

CXXV.—*The System Sodium-Tin.*

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IN connexion with the problem of intermetallic compounds, the alloys of the alkali and alkaline-earth metals are of particular interest, since in these one metal at least is of well-defined chemical nature. The present author (*J. Inst. Metals*, 1926, **35**, 295) has already investigated the alloys of tin with calcium and magnesium, and the work is now extended to the alloys with sodium.

According to Mathewson (*Z. anorg. Chem.*, 1905, **46**, 94), the system sodium-tin is very complex, and contains the compounds Na_4Sn , Na_2Sn , Na_4Sn_3 , NaSn , and NaSn_2 . Of these, the last three were regarded as undergoing polymorphic transformations, but the evidence on this point was inconclusive, since only cooling curves were studied. No systematic examination by means of annealing experiments and microscopical investigation was made.

The only other detailed work on this system appears to be that of Kremann and Gmachl-Pammer (*Inter. Z. Metal.*, 1920, **12**, 257), who investigated the electromotive behaviour of these alloys in solutions of sodium iodide in pyridine, and of the tin-rich alloys in aqueous solutions. They confirmed the existence of the compounds Na_4Sn , Na_2Sn , NaSn , and NaSn_2 , but not of Na_4Sn_3 .

EXPERIMENTAL.

Materials.—The sodium used in the present work was pure electrolytic metal. No other metals could be detected by the ordinary methods of analysis, and, apart from superficial oxidation and occasional inclusions of hydroxide, the material appeared satisfactorily pure. It froze at a constant temperature. The tin was the "Chempur" tin of Messrs. Capper Pass and Co., and was accepted as being of sufficient purity.

Procedure.—The reactivity of these alloys necessitated the use of closed vessels for all the cooling-curve experiments, which were carried out in an atmosphere of nitrogen. The alloys were melted

in hard glass tubes of 1—1.3" diameter, and for the sodium-rich alloys Pyrex glass was the most suitable; no appreciable error is likely to have resulted from action between the alloy and the glass, since the two could always be separated cleanly, and, except for a very thin dark film on the inside, the tubes appeared unaffected. These tubes were then placed inside a large, hard-glass tube about 12—14" long and 1.5" in diameter, fitted with a rubber bung through which passed glass tubes carrying the stirrer, the thermocouple, and a tube for the passage of a slow current of nitrogen. The general arrangement was similar to that used by the author for the calcium alloys (*loc. cit.*) but on a rather smaller scale. The thermocouples were of alumel-chromel (No. 26 S.W.G.) and were standardised against the melting points of pure aluminium, zinc, lead, and tin. The thermocouple sheath was made by drawing out a hard-glass tube into a thin capillary just wide enough to contain the wires; for some of the tin-rich alloys, a thin silica sheath coated with alundum cement was used. The thermoelectric force was measured on a Carpenter-Stansfield potentiometer.

For the cooling-curve experiments two types of furnace were used—a well-lagged electric crucible furnace, and a large gas-fired furnace with a damper in the flue to stop the draught during cooling. These gave rates of cooling of about 5° and 10° per minute at 400°, and for convenience these will be referred to as "slow" and "normal" cooling respectively. Heating and cooling curves at slower rates were also taken in special cases.

The weights of alloys used in the cooling-curve experiments varied from about 120 g. at the tin end of the diagram to 35 or 40 g. for the sodium-rich alloys. In all cases, thorough stirring was necessary during melting, since there was a great tendency for the sodium to float on the top.

As will be shown later, it was necessary to prepare chill castings of many alloys in order to obtain samples with a very fine structure suitable for annealing experiments. Alloys containing not more than 8% of sodium were melted in an atmosphere of nitrogen, and were then cast in heavy copper moulds bored with holes $\frac{1}{4}$ " and $\frac{3}{8}$ " diameter respectively, so as to give ingots of these diameters and about 4" long. The large mass and high thermal conductivity of the copper gave a very rapid cooling, and it was largely owing to the very fine structure obtained in this way that the annealing experiments were successful. For the sodium-rich alloys the whole of the casting operation had to be carried out in a closed vessel, and for this purpose an apparatus was devised consisting of a hard-glass tube about 15" long and 1.4" in diameter, closed at one end and fitted with a wide side-tube about 6" from the bottom. In this

side-tube was placed a copper mould made from a 1" circular bar of pure copper so as to give a square ingot $3'' \times \frac{1}{4}'' \times \frac{1}{4}''$. The alloy was melted in a narrower tube provided with a spout, and of a length such that the spout was situated immediately over the opening of the mould, so that, when the alloy was molten, a casting could be made by carefully tipping the whole apparatus to one side. In this way it was possible to prepare chill castings of sodium-rich alloys from a temperature of about 500° . It is hoped to publish elsewhere further details of this apparatus.

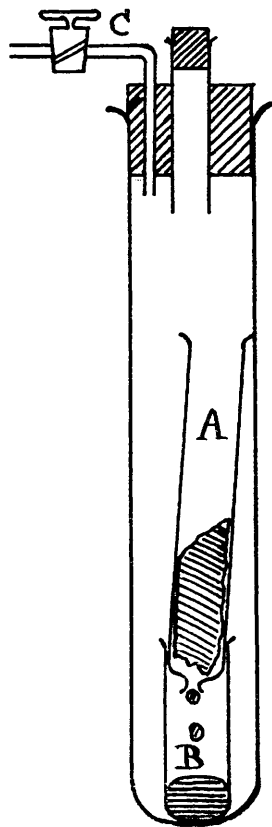
For microscopical examination the alloys were mounted in fusible metal, and in all except the tin-rich alloys, the grinding, polishing, and photography had to be carried out under oil.

