

**Chemistry.** — *On the Law of Additive Atomic Heats in Intermetallic Compounds. IX. The Compounds of Tin and Gold, and of Gold and Antimony.* By J. A. BOTTEMA and F. M. JAEGER.

(Communicated at the meeting of September 24, 1932.)

§ 1. In just the same way as in the case of the compound  $PtSn^1$ ), the question of the validity of the rule of additive atomic heats in compounds was studied in that of the compounds  $AuSn$  and  $AuSb_2$ . The alloy  $AuSn$  was prepared by carefully melting together the components, mixed in the theoretical proportion, in an atmosphere of pure hydrogen; the melting was repeated until a microscopically homogeneous mass was finally obtained. That the compound  $AuSn$  was really present, was controlled by means of  $X$ -ray-analysis<sup>2</sup>). Table I contains the data collected in this way. They prove, that the *hexagonal* compound  $AuSn$ , formerly studied by OWEN and PRESTON<sup>3</sup>), is really present here. No superstructure-lines were observed; the chemical analysis, moreover, yielded: 62.40%  $Au$  and 37.58%  $Sn$ , while the calculated values are: 62.42%  $Au$  and 37.58%  $Sn$ ; so that the preparation may be considered as being chemically pure.

The structure of the compound  $AuSn$  is evidently quite analogous to that of  $PtSn$ : the dimensions of the elementary cell:  $a_0 = 4.307 \text{ \AA}$  and  $c_0 = 5.496 \text{ \AA}$  are somewhat greater than in the case of the *platinum*-compound. If 2 molecules are present within the elementary cell, the specific gravity of  $AuSn$  is calculated to be: 11.807 at  $0^\circ \text{C.}$ ; the specific volume of the compound is about 12% smaller than the sum of the specific volumes of its components.

1) F. M. JAEGER and J. A. BOTTEMA, *Proceed. R. Acad. Sciences Amsterdam*, **35**, (1932), 352.

2) Spectrogram by J. BEINTEMA.

3) E. A. OWEN and G. D. PRESTON, *Phil. Mag.*, **4**, (1927), 133.

TABLE I. Powder-Spectrogram of AuSn.

No. of Line:	2l in m.M.:	Estim. Intens.:	Wave-length $\lambda$ :	Angle $\theta$ :	$\text{Sin}^2 \theta$ (observed):	$\text{Sin}^2 \theta$ (calculated):	Indices (hkl) or (hkil):
1	42.36	1	$\beta$	10° 35'	0.0337	0.0347	(100) = (10 $\bar{1}$ 0)
2	47.58	4	$\alpha$	11 54	0.0425	0.0426	(100) = (10 $\bar{1}$ 0)
3	52.16	1	$\beta$	13 2	0.0509	0.0506	(101) = (10 $\bar{1}$ 1)
4	57.80	4	$\alpha$	14 27	0.0623	0.0622	(101) = (10 $\bar{1}$ 1)
5	73.30	3	$\beta$	18 19	0.0988	0.0985	(102) = (10 $\bar{1}$ 2)
6	75.38	3	$\beta$	18 51	0.1044	0.1040	(110) = (11 $\bar{2}$ 0)
7	81.56	10	$\alpha$	20 23	0.1213	0.1210	(102) = (10 $\bar{1}$ 2)
8	83.98	8	$\alpha$	21 0	0.1284	0.1277	(110) = (11 $\bar{2}$ 0)
9	97.44	2	$\alpha$	24 22	0.1702	0.1702	(200) = (20 $\bar{2}$ 0)
10	99.92	1	$\beta$	24 59	0.1784	0.1783	(103) = (10 $\bar{1}$ 3)
11	103.24	2	$\alpha$	25 49	0.1897	0.1898	(201) = (20 $\bar{2}$ 1)
12	107.22	2	$\beta$	26 48	0.2033	0.2025	(202) = (20 $\bar{2}$ 2)
13	111.76	2	$\alpha$	27 56	0.2194	0.2190	(103) = (10 $\bar{1}$ 3)
14	119.92	5	$\alpha$	29 59	0.2497	0.2486	(202) = (20 $\bar{2}$ 2)
15	132.46	1	$\alpha$	33 7	0.2985	0.2979	(210) = (21 $\bar{3}$ 0)
16	134.54	1	$\beta$	33 38	0.3068	0.3066	(212) = (21 $\bar{2}$ 2)
17	136.22	2	$\alpha$	34 3	0.3135	0.3136	(004) = (00 $\bar{0}$ 4)
18	137.58	1	$\alpha$	34 24	0.3192	0.3175	(211) = (21 $\bar{3}$ 1)
19	144.16	1	$\alpha$	36 2	0.3460	0.3466	(203) = (20 $\bar{2}$ 3)
20	146.76	2	$\beta$	36 41	0.3577	0.3562	(104) = (10 $\bar{1}$ 4)
			$\alpha$			0.3593	(114) = (11 $\bar{2}$ 4)
21	151.62	5	$\alpha$	37 54	0.3773	0.3763	(212) = (21 $\bar{3}$ 2)
22	153.50	2	$\alpha$	38 22	0.3853	0.3830	(300) = (30 $\bar{3}$ 0)
23	166.62	5	$\alpha$	41 39	0.4417	0.4418	(114) = (11 $\bar{2}$ 4)
24	174.42	1	$\alpha$	43 36	0.4756	0.4743	(213) = (21 $\bar{3}$ 3)
25	176.58	1	$\alpha$	44 9	0.4852	0.4838	(204) = (20 $\bar{2}$ 4)
26	182.84	1 $\bar{}$	$\alpha$	45 43	0.5125	0.5107	(220) = (22 $\bar{4}$ 0)
27	187.38	1 $\bar{}$	$\alpha$	46 51	0.5323	0.5303	(221) = (22 $\bar{1}$ 1)
28	196.74	1 $\bar{}$	$\alpha$	49 11	0.5727	0.5729	(311) = (31 $\bar{1}$ 1)
29	205.64	2	$\alpha$	51 25	0.6111	0.6115	(214) = (21 $\bar{3}$ 4)
30	210.42	3	$\alpha$	52 36	0.6311	0.6317	(312) = (31 $\bar{4}$ 2)
31	226.18	4	$\alpha$	56 33	0.6962	0.6966	(304) = (30 $\bar{3}$ 4)
32	238.96	4	$\alpha$	59 44	0.7460	0.7482	(106) = (10 $\bar{1}$ 6)
33	242.60	1	$\alpha$	60 39	0.7598	0.7594	(402) = (40 $\bar{2}$ 2)

