Title
THE HEATS OF FORMATION OF SODIUM-TIN ALLOYS

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The Heats of Formation of Sodium-Tin Alloys

Raleigh L. McKisson and LeRoy A. Bromley

May 1, 1950

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The Heats of Formation of Sodium-Tin Alloys.

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May 1, 1950

Abstract

The new high-temperature calorimeter was used to measure the heats of formation of liquid sodium-tin alloys at 880°K. The $\Delta H_{f_{880}}$ of the alloys of composition NaSn, $Na_{1.105}Sn$, and Na_2Sn are found to be -4.80 ± 0.14, -4.86 ± 0.04, and -4.03 ± 0.08 kcal./g. atom alloy respectively. In addition to these results, a curve of $\Delta H_{f_{880}}$ vs. mole fraction sodium is presented in Figure 1. These values have been qualitatively compared with those of other workers and tend to agree with the values given by Kubaschewski and Seith[9], and to disagree with those of Biltz and Meyer[5].

Introduction

The system sodium-tin was chosen for investigation in the newly developed high-temperature calorimeter described by McKisson and Bromley[11]. The selection of this system was made principally because of the temperature involved, since this temperature, 600°C., is sufficiently high to adequately test the operation of the calorimeter. However, the data reported in the literature for the various alloys of sodium and tin differs markedly, and it was hoped that this investigation would help to fix the values of the heats of formation in this system.

Biltz and Holverscheit[4] in 1924 measured the heats of formation of sodium-tin alloys by a differential solution method using a ferric chloride-hydrochloric acid solvent and reported the following values in kilocalories per mole for ΔH_f at 298°K.: Na_4Sn, -21.; Na_2Sn, -12.; Na_4Sn_3, -36.; NaSn, -11.; and $NaSn_2$, -15. In 1928, Biltz and Meyer[5] reported a recalculated set of values. These values were also listed by Biltz[3] in 1937, and by Bichowsky and Rossini[2] in 1936; these ΔH_f are, in kilocalories per mole at 298°K: Na_4Sn, -34.; Na_2Sn, -21.; Na_4Sn_3, -56.; NaSn, -16.; and $NaSn_2$, -20. Kubaschewski and Seith[9] in 1938, Kubaschewski and Wittig[10] in 1941, and Kubaschewski[8] in 1942 reported a series of values for the heats of formation of sodium-tin alloys from direct measurements using a copper-block calorimeter. These values, in kilocalories per mole at 298°K., are Na_4Sn, -14.4; Na_2Sn, -14.4; and NaSn, -12.0. In 1948, Barber et al.[1] report the results of a direct measurement of the compound NaSn in an induction-heated high-temperature calorimeter. The value given for the heat of formation of the liquid alloy at 873°K. is -9.63 ± 0.40 kilocalories per mole; for the solid alloy at 298°K., -10.6 ± 0.6 kilocalories per mole.

Operating Procedure

Preparation of Samples:

The preparation of the samples consisted of purifying the metals and forming them into suitable shapes for use. Mallinkrodt analytical reagent sodium was used and samples were prepared in a dry-box[6] using a molten sodium scavenger to absorb any water vapor or oxygen present in the argon atmosphere. The criterion for a satisfactory atmosphere was that no perceptible tarnishing of the surface of a molten drop of sodium be noticed in two minutes. When such an atmosphere was obtained, the sodium metal was trimmed of oxide and bright pieces of sodium metal were melted in a clean molybdenum crucible. The sodium was cast to form cylindrical samples in an iron mold, and after weighing inside the dry-box the samples were wrapped in 3" x 3" x 0.002" pieces of tin foil. The tin foil covering was satisfactory, since a weight gain of less than 0.1 mg./hr. was found in three samples which were exposed to air for two days. Spectrographic analysis of the prepared sodium indicated a purity of 99.9+%.

The bar stock tin used was obtained from the American Smelting and Refining Co.; the foil was obtained from the Reynolds Metals Co. The bar stock was merely cut with a cleaned bolt-cutter and the pieces used directly. The foil was cut to size, weighed, and used as wrappers for the samples. The tin samples used in the heat capacity additions were made by casting molten tin from the bar stock in pyrex test tubes and machining off the surface to give a clean sample. Spectrographic analysis of the bar stock tin indicated a purity of 99.9+%, the principle impurity being a trace of lead. Spectrographic analysis of the foil indicated a purity of 99.9+%, the principle impurity being a trace of iron.

