EQUILIBRIUM IN THE SYSTEM HYDROGEN, WATER VAPOR

AND THE OXIDES OF TIN

Thesis

by

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Outline of Investigation and Review of Previous Work

Wöhler and Balz (Zs. El-Chemie, 1921, pg. 414) determined the equilibrium for the reactions $SnO_2 + H_2 \rightleftharpoons SnO + H_2O$, $SnO + H_2 \rightleftharpoons Sn + H_2O$ and $SnO_2 + 2H_2 \rightleftharpoons Sn + 2H_2O$ at 700° and 800°. It was thought desirable to obtain the equilibrium conditions at some lower temperature and thus avoid some of the error in extropolation to standard temperature. Furthermore, the heat effect calculated from the results of Wöhler and Balz differs by over 9,000 calories from that calculated from the thermochemical data of W. G. Mixter (Am. J. Sci., 27, 229-34) who determined the heats of formation of stannous and of stannic oxide.

The purpose of the present investigation was to obtain the equilibrium constants of the above reactions at as low a temperature as practicable.

A series of experiments was made to determine whether or not the reaction could be carried on at temperatures as low as 350° and 450°. Experiments were made to prove the decomposition of stannic oxide from 300° to 600° was negligible.

The final equilibrium measurements for the above reactions were made at 444°.

The atomic weights used throughout this work are as follows: Sn, 118.7; H, 1.0; O, 16.0

Preparation of Materials

The stannic oxide used was made by treating a good grade of imported tin with C.P. concentrated nitric and then drying and heating the product at a red heat for eight hours.

The stannous oxide was prepared by boiling a good grade of domestic stannous chloride with finely divided metallic tin in acid solution until the liquid became clear. The flask containing the stannous chloride was then washed clean of all air by means of hydrogen. From this point to the drying of the final product the solutions were kept in an atmosphere of hydrogen. Stannous hydroxide was first precipitated by means of sodium hydroxide. The stannous oxide, in the form of blue black crystals, was obtained by boiling the stannous hydroxide in a dilute alkaline solution. The oxide thus obtained was washed by decantation until the washings gave no test for chlorides. After allowing to drain, the oxide was washed first with alcohol and then with ether. It was allowed to dry in a vacuum desiccator, over sulfuric acid for two weeks. The results of later experiments seemed to show that the stannous oxide prepared in this way contained water. The black crystals of stannous oxide were then placed in a hard glass tube attached to a vacuum pump and heated for several hours in an electric furnace at 600°. Upon removal from the furnace, the stannous oxide appeared as an olive green powder.

The metallic tin was precipitated from a solution of stannous hydroxide, prepared as above, by boiling the hydroxide in a strongly alkaline solution. The finely-divided tin, prepared in this way, was washed until free from chlorides then melted to a button in an atmosphere of hydrogen, after which it was cut into small pieces.

The hydrogen used was prepared by the action of hydrochloric acid on zinc. It was washed by means of concentrated sulfuric acid and alkaline pyrogallol.

Apparatus and Method

In the early part of the work a flow method was tried. However, at the temperature 500° it was found that equilibrium could not be obtained in a reasonable length of time. The static method was then tried at 357°. The method was as follows. Into a flask of about sixty cubic centimeters capacity was introduced several grams of a mixture consisting of the initial and final solid substances which took part in the reaction. In the case of the reaction $SnO + H_2O \rightleftharpoons SnO_2 + H_2$ and $Sn + H_2O \rightleftharpoons SnO + H_2$, in which water was one of the initial reacting substances, a small weighed quantity of water was introduced into the flask by means of a sealed bulb. With the bulb was introduced a small solid glass rod. The neck of the flask was drawn down to a small capillary and the whole attached to a vacuum pump, capable of evacuating to a pressure of less than one one-hundredth of a milli-meter. After the flask had been evacuated, it was sealed by fusing the capillary neck. The bulb containing the water was then fractured by jarring the flask sufficiently to cause the impact of the rod to crack the bulb. The flask was then placed in a vapor bath and allowed to heat for several days. When it was thought that equilibrium was reached, the flask was removed from the bath and rapidly cooled in a strong blast of air. The cooling usually required from one and one-half to two minutes. It was then weighed after which the tip was broken off under water and the water allowed to rise in the flask. There was a second weighing to determine the volume occupied by the water vapor at equilibrium. The space left above the water was filled with hydrogen in the quantity at which it was present at equilibrium. The partially

filled flask was then filled completely with water and weighed again.