Radius of Camera: 57.2 m.M. Exposure: 100 m. Amp. hours.  
Wave-Length:  $\lambda_{\text{Cu}\alpha} = 1.539 \text{ \AA}$ .;  $\lambda_{\text{Cu}\beta} = 1.389 \text{ \AA}$ .  
Quadratic Equation:  $\text{sin}^2 \theta = 0.04256 (h^2 + hk + k^2) + 0.01960 . l^2$ . . . . ( $\alpha$ )  
 $\text{sin}^2 \theta = 0.03466 (h^2 + hk + k^2) + 0.01596 . l^2$ . . . . ( $\beta$ )  
Parameter of Lattice:  $a_0 = 4.307 \text{ \AA}$ .;  $c_0 = 5.496 \text{ \AA}$ . Hexagonal.

§ 2. The quantities of heat developed by 1 gramme of *AuSn* were determined in a series of measurements which proved to be reproducible within 0.1%. The results obtained were the following:

Temperature $t$ in °C.:	Final temp. $t'$ of the Calorimeter:	Quantities of heat $Q$ developed between $t$ and $t'$ :	Quantities of heat $Q_0$ developed between $t$ and 0° C.:
100°	20.3	3.1680	3.9730
190	20.7	6.7652	7.5862
219.5	20.7	7.9778	8.7988
307.7	20.7	11.6493	12.4703

At 410° C. indications were obtained of an initial melting of the compound; no measurements at temperatures exceeding 400° C. could, therefore, be made.

The quantities of heat  $Q_0$  mentioned can be very accurately expressed by the formula:

$$Q_0 = 0.039649 \cdot t - 0.1679 \cdot 10^{-6} \cdot t^2 + 0.9779 \cdot 10^{-8} \cdot t^3.$$

The true specific heats  $c_p$  of *AuSn* at each temperature can, therefore, be calculated by means of the equation:

$$c_p = 0.039649 - 0.3358 \cdot 10^{-6} \cdot t + 2.9337 \cdot 10^{-8} \cdot t^2.$$

Some values of  $c_p$  and of the molecular heats  $C_p$  of the compounds are thus calculated and, in Table III, compared with the sum  $\Sigma$  of the atomic heats of *gold* and *tin*, as deduced from previous experiments<sup>1)</sup>:

Temperature $t$ in °C.:	$c_p$ :	$C_p$ :		Diff. ( $\Sigma - C_p$ ) in %:
0°	0.03965	12.525	12.544	+ 0.15 %
100	0.03991	12.607	12.911	2.42
200	0.04075	12.873	13.406	4.25
300	0.04219	13.328	—	—
400	0.04421	13.966	—	—

<sup>1)</sup> F. M. JAEGER and J. A. BOTTEMA, loco cit.; F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA, these Proceed., 35 (1932), 772. For *gold* the values for the "molten and solidified" metal are taken, as they are given in the last mentioned paper.