Temperature Adjustment:

The second phase of the operation consisted of adjusting the temperature of the calorimeter. The prepared samples were put into the sample chamber in the afternoon prior to the day on which the run was to be made. The gas flows were turned on (at a low rate) and the e.m.f. delivered to the main heating unit by the Variac and set as close as possible to give the desired equilibrium temperature, and all controls were turned off.

On the morning of a run, the inert gas flows were turned up to deliver about 0.05 ft.^{3}/min. of argon, and about 0.02 ft.^{3}/min. of helium, the control system was turned on and the temperature of the bath was adjusted as required (usually only a few degrees). When the temperature had reached the desired level, and had remained there for a half-hour, the system was considered in adjustment.

Measurement:

The measurement proper consisted of recording the temperatures of the reaction crucible melt, the two tin bath thermocouples, and the sample chamber. The sample was transferred to the dispenser tube (with the helium flow turned up to about 0.10 ft.^{3}/min.) and a final check on the reaction crucible temperature was made. The timer was started when the sample was ejected into the melt and temperatures (e.m.f.'s) were read on the Leeds and Northrup Portable Precision Potentiometer as rapidly as possible. These e.m.f.'s were recorded, together with the corresponding times. This record was then compared with the trace of the temperature vs. time from the Leeds and Northrup Micromax and if there was a gap in the Potentiometer data, the Micromax tracing was used to provide supplementary data.

Calculations:

The calculations were made as outlined in detail by McKisson and Bromley[11]. In brief, the method consists of using the temperature-time curve from the addition of an inert material to find the heat capacity and the cooling-rate parameters of the system. Once these quantities are known, one can calculate the "q-function" which gives the rate of heat loss (or gain) from the crucible system in cal./min. as a function of the temperature difference between the crucible and the cavity. By plotting this function vs. the time, one graphically integrates for the heat liberation of an addition.

Summary of Experimental Results

Six runs were completed, yielding fifty-eight individual measurements. One entire run, consisting of eleven additions, was discarded because the stirring was inadequate. In addition, seven other additions were discarded; five because of stirring rate, and two because of obvious experimental error. Thus forty additions were usable, yielding forty individual measurements. Of these, twelve were for the composition NaSn, six for the composition $Na_{1.105}Sn$, and four for the composition Na_2Sn. These three averages are plotted in Figure 1 together with the other eighteen results. The phase diagram shown below the curve of experimental results is taken from Hansen[7]. Table 1 shows the serial number, the reaction for which the heats were determined, the temperature of the reaction, the heat (calories) measured in the q vs. Θ plot, the ΔH_{Rx} in calories for the isothermal reaction at the quoted temperature, and the ΔH_f of the product of the reaction in kcal/g. atom alloy were applicable.

Table 2 consists of a summary of the various combinations of the direct determinations of Table 1. Table 2 shows a serial number, the combination of

