

AD 722799

This document has been approved for public release and sale; its distribution is unlimited.

AD

THERMODYNAMICS OF ALLOYS

Calorimetric Studies of Palladium-Silver-Tin Solid Solutions and the Intermediate Compounds  $Pt_2Al_3$ ,  $RhAl$ ,  $NiAl$  and  $PdGa$

Final Technical Report

by

J.N. PRATT, A.W. BRYANT AND D.T. UNDERHILL

January 1971

EUROPEAN RESEARCH OFFICE

United States Army

Contract Number DAJA37-70-C-0632

Department of Physical Metallurgy and Science of Materials  
University of Birmingham.  
England.

DDC  
RECEIVED  
MAY 6 1971  
B

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Reproduced by  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
Springfield, Va. 22151

~~UNCLASSIFIED~~  
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Department of Physical Metallurgy and Science of Materials, The University of Birmingham, P.O.Box 363, Birmingham B15 2TT, England		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP N/A	
3. REPORT TITLE Thermodynamics of Alloys			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Technical Report January 1970 - December 1970			
5. AUTHOR(S) (First name, middle initial, last name) John N. Pratt; A.W. Bryant; D.T. Underhill			
6. REPORT DATE January 1971		7a. TOTAL NO. OF PAGES 26	7b. NO. OF REFS 24
8a. CONTRACT OR GRANT NO. DAJA37-70-C-0632		8b. ORIGINATOR'S REPORT NUMBER(S)	
8c. PROJECT NO. 20061102B 32D			
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.		E-1385	
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY US Army Research & Development Gp (EUR) Box 15, FPO New York 09510	
13. ABSTRACT Tin solution calorimetry has been used to measure the heats of formation of selected face-centred cubic palladium-rich solid solutions of the palladium-silver-tin system. The results show that alloys of constant electron concentration are characterised by heats of formation which vary almost exactly linearly between the values for the terminal binary alloys (60 Pd 40 Ag, $\Delta H = -890$ cal/g.atom.; 90 Pd 10 Sn, $\Delta H = -6200$ cal/g.atom.). The results are discussed in relation to the possible contributions associated with electronic energy and ion-ion interaction effects. Lattice parameters of the alloys have been measured and a linear variation of these is also observed. The technique based on the precipitation of an alloy phase from liquid tin has been used for the study of the aluminides $Pt_2Al_3$ ( $Ni_2Al_3$ -type), $RhAl$ (CsCl-type) and $NiAl$ (CsCl-type), while normal solution calorimetry has been used to investigate the compound $PdGa$ (FeSi-type). Values ob- tained for the heats of formation of these are: $Pt_2Al_3, \Delta H = -23.05 \pm 0.2$ ; $RhAl, \Delta H = -25.81 \pm 0.2$ ; $NiAl, \Delta H = -14.64 \pm 0.2$ ; $PdGa, \Delta H = -17.25 \pm 0.06$ Kcal/ g.atom. These and previously determined heats of formation of related compounds are compared and trends and influences in the heats of for- mation of transition metal aluminides and palladium - Group IIIB com- pounds are discussed. Key words: Calorimetric studies, Palladium-Silver-Tin solid solutions, Phase precipitation, Heats of formation, Alloy			

DD FORM 1473  
1 NOV 66

REPLACES DD FORM 1373, 1 JAN 66, WHICH IS  
OBSOLETE FOR ARMY USE.

UNCLASSIFIED

THERMODYNAMICS OF ALLOYS

Calorimetric Studies of Palladium-Silver-Tin Solid Solutions and  
the Intermediate Compounds  $Pt_2Al_3$ ,  $RhAl$ ,  $NiAl$  and  $PdGa$

Final Technical Report

by

J.N. PRATT, A.W. BRYANT AND D.T. UNDERHILL

January 1971

EUROPEAN RESEARCH OFFICE

United States Army

Contract Number DAJA37-70-C-0632

Department of Physical Metallurgy and Science of Materials  
University of Birmingham  
England.

## Contents

	<u>Page</u>
<u>Synopsis</u>	
1. Introduction	1
2. The Palladium-Silver-Tin Solid Solutions	2
2.1. Experimental	2
2.2. Discussion	3
3. Transition Metal Aluminides	6
3.1. Experimental Technique	6
3.2. Platinum-Aluminium System	8
3.3. Rhodium-Aluminium System	9
3.4. Nickel-Aluminium System	10
4. Palladium-Gallium System	11
5. Discussion of Intermediate Phases	12
6. Further Work	13
7. References	15

## Figures

1. Schematic phase diagram of Pd-Ag-Sn solid alloys.
2. Lattice parameters of Pd-Ag-Sn f.c.c. solid solutions.
3. Heats of formation of Pd-Ag-Sn f.c.c. solid solutions.

### Synopsis.

Tin solution calorimetry has been used to measure the heats of formation of selected face-centred cubic palladium-rich solid solutions of the palladium-silver-tin system. The results show that alloys of constant electron concentration are characterised by heats of formation which vary almost exactly linearly between the values for the terminal binary alloys (60 Pd 40 Ag,  $\Delta H = - 890$  cal/g.atom.; 90 Pd 10 Sn,  $\Delta H = - 6200$  cal/g.atom). The results are discussed in relation to the possible contributions associated with electronic energy and ion-ion interaction effects. Lattice parameters of the alloys have been measured and a linear variation of these is also observed.

The technique based on the precipitation of an alloy phase from liquid tin has been used for the study of the aluminides  $Pt_2Al_3$  ( $Ni_2Al_3$  - type),  $RhAl$  (CsCl - type) and  $NiAl$  (CsCl - type), while normal solution calorimetry has been used to investigate the compound  $PdGa$  (FeSi - type). Values obtained for the heats of formation of these are:  $Pt_2Al_3$ ,  $\Delta H = - 23.05 \pm 0.2$ ;  $RhAl$ ,  $\Delta H = - 25.81 \pm 0.2$ ;  $NiAl$ ,  $\Delta H = - 14.64 \pm 0.2$ ;  $PdGa$ ,  $\Delta H = - 17.25 \pm 0.06$  K.cal/g.atom. These and previously determined heats of formation of related compounds are compared and trends and influences in the heats of formation of transition metal aluminides and palladium - Group III B compounds are discussed.

