

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

**Equilibria in the Stannous Oxide-Sodium Hydroxide and in the Stannous Oxide-Hydrochloric Acid Systems at 25°. Analysis of Dilute Solutions of Stannous Tin**

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The purpose of this paper is to present data on the solubility of stannous oxide in dilute solutions of sodium hydroxide and of hydrochloric acid. Such data make possible the evaluation of the equilibrium constants involved in these equilibria. These data also make possible the evaluation of the equilibrium constants for the first and second basic dissociation, the first acidic dissociation, the solubility product constant, the free energy of formation and the heats of formation of stannous hydroxide and stannous oxide, as well as the heat of hydration of stannous oxide.

During the course of this work it was possible and necessary to make certain important observations relevant to the development of a method for the quantitative analysis of dilute solutions of tin; accordingly, data are presented on the potentiometric as well as the polarographic methods of analysis of tin.

Early work on this problem is of interest to report here. Goldschmidt and Eckhardt<sup>1</sup> measured the solubility of stannous hydroxide from 0.004 to 0.03 molar sodium hydroxide. Prytz<sup>2</sup> obtained the value  $5 \times 10^{-26}$  for the solubility product constant of stannous hydroxide from data on the titration of stannous chloride with sodium hydroxide. Smrz<sup>3</sup> obtained a value of  $1.4 \times 10^{-28}$  for the solubility product constant and  $6 \times 10^{-18}$  for the acid dissociation constant from data on the half-wave potentials of polarographic data. Randall and Murakami<sup>4</sup> determined the hydrolysis constant for stannous chloride in accordance with the equilibrium  $\text{Sn}^{++} + \text{Cl}^- + 2\text{H}_2\text{O} = \text{SnOHCl} \cdot \text{H}_2\text{O}_{(s)} + \text{H}^+$ .

An additional interest is given to this problem since it was shown by Garrett, Vellenga and Fontana<sup>5</sup> from a similar study of lead oxide that lead hydroxide forms a monobasic acid and may have the formic acid type of structure; since the tin ion has a similar electron configuration as the lead ion, it might be expected that tin hydroxide should also form a monobasic acid. This expectation has been realized in this study.

(1) Goldschmidt and Eckhardt, *Z. physik. Chem.*, **56**, 386 (1906).(2) Prytz, *Z. anorg. allgem. chem.*, **174**, 371 (1928).(3) Smrz, *Rec. trav. chim.*, **44**, 590 (1925).(4) Randall and Murakami, *THIS JOURNAL*, **52**, 3967 (1930).(5) Garrett, Vellenga and Fontana, *ibid.*, **61**, 367 (1939).**Procedure**

The general procedure was similar to that described in similar papers.<sup>5</sup>

**Preparation of Reagents**

a. **Conductivity Water.**—Conductivity water ( $2 \times 10^{-6}$  mho) was used for the preparation of all solutions.

b. **Sodium Hydroxide Solutions.**—Baker and Adamson Reagent sodium hydroxide pellets were dissolved in conductivity water, which had previously been boiled free of carbon dioxide and oxygen; saturated barium hydroxide solution was added in slight excess to precipitate all the carbonate. Solutions of less than 0.1 molar sodium hydroxide were prepared by decomposition of sodium-mercury amalgams in the absence of carbon dioxide.<sup>5</sup> The solutions were standardized by titration against potassium acid phthalate using phenolphthalein as indicator.

c. **Stannous Chloride Solutions.**—The stannous chloride solutions used were prepared by dissolving Baker and Adamson Reagent metallic tin in Grasselli c. p. hydrochloric acid in the presence of platinum as a catalyst.

d. **Other Reagents.**—Recrystallized c. p. quality potassium dichromate was dried in an oven at 130° for fifteen hours, ground to a fine powder in an agate mortar, and dried for twenty-four hours more. This material was used for the preparation of standard solutions for titration purposes.

Standard solutions of hydrochloric acid were prepared by dilution of Grasselli c. p. acid. These were standardized against standard sodium hydroxide solutions.

