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THERMODYNAMICS OF ALLOYS

Studies of Palladium-Copper-Silver
and Palladium-Indium Alloys.

Final Technical Report

by

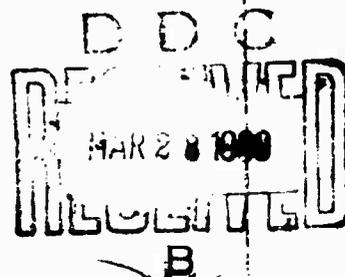
J.N. PRATT, A.W. BRYANT & W.G. BUGDEN

November 1968

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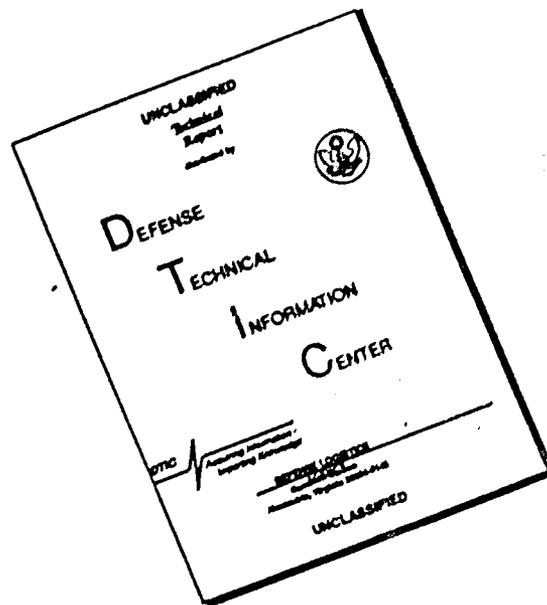
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Synopsis

Reversible galvanic cells employing zirconia-calcia solid electrolytes have been used to investigate the thermodynamic properties of the f.c.c. solid solutions of the ternary system palladium-copper-silver. Measurements have been made between 870 and 1250°K over a wide range of compositions and the data used to calculate activities of copper and integral free energies of formation of the entire range of ternary alloys at 1000°K. The results are discussed in terms of the influence of electronic (d-band filling) and misfit effects.

Tin solution calorimetry has been used to measure the heats of formation of solid palladium-indium alloys. Values are reported for the palladium-rich f.c.c. solid solution and for the intermediate phases Pd_3In , Pd_2In , Pd_5In_3 , $PdIn$, Pd_2In_3 and $PdIn_3$. The system is observed to be extremely exothermic in character. This is considered to be due to electron transfer to the subvalency transition metal electron levels which contributes a large heteropolar component to the bonding in the intermediate phases. The phase $PdIn$ has been investigated in detail; the occurrence of defect structures is indicated.

New measurements are reported of the heats of solution of palladium and indium in liquid tin.

1. INTRODUCTION

The thermodynamic properties of transition metal alloys are of considerable technological and fundamental interest and the work reported here is a continuation of the programme of experimental studies¹⁻⁶ investigating the influence of electronic structure, atomic size and other component characteristics upon these properties. Because of the comparative simplicity and reasonably well established state of the electronic structure of palladium, attention continues to be directed principally towards alloys of this element with others from the B-sub-groups. Past investigations have been mainly confined to binary solid solutions, but the field of studies is now being extended to ternary solutions and intermediate phases in an effort to provide a further resolution of the role of the various alloying factors. The present report describes measurements on ternary palladium-copper-silver alloys, made using the solid oxide electrolyte e.m.f. technique⁷, and tin solution calorimetric measurements over the complete composition range of the palladium-indium alloy system.

2. EXPERIMENTAL DETAILS

The apparatus and experimental procedures employed are identical with those used in previous studies in this research programme. In the e.m.f. studies the solid electrolyte (calcia stabilized zirconia) has again been employed in the form of small crucibles and the cells established under an atmosphere of purified argon. The solution calorimetry has again been performed using an isoperibol calorimeter of

a design similar to that of Orr, Goldberg and Hultgren⁸. Full details of both experimental techniques may be found in previous reports and publications^{6,9}.

For the present work alloys were prepared from 99.999% pure palladium, copper, silver and indium. Approximately 2g. samples were obtained by direct combination of the pure components by H.F. induction melting under argon in sealed silica capsules. The resulting ingots were homogenised by annealing, after heavily cold-working where possible, in argon-filled silica capsules for approximately 14 days or until equilibrium was obtained. Annealing temperatures were approximately 1150°C for palladium-rich alloys or 50° below the solidus elsewhere. In the case of palladium-indium phases undergoing high temperature transformations, the anneals were performed at the highest temperatures consistent with the stability of the phase. Compositions were checked by weighing and occasional chemical analysis and phase equilibria were confirmed by metallographic and x-ray examination.

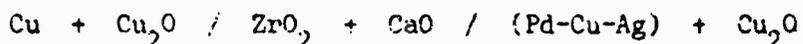
For the e.m.f. studies, filings were prepared from the homogenised Pd-Cu-Ag alloy ingots and, after washing and drying, mixed with Cu₂O powder before compression in a die to prepare the electrode tablets. Preparation of Pd-In alloys for solution calorimetry depended on mechanical properties. The malleable solid solutions (5,10,15% In) were rolled to thin strip, while the harder intermediate phase alloys were crushed to provide coarse powder. Cold work was removed from the strip and powder specimens by annealing at 900°C or below the solidus or other

transformation temperature for approximately 45 minutes. Samples of the strip were formed into small coils, while powder samples were enclosed in small thin-walled capsules of pure tin to provide suitable samples for use in the calorimeter.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. The Palladium-Copper-Silver System

Measurements were made on reversible galvanic cells of the form



37 single - or two-phase solid solution alloys, representing a fairly complete range of ternary compositions, were investigated at temperatures between 600 and 950°C. The observed cell potentials (E) showed near linear temperature dependence and may be satisfactorily expressed by equations of the form

$$E \text{ (mV)} = E_0 + T dE / dT$$

where T is the cell temperature in °K; the experimental e.m.f. data summarised in this manner are presented in Table I. The activities of copper in the alloys at 1000°C, calculated directly from these data are also included in this table.