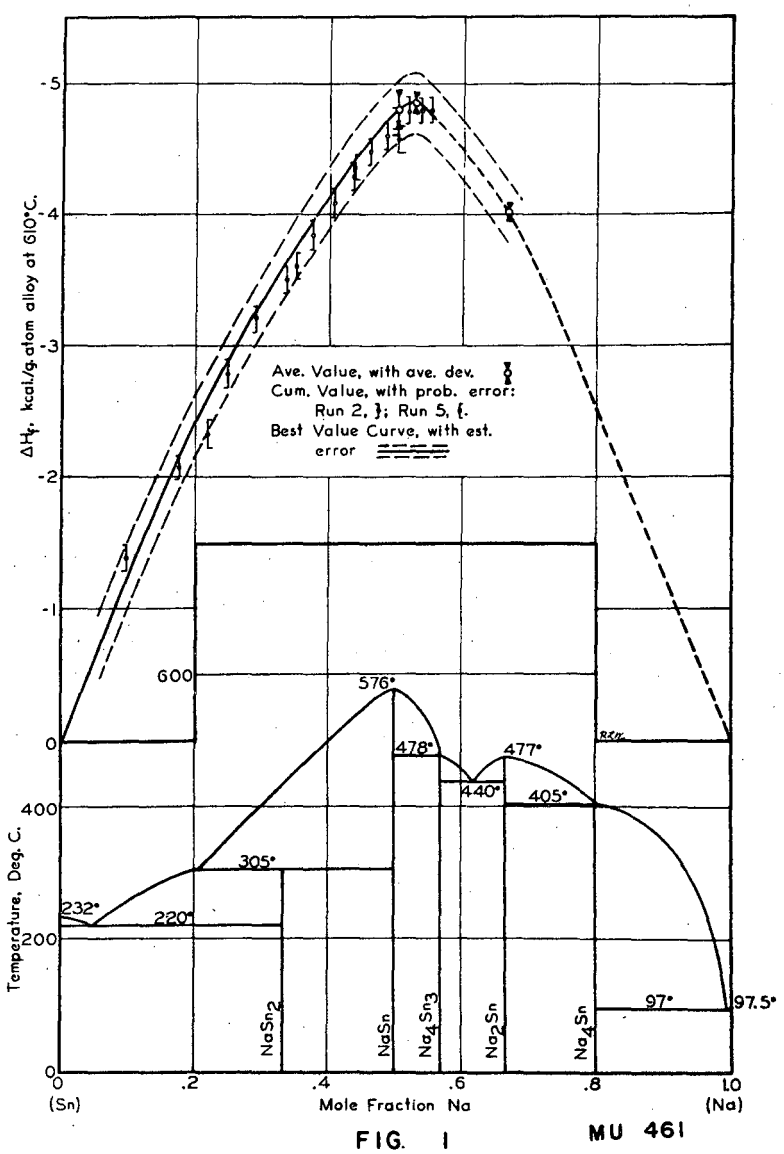

FIG. 1

Figure 1.

ΔH_f vs. N_{Na} Curve for Liquid Sodium-Tin Alloys,

and Phase Diagram for the Sodium-Tin System.

Table 1

Summary of Direct Measurements

Serial	Reaction	Temp. °K.	ΔH q - θ plot cal.	ΔH_{Rx} cal.	ΔH_f of Products kcal./g. atom
1	0.1348 Na + 0.0185 Sn + 1.2553 Sn $\longrightarrow$ 1.274 $Na_{0.1058}$ Sn	864	-1242±10%	-1951±7%	-1.385±7%
2	0.1348 Na + 0.0185 Sn + 1.274 $Na_{0.106}$ Sn $\longrightarrow$ 1.292 $Na_{0.209}$ Sn	866	-689±10%	-1408±5%	
3	0.1348 Na + 0.0185 Sn + 1.292 $Na_{0.209}$ Sn $\longrightarrow$ 1.311 $Na_{0.309}$ Sn	866	-698±10%	-1417±5%	
4	0.1348 Na + 0.0185 Sn + 1.311 $Na_{0.309}$ Sn $\longrightarrow$ 1.329 $Na_{0.406}$ Sn	866	-504±10%	-1223±4.2%	
5	0.1348 Na + 0.0185 Sn + 1.329 $Na_{0.406}$ Sn $\longrightarrow$ 1.348 $Na_{0.500}$ Sn	866	-369±10%	-1088±4.1%	
6	0.1348 Na + 0.0185 Sn + 1.348 $Na_{0.500}$ Sn $\longrightarrow$ 1.366 $Na_{0.592}$ Sn	866	-561±10%	-1280±4.5%	
7	0.1348 Na + 0.0185 Sn + 1.366 $Na_{0.592}$ Sn $\longrightarrow$ 1.385 $Na_{0.681}$ Sn	866	-431±10%	-1150±4%	
8	0.1348 Na + 0.0185 Sn + 1.385 $Na_{0.681}$ Sn $\longrightarrow$ 1.404 $Na_{0.768}$ Sn	866	-405±10%	-1124±4%	
9	0.1348 Na + 0.0185 Sn + 1.404 $Na_{0.768}$ Sn $\longrightarrow$ 1.422 $Na_{0.853}$ Sn	866	-424±10%	-1143±4%	
10	0.1348 Na + 0.0185 Sn + 1.422 $Na_{0.853}$ Sn $\longrightarrow$ 1.441 $Na_{0.935}$ Sn	866	-312±10%	-1031±3%	
11	0.1113 Na + 0.0185 Sn + 1.441 $Na_{0.935}$ Sn $\longrightarrow$ 1.459 NaSn	866	-308±10%	-920±3.5%	
12	0.1348 Na + 0.0185 Sn + 1.459 NaSn $\longrightarrow$ 1.478 $Na_{1.078}$ Sn	867	-218±10%	-937±2.5%	
13	0.1348 Na + 0.0185 Sn + 1.478 $Na_{1.078}$ Sn $\longrightarrow$ 1.496 $Na_{1.156}$ Sn	866	-53±10%	-772±2%	
14	0.1348 Na + 0.0185 Sn + 1.496 $Na_{1.156}$ Sn $\longrightarrow$ 1.515 $Na_{1.230}$ Sn	866	-32±10%	-751±2%	

Table 1 (cont.)

