THE STRUCTURE OF URANIUM PALLADIUM RHODIUM ALLOYS

by

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A thesis submitted to the University of Surrey for the
Degree of Doctor of Philosophy
ABSTRACT

The structure and phases of alloys of uranium and two of the light platinum metals, Pd and Rh have been studied. Using X-ray diffraction, metallography and electron microscopy, the phase diagram of the noble metal-rich end of the ternary system, U-Pd-Rh has been established. Portions of the binary systems, U-Pd and U-Rh have also been studied and the Pd-Rh phase diagram re-established. The structure of the solid phases which are stable at 1050°C, 1150°C and 1250°C have been determined.

A thermodynamic calculation of the isothermal sections of the ternary U-Pd-Rh system at 1350°K, 1450°K and 1550°K was carried out. This confirms the phases that the conventional methods were used to establish. It has been suggested that UPd₄ has a defect lattice with some of the uranium sites being vacant. On addition of Rh this compound phase (UPd₄ or α₁) extends continuously to include the 1:3 ratio which characterises the A-B compounds with L12 structures. It is also shown that whereas Pd is dissolved in URh₃, solubility of Rh in UPd₃ is very restricted. It has been found that the miscibility gap in the Pd-Rh system widens upon addition of uranium and that the critical point therefore rises in the ternary system although the ternary critical point is unstable.

Electronic effects are responsible for the large solubility of U in Pd (δ-solid solution) as compared with the other Pt metals. The pseudo-binary system UPd₄ and URh₃ (both having the L12 structure) has a miscibility gap.
DEDICATION

To My Daughters
Aba, Ama and Mansa
Who were starved of my care and affection
While I was pursuing this study

and

Nemata
Errata

Page 14  Paragraph 2  line 10 should read "forms and hence are found in the inclusions. Phase studies of the UC-Mo"

Page 17  Paragraph 1  line 3 should read "extracted inclusions was Mo 43.3 w/o, Tc 15.7 w/o, Ru 33.6 w/o and Rh 7.4 w/o

Page 27  Paragraph 2  line 3 should read "solution had limit at 16.5 at. % at 1300°C but breaks down eutectoidally"

Page 62  Paragraph 2  line 2 should read "pure metals has been solved with variable success by applying the method"

Page 70  Paragraph 2  line 10 should read "(b) the model of Miedema, de Boer and de Chatel (113),(114)"

Page  Paragraph 1  line 3 should read "considerable differences in the critical temperatures of the different"

Page 80  Paragraph 3  line 8 should read "section at 793K for the Bi-P-Zn system. The NPL formalism which the"

Page 152 last paragraph  line 1 should read "Two coefficients are stored in the computer to represent the Gibbs"
ACKNOWLEDGEMENTS

The completion of this thesis would have been impossible without the generous co-operation of many devoted people and sources. I am deeply and sincerely grateful to the following:

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- Nemata for kindly agreeing to rescue me at a time when I was almost sinking, and for proof reading the material.
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1. INTRODUCTION

During fission, nuclides are produced which are entirely different from those originally present. Most of these new nuclides are radioactive. They then decay to stable conditions via other isotopes. Yield curves, whose shapes depend on the particular fissile species originally present, on the irradiation time and on the cooling time (time for which the sample has been out of the reactor) can be used to represent the proportion of various fission and decay products in the fuel at any time.

Accumulation of fission products can drastically change the properties and dimensions of solid fuels. At large burn-ups, such as 10% in highly enriched uranium, the character of the fuel material will bear no resemblance to that of the starting material. The removal of fission products is obviously of great concern and hence constitutes the major problem of fuel reprocessing. The chemical state of fission products is, therefore, of considerable relevance to processing economics.

One of the primary objectives of studying uranium alloys is to improve dimensional stability of uranium as a fuel material. The effects which determine dimensional stability are structure sensitive, therefore in the very selection of fuel alloys importance is attached to the structure. This has led to investigations of binary systems of uranium and several other metals e.g. Mo, Nb, Zr, Ti, Ru, Pd etc most of which are fission products. These elements form extended solid solutions with $\gamma$-uranium, and some of these solutions on quenching from the $\gamma$-phase are known to yield a variety of metastable phase of great technological interest.