By interpolation from these activities at the investigated compositions a series of isoactivity compositions have been derived and the contours of isoactivity for the ternary alloys at 1000°C are plotted in Figure 1. Gibbs-Duhem integration of the copper partial free energy data, using Darken's method¹⁰ for a ternary system, has been performed to

Table 1.

Palladium-Copper-Silver: E.m.f.'s of
Cells $\text{CuCu}_2\text{O} / \text{ZrO}_2\text{CaO} / (\text{Pd-Cu-Ag})_x \text{Cu}_2\text{O}$
and Activities of Copper at 1000°K

$$E(\text{mV}) = E_o + T \frac{dE}{dT}$$

<u>N_{Pd}</u>	<u>Cu/Ag ratio</u> (atom %)	<u>E_o</u> (mV)	<u>$\frac{dE}{dT}$</u> (mV/deg) $\times 10^2$	<u>a_{Cu} (1000°K)</u>
0.881	92/8	632.3	-27.0	0.017
0.100	90/10	-4.75	2.2	0.820
0.200	90/10	9.30	3.5	0.600
0.300	90/10	16.9	6.7	0.380
0.400	90/10	53.7	9.5	0.180
0.719	85/15	119.1	16.0	0.040
0.500	84/16	113.4	8.2	0.105
0.603	84/16	163.4	6.0	0.075
0.775	83/17	150.0	16.0	0.028
0.781	83/17	38.4	26.0	0.032
0.556	81/19	100.3	12.9	0.071
0.630	81/19	208.8	6.2	0.044
0.710	81/19	203.7	14.0	0.019
0.975	80/20	-446.3	95.0	0.003
0.100	75/25	-23.0	4.0	0.821
0.200	75/25	-12.5	4.2	0.533
0.300	75/25	-24.0	6.6	0.354
0.400	75/25	-110.0	4.7	0.163
0.765	64/36	166.6	21.0	0.013
0.599	63/37	463.6	-18.0	0.038
0.664	63/37	200.0	11.0	0.028
0.100	50/50	-64.5	8.8	0.763
0.200	50/50	10.0	5.3	0.483
0.300	50/50	41.0	6.5	0.294
0.400	50/50	106.0	6.1	0.146
0.500	45/55	167.8	7.9	0.058
0.554	43/57	239.9	8.0	0.025
0.100	25/75	-3.0	4.0	0.653
0.200	25/75	13.0	5.4	0.462
0.300	25/75	87.0	5.2	0.201
0.400	25/75	130.0	33.5	0.094
0.710	25/75	310.1	6.0	0.014
0.860	25/75	73.6	37.0	0.006
0.635	23/77	441.5	-12.5	0.028
0.200	10/90	-20.3	22.0	0.100
0.603	5/95	8.3	34.0	0.018