Just as in the case of *PtSn*, the sum  $\Sigma$  of the atomic heats of the components here appeared to be *greater* than the molecular heats actually observed: the differences are, also in this case, augmenting with an increase of the temperature. (Fig. 1).

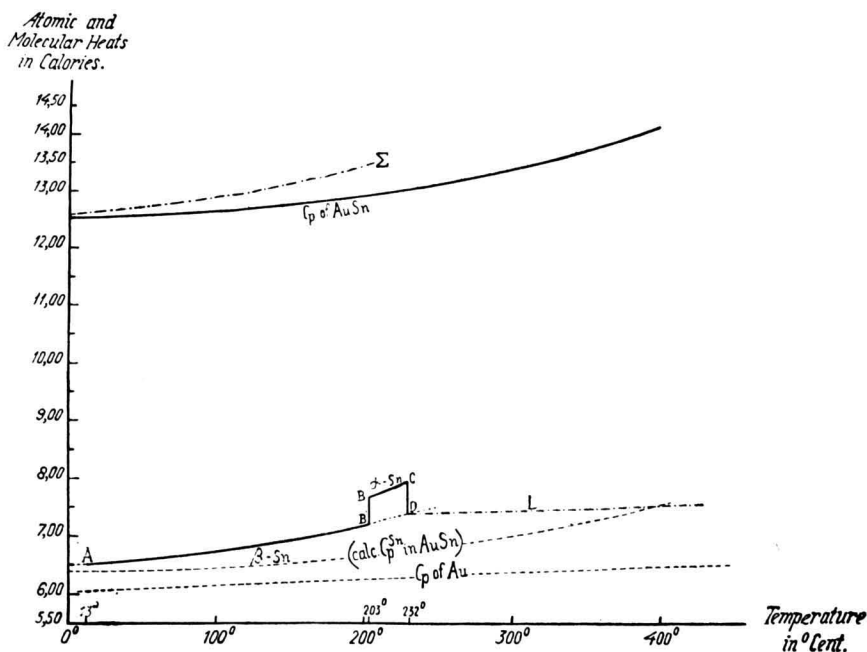


Fig. 1

If however, the values of the atomic heats of *gold* are subtracted from the molecular heats  $C_p$  of the compound, the (virtual) values of the atomic heats of *tin*, as present in the compound, no longer show any analogy with those of *grey tin*, — as was emphasized in the case of the *platinum*-compound. These virtual values  $C_p^{Sn}$  prove to be much higher than in the previous case, although much lower than those for tetragonal *tin* at the same temperatures:

$t$ :	$C_p^{Sn}$ (virt.) :
0 $^{\circ}$	6.382
100	6.415
200	6.612
300	6.980
400	7.529

They are represented by a *continuous* curve which starts at  $0^\circ$  with a value of  $C_p^{Sn}$ , which is somewhat lower than  $C_p$  for tetragonal *tin*; it ends at  $400^\circ$  C. with a value which is about equal to the corresponding value of  $C_p$  for liquid *tin* at these temperatures and the curve is convex towards the axis of the temperatures.

These data prove that the specific heats of *tin* in the compound *AuSn* have values which are *completely different* from those in *PtSn* and also, that their dependence on the temperature is quite an other than in the case previously studied. Notwithstanding the perfect analogy between the crystallographical structures of *PtSn* and *AuSn*, the substitution of *Pt*-atoms in the lattice by *Au*-atoms evidently causes a quite different way of thermal oscillation of the *tin*-atoms present in these two cases. The law of NEUMANN-KOPP, etc., however, is here followed no more than in the previous case; the deviations are, as well with *AuSn*, as with *PtSn*, situated in *the same* direction, but they are smaller in the first, than in the second case.

§ 3. The behaviour of *AuSb<sub>2</sub>*, however, is a much more complicated one.

This compound was prepared by melting together the theoretical quantities of the components in an atmosphere of pure, dry hydrogen, and by tempering and re-melting the mass obtained, till a homogeneous product finally was produced. The analysis yielded: 44.72% *Au* and 55.22% *Sb*; calculated: 44.74% *Au* and 55.26% *Sb*. An *X-ray-analysis* gave the results collected in Table IV; the powder-spectrogram appeared to be identical with that obtained by OFTEDAL<sup>1)</sup> and did not show any extra diffraction-lines. The compound possesses a *pyrite*-structure; the simple cubic cell has an edge:  $a_0 = 6.636 \text{ \AA}$  and contains 4 molecules *AuSb<sub>2</sub>* pro cell. The space-group is evidently  $T_H^6$ .

