THE SYSTEM TIN + OXYGEN

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It is shown experimentally that solid stannous oxide is unstable and decomposes into tin and tin dioxide at 300° C and higher. Probably this instability exists at all temperatures. Gaseous stannous oxide on the other hand, is stable. The vapour pressure of gaseous stannous oxide over the temperature range 1280-1400° K was determined in the presence of mixtures of Sn(I) and SnO₂(s). The results can be expressed as $\log_{10}p$ (mm) = -13,160/T + 10.775. From the results of measurements on the SnO₂ + Sn + CO + CO₂ equilibrium the following data for the heat and free energy of formation for SnO₂(s) are derived: $\Delta H_{298} = -138.7 \pm 0.2$ kcal/mole, $\Delta G^{\circ}_{298} =$ -123.9 ± 0.1 kcal/mole. From this work a new estimate of the heat of dissociation of SnO(g) at 0° K was made, $D_0(SnO) = 134 \pm 2$ kcal/mole. The rates of reactions producing SnO(g) are qualitatively compared.

Conflicting opinions in the literature on the occurrence and stability of compounds in the tin + oxygen system gave the incentive to this investigation. The lower oxide of tin, stannous oxide, has been prepared by several authors. It crystallizes in a form analogous to that of red PbO.¹⁻⁴ Various temperatures have been reported for the decomposition into Sn and SnO₂: 510° C,⁵ 385° C,⁶ 400° C,¹ and 370° C.² On the other hand, Weiser and Milligan ³ report that heating of stannous oxide in vacuum at 550° C gives rise to a product which is neither SnO, Sn, nor SnO₂ and which they call β -SnO. According to Spandau et al.⁷ stannous oxide decomposes into Sn and Sn₃O₄ from about 400° C upwards. The latter compound is stated to be stable to about 1040° C. At higher temperatures stannous oxide is said to exist in the liquid phase. The occurrence of β -SnO and of Sn₃O₄ as stable compounds does not agree with the measurements the equilibria $Sn + SnO_2 + CO_2 + CO_5$, 8, 9 and $Sn + SnO_2 + H_2 + H_2$ on $H_2O^{8, 10, 11}$ in the temperature range of about 500° to 850° C. In all cases the

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equilibria were approached from both sides, so that no stable intermediate oxide in the condensed phase could be detected. Fraenkel ⁵ and Klärding,¹² on determining the equilibrium $\text{SnO}_2 + \text{Sn} + \text{CO}_2 + \text{CO}$ at higher temperatures from the SnO_2 -side, find CO_2 contents higher than those to be expected from an extrapolation of their low-temperature results. This might indicate that another oxide exists at temperatures higher than about 900° C. Brewer's data,¹³ based on a statement of Veselovsky,¹⁴ indicate that SnO(s) is stable only in the temperature range of about 300° to 650° K. Recent calorimetric determinations of the heats of formation of the tin oxides by Humphrey *et al.*,¹⁵ on the other hand, indicate that SnO(s) is unstable at all temperatures.

The lowest temperature found so far for the decomposition of SnO(s) into tin and tin dioxide is 370° C.² Veselovsky ¹⁴ assumes that at this temperature SnO(s)is in equilibrium with Sn(l) and $SnO_2(s)$. On using the known heat content data,¹⁶ one then finds that SnO(s) is stable between about 300° and 650° K. There is no reason, however, to suppose that 370° C is actually the lowest temperature at which SnO(s) decomposes, because the reaction might proceed extremely slowly at still lower temperatures. The measurements of the $SnO_2 + Sn + CO_2 + CO$ equilibrium do not agree with the existence of β -SnO at 550° C.³ These considerations gave rise to an investigation into the stability of SnO(s) at 300° C and at 550° C.

Generally speaking the results obtained by various authors on the $\text{SnO}_2 + \text{Sn} + \text{CO}_2 + \text{CO}$ equilibrium do not agree. Such measurements, when applied in a correct way, may be useful in tracing intermediate stable compounds. In order to evaluate the equilibrium data more accurately and to study the deviations at higher temperatures reported by Fraenkel ⁵ and Klärding,¹² these measurements have been repeated.