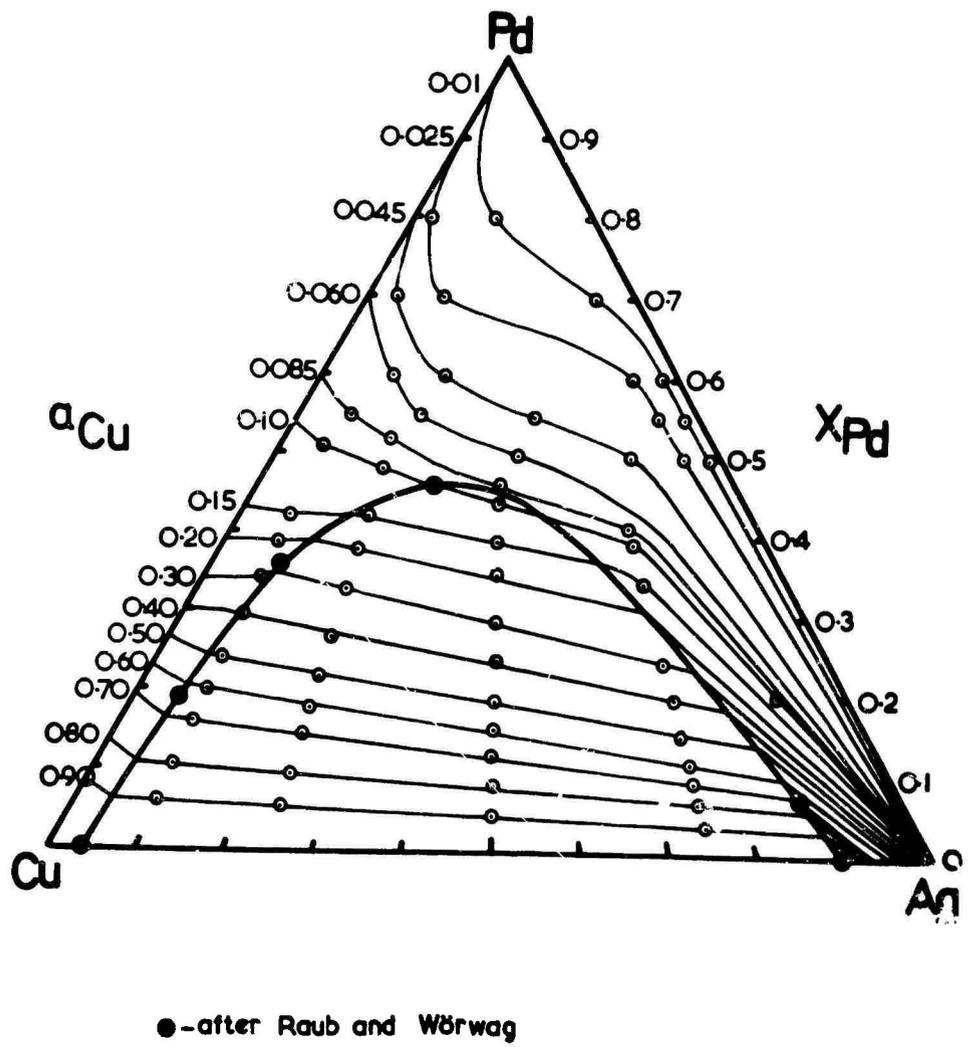


Fig. 1. Isoactivities of copper in Pd-Cu-Ag alloys at 1000°K.

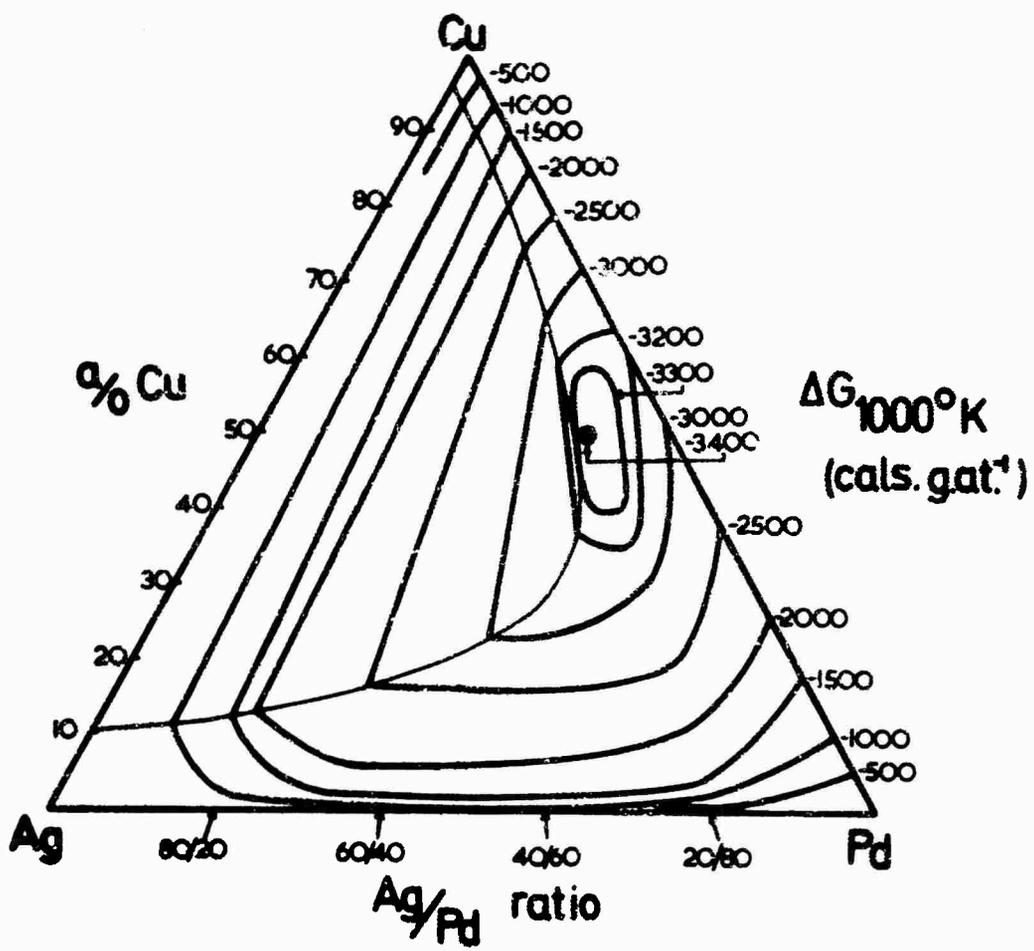


Fig. 2. Free energies of formation of Pd-Cu-Ag alloys at 1000^oK.

obtain integral free energies of formation of the alloys; the resulting values are shown in Figure 2. The system has not yet been studied in sufficient detail to justify the calculation of partial values for the other components, nor to establish purely thermodynamically the extension of the Ag-Cu miscibility gap into the ternary system. The limits of the miscibility gap shown in Figures 1 and 2 are estimated from the x-ray studies of Raub and Worwag¹¹ together with metallographic examination of present alloys.

The thermodynamic properties of the constituent binary systems reflect the dominance of two different factors. The strong negative deviations from ideal behaviour of the Pd-Cu and Pd-Ag systems have been attributed^{1,6,12} to electronic influences resulting from the filling of the d-band of the transition metal on alloying. On the other hand the extreme positive deviations and consequent limited solid state miscibility of the Ag-Cu system is certainly a consequence of the large size difference between these latter components. The thermodynamic properties of the ternary alloys manifest the influence of both of these factors. This is perhaps most clearly revealed by considering the effects of adding the second noble metal (Ag or Cu) to the Pd-Cu and Pd-Ag binaries. Since the silver ion is large compared with palladium or copper large misfit energies may be expected when it is introduced into the copper-palladium lattice. Nevertheless, as consideration of lines of constant copper content in the isoactivity plot (Fig. 1) shows, the initial additions of silver are in the palladium-

