3	9	.02730	.11558	.06098	1.283	.412	2.23	.428	.3491
4	12	.03140	.15223	.08943	1.274	.423	2.84	.425	.3461
5	15	.01006	.04789	.02777	1.760	.241	2.70	.587	.5280
6	13	.01234	.05602	.03134	1.662	.261	2.58	.554	.4921
7	15	.003261	.01491	.008387	2.237	.135	2.56	.746	.7083
8	16	.002987	.01227	.006290	2.233	.124	2.10	.744	.7103
9	9	.002981	.01225	.006290	2.236	.123	2.10	.745	.7113
10	13	.002802	.01085	.005242	2.237	.117	1.87	.746	.7123
11	11	.002802	.01085	.005242	2.237	.117	1.87	.746	.7123
12	21	.002824	.01089	.005242	2.231	.117	1.86	.744	.7103
13	46	.01176	.07560	.05208	1.770	.296	4.43	.590	.5238
14	5	.01410	.06790	.03970	1.618	.286	2.82	.539	.4738
15	8	.006407	.03294	.02011	1.980	.198	3.12	.658	.6078
16	12	.02329	.10949	.06290	1.392	.360	2.70	.464	.3900
17	9	.008168	.03731	.02097	1.838	.213	2.56	.613	.5587
18	19	.009081	.03879	.02062	1.768	.218	2.21	.589	.5347
19	20	.009248	.03825	.01975	1.747	.218	2.14	.582	.5277
20	45	.009907	.04363	.02382	1.741	.231	2.40	.580	.5230
21	78	.008825	.04023	.02358	1.822	.220	2.66	.607	.5520

solution or water was added, the flasks were sealed and rotated in the thermostat at 25 ± 0.02.[2]

After the time of rotation indicated in Col. 2 of Table I, the solution was filtered[2] and analyzed (moles per 1000 g. of water in vacuum). The stannous-ion constituent (Col. 3) was determined by titration with potassium permanganate solution. Dilute nitric acid was added to give a sufficient hydrogen-ion concentration for the titration. After titration the chloride-ion constituent (Col. 4) was determined as silver chloride by precipitation. The hydrogen-ion constituent was determined by difference. In Expts. 7 to 12 in which the stannous ion was very small the hydrogen-ion constituent was determined by titration with sodium hydroxide solution (phenolphthalein indicator) and chloride-ion constituent was taken equal to twice the stannous ion plus the hydrogen-ion constituent.

In plotting Fig. 1, the scale of the square root of the ionic strength (Col. 7) was made the same, and the scale of log K (Equation 1, Col. 6) was made one-fourth that of Fig. 2 of Randall and Vietti,[2] for the following reason. If we again consider Equation 1, the expression for the equilibrium constant is

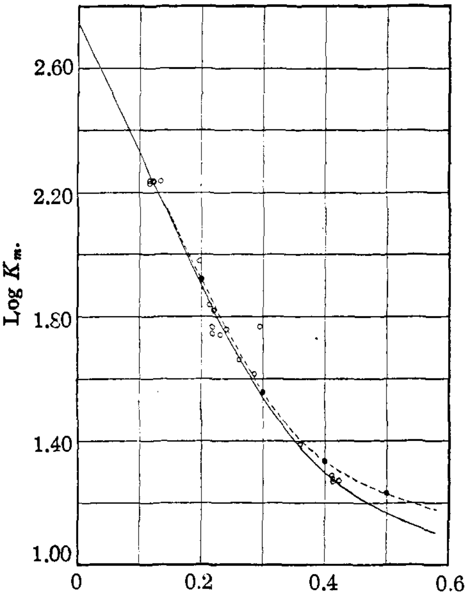

Fig. 1.—$Sn^{++} + Cl^- + 2H_2O(l) = SnOHCl{\cdot}H_2O(s) + H^+(25°)$.

$$K = m\gamma(H^+)/m\gamma(Sn^{++})m\gamma(Cl^-) \qquad (2)$$

The individual activity coefficient of H^+ is very nearly the same as that of Cl^-, especially in the more dilute solutions. Furthermore, we should expect the activity coefficient of these ions to be more nearly alike in mixtures with stannous ion, and in the presence of the large excess of chloride ion.[3] We also find as a consequence of the Debye–Hückel treatment of dilute solutions that at near zero molality[3,4]

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[2] See Randall and Vietti, This Journal, 50, 1526 (1928).

[3] (a) Brönsted, *ibid.*, 44, 938 (1922); (b) *ibid.*, 45, 2898 (1923); (c) Brönsted and La Mer, *ibid.*, 46, 555 (1924); (d) see Randall and Breckenridge, *ibid.*, 49, 1435 (1927).