§ 4. A sample weighing 22.5578 grammes was included within a vacuum-crucible of the usual shape; it weighed 30.2202 grammes. For the purpose of controlling the exactness of the indications of the thermocouple, the sequence of the experiments was taken quite arbitrarily, as is indicated by the numbers of the first column in Table V.

These measurements proved to be reproducible within 0.1 to 0.2% of the absolute values.

The compound *AuSb<sub>2</sub>* evidently occurs in *three* polymorphous modifications; the transformations prove to be quite reversible. From the data obtained, the first transition-temperature:  $\gamma\text{-AuSb}_2 \rightleftharpoons \beta\text{-AuSb}_2$  was calculated to be: about  $355^\circ$  C.; the second:  $\beta\text{-AuSb}_2 \rightleftharpoons \alpha\text{-AuSb}_2$  must be situated in the neighbourhood of  $405^\circ$  C.

<sup>1)</sup> I. OFTEDAL, Zeits. f. phys. Chem., **135**, (1928), 291, 296.

TABLE IV.  
Powder-Spectrogram of the Compound  $AuSb_2$ .

No. of Line:	$2l$ in m.M.:	Estim. Intens.:	Wave-length $\lambda$ :	Angle $\theta$ :	$\text{Sin}^2\theta$ (observed):	$\text{Sin}^2\theta$ (calculated):	Indices ( $hkl$ ):
1	46.46	3	$\alpha$	11° 37'	0.0405	0.0403	(111)
2	48.64	2	$\beta$	12 10	0.0444	0.0438	(200)
3	53.82	6	$\alpha$	13 27	0.0541	0.0538	(200)
4	60.06	6	$\alpha$	15 2	0.0673	0.0672	(210)
5	66.10	5	$\alpha$	16 33	0.0808	0.0807	(211)
6	68.98	2	$\beta$	17 15	0.0879	0.0876	(220)
7	76.70	5	$\alpha$	19 10	0.1078	0.1076	(220)
8	81.36	4	$\left\{ \begin{array}{l} \alpha \\ \beta \end{array} \right.$	20 20	0.1207	$\left\{ \begin{array}{l} 0.1210 \\ 0.1205 \end{array} \right.$	(300) or (221) (311)
9	90.50	10	$\alpha$	22 37	0.1476	0.1479	(311)
10	94.80	3	$\alpha$	23 42	0.1616	0.1614	(222)
11	98.78	4	$\alpha$	24 42	0.1746	0.1748	(320)
12	102.86	5	$\alpha$	25 43	0.1883	0.1882	(321)
13	111.54	1	$\beta$	27 53	0.2187	0.2190	(420)
14	114.76	1	$\beta$	28 41	0.2304	0.2300	(421)
15	121.44	1	$\alpha$	30 22	0.2556	0.2555	(331)
16	124.94	3	$\alpha$	31 14	0.2689	0.2689	(420)
17	128.34	2	$\alpha$	32 5	0.2821	0.2824	(421)
18	131.86	2	$\left\{ \begin{array}{l} \alpha \\ \beta \end{array} \right.$	32 58	0.2961	$\left\{ \begin{array}{l} 0.2958 \\ 0.2957 \end{array} \right.$	(332) (333) or (511)
19	138.50	2	$\alpha$	34 37	0.3227	0.3227	(422)
20	145.42	1	$\left\{ \begin{array}{l} \alpha \\ \beta \end{array} \right.$	36 21	0.3513	$\left\{ \begin{array}{l} 0.3496 \\ 0.3504 \end{array} \right.$	(431) or (510) (440)
21	148.16	8	$\alpha$	37 2	0.3627	0.3630	(333) or (511)
22	154.32	2	$\alpha$	38 35	0.3889	0.3899	(432) or (520)
23	157.58	2	$\alpha$	39 24	0.4029	0.4034	(521)
24	163.82	5	$\alpha$	40 57	0.4296	0.4303	(440)
25	172.72	2	$\left\{ \begin{array}{l} \alpha \\ \beta \end{array} \right.$	43 11	0.4683	$\left\{ \begin{array}{l} 0.4706 \\ 0.4709 \end{array} \right.$	(531) (533)

TABLE IV. (Continued).  
Powder-Spectrogram of the Compound  $AuSb_2$ .

