Between 0 and 32 per cent. copper, grains and dendrites of aluminium occur in an increasing ground-mass; between 32 and 54 per cent. copper, crystals of the compound Al_2Cu occur in a decreasing ground-mass of the eutectic. In neither case are the dendrites or crystals pure but contain about 2 per cent. of copper,[1] or of aluminium, as the case may be, in solid solution.

(2) From 54 per cent. copper onwards we find a decreasing ground-mass of Al_2Cu, while a new constituent, in the form of dendrites and then irregular masses, increases until at about 78 per cent. copper the alloys are homogeneous.

(3) The alloys remain homogeneous from 78 per cent. to about 83 per cent. copper (from Al_2Cu_3 to $AlCu_2$).

(4) It is open to question whether this new constituent is $AlCu$, Al_2Cu_3 or $AlCu_2$, for in any case it forms solid solutions. There may even be two isomorphous compounds present.

(5) Above 83 per cent. to about 90 per cent. copper the alloys solidify as solid solutions, which, at a lower temperature, rearrange themselves, according as the alloy contains more or less than 87 per cent. copper—the eutectoid point. This change is similar to that which takes place in steel or in the bronzes.

(6) From 92 per cent. to 100 per cent. copper, the alloys form a series of solid solutions isomorphous with copper and show no rearrangement in the solid state.

In conclusion, my thanks are due to M. N. Bolles, Ph.D., who made several electrolytic copper determinations; to Professor Howe, in whose laboratory the work was carried out; and to Professor E. H. Miller, for his interest in the work.

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ON THE STRUCTURE OF ALLOYS. PART II. SOME TERNARY ALLOYS OF TIN AND ANTIMONY.[2]

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THE alloys of tin and antimony have been studied by Stead,[3] Behrens,[4] Reinders,[5] and others. Between 0 and 7.5 per cent. of

[1] This would probably be in solution as Al_2Cu.
[2] Read before the New York Section of the American Chemical Society, June 10, 1904.
[3] *J. Soc. Chem. Ind.*, March-June, 1897; December, 1898.
[4] *Verslagen d. Kon. Acad. v. Wetensch. te. Amst.*, June 25, 1898, 58; and *Baumaterialkunde*, Vol. IV, Part 6 and 7 (*Metallographist*, Vol. III, p. 4).
[5] *Ztschr. anorg. Chem.*, **25**, 113 (1900).

antimony we have a series of solid solutions of antimonide of tin in tin, whose structure is isomorphous with tin. Fig. 1, $\times$ 35 v., shows the alloy containing 5 per cent. antimony and 95 per cent. tin, and this is characteristic of this part of the series. The freezing-point curve shows a rise from pure tin at 232° C. to the 7.5 per cent. alloy at 256° C. (Stead), or to the 8 (molecular) per cent. alloy at 243° C. (Reinders).

Above 7.5 per cent. antimony hard, bright white cubes make their appearance. They are lighter than the mother-liquor out of which they crystallize and so they float to the top and form a layer there. Each addition of antimony produces an increase in the number and size of the cubes until at about 25 per cent. antimony they are found to reach the bottom of the alloy. Their shape is shown in Fig. 2, $\times$ 33 v., which is a horizontal section through the 20 per cent. alloy, etched with dilute nitric acid. The ground-mass is the same as the 7.5 per cent. alloy. These cubes continue to increase with the antimony present up to 40 per cent. when their form changes, and as the antimony increases they become plate-like, as seen in Fig. 3, $\times$ 16 o., which shows the alloy containing 45 per cent. antimony and 55 per cent. tin deeply etched. The composition of these crystals is in dispute. Stead found them to correspond to SbSn up to the 40 per cent. antimony alloy, but beyond that point they contain more antimony. Behrens, on the other hand, isolated them by another method and found them to be $SbSn_2$.

At 55 per cent. antimony the ground-mass disappears. On polishing, the mass appears homogeneous, but by deep etching harder cores are found within the plates. These increase with the antimony present, develop into well-defined antimony dendrites and finally occupy the whole field. Fig. 4, $\times$ 16 o., shows the 60 per cent. antimony alloy etched with nitric acid.

