

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.

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§ 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*.

method applicated involves an almost sudden quenching of the heated material at 20° C., — it is, therefore, by no means excluded that a partial or even complete change of the composition of the preparations, — especially after heatings at temperatures above 600° C., — will set in; so that, besides the compounds, a certain portion or even the whole mass may be transformed into a solid solution of *copper* and *palladium*. This possibility must perhaps be taken into account in the interpretation of the results obtained. It may be remarked, however, in this connection, that the calorimetrical behaviour of both substances studied, appeared to be almost normal, no indication whatsoever being found of retardation-phenomena or of a lack of reproducibility of the values observed. In both cases the maximum temperature of the calorimeterblock was reached within 7 or 8 minutes and the instrument regained its normal course of cooling after 1 hour. The experiments were not continued above 900° C., because the granules of the two compounds then proved to begin to stick to the walls of the platinum crucible and thus an interaction with the platinum was to be feared on heating at still higher temperatures.

§ 2. *The supposed compound PdCu.* 16,852 grammes of the substance were enclosed in a vacuum platinum crucible weighing 29,017 grammes and the specific heats determined with the usual precautions. The results obtained are collected in Table I; for the reduction of Q_{20} to Q_0 , as the most probable value of \bar{c}_p between 0° and 20° C. we used: $c_p = 0,06580$.

Number of the Exp.	Temperature t in °C.:	Final temperature t' of the Calorimeter:	Increase of the temp. Δt of the Calorimeter in M.V.:	Quantity of Heat Q_0 delivered by 1 Gr. between t° and 0° C. in Calories:	Mean Specific Heats between t° and 0° C.:
3	196.19	21.383	459.2	13.552	0.06908
9	196.05	21.657	458.0	13.537	0.06905
4	306.77	21.535	764.8	21.780	0.07100
1	414.53	21.823	1068.2	29.966	0.07229
6	414.48	21.944	1069.6	30.039	0.07248
2	553.61	22.206	1473.0	40.986	0.07403
5	713.18	22.521	1947.9	53.821	0.07547
7	713.41	22.482	1946.9	53.761	0.07536
8	900.28	22.564	2517.3	69.090	0.07674

The quantities of heat delivered by 1 gramme of the substance between t° and 0° C. can fairly well be represented by means of the formula:

$$Q_0 = 0,065396 \cdot t + 0,20541 \cdot 10^{-4} \cdot t^2 - 0,088685 \cdot 10^{-7} \cdot t^3.$$

The true specific heats c_p , therefore, by the equation:

$$c_p = 0,065396 + 0,41082 \cdot 10^{-4} \cdot t - 0,266055 \cdot 10^{-7} \cdot t^2,$$

and the molecular heats C'_p by:

$$C'_p = 11,1346 + 0,699483 \cdot 10^{-2} \cdot t - 0,453 \cdot 10^{-5} \cdot t^2.$$

§ 3. Some of the values of C'_p thus calculated for temperatures between 200° and 900° C. are, in the following table, compared with the sum Σ of the atomic heats of *copper*¹⁾ and *palladium*²⁾ at the same temperatures. In the last column the differences: $\Delta = (C'_p - \Sigma)$ are expressed in percents.

Temperature t :	Molecular Heats C'_p :	Sum Σ :	Differences $C'_p - \Sigma$:	Δ (in Proc.):
200°	12.3524	12.638	- 0.286	- 2.0
300	12.8253	12.901	- 0.076	- 0.6
400	13.2077	13.164	+ 0.044	+ 0.3
500	13.4995	13.427	+ 0.072	+ 0.6
600	13.7007	13.691	+ 0.010	+ 0.08
700	13.8113	13.955	- 0.144	- 1.0
800	13.8313	14.222	- 0.391	- 2.8
900	13.7606	14.487	- 0.726	- 5.3

The differences Δ have an *uncertain* oscillating algebraic sign and are, moreover, *very small*, only becoming somewhat greater at temperatures above 700° C. This behaviour is quite similar to that previously stated *with mixed crystals*, — as illustrated by us in the case of the solid solutions of *gold* and *silver*³⁾. Also the fact that C'_p evidently has a maximum in the vicinity of 800° C. proves, that at least some change in the solid phase partially sets in, if it is heated at higher temperatures and then repeatedly quenched in the calorimeter. But there can be no doubt, *that the major part of the preparation consists of mixed crystals and not of the compound*

¹⁾ F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA, Rec. d. trav. d. Chim. Pays-Bas, **52**, (1933), 77.