[4] Debye and Hückel, *Physik. Z.*, 24, 185 (1923).

$$\log \gamma = -z^2A\mu^{1/2} = -z_1z_2A\mu^{1/2} \qquad (3)$$

where z is the valence of an ion, A is a constant = 0.503 at 25°, and μ is the ionic strength. In the case of the mean activity coefficient z^2 is replaced by 2 for uni-bivalent salts. In order, therefore, to have the plot of the logarithm of the activity coefficient of a bivalent ion, or its value plus a constant superimpose on our standard plot, we must make the scale one-fourth that of a univalent salt. By comparison with the standard curves[2] we find $\log K = 2.75$, or

$$Sn^{++} + Cl^- + 2H_2O(l) = SnOHCl\cdot H_2O(s) + H^+;\ \Delta F^\circ_{298.1} = -3750 \text{ cal.} \qquad (4)$$

Using the values of the free energy of chloride ion given by Randall and Young[5] and the value of −6276 cal. for the free energy of stannous ion[6] we find for the free energy of formation of stannous hydroxyl chloride

$$Sn(s) + {}^1/_2Cl_2(g) + 1{}^1/_2H_2(g) + O_2(g) = SnOHCl\cdot H_2O(s);$$
$$\Delta F^\circ_{298.1} = -154{,}491 \text{ cal.} \qquad (5)$$

If we assume the individual-ion activity coefficients given by Lewis and Randall,[6] we find at four molalities the values for $\log \gamma\ (Sn^{++}) + \log K$ indicated on the dotted curve. The values of the activity coefficient of stannous ion found by subtracting $\log K$ from the values of $\log K_m$ are, however, probably more nearly the correct values than those found by using the individual-ion activities which are based on the values in pure hydrochloric acid. The values of the activity coefficient of stannous ion are smaller than those of the alkali earth bivalent ions.

We may also write Equation 1 in the form

$$Sn^{++} + 2Cl^- + 2H_2O(l) = SnOHCl\cdot H_2O(s) + H^+ + Cl^-;$$
$$K = m\gamma(H^+)m\gamma(Cl^-)/m\gamma(Sn^{++})m^2\gamma^2(Cl^-) \qquad (6)$$

where the numerical value of K is obviously identical with that in Equation 1. We may also write

$$\log K = \log K_m + \log \gamma^2_\pm(HCl) - \log \gamma^3_\pm\ (SnCl_2)$$

whence, rearranging

$$\log \gamma_\pm(SnCl_2) + {}^1/_3 \log K = {}^1/_3 \log K_m + {}^2/_3 \log \gamma_\pm(HCl) \qquad (7)$$

TABLE II

ACTIVITY COEFFICIENT OF STANNOUS CHLORIDE AND OF STANNOUS ION

m	Log $\gamma_\pm(Sn^{++})$	$\gamma_\pm(Sn^{++})$	Log $\gamma_\pm(SnCl_2)$	$\gamma_\pm(SnCl_2)$
0.0001	−0.074	0.843	−0.028	0.938
.0010	− .234	.583	− .092	.809
.0025	− .366	.431	− .145	.716
.0050	− .518	.303	− .205	.624
.01	− .726	.188	− .291	.512
.02	−1.002	.0995	− .400	.398
.05	−1.394	.0404	− .548	.283
.1000	−1.554	.0279	− .633	.233

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[5] See Randall and Young, THIS JOURNAL, 50, 989 (1928).

[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York and London, 1923.

The values of log $\gamma_\pm$ ($SnCl_2$) given by this procedure will be those in the presence of hydrochloric acid, and the values of log $\gamma_\pm$(HCl) which should be used are those in the presence of stannous chloride. We give in Table I along with the values of $^1/_3$ log K_m (Col. 9), the values for the ratio of the molality of the hydrochloric acid to that of stannous chloride, and the values of $^1/_3$ log K_m + $^2/_3$ log $\gamma_\pm$(HCl) = log $\gamma_\pm$($SnCl_2$) + const., where the value of $^2/_3$ log $\gamma_\pm$(HCl) is taken from the curves of Randall and Breckenridge in mixtures of hydrochloric acid and barium chloride at the same ratio and same ionic strength. This approximation is not entirely justified as the stannous chloride is a "weaker" salt than barium chloride, but the approximation is better than taking the activity coefficient in pure hydrochloric acid. The values of $^1/_3$ log K_m and of $^1/_3$ log K_m + $^2/_3$ log $\gamma_\pm$(HCl) are plotted against $\mu^{1/2}$ in Fig. 2 and lead to an extrapolated value of $^1/_3$ log K which is identical with $^1/_3$ log K, as was found from Fig. 1. The values of log $\gamma_\pm$(Sn^{++}) and of log $\gamma_\pm$($SnCl_2$) at round molalities, as determined by substituting log K in Equations 2 and 7, are given in Table II.

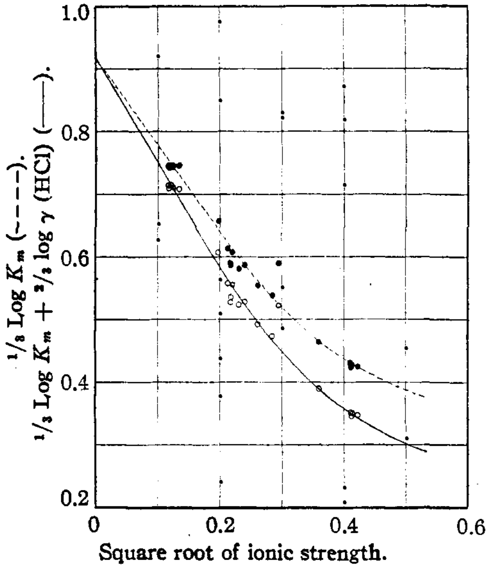

Fig. 2.—$Sn^{++} + 2Cl^- + 2H_2O(l) = SnOHCl{\cdot}H_2O(s) + H^+ + Cl^-$(25°).

Summary

The equilibrium in the hydrolysis of stannous chloride has been measured at 25°. The free energy of the solid stannous hydroxyl chloride and the activity coefficient of stannous chloride and of stannous ion have been calculated.

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