The arrangements for the annealing and quenching experiments were the same as those used by the author and S. W. Rowell (*J. Inst. Metals*, 1927, **38**, 137).

Analytical Methods.—The difference between the atomic weights of sodium and tin, and the steepness of many of the lines in the equilibrium diagram made the accurate analysis of the alloys a matter of great importance, a difference of 0.1% of sodium sometimes corresponding to as much as 10° in the freezing-point curve. The extreme reactivity of the alloys made it essential to determine both constituents, in order to avoid any errors introduced by slight oxidation during weighing, and this has been done in the case of all alloys containing more than 0.5% of sodium, the tin being weighed as dioxide, and the sodium as sulphate.

For the tin-rich alloys, a complete vertical strip of the cooling curve ingot was cut for the analysis, to avoid the effects of any slight segregation. The alloys of intermediate composition were too brittle for this treatment, and large lumps from the top, bottom, and middle of the ingot were therefore taken and

FIG. 1.
Apparatus for obtaining sodium free from oxide for accurate weighing.



- A. Filter tube.
- B. Weighed hard-glass tube subsequently used for the cooling-curve experiment.
- C. Tap to vacuum pump and nitrogen supply.

ground to powder under benzene. A suitable amount of the powder was then added to water, and the small amount of benzene boiled off. This was satisfactory for alloys containing up to 35% of sodium, but beyond this point increasing amounts of the compound Na_4Sn are present, and as this reacts explosively with water, it was necessary to allow the powder to oxidise in a porcelain dish before adding water.

In alloys containing more than 44% of sodium, some of this element is in the free state, and the mass cannot be ground to powder; these alloys are, in fact, so dangerous to handle that it was thought better to adopt special methods to avoid oxidation during the melting

TABLE I.

Cooling curve experiments for the determination of the liquidus.

Tin-rich Alloys.

No. of alloy.	Sodium.		Arrests on cooling curve.				
	% by weight.	Atomic %.	Primary.	Later arrests.			
A1	0	0	232°				
A2	0.073	0.38	231			218°	
A3	0.20	1.02	230			221	
A4	0.37	1.88	225			220	
A5	0.62	3.12	223			220	
A6	0.82	4.09	221				
B1	0.99	4.91	224			220	
B2	1.18	5.81	232		225°	221	
B3	1.24	6.09	238		225	221	
B4	1.61	7.79	248		226	220	
B5	1.72	8.28	253		227°	225	221
B6	1.80	8.63	254		227	225	221
B7	2.15	10.19	266		228	226	221
B8	2.10	9.97	267		226	225	221
B9	2.29	10.79	268		228	225	221
B10	2.34	11.01	269		228	225	221
B11	2.77	12.82	278		227	224	219
B12	3.03	13.89	289		228	226	221
B13	3.12	14.25	289	286°	229	225	221
B14	3.53	15.91	293	283	231	225	220
B15	3.78	16.85	297	290	229	225	221
C2	4.47	19.45	308	289	228	226	
C3	4.61	19.97	312	309	284	229	226
C4	5.05	21.54	321	303	292	229	226
C5	5.19	22.03	331	304	288	231	226
C6	7.20	28.59	381	303	292	231	220
C7	9.33	34.68	433	302	278		220
C8	9.76	35.83	450	303	279		
C9	11.04	39.05	489	455	303	274	
C10	11.88	41.03	523	466	302	289	
C11	12.87	43.26	543	473	303	281	
C12	14.27	46.21	564	482	304	272	
C13	15.44	48.52	575	486	305		
Purest possible Na_3Sn , mean of two determinations			578	483			

TABLE II.

Alloys of Intermediate Composition.

No. of alloy.	Sodium.		Arrests on cooling curve.		
	% by weight.	Atomic %.	Primary.	Second.	Third.
X1	27.22	65.88	466°	433°	
X2	25.46	63.81	449	435	
X3	25.75	64.15	438	432	
X4	23.96	61.93	443	441	
X5	23.33	61.10	448	441	
X6	23.18	60.90	450	430	335°
X7	22.75	60.31	457	425 †	336
X8	22.60	60.11	458	429	358
X9	21.62	58.73	473	435	356
X10	20.88	57.66	480		352
X11	19.98	56.31	— *	479 & 469	349
X12	19.53	55.61	529	479 & 471	348
X13	18.47	53.90	559	478	340
X14	17.60	52.43	574	481 & 483	355

* In this alloy the primary arrest was too slight to be located accurately.

† Marked supercooling and recalescence.

of the alloy, and to estimate the composition from the weights of sodium and tin used. When the sodium was cut under petroleum, quickly dried in filter paper, and at once corked up in the hard-glass tube, the sodium contents of the alloys determined by analysis were about 1% less than those calculated from the weighed quantities over the range 30—44% of sodium. In order to reduce the loss by oxidation, the apparatus shown in Fig. 1 was used: the sodium was placed in the upper tube which stands on top of the weighed hard-glass tube. The whole was filled with nitrogen, and then on heating it was possible, by gently tapping the tube, to filter the sodium into the lower tube, leaving the skin of oxide in the upper. In this way the sodium could be weighed without any oxidation, and since, for these sodium-rich alloys, larger quantities of sodium are used at lower temperatures, it is unlikely that the true composition of the alloy differed by more than a few tenths of a unit % from that calculated from the weighed amounts.

Results.

The experimental results can conveniently be divided into three sections. In order to save space the system of Heycock and Neville is adopted: an alloy described as, *e.g.*, "alloy 24.5" means one containing 24.5 *atoms* % of sodium. The results of the cooling-curve experiments are given in Tables I—III, and are plotted in Fig. 2; Fig. 3 shows the tin-rich end of the diagram on an enlarged scale.

