

The Electromotive-Force of Cells Containing Stannous
Sulphate and Stannic Oxide.

A Thesis

by

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Object of this Research and Review of Previous Work.

The objects of this research were to determine:

- (1) The free energy of SnO_2 .
- (2) The difference between the free energy of $\text{SnSO}_4(\text{s})$ and of $\text{Hg}_2\text{SO}_4(\text{s})$.
- (3) The heat of formation of SnSO_4 .

It had been hoped to use these data in connection with measurements of the equilibrium in the reaction,
$$\text{SnSO}_4(\text{s}) = \text{SnO}_2(\text{s}) + \text{SO}_2(\text{g}).$$

but complications have prevented the obtaining of the latter measurements so that the results of the following work are presented in advance as a separate contribution to our knowledge of the compounds of tin.

Apparently neither the free energy nor the heat of formation of $\text{SnSO}_4(\text{s})$ have been determined. However the equilibrium between SnO_2 , Sn , SnO , H_2 , and H_2O , was determined by Wöhler and Balz,

****Zeitschrift für Elektrochemie. 27, 414, (1911).****

but the results seem to be in error. Thus, the heat effect of the reaction calculated from the temperature coefficient of the equilibrium is several thousand calories different from that obtained from thermochemical data. Also experiments made by Mr. P. L. Magill in this laboratory seem to lead to different results. It was thought desirable, there-

fore, to get at least an approximate value for the free energy of SnO_2 at room temperature and avoid uncertainty in extrapolation from high temperatures.

It was proposed to measure the electromotive force of cells containing Hg, HgO, SnO_2 , and Sn; and Hg, Hg_2SO_4 , SnSO_4 , and Sn. One of the hardest problems was the preparation of materials of sufficient purity. In this connection the author wishes to acknowledge his indebtedness to Mr. V. Kalichevsky for the preparation of the HgO and the solution of Na_2SnS_3 for plating the electrodes; and to Mr. F. A. Hough for the preparation of the SnSO_4 .

This research was carried on under the direction of Dr. David F. Smith to whom the author is indebted for much valuable advice and aid both in the laboratory work and in the writing of this report.

Preparation of Materials.

Alcohol: The absolute alcohol was made by refluxing 94% alcohol with a large quantity of lime and anhydrous KOH for two days. It was then distilled into a flask which contained finely powdered lime and anhydrous KOH. This mixture was refluxed for two days and distilled. The first ten cubic-centimeters were discarded and the remainder was caught in 250 cc. flasks which were then sealed off.

KOH: The KOH used in the oxide cell was prepared by fusing KOH in a polished iron crucible. The resulting mass was powdered, was shaken with absolute alcohol, and was filtered out of contact with air. The filtrate was placed in a vacuum dessicator over CaCl_2 and the air exhausted. Upon standing the solution first became brown and then crystals of KOH appeared. These were washed with absolute ether.

SnO_2 : The SnO_2 was prepared by igniting SnSO_4 . The product was a light yellow powder.

HgO: This was made by heating the nitrate, HgNO_3 .

Tin: The tin was prepared by boiling a solution of SnCl_2 with a strong solution of NaOH. The precipitate of metallic tin was washed until it gave a neutral washing which showed no test for chlorides. It was then placed in a tube, evacuated, dried, and finally melted to a button

of pure metallic tin. This tin was powdered by filing with a clean new file.

SnSO_4 : A solution of pure SnCl_2 of commerce was treated with NaOH and the $\text{Sn}(\text{OH})_2$ washed with water until free from chlorides. The $\text{Sn}(\text{OH})_2$ was dissolved in dilute H_2SO_4 and from this solution the SnSO_4 was precipitated by adding alcohol. This product was dissolved in dilute H_2SO_4 and was shaken with finely powdered tin for several days. The solution was then filtered and the SnSO_4 precipitated with alcohol. This product was washed with alcohol and ether and dried in a vacuum dessicator. The SnSO_4 prepared by this method was used in the solubility measurements and, after shaking with tin, was used in the alcohol- H_2SO_4 cells. For the cell containing the amalgam the SnSO_4 was dissolved in dilute H_2SO_4 and was shaken with finely powdered tin for three days. It was then re-precipitated by adding eighteen normal H_2SO_4 until the solution was approximately ten normal. After washing the SnSO_4 with alcohol it was dried in a dessicator. The final product was a fine white powder. All the above processes were carried on in an atmosphere of CO_2 to prevent oxidation.