The cooling- or freezing-point curve, as determined by Reinders, shows some interesting points, for when the alloys contain more than 20 (molecular) per cent. antimony the cooling curves show three retardations, the middle one being feeble at 310° C. and the lower at 243° C., corresponding to the solidification of the ground-mass. From 51 to 60 (molecular) per cent. antimony the cooling curves show four halts. The first and second (430° C.) are well marked, the third and fourth (310° and 243° C.) are feeble and die out above this percentage. This shows that above

25 per cent. antimony the alloys become complex and are not the simple series with the single compound SbSn, as previous authorities have stated. Reinders concludes from his researches that tin and antimony form two solid solutions, tin containing a maximum of 11 per cent. antimony, and antimony containing an unknown quantity of tin. They also form two compounds: The cubic form, SbSn or $SbSn_2$; the plate-like form, Sb_4Sn_3 or Sb_5Sn_4. Until these two compounds have been isolated and analyzed their formulae can only be guessed at.

The importance of the ternary alloys of tin and antimony in the arts made it seem desirable to examine their structure. As a basis of study, the 25 per cent. antimony and 75 per cent. tin alloy was taken, because, in it, the bright cubes of SbSn (following Stead for convenience) are distributed throughout the whole mass of the alloy. For industrial purposes, such as bearings, etc., the antimony would not exceed 12 per cent., but in this case we would be dealing with comparatively rapid cooling. A large amount of the alloy was carefully made and cast. Convenient weights were then alloyed with 10 per cent. of the following metals: Lead, cadmium, bismuth, copper, silver, zinc, arsenic and aluminium. The melts were made in a small Fletcher gas-furnace. Ninety parts of the 25 per cent. antimony and 75 per cent. tin alloy were melted under potassium cyanide and then 10 parts of the third metal added. The alloy was well shaken around to produce a uniform liquid, and, shortly afterwards, the gas and air were shut off and the crucible allowed to cool down slowly in the furnace. In the case of aluminium, potassium cyanide cannot be used and charcoal was substituted. The alloys can be divided into groups according to their resulting structure.

Group I. The third metal forms a simple alloy with tin, and the whole consists of bright cubes of SbSn set in a ground-mass, which is composed of grains and dendrites of tin, surrounded by the eutectic.

10 per cent. Pb, 22.5 per cent. Sb, 67.5 per cent. Sn. Lead and tin form a simple series of alloys with a eutectic point 68 per cent. tin, melting at 180° C., and intermediate alloys are composed of grains and dendrites of tin or lead set in the eutectic. If the whole of the antimony present combines with tin to form SbSn (and this is likely for lead and antimony also form simple alloys whose eutectic point is at 12.5 per cent. antimony and melts

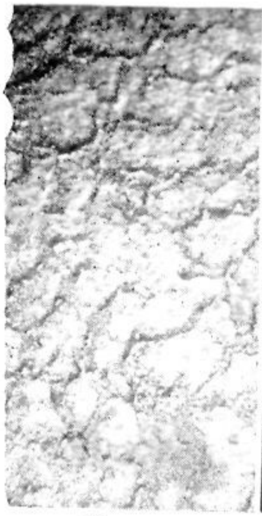


Fig. 1.

Fig. 2.

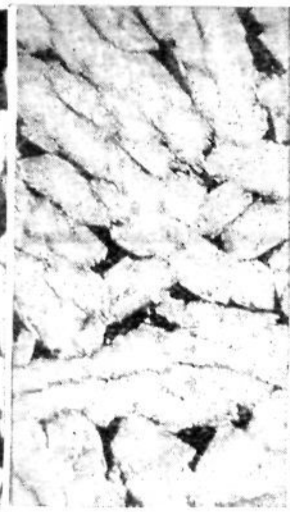
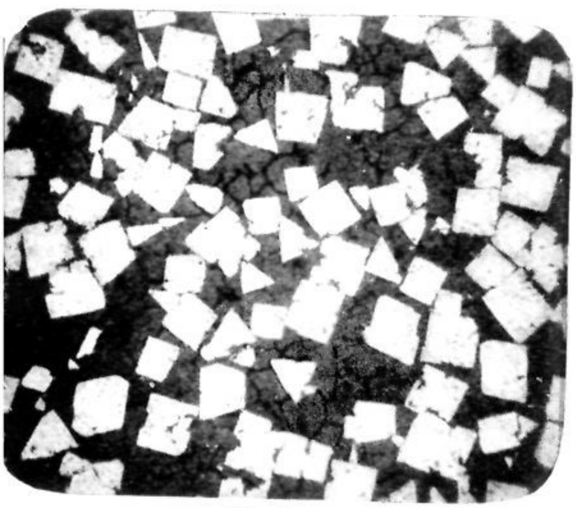


Fig. 3.