rich alloys accompanied by a rapid fall in copper activities. Further silver additions cause a slow increase to ensue, but rapid increases in copper activities leading eventually to positive deviation from ideality occur as the total noble metal content (Cu + Ag) approaches and exceeds that associated with the probable filling of the d-band of the alloys. At lower concentrations of palladium, however, when there are few or no holes in the d-band, the repulsive forces between the silver and copper ions manifest themselves by an immediate increase of copper activities and the consequent extension of the miscibility gap into the ternary system. It would thus appear that in the regions where alloys are able to accept extra electrons into the sub-valent levels this process is able to reduce the influence of the size factor. This could result from the counter-balancing of positive misfit energies by negative energies of electron demotion, but also the misfit might be directly reduced by the modification of the effective sizes of the components as a result of the electronic changes. The actual lowering of Cu activities by the initial silver additions to palladium-rich alloys is surprising and contrary to the expected effect of both the Cu-Ag repulsions and the increasing electron concentration and suggests that the effect of these is at first completely outweighed by other factors; one possibility is perhaps the reduction in the Fermi level in the alloys as a result of the expansion of the lattice by the addition of silver. A similar dependence of thermodynamic behaviour upon the state of filling of the d-band is again suggested by the activities of copper considered as a solute addition to various Ag-Pd (solvent) alloys.

AgCuPd system

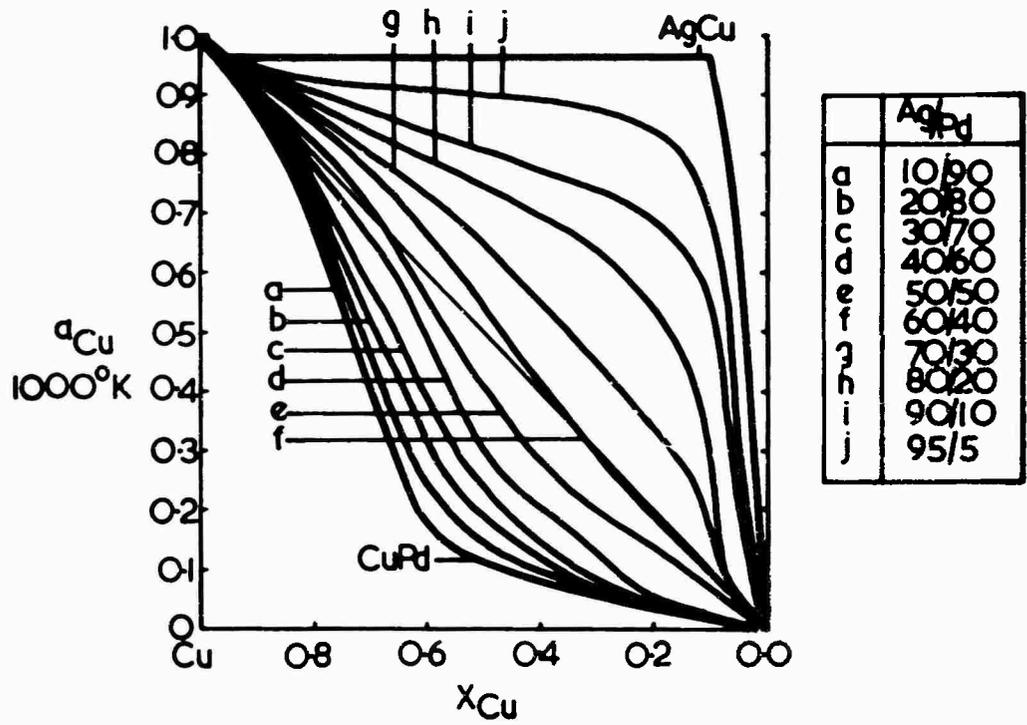


Fig. 3. Activities of copper in Cu - ("Ag-Pd") alloys at $1000^{\circ}K$.

Activities along sections through the Cu corner of the ternary are shown in Figure 3; negative deviations from Raoultian behaviour decreasing rapidly as the d-band is filled are apparent for Pd-rich alloys, while positive deviations of the copper activities occur at all compositions with silver rich (filled band) alloys.

In the Cu-Pd and Ag-Pd binaries the free energies of formation^{1,6,12} have their maximum (-ve) values at approximately 40 atom % Pd, but a shift of contours towards higher Pd concentrations in ternary alloys probably reflects the influence of the (Cu-Ag) misfit factor. The location of the overall maximum (-ve) free energy very near the Cu-Pd binary may reflect the persistence of the ordered Cu_5Pd_4 phase to higher temperatures in the ternary system than in the binary, as found by Raub and Worwag¹¹.

3.2. The Palladium-Indium System

The phase diagram of the Pd-In system, according to Elliott¹³, is shown in Figure 4. Using the solution calorimetric technique, the heats of formation of the solid alloy phases of this system have been obtained in the usual manner from the difference in heats of solution in molten tin of the alloys and the individual pure components. A tin bath temperature of approximately 656°K was employed, providing optimum solution rates and heat transfer conditions, and samples were dropped from an initial temperature of 320 (+ 5)°K.

Investigations have extended over the complete composition range and heats of formation have been obtained for the f.c.c. Pd-rich α -solid solution and for the intermediate phases Pd_3In , Pd_2In , PdIn , Pd_2In_3 , PdIn_3 .