**Preparation of Stannous Oxide.**—Special care was observed in the preparation of stannous oxide, not only to protect it from carbon dioxide, hydrogen sulfide, etc., but also to protect it from oxygen, since the stannous ion changes very rapidly to the stannic ion in the presence of atmospheric oxygen. Consequently, all the work was done in an atmosphere of nitrogen which was passed through a purification train of sodium stannite, barium hydroxide, silver nitrate, sulfuric acid, heated copper turnings, pyrogallol acid and distilled water. The stannous hydroxide was prepared by the action of the sodium hydroxide on the stannous chloride. The stannous hydroxide was dehydrated in warm conductivity water in the presence of a small amount of sodium hydroxide. The resulting material (SnO) was washed fifteen times with conductivity water. The samples of stannous oxide were then prepared from standard solutions (oxygen-free) of sodium hydroxide or of hydrochloric acid. A pair of samples was made for each desired concentration and equilibrium was approached from supersaturation (s) and undersaturation (u); an equilibrium period of twenty days at  $25 \pm 0.02^\circ$  was used.

**Sedimentation, Filtration, and Analysis.**—The samples were allowed to sediment for a period of seven days.

They were then filtered through a Jena glass filter and analyzed by means of a polarographic method and a potentiometric method.

**Polarographic Method of Analysis.**—Standard solutions of stannous chloride were prepared and a calibration curve established for the concentration range  $10^{-5}$  to  $10^{-2}$  mole of stannous chloride. A Sargent-Heyrovsky micro-polarograph was used for this work. The analysis by such a procedure could be reproduced to  $\pm 4\%$  at the low range and  $\pm 2\%$  at the high range. The results of this research obtained by this method are shown in column 2 of Tables I and II.

**Potentiometric Analysis.**—This method of analysis was a modification of the potentiometric procedure described by Hostetter and Roberts<sup>6</sup> in which stannous tin is oxidized to stannic tin by potassium dichromate. Since the stannous ion is unstable in atmospheric oxygen, a titrating beaker was arranged whereby oxygen could be excluded during a titration. It consisted of a 250-ml. beaker with a stationary all glass cap. The beaker could be lowered away from the cap to permit refilling. Holes in the top of the glass cap allowed for a mechanical stirrer, a salt bridge, a thermometer, a platinum electrode, and the buret tip. A stream of carbon dioxide was passed over the buret tip and into the beaker during a titration. Passing the carbon dioxide over the buret tip prevented condensation of vapor on the tip which would carry some of the potassium dichromate into the solution. Also in the top of the glass cap was a narrow slit which allowed a platinum-lead couple to be inserted into the solution. This titration cell was connected to a calomel half-cell by a potassium chloride salt bridge. The electrode consisted of a small platinum wire sealed in a soft glass tube filled with mercury. During the course of this investigation it was found necessary to eliminate the glass-platinum-solution interface as described by Garrett, Hogge and Heiks.<sup>7</sup> This was done by allowing only the platinum wire to come in contact with the solution.

The stannous ion was titrated with standard solutions of potassium dichromate, and the change of potential followed by a Leeds and Northrup type K potentiometer. A very large increase in the potential upon the addition of a few drops of potassium dichromate indicated the end-point of the titration.

It was found that an unavoidable oxidation of the stannous ion occurred during the handling of the solutions. For this reason it was necessary to reduce the stannic tin to the stannous form before titration. Preliminary work showed that stannic tin could be reduced with a platinum-lead couple. The couple consisted of a strip of lead foil (free from tin) with a piece of platinum foil, 2 cm. square, fastened securely to the end.

The solutions to be analyzed were made 6 molal with hydrochloric acid and heated to 75–80° in the titrating beaker, described above, with a stream of carbon dioxide flowing into the beaker. The platinum-lead couple was then inserted into the solution and the solution stirred vigorously. The total volume of the solution at this point was 100 ml. After thirty minutes the couple was removed and the solution titrated.

Early work indicated that complete reduction was not obtained by the platinum-lead couple. Accordingly it was found necessary to establish an empirical titration curve for each standard potassium dichromate solution used. This was done by titrating standard tin solutions against standard potassium dichromate solutions. Using the normality of the standard tin solution and the normality of the standard potassium dichromate solution it was possible to calculate the true end-point (ml. of potassium dichromate) for a titration. However, the observed end-point (ml. of potassium dichromate) was always less than the calculated end-point. By plotting the end-point cal-