Fig. 4.



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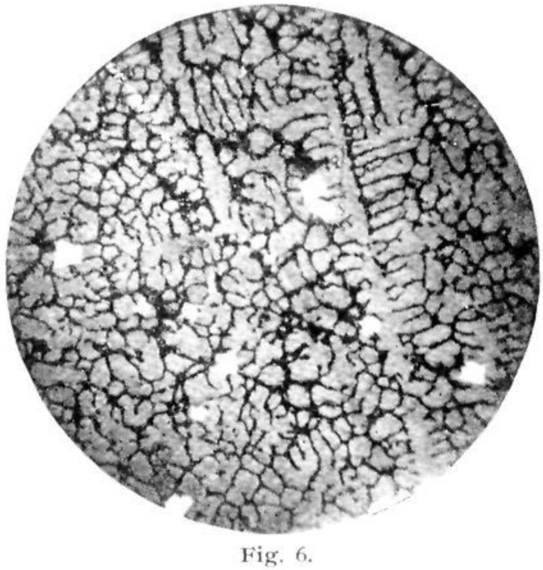

Fig. 6.

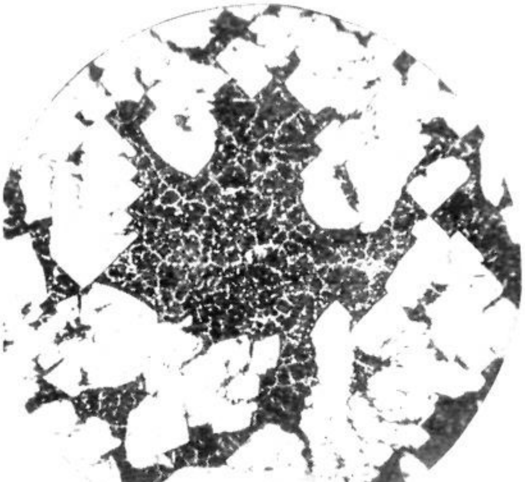

Fig. 7.

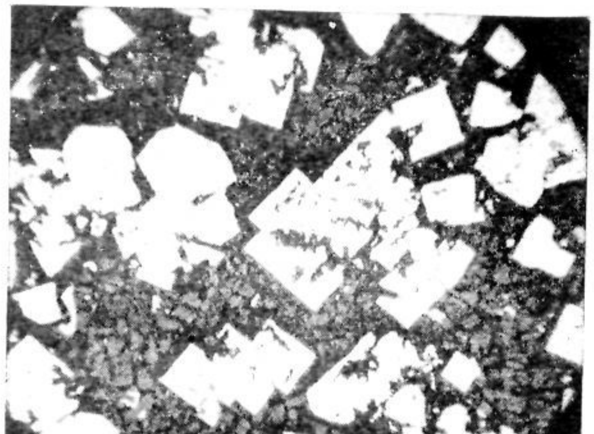

Fig. 8.

Fig. 9.

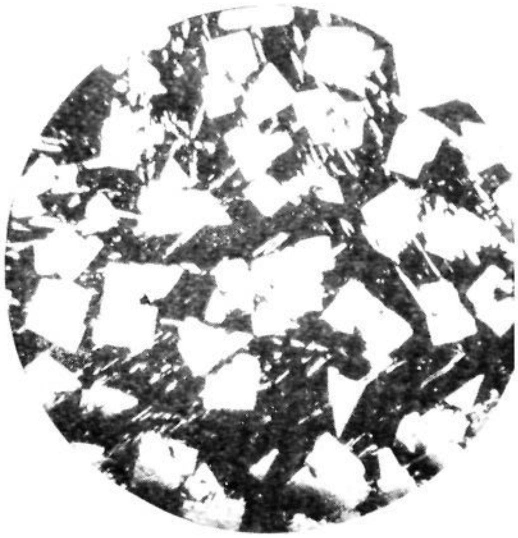

Fig. 10.