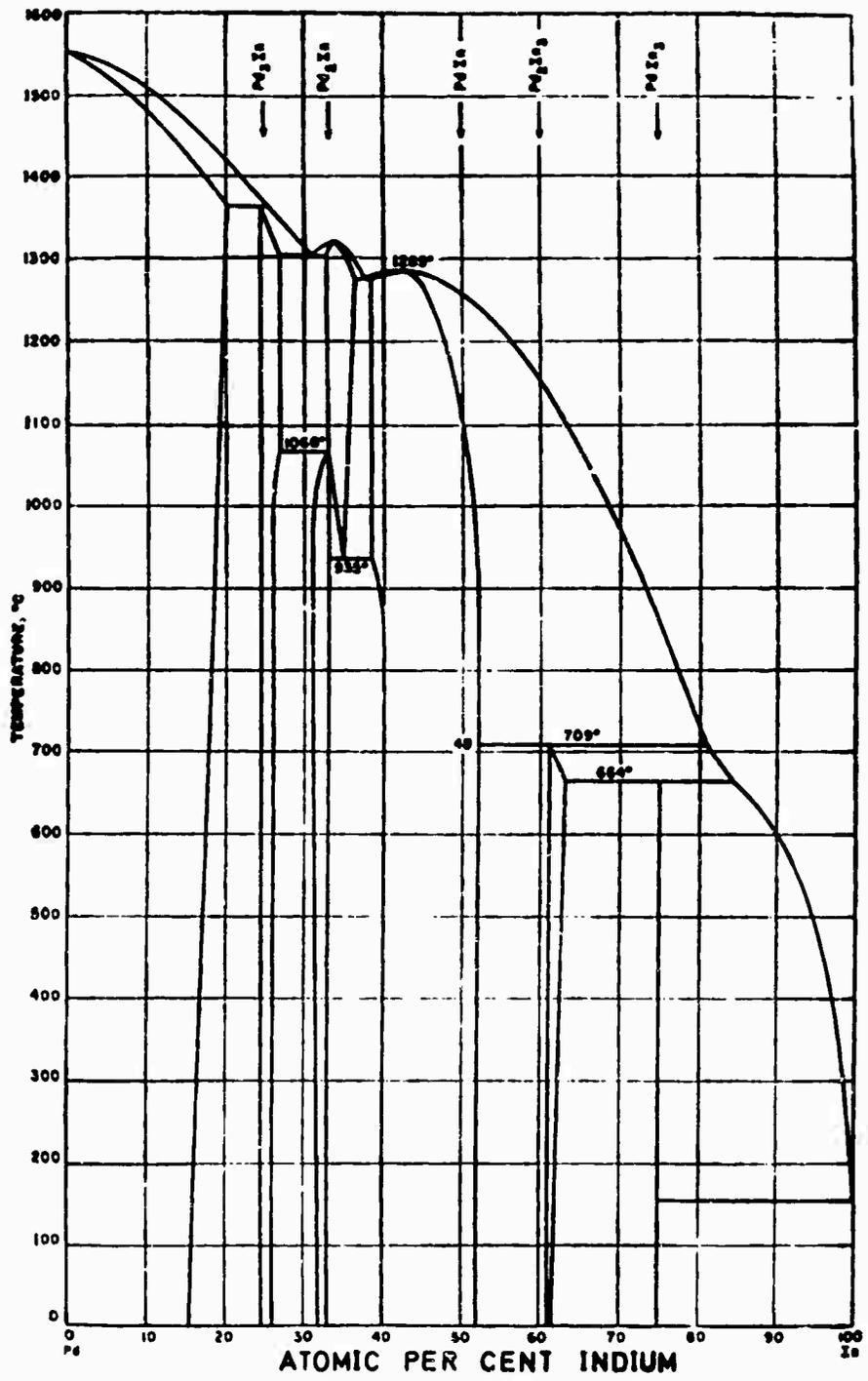


Fig. 4. The Pd-In phase diagram.

Table 2.

Heats of Formation of Solid Palladium-

Indium Alloys at 320°K

<u>N_{In}</u>	<u>Phase</u>	<u>ΔH</u> (cal/g. atom)	<u>No. of</u> <u>Measurements</u>
0.05	α	-2640 ± 148	10
0.10	α	-5404 ± 223	14
0.15	α	-7783 ± 170	12
0.25	Pd ₃ In	-12704 ± 53	9
0.33	Pd ₂ In	-14438 ± 25	6
0.37	Pd ₂ In+Pd ₅ In ₃	-14502 ± 30	3
	Pd ₅ In ₃	-14510	interpolated
0.40	Pd ₅ In ₃ +PdIn	-14462 ± 20	5
0.43	PdIn	-14566 ± 30	4
0.45	PdIn	-14606 ± 37	9
0.46	PdIn	-14649 ± 20	3
0.49	PdIn	-14684 ± 32	4
0.50	PdIn	-14675 ± 35	9
0.52	PdIn	-14360 ± 20	3
0.54	PdIn+Pd ₂ In ₃	-14071 ± 20	3
0.60	Pd ₂ In ₃	-13204 ± 63	7
	PdIn ₃	-8486	interpolated
0.875	PdIn ₃ +In	-4243 ± 20	3