Veselovsky ¹⁴ studied the volatility of $Sn(l) + SnO_2$ mixtures in a Knudsen cell by means of the effusion method. This author used a cell made of quartz in which he placed a mixture of tin and tin dioxide. Silicious materials, however, are not inert with respect to the system to be studied. Especially at elevated temperatures silica is heavily attacked by SnO(g). If this compound partly reacts with the cell, the loss in weight of the latter will be too small and too low vapour pressures are calculated. These measurements have therefore been carried out by an entrainment technique in an alundum apparatus. The volatility of tin or tin dioxide as a function of the oxygen pressure has also been studied.

EXPERIMENTAL

INVESTIGATION OF THE STABILITY OF STANNOUS OXIDE AT LOWER TEMPERATURES

PREPARATION OF SnO(s) AND SnO₂.—Stannous oxide was prepared by adding a sodium carbonate solution to a solution of chemically pure tin in hydrochloric acid and heating the resulting mixture at about 110° C until the precipitate turned black. The stannous oxide precipitate was washed until free from chloride and dried at 100° C in an inert atmosphere.

Stannic oxide was prepared by drying and calcining the product obtained by the reaction of concentrated nitric acid with chemically pure tin.

STABILITY.—SnO(s) was sealed in a Pyrex tube *in vacuo* and kept at 300° C for three weeks. Another glass tube containing a finely divided mixture of tin and tin dioxide was treated in the same way. Both experiments were repeated at 550° C for 60 h. The tubes were quenched to room temperature, opened and X-ray spectrograms of the contents were taken, using CuK_{α} radiation in a Debye-Scherrer camera with a circumference of 360 mm.

measurements on the $SnO_2 + Sn + CO_2 + CO$ equilibrium

APPARATUS AND PROCEDURE.—The experiments were performed in a circulation apparatus, which consisted essentially of a silica tube placed in an electric furnace and a pumping system. The details have been described previously.⁹ An alundum boat containing tin dioxide or a mixture of metallic tin and alumina powder was placed in the

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silica tube and the circulation system filled with carbon monoxide or carbon dioxide. The amount of reacting gas was always insufficient to convert the contents of the boat into one phase. One end of the silica tube was a capillary, so that the gaseous mixture left the reaction zone quickly and thermal diffusion backwards was prevented. Facilities for taking gas samples were present. The central zone of the silica tube, about 8 cm in length, could be heated to an even temperature, the variation not exceeding \pm 1° C. Temperatures were measured by Pt—Pt/Rh thermocouples which were calibrated at fixed points. In each experiment the temperature was held constant to within 1.5° C.

ANALYSIS OF GASEOUS MIXTURES.—Gas samples were taken by means of mercuryfilled burettes and analysed in an apparatus described earlier.¹⁷ Carbon dioxide was condensed in liquid air and the uncondensed gases (CO + N₂) pumped into a gas burette. The carbon dioxide was next evaporated into another gas burette and the volume measured. The uncondensed gases were led over copper oxide at 300° C in order to convert CO into CO₂. The latter was condensed again, inert gas pumped away and CO₂ evaporated and measured. The ratio of both volumes in the sequence mentioned under the same conditions of temperature and pressure is equal to p_{CO_2}/p_{CO} .

VAPOUR EVOLVED ON HEATING A MIXTURE OF TIN AND TIN DIOXIDE

A finely divided mixture of tin and tin dioxide was heated at elevated temperatures in vacuum and the vapour evolved quenched on a cooled surface. X-ray spectrograms of the mirror obtained were taken, using CuK_{α} radiation in a Debye-Scherrer camera with a circumference of 360 mm.

STABILITY OF STANNOUS OXIDE AT HIGHER TEMPERATURES

 $CO + CO_2$ mixtures of known composition were slowly passed without recycling over an excess of SnO_2 or an excess of condensed SnO at elevated temperatures. The gas mixtures left the hot reaction zone quickly through a capillary condenser in order to prevent reaction with the volatilized product. A gas-tight alundum tube 30 mm int. diam. and 600 mm in length, was placed in an electric furnace. The capillary condenser, 2 mm int. diam., and the thermocouple sheath, both placed in the larger tube, were also made of gas-tight alundum, a material which is resistant to SnO(g) at the temperatures employed. The apparatus was heated and allowed to cool in a stream of purified nitrogen.

