

is evident that the absolute values of the differences Δ here indicated have only a restricted significance. As could beforehand be expected at these low temperatures and within their short interval of only 200° to 600° C., — the deviations from the additive law observed are only small. They regularly increase with the quantity of *palladium* in the compounds and their correspondingly increasing meltingpoints: they are *greatest* for Pd_3Sb (from 3—6 %) and *negative; smallest* and almost unappreciable for $PdSb_2$ (from 1,5—2 %, with a maximum at 400° C. and with an oscillating algebraic sign) ¹⁾. For $PdSb$ they also are *negative* and vary from 1 %—4 %. As was observed in all previous cases, also here the differences Δ prove to be a *function of the temperature*, — in so far as they clearly augment with increasing temperatures, especially above 500° or 600° C. An analogous comparison is excluded in the case of the α -modification of Pd_3Sb , because its transformation-temperature (about 950° C.) is higher than the melting-point of *antimony*.

¹⁾ In connection with the experience made in the case of $CuPd$, the possibility exists, that also in the case of $PdSb_2$ a kind of transformation into solid solutions may be the real cause of this behaviour.

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Chemistry. — *The Exact Measurement of the Specific Heats of Solid Substances at Higher Temperatures. XXI. On the Molecular Heats of the Compound $PtSb_2$ in Comparison with the Sum of the Atomic Heats of the free composing Elements.* By T. J. POPPEMA and F. M. JAEGER.

(Communicated at the meeting of September 28, 1935).

§ 1. In the binary system: Pt — Sb , FRIEDRICH and LEROUX ¹⁾ stated the occurrence of a compound $PtSb_2$, showing a congruent meltingpoint at 1226° C.; its crystalstructure (*pyrite*-type) was afterwards determined by THOMASSEN ²⁾. Moreover, they proved the occurrence of a compound: Pt_5Sb_2 in the solid mass, this being generated in it at about 683° C. and stable at lower temperatures. The existence of a compound $PtSb$, melting at about 1050° C. under decomposition, is still problematic, as the phenomena observed may as well be interpreted by assuming a formation of mixed crystals. For this reason, we have, in the present paper, confined ourselves to the study of the compound $PtSb_2$ only.

§ 2. The specific heats of this substance were measured in the usual way, 22,858 grammes of it being enclosed within a vacuum crucible of

¹⁾ K. FRIEDRICH and A. LEROUX, *Die Metallurgie*, 6, (1909), 1.

²⁾ L. THOMASSEN, *Zeits. f. phys. Chem.*, B 2, (1929), 349.

platinum, weighing 29,620 grammes. As the meltingpoint of *antimony* is 629° C., the measurements were not continued above that temperature, — a comparison with the atomic heats of the composing elements at higher temperatures being beforehand excluded. The maximum temperature of the calorimeter in this case was reached in 4—5 minutes after the moment of dropping the sample into the instrument; the normal course of the latter was reached within 1 hour since that moment.

The data obtained are collected in the following table; as the most probable value of \bar{c}_p between 0° and 20° C., $\bar{c}_p = 0,03830$ was used.

The quantity of heat delivered by 1 gramme of the substance between t° and 0° C. can very well be expressed by means of the equation:

$$Q_0 = 0,03820 \cdot t + 0,66248 \cdot 10^{-5} \cdot t^2 - 0,26254 \cdot 10^{-8} \cdot t^3.$$

The true specific heats c_p , therefore, by:

$$c_p = 0,03820 + 0,132496 \cdot 10^{-4} \cdot t - 0,78762 \cdot 10^{-8} \cdot t^2,$$

and the molecular heats C'_p by the formula:

$$C'_p = 16,6400 + 0,577143 \cdot 10^{-2} \cdot t - 0,35108 \cdot 10^{-5} \cdot t^2.$$

No. of the Experiment:	Temperature t in °C.:	Final temperature t' of the Calorim.:	Increase of the temperature Δt of the Calorimeter in M.V.:	Quantity of Heat Q_0 set free by 1 Gr. of the substance in Cal.:	Mean specific Heats \bar{c}_p between t° and 0° C.:
1	406.94	21.697	915.2	16.474	0.04048
2	500.31	21.855	1146.1	20.423	0.04082
3	310.15	21.695	678.0	12.412	0.04002
4	196.69	21.627	405.6	7.740	0.03935
5	196.76	21.520	406.4	7.757	0.03942
6	407.04	21.728	914.6	16.464	0.04045
7	600.43	22.077	1398.5	24.743	0.04121
8	600.57	21.920	1400.1	24.778	0.04126

§ 3. Some of the values of C'_p thus calculated are, in the following table, compared with the sum Σ of the atomic heats of the free elements at the same temperatures, — for *antimony* as well the values A as B ¹⁾ being

¹⁾ For *antimony*, conf. these Proceed. 38, (1935), 822—833; for *platinum*: F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA, Rec. d. Trav. d. Chim. d. Pays Bas, 52, (1933), 70—74.

taken into account. The differences: $\Delta = (C'_p - \Sigma)$, — also in percents, — are simultaneously indicated in the last column.