## 1. Introduction

The present investigations of selected ternary solid solutions and binary intermediate phases form part of the continuing programme of acquisition and analysis of critical thermodynamic data for transition metal alloys<sup>1-6</sup>. Measurements on the face-centred-cubic phases of the Pd-Ag-Sn system were undertaken in the course of current attempts to investigate the different factors influencing the behaviour of Pd-rich solid solutions; alloys were selected with a view to controlling the predominant electronic energy contribution in order to examine the nature of the influence of ion-ion interactions in the ternary alloys. Systemic studies of intermediate phase of transition metal systems were initiated by earlier investigations of Pd-Sn<sup>4</sup>, Pd-In<sup>6</sup> and Pd-Al<sup>7</sup> alloys. This section of the programme is continued with the measurements on the CsCl and related structures in the Pt-Al, Rh-Al, Ni-Al and Pd-Ga which are reported here. The principal technique used has again been tin-solution calorimetry; the isoperibol calorimeter has been operated in both the normal and precipitation modes. Details of the apparatus and the alternative modes of operation have been described previously<sup>7,8</sup>.

## 2. The Palladium-Silver-Tin Solid Solutions

### 2.1 Experimental

The equilibrium diagram of the palladium-silver-tin ternary system has not been investigated, but the phases involved in the constituent binaries<sup>9,10</sup> at near room temperature are indicated in the schematic diagram shown in Figure 1. At such temperatures the solubilities of tin in palladium and in silver are of the order of 16 and 9.4 atom per cent of tin respectively while silver and palladium are mutually soluble at all concentrations. Thus a continuous range of solid solutions may be expected to exist between the binary phases  $\alpha(\text{Ag-Sn})$  and  $\alpha(\text{Pd-Sn})$ . It is likely, however, even if no new ternary phases are involved, that the exceptionally high stability of the Pd-Sn binary intermediate phases<sup>4</sup> will force the ternary  $\alpha$  solid solution limits to much lower tin contents than those corresponding to the indicated linear boundary joining the binary  $\alpha(\text{Ag-Sn})$  and  $\alpha(\text{Pd-Sn})$  limits. The present measurements were undertaken for the purpose of observing the variation of the heat of formation in a series of f.c.c. palladium based alloys of constant electron: atom ratio. Assuming effective valencies of 0, 1 and 4 for palladium, silver and tin respectively, lines of constant  $e/a$  will be as indicated in Figure 1. In order to satisfy both the necessity of keeping within the ill defined  $\alpha$ -phase field and the desirability of having comparatively large heats of formation for examination, a series of alloys along the line  $e/a = 0.4$  were selected for study. In addition to the terminal binary alloys 90 Pd.10Sn and 60 Pd.40Ag, four equally spaced intermediate alloys were investigated.

Alloys were prepared from 99.999% pure palladium, silver and tin. Approximately 4g samples were obtained by direct combination of the pure components by H.F. induction melting under argon in sealed silica capsules

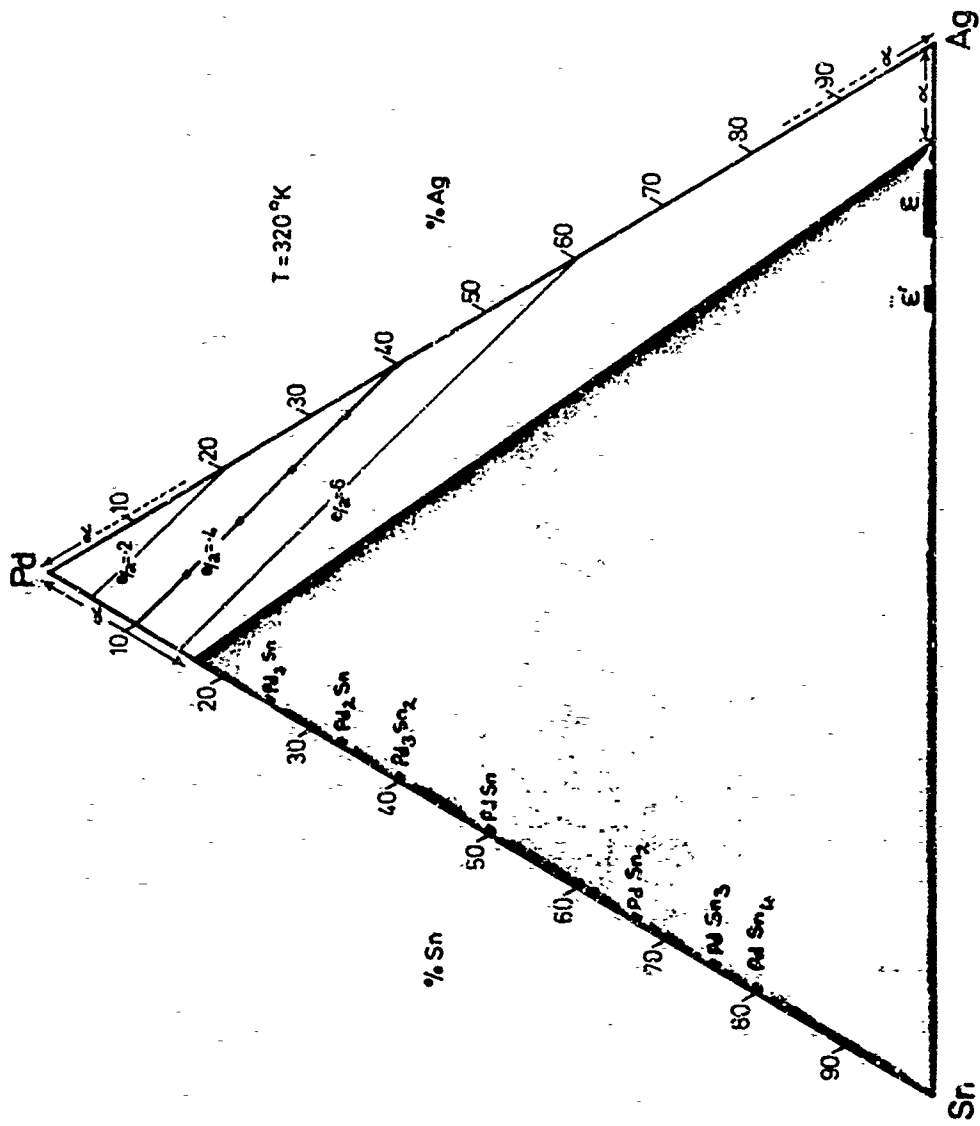


Figure 1. Schematic phase diagram of Pd-Ag-Sn solid alloys.