Serial	Reaction	Temp. °K.	ΔH q - $\int C_p dT$ plot cal.	ΔH_{Rx} cal.	ΔH_f of Products kcal./g. atom
15	0.0739 Na + 0.0739 Sn $\rightarrow$ 0.0739 NaSn	882	+95±9%	-679±2%	-4.60±2.5%
16	0.0739 Na + 0.0739 Sn $\rightarrow$ 0.0739 NaSn	881.5	+43±9%	-730±2%	-4.94±2%
17	0.0739 Na + 0.0739 Sn $\rightarrow$ 0.0739 NaSn	881.5	+65±9%	-708±2%	-4.79±2%
18	0.0739 Na + 0.0739 Sn $\rightarrow$ 0.0739 NaSn	881	+27±9%	-746±2%	-5.05±2%
19	0.1391 Na + 0.0185 Sn + 0.9263 NaSn $\rightarrow$ 0.9448 $Na_{1.1274}$ Sn	881.5	-223±9%	-993±2.5%	
20	0.0739 Na + 0.0739 Sn + 0.9448 $Na_{1.1274}$ Sn $\rightarrow$ 1.0187 $Na_{1.1182}$ Sn	881.5	+224±9%	-551±4%	
21	0.0739 Na + 0.0739 Sn + 1.0187 $Na_{1.1182}$ Sn $\rightarrow$ 1.0926 $Na_{1.1102}$ Sn	881.3	+86±9%	-694±2%	
22	0.0739 Na + 0.0739 Sn + 1.0926 $Na_{1.1102}$ Sn $\rightarrow$ 1.1665 $Na_{1.1033}$ Sn	881.5	+88±9%	-688±2%	
23	0.0870 Na + 0.0435 Sn $\rightarrow$ 0.0435 Na_2Sn	887	+149±7%	-516±3%	-3.95±3%
24	0.0870 Na + 0.0435 Sn $\rightarrow$ 0.0435 Na_2Sn	885	+117±7%	-545±2.1%	-4.18±2.5%
25	0.0870 Na + 0.0435 Sn $\rightarrow$ 0.0435 Na_2Sn	885	+139±7%	-524+2.5%	-4.02±2.7%
26	0.0870 Na + 0.0435 Sn $\rightarrow$ 0.0435 Na_2Sn	884	+144±7%	-518±2.5%	-3.97±2.7%
27	0.1391 Na + 0.0185 Sn + 0.4827 Sn $\rightarrow$ 0.5013 $Na_{0.277}$ Sn	885	-726±7%	-1494±3.5%	-2.334±4%
28	0.1391 Na + 0.0185 Sn + 0.5013 $Na_{0.277}$ Sn $\rightarrow$ 0.5198 $Na_{0.535}$ Sn	884	-638±7%	-1395±3.2%	
29	0.1391 Na + 0.0185 Sn + 0.5198 $Na_{0.535}$ Sn $\rightarrow$ 0.5383 $Na_{0.775}$ Sn	885.5	-470±7%	-1232±2.7%	

Table 1 (cont.)