By making the proper corrections for barometric pressure, heights of

water, temperature of water and air, vapor tension etc., the quantity

of hydrogen was computed. It was possible from these results, as will

be shown later, to calculate the equilibrium constants.

In the case of the reactions $SnO + H_2 \rightleftharpoons Sn + H_2O$ and $SnO_2 + H_2$

$\rightleftharpoons SnO + H_2O$, in which hydrogen was one of the initial reacting sub-

stances, the flask was filled with the substances and the neck was

drawn down as before. Connection to the flask was made by means of a

two-way stop cock. One position would connect the flask to the vacuum

pump and the other position would connect it to a source of hydrogen.

The pressure at which the flask was filled was measured by means of a

mercury manometer.

In order to facilitate the reactions in which metallic tin was one

of the reacting substances an apparatus was devised which would cause

the molten tin to be agitated. It consisted of a flask of about thirty

cubic centimeters capacity whose shape was somewhat conical. When the

flask was rapidly rotated the molten tin would be thrown on the wall in

a thin layer, thereby increasing the surface of the tin and keeping the

metal separated from its oxide. The determination of the equilibrium

mixture was made in the same manner as the above.

Experimental Results

The first part of the work was tried at $357°$. At this temperature

the reactions $SnO + H_2 \rightleftharpoons Sn + H_2O$ and $SnO_2 + H_2 \rightleftharpoons SnO + H_2O$ seemed

to go rather slow. The reaction $SnO_2 + 2H_2 \rightleftharpoons Sn + 2H_2O$ after heating

for two days was found to have gone so far to the right that an accurate

determination of the constant was not feasible.

Before going to a higher temperature an experiment was made to determine whether or not stannic oxide had an appreciable dissociation pressure. It was found by the use of a mercury manometer that between 300° and 600° the pressure of the oxygen was negligible.

The temperature was increased to 444° and the following results were obtained.

Table 1

Initial substances	Total mols	Total Vol. (cc.)	P_{H_2O} (atm.)	P_{H_2} (atm.)	$\dfrac{P_{H_2O}}{P_{H_2}} = K$	Total pressure	Hours heated
SnO, SnO$_2$, H$_2$	0.00256	64.40	0.454	1.88	0.242	2.34	41
SnO, SnO$_2$, H$_2$	0.00252	64.20	0.477	1.835	0.260	2.31	72
SnO, SnO$_2$, H$_2$	0.00262	66.50	0.481	1.820	0.270	2.31	86
SnO$_2$, SnO, H$_2$O	0.00312	64.40	1.01	1.75	0.576	2.76	41
SnO$_2$, SnO, H$_2$O	0.00165	66.36	0.425	1.035	0.408	1.46	66
SnO$_2$, SnO, H$_2$O	0.00106	63.79	0.208	0.638	0.326	0.846	86
SnO, Sn, H$_2$O	0.00269	47.80	1.775	1.530	1.150	3.31	86
SnO, Sn, H$_2$O	0.00250	66.67	0.730	1.470	0.667	2.20	21
SnO, Sn, H$_2$O	0.00200	65.69	0.639	1.790	0.554	1.79	41
Sn, SnO, H$_2$	0.00192	48.34	0.807	1.533	0.415	2.34	86
Sn, SnO, H$_2$	0.00272	68.40	0.808	1.512	0.528	2.32	40

Although there is a close agreement of the results in several cases, the variation in the remaining determinations seems to be greater than that accounted for by experimental error.

An experiment was made to determine if the reaction $2SnO \rightleftharpoons Sn + SnO_2$ would take place at 444°. After heating a sample of stannous oxide in boiling sulfur for ten hours, the following differences were noticed.

Before heating.

The stannous oxide existed as blue black crystals. The crystals dissolved in concentrated hydrochloric acid leaving no residue. No gas was evolved during the solution of the black crystals.

After heating. ·

The material existed as an olive green powder. The powder partially dissolved leaving a white residue. Gas seemed to be evolved in small amount upon the addition of concentrated hydrochloric acid.