All alloys were then homogenised by cold working and annealing, again in argon filled capsules, at  $1100^{\circ}\text{C}$  for 2 weeks. Compositions were checked by weighing; weight losses during melting and heat treatment were found to be negligible, so that the maximum final uncertainty in composition was equivalent to only 0.03 atom per cent Sn. The alloys were finally rolled into thin foil (0.02 cm thick), annealed at  $900^{\circ}\text{C}$  for 30 minutes to remove cold work and finally cut and coiled to provide calorimetric samples.

Metallographic and X-ray examination showed all the alloys prepared as above to be homogeneous single phase f.c.c. solid solutions. Debye-Scherrer patterns were obtained from annealed filings using Cu radiation with Ni filter and 3 hr. exposures. Values determined for the lattice parameters are given in Table 1 and plotted in Figure 2.

Using the solution calorimetric technique, the heats of formation of these alloys 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. Samples were dropped from an initial temperature of  $320^{\circ}\text{K}$  into a tin bath at  $656^{\circ}\text{K}$ . Under these conditions a strongly exothermic solution process of about 2 minutes duration and yielding good thermograms was observed for all alloys. In view of the desirability of obtaining data of the highest possible precision in this study, a somewhat larger number of measurements than usual were made on each alloy. The results obtained are summarised in Table 2 and plotted in Figure 3.

## 2.2. Discussion

No thermodynamic measurements have been made previously on solid ternary alloys of this system, but within the limits of experimental precision the  $\Delta H$  value for the 60 Pd. Ag 40 binary alloy shows good agreement with data obtained by Hultgren<sup>11</sup>. The precision of the heats of formation obtained

Table 1. Lattice Parameters of Ternary Palladium  
 - Silver - Tin F.C.C. Solid Solutions of  
 Constant Electron Concentration.

Alloy (atom %)	Lattice parameter a, (KX units)
60Pd.40Ag.	3.9517
66Pd.32Ag.2Sn.	3.9442
72Pd.24Ag.4Sn.	3.9366
78Pd.16Ag.6Sn.	3.9290
84Pd.8Ag.8Sn.	3.9213
90Pd.10Sn.	3.9134

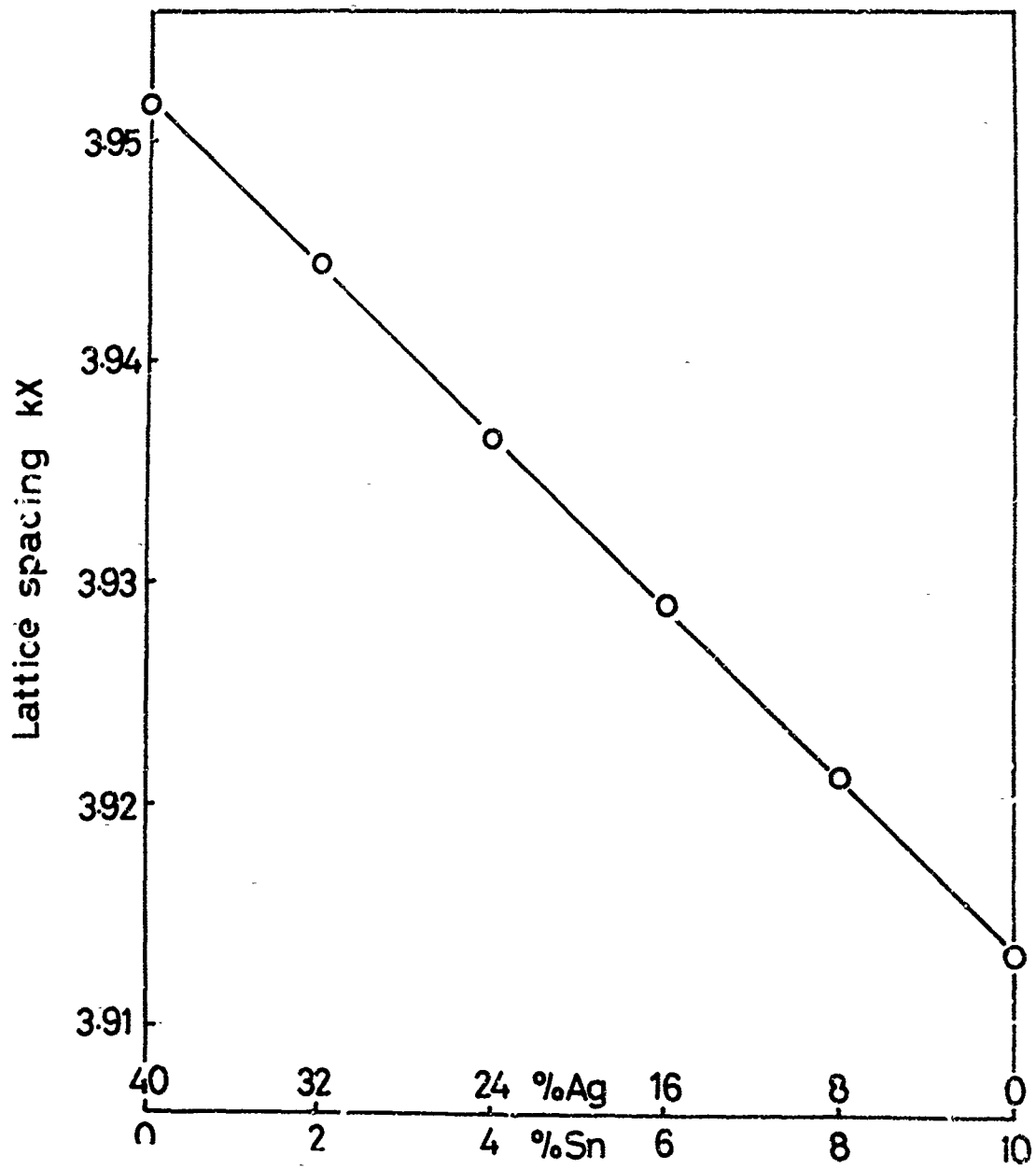


Figure 2. Lattice parameters of Pd-Ag-Sn f.c.c. solid solutions.