²⁾ F. M. JAEGER and W. A. VEENSTRA, these Proceed., **37**, (1934), 280.

³⁾ F. M. JAEGER and J. A. BOTTEMA, Rec. d. Trav. d. Chim. d. Pays-Bas, **52**, (1933), 109. The absolute values of Δ in the case of *silver + gold* were somewhat smaller; a very slight admixture of the compound, — no longer detectable by the X-ray-method, — may perhaps be the cause of the greater differences in the present case.

PdCu. Indeed, the authors mentioned stated, that in preparations containing 49,8 atom. percents of *Pd*, the compound *PdCu* still appears, but in such containing 49,95 % of *Pd* the latter no longer exists. As our preparation contained a little more than 50 atom. percents of *Pd*, it is highly probable that it really consists of mixed crystals. An investigation of the original and of the heated preparation by means of *X*-rays now proved beyond any doubt, that really only the face-centred grating was present; so that it is certain that the data obtained only correspond to the solid solution and *not* to the supposed compound.

§ 4. *The supposed Compound Cu₃Pd*. 11,573 grammes of *Cu₃Pd* were enclosed in a vacuum crucible of platinum, weighing 28,090 grammes and the specific heats measured in the usual way. After 1 hour since the introduction of the sample into the calorimeter, the latter had re-assumed its normal cooling-rate. As the most probable value of \bar{c}_p between 0° and 20° C., the number: $\bar{c}_p = 0,07475$ was used. As above 900° C. there proved to be a danger that the platinum crucible became attacked, no measurements above this temperature were made.

The data obtained are collected in the following table II.

No. of the Experiment:	Temperature <i>t</i> in °C.:	Final temperature <i>t'</i> of the Calorimeter:	Increase of temperature Δt of the Calorimeter in M.V.:	Quantity of Heat Q_0 delivered by 1 gr. substance between <i>t</i> ° and 0° C. in Cal.:	Mean Specific Heats \bar{c}_p between 0° and <i>t</i> ° C.:
3	210.65	21.507	428.9	16.500	0.07833
11	210.77	21.633	429.6	16.557	0.07855
5	305.35	21.574	655.6	24.560	0.08043
10	305.41	21.681	655.0	24.530	0.08032
2	450.75	21.760	1014.9	37.480	0.08315
4	450.97	21.752	1016.2	37.549	0.08326
1	608.29	21.977	1423.1	52.438	0.08620
6	608.65	21.959	1424.7	52.519	0.08629
7	700.20	22.498	1667.6	61.496	0.08783
8	800.22	22.391	1935.5	71.221	0.08900
9	900.18	22.668	2211.4	81.387	0.09041

Between 200° and 900° C. these quantities of heat Q_0 can very well be represented by the formula:

$$Q_0 = 0,07345 \cdot t + 0,25082 \cdot 10^{-4} \cdot t^2 - 0,069444 \cdot 10^{-7} \cdot t^3.$$

The true specific heats c_p , therefore, can be calculated from the equation:

$$c_p = 0,07345 + 0,50164 \cdot 10^{-4} \cdot t - 0,208332 \cdot 10^{-7} \cdot t^2,$$

and the molecular heats C'_p by means of the formula:

$$C'_p = 21,8445 + 0,14919 \cdot 10^{-1} \cdot t - 0,6196 \cdot 10^{-5} \cdot t^2.$$

§ 5. Some of the values of C'_p thus calculated for a series of temperatures are here compared with the sum Σ of the atomic heats of the free elements measured at the same temperatures and the values of $(C'_p - \Sigma)$ indicated; these differences Δ , expressed in procents, are given in the last column. The behaviour of this compound in comparison with the former, is graphically represented in the figure 1.