No. of Line:	2l in m.M.:	Estim. Intens.:	Wave length $\lambda$ :	Angle $\theta$ :	$\text{Sin}^2\theta$ (observed):	$\text{Sin}^2\theta$ (calculated):	Indices (hkl):
26	175.86	2	$\alpha$	43° 58'	0.4820	0.4841	(442) or (600)
27	182.00	2	$\alpha$	45 30	0.5087	0.5109	(532) or (611)
28	188.34	2	$\alpha$	47 5	0.5363	0.5378	(620)
29	197.54	3	$\alpha$	49 23	0.5762	0.5782	(533)
30	200.80	1	$\left\{ \begin{array}{l} \alpha \\ \beta \end{array} \right.$	50 12	0.5903	$\left\{ \begin{array}{l} 0.5916 \\ 0.5914 \end{array} \right.$	(622) (552), (633), or (721)
31	203.62	1	$\alpha$	50 54	0.6023	0.6051	(542) or (630)
32	213.52	2	$\left\{ \begin{array}{l} \alpha \\ \beta \end{array} \right.$	53 23	0.6442	$\left\{ \begin{array}{l} 0.6454 \\ 0.6461 \end{array} \right.$	(444) (553) or (731)
33	233.50	2	$\alpha$	58 22	0.7249	0.7261	(552), (633), or (721)
34	240.64	3	$\alpha$	60 10	0.7525	0.7530	(642)
35	251.38	6	$\alpha$	62 51	0.7918	0.7933	(553) or (731)

Radius of Camera: 57.2 m.M. Exposure: 100 m. Amp. hours.  
Wave-Length: = 1.539 Å.; = 1.389 Å.  
Quadratic Equations:  
 $\text{sin}^2 \theta = 0.013446 \cdot (h^2 + k^2 + l^2) \dots \dots \dots (\alpha)$   
 $\text{sin}^2 \theta = 0.010951 \cdot (h^2 + h^2 + l^2) \dots \dots \dots (\beta)$   
Parameter of the Lattice:  $a_0 = 6.636 \text{ \AA.}$  Simple cubic cell.

Special experiments were made to fix these transition-temperatures more accurately: in a block of ATCHESON-graphite two big holes were bored, parallel and very close to each other; the one was filled with purest *silver*, the other with the compound in a sufficient quantity and two thermocouples were inserted into the two masses. Then the furnace was slowly heated, with a gradient of about 1.1° C. pro minute. The first transition:  $\gamma$  - modification  $\rightleftharpoons$   $\beta$  - modification proved to be a rather rapid one; the heat-effect is only small, but the temperature of inversion could be very accurately fixed at 2830 M.V. (corrected), i. e. at 355.2° C. The inversion  $\beta$  - modification  $\rightleftharpoons$   $\gamma$  - modification seems to be very sluggish; there is a temperature-interval and it proved impossible accurately to determine the temperature of transition in this way.

The amounts of heat developed in the calorimetric measurements are very well expressed by the following equations:

TABLE V.

No. of the Experim. :	Temperature $t$ in °C :	Final temp. $t'$ of the Calorim. :	$Q$ in calor. between $t$ and $t'$ :	$Q_0$ in calor. between $t$ and 0° C. :	$Q_0$ (calcul.) :
1	190°	20.6	7.2587	8.1373	$\gamma$ —
2	250.8	20.63	9.8880	10.7679	$\gamma$ 10.7788
3	280.8	20.8	11.2219	12.1090	$\gamma$ —
5	316.8	20.75	12.8518	13.7368	$\gamma$ —
6	354.14	21.00	14.5350	15.4307	$\gamma$ 15.4705
9	404.37	21.11	17.3006	18.2009	$\beta$ —
8	378.73	20.97	16.1741	17.0685	$\beta$ —
7	365.51	21.20	15.3150	16.2192	$\beta$ —
4	315.53	20.47	12.8027	13.6758	$\gamma$ 13.6789
12	439.47	20.86	19.5241	20.4138	$\alpha$ —
10	419.80	20.90	18.1417	19.0331	$\alpha$ —
11	430.51	21.23	18.7737	19.6792	$\alpha$ —

$\gamma$ -Modification:  $Q_0 = 0.043626 \cdot t - 0.94532 \cdot 10^{-5} \cdot t^2 + 0.26521 \cdot 10^{-7} \cdot t^3$ .

$\beta$ -Modification:  $Q_0 = -0.169785 \cdot t + 0.11007 \cdot 10^{-2} \cdot t^2 - 0.14084 \cdot 10^{-5} \cdot t^3$ .

$\alpha$ -Modification:  $Q_0 = 0.45389 \cdot t - 0.195633 \cdot 10^{-2} \cdot t^2 + 0.23419 \cdot 10^{-5} \cdot t^3$ .