Table 2. Heats of Formation of Ternary Palladium  
- Silver - Tin F.C.C. Solid Solutions of  
Constant Electron Concentration.

Alloy (atom %)	Number of Measurements	$\Delta H$ formation, 320°K (cal./g.atom)
60Pd.40Ag.	10	- 892 $\pm$ 63
66Pd.32Ag.2Sn.	13	- 2064 $\pm$ 68
72Pd.24Ag.4Sn.	13	- 2989 $\pm$ 69
78Pd.16Ag.6Sn.	16	- 3958 $\pm$ 71
84Pd.8Ag.8Sn.	12	- 5048 $\pm$ 90
90Pd.10Sn.	13	- 6197 $\pm$ 102

Reference states: Pd(S), Ag(S), Sn(S)

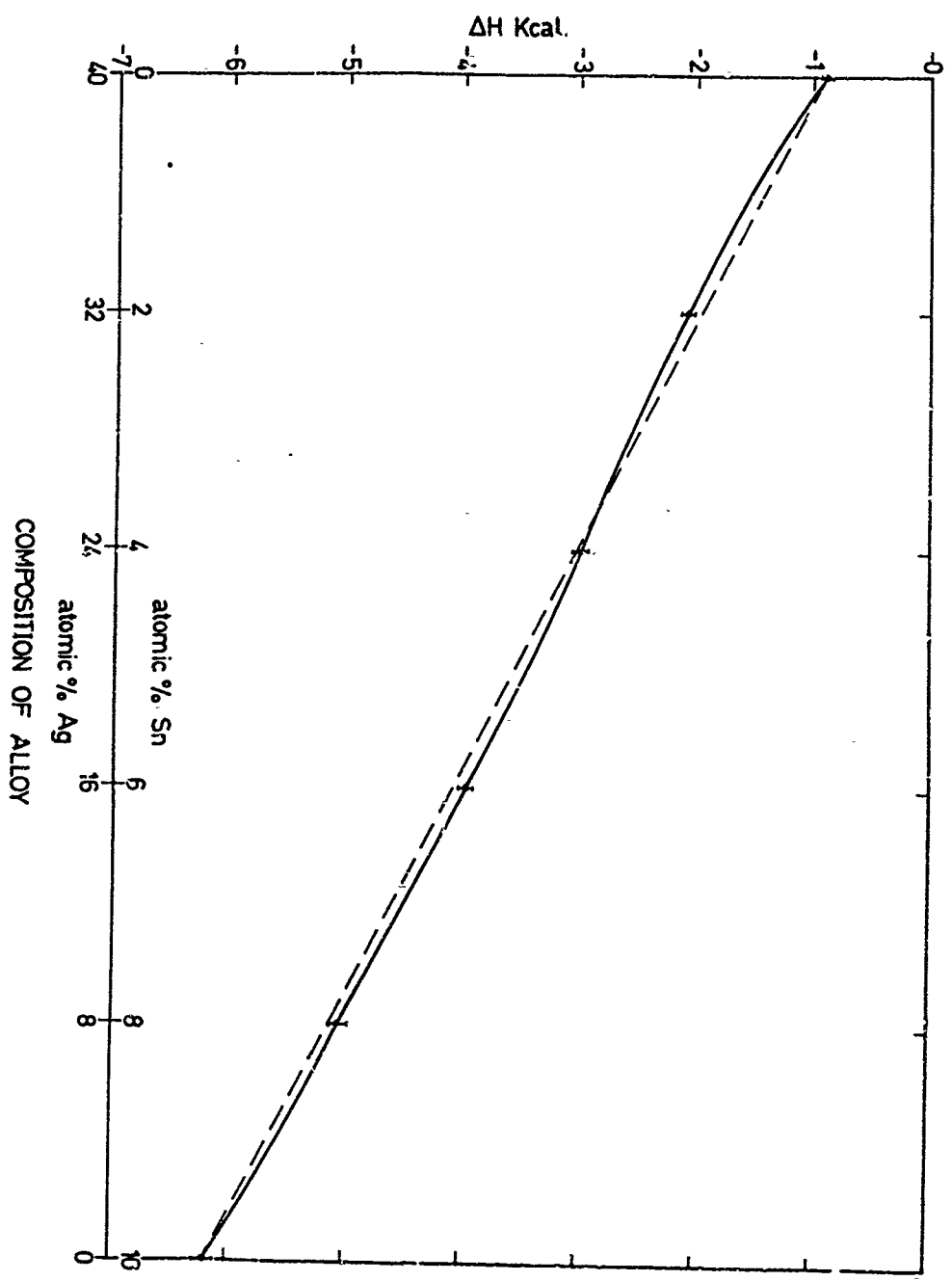


Figure 3. Heats of formation of Pd-Ag-Sn f.c.c. solid solutions with  $e/a = 0.4$ .

for the ternary alloys is particularly high and corresponds to only  $\frac{1}{2}$  of the measured heats of dissolution of samples in the solvent tin bath.

From Figure 3 it will be seen that the plot of  $\Delta H$  for the alloys in the chosen ternary section is essentially linear and no obvious inconsistencies in the  $\Delta H$  values are indicated. The small deviations from linearity only slightly exceed the limits of experimental uncertainty and are of the order of 100 cal./g. atom.