FIG. 3.

The Equilibrium Diagram of the System Sodium-Tin: Tin-rich Alloys.

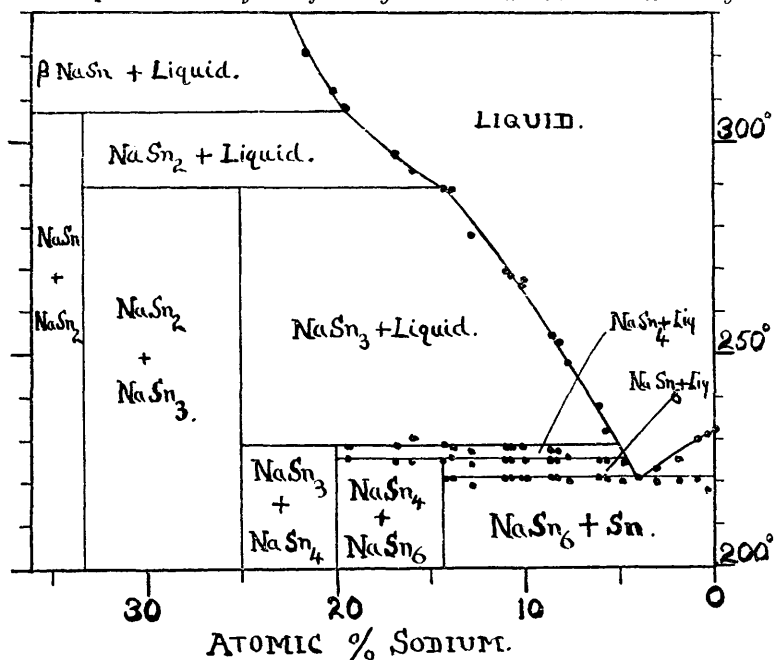


TABLE III.

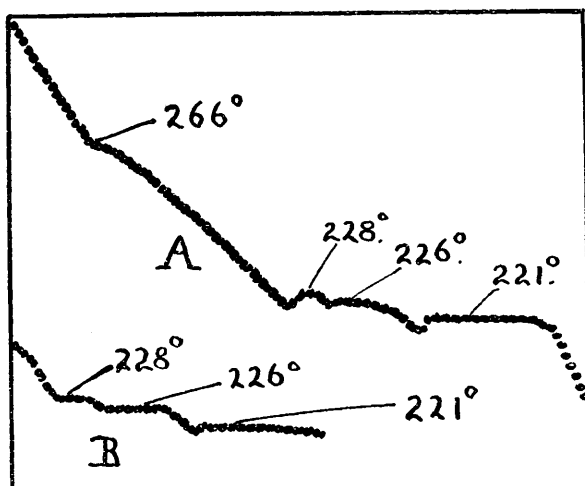
Sodium-rich Alloys.

No. of alloy.	Sodium.		Arrests on cooling curve.		
	% by weight.	Atomic %.	Primary.	Second.	Third.
Z1	100	100	97°		
Z2	90.03	97.90	290	97°	
Z3	79.36	95.20	333	96	
Z4	63.69	90.06	367	97	
Z5	52.39	85.04	391	97	
Z6	48.69	83.05	398	97	
Z7	45.59	81.12	406	96	
Z8					
Purest possible Na ₄ Sn.	Mean of two determinations.	80.0	407-408		
Y1	40.86	78.10	419	407	370°
Y2	39.14	76.85	430	406	368
Y3	36.55	74.84	449	408	364
Y4	33.49	72.21	469	404	377
Y5	31.27	70.13	476	403	
Y6	28.64	67.43	478		
Y7					
Purest possible Na ₂ Sn		66.67	478		

I. *Tin-rich Alloys.*

When sodium is added to tin, the liquidus falls to a eutectic point at 220—221°, the eutectic composition being 4 atoms % of sodium (Mathewson gives 220° for this arrest). From this point the liquidus rises steeply with various breaks (see later) to a well-defined maximum at 50 atoms % corresponding to NaSn. According to Mathewson this compound is in equilibrium with liquid from its melting point down to 305°, at which temperature the compound NaSn₂ is formed by a peritectic reaction between NaSn and liquid. The compound

FIG. 4.



Examples of cooling curves for tin-rich alloys. Curve A shows that for alloy 10·19. This is typical of unstirred alloys at normal rates of cooling, showing the supercooling of the 228° arrest and also of the eutectic at 221°. Curve B shows the lower part of the cooling curve of an alloy of almost the same composition, the curve being taken at a slower rate of cooling, and with vigorous stirring of the alloy. In this case the supercooling of the 228° arrest is prevented, and that of the eutectic is greatly reduced. In both curves the presence of two arrests besides that of the eutectic is made clear.

NaSn₂ was described as undergoing a "transformation" extending over the range 220—225°, and its low-temperature polymorphic form was regarded as forming one of the constituents of the 220° eutectic, the other constituent being pure tin.

The present author's cooling curves at once showed that this "transformation" of Mathewson was in reality composed of two distinct arrests, one at 225—226°, and the other at 228—229°. At normal rates of cooling the 229° arrest usually showed undercooling followed by recalescence, but even so the double nature of the arrest was apparent, whilst by using very slow cooling with

vigorous vibration of the tube containing the alloy, the two arrests could be obtained quite distinct, and with no appreciable under-cooling. Examples of these curves are shown in Fig. 4.