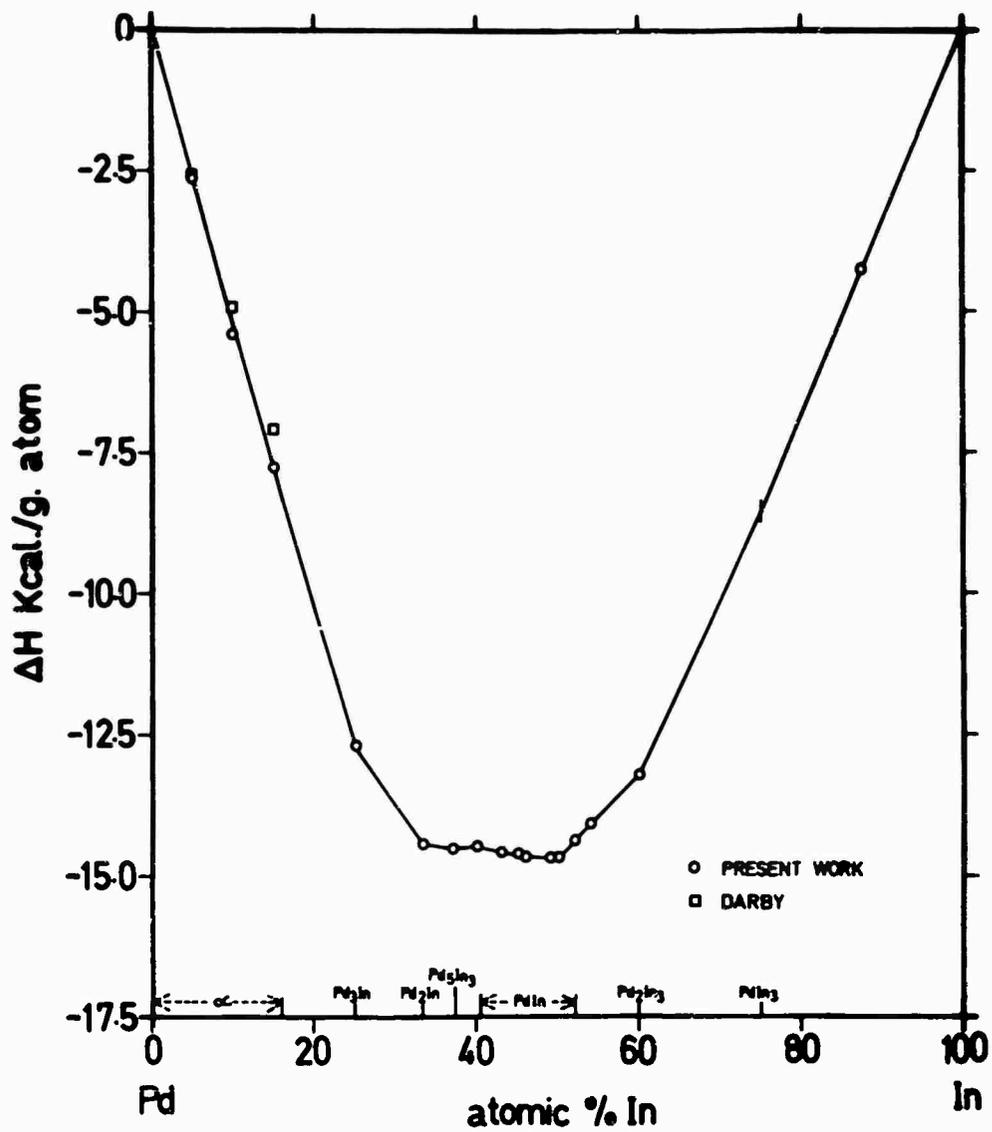


Fig. 5. Heats of formation of solid Pd-In alloys at 320° K.

and possibly Pd_5In_3 . The integral heats of formation of solid Pd-In alloys at 320°K are listed in Table 2. They are illustrated diagrammatically in Figure 5; values obtained for the α -phase by Darby¹⁴ are included and good agreement is indicated. Since it proved impossible to obtain single phase samples of PdIn_3 , the heat of formation of this phase was determined from measurements on the 87.5%In ($\text{PdIn}_3 + \text{In}$) alloy.

The results show that the Pd-In system is strongly exothermic in character, with heats of formation of magnitudes very similar to those of the Pd-Sn system reported earlier⁶. In the present system, however, the asymmetry of the enthalpies with respect to composition is less pronounced; the most negative heats of formation are slightly smaller than in the former and are at approximately equiatomic compositions in contrast with the sharper maximum (-ve) at Pd_2Sn in the former case. This suggests that similar bonding mechanisms are involved except for a smaller electron transfer per solute atom in the present system. These observations are consistent with the fact that the size and electrochemical factors are similar in the two systems, solute valency being the only significant difference in component characteristics.

The heats of formation of the Pd-In α -phase are almost linearly dependent on composition. Comparison with observations on other Pd-B sub-group f.c.c. solid solutions^{6,15} indicates that the general magnitudes correspond closely to those expected if the dominant energetic contribution is due to the transfer of electrons from the s to d band of the alloy at a rate proportional to the

solute valency. The existence of such an electronic factor is demonstrated by the similarity of the heats of formation of several such Pd-based f.c.c. phases when plotted as a function of electron concentration. Indeed it is likely that the quite extensive α -solid solutions of In and of Sn in Pd despite the existence of significant electrochemical factors and borderline size factors, may depend on the stabilising effect of the electron band transfer mechanism. The opposing effect of the size factor is apparent in the fact that while the solid solution of Sn in Pd continues until the d-band is filled (Ca 15 atom % Sn), the higher concentration of 3-valent In required to achieve this electronic state (20 atom % In) is not tolerable as a random substitutional solution and the α -phase terminates at approximately 18 atom % In before band filling is achieved. The first intermediate phase Pd₃In (ordered face centred tetragonal) however, may be considered as derived from an f.c.c. structure by ordering and may be regarded as equivalent to a local re-stabilisation of the α -phase as a result of ordering reducing misfit and electronic energies. It may be noted that the heat of formation of this phase extrapolates directly from those of the α -solid - solutions.

In the intermediate phases the tendency to complete the palladium d - shell by electron transfer may be expected to lead to considerable heteropolar character and this is apparent from the structural types occurring, all are characterised by mixed metallic-covalent bonding and except for PdIn₃ have very similar heats of formation.