Fig. 11.

Fig. 12.

Fig. 13.

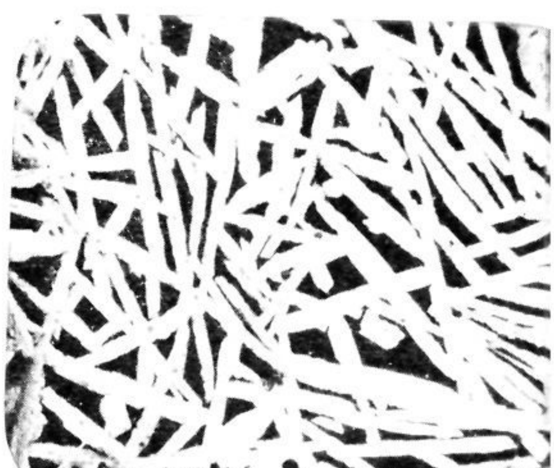

Fig. 14.

at 247° C.[1]) we should have a ground-mass consisting of 18 per cent. lead and 82 per cent. tin. This would give us an excess of tin which would crystallize out as large dendrites and be surrounded by a ground-mass of the eutectic. It is possible, however, that the ground-mass contains antimony and consists of dendrites of tin, surrounded by a lead-tin-antimony eutectic.

A section of the alloy was cut and polished. Etching with dilute nitric acid intensifies the contrast, but the structure can be seen after polishing alone. Bright white cubes, in all respects similar to SbSn, are seen, but they do not extend to the bottom of the alloy, having concentrated in the upper two-thirds by gravity where free. The attached ones remain in place round the base and sides of the alloy, of course. Fig. 5, $\times$ 38 v., etched with dilute nitric (5 per cent.) acid shows a section from near the top of the alloy. The cubes are seen set in a ground-mass, which is composed of two constituents. The structure of the ground-mass can best be seen at the base of the alloy from which the cubes have nearly all separated out and floated to the top. Fig. 6, $\times$ 38 v., shows this part of the section. A few stray cubes are still left, but the rest of the field is filled with comparatively large grains and dendrites of tin, surrounded by a dark ground-mass, which is apparently composed of alternate flakes of lead and tin and is the eutectic. From the manner of etching it would seem that the dendrites were not pure, but contained a certain small amount in solid solution.

10 per cent. Bi, 22.5 per cent. Sb, 67.5 per cent. Sn. Bismuth and antimony are said to form a series of isomorphous solid solutions like gold and silver. Bismuth and tin form a simple series of alloys with a eutectic at 58 per cent. bismuth, melting at 133° C. The dendrites of tin which separate out contain about 10 per cent. bismuth in solid solution, however. If, as before, the antimony combined with the tin to form SbSn, we should have a ground-mass of 18 per cent. bismuth and 82 per cent. tin, which would be formed of grains and dendrites of tin (10 per cent. bismuth in solid solution), surrounded by an envelope of the eutectic of Bi-Sn (58 per cent.). Fig. 7, $\times$ 38 v., shows a horizontal section of an alloy containing 10 per cent. bismuth, 28 per cent. antimony and 62 per cent. tin, etched with 5 per cent. nitric acid. It shows bright cubes whose parallel growth is very similar to

[1] Stead : *J. Soc. Chem. Ind.*, 1897, p. 203.

that found in a slowly-cooled 25 to 30 per cent. antimony, 75 to 70 per cent. tin alloy. Deep etching attacks these crystals much in the center and at a little distance from the edge, which seems to show that they contain either tin or bismuth in solid solution. The ground-mass is composed of black-etching grains of tin (10 per cent. bismuth in solution), surrounded by a brighter envelope. This has a pinkish tinge and is the BiSn eutectic, the tin of which has mostly migrated into the grains adjoining. Under a high power the black-etching grains of tin are seen to contain minute white dots of the color of SbSn, which seem to have been thrown out after solidification.

Group II. The third metal forms a compound with tin and the whole consists of cubes of SbSn and crystals of the new compound set in a matrix, which is the eutectic.