From 228° , the liquidus rises steeply to 289° , where a break occurs. In agreement with this, it was found that the cooling curves showed an arrest at this temperature in addition to their primary arrests. This arrest, which escaped Mathewson's notice, was always slight, and was apt to be masked by the much more pronounced arrest at 307° . The arrest found by Mathewson at 305° was confirmed, and, as will be shown later, his interpretation of it as due to the formation of the compound NaSn_2 is correct. The true temperature of this arrest, as given by very slow rates of cooling or by vigorously stirred alloys at normal rates of cooling, was 307° , but at normal rates of cooling the arrest is apt to show under-cooling, and may occur at any temperature between 300° and 307° .

None of the arrests at 307° , 289° , 229° , or 226° corresponded to an alloy freezing at constant temperature, but all were due to peritectic reactions, and these never reached true equilibrium in the cooling-curve experiments owing to a sheath of the secondary solid being formed round the primary solid and so preventing the latter from further action with the liquid. Consequently, alloys which began to freeze above 307° showed the whole series of these arrests in the cooling curves, and only became completely solid below the eutectic temperature at 220° . This was confirmed by the microscopic examination of the cooling-curve ingots, which showed the solid adjoining the eutectic to consist of a whole series of layers which became more and more reactive as the centre was approached, indicating a series of compounds in which the sodium content increased towards the interior.

As these transformations never attained true equilibrium, the only chance of finding the compositions of the various phases was to prepare and anneal chill castings. Two series of experiments were carried out in which the alloys were annealed for 17 days at 200° , and for 4 weeks at 210° , respectively. The results are shown in Table IV and may be summarised as follows. No solid solution in tin could be detected. Even the alloy 0.52 showed two constituents quite clearly after annealing. With increasing sodium content the tin was gradually replaced by a constituent which is denoted by α . This was only slowly oxidised in air, and tarnished to a characteristic brownish colour with a curious shining appearance. Alloy 14.05 consisted almost entirely of this constituent with traces of free tin, showing that the phase must contain slightly more sodium than 14.05 atoms %. Alloys 14.21 and 14.41 showed almost entirely α , with traces of a more reactive constituent in some

TABLE IV.

Details of annealing experiments.

Temp. of annealing.	Time of annealing.	Compositions of alloys annealed. (Na, atoms %).	Notes.
200°	17 days	0·52, 1·23, 3·02, 10·23, 11·13, 12·99	Free tin with increasing amounts of NaSn ₄ . All chill cast.
210	28 "	12·99, 13·81, 14·05, 14·21, 14·41, 15·26	See pp. 954 and 957. All chill cast.
200	17 "	16·70, 18·61	NaSn ₅ and "spotted tarnish" constituent.
210	28 "	16·70, 18·61	NaSn ₅ and "spotted tarnish" constituent. All chill cast.
210	28 "	19·97, 20·47, 21·03	See pp. 956 and 957. All chill cast.
210	28 "	21·03	NaSn ₄ ("spotted tarnish" constituent) and NaSn ₃ . Chill cast.
200	17 "	22·03	
200	17 "	24·97	See p. 957. Chill cast.
210	28 "	24·97, 25·34, 25·37, 25·89	
210	28 "	26·28, 30·74, 31·38	NaSn ₃ with increasing amounts of NaSn ₂ . Chill cast.
210	28 "	33·77, 33·96, 37·49, 38·67	NaSn ₂ with increasing amounts of NaSn. Chill cast.
210	14 "	48·52	These experiments were made to see if there were any signs of solid solutions in the compounds of intermediate composition, and to see the effect of annealing Na ₄ Sn ₃ below the transformation temperature. As no indication of solid solubility was obtained, chill castings were not prepared on account of the dangerous manipulation.
330	14 "	52·43, 56·31, 57·66, 65·88, 67·43, 78·10	
330	14 "	74·42, 76·26, 77·90	

parts, and a very little free tin in some areas, whilst alloy 15·26 showed α and a more reactive constituent, with a few areas in which traces of free tin could be seen. From this it is concluded that the constituent α is the compound NaSn₆ (14·3 atoms % of sodium), and that no appreciable solid solution exists, since no range of homogeneous alloys was observed. This last conclusion is supported by the fact that, even after 4 weeks' annealing, the alloys of composition very near NaSn₆ showed traces of both more and less reactive constituents, indicating that equilibrium had not

been completely reached, such slowness of reaction being characteristic of cases where no solid solution exists. Since the alloys annealed for 2 and for 4 weeks showed no differences, the annealings were stopped, as the work shows conclusively that the variation (if any) must be considerably less than 1 atom %. Fig. 5 shows alloy 14.4 after 4 weeks at 210°, consisting almost entirely of α with traces of a darker constituent.

To confirm this conclusion some of these annealed alloys were quenched from temperatures between 220° and 230°; the results are shown in Table V. In all these cases the inevitable handling of the alloy caused a thin surface film to oxidise and melt above 220°, but this was ignored. These experiments showed that from 220° to 224° the phase in equilibrium with the liquid was the constituent α , but that at 227° a new darker-etching phase was in equilibrium with the liquid. This is well shown in Fig. 6, which represents alloy 13.81 quenched from 227°: dark compact crystals of the new constituent, which we may call β , are surrounded by a thin film of light-etching α formed during the quenching, these being embedded in eutectic, the structure of which is not resolved at this magnification. From the quenching experiments we may therefore conclude that the α , or NaSn_6 , is formed by a peritectic reaction between 224° and 227°, and this clearly corresponds to the 226° arrest found on the cooling curves.