The reaction $SnO_2 + 2H_2 \rightleftharpoons Sn + 2H_2O$ was tried at 444° and the following results were obtained.

Table 2

Initial substances	Total mols	Total vol.	P_{H_2O} (atm.)	P_{H_2} (atm.)	$\dfrac{P_{H_2O}}{P_{H_2}} = K$	Total pres.	Hours heated
SnO_2, Sn, H_2	0.00252	64.20	1.16	1.16	1.00	2.32	62
SnO_2, Sn, H_2	0.00148	37.00	1.563	0.803	1.938	2.36	71
SnO_2, Sn, H_2O	0.00266	46.40	3.100	0.280	10.99	3.38	62
SnO_2, Sn, H_2O	0.00304	66.20	2.63	0.0703	42.40	2.70	62

Calculations

The heat effect for the reaction $SnO_2 + 2H_2 \longrightarrow 2H_2O + Sn$ was calculated from the results of Wöhler and Balz by means of the integrated van't Hoff equation from the constants 107.0 at 700 and 184.5 at 800° C. The heat effect is $-\triangle H = 11,280$ between 700 and 800°. By using the specific heat of stannic oxide as 0.0938 the specific heat of tin as 0.05876 and the heat of fusion of tin as 1,700 calories for 1 gm. atom, the heat effect was calculated to be $-\triangle H = 23,380 - 1.50\ T - 0.0028T^2 + 0.000,001,48T^3$ above 233° C. Or $-\triangle H = 20,530$ calories at 750° C. The heat effect below 233°

is $-\Delta H = 22{,}167 - 2.67\,T - 0.0028T^2 + 0.000{,}00148\,T^3$. By using the value $11{,}280$ for $-\Delta H$ and calculating the equilibrium constant from $800°$ to $444°$ C, the value for $\left(\dfrac{P_{H_2O}}{P_{H_2}}\right)^2$ was found to be 13.13. If the value for $-\Delta H$ is used that was determined from heat data, the value for $\left(\dfrac{P_{H_2O}}{P_{H_2}}\right)^2$ is found to be 1.398 when calculated from $800°$ to $444°$, and 2.46 when calculated from $700°$ to $444°$. The equilibrium constant $\left(\dfrac{P_{H_2O}}{P_{H_2}}\right)^2$ when calculated from $800°$ to $25°$ is 7.95×10^{-10}; and when calculated from $700°$ to $25°$ is 14.4×10^{-10}. These values give the free energy of stannic oxide to be $-121{,}364$ calories and $-121{,}134$ calories respectively when the free energy of H_2O (gas) is taken as $-54{,}507$ calories at $25°$.

An average of the best experimental results of the present work was taken and the value for $\left(\dfrac{P_{H_2O}}{P_{H_2}}\right)^2$ was found to be 0.188 at $444°$ C. When this values is calculated to $233°$ C (melting-point of tin) it was found to be 3.19×10^{-4}. The value for $\left(\dfrac{P_{H_2O}}{P_{H_2}}\right)^2$ was found to be 1.63×10^{-10} at $25°$. These values give the free energy of stannic oxide to be $-126{,}488$ calories at $506°$ A and $-122{,}364$ calories at $298°$ A.

An average value for $\dfrac{P_{H_2O}}{P_{H_2}}$ for the reaction $SnO + H_2 \rightleftharpoons Sn + H_2O$ was found to be 0.541 at $444°$ C. When this is calculated to $233°$ C it was found to be 0.0633 and when calculated to $25°$ C it was 3.96×10^{-5}. This gives the free energy of stannous oxide to be $-62{,}009$ calories at $233°$ C and $-60{,}507$ calories at $25°$ C. The heat effect used was $-\Delta H = 7{,}947 - 1.1T - 0.0014T^2 + 7.4 \times 10^{-7}T^3$ below $233°$ C, and $-\Delta H = 8495 - 1.4T - 0.0014T^2 + 7.4 \times 10^{-7}T^3$, above $233°$ C.