*Atomic and Molecular Heats
in Calories.*

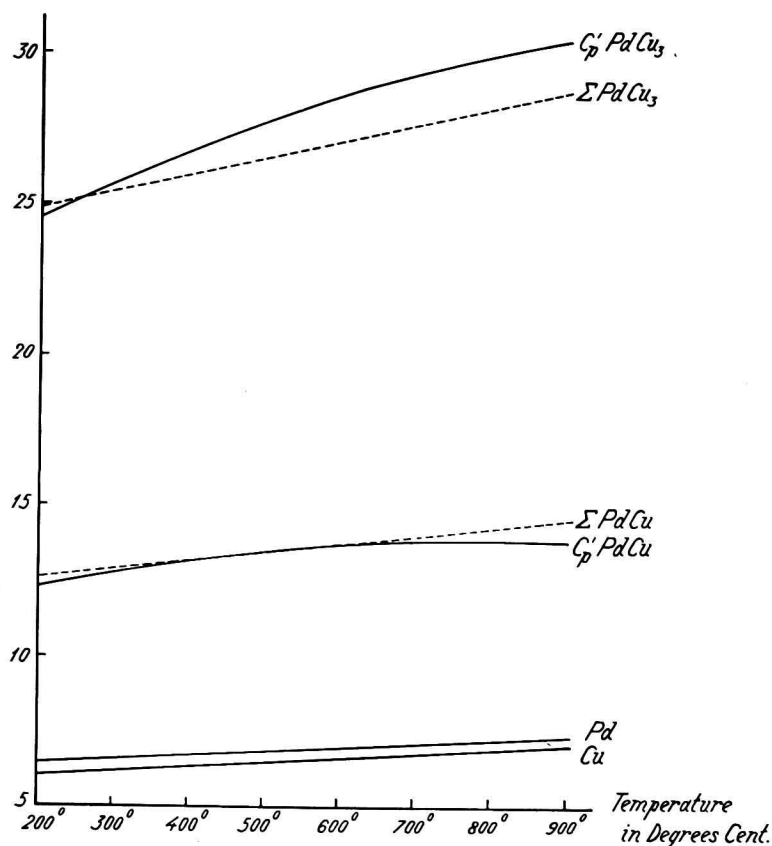


Fig.1. Deviations from the Additive Law for PdCu and PdCu₃.

The differences Δ are here *positive*, — with the exception of the value for the lowest temperature of 200° C.; they regularly increase with increasing temperature to a maximum of 5.7 %, which is reached at 700°—800° C., — just as in the preceding case, where also this temperature seemed to be a particular one with respect to values of the molecular heats C'_p themselves.

Temperature t in °C.:	Molecular Heats C'_p :	Sum Σ :	$(C'_p - \Sigma)$	Differences Δ in Percents:
200°	24.580	24.941	− 0.361	− 1.4 %
300	25.763	25.468	+ 0.295	+ 1.14
400	26.821	25.996	+ 0.825	+ 3.07
500	27.755	26.524	+ 1.231	+ 4.43
600	28.565	27.053	+ 1.512	+ 5.29
700	29.252	27.582	+ 1.670	+ 5.71
800	29.814	28.113	+ 1.701	+ 5.70
900	30.253	28.644	+ 1.609	+ 5.32

A *Roentgen* analysis of the original and finally of the repeatedly heated preparations proved, that no real difference between them existed: the powerspectrograms in the two cases show the typical characteristics of those to be expected in the case of solid solutions between the components. No super-structure lines whatsoever could be detected. It seems, therefore, that from this fact we must conclude, that also in this case *no* true compound, or only in unappreciable quantity, was present in the alloy studied. The results of the calorimetrical measurement thus chiefly seem to refer to solid solutions. As well from the maximum of the procentual deviations observed at about 800° C., as from the change of their algebraic sign between temperatures as low as 200°—300°-C., suspicion can, however, arise as to the presence, — be it in only very small amounts, — of the compound Cu_3Pd amongst the excess of mixed crystals. This fact perhaps may in some way be connected with the for mixed crystals rather exceptionally high procentual values of Δ and, on the other hand, with the rapid increase of the specific heats of the alloy with augmenting temperatures, when compared with that in the case of the pure components.

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