From alloy 14.41, with increasing quantities of sodium the alloys consisted of NaSn_6 with increasing amounts of the darker-etching constituent β , which etched in air or under oil with a curious "spotted tarnish" effect. Alloy 19.97 consisted almost entirely of this constituent, whilst alloy 20.47 showed chiefly this constituent with some of a more reactive phase, which we may call γ , in the grain boundaries. It was difficult to decide whether this "spotted tarnish" constituent (see Fig. 7) was really composed of one phase or two, but it is considered to be a single phase on the following grounds: (1) The fineness of the tarnish pattern appeared to vary with the conditions of formation (*e.g.*, tarnishing under oil or in air). (2) In alloy 21.03 a more reactive phase was undoubtedly present in the grain boundaries; if the "spotted tarnish" constituent were in reality due to two phases, this would indicate that the alloy had three phases, and had not yet reached equilibrium, and if this were so, we should not expect to find the most reactive constituent in the grain boundaries, but rather as unchanged cores in the middle of the grains. (3) The dark-etching crystals shown in Fig. 6 were themselves etched with a distinctly spotted appearance, although here there can be no doubt that they represent the phase in equilibrium with the liquid. (4) Finally, if the effect indicated two phases, it

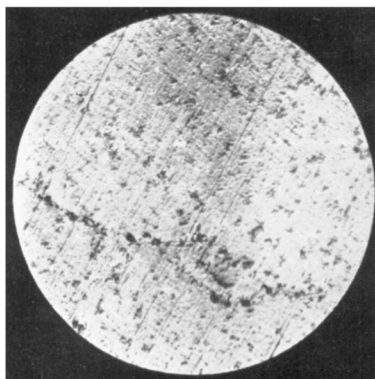


FIG. 5.—Alloy 14.4 annealed for 4 weeks at 210°. Magnification, 300.

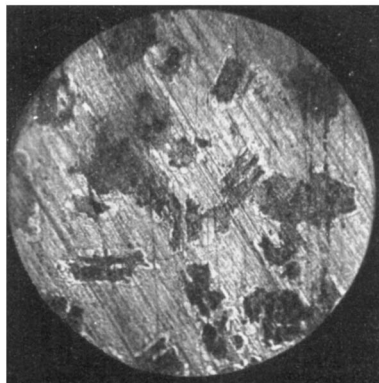


FIG. 6.—Alloy 13.81, annealed for 4 weeks at 210°, then heated to 227°, and quenched in oil. Magnification, 150.

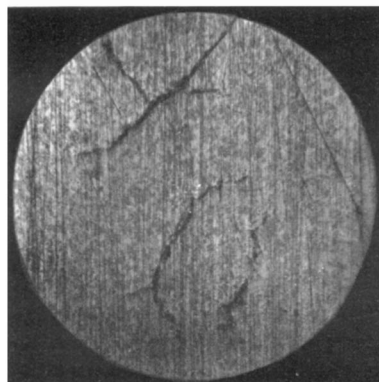


FIG. 7.—Alloy 20.47 after annealing for 4 weeks at 210°, showing the "spotted tarnish" constituent with small amounts of a more reactive phase. Magnification, 150.

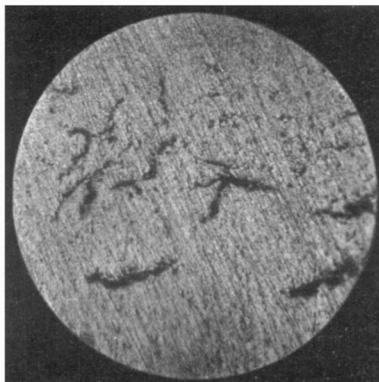


FIG. 8.—Alloy 25.34 after annealing for 4 weeks at 210°, showing chiefly γ (Na_3Sn_3) with traces of a more reactive constituent. Magnification, 150.

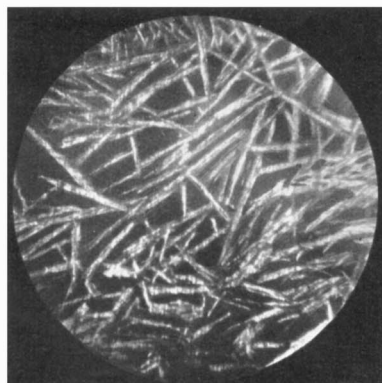


FIG. 9.—Alloy 76.26, chill cast, showing Na_2Sn (white) and Na_4Sn (black). Magnification, 150.

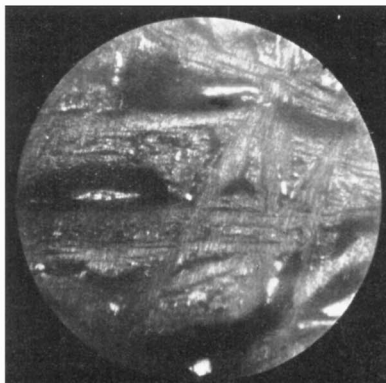


FIG. 10.—Alloy 76.26 after annealing for 2 weeks at 330°, showing chiefly Na_3Sn , with holes, and fine dark lines which are probably Na_4Sn .

Magnification, 150.

[To face page 956.]

would be a remarkable coincidence that it should reach a maximum at exactly 20 atoms % of sodium.

TABLE V.

Results of quenching experiments on tin-rich alloys.

(All these experiments refer to chill-cast alloys which had received a preliminary annealing of either 17 days at 200° or 28 days at 210°.)

Comp. of alloy (atomic % Na).	Quenching temp.	Whether melted or not.	Notes.
12.99	222°	Very slightly melted.	NaSn ₆ in equilibrium with liquid.
14.41	222	Solid.	
14.41	226	"	
13.81	224	Very slightly melted.	NaSn ₆ in equilibrium with liquid.
13.81	227	Melted.	Dark crystals in equilibrium with liquid.
14.41	230	"	" "
19.97	230	"	" "
21.03	230	Slightly melted.	" "
19.97	227	Solid.	
16.70	227	Melted.	" "
24.97	230	Solid.	
25.89	230	"	

NOTE.—In the above experiments a thin surface layer of the alloy always melted above 220° owing to the inevitable slight oxidation during handling. This has been ignored. There was some slight evidence that the dark crystals in equilibrium with the liquid at 230° were different in shape from those in equilibrium at 227°, but this could not be considered conclusive, although it is in agreement with the author's diagram.