The phase Pd_2In has the C 23 (Ni_2Si) structure; this type is common in Pd-B sub-group metal alloys but no heats of formation are known for previously comparable examples; the heat of formation of the present phase is however similar to that of its non-transitional metal isomorph Ca_2Pb ¹⁶.

The CsCl type phase PdIn exists over a range of compositions and the results of the detailed study of the heats of formation of this phase may be seen in Figure 6. Many characteristics of this phase closely parallel those of its isomorph NiAl and it may be similarly classified as $3/2$ electron compound if Pd is treated as zero valent as a result of electron transfer; the existence of a considerable covalent contribution to its bonding is evident from the marked lattice contraction which accompanies the formation of the phase. The change in effective size of the components may be attributed in terms of the Pauling model, to the increase in available bonding electrons which would be produced by the transfer of electrons to the metallic orbitals of In and from In to the Pd atomic orbitals. Lattice parameter and gravimetric density measurements¹⁷ across the homogeneity range of the PdIn phase are shown in Figure 7. These reveal that, as with NiAl, when the non-transition metal content exceeds the stoichiometric composition a defect structure is produced by the appearance of vacancies on the transition metal sub-lattice. This effect is probably once more the consequence of an attempt to maintain a constant Fermi energy by keeping

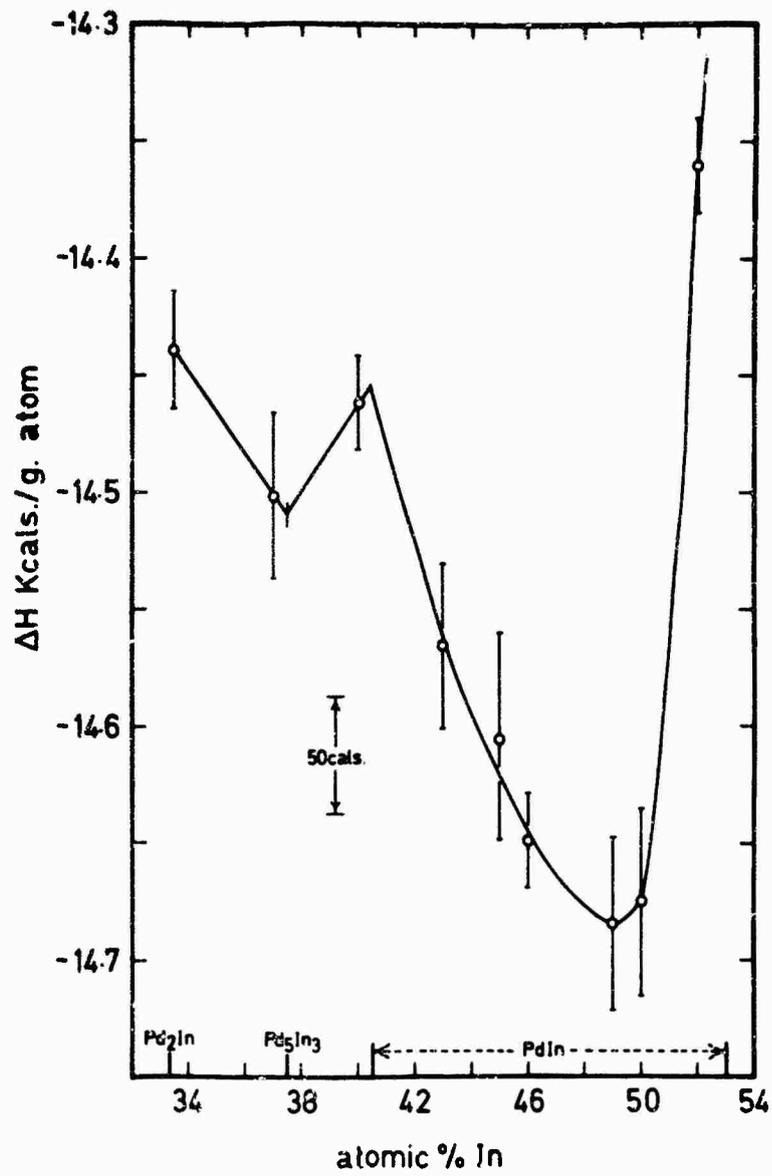


Fig. 5. Heats of formation of the phases $PdIn$, Pd_2In and Pd_5In_3 .