Hg_2SO_4 : This was prepared by the method described by G. A. Hulett using two crystallizing dishes and an automatic stirrer.

The Hg_2SO_4 was shaken several times with the cell solution before using.

Hg: The mercury used; in the cells, in the preparation of the Hg_2SO_4 , and in the amalgam, was purified by electrolyzing and distilling.

Mercury amalgam: The amalgam of approximately 0.6 weight percent tin was prepared by weighing out the required quantities and sealing them in an exhausted tube. Upon heating, the tin completely dissolved.

SnCl_2 : A solution of pure SnCl_2 of commerce was shaken with tin for three days. This solution, after being filtered, was concentrated and was cooled in a vacuum dessicator. The SnCl_2 , which crystallized out in large needle like crystals, was dissolved in water. This solution was shaken with tin for three days and was then filtered and sealed until used.

Na_2SnS_3 : This solution, which was used to plate the tin electrodes was made as follows: Chlorine gas was passed over commercial tin at a temperature below 100° . The SnCl_4 thus obtained was distilled and the fraction boiling at 114° was collected. It was then diluted four times its volume with water and a concentrated solution of Na_2S added until the precipitate re-dissolved, after which a fifty percent excess was added.

The plating of the electrodes was done with a current

of from 0.02 to 0.03 amperes. Tin is precipitated quantitatively in this way without occlusion of impurities in the deposit, and is a white closely adhering mass.

****Berichte. 21, 2, 2900.****

****J. A. Ch. S. Trans. 1915, CVII, 71.****

Apparatus.

The cells were of the common "H" type with the electrodes at the bottom.

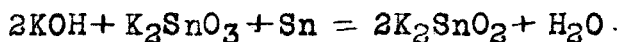
The oil thermostats, one of which was at 25° and the other at 45°, were both regulated to keep the temperature constant to 0.02°.

The electromotive-force measurements were made with a Leeds and Northrup potentiometer against a Weston standard cell.

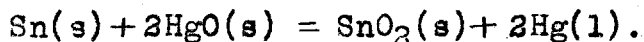
For shaking the various solutions a motor driven revolving wheel was employed.

The Oxide Cell.

The oxide cell is represented in the following manner; $\text{Sn}(s) + \text{SnO}_2(s)$, sol'n. of KOH in absolute alcohol, $\text{HgO}(s) + \text{Hg}(l)$. Alcoholic KOH was used to prevent hydration of the SnO_2 and also to cut down the OH^- ion concentration and thus prevent the reaction



which proceeds in aqueous alkaline solutions. The cell reaction when four faradays are passed through the cell from left to right, is



In setting up this cell two bottles were filled with the absolute alcohol KOH solution. The stoppers were waxed in after some HgO and Hg was placed in one and SnO_2 and Sn in the other. The two bottles were then shaken for two days. After the cell was cleaned, dried, and filled with nitrogen, the suspensions were poured in the respective sides of the cell up to the connecting tube. When the suspensions had settled the rest of the cell was filled with the original solution. The glass stoppers were then waxed in and the cell placed in the 25° thermostat.

Data.

Temperature 25°

E.M.F. 1.0267 volts.

For six days the measured electromotive-force of this cell was not different from the value 1.0267 by more than three millivolts and was within 0.1 millivolt of this value the last three days.

Results and Calculations.

$$-\Delta F_{250} = ENF = 94,758. \text{ calories.}$$

$$2(F_{\text{HgO}}) = F_{\text{SnO}_2} - \Delta F.$$

$F_{\text{SnO}_2} = -122,374$ calories, assuming the value of -13808 calories for the free energy of HgO given by Lewis and Randall.