On these grounds the phase β was considered to be NaSn₄, and this was confirmed by the quenching experiments (Table V), which showed alloy 19.97 to be solid at 227°, but to have melted at 230°. The compound NaSn₄ thus corresponds to a peritectic reaction between these two temperatures, agreeing with the 229° arrest on the cooling curves.

With increasing sodium content, the alloys consisted of NaSn₄ together with the more reactive phase γ . After 4 weeks at 210°, alloy 24.97 consisted almost entirely of γ , with occasional traces of both more and less reactive phases in some areas, but with large patches entirely homogeneous. Alloy 25.34 consisted chiefly of the new phase γ with a little of a still more reactive phase in the grain boundaries, as shown in Fig. 8. On these grounds the constituent γ is considered to be the compound NaSn₃, and in agreement with this the quenching experiments showed alloys 24.97 and 25.89 to be solid at 230°. No evidence could be found for the existence of any solid solution. As shown in Fig. 8, NaSn₃ etches in air or under oil with a very much more finely divided tarnish pattern than NaSn₄.

On further raising the sodium content, the annealed alloys consisted of NaSn_3 with increasing amounts of a more reactive constituent which was readily identified as NaSn_2 , reported by Mathewson. This compound takes a very high polish if kept out of contact with air. There again appears to be no appreciable region of solid solubility.

There is thus one phase corresponding to each arrest on the cooling curves, and this fact gives considerable support to the results obtained in this part of the diagram, which is much more complex than previously supposed. Mathewson only examined nine alloys between 0 and 33.3 atoms % of sodium, and as he did not prepare chill castings for annealing purposes, his work could not have led to the identification of the numerous phases concerned. The present work also explains why the composition-potential curves of Kremann and Gmachl-Pammer did not fit in with the theoretical requirements of the old diagram in this region, for their alloys too were not annealed.

II. Alloys of Intermediate Composition.

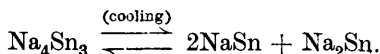
The compound NaSn corresponds to a well-defined maximum on the liquidus, the freezing point being determined as 578° from two closely-agreeing measurements; the value found by Mathewson was 575° . This compound, as stated by Mathewson, undergoes a transformation, the true temperature of which was determined as 483° , whereas he gave $480\text{--}483^\circ$. This transformation usually shows marked undercooling, and the true temperature can only be determined by reducing the rate of cooling to about 1° per minute. Mathewson's identification of this change as a polymorphic transformation of the compound NaSn appears to be correct for the following reasons. (1) The change is shown by alloys on both sides of the maximum on the freezing-point curve, and hence it is very improbable that it is due to a reaction between NaSn and liquid to form a new phase, since there would have to be two such phases, one containing more and one less sodium than the compound NaSn , and it would be a very remarkable coincidence if both these reactions occurred at the same temperature. (2) The fact that Kremann and Gmachl-Pammer (*loc. cit.*), with slowly cooled specimens, found a break at 50 atoms % in the potential-composition curves, indicates that one form of this compound exists at low temperatures. On these grounds, the line AB is drawn in Fig. 2 as showing the transformation from the high-temperature (α -) form of NaSn to the low-temperature (β -) form.

With higher sodium content, the liquidus falls steeply until there is a distinct break at $479\text{--}480^\circ$, at which the compound Na_4Sn_3

freezes at constant temperature (Mathewson gave 478°). The cooling curves in this region are apt to be very complex on account of the supercooling shown by the change $\alpha\text{-NaSn} \rightleftharpoons \beta\text{-NaSn}$, since if this cools below 479°, the compound Na_4Sn_3 may begin to freeze, and then the NaSn transformation takes place with a rise in temperature. The present work, however, completely confirmed Mathewson's conclusion that the 483° and 479° transformations were distinct, although Kremann and Gmachl-Pammer had doubted this.

From here, the liquidus falls to a eutectic point at 62 atoms % of sodium, and 441° (Mathewson gave 61.7% and 440°). This arrest is prone to show under-cooling, and, with normal rates of cooling, may occur at any temperature between 430° and 440°. From the eutectic the liquidus rises steeply to a maximum at 478°, at which the compound Na_2Sn freezes at constant temperature; the value found by Mathewson was 475°.

According to Mathewson the compound Na_4Sn_3 underwent a polymorphic change in the range 320—350°, and, in agreement with this, the author's cooling curves showed arrests in this region. These transformations exhibited marked hysteresis on both heating and cooling curves, and even when the rate of change of temperature was reduced to 1° per minute, there was still a difference of 10° between the values given on heating and cooling curves; the mean values from curves of this nature with two different alloys were 358° and 357°. In order to determine the nature of this change, alloys were annealed for 2 weeks at 330°, *i.e.*, just below the transformation temperature. If Mathewson's interpretation of the transformation as a polymorphic change of Na_4Sn_3 be correct, the alloy 57.66, on annealing at 330°, should show almost all one constituent (the supposed low-temperature form of Na_4Sn_3) with a slight excess of Na_2Sn . Actually, however, it showed a finely divided two-constituent structure characteristic of the changes in which one phase on cooling splits into two phases. This was confirmed by the microstructure of the other slowly-cooled ingots in this region, for in all these the phase which, according to Mathewson, should have been homogeneous Na_4Sn_3 , possessed this finely-divided eutectoid-like structure. On these grounds, therefore, the transformation at 357° is regarded, not as a polymorphic change of Na_4Sn_3 , but as the decomposition of this compound on cooling into two other phases; and since, on annealing at 330°, all the alloys between NaSn and Na_2Sn showed two constituents, it is concluded that the Na_4Sn_3 splits up into NaSn and Na_2Sn , the transformation at 357° corresponding to the change



This also explains why Kremann and Gmachl-Pammer (*loc. cit.*), using slowly cooled alloys, found no evidence for the existence of the compound Na_4Sn_3 at the ordinary temperatures at which their measurements were made.