From this, the true specific heats  $c_p$  and the molecular heats  $C_p$  can be calculated to be:

$\gamma$ -Modification:  $c_p = 0.043626 - 0.189064 \cdot 10^{-4} \cdot t + 0.79563 \cdot 10^{-7} \cdot t^2$ .

$\beta$ -Modification:  $c_p = -0.169785 + 0.22014 \cdot 10^{-2} \cdot t - 0.42252 \cdot 10^{-5} \cdot t^2$ .

$\alpha$ -Modification:  $c_p = 0.45389 - 0.39127 \cdot 10^{-2} \cdot t + 0.70257 \cdot 10^{-5} \cdot t^2$ .

The first formula is valid between 150° C. and 355° C.; the second between 360° and 405° C.; the third between 415° C. and 450° C.

In Table VI some values of  $c_p$  for the different modifications are collected; (see following page).

The values of  $c_p$  for the  $\beta$ -modification appear to decrease with the temperature within the interval of 355° — 405° C.

In Table IX a series of the values of  $C_p$  for different temperatures  $t$  are thus calculated and compared with the sum  $\Sigma$  of the atomic heats of gold and antimony ( $2 \times$ ), as deduced from the corresponding measurements.



TABLE VI.  
Specific Heats  $c_p$  of the Compound  $AuSb_2$ .

Temperature $t$ in °C.:	Specific Heat $C_p$		
	$\gamma$ -Modification:	$\beta$ -Modification:	$\alpha$ -Modification:
150°	0.04258	—	—
200	0.04303	—	—
250	0.04388	—	—
300	0.04509	—	—
350	0.04673	—	—
360	—	0.07513	—
370	—	0.06631	—
380	—	0.05663	—
390	—	0.04612	—
400	—	0.03475	—
420	—	—	0.04988
430	—	—	0.07054
440	—	—	0.09244
450	—	—	0.1159

§ 5. *Antimony*. The calorimetric measurements necessary for the exact determination of the specific heats of *antimony* were executed with a massive, previously stabilized lump of the pure element, brought into the shape of our usual vacuum-crucibles and weighing 59.492 grammes. The data obtained (in the sequence of the experiments as indicated in the first column) are collected in Table VII.

TABLE VII  
Specific Heats  $c_p$  of Antimony at Different Temperatures.

No. of Experim.	Temperature in °C.:	Final temp. $t'$ of Calori- meter:	Quantity of Heat $Q_0$ devel. between $t$ and $t'$ :	Quantity of Heat $Q$ devel. betw. $t^0$ and $0^0$ :	$Q'_0$ as cal- culated from the formulae:
1	233.35	21.36	10.822	11.886	—
2	324.85	21.67	15.632	16.711	—
4	386.00	21.57	18.055	19.129	—
3	411.46	21.95	20.609	21.702	21.699
8	415.00	21.16	20.633	21.687	—
7	418.20	21.04	20.771	21.819	21.799
6	424.8	21.70	20.957	22.037	—
5	440.10	22.10	21.932	23.033	—

The element evidently has a transformation-point<sup>1)</sup> in the neighbourhood of 413° C., although we were not able to fix this temperature more exactly by means of the thermal method.

The quantities of heat  $Q_0$  mentioned can very satisfactorily be expressed by the equations:

$$\beta\text{-Modification: } Q_0 = 0.0535656 \cdot t - 0.233176 \cdot 10^{-4} \cdot t^2 + 0.051656 \cdot 10^{-6} \cdot t^3.$$

$$\alpha\text{-Modification: } Q_0 = 0.534496 \cdot t - 0.2261 \cdot 10^{-2} \cdot t^2 + 0.2648 \cdot 10^{-5} \cdot t^3.$$

The first formula is valid between 150° and 411° C., the second above 413° C.

The true specific heats of *antimony*, therefore, can, within the intervals of temperatures indicated, be calculated by means of the formulae:

$$\beta\text{-Modification: } c_p = 0.0535656 - 0.46635 \cdot 10^{-4} \cdot t + 0.15497 \cdot 10^{-6} \cdot t^2.$$

$$\alpha\text{-Modification: } c_p = 0.534496 - 0.4522 \cdot 10^{-2} \cdot t + 0.7944 \cdot 10^{-5} \cdot t^2.$$

In Table VIII a survey is given of a series of values  $c_p$  and  $C_p$  at different temperatures.