10 per cent. Ag, 22.5 per cent. Sb, 67.5 per cent. Sn. According to Charpy[1] silver and tin form a compound Ag_2Sn. Between 100 and 65 per cent. silver we have isomorphous mixtures of Ag and Ag_2Sn, while below this we have a simple series of alloys of Ag_2Sn and Sn with a eutectic at 3.5 per cent. silver, melting at 222° C.[2] Supposing the antimony all combines to form SbSn, the ground-mass would consist of 18 per cent. silver and 82 per cent. tin, and, therefore, would consist of crystals of Ag_2Sn set in the silver-tin eutectic. Fig. 9, $\times$ 38 v., shows the alloy. Bright cube-like forms of SbSn are seen, together with long needles and rods of the compound (characteristic of silver-tin alloys from 3.5 per cent. silver onwards) set in a ground-mass identical with the silver-tin eutectic. The freezing-point curve for silver and antimony is composed of two branches, the one from pure antimony to 55 per cent. silver, the eutectic point (485° C.) being quite normal, the other from pure silver having a decided angle at 72 per cent. silver, corresponding to the formula Ag_3Sb. Hence, by increasing the silver and decreasing the tin, points would be reached where either Ag_3Sb and SbSn or Ag_3Sb and Ag_2Sn would be found in the alloy.

5 per cent. Cu, 23.75 per cent. Sb, 71.25 per cent. Sn. Copper and tin form a eutectic at 1 per cent. copper, above which point to about 8 per cent. crystals of CuSn are found set in the eutectic. From 8 per cent. copper onwards the series is complicated by changes which take place after solidification has begun. The

[1] *Bull. de la Soc. d'Enc.*, March, 1897, p. 418.

[2] Heycock and Neville: *Phil. Trans. Roy. Soc.* (1897), 189 A.

series contains $SnCu_3$ and $SnCu_4$. If, as before, the antimony and tin combine, the rest of the alloy would be composed of about 9.5 per cent. copper and 90.5 per cent. tin, which would consist of needles and skeleton stars of CuSn in the copper-tin eutectic. Fig. 10, $\times$ 30 v., shows the alloy etched with 5 per cent. nitric acid. Bright white cubes are seen, together with needles giving a curious arrow-head shape in cross-section, surrounded by the dark ground-mass, which is apparently the copper-tin eutectic. It is noticed that some of the CuSn has solidified first of all and the SbSn has grown around it, resembling the ophitic structure of plagioclase and pyroxene in certain diabases.

The curve of fusibility of antimony and copper, as determined by Le Chatelier, consists of four branches, which cross at the two eutectic points at 25 and 71 per cent. copper. The summit occurs at 60 per cent. copper. Stansfield[1] has published a similar curve with a summit at 57 per cent. copper. According to Stead[2] there are two compounds in this region, $SbCu_2$, the purple compound, and $SbCu_3$, which is white. By varying the percentages of tin, copper and antimony we obtain alloys with the purple compound of copper and antimony. An alloy containing 16 per cent. tin, 56 per cent. copper and 48 per cent. antimony showed very coarse plates of the purple compound which had crystallized out first of all. Between these coarse plates the spaces were filled with white rods, or smaller plates of a white compound and a ground-mass, which is evidently a eutectic composed of needles of the purple and white compounds and white grains.

Group III. The third metal has a greater affinity for the antimony and forms a compound with it. If the whole of the antimony is combined, the ground-mass is an alloy of the third metal and tin; if some antimony remains over, the ground-mass is an antimony-tin alloy.

10 per cent. Al, 22.5 per cent. Sb, 67.5 per cent. Sn. Antimony and aluminium combine to form a compound SbAl (81.5 per cent. antimony), which solidifies at a slightly lower temperature than copper.[3] Tin and aluminium form a series of alloys in which aluminium crystallizes out in a ground-mass containing about 0.5 per cent. aluminium in solid solution. If the whole of the antimony combined with the aluminium to form SbAl, we should have left

1 *Congrès Internationale de Physique*, Paris, 1900.

2 *J. Soc. Chem. Ind.*, December, 1898, p. 1111.