Another calculation was made to determine at what temperature stannic oxide, stannous oxide, and tin are in equilibrium. Values taken from the results of Wöhler and Balz give 1040° A, experimental data from the present work give 786° A. The change of the free energy with the temperature of the reaction $2SnO \rightleftharpoons SnO_2 + Sn$ is in such a direction that at temperatures below those given tin will reduce stannic oxide to stannous oxide.

Discussion of Results

Although the results of this research are not conclusively quantitative, it has been shown that the above reactions do take place at 444° C at a moderately rapid rate. Application of the phase rule to the system Sn, SnO, SnO_2, H_2O and H_2 shows that there is but one temperature at which the three solid phases can be in equilibrium, and at this temperature both the total pressure and the ratio of H_2O to H_2 are fixed. At temperatures below this point the foregoing calculations show that the stable phases are Sn and SnO, above this SnO_2 and Sn are the stable phases. This, however, does not exclude the possibility of a metastable equilibrium between any two of these three phases at any temperature where the rates of reaction between the solids (such as $Sn + SnO_2 \longrightarrow 2SnO$) are very slow. But to obtain this metastable equilibrium the ratios of H_2O to H_2 and the total pressure would have to be such as not to produce a third phase or else the rate of attainment of equilibrium with any third phase appearing would have to be slow. This would doubtless be the case when only small quantities of the third phase appeared.

It is possible though improbable that the equilibrium changed during the cooling of the tube. It is likely that a continuous flow method could be used, to better advantage.

The disagreement of the data in the second table was due, no doubt, to the reduction of the stannic oxide by the tin; thereby preventing equilibrium from being reached. The calculations show that this is possible at 444° C.

It can be seen from the data in the first table that with the exclusion of one value, the greatest variation is about two fold. In calculating the free energy of stannic oxide at 25° a two fold variation in the equilibrium constant would make a difference of about 360 calories. The free energy of stannic oxide was found by electromotive-force measurements to be -122,374[*] cal. at 25° which is only ten calories different from the above value.

Summary

In this article results are given to show that the reactions $SnO_2 + H_2 \rightleftharpoons SnO + H_2O$, $SnO + H_2 \rightleftharpoons Sn + H_2O$ and $SnO_2 + 2H_2 \rightleftharpoons Sn + 2H_2O$ take place at a fairly rapid rate at 444° C.

Results have been obtained which indicate that the reaction $Sn + SnO_2 \rightarrow 2SnO$ takes place below 513° C.

The decomposition of stannic oxide was found to be negligible between 300° and 400° C.

The equilibrium constant for the reaction $SnO_2 + 2H_2 \rightleftharpoons Sn + 2H_2O$ was found to be 1.63×10^{-10} at 25°. It was calculated from the results of Wöhler and Balz to lie between 7.95×10^{-10} and 14.4×10^{-10} at 25° C.

The equilibrium constant for the reaction $SnO + H_2 \rightleftharpoons Sn + H_2O$ was found to be 3.96×10^{-5} at 25° C.

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[*] Palmer Miller's Thesis, C.I.T., 1923.

The free energy of stannic oxide was found to be -122,364 calories at 25°. It was calculated from the results of Wöhler and Balz to lie between -121,364 calories and -121,134 calories at 25°.

The free energy of stannous oxide was found to be -60,507 calories at 25° C.

Note: From the results presented in an abstract (Chem. Abstr., 17, 3124) of the data obtained by Tsutomu Maeda (Bull. Inst. Phys. Chem., Res., Japan) on the equilibrium $SnO_2 + 2CO = Sn + 2CO_2$, the reaction $2SnO = SnO_2 + Sn$ was found to take place in the temperature interval from 700 to 950° C. From the calculated pressure of oxygen of 4.47 x 10^{-15} atm. at 927° C, as reported in the abstract, the free energy of SnO_2 at 25° is calculated by me to be -122,350 cal.

Moreover, from the temperature coefficient of the equilibrium, Maeda calculates ΔH for the reaction $SnO_2 = Sn + O_2$ to be 130,260 cal., while thermochemical data give 133,570 cal.which is perhaps as good agreement as could be expected.

It seems certain then that the free energy of SnO_2 at 25° is very close to the value -122,360 cal. and also that at temperatures above about 500° C Sn and SnO_2 are the stable phases and below this temperature Sn and SnO are the stable phases.