Serial	Reaction	Temp. °K.	ΔH q - Θ plot cal.	ΔH_{Rx} cal.	ΔH_f of Product kcal./g. atom
30	0.1391 Na + 0.0185 Sn + 0.5383 $Na_{0.775}$ Sn $\longrightarrow$ 0.5569 $Na_{0.999}$ Sn	885.5	-206±7%	-966±2.0%	
31	0.0739 Na + 0.0739 Sn $\longrightarrow$ 0.0739 NaSn	887.5	+59±7%	-723±1.6%	-4.89±2.1%
32	0.0739 Na + 0.0739 Sn $\longrightarrow$ 0.0739 NaSn	888	+62±7%	-719±1.6%	-4.87±2.1%
33	0.0739 Na + 0.0739 Sn $\longrightarrow$ 0.0739 NaSn	888	+59±7%	-722±1.6%	-4.89±2.1%
34	0.0774 Na + 0.0774 Sn $\longrightarrow$ 0.0774 NaSn	878.5	+81±10%	-728±2%	-4.71±2.4%
35	0.0774 Na + 0.0774 Sn $\longrightarrow$ 0.0774 NaSn	878	+50±10%	-759±1.7%	-4.91±2.2%
36	0.0774 Na + 0.0774 Sn $\longrightarrow$ 0.0774 NaSn	877	+55±10%	-753±1.7%	-4.87±2.2%
37	0.0774 Na + 0.0774 Sn $\longrightarrow$ 0.0774 NaSn	878	+105±10%	-703±2.2%	-4.54±2.7%
38	0.0774 Na + 0.0774 Sn $\longrightarrow$ 0.0774 NaSn	878.5	+117±10%	-693±2.4%	-4.48±2.9%
39	0.1304 Na + 0.0185 Sn + 1.040 NaSn $\longrightarrow$ 1.058 $Na_{1.106}$ Sn	879	-223±10%	-939±2.5%	
40	0.0774 Na + 0.0774 Sn + 1.058 $Na_{1.106}$ $\longrightarrow$ 1.136 $Na_{1.098}$ Sn	878	+109±10%	-705±2.3%	

Table 2

Summary of Combinations of Direct measurements

Serial	Combination	Reaction	Temp. °K.	ΔH_{Rx} cal.	ΔH_f of Product kcal./g. atom
41	1 and 2	$0.2696\ Na + 1.292\ Sn \rightarrow 1.292\ Na_{0.209}\ Sn$	865	-3359±143	-2.150±4.5%
42	1 thru 3	$0.4044\ Na + 1.311\ Sn \rightarrow 1.311\ Na_{0.309}\ Sn$	865	-4776±160	-2.783±4%
43	1 thru 4	$0.5392\ Na + 1.329\ Sn \rightarrow 1.329\ Na_{0.406}\ Sn$	866	-5999±168	-3.210±3%
44	1 thru 5	$0.6740\ Na + 1.348\ Sn \rightarrow 1.348\ Na_{0.500}\ Sn$	866	-7087±173	-3.505±3%
45	1 thru 6	$0.8088\ Na + 1.366\ Sn \rightarrow 1.366\ Na_{0.592}\ Sn$	866	-8367±182	-3.847±3%
46	1 thru 7	$0.9436\ Na + 1.385\ Sn \rightarrow 1.385\ Na_{0.681}\ Sn$	866	-9517±187	-4.088±2.5%
47	1 thru 8	$1.0784\ Na + 1.404\ Sn \rightarrow 1.404\ Na_{0.768}\ Sn$	866	-10641±192	-4.287±2%
48	1 thru 9	$1.2132\ Na + 1.422\ Sn \rightarrow 1.422\ Na_{0.853}\ Sn$	866	-11784±198	-4.472±2%
49	1 thru 10	$1.3480\ Na + 1.441\ Sn \rightarrow 1.441\ Na_{0.935}\ Sn$	866	-12815±201	-4.596±2%
50	1 thru 11	$1.4593\ Na + 1.459\ Sn \rightarrow 1.459\ NaSn$	866	-13735±203	-4.707±2%
51	1 thru 12	$1.5941\ Na + 1.478\ Sn \rightarrow 1.478\ Na_{1.078}\ Sn$	867	-14672±205	-4.778±2%
52	1 thru 13	$1.7289\ Na + 1.496\ Sn \rightarrow 1.496\ Na_{1.156}\ Sn$	866	-15444±205	-4.789±2%
53	1 thru 14	$1.864\ Na + 1.515\ Sn \rightarrow 1.515\ Na_{1.230}\ Sn$	866	-16195±206	-4.794±2%

Table 2 (cont.)