 $CO + CO_2$ mixtures were prepared in a cylinder from pure CO_2 and pure CO supplied in steel bottles. The mixtures obtained were homogenized by shaking the cylinder vigorously, efficient mixing being promoted by the presence of stainless steel strips. Pure nitrogen was prepared by passing an oxygen-free sample over red-hot copper, solid KOH and by drying over P_2O_5 .

VAPOUR PRESSURE MEASUREMENTS.—The general arrangement of the apparatus was similar to that described by Jellinek and Rosner.²⁰ Particulars have been given above. Alundum boats, placed in the central zone of the alundum tube, were filled with SnO(s), which gives an extremely finely divided mixture of Sn(l) and $SnO_2(s)$ at elevated temperatures. During the heating period nitrogen was passed over the boats in a reverse direction to the one applied during the experiment proper, in order to prevent SnO(g) from entering the capillary condenser. Vapour pressure measurements were conducted by passing a known volume of nitrogen over the $Sn + SnO_2$ mixture at a known temperature and suitable flow rate, and collecting the condensed stannous oxide in the cooler regions of the capillary condenser. After each run the furnace was allowed to cool and the condenser was removed and weighed. The gas flow rate used in all experiments was 35 ml/min. Reducing the flow rate to 20 ml/min and increasing the flow rate to 50 ml/min produced no change in the measured vapour pressure of the stannous oxide at the temperature involved.

 $\rm CO + \rm CO_2$ mixtures of known composition were used as carrier gas for the determination of the volatility of tin and/or tin dioxide in these gas mixtures. Because of the solubility of $\rm CO_2$ in almost all kinds of liquid, the volume of the gas mixture used could not be determined by collecting it in a gas bottle. Therefore the effluent gas was passed through a sequence formed by a cold trap placed in liquid air, a tube filled with P₂O₅ and a tower with soda-lime. Soda-lime and P₂O₅ prevent atmospheric CO₂ and H₂O from entering the cold trap. CO₂ was quantitatively condensed from the effluent gas mixture. Subsequently the contents of the trap were distilled in vacuum into a small monel cylinder and weighed. From the analysis of the effluent gas and the increase in weight of the monel vessel, the volume of the carrier gas used during an experiment was calculated.

RESULTS

The X-ray patterns of the samples treated at 300° C showed that stannous oxide partly decomposed into tin and tin dioxide and that the Sn + SnO₂ mixture remained unchanged. The SnO(s) sample treated at 550° C was completely disproportionated. No change could be observed in the Sn + SnO₂ mixture treated under the same conditions.



FIG. 1.—The $SnO_2 + Sn + CO_2 + CO$ equilibrium.

In fig. 1 the data obtained for the $SnO_2 + Sn + CO_2 + CO$ equilibrium from 533° to 834° C are shown. Our data were combined with those of Meyer and Scheffer,⁹ the latter (indicated in fig. 1 by open circles) being as probable as ours. The best straight line through the points was determined by the method of least squares, which gives

$$\log_{10} (p_{\rm CO}/p_{\rm CO_2}) = (404 \pm 19)/T - 0.968 \pm 0.02, (806^{\circ}-1107^{\circ} \text{ K}).$$
 (1)

Thus, for $\frac{1}{2}Sn(l) + CO_2 = \frac{1}{2}SnO_2(s) + CO$:

 $\Delta H_{930} = -1.848 \pm 0.087$ kcal/mole,

 $\Delta S_{930} = -4.43 \pm 0.09$ cal/mole deg.

For $CO + \frac{1}{2}O_2 = CO_2$ the calculated data are $\Delta H_{930} = -67.607$ kcal/mole and $\Delta S_{930}^{\circ} = -20.96$ cal/mole deg.¹⁶, ¹⁸, ¹⁹ By combining these values with the experimental results, we find for $Sn(l) + O_2 = SnO_2(s)$:

$$\Delta H_{930} = -138.91 \pm 0.17$$
 kcal/mole,
 $\Delta S_{030}^{\circ} = -50.78 \pm 0.18$ cal/mole deg.

Extrapolation to room temperature ¹⁶ results in the heat and free energy of formation of tin dioxide :

$$\Delta H_{298} = -138.7 \pm 0.2$$
 kcal/mole,
 $\Delta G_{298}^{\circ} = -123.9 \pm 0.1$ kcal/mole.