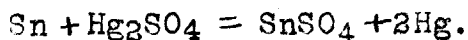
****Lewis and Randall, "Thermodynamics".****

The Sulphate Cell.

In order to determine the concentration of sulphuric acid necessary to cause the solubility of SnSO_4 to fall to such a value as would not appreciably effect the activity of the H_2SO_4 , the solubility of SnSO_4 in various solutions of H_2SO_4 was determined. The total stannous tin concentration was determined by titration with standard iodine, and these values, after being calculated to moles per Kg. of solution, were plotted against the respective normalities of the sulphuric acid. The saturation point was approached merely from the unsaturated side and may be in error by a few percent.

While the solubility of SnSO_4 was being determined the cell was set up three times with alcohol- H_2SO_4 solutions in which SnSO_4 is but slightly soluble. Two cells were set up with a solution of equal volumes of eight normal H_2SO_4 and alcohol, and one with equal volumes of eighteen normal H_2SO_4 and alcohol. The cell in these cases is represented in the following manner:

$\text{Hg}(l) + \text{Hg}_2\text{SO}_4(s)$, sol'n. of H_2SO_4 in alcohol; $\text{SnSO}_4(s) + \text{Sn}(s)$. The cell reaction was

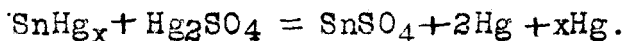


From the solubility curve of SnSO_4 in H_2SO_4 , it was decided that a solution of approximately ten normal or more in H_2SO_4 would make a suitable cell solution since

the solubility of SnSO_4 in this solution is but 0.03 molal. However an acid of this concentration reacted with the metallic tin and therefore a liquid amalgam of about 0.6 weight percent of tin was used. For this cell, represented by the expression

$\text{SnHg}_x(\text{l}) + \text{SnSO}_4(\text{s}), \text{sol'n. of } 10 \text{ N. H}_2\text{SO}_4, \text{Hg}_2\text{SO}_4(\text{s}) + \text{Hg}(\text{l})$., .

the reaction was



A portion of the same amalgam was then placed in a cellof the type

Sn, SnCl_2 sol'n approximately 0.4 molal, SnHg_x .

in order to refer the above electromotive-force to pure tin.

The change in electromotive-force with the temperature was found by first letting the cell come to equilibrium at 25° and then at 45° . From these values the heat effect of the cell reaction could be calculated.

Data.

From the alcohol- H_2SO_4 cells the value for the electromotive-force was approximately 0.855 volts. This value was not used in the calculations because the alcohol- H_2SO_4 cells did not give as sensitive readings nor as constant a value as did the amalgam cells.

Results and Calculations.

(1)	(2)	(3) = (1) + (2)
$\text{SnHg}_x + \text{Hg}_2\text{SO}_4 =$	$\text{Sn} + x\text{Hg} = \text{SnHg}_x$	$\text{Sn} + \text{Hg}_2\text{SO}_4 =$
$\text{SnSO}_4 + 2\text{Hg} + x\text{Hg}$		$\text{SnSO}_4 + 2\text{Hg}.$
Temp.	E.M.F.	E.M.F.
1 25°	0.85472	0.00385
2 35°	0.85480	0.00100
3 25°	0.85405	0.00120
4 25°	--	--
1 45°	0.85364	0.00848
		0.85830
		0.85580
		0.85525
		0.855
		0.86206.

Value no.1 was obtained from a cell having for the tin electrode a platinum coil plated with tin. Values 2 and 3 were from a cell in which the tin electrode was a coil of platinum wire about which finely powdered tin was packed. Value number 4 is the average value for those cells containing alcohol and H_2SO_4 as the cell solution. The average of values 1,2,3,&4 is

0.856 calories.

$$-\Delta F_{25} = ENF = \frac{.856 \times 2 \times 96494}{4.183} = 39500 \text{ calories.}$$

$$-\Delta F_{45} = ENF = 39780 \text{ calories.}$$

$$\frac{E_2}{T_2} - \frac{E_1}{T_1} = \frac{4.183 \times (\Delta H)}{192988} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$-\Delta H = 37000 \text{ calories.}$$