3 Gautier : *Bull. de la Soc. d'Enc.*, 1896 ; Campbell and Matthews ; This Journal, 1902

a ground-mass consisting of about 6 per cent. aluminium to 94 per cent. tin. This would be composed of dendrites of aluminium set in a tin-rich ground-mass isomorphous with tin. In making the alloy, great difficulty was met with. On adding the aluminium to the molten SbSn alloy combination immediately takes place and SbAl is formed which, on account of its high melting-point, makes the alloy very gritty. Potassium cyanide must not be used as a cover, for it attacks the alloy and makes an incoherent mass. By keeping the alloy melted for some time under a cover of charcoal, good results are obtained. Fig. 11, × 38 o., shows a section of the alloy lightly etched with nitric acid. Well-defined crystals of SbAl are seen set in the ground-mass composed of dendrites of aluminium in the matrix of tin (0.5 per cent. aluminium). Deep etching and slightly repolishing reveals the structure of the ground-mass. Fig. 12, × 38 v., etched with 2 per cent. nitric acid deeply and repolished to remove oxide, shows the crystals of SbAl in relief. The dendrites of aluminium are seen, set in the tin-rich ground-mass. On exposure to the atmosphere for a few weeks the alloy disintegrates to a black powder, due to oxidation.

10 per cent. Zn, 22.5 per cent. Sb, 67.5 per cent. Sn. The fusibility curve of zinc and antimony, as given by Gautier,[1] shows a summit near 64 per cent. antimony, with two eutectic points at about 4 per cent. and about 77 per cent. antimony. This would point to the formation of a compound, probably SbZn. Three alloys were made: 10, 50 and 95 per cent. antimony. The first showed needles, rods, and grains of a compound in a well-marked eutectic ground-mass. The second showed the massive crystals of the same compounds in the eutectic, while the last showed beautiful crystals of antimony in the second eutectic. A compound is certainly formed. Tin and zinc form a simple series, with the eutectic at 8 per cent. zinc, melting at a little above 200° C. If the zinc combined with the antimony to form the compound SbZn, a ground-mass would be left containing approximately 11 per cent. antimony and 89 per cent. tin, which would show cubes of SbSn in the tin-antimony solid solution. On examining the alloy three constituents can be seen. Hard cores or crystals which stand out in relief, surrounded by a softer white constituent, the whole being surrounded by a tin-rich ground-

[1] *Bull. de la Soc. d'Enc.*, 1896, p. 1293.

mass, isomorphous with tin. The harder constituent, apparently SbZn, often occurs free and the composite crystals are larger towards the top of the alloy. Fig. 13, × 30 v., shows a part of the alloy near the top. The fact that no cubes of SbSn are seen and that the second constituent always covers the zinc-antimony compound like an envelope and, as a rule, has the same form, would suggest that it was the result of a reaction between the liquid ground-mass and solid crystals of the SbZn compound. Further work is needed on this point.

10 per cent. Cd, 22.5 per cent. Sb, 67.5 per cent. Sn. According to Kapp[1] tin and cadmium form a eutectic at 70 per cent. tin to 30 per cent. cadmium. The alloys of antimony and cadmium do not appear to have been worked out. On alloying two parts of cadmium with one part of antimony, an alloy is produced consisting of massive crystals of a compound in a small amount of eutectic with a fairly coarse structure. The eutectic is apparently that of cadmium and the compound, and the compound probably contains more cadmium than CdSb. Fig. 8, × 30 v., shows the antimony-tin alloy with 10 per cent. cadmium. The view is from the upper part of the alloy and shows cube-like forms of SbSn, with which are mixed a few short prisms and irregular laths of a pinkish constituent set in a matrix which is isomorphous with tin. There is a slight layer at the base of the alloy in which no SbSn is seen, but where the other compound occurs in the tin-rich ground-mass. It seems probable that the cadmium and antimony have combined to form the pinkish compound, but unless this is rich in cadmium the amount formed would not account for all. On the other hand, the ground-mass under high powers is seen to differ from that of the typical SbSn alloys, for it contains light-colored dots and in places needles, and etches much more lightly; it may contain cadmium in solid solution. Lastly, an alloy containing arsenic was examined.