It has been pointed out earlier<sup>1,4</sup> that the unusually exothermic heats of formation of the Pd-B sub group f.c.c. solid solutions are probably a consequence of a filling of the incomplete 4d band of palladium on alloying. With the B-sub group elements Cd, In, Sn and Sb there exists a good correlation between the relative heats of formation and the rate of filling of the d-band as indicated by specific heat or magnetic property measurements<sup>5,12</sup>. Furthermore the similarity of the heats of formation of these phases, viewed as a function of electron concentration, suggests that a localized redistribution of electrons between the s and d bands of palladium, rather than inter-component transfer, is involved<sup>4</sup>. Much larger differences between the heats of formation with different solutes would be expected, if the latter mechanism operated, because of the likely wide variation of the valence band energies of the different solutes. The above interpretation is consistent with the "sliding band model" recently proposed by Montgomery et al<sup>13</sup> for the electronic structure of binary alloys of Pd with noble and polyvalent elements. In contrast with its alloys with the above polyvalent elements, the heats of formation of Pd-Ag binary solid solutions are of an order of magnitude less exothermic and it has been suggested that this is due to a large endothermic contribution associated with the ion core repulsion energy<sup>5,12</sup>. Unfortunately, it is impossible to resolve the separate electronic and ionic contribution from

an examination of individual binary systems, since both contributions will vary with composition in manners which cannot be readily defined. However, by examining a series of ternary alloys of constant electron concentration, it is reasonable to assume from the characteristic behaviour of the binaries that a constant state of Pd alloy d-band filling will be maintained while the number and type of ion-ion interaction will still vary. Along such a line the electronic (Fermi energy) contribution to the heat of formation might be expected to be constant if, as suggested above, an s-d redistribution without inter-component transfer is the electronic process involved. Observed deviations from such a constant value in the experimental heats of formation may thus give a clearer indication of the nature of ion-ion interactions.

As is clearly shown by the data plotted in Figure 3, the heats of formation of the chosen series of ternary alloys of expected identical band filling are not constant, but vary in a simple near-linear fashion between the values for the terminal binary alloys. While it should be noted that this variation would be consistent with a rigid band model and inter-component transfer, provided ion-ion effects are negligible throughout, such an explanation of the ternary alloy behaviour appears improbable in view of the incompatibility of the specific heats, magnetic and thermodynamic properties of the binary alloys with this model. It is considered therefore that observed variation of the heats of formation must be treated as a manifestation of ion-ion interaction effects.

No suitable model exists permitting the exact theoretical calculation of ion interactions in complex transition metal alloys. For heuristic purposes, however, consideration has been given to the possibility that experimental heats of formation of the alloys investigated may be represented empirically in the

form

$$\Delta H (\text{observed}) = \Delta H_{\text{elec}} + \lambda_1 x_{\text{Pd}} x_{\text{Ag}} + \lambda_2 x_{\text{Pd}} x_{\text{Sn}} + \lambda_3 x_{\text{Ag}} x_{\text{Sn}}$$

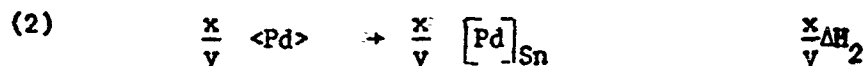
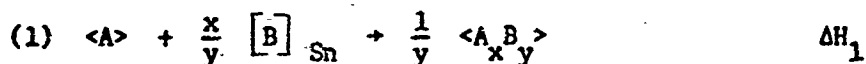
This is based on the assumption that the electronic contribution ( $\Delta H_{\text{elec}}$ ) and the ion-ion interactions ( $\lambda_1, \lambda_2, \lambda_3$ ) between particular pairs of components are independent of composition; it further assumes that the total ion-ion contribution to the heats approximates to the sum of nearest neighbour pair-wise interactions. Preliminary attempts have been made to evaluate  $\Delta H_{\text{elec}}$  and the  $\lambda$  coefficients using the data of Table 2. While it has been established that the observed linear variation can be surprisingly well fitted to the pairwise model, unambiguous evaluation of the coefficients without making additional assumptions has not so far proved possible. The  $\lambda$  values are extremely sensitive to the assumed magnitude of the electronic contribution. Using an early crude estimate<sup>1</sup> of  $\Delta H_{\text{elec}}$  as  $-4$  Kcal/g.atom for alloys of this composition yields the values  $\lambda_1 = +13$  Kcal/g.atom  $\lambda_2 = -24$  K.cal/g.atcm and  $\lambda_3 = -55$  K.cal/g.atom for the Pd-Ag, Pd-Sn and Ag-Sn interactions. Little significance should be attached to these values, however, and re-examination of these data using a more specific model for ion interactions is being undertaken.

### 3. Transition Metal Aluminides

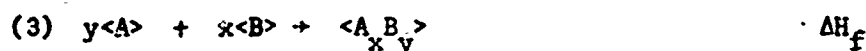
#### 3.1. Experimental Technique

In the investigation of the heats of formation of phases of exceptionally high stability, normal use of the solution calorimetric technique may be inhibited by an extremely low solubility of the alloy compound in the liquid solvent. This problem was first encountered in attempts to measure heats of formation of Pd-Al<sup>7</sup> alloys for, although Pd and Al separately have moderate solubilities in liquid tin at the calorimeter operating temperature

the Pd-Al alloys were found to be virtually insoluble. Nevertheless good values for the heat of formation of the equiatomic phase PdAl (FeSi structure) were obtained<sup>7</sup> by using the solution calorimeter in a precipitation mode. This precipitation technique has now been employed for measurements on other transition metal aluminides. A fuller description of the technique was given in the previous report<sup>7</sup> so a brief reiteration of the principle of the precipitation mode of operation of the tin-solution calorimeter will suffice here. The heat of formation of the most stable compound of the A-B system may be determined by the addition of A to a dilute solution of B in liquid tin, thereby causing the precipitation of the insoluble equilibrium phase, say  $A_x B_y$ . The heat effect accompanying this precipitation is measured in the normal way and, by combining its value with that for the heat of solution of B in tin, the heat of formation of  $A_x B_y$  at the tin bath temperature calculated from the following relationships,



which combined, using Hess's Law gives



$$\Delta H_f = y \Delta H_1 + x \Delta H_2$$

Satisfactory results were obtained by making successive drops, of about .001 -.002 g. atom Al, into liquid solutions of the respective transition elements in tin; the concentration of the solutions employed depended on the solubility of the element involved. Where possible, after removal of the tin bath from the calorimeter at the end of the precipitation experiments, the precipitated phase was leached out by immersion in concentrated hydrochloric acid and the compound identified by X-ray parameter measurements. In cases

where this is not possible the composition of the precipitating phase may be established within close limits by observing the "equivalence" of the reaction, i.e. from a knowledge of the quantities of the elements present in or added to the tin bath and noting the number of consistent values obtained for the heat of precipitation.