TABLE I  
SOLUBILITY OF SnO IN SODIUM HYDROXIDE

Moles of NaOH/1000 g. H <sub>2</sub> O	Moles of SnO/1000 g. H <sub>2</sub> O (polarograph)	Moles of SnO/1000 g. H <sub>2</sub> O (titration)
0.00		$5.0 \times 10^{-6}$
$5.00 \times 10^{-3}$	$67.9^u \times 10^{-5}$	$70.5^u \times 10^{-5}$
5.00	69.6 <sup>u</sup>	
7.64	95.7	$94.1^s \times 10^{-5}$
10.23	134	
18.74	238	$254 \times 10^{-5}$
36.97	440	460
55.4	700	700
73.4	880	850
93.1	1100	1100
187.9	1800	2000
375.8	4200	4400
563.1	6000	5600
751	7300	7100
1131	9700	9800 <sup>u</sup>

<sup>u</sup> Average of five determinations.

<sup>u</sup> refers to undersaturation.

<sup>s</sup> refers to supersaturation.

TABLE II  
SOLUBILITY OF SnO IN HYDROCHLORIC ACID

Moles of HCl/1000 g. H <sub>2</sub> O	Moles of SnO/1000 g. H <sub>2</sub> O (polarograph)	Moles of SnO/1000 g. H <sub>2</sub> O (titration)
0.00		$5.0 \times 10^{-6}$
$4.44 \times 10^{-4}$	$1.43^u \times 10^{-5}$	$1.15^s \times 10^{-5}$
8.89	7.50 <sup>u</sup>	4.77
17.7	23.7 <sup>s</sup>	22.7
22.4	50.9	
44.8	164	156 <sup>u</sup>
89.3	334	304
358	1600 <sup>u</sup>	
895	3600	3700
965	4100	4300 <sup>u</sup>

<sup>u</sup> Average of five determinations.

TABLE III  
WATER SOLUBILITY OF SnO

Sample	Moles SnO/1000 g. H <sub>2</sub> O (titration)
1	$5.82^s \times 10^{-6}$
2	5.82 <sup>s</sup>
3	4.66 <sup>u</sup>
4	4.32 <sup>s</sup>
5	4.49 <sup>u</sup>

Average  $5.0 \times 10^{-6}$

(6) Hostetter and Roberts, *THIS JOURNAL*, 41, 1337 (1919).

(7) Garrett, Hogge and Heiks, *Science*, 92, 18 (1940).

TABLE IV  
 ROUNDED VALUES OF MOLES OF SnO IN ALKALI; CALCULATED VALUES OF  $K_2$  AND  $K_3$

Initial moles of NaOH/1000 g. H <sub>2</sub> O	Moles of SnO/1000 g. H <sub>2</sub> O	Moles of free OH <sup>-</sup> /1000 g. H <sub>2</sub> O	$K_2 = \frac{m_{\text{HSnO}_2^-} \gamma_{\text{HSnO}_2^-}}{m_{\text{OH}^-} \gamma_{\text{OH}^-}}$	$K_3 = \frac{m_{\text{SnO}_2} \gamma_{\text{SnO}_2}}{m_{\text{OH}^-} \gamma_{\text{OH}^-}}$
$5 \times 10^{-3}$	$0.65 \times 10^{-3}$	$4.35 \times 10^{-3}$	0.149	0.0475
10	.128	8.72	.147	.0231
15	.193	13.07	.148	
20	2.56	17.44	.147	
25	3.19	21.81	.146	
30	3.81	26.19	.146	
35	4.42	30.58	.145	
40	5.02	34.98	.144	.00559
50	6.18	43.8	.141	
60	7.32	52.7	.139	
70	8.43	61.6	.137	.00299
80	9.48	70.5	.134	
85	9.98	75.0	.133	.00236
100	12.00	88.0	.136	.00199
200	23.6	176	.134	
300	34.6	265	.130	
400	44.3	356	.125	

Average  $K_2 = 0.140$ .

culated from the standard solutions as the ordinate and the observed end-point as the abscissa a smooth curve was obtained in each case. In most cases the curves are nearly linear. These curves are shown in Fig. 1 for 0.10, 0.01, 0.001507 and 0.000742 *N* potassium dichromate solutions.