Temperature $t$ in °C.:	$c_p$ of the $\beta$ -Modifi- cation:	$C_p$ of the $\beta$ -Form.:	Temperature $t$ in °C.:	$C_p$ of the $\alpha$ -Modifi- cation:	$c_p$ of the $\alpha$ -Form:
150°	0.05006	6.017	415°	0.02600	3.125
200	0.05044	6.063	420	0.03656	4.394
250	0.05159	6.201	430	0.06217	7.473
300	0.05352	6.433	440	0.08274	9.945
350	0.05623	6.759	450	0.1082	13.005
400	0.05971	7.177	460	0.1354	16.270
411.5	0.06062	7.286			

Most remarkable is the rapid increase of  $c_p$  with the temperature above 413° C. The data for  $C_p$  are graphically represented in Fig. 2; the same break was also found in the curve representing the dependency of the *mean* specific heats  $\bar{c}_p$  on the temperature:

<sup>1)</sup> It may be remarked in this connection, that in the Physical Laboratory of this University recently such a transformation-point was found, by means of X-ray-analysis at higher temperatures, in the case of the quite analogously built *bismuthum*. (Private communication by Prof. COSTER).

Between $t$ and $t'$ :	Mean Specific Heats $\bar{c}_p$ :
233.35	0.05105
324	0.05156
368	0.05212
411	0.05291
415	0.05239
418	0.05230
424.8	0.05199
440.1	0.05247

In fairly good agreement with this are the values of the mean specific heats  $\bar{c}_p$  given in the literature <sup>1)</sup> between 100° and 20° C. ( $\bar{c}_p = 0.05037$ ). In Fig. 2 a curve indicated by *Sch* gives the values of  $C_p$  as calculated

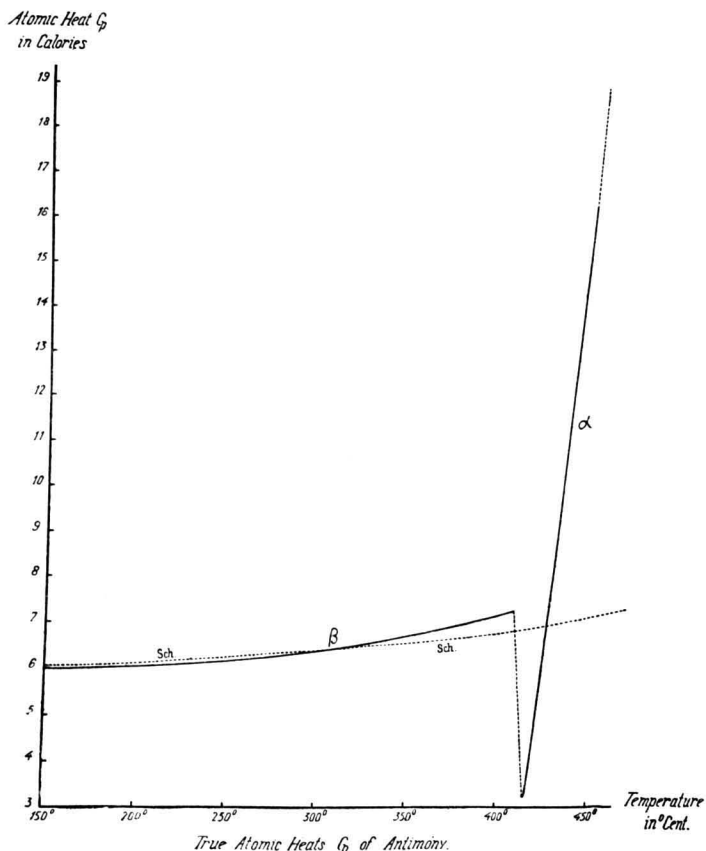


Fig. 2.

<sup>1)</sup> J. A. LINNAVUOP, Soc. Scient. Fenn. Comm. 1, (10), (1922); P. SCHÜBEL, Zeits. f. anorg. Chem. 87, (1914), 81; H. SCHIMPF, Zeits. f. phys. Chem., 71, (1910), 257. The most probable value of  $c_p$  between 100° and 20° C. is: 0.0503; between 20° and 0° C.: 0.0498.

by SCHÜBEL (*loco cit.*), from which it may be seen that the true dependence of  $C_p$  on  $t$  is rather different from that indicated by this author.

§ 6. With the aid of the values for the atomic heats of *antimony* (and *gold*) thus determined, we are now able to compare the sum  $\Sigma$  of these atomic heats at different temperatures with the molecular heats  $C_p$  directly observed. The results are collected in Table IX and in Fig. 3 they are graphically plotted against the temperatures  $t$ .