### 3.2 Platinum-Aluminium System

Preliminary measurements of the heat of solution of platinum in tin at 656°K were made using samples consisting of Pt filings enclosed in small tin capsules. Observations were made difficult by the slow rate of solution at this temperature, but three satisfactory values were obtained yielding a value of  $\Delta\bar{H}_{Pt} = -26,758 \pm 250$  cal/g.atom. This is in reasonable agreement with values reported by Walker and Darby<sup>14</sup> ( $\Delta\bar{H}_{Pt} = -27302$  cal/g.atom; 698°K) and by Geiken<sup>15</sup> ( $\Delta\bar{H}_{Pt} = -26951$  cal/g.atom; 900°K). For the purpose of the present calculations a value of  $\Delta\bar{H}_{Pt} = -27000 \pm 300$  cal/g.atom was therefore employed.

Once again it was observed that the addition of aluminium to dilute solutions of platinum in tin resulted in large exothermic heat effects - in contrast to the behaviour observed when platinum is absent. Initial attempts to use the technique were, however, unsatisfactory since the platinum contents used proved to be in excess of the liquidus composition of the Pt-Sn binary system. From observations made during these early runs it is apparent that this, at the bath temperature (656°K), is only about 0.35 - 0.45 atom per cent Pt, rather than the much higher value reported in the literature<sup>9,10</sup>. By reducing the initial Pt content of the baths to lower values therefore, satisfactory precipitation results were obtained. In calculating the heats of precipitation ( $\Delta H_1$ ) in this and all other aluminide studies, the heat content change of aluminium between the sample drop temperature (320°K) and bath temperature

Table 3. Heats of Precipitation and Formation at  
656°K of the Compound  $Pt_2Al_3$ .

Expt. No.	Initial Conc. of Pt in solution at. %	$\Delta H_1$ , Heat of Pptn (cal/g.at Al)	$\Delta H_c$ , Heat of form. of $Pt_2Al_3$ (cal/g.at)
1.1	0.35	-20391	-23035
1.2		-20395	-23037
1.3		-20475	-23085
2.1	0.35	-20628	-23177
2.2		-20219	-22931
2.3		-20436	-23026

Heat of Formation of  $Pt_2Al_3$  at 656°K =  
-23.049  $\pm$  0.2 k.cal/g.atom.

(656°K), which must be deducted from the measured heats, was obtained from the data assessment by Hultgren et al<sup>16</sup>.

The overall "equivalence" of the reaction indicated a composition for the precipitating phase of 60 ± 1 atom per cent Al, suggesting the formation of Pt<sub>2</sub>Al<sub>3</sub> rather than the equiatomic compound. Crystals of the precipitated phase were successfully extracted from the tin bath on removal from the calorimeter and confirmed as Pt<sub>2</sub>Al<sub>3</sub> (Ni<sub>2</sub>Al<sub>3</sub> type structure). Lattice parameters were measured and found to be

$$a = 4.210 \text{ \AA}, c = 5.175 \text{ \AA}$$

These may be compared with values of  $a = 4.208 \text{ \AA}$  and  $c = 5.172 \text{ \AA}$  reported by Ferro et al<sup>17</sup>.

Six measurements were made of the heat of precipitation of Pt<sub>2</sub>Al<sub>3</sub>. These and the corresponding values for the heat of formation of this compound are collected in Table 3.

### 3.3 Rhodium - Aluminium System

Since difficulties in obtaining heats of solution of Rh were anticipated, owing to its low solubility in tin, no attempt was made to remeasure  $\Delta\bar{H}_{\text{Rh}}$ . Satisfactory values for this quantity have been reported by Darby<sup>18</sup> ( $\Delta\bar{H}_{\text{Rh}} = -30,000 \text{ cal./g. atom; } 698^\circ\text{K}$ ) and by Miner, Spencer and Pool<sup>19</sup> ( $\Delta\bar{H}_{\text{Rh}} = -29950 \text{ cal./g. atom; } 700^\circ\text{K}$ ) and the more precise of these,  $\Delta\bar{H}_{\text{Rh}} = -29950 \text{ cal./g. atom}$ , was adopted in the present calculations.

As with the case of Pt, difficulties were encountered in the early precipitation experiments due to the solubility of Rh being even less than previously reported. Present experience showed that at 656°K the liquidus is in the range 0.3 - 0.4 atom % Rh, considerably lower than suggested previously<sup>9</sup>. Reduction of the starting Rh contents of the tin baths to 0.3 atom % Rh or less yielded satisfactory results. Attempts to extract samples of the precipitated

Table 4. Heats of Precipitation and Formation at  
656°K of the Compound RhAl.

Expt. No.	Initial conc. of Rh in sol. (at. %)	$\Delta H_p$ , Heat of Pptn. (cal./g.atom Al)	$\Delta H_f$ , Heat of form of RhAl (cal./g.at.)
1.1	0.30	-21454	-25715
1.2		-21659	-25805
1.3		-21540	-25745
2.1	0.20	-22042	-25996
2.2		-21381	-25666
2.3		-21760	-25855
2.4		-21770	-25860

Heat of Formation of RhAl at 655°K =  
-25.806  $\pm$  0.2 k.cal./g.atom.

phase proved to be impossible owing to its attack and decomposition by solvent acids. X-ray structural data and identification have therefore not been obtained. From the equivalence of the precipitation reactions, however, its composition has been unambiguously established as  $50 \pm 1$  atom per cent Al. There is no doubt therefore that the observations refer to the phase RhAl (CsCl structure). From the observed behaviour in the precipitation experiments it can further be seen that the solubility of the phase RhAl in liquid tin at  $656^{\circ}\text{K}$  does not exceed 0.0001 mole fraction. Seven measurements have been made of the heat of precipitation of RhAl, these and the derived heats of formation are given in Table 4.

#### 3.4 Nickel-Aluminium System

Although heats of formation of the NiAl phase (CsCl structure) have been measured previous by Kutaschewski<sup>20</sup> and by Oelsen and Middel<sup>21</sup>, direct reaction or liquid mixing techniques were employed and quite large uncertainties ( $\pm 1000$  cal./g.atom) attach to the reported values. A re-determination using the precipitation technique therefore appeared to be of interest. Several studies have been made of the heat of solution of Ni in liquid tin at near the present operating temperatures. Values are reported by Hertz<sup>22</sup> ( $\Delta\bar{H}_{\text{Ni}} = -12750$  cal./g.atom;  $623^{\circ}\text{K}$ ), Leach and Bever<sup>23</sup> ( $\Delta\bar{H}_{\text{Ni}} = -9940$  cal./g. atom;  $623^{\circ}\text{K}$ ) and Darby<sup>18</sup> ( $\Delta\bar{H}_{\text{Ni}} = -10918$  cal./g.atom;  $698^{\circ}\text{K}$ ). Of these the last appears to be the most reliable and has been used in present calculations.