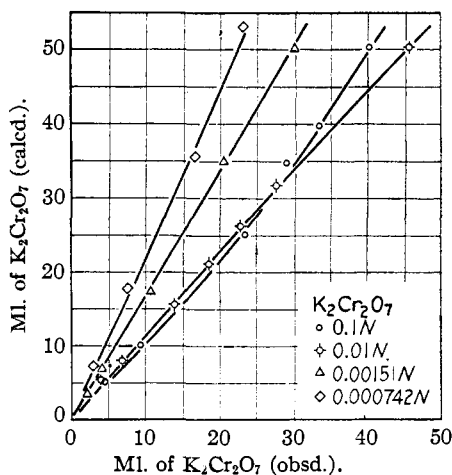


Fig. 1.

The concentrations of the unknown samples were then found by titrating with potassium dichromate as described above; after finding the observed end-point the true end-point was determined from large scale plots of the above curves. The results of this research obtained by this method are shown in column 3 of Tables I and II.

A comparison of each individual sample analyzed by the potentiometric and polarographic methods showed the average deviation to be  $\pm 4\%$  over the whole range of concentrations studied.

**Analysis of the Solid Phase.**—The solid phase was analyzed both before and after equilibration; the results indicated that no phase change occurred. The results of

TABLE V  
 ROUNDED VALUES OF MOLES OF SnO IN ACID; CALCULATED VALUES OF  $K_4$  AND  $K_5$

Initial moles of HCl/1000 g. H <sub>2</sub> O	Total moles of SnO/1000 g. H <sub>2</sub> O	Moles of Sn(OH) <sup>+</sup> from 4th approximation	Moles of Sn <sup>++</sup> from 4th approximation	Moles of free H <sup>+</sup>
0.005	0.00175	0.00139	0.00036	0.00289
.010	.00390	.00212	.00178	.00432
.015	.00600	.00294	.00306	.00594
.020	.00815	.00366	.00448	.00737
.030	.01245	.00513	.00732	.01023
.040	.01680	.00651	.01029	.01291

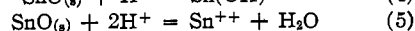
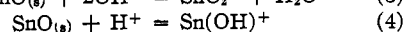
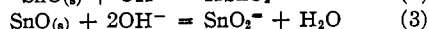
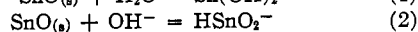
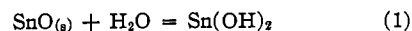
Average  $K_4 = 0.495$ . Average  $K_5 = 57.5$ .

six analyses gave an average 87.6% for the tin content of the solid phase (theoretical Sn/SnO = 88.1%).

### The Data

The data are shown in Tables I, II, III, IV, V, and Figs. 2, 3 and 4. All the data are expressed as moles per 1000 grams of water. The data in Tables IV and V are smoothed data taken from large-scale graphs.

It is assumed that several or all of the reactions represented by the following equations will account for the solubility of stannous oxide in water, in alkali and in acid



The equilibrium constants for the reactions represented by Equations (2) and (4) are evaluated on the assumption that the ratios

$$\gamma_{\text{HSnO}_2^-} / \gamma_{\text{OH}^-} \text{ and } \gamma_{\text{Sn(OH)}^+} / \gamma_{\text{H}^+} \text{ are unity.}$$

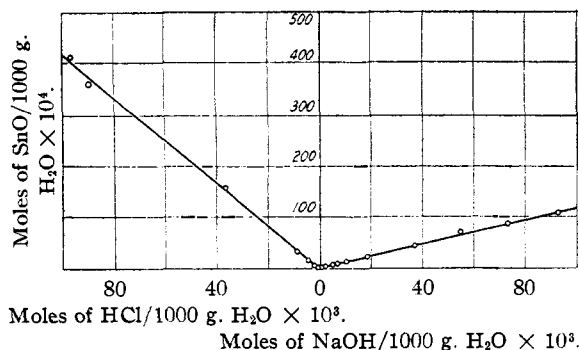


Fig. 2.

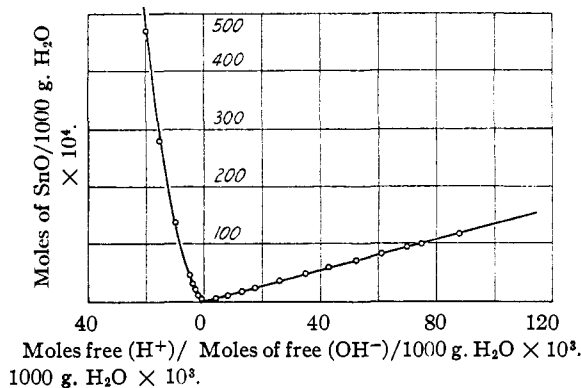


Fig. 3.