In the present study, a particular ternary system has been investigated owing to its relevance to the understanding of fuel/fission
product interaction. As a result of this investigation, a partial phase diagram has been established by conventional methods. The component binary systems were reassessed to enhance the study of the ternary system. The structures of the different phases have been determined by conventional methods. Lattice parameter data together with data from the literature have been used to determine the chemical states of uranium in the noble-metal-rich end of the system and the phase equilibria confirmed by thermodynamic calculation.
2.1 Introduction

As a result of the continued growth of the world's population, combined with generally rising living standards, the rate of utilization of energy has been increasing rapidly. Conventional sources, such as water power and fossil fuels - namely coal, oil and natural gas - have become insufficient to supply the world's energy requirement. This has made it necessary that other energy sources be found, such as solar energy, wind energy, tidal energy, geothermal energy and nuclear energy. Energy which can be obtained from nuclear fission has been so successful that it is being used considerably in most of the industrialised world.

Instead of coal and oil, the basic sources of energy are the elements uranium, thorium and plutonium. In most reactors, the nuclear fuel material is in solid form and the structural unit containing, or consisting of, this material is called a fuel element. This preparation of nuclear fuel material has introduced a number of novel, interesting, and often difficult metallurgical problems. Some of these problems have led to the determination of phase diagrams, mainly involving uranium, plutonium, their oxides and fission product elements. Since it is the aim of this thesis to determine the structure of U-Pd-Rh alloys this chapter will review data which is needed in establishing the U-Pd-Rh system.

Until about two decades ago, the majority of previous work on phase equilibria had not dealt with the thermodynamic approach, but as the work of Kubaschewski (1) and others (2) (3) have shown, the application of thermodynamics to phase equilibria can provide useful checks on experimental data and allow its extension to regions
<table>
<thead>
<tr>
<th>Property</th>
<th>Uranium Metal (Natural)</th>
<th>Thorium Metal (Natural)</th>
<th>Uranium Oxide</th>
<th>Plutonium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Stability</td>
<td>Oxidises readily, easily corroded by air or water, easily alloyed</td>
<td>Oxidizes less than Uranium but still active</td>
<td>Chemically stable</td>
<td>-</td>
</tr>
<tr>
<td>Phases Changes</td>
<td>Exists in three phases: $\alpha$ below 663°C $\beta$ between 663°C-772°C $\gamma$ between 777°C-1133°C Distorts on change of phase from $\alpha$ to $\beta$</td>
<td>Exists in two phases, but change is at 1398.9°C</td>
<td>-</td>
<td>$\alpha - \beta$ 122 ± 2°C $\beta - \gamma$ 206 ± 3°C $\gamma - \delta$ 319 ± 5°C $\delta - \delta'$ 451 ± 4°C $\delta' - \epsilon$ 476 ± 5°C $\epsilon$-liq 6395 ± 2°C</td>
</tr>
</tbody>
</table>

* Obtained from various sources. (7) (8) (9) (10) (12) (13)
<table>
<thead>
<tr>
<th>Property</th>
<th>Uranium Metal (Natural)</th>
<th>Thorium Metal (Natural)</th>
<th>Uranium Oxide</th>
<th>Plutonium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g.0m⁻³)</td>
<td>18.5 - 19</td>
<td>11.5 - 11.7</td>
<td>10 - 11</td>
<td>16.5</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>1133</td>
<td>1671</td>
<td>2760</td>
<td>633</td>
</tr>
<tr>
<td>Thermal Conductivity (W.M⁻¹ oK⁻¹)</td>
<td>26 - 40</td>
<td>38 - 52</td>
<td>2.6 - 5.2</td>
<td>-</td>
</tr>
<tr>
<td>Yield Stress (KN.m⁻²)</td>
<td>Room Temp</td>
<td>500°C</td>
<td>Room Temp</td>
<td>500°C</td>
</tr>
<tr>
<td></td>
<td>41,400 - 760,000</td>
<td>69,000</td>
<td>255,000</td>
<td>117,500</td>
</tr>
<tr>
<td></td>
<td>(x10⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tons Recoverable</td>
<td>25 x 10⁶</td>
<td>1 x 10⁶</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Machinability</td>
<td>Good</td>
<td>Very Good</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Must be converted from U²³⁵
difficult to determine by experiment. Due to the above fact and the fact that the thermodynamic calculation will be carried out on this particular system, a section is devoted to the thermodynamic aspects of phase diagrams.