The composition of the precipitating phase was established from the observed equivalence of the reaction to lie between 48 and 52 atom per cent Al and hence is clearly the phase NiAl (CsCl-structure). As with RhAl, the NiAl phase was attacked by solvent acids and hence no enriched samples could be extracted for X-ray examination. The solubility of NiAl in liquid tin at  $656^{\circ}\text{K}$  was indicated by observed precipitation behaviour to be not more than

Table 5. Heats of Precipitation and Formation at 656°K of the Compound NiAl.

Expt. No.	Initial conc. of Ni in sol. (at. %)	$\Delta H_p$ , Heat of Pptn. (cal./g.at Al)	$\Delta H_f$ , Heat of form. of NiAl (cal./g.at.)
1.1	0.49	-18456	-14687
1.2		-18454	-14686
1.3		-18603	-14761
1.4		-18320	-14619
1.5		-18306	-14612
2.1	0.23	-17985	-14451
2.2		-18408	-14663

Heat of Formation of NiAl at 656°K =  
 $-14.64 \pm 0.2$  k.cal/g.atom.

0.0001 mole fraction.

Heats of formation of NiAl obtained using the present technique are shown in Table 5. They must be compared with the value of  $\Delta H = -14.05 \pm 1.0$  k.cal/g.atom reported by Kubaschewski<sup>20</sup> for the equiatomic composition. It may be noted that the uncertainty of  $\pm 0.2$  k.cal/g.atom associated with the present values is largely attributable to deviations in the value of  $\bar{\Delta H}_{Ni}$  which was employed.

In experiments with this system it was found that the addition of excess aluminium to the Sn(-Ni) solution resulted in the onset of a very slow slightly exothermic reaction which possibly corresponds to the entry of the bath composition into the NiAl + Ni<sub>2</sub>Al<sub>3</sub> + Sn phase field.

#### 4. Palladium-Gallium System

To complete the comparison with the other Pd-IIIIB equiatomic phases examined previously<sup>6,7</sup>, measurements were made of heats of formation of the phase PdGa (FeSi-structure). In this case the phase has significant solubility in liquid tin and therefore the normal technique of tin-solution calorimetry was employed. Alloys were prepared by the procedure described in section 2.1 and their homogeneity and structure checked by X-ray diffraction.

Preliminary measurements of the heat of solution of Ga in tin showed good agreement with previously reported values<sup>16</sup>. The present measurements yielded for the isothermal heat of solution of liquid Ga in liquid Sn at 656°K,  $\bar{\Delta H}_{Ga} = + 737$  cal./g.atom (mean of 12 measurements; standard deviation = 25 cal./g.atom).

The results obtained for the heat of formation of PdGa are shown in Table 6. It should be noted that although Ga is liquid at the reference temperature of 320°K, the data in the table are expressed relative to solid Pd and superheated solid Ga for better comparison with other systems. Cp for

Table 6. Heats of Formation of the Compound PdGa at 320°K. (Reference states: Pd (solid and Ga (superheated solid)).

Expt. No.	$\Delta H_{\text{form.}}$ (cal/g. atom)
1.1	-17342
2.1	-17285
2.2	-17303
2.3	-17261
2.4	-17335
2.5	-17330
2.6	-17257
3.1	-17155
3.2	-17105
4.1	-17108
4.2	-17177
5.1	-17276
5.2	-17352
5.3	-17183
6.1	-17266

Heat of Formation PdGa (FeSi structure)  
 = -17.254 k.cal/g. atom (mean deviation  
 0.062).

solid Ga<sup>16</sup> has been directly extrapolated to higher temperatures for the change of standard state calculations.

#### 5. Discussion of Intermediate Phases

The heats of formation of the transition metal -B sub group element intermediate phases studied thus far in the current programme are assembled in Table 7. Also included for the purpose of discussion are two values measured by other workers. Although the present systematic studies are not yet complete, a number of interesting trends are evident from the data already available.

The strongly exothermic character of all the phases is certainly associated with a strong heteropolar component in their bonding. This may be regarded as probably deriving from a mixture of electronegativity effects of a conventional kind, combined with electron redistribution between the components due to the tendency of the transition elements to take electrons into their incomplete d-states. These influences are well illustrated by the aluminides.

Although no data are yet available for the PdAl (CsCl structure) phase, previous studies<sup>7</sup> indicate that its heat of formation will not differ greatly from that shown for the FeSi form. Similarly, an almost equal stability of the PtAl (CsCl) and Pt<sub>2</sub>Al<sub>3</sub> phases is suggested by the Pt-Al phase diagram<sup>9</sup> indicating that the heats of formation of these two phases are closely comparable. Considering these estimated values in conjunction with the experimental measurements on CsCl aluminides given in the table shows a systematic increase of the heats of formation in the order NiAl, PdAl, PtAl, RhAl. The very large difference between the values for NiAl and PdAl and the smaller one between the latter and PtAl clearly reflect the variation of the electronegativity differences between the components. On the other hand, the

Table 7. Heats of Formation of Selected Transition Metal - Group B Element Intermediate Phases (k.cal/g.atom)