10 per cent. As, 22.5 per cent. Sb, 67.5 per cent. Sn. When arsenic is added to tin, thick rough plates are formed. These have been found by Stead to have a composition corresponding to Sn_3As_2, while the ground-mass solidifies at 235° C. and contains a trace of arsenic in solid solution. I have been able to find no reference to the alloys of arsenic and antimony. Fig. 14, × 38 v., etched with nitric acid, shows the 10 per cent. arsenic alloy. It

[1] *Ann. Phys. Chem.* [4], **6**, 754-773 (1901).

is of whitish color, very brittle, with a beautifully crystalline fracture. The section shows light-colored plates set in a matrix, which etches like the SbSn or SnAs solid solution. The plates form a regular network and are really composed of a harder, slightly colored core surrounded by a white envelope. There is a sharp line between the two. The outer portion is SbSn. This was proved by making a diffusion alloy. The 25 per cent. antimony and 75 per cent. tin alloy was melted and well covered with potassium cyanide. Massive arsenic was carefully dropped in and when melted the whole was allowed to slowly cool. The base of the alloy was the same as the typical 25 per cent. antimony and 75 per cent. tin, but the ton was similar to Fig. 14, only coarser. On deeply etching, the cubes of SbSn were seen to pass up into and become part of the white outer constituent of the composite plates. The inner cores contain the arsenic, for they increase with the arsenic present. An alloy was made by adding arsenic to the SbSn alloy at a dull red heat until dense fumes came off. The alloy consisted of very coarse, thick plates, with very broad cores. The white envelopes were present in about the same amount as in the 10 per cent. alloy, but the ground-mass had greatly diminished, which would seem to show that the central cores were As_2Sn_3. The appearance of the envelopes of SbSn around the cores of the other constituent resembles that of the zinc alloy. They are both similar to composite crystals of Cu_3Sn and CuSn found in the copper-tin series,[1] which are caused by reaction of the mother-liquor on crystals of Cu_3Sn, which have formed at a higher temperature. In other words, they are due to imperfect equilibrium.[2] We may have such a case here, which will be ascertained when cooling curves have been obtained for these alloys.

The arsenic alloy was placed last because it is doubtful where it belongs.

The above examples show that by alloying the tin-antimony alloy with 10 per cent. of the third metal three types of structures may occur:

(1) Cubes of SbSn are found in a ground-mass of tin dendrites, surrounded by the eutectic of tin and the third metal: lead and bismuth.

[1] Campbell: *Proc. Inst. Mech. Eng.* (London), 1901. Appendix Alloys Research Committee Report.

[2] Heycock and Neville: *Phil. Trans. Roy. Soc.* (London), A **202**, 1-69.

(2) Cubes of SbSn and crystals of a compound of tin and the third metal are found set in the eutectic of tin and the second (new) compound: copper and silver.

(3) A compound of antimony and the third metal is formed; the ground-mass consists of (*a*) crystals of the third metal in its eutectic with tin: aluminum. (*b*) Crystals of SbSn and a tin-rich solid solution: zinc and perhaps cadmium.

Arsenic probably belongs to a sub-group of (2) where SbSn and crystals of a compound of tin and the third metal occur in a ground-mass, which is a solid solution of tin.

It may be that most of the eutectics are not binary, but contain the three metals; however, only two constituents apparently are revealed by the microscope.

It remains to run cooling curves on each of the alloys and as far as possible to isolate and analyze their harder crystalline constituents by which means more light would be thrown on their constitution. It is intended to expand the work by making similar series with different percentages of tin and antimony, and different amounts of the added metal, from which, it is hoped, much more may be learned of the constitution of these ternary alloys.

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THE VISCOSITY OF SOLUTIONS IN RELATION TO THE CONSTITUTION OF THE DISSOLVED SUBSTANCE.

BY ARTHUR A. BLANCHARD.

Received July 28, 1904.

WORK upon this theme was first undertaken by Mr. M. A. Stewart in the laboratories of the New Hampshire College. The method herewith described was worked out by him and was presented in June, 1903, together with a considerable amount of experimental data as a thesis for the Bachelor's degree at the above-named college. A brief account of his work was given by the author at the June, 1903, meeting of the American Chemical Society at Cleveland.[1] Since then the work has been further carried on, partly at that college and partly at the Massachusetts Institute of Technology. The author wishes to acknowledge his

[1] *Science*, **18**, 98 (July 24, 1903).