Temperature t in $^{\circ}\text{C}.$:	Molecular Heats C'_p observed:	Sum Σ		$(C'_p - \Sigma)$		Differences Δ in Percents	
		A:	B:	A:	B:	A:	B:
100 $^{\circ}$	(17.1820)	18.198	18.572	(-1.016)	(-1.390)	(-5.91 $^{\circ}/_0$)	(-8.09 $^{\circ}/_0$)
200	17.6570	18.660	18.964	-1.003	-1.307	- 5.68	- 7.40
300	18.0626	19.272	19.554	-1.209	-1.491	- 6.69	- 8.25
400	18.3996	20.034	20.341	-1.634	-1.941	- 8.89	-10.55
500	18.6679	20.946	21.326	-2.278	-2.658	-12.20	-14.24
600	18.8677	22.005	22.506	-3.137	-3.638	-16.62	-19.29

From these data (Fig. 1) it can be concluded, that the deviations from the "law" of NEUMANN-KOPP-REGNAULT in this case are really *enormous*

*Atomic and Molecular Heats
in Calories.*

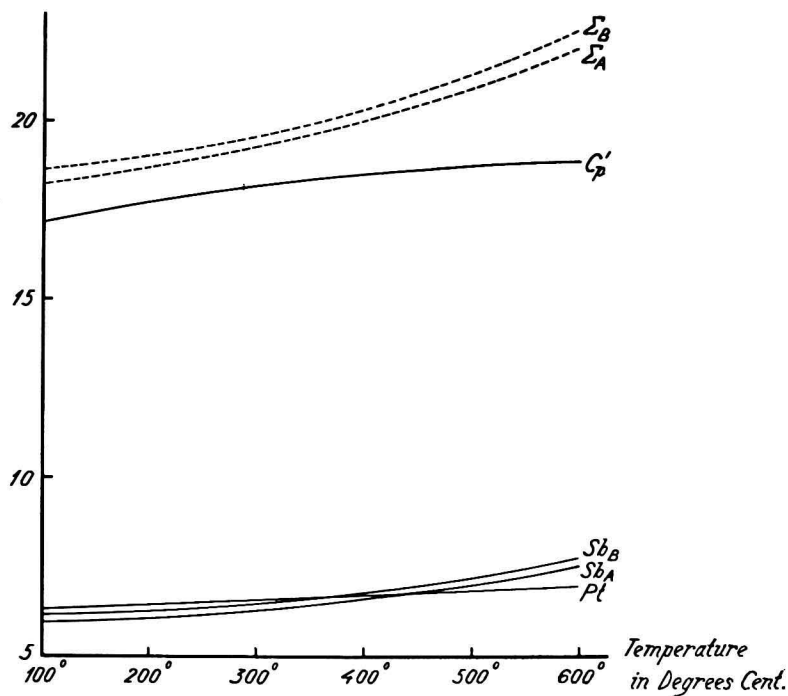


Fig.1. Deviations from the Additive Law for PtSb_2 .

and *negative*; a fact which surely is connected with the rather feeble variation of the specific heat of the compound in relation to the temperature in comparison with that of the free components. They are, as in all previous

cases, a function of the temperature and here they augment with great and gradually growing rapidity with increasing temperature, varying between 200° and 600° C. from 6—8 % to 17—19 %; i.e. much more rapidly than in the case of the alloys of *palladium* and *antimony*, as well as in all other cases of intermetallic compounds hitherto investigated.

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Chemistry. — *The Exact Measurement of the Specific Heats of Solid Substances at Higher Temperatures. XXII. The Molecular Heats of the supposed Binary Compounds of Copper and Palladium.* By T. J. POPPEMA and F. M. JAEGER.

(Communicated at the meeting of September 28, 1935).

§ 1. For a long time considerable uncertainty has been present as to the occurrence of binary compounds in the system: *Cu—Pd*. *Copper* and *palladium* at higher temperatures form an uninterrupted series of solid solutions¹⁾; but, as later investigations²⁾ have proved beyond doubt, by heating below their meltingpoints and by careful and repeated annealing during a long time and slow cooling, within certain limits of concentration the compounds: *CuPd* and *Cu₃Pd* are separated out from these mixed crystals in the solid phase. Their existence in carefully tempered preparations has been established as well by the study of their crystalline structure by means of *X*-rays, as by that of the thermoelectric properties and of the thermal and electrical conductivity of alloys of different composition. The compounds prove to be most stable in alloys tempered at about 400° C. and having an excess of *copper* of about 8—10 atom. proc. above that corresponding to the stoichiometrical composition of the two compounds: *PdCu* is cubic, with a bodily-centred grating (*cesiumchloride*-type) and $a_0 = 2,988$ A.U. Its density is: 10,35 and it occurs in mixtures having 40—50 atom. proc. of *palladium*. The compound *Cu₃Pd* is also cubic, but has a face-centred grating with: $a_0 = \text{about } 3,7$ A.U.; it occurs, after repeated annealing, in mixtures containing 10—30 atom. percents of *palladium* and its presence is betrayed by a strong decrease of the electrical resistance. As in our calorimetrical experiments we made use of preparations having almost the true stoichiometrical composition³⁾ and the

¹⁾ R. RUER, *Zeits. f. anorg. Chem.*, **51**, (1906), 223, 391.

²⁾ G. BORELIUS, C. H. JOHANSSON, and J. O. LINDE, *Ann. d. Phys.*, **86**, (1928), 291; S. HOLGERSSON and E. SEDSTRÖM, *Ann. d. Phys.*, **75**, (1923), 143; C. H. JOHANSSON and J. O. LINDE, *Ann. d. Phys.*, **78**, (1925), 439; **82**, (1927), 449; **86**, (1928), 291.

³⁾ Analysis yielded the following data: For the phase of the composition *CuPd*: 62,68 % *Pd* and 37,39 % *Cu*; theoretically: 62,67 % *Pd* and 37,33 % *Cu*. For *Cu₃Pd*: 36,02 % *Pd* and 64,02 % *Cu*; theoretically: 35,78 % *Pd* and 64,12 % *Cu*.