	<u>Al</u>	<u>Ga</u>	<u>In</u>	<u>Sn</u>
<u>Ni</u>	NiAl (CsCl) -14.67 <sup>(a)</sup> Ni <sub>2</sub> Al <sub>3</sub> (Ni <sub>2</sub> Al <sub>3</sub> ) -13.85 <sup>(e)</sup>	NiGa (CsCl)  Ni <sub>2</sub> Ga <sub>3</sub> (Ni <sub>2</sub> Al <sub>3</sub> )		
<u>Pd</u>	PdAl (CsCl)  PdAl (FeSi) -22.07 <sup>(b)</sup> Pd <sub>2</sub> Al <sub>3</sub> (Ni <sub>2</sub> Al <sub>3</sub> ) -19.20 <sup>(f)</sup>	PdGa (FeSi) -17.15 <sup>(a)</sup>	PdIn (CsCl) -14.70 <sup>(c)</sup>  Pd <sub>2</sub> In <sub>3</sub> (Ni <sub>2</sub> Al <sub>3</sub> ) -13.20 <sup>(c)</sup>	PdSn (MnP) -14.60 <sup>(d)</sup>
<u>Pt</u>	PtAl (CsCl) Pt <sub>2</sub> Al <sub>3</sub> (Ni <sub>2</sub> Al <sub>3</sub> ) -23.05 <sup>(a)</sup>		Pt <sub>2</sub> In <sub>3</sub> (Ni <sub>2</sub> Al <sub>3</sub> )	PtSn (NiAs)
<u>Rh</u>	RhAl (CsCl) -25.81 <sup>(a)</sup>		RhIn (CsCl)	

(a) Present work

(b) J.N. Pratt and A.W. Bryant. (Ref. 7)

(c) J.N. Pratt, A.W. Bryant and W.G. Bugden (Ref. 6)

(d) J.N. Pratt, A.W. Bryant and W.G. Bugden (Ref. 4)

(e) O. Kubaschewski (Ref. 20)

(f) R. Ferro and R. Capelli (Ref. 24)

even larger heat formation of RhAl is considered to result from the possibility of a greater electron transfer to the initially less-filled d-states of Rh.

The phases  $Ni_2Al_3$ ,  $Pd_2Al_3$  and  $Pd_2In_3$  have heats which are very similar to, but consistently less exothermic, than their corresponding equiatomic neighbours. This is consistent with the fact that the  $Ni_2Al_3$  (ordered trigonal) -type structures are related to CsCl, but involve an ordered arrangement of a large number of vacancies and with the expectation that, owing to the composition differences, a smaller electron transfer per mole of alloy may occur. The effect of electronegativity differences is again apparent from a comparison of the heats of formation of  $Ni_2Al_3$ ,  $Pd_2Al_3$  and  $Pt_2Al_3$ .

Finally it is of interest to compare the heats of formation of the equiatomic compounds of Pd with different IIIB element partners. It will be noted that these values become less exothermic as the difference between the Periods of the components decreases. No significant variation of electronegativities or electron structure is involved in this group of phases, but the observation that the ionic size of the B-components increase in the sequence Al, Ga, In suggests that a variation of ion repulsion may be a significant factor in this series.

Attempts will now be made to complete the present studies by the examining of the similar isomorphous phases occurring in the remaining binary systems represented in the array in Table 7. This should define more precisely the present trends and influences and begin to quantify the factors responsible for the choice of specific structural type (CsCl, FeSi, MnP, NiAs) which may be adopted by the equiatomic phase.

#### 6. Further Work

In addition to the investigations reported here, solid electrolyte studies of Pd-In alloys and vapour pressure measurements of selected rare-earth

= 14 =

- group V element systems are also in progress. Some further measurements on these are necessary before computation of their thermodynamic properties can be undertaken. These are now in progress and the complete studies will be described in a subsequent report.

7. References,

1. J. N. Pratt, Trans. Faraday Soc., 1960, 56, 975.
2. W. G. Bugden and J. N. Pratt, J. Chem. Thermodynamics, 1969, 1, 353.
3. J. N. Pratt and P. J. Spencer, Final Tech. Rep. U.S.D.A. Contract No. DA-91-591-EUC-3762 (Nov. 1966).
4. A. W. Bryant, W. G. Bugden and J. N. Pratt, Acta Met., 1970, 18, 101.
5. J. B. Darby, K. M. Myles and J. N. Pratt, Acta Met., 1971, (Jan).
6. J. N. Pratt, A. W. Bryant and W. G. Bugden, Final Tech. Rep. U.S.D.A. Contract No. DAJA37-68-C-0027 (Nov. 1968).
7. J. N. Pratt and A. W. Bryant, Final Tech. Rep. U.S.D.A. Contract No. DAJA37-69-C-0472 (Dec. 1969).
8. A. W. H. Morris and J. N. Pratt, Brit. J. App. Phys., 1965, 16, 517.
9. M. Hansen and K. Anderko, "Constitution of Binary Alloys", McGraw-Hill, N.Y., 1958.
10. R. P. Elliot, "Constitution of Binary Alloys, 1st Supplement", McGraw-Hill, N.Y., 1965.
11. J. P. Chan, P. D. Anderson, R. L. Orr and R. Hultgren, 4th Tech. Rep., Minerals Research Lab., Univ. of California (Oct. 1959).
12. J. N. Pratt and W. G. Bugden, Final Tech. Rep. U.S.D.A. Contract No. DA-91-591-EUC-4132 (Nov. 1967).
13. H. Montgomery, G. P. Pells and E. M. Wray, Proc. Roy. Soc., 1967, A301, 261.
14. R. A. Walker and J. B. Darby, Acta Met., 1970, 18, 1261.
15. G. W. Geiken, U.S.A.E.C. Rep. UCRL-17615, Univ. of California, 1967.
16. R. Hultgren, R. L. Orr, F. D. Anderson and K. K. Kelley, "Selected Values for the Thermodynamic Properties of Metals and Alloys", Wiley, N.Y., 1963.
17. R. Ferro, R. Capelli and G. Rambaldi, Atti. Accad. Nazl. Lincei, Rend. Classe. Sci. Fis. Mat. Nat., 1963, 34, 45.
18. J. B. Darby, Private communication, (Argonne National Laboratory), 1970.
19. R. V. Miner, P. J. Spencer and M. J. Pool, Trans A.I.M.E., 1968, 242, 1553.
20. O. Kubaschewski, Trans. Faraday Soc., 1958, 54, 814.
21. W. Oelsen and W. Middel, Mit. Kaiser Wilhelm Inst. Eisenforsch., 1937, 19, 1.
22. J. Hertz, C.R. Acad. Sci. Paris, 1966, 262C, 1652.

23. J. S. Ll. Leach and M. B. Bever, Trans. A.I.M.E., 1959, 215, 728.
24. R. Ferro and R. Capelli, Atti. Accad. Nazl. Lincei, Rend. Classe Fis. Mat. Nat. 1963, 34, 659.