In the above ratios the symbols  $\gamma_{\text{HSnO}_2^-}$ ,  $\gamma_{\text{OH}^-}$ ,  $\gamma_{\text{Sn(OH)}^+}$  and  $\gamma_{\text{H}^+}$  represent the activity coefficients of the  $\text{HSnO}_2^-$ ,  $\text{OH}^-$ ,  $\text{Sn(OH)}^+$  and  $\text{H}^+$  ions, respectively.

The value of  $K_2$  shows a remarkable constancy from 0.005 to 0.1 molar sodium hydroxide and does not vary appreciably up to 1.0 molar. This near constancy of  $K_2$  is substantial evidence of the fact that tin hydroxide forms a monobasic acid (see column 4, Table IV). That there is little or no second acid dissociation of tin hydroxide is indicated by the wide variation of the value calculated for  $K_3$  (see column 5, Table IV).<sup>8</sup>

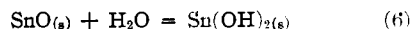
The values of the equilibrium constants for the reactions represented

(8) In the expressions for  $K_3$  and  $K_5$  the activity coefficient ratios  $\gamma_{\text{HSnO}_2^-}/\gamma_{\text{OH}^-}$  and  $\gamma_{\text{HSn}^{++}}/\gamma_{\text{H}^+}$  occur. These ratios were replaced by  $\gamma^{\text{NaOH}}$  and  $\gamma^{\text{HCl}}$ , respectively. This is valid since  $\gamma_{\text{HSnO}_2^-}/\gamma_{\text{OH}^-}$  can be accurately replaced with  $\gamma^{\text{Na}_2\text{SnO}_3}/\gamma^{\text{NaOH}}$ , and  $\gamma^{\text{Na}_2\text{SnO}_3}$  can be, in turn, replaced by  $\gamma^{\text{NaOH}}$ . This follows from the fact that at low ionic strength, where the Debye-Hückel limiting law is obeyed, the activity coefficient of a 1-2 electrolyte is the square of that of a 1-1 electrolyte at the same ionic strength. Attention was called to this relationship by Walker, Bray and Johnston [THIS JOURNAL, 49, 1235 (1927)] and by McDowell and Johnston [*ibid.*, 58, 2009 (1936)].

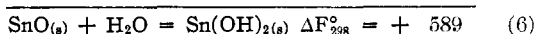
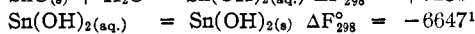
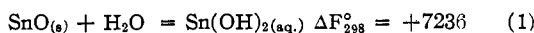
by Equations 4 and 5 were determined by a method of approximation; the third and fourth approximations of this solution yielded constant values of  $K_4$  and  $K_5$ ; such constancy is indicative of the fact that the values of  $K_4$  and  $K_5$ , so determined, are the true constants (see Table V).

**Free Energy of Hydration of Stannous Oxide.**

—The free energy of hydration of stannous oxide



was evaluated by using the water solubility of stannous oxide determined in this research; and the water solubility of stannous hydroxide, reported by Goldschmidt and Eckhardt<sup>1</sup> as  $1.35 \times 10^{-5}$  mole per 1000 g. water. The desired quantity was obtained by addition of the following equations



**The Basic Ion Product Constants.**—The

primary basic ion product constant,  $K_7$



for stannous oxide was evaluated from the value of  $K_4$  and the ion product constant of water,  $K_w$ . This treatment gives  $K_7$  a value of  $5.0 \times 10^{-15}$ .

Using Equations (6) and (7) the ion product con-

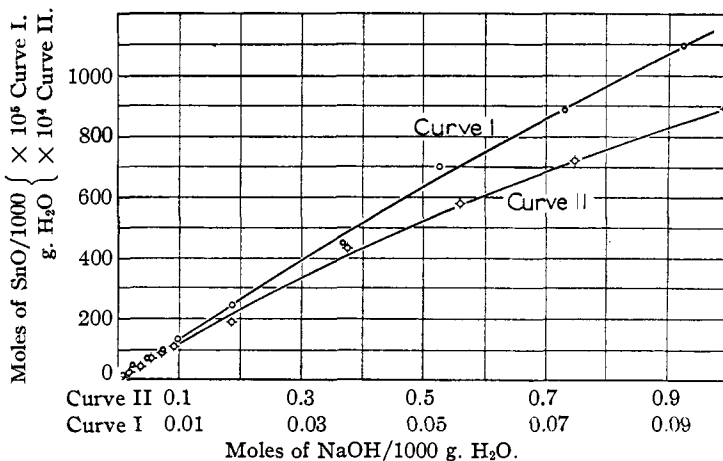
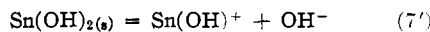