Serial	Combination	Reaction	Temp. °K.	ΔH_{Rx} cal.	ΔH_f of Product kcal./g. atom
54	27 and 28	0.2782 Na + 0.5198 Sn $\longrightarrow$ 0.5198 $Na_{0.535}$ Sn	884.5	-2889±68	-3.621±2.6%
55	27 thru 29	0.4173 Na + 0.5383 Sn $\longrightarrow$ 0.5383 $Na_{0.775}$ Sn	885	-4121±76	-4.313±2.1%
56	27 thru 30	0.5564 Na + 0.5569 Sn $\longrightarrow$ 0.5569 $Na_{0.999}$ Sn	885	-5087±78	-4.57±2%
57	63 and 19	1.0654 Na + 0.9448 Sn $\longrightarrow$ 0.9448 $Na_{1.1274}$ Sn	881.6	-9876±259	-4.913±3%
58	63, 19, and 20	1.1393 Na + 1.0187 Sn $\longrightarrow$ 1.0187 $Na_{1.1182}$ Sn	881.6	-10427±260	-4.832±3%
59	63, 19 thru 21	1.2132 Na + 1.0926 Sn $\longrightarrow$ 1.0926 $Na_{1.1102}$ Sn	881.6	-11121±260	-4.823±3%
60	63, 19 thru 22	1.2871 Na + 1.1665 Sn $\longrightarrow$ 1.1665 $Na_{1.1033}$ Sn	881.6	-11809±260	-4.813±3%
61	63 and 39	1.1704 Na + 1.0585 Sn $\longrightarrow$ 1.058 $Na_{1.106}$ Sn	881.	-10913±291	-4.898±3%
62	63, 39, and 40	1.2478 Na + 1.136 Sn $\longrightarrow$ 1.136 $Na_{1.098}$ Sn	881.	-11618±291	-4.875±3%

items in Tables 1 and 3 which are used, the resulting reaction, the temperature of the resulting reaction, the ΔH in calories at the high temperature of the reaction shown, and the ΔH_f in kcal./g. atom of the product of the reaction where applicable.

Table 3 consists of a summary of the averaged values for the ΔH_f of those alloys for which multiple determinations were made. Table 3 shows a serial number, the combination of serial numbers from Table 1 and Table 2 from which the average was computed, the average temperature, and the average ΔH_f of the product in kcal./g. atom alloy.

Discussion

An examination of Table 1 will show that the heats found in the q - θ plots for the same reaction vary widely. For the twelve direct determinations of the composition NaSn, these values average +898 cal./mol. with an average deviation of 267 cal./mol. or 30%. This greatly exceeds the maximum probable error ($\pm$10%) estimated. However, for the four direct determinations of the composition Na_2Sn, the q - θ plot values average +3148 cal./mol. with an average deviation of 230 cal./mol. or 7.3%. This is of the order of the estimated probable error.

The cause of the very large probable error above cannot be positively determined, but one factor which would have a marked effect on these quantities is the stirring rate, or more particularly, the extent to which uniformity of composition and temperature was attained. The development of the equations used is based on a uniform temperature in the reaction crucible, and the entire Run 1 was discarded because its results deviated markedly from those of the later runs. Since the stirring rate in Run 1 was about 250 RPM, and the rate

Table 3

Summary of Averaged Values

Serial	Combination	Reaction	Temp.	ΔH_f of Product kcal./g. atom
63	Ave. of 15, 16, 17, 18, 31, 32, 33, 34, 35, 36, 37, and 38.	$Na + Sn \longrightarrow NaSn$	881.6	-4.795±0.143 av. dev.
64	Ave. of 23 , 24, 25, and 26.	$2Na + Sn \longrightarrow Na_2Sn$	885.3	-4.03±0.075 av. dev.
65	Ave. of 57, 58, 59, 60, 61, and 62.	$1.105\ Na + Sn \longrightarrow Na_{1.105}\ Sn$	881.	-4.859±0.036 av. dev.

was increased to >400 RPM in the later runs (which gave better agreement), the slower stirring was assumed to be the cause of the poor results in Run 1. It is possible that the stirring rate, although high, in the NaSn additions was not always effective in maintaining a uniform temperature and composition in the crucible. Although the 30% deviation is large, its effect on the ultimate result is minimized by the fact that the total heat effect is -9590 calories which means that the inaccurate measurement involves less than 10% of the total heat effect. This is because the q - θ plot measures the heat for the reaction: cold sodium plus cold tin yield hot alloy; and more heat is required to heat the reactants up to the high temperature (10490 cal.), than is liberated in the reaction (9590 cal.), therefore there is a net heat absorption by the crucible. The heat capacities of tin and sodium are known to about 1% so that the large error in the q - θ plot heat is absorbed in the final result.

The only data on the sodium-tin system taken at high temperature was that of Barber et al.[1] The other values by Biltz and Holverscheit[4], Biltz and Meyer[5], Biltz[3], Bichowsky and Rossini[2], Kubaschewski and Seith[9], Kubaschewski and Wittig[10], and Kubaschewski[8], are reported at room temperature (298°K.). Table 4 lists all the available values for the heats of formation of sodium-tin alloys, the temperature of the measurement, and the reference.