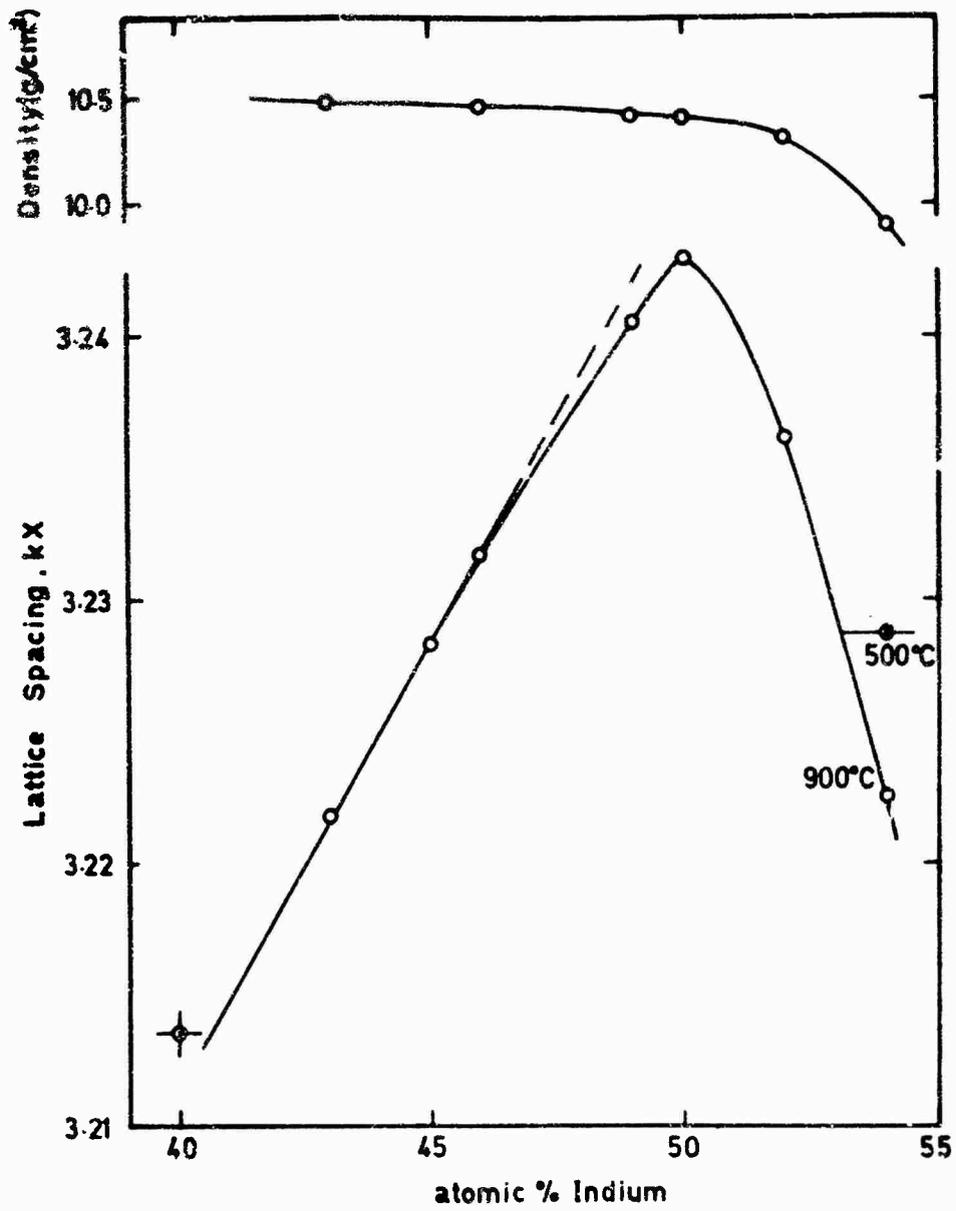


Fig. 7. Lattice parameters and densities of the phase PdIn.

although from the existing evidence it is not possible to preclude a size factor effect, i.e. the simple reluctance of the much larger In atoms to occupy Pd sub-lattice sites. As may be seen from Figure 6, the heats of formation of PdIn are markedly asymmetric about the stoichiometric composition, the heats of formation varying more rapidly with composition in the defect lattice range. It will be noted that the most exothermic value is observed at approximately 49 atom % In and not at the idealized stoichiometry; the value of -14.7 k cal/g.atom may be compared with that of -14 k cal reported for the corresponding NiAl alloy.

The heat of formation of Pd_2In_3 (-13.2 k cal/g.atom) is very close to the value indicated at this composition by an extrapolation of the trend observed in the PdIn defect structure range. This reflects the related character of the two phases since Pd_2In_3 (Ni_2Al_3 ordered trigonal structure) is similar to PdIn but involving an ordered arrangement of numerous vacancies. The final indium-rich intermediate phase PdIn_3 has a much smaller heat of formation; this would be expected as the electron transfer per mole of alloy and hence the degree of heteropolarity is reduced as a result of the smaller number of electron-absorbing Pd 4d states.

Finally attention is drawn to studies of alloys in the region between Pd_2In and the Pd-rich boundary of PdIn (see Figure 6). The heats of formation are indicative of the presence of an additional phase in this

region and this has been confirmed by metallographic and x-ray examination. The present observations appear to confirm the existence of the phase Pd_5In_3 which has also been reported by Schubert¹⁸; interpolation yields a heat of formation of $-14.5/k$ cal/g.atom for this phase.

In the course of the present studies numerous re-measurements of the heats of solution of the pure elements in tin have been made. The mean values for solid Pd and liquid In in liquid tin at 656°K are given below:

$$\Delta H_{\text{In}} = -154 \text{ cal/g.atom In (mean of 17 measurements;}$$

standard deviation = 19 cal/g.atom).

$$\Delta H_{\text{Pd}} = -26,235 \text{ cal/g.atom Pd (mean of 23 measurements;}$$

standard deviation = 88 cal/g.atom).

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Final sentence, page 9, to read:-

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13. ABSTRACT			
Reversible galvanic cells employing zirconia-calcia solid electrolytes were used to investigate the thermodynamic properties of the f.c.c. solid solutions of the ternary system palladium-copper-silver. Measurements were made between 870 and 1250°K over a wide range of compositions and the data used to calculate activities of copper and integral free energies of formation of the entire range of ternary alloys at 1000°K. Tin solution calorimetry was used to measure the heats of formation of solid palladium-indium alloys. Values for the palladium-rich f.c.c. solid solution and for the intermediate phases Pd ₃ In, Pd ₂ In, Pd ₅ In ₃ , PdIn, Pd ₂ In ₃ and PdIn ₃ were obtained. The system is extremely exothermic in character. This is considered to be due to electron transfer to the subvalency transition metal electron levels which contributes a large heteropolar component to the bonding in the intermediate phases. The phase PdIn has been investigated in detail; the occurrence of defect structures is indicated. New measurements of the heats of solution of palladium and indium in liquid tin were obtained.			

18. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
ALLOYS ALLOY CHEMISTRY THERMODYNAMICS INTERMEDIATE PHASES						