TABLE IX.						
Temperature in °C.:	Atomic Heats $C_p$		Sum of the Atomic Heats of $Au + 2Sb$ :	Observed Molecular Heat $C_p$ of $AuSb_2$ :	Difference ( $\Sigma - C_p$ ) in %:	
	Gold:	Antimony:				
150°	6.228	6.017	18.262	18.633	} $\gamma$	- 2.03
200	6.261	6.063	18.387	18.830		- 2.40
250	6.298	6.201	18.700	19.202		- 2.68
300	6.340	6.433	19.206	19.731		- 2.73
350	6.386	6.759	19.904	20.458		- 2.78
360	6.396	6.835	20.066	32.877	} $\beta$	- 63.3
370	6.406	6.915	20.236	29.017		- 43.3
380	6.416	6.999	20.414	24.782		- 21.4
390	6.426	7.085	20.596	20.182		- 2.0
400	6.437	7.177	20.791	15.206		+ 26.9
415	6.453	3.125	12.703	(20.20)	} $\alpha$	(- 59.0)
420	6.458	4.394	15.246	21.828		- 43.1
430	6.469	7.473	21.415	30.868		- 44.1
440	6.481	9.945	26.371	40.452		- 53.4
450	6.482	13.005	32.492	50.705		- 56.0

Contrary to the previous cases of  $PtSn$  and  $AuSn$ , the deviations from the rule of additive atomic heats here are situated in the *opposite* direction: the observed molecular heat of the compound, in all its modifications, proves always to be *greater* than the sum of the atomic heats of its components at the same temperature.

Only for the  $\gamma$ -modification of  $AuSb_2$ , however, it is still possible really

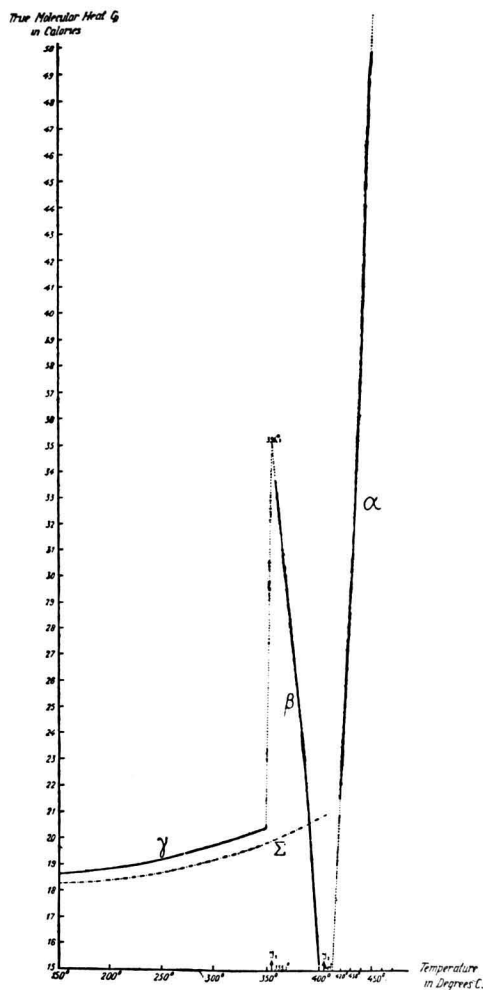


Fig. 3

volumes of their components on the one hand, and between the algebraic sign of the deviations ( $\Sigma - C_p$ ) from the rule of the additive atomic heats on the other hand, — as suggested by TAMMANN and ROHMANN<sup>1)</sup>, — could not be stated.

Groningen, Laboratory for Inorganic and Physical  
Chemistry of the University.

<sup>1)</sup> G. TAMMANN and A. ROHMANN, *Zeits. f. anorg. Chem.*, **190**, (1930), 227.

to compare the two sets of values: as well for the  $\beta$ -, as for the  $\alpha$ -modifications the two series of numbers prove to be *completely incomparable*, with the exception of a value in the vicinity of  $400^\circ$  and of one in the neighbourhood of  $393^\circ$  C. ( $\beta$ -modification, -which, however, represents a purely accidental coincidence. The behaviour of the  $\beta$ -modification in this respect convincingly illustrates the important fact, that even an approximating validity of the rule of additive atomic heats may completely disappear by the occurrence of a polymorphous transformation; so that evidently a change in the crystal-line structure can, in this respect, have a rather catastrophic influence.

The facts mentioned are graphically represented in Fig. 3; they show a slow increase of the deviations with the temperature. A definite relationship between an occurring increase or diminution of the specific volume in the formation of the compounds  $PtSn$ ,  $AuSn$  and  $AuSb_2$ , compared with the sum of the atomic