Fig. 4.

stant,  $K_7'$ , for the primary basic dissociation of stannous hydroxide

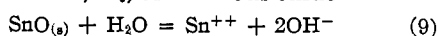


was evaluated:  $K_7' = 1.35 \times 10^{-14}$

The secondary ion product constant,  $K_8$

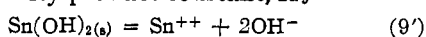


for stannous hydroxide was evaluated from values of  $K_4$ ,  $K_5$  and the ion product constant of water. The value of  $K_5$  is  $1.17 \times 10^{-12}$ . The solubility product constant,  $K_9$ , of stannous oxide



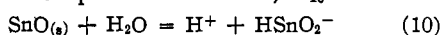
was evaluated from the value of  $K_5$  together with the ion product constant for water:  $K_9 = 5.75 \times 10^{-27}$ .

The solubility product constant,  $K_9'$



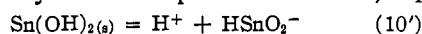
of stannous hydroxide was evaluated by addition of Equations (6) and (9).  $K_9'$  is  $1.55 \times 10^{-26}$ . This value for  $K_9'$  is in agreement with the value obtained by Prytz<sup>2</sup> of  $5.0 \times 10^{-26}$  and is probably the most reliable value reported.

**The Acid Ion Product Constants.**—The primary acidic ion product constant,  $K_{10}$



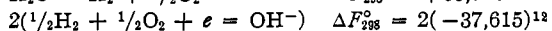
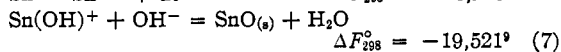
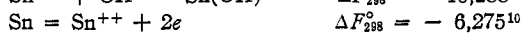
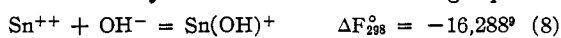
was evaluated from the value of  $K_2$  and the ion product of water.  $K_{10} = 1.40 \times 10^{-15}$ .

The primary acidic ion product constant,  $K_{10}'$ ,



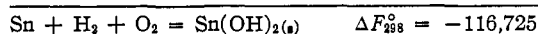
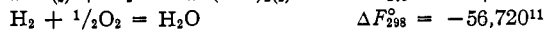
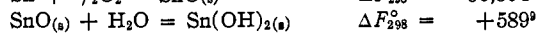
was evaluated by addition of equations (6) and (10).  $K_{10}' = 3.78 \times 10^{-15}$ . Smrz,<sup>3</sup> from rather doubtful polarographic data, reports  $6 \times 10^{-18}$  for the value of  $K_{10}'$ .

**The Free Energy of Formation of Stannous Oxide and Stannous Hydroxide.**—The free energy of formation of stannous oxide was calculated by addition of the following equations



Maier<sup>13</sup> reports a value of  $-61,332$  calories for the free energy of formation of stannous oxide, obtained from cell measurements.

The free energy of formation of stannous hydroxide was then evaluated by addition of the equations



(9) This research.

(10) "International Critical Tables," Vol. 7, page 247.

(11) Giaque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

(12) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, page 487, corrected for new value of  $\Delta F_{298}^\circ$  of formation of water =  $-56,720$  calories.<sup>11</sup>

(13) Maier, *THIS JOURNAL*, **51**, 194 (1929).

This value agrees very well with the other data in the literature. Latimer<sup>14</sup> gives a value of  $-115,950$  calories for the free energy of formation of stannous hydroxide which was evaluated from the solubility product constant obtained by Prytz.<sup>2</sup> Calculations from thermal data by Latimer yield  $-115,200$  calories for this quantity.