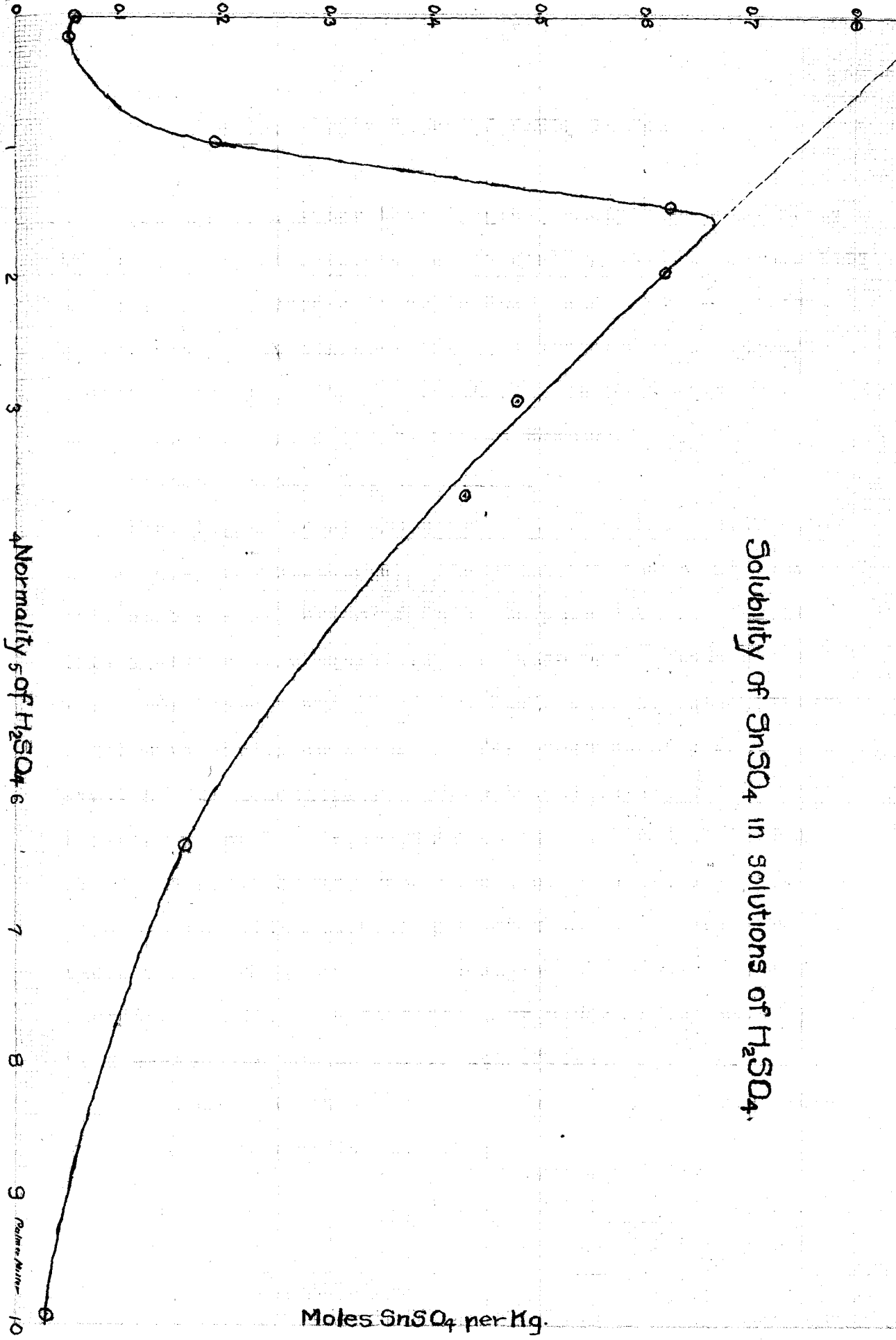
$$H_{\text{Hg}_2\text{SO}_4} = H_{\text{SnSO}_4} - \Delta H$$

$H_{\text{SnSO}_4} = 212000$ calories assuming the value of -175000 calories

for the heat of formation of Hg_2SO_4 , taken from

Landolt Börnstein. "Tabellen".