On extending the measurements to higher temperatures deviations were observed. When starting with carbon monoxide and an excess of tin dioxide, it was found that the CO_2 content of the stationary gas mixtures was higher than predicted by extrapolation of the low-temperature measurements. These deviations were still greater at higher temperatures. Gas mixtures with too high a CO content were obtained if the circulation system was filled with carbon dioxide and an excess of metallic tin. A volatile product was formed, as could be seen by the occurrence of a deposit near the capillary end of the silica tube; furthermore, the silicious material was heavily attacked. X-ray patterns of the deposit showed it to be a mixture of tin and tin dioxide.

The X-ray pattern of the mirror, obtained by quenching the vapour evolved by a mixture of Sn and SnO_2 at elevated temperatures, revealed that the deposit was substantially identical with SnO(s), the balance being tin and tin dioxide.

The results obtained by passing various $CO + CO_2$ mixtures over SnO_2 and SnO in a "once-through" operation are shown in table 1.

The vapour pressure of stannous oxide was calculated from the expression $p_{\text{SnO}} = n_1 P/(n_1 + n_2)$, where P = pressure in system, $n_1 =$ moles of SnO collected in n_2 moles of nitrogen. The vapour pressure at various temperatures as found by experiment

TABLE 1.--REACTIONS OCCURRING IN THE "ONCE-THROUGH" OPERATION

no.	composition of the gas introduced		contents of	temp. °C	gas rate	composition of the effluent gas	
	vol % CO	vol % CO2			1111/11111	vol % CO	vol % CO2
1	29.8	70-2	SnO(s)	1050	20	18.6	81.4
2	29.6	70·4	SnO(s)	1050	40	18.6	81.4
3	29.8	70·2	$SnO_2(s)$	1050	20	18.5	81.5
4	10.0	90.0	SnO(s)	1055	20	18·2	81.8
5	10.0	90.0	SnO(s)	1055	30	18-4	81.6

is plotted in the form $\log_{10}p$ (mm) against $1/T^{\circ}$ K in fig. 2. Weight numbers proportional to the amount of collected product were attached to the observations of $\log_{10}p$ in order to account for the fact that the results are more accurate the larger the amount of product collected. Using the method of least squares we obtain

$$\log_{10} p(\text{mm}) = -(13,161 \pm 156)/T + 10.775 \pm 0.114,$$
 (1280°-1400° K). (2)





Thus, for $\frac{1}{2}$ SnO₂(s) + $\frac{1}{2}$ Sn(l) = SnO(g):

 $\Delta H_{1340} = 60.220 \pm 0.723$ kcal/mole,

- $\Delta S^{\circ}_{1340} =$ 36.12 \pm 0.50 cal/mole deg.,
- $\Delta G_{1340}^{\circ} = 11.820 \pm 0.095$ kcal/mole.

Extrapolation to room temperature ¹⁶ results in the following data:

 $\Delta H_{298} = 65.6 \pm 0.8$ kcal/mole, $\Delta S^{\circ}_{298} = 43.8 \pm 0.6$ cal/mole deg., $\Delta G^{\circ}_{298} = 52.5 \pm 0.2$ kcal/mole. Heat-content data ¹⁶ enable us to give the vapour pressures over a longer range of temperatures :

$$\log_{10} p \text{ (mm)} = -14,550/T - 2.043 \log_{10} T - 0.096 \times 10^{-3}T + 0.19 \times 10^{5}T^{-2} + 18.319,$$
(505°-1500° K).

The experiments in which $CO + CO_2$ mixtures were slowly passed without recycling over SnO_2 or SnO were combined with vapour pressure measurements. The results additional to table 1 are given in table 2. The data in the last row of table 2 are calculated by means of eqn. (2).

	TABLE 2.—	DATA ADDITIC	ONAL TO TABL	ΕI	
no.	1	2	3	4	5
P _{SnO} (mm Hg) expt. calc.	6·7 6·7	6·5 6·7	6·7 6·7	7·1 7·3	7·3 7·3

Table 3 shows the data obtained when $CO + CO_2$ mixtures, not capable of forming a second condensed phase, are passed over SnO_2 or Sn. For the equilibria

 $\frac{1}{2}Sn(l) + CO_2 = \frac{1}{2}SnO_2(s) + CO_1$, and $\frac{1}{2}Sn(l) + \frac{1}{2}SnO_2(s) = SnO(g)$

eqn. (1) and (2) were found respectively. For the equilibria

$$SnO_2(s) + CO = SnO(g) + CO_2, \qquad (a)$$

$$Sn(l) + CO_2 = SnO(g) + CO, \qquad (b)$$

it therefore follows respectively that

$$\log_{10}K_a \,(\mathrm{mm}) = -13,565/T + 11.743,\tag{3}$$

$$\log_{10}K_b \text{ (mm)} = -12,757/T + 9.807.$$
 (4)

The data in the last column of table 3 are calculated from the composition of the effluent gas mixture and eqn. (3) or (4).