**The Free Energy of Formation of the  $\text{HSnO}_2^-$  Ion and the  $\text{Sn}(\text{OH})^+$  Ion from Their Elements.**

—The free energy of formation of the  $\text{HSnO}_2^-$  ion from its elements was found from Equation (2), the free energy of formation of stannous oxide and the free energy of formation of the hydroxyl ion;  $\Delta F_{298}^\circ = -97,040$  calories.

Free energy of formation of the  $\text{Sn}(\text{OH})^+$  ion from its elements was evaluated from Equation (8), the free energy of formation of the stannous ion and the free energy of formation of the hydroxyl ion;  $\Delta F_{298}^\circ = -60,200$  calories.

**The Heats of Formation of Stannous Oxide and Stannous Hydroxide.**—The heats of formation of stannous oxide and stannous hydroxide were evaluated by using the relation

$$\Delta H^\circ = \Delta F^\circ + T\Delta S^\circ$$

$\Delta S^\circ$  was calculated from reliable data in the literature;  $\Delta F^\circ$  was calculated from data of this research. The following entropy values were used:  $S_{\text{Sn}}^\circ = 12.4^{15}$ ;  $S_{\text{O}_2}^\circ = 49.03^{16}$ ;  $S_{\text{H}_2}^\circ = 31.23^{17}$ ;  $S_{\text{SnO}}^\circ = 13.5^{18}$ ;  $S_{\text{Sn}(\text{OH})_2}^\circ = 22^{14}$ .

The resulting heat of formation of stannous oxide is  $-67,600$  calories; the heat of formation of stannous hydroxide is  $-137,800$  calories.

This value for the heat of formation of stannous oxide is probably the best value determined to date, since it is calculated from very reliable entropy values and from the equilibrium constants determined in this research, together with other reliable data.<sup>10,11,12</sup> The equilibrium constants were determined from very reproducible solubility measurements. If the equilibrium constants involved in these calculations are all changed by 10%, in such a way that the effects do not cancel out in the addition of the free energies, then the value obtained for the heat of formation of stannous oxide is  $-67,636$  calories, which is within 0.1% of the former value.

(14) Latimer, "Oxidation Potentials," Prentice-Hall Book Co., Inc., New York, N. Y., 1938, p. 137.

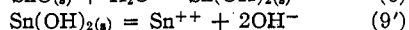
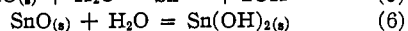
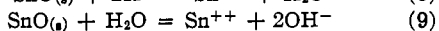
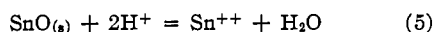
(15) "International Critical Tables," Vol. 5, p. 84.

(16) Giaque and Johnston, *THIS JOURNAL*, **51**, 2300 (1929).

(17) Giaque, *ibid.*, **52**, 4816 (1930).

(18) Kelley, *U. S. Bur. Mines Bull.*, No. 394 (1935).

Heats of Several Other Reactions.—In a similar manner the heats of the reactions



were calculated. The following entropy values were used:

$$S_{\text{Sn}^{++}}^{\circ} = -4.9^{19}; \quad S_{\text{H}_2\text{O}}^{\circ} = 16.7^{20}; \quad S_{\text{SnO}}^{\circ} = 13.5^{18}; \\ S_{\text{H}^+}^{\circ} = 0.1^9$$

The resulting  $\Delta H^{\circ}$ s are Eq. 5,  $-2909$  calories; Eq. 9,  $+23,869$  calories; Eq. 6,  $-1807$  calories and Eq. 9',  $+25,724$  calories, respectively.

### Discussion

It is interesting to note that the minimum in the solubility of stannous oxide occurs at approximately water solubility. This indicates that stannous hydroxide is approximately a neutral amphoteric hydroxide. It is also of interest to note that the first acidic and first basic ion product constants are the same order of magnitude, hence, stannous hydroxide should give about as many

stant is about 3000 times as large as the first acidic dissociation constant. This indicates that lead hydroxide is predominately basic in character. One would then predict on this basis that germanous hydroxide would be predominately acidic.

It was noted during the course of this research that in the stannous oxide-sodium hydroxide systems, all the samples below a concentration of approximately 0.005 molar sodium hydroxide were colloidal. Whether this fact is significant in the preparation of colloidal stannous oxide is not known.

**Acknowledgment.**—The authors wish to express their appreciation to Professor William MacNevin for the help and coöperation extended to them in obtaining the polarographic data reported in this paper.