Solubility of SnSO_4 in solutions of H_2SO_4 .



The Solubility Curve of SnSO_4 in H_2SO_4 .

All the values for this diagram, except the solubility in pure water, were determined by shaking various normalities of acid with an excess of solid SnSO_4 and finding the concentration of the stannous tin by titration with standard iodine. The value for the solubility in pure water was taken from the value determined by Margnac.

Comp. Rend. 45, 650, (1857).

The diagram shows the phases in equilibrium with acids of various concentrations. The point "A" represents the meta-stable equilibrium of SnSO_4 in pure water. This is only a meta-stable equilibrium because upon standing the salt hydrolyzes readily and the basic salt is precipitated until equilibrium is reached. The presence of even a small H^+ ion concentration seems to catalyze the hydrolysis reaction to such a degree that a meta-stable equilibrium is not attained in any case except pure water. When the acid concentration becomes greater than 1.6 normal the basic salt $\text{SnSO}_4 \cdot 2\text{SnO} \cdot x\text{H}_2\text{O}$ changes to SnSO_4 . Further increases in the acid concentration cause the solubility to decrease due to the common ion effect.

In this connection Dr. D. F. Smith made some calculations on the activities of SnSO_4 .

ΣSn^{++}	H_2SO_4	E.	A Sn^{++} calculated	A Sn^{++} from E.
0.096	0.5	0.203	0.00643	0.00533.
0.0105	0.5	0.221	0.000704	0.000704
0.048	0.05	0.204	0.0104	0.00494
0.105	0.05	0.223	0.00227	00.00112
0.429	0.00	0.190	0.0335	0.0146
0.095	0.00	0.198	0.0152	0.00185
0.010	0.00	0.211	0.0040	0.00286.

The activity values in the fourth column are those of CuSO_4 taken from Lewis and Randall.

****Lewis and Randall, "Thermodynamics".****

The values in the fifth column are calculated from the measured electromotive-forces of F. Foester and J. Yamasaki, of the cell $\text{Sn}, \text{H}_2\text{SO}_4 + \text{SnSO}_4, \text{N.E.}$,

****Zeitschrift für Elektrochemie. 17, 362, (1911).****
 assuming the values in the second row to be identical by the two methods. It can readily be seen that the smaller the concentration of the acid, the more the activity calculated varies from the actual. This is further proof of the large hydrolysis in weakly acid solutions. It shows furthermore that upon the basis of known activity values it would be impossible to calculate the Sn^{++} ion concentration in any case except strongly acid solutions since the hydrolysis is so large.

The Electrode Potential of Tin.

If the activity of SnSO_4 at this concentration were known the electrode potential of tin could be calculated, since we have all the other necessary data (ie) the electromotive-force of the sulphate cell containing ten normal H_2SO_4 and the activity of H_2SO_4 at this concentration.

Summary.

From the electromotive force of the oxide cell and from the assumed value of -13808 calories for the free energy of HgO, the free energy of SnO₂ was calculated to be -123374 calories. Since only one measurement of this electromotive force was made, it is impossible to estimate how much this value may be in error.

The free energy of SnSO₄ is greater than the free energy of Hg₂SO₄ at 25° by ~~39500~~ 39780 calories, and at 45° by 39780 calories. It is unlikely that these values are in error by more than 100 calories, corresponding to an error of about two millivolts in the electromotive force.

When the reaction $\text{Sn} + \text{Hg}_2\text{SO}_4 = \text{SnSO}_4 + 2\text{Hg}$ takes place at an average temperature of 35°, 37000 calories of heat are evolved. This value is probably in error by less than 1000 calories.

Assuming the value of -175000 calories for the heat of formation of Hg₂SO₄, the heat of formation of SnSO₄ becomes -212000 calories.