Apart from this one point, the present results are in good agreement with those of Mathewson, for alloys within this range.

III. Sodium-rich Alloys.

Over the range 66.6—100 atoms % of sodium, the author's determination of the liquidus agrees remarkably well with that of Mathewson, the curve falling from the freezing point of Na_2Sn to 408° (Mathewson 405°) at which the compound Na_4Sn freezes at constant temperature; from here the liquidus falls steeply to the melting point of pure sodium. Mathewson, however, concluded that the liquidus and solidus did not exactly coincide at his 405° transformation line, but that the composition of the liquid was here 80.8 atoms % of sodium, the compound thus melting over a slight range of temperature. The present work does not confirm this. The smooth curves through the three points on either side of the compound meet almost exactly at the 80% line. That the solidus and liquidus meet at this point is further shown by the fact that the 97° arrest, at the melting point of sodium, was shown by alloys 83.05 and 81.12, but not by alloy 80.0 or 78.10. If the compound Na_4Sn did not melt at constant temperature, but corresponded to a peritectic reaction at 408° , we should not expect this to proceed to complete equilibrium in the cooling-curve experiments (owing to the effect of the film of solid first formed round the primary crystals) and we should expect to find traces of the 97° arrest continuing in the last two alloys in the same way that the low-temperature arrests persisted in the tin-rich alloys. The evidence is therefore that the compound Na_4Sn melts at constant temperature.

On the other hand, the author's cooling curves showed a brief arrest in the region $360\text{--}380^\circ$ for alloys between 66.6 and 80 atoms % of sodium, and from slow heating and cooling curves the true temperature of this was found to be 377° (heating, 380° ; cooling, 374°). This was not given by either pure Na_4Sn or pure Na_2Sn , and the only reasonable explanation seems to be that at this temperature these two compounds react to form another phase of intermediate composition. The arrest was a maximum between 75 and 80 atoms % of sodium, indicating that the new phase might be Na_3Sn , and with very great difficulty chill castings were prepared in this range of composition, and were annealed for 2 weeks at 330° . Fig. 9 shows the casting of alloy 76.26. Here will be seen light needles (indicating plate-like crystals) of Na_3Sn in a ground mass of

Na_4Sn . In spite of the great reactivity of its constituents, this alloy could be photographed under an oil film at any time up to 50 seconds after polishing, although the structure of the Na_4Sn could never be seen. After annealing, the whole structure had changed, no Na_2Sn could be seen, and the alloy was so very much more reactive that, even under oil, it was almost impossible to photograph it before the whole surface appeared black. After many failures, however, Fig. 10 was obtained; the structure here shows numerous holes (indicating a volume change), and chiefly one constituent appearing dark grey in the photograph, and small dark lines which are either a second more reactive constituent or else fine cracks. The white spots are bubbles of hydrogen. On the other hand, alloy 74.42 showed some of the light Na_2Sn left over after annealing, whilst alloy 77.9 looked very much like Fig. 10 with more of the fine dark lines. On these grounds, therefore, it is considered that the transformation at 377° corresponds to the combination of Na_4Sn and Na_2Sn to form Na_3Sn , which decomposes to its constituent compounds on heating through the transformation temperature. That Na_3Sn forms little or no solid solution is shown by the fact that the annealed alloy 74.42 showed some Na_2Sn to be present, whilst if the fine dark lines in alloys 76.26 and 77.90 indicate Na_4Sn , it is clear that there is little solid solubility on the sodium side. It must be admitted that this evidence is not entirely conclusive, but it is not unsatisfactory in view of the intense reactivity of these alloys, for they explode when dropped into water, and even under oil become black within 30 seconds.

The annealing experiments failed to show any solid solutions in the compound Na_2Sn , or on the tin side of Na_4Sn . Alloy 81.12 showed a clear arrest at 96° on the cooling curve, indicating that little or no solid solubility exists on the sodium side of Na_4Sn , but as this alloy is partially liquid above 97° annealing experiments were not carried out.

Discussion.

The system sodium-tin contains the compounds Na_4Sn , Na_3Sn , Na_2Sn , Na_4Sn_3 , NaSn , NaSn_2 , NaSn_3 , NaSn_4 , and NaSn_6 . All these are definitely metallic, and conduct electricity, the least metallic-looking being Na_2Sn , which is bluish-black and closely resembles the bluish-black Mg_2Sn (probably Mg_4Sn_2), as has been previously pointed out by the author. The density of Na_2Sn was determined as 2.94 by using xylene as the immersion fluid, and a stoppered pycnometer.

As the author has previously suggested, the metallic properties of compounds of this nature indicate that some of the valency electrons are not bound into stable octets, or other groupings,

but remain more loosely held. Of the compounds discovered, NaSn_6 and NaSn_4 readily suggest themselves as co-ordination compounds of the sodium *ion*, with 6 and 4 atoms, respectively, surrounding the positively charged ion, and thus leaving the one free valency electron over to give the substance its metallic properties. For the other compounds, electronic structures must remain speculative until methods have been devised for determining the true molecular weights and the number of "free" electrons present, or alternatively, until the crystal structure has been investigated.