### Summary

A summary of all the calculations made in this paper, together with the corresponding values in the literature, is shown in Table VI.

TABLE VI  
SUMMARY

Reaction	$K$		$\Delta F_{298}^{\circ}$		$\Delta H_{298}^{\circ}$	
	This research	Literature	This research	Literature	This research	Literature
$\text{SnO}(s) + \text{H}_2\text{O} = \text{Sn}(\text{OH})_2(aq)$	$5.0 \times 10^{-6}$		+ 7,240			
$\text{SnO}(s) + \text{H}_2\text{O} = \text{Sn}(\text{OH})_2(s)$	0.370		+ 589		- 1,810	
$\text{SnO}(s) + \text{OH}^- = \text{HSnO}_2^-$	.140		+ 1,170			
$\text{SnO}(s) + \text{H}^+ = \text{Sn}(\text{OH})^+$	.495		+ 417			
$\text{SnO}(s) + 2\text{H}^+ = \text{Sn}^{++} + \text{H}_2\text{O}$	57.5		- 2,400		- 2,910	
$\text{SnO}(s) + \text{H}_2\text{O} = \text{Sn}(\text{OH})^+ + \text{OH}^-$	$5.0 \times 10^{-15}$		+ 19,500			
$\text{Sn}(\text{OH})_2(s) = \text{Sn}(\text{OH})^+ + \text{OH}^-$	$1.35 \times 10^{-14}$		+ 18,900			
$\text{Sn}(\text{OH})^+ = \text{Sn}^{++} + \text{OH}^-$	$1.17 \times 10^{-12}$		+ 16,300			
$\text{SnO}(s) + \text{H}_2\text{O} = \text{Sn}^{++} + 2\text{OH}^-$	$5.75 \times 10^{-27}$		+ 35,800		+ 23,900	
$\text{Sn}(\text{OH})_2(s) = \text{Sn}^{++} + 2\text{OH}^-$	$1.55 \times 10^{-26}$		+ 35,200		+ 25,700	
$\text{SnO}(s) + \text{H}_2\text{O} = \text{H}^+ + \text{HSnO}_2^-$	$1.40 \times 10^{-15}$		+ 20,300			
$\text{Sn}(\text{OH})_2(s) = \text{H}^+ + \text{HSnO}_2^-$	$3.78 \times 10^{-15}$	$6.0 \times 10^{-18(3)}$	+ 19,700	+ 23,500 <sup>14</sup>		
$\text{Sn}(s) + 1/2\text{O}_2(g) = \text{SnO}(s)$	$2.46 \times 10^{44}$		- 60,600	- 61,332 <sup>13</sup>	- 67,600	
$\text{Sn}(s) + \text{H}_2(g) + \text{O}_2(g) = \text{Sn}(\text{OH})_2(s)$	$3.26 \times 10^{35}$		- 116,700	- 115,950 <sup>14</sup>		
$\text{Sn}(s) + 1/2\text{H}_2(g) + \text{O}_2(g) + e = \text{HSnO}_2^-$	$1.24 = 10^{71}$		- 97,000	- 92,450 <sup>14</sup>		
$\text{Sn}(s) + 1/2\text{H}_2(g) + 1/2\text{O}_2(g) - e = \text{Sn}(\text{OH})^+$	$1.22 \times 10^{44}$		- 60,200			

$\text{H}^+$  ions as  $\text{OH}^-$  ions on dissociation. The data indicate that stannous hydroxide forms a mono-basic acid as does lead hydroxide. In the case of lead hydroxide<sup>5</sup> the first basic dissociation con-

(19) Latimer, Pitzer and Smith, THIS JOURNAL, 60, 1829 (1938).

(20) Calculated from  $\Delta S^{\circ}$  of formation of water given by Bichowsky and Rossini as  $-39.0$  using an entropy of  $31.23^{17}$  for hydrogen and  $49.03^{18}$  for oxygen.

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- (21) Dulong, *Compt. rend.*, 7, 871 (1838).  
 (22) Mixer, *Am. J. Sci.*, [4] 177, 229 (1909).  
 (23) Andrews, *Phil. Mag.*, [3] 32, 321 (1848).  
 (24) Chandron, *Ann. chim. phys.*, [9] 16, 220 (1921).  
 (25) Delépine and Hallopean, *Compt. rend.*, 129, 600 (1899).  
 (26) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 56.