The results at high temperature check very well with those of Barber et al.[1]. A quantitative comparison between the results of this research and the other values shown in Table 4 is possible only if the heats of fusion and heat capacities are known for all the alloys and the elements. Since this data data is not available for the alloys, only a qualitative comparison is possible. Such a comparison can be made by solving for the various combinations of heat capacities and heats of fusion which are required to convert the high temperature data to the low temperature data. Any result requiring absurd values of

Table 4

Heats of Formation of Sodium-Tin Alloys

Compound or Composition	ΔH_f kcal./ g. atom	Temp. °K.	Remarks	References
$NaSn_2$	-5.	298		(4)
	-6.7	298		(2), (3), (5)
	-3.65±0.25	880	from curve, Figure 1	This research
NaSn	-5.5	298		(4)
	-8.	298		(2), (3), (5)
	-6.	room		(8), (9), (10)
	-5.3±0.3	298	Est. value	(1)
	-4.9±0.2	873	Recalculated value	(1)
	-4.80±0.14	882		This research
$Na_{1.105}Sn$	-4.86±0.04	881		This research
Na_4Sn_3	-5.1	298		(4)
	-8.	298		(2), (3), (5)
	-4.65±0.3	880	Est. from curve, Fig. 1	This research
Na_2Sn	-4.	298		(4)
	-7.	298		(2), (3), (5)
	-4.8	room		(8), (9), (10)
	-4.03±0.08	885		This research
Na_4Sn	-4.2	298		(4)
	-6.8	298		(2), (3), (5)
	-2.9	298		(8), (9), (10)
	-2.5±0.5	880	Est. from curve, Fig. 1	This research

heat capacity and/or heat of fusion cannot be considered compatible with the results presented here. The limits considered acceptible for the liquid alloy heat capacity are from 7 to 10 cal./deg. g. atom; for the entropy change in melting, 1.5 to 3.5 e.u./g. atom; and for the solid alloy heat capacity, 6 to 9 cal./deg. g. atom. Using these criteria, and starting with the values of $\Delta H_{f_{880}}$ read from Figure 1, one can readily find the range of values of $\Delta H_{f_{298}}$ which are compatible. For $NaSn_2$ these limits for $\Delta H_{f_{298}}$ are from -2.8 to -5.7 kcal./g. atom. For NaSn, the limits are from -4.3 to -7.7 kcal./g. atom. For Na_4Sn_3, the limits are from -4.2 to -7.4 kcal./g. atom. For Na_2Sn, the limits are from -3.6 to -6.9 kcal./g. atom. For Na_4Sn, the limits are from -2.2 to -5.3 kcal./g. atom.

A comparison of the limits noted above with the data of Table 4 shows that all of the values of Biltz and Holverscheit[4], are within the compatible range, that all the values of Kubaschewski[8] and Kubaschewski and co-workers[9], [10] are near the center of the compatible range, that the estimated value of Barber et al.[1] for NaSn is in the compatible range, but that the values reported by Bichowsky and Rossini[2], who reviewed the work of Biltz[3], and Biltz and Meyer[5], are higher than the upper compatible limit. This, although not conclusive, is evidence indicating that the revised data, with which Biltz and Meyer recalculated the experimental results of Biltz and Holverscheit, was incorrect, and further, it tends to support the values of Kubaschewski.

Conclusion

Heats of formation of sodium-tin alloys have been measured in the new high-temperature calorimeter at 610°C. (880°K.), and the results tend to support the values originally reported by Kubaschewski and Seith[9]. A summary of the heats of formation found in this research appear in Table 5.

This work was performed under the auspices of the Atomic Energy Commission.

Table 5

Heats of Formation of Liquid Sodium-Tin Alloys

Composition	$\Delta H_{f_{880}}$
$NaSn_2$	-3.65 ± 0.25 kcal./g. atom
NaSn	-4.80 ± 0.14 kcal./g. atom
$Na_{1.105}Sn$	-4.86 ± 0.04 kcal./g. atom
Na_4Sn_3	-4.65 ± 0.3 kcal./g. atom
Na_2Sn	-4.03 ± 0.08 kcal./g. atom
Na_4Sn	(-2.5 ± 0.5) kcal./g. atom

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