Summary.

The equilibrium diagram of the system sodium-tin has been investigated by thermal and microscopic methods. More than 60 alloys have been annealed or quenched under different conditions, and 63 independent cooling-curve experiments have been carried out.

The system has been shown to be very complex, and to contain the nine compounds Na_4Sn , Na_3Sn , Na_2Sn , Na_4Sn_3 , NaSn , NaSn_2 , NaSn_3 , NaSn_4 , and NaSn_6 .

Of these, the compounds Na_2Sn (m. p. 478°) and NaSn (m. p. 578°) correspond to maxima on the liquidus, and melt at constant temperatures. The compound NaSn undergoes a polymorphic transformation at 483° .

The compounds Na_4Sn (m. p. 408°) and Na_4Sn_3 (m. p. 479°) also melt at constant temperatures, but correspond to breaks in the liquidus and not to maxima. The compound Na_4Sn_3 is only stable above 357° , and on cooling below this temperature it splits up into the compounds Na_2Sn and NaSn , the reverse change taking place on heating above 357° .

The compound Na_3Sn exists only in the solid state, and on heating above 377° it decomposes into a mixture of the compounds Na_4Sn and Na_2Sn .

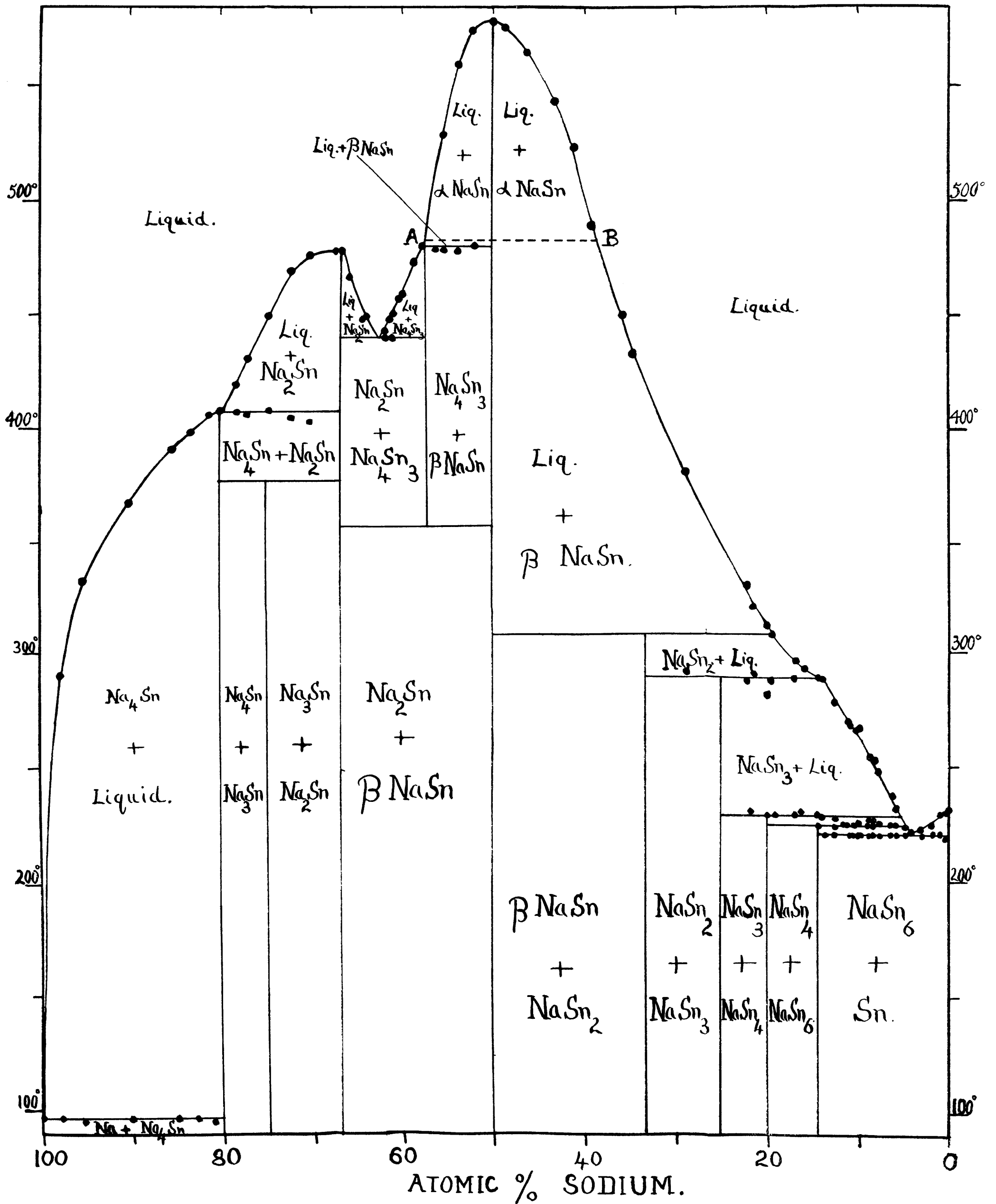
The compound NaSn_2 is formed at 307° by a reaction between the compound NaSn and liquid; the compound NaSn_3 is formed at 289° from NaSn_2 and liquid; the compound NaSn_4 is formed at 229° from NaSn_3 and liquid; and the compound NaSn_6 is formed at 226° from NaSn_4 and liquid. None of these compounds melts at a constant temperature, but all correspond to peritectic reactions indicating extensive decomposition on melting.

No evidence has been found for the existence of any solid solutions. The results are discussed in the light of previous work.

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FIG. 2.

The Equilibrium Diagram of the System Sodium-Tin.



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