TABLE 3.—VOLATILITY OF $SnO_2(s)$ or Sn(l) in CO + CO₂ mixtures at 1033° C

no.	composition of the gas introduced		contents of	gas rate	composition of the effluent gas		pSnO (mm Hg)	
	vol % CO	vol % CO2	the boats	ml/min	vol % CO	vol % CO ₂	expt.	calc.
1	16.4	83.6	SnO ₂	40	16.0	84 •0	3.7	4.3
2	16.4	83.6	SnO_2	15	16.0	84.0	3.7	4.3
3	16.4	83.6	SnO_2	10	16.0	84·0	3.5	4.3
4	5.2	94.8	SnO_2	38	5.2	94·8	0.2	1.2
5	26.8	73.2	Sn*	30	26.8	73·2	0.8	3.0
6	26.8	73.2	Sn	30	26.8	73.2	0.7	3.0
7	26 ·8	73-2	Sn	15	26 ·8	73·2	0.7	3.0

* In an attempt to obtain a high surface area the boats were filled with a finely divided mixture of tin and alumina powder. After the experiment tin had accumulated in some places.

DISCUSSION

The results show that, even at 300° C, SnO(s) is unstable and decomposes into Sn(l) and $SnO_2(s)$. That an appreciable amount of SnO(s) is still present only means that under these conditions the reaction is extremely slow, so that even three weeks are insufficient to terminate the disproportionation. No conversion of stannous oxide into β -SnO could be observed. These findings are in accordance with recent calorimetric determinations,¹⁵ showing that SnO(s) is unstable at the temperatures applied.

The values obtained for the heat and free energy of formation of tin dioxide are in excellent agreement with the calorimetric data given by Rossini *et al.*: 18

and

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 $\Delta H_{298} = -138.8$ kcal/mole, $\Delta G_{298}^{\circ} = -124.2$ kcal/mole. This agreement, together with the fact that the present authors' data were obtained by approaching the equilibrium from both sides, furnishes clear proof that no stable lower oxide exists in condensed phase between the temperature limits investigated (533-834° C).

At higher temperatures the results obtained with an excess of tin dioxide are in accordance with Klärding's ¹² observations in giving too high CO_2/CO ratios. The results obtained by quenching the vapour evolved when a mixture of Sn(l)and $SnO_2(s)$ is heated at elevated temperatures indicate that the gaseous product formed in the circulation apparatus is gaseous stannous oxide. This product leaves the reaction system continuously by being deposited at lower temperatures. Consequently no real equilibria will be established. Gas mixtures with changing composition enter the reaction tube in the circulation apparatus. These gas mixtures continue to react with the contents of the boat until practically no more SnO(g) is formed. The reactions producing SnO(g) proceed to a greater extent at increasing temperatures and this gives rise to increasing deviations from the gas compositions predicted by extrapolation of the low-temperature measurements,

The circulation system is evidently not suited for finding out whether or not SnO occurs as a stable condensed phase at higher temperatures. This is the reason why the "once-through" operations were carried out (table 1). Extrapolation of the low-temperature data of the $\text{SnO}_2 + \text{Sn} + \text{CO}_2 + \text{CO}$ equilibrium gives a gas composition of 18 vol % CO and 82 vol % CO₂ at the temperatures mentioned in table 1. It is clear that SnO(s) behaved like a mixture of tin and tin dioxide in these experiments. Therefore solid or liquid stannous oxide does not occur and liquid tin and solid tin dioxide are the only stable condensed phases.

Standard entropies based on calorimetric and spectrographic data for Sn, SnO₂ and SnO(g) have been collected by Kelley.¹⁹ From these data one derives for $\frac{1}{2}$ Sn $+ \frac{1}{2}$ SnO₂ = SnO(g), $\Delta S_{298}^{\circ} = 43.1 \pm 0.3$ cal/mole deg., a figure in good agreement with the experimental value. Evidently the solubility of stannic oxide in liquid tin is negligible even at higher temperatures and stannous oxide is present in the gas phase as an unassociated molecule. Our values are appreciably higher than those found by the effusion method.¹⁴ The possibility that the presence of some condensed SnO might account for this difference is ruled out completely. This is shown by the perfect agreement of the experimental vapour pressures with the data calculated from the entrainment measurements in nitrogen (table 2). The experimental values were obtained in the experiments given in table 1, where the composition of the effluent gas furnished clear proof that only liquid tin and solid tin dioxide occurred. The difference between Veselovsky's results and those of the present paper is probably caused by reaction of SnO(g) with the walls of the Knudsen cell.

The data obtained so far enable us to calculate the heat $D_0(SnO)$ of dissociation of SnO(g) at $0^\circ K$:

$\frac{1}{2}$ Sn(s) + $\frac{1}{2}$ O ₂ (g) = $\frac{1}{2}$ SnO ₂ (s),	$\Delta H_{298} = -69.3 \text{ kcal/mole,}$			
$\frac{1}{2}\operatorname{Sn}(s) + \frac{1}{2}\operatorname{SnO}_2(s) = \operatorname{SnO}(g),$	$\Delta H_{298} = + 65.6 \text{ kcal/mole,}$			
$\operatorname{Sn}(g) = \operatorname{Sn}(s),$	$\Delta H_{298} = -72 \text{ kcal/mole},^{21}$			
$\mathcal{O}(g)=\tfrac{1}{2}\mathcal{O}_2(g),$	$\Delta H_{298} = -59.3 \text{ kcal/mole.}^{22}$			
$\operatorname{Sn}(g) + \operatorname{O}(g) = \operatorname{SnO}(g),$	$\Delta H_{298} = -135 \text{ kcal/mole.}$			
$D_0(\text{SnO}) = 134 \pm 2 \text{ kcal/mole.}$				

Thus

In expt. 1-4 of table 3 the only reaction which can take place is $SnO_2(s) + CO \rightarrow SnO(g) + CO_2$. The experimental vapour pressures are smaller than calculated; this signifies that the reaction mentioned is somewhat slow. Runs 5-7 show that $Sn(l) + CO_2 \rightarrow SnO(g) + CO$ is extremely slow.

On comparing the reactions which produce gaseous stannous oxide, it may be concluded that their rates, on a rough qualitative basis, are as follows:

$$\frac{1}{2}\operatorname{SnO}_2(s) + \frac{1}{2}\operatorname{SnO}(l) \to \operatorname{SnO}(g) \qquad \text{fast,}$$

$$\operatorname{SnO}_2(s) + \operatorname{CO} \to \operatorname{SnO}(g) + \operatorname{CO}_2 \qquad \text{slow,}$$

$$\operatorname{Sn}(l) + \operatorname{CO}_2 \to \operatorname{SnO}(g) + \operatorname{CO} \qquad \text{extremely slow.}$$

The small surface area of liquid tin will be an important reason why the latter reaction is very slow. A good illustration of the fact that both $\frac{1}{2}$ SnO₂(s) + CO \rightarrow $\frac{1}{2}$ Sn(l) + CO₂, and $\frac{1}{2}$ Sn(l) + $\frac{1}{2}$ SnO₂(s) \rightarrow SnO(g), are fast is given by run no. 3 in table 1 and 2. Here the maximum vapour pressure is attained, although metallic tin must be formed first.

Spandau and Kohlmeyer ⁷ give a T - x diagram at one atmosphere for the binary system Sn + SnO₂, based on the occurrence of Sn₃O₄ up to about 1040° C and of SnO(*l*) at higher temperatures. In the authors' opinion the latter premises are open to doubt. The present work clearly shows that, at least in the temperature range of 300-1127° C, liquid tin, solid tin dioxide and gaseous stannous oxide are the only stable phases.

Finally we may comment on the standard entropy of tin dioxide as calculated by Kelley ¹⁹ (12.5). This value was obtained from molar heats measured at temperatures not lower than 71° K and is therefore found to be uncertain. From the results on the $SnO_2 + Sn + CO_2 + CO$ equilibrium we calculate 11.6 and from those on the vapour pressures of SnO(g), 11.1. Therefore we believe that Kelley's value is about one unit of entropy too high.

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