Experimental data on existing related phase diagrams are also reviewed in another section. Finally, the problems which have led to research on uranium fuels are briefly discussed in the following section followed by an account on fission product of which two of the elements encountered in the present project are members.

2.2 General

Owing to the intense heat and irradiation on which the fuel is subjected, the latter should have some characteristic properties to meet the conditions encountered in a reactor. Some of the desirable characteristics for solid fuels are:

(a) Reasonable tensile strengths at high temperatures
(b) Ductility, machinability
(c) High thermal conductivities
(d) Corrosion resistance
(e) High melting point
(f) Radiation stability
and (g) Lack of toxicity

Solid fuels include the metals uranium, thorium and plutonium. However, owing to the fact that these metals meet the above requirements poorly, the alloys of the above metals and ceramic fuels e.g. UO$_2$, UC, PuO$_2$ etc. have replaced, to a great extent, the metal fuels. Table I shows a comparison of properties between the metals and a typical ceramic oxide, UO$_2$. The desirable characteristics listed above mainly concern the control of mechanical failure of the fuel elements, but in an attempt to control or alleviate these problems, other properties may well be affected. For instance, in choosing alloying elements to combat some of
Fig. 2.1 The uranium-zirconium phase diagram showing that Zr is a $\gamma$-stabilizer (175).

Fig. 2.2 The phase diagram of the $\gamma$-stabilizer, Mo and U (176).
Fig. 2.3 The phase diagram of Nb ($\gamma$-stabilizer) and U (177)

Fig. 2.4 The Ti-U system (178)
Fig. 2.5 The variation of corrosion rate of alloyed uranium with temperature (6)

![Graph showing the variation of corrosion rate of alloyed uranium with temperature.](image)

Fig. 2.6 The variation of corrosion rate of unalloyed uranium with temperature (6)

![Graph showing the variation of corrosion rate of unalloyed uranium with temperature.](image)
the problems, consideration should be given to neutron absorption
cross section of the alloying element otherwise neutron economy will
suffer. An example of such a development is provided by work on
U - 12a/oMo alloy which is single phase (4) over a wide range of
both composition and temperature. Owing to the high or marked
anisotropy of γ-uranium, it became necessary that alloying elements
which will stabilize the γ-form of uranium, which does not show
anisotropy, should be sought for. Constitutional studies of binary
systems of uranium and other metals indicated that Mo, Zr, Nb and Ti
were very good γ-stabilizers. (Figs. 2.1, 2.2, 2.3 and 2.4 show the
phase diagrams of U and the metals Zr, Mo, Nb and Ti respectively -
all showing large γ-U regions.) However, the neutron cross-sections
for Mo and Ti are very high (2.65 and 6.1 barns respectively) (5)
and hence this limited the amounts of alloying material which could
safely be introduced.

The chemical stabilities of the metals, as can be seen from
Table I are very poor. U and Th readily react with atmospheric oxygen
and are easily corroded by water. Alloying of the metal has been used
to increase the corrosion resistance of the metals as can be seen from
Figs. 2.5 and 2.6. The corrosion rate of uranium is reduced \( 10^3 \)
dramatically upon alloying with Nb, Zr, Si and Mo. Al has also been used
as an alloying material for the same purpose (6).

2.3 Fission Products

Basically, during fission, a nucleus of high atomic number captures
a neutron resulting in an excited compound nucleus which, instead of
emitting its excess energy, splits into two lighter nuclei having masses
very different to the original heavy nucleus i.e.

\[
X + n \rightarrow X^* \rightarrow A + B + \text{neutrons} + \text{Energy}
\]  

(1)

The lighter nuclei formed in the fission process are called fission
fragments and referring to equation (1), A and B are therefor the
fission fragments or fission products.
Fig. 2.7a
Yield-mass curve for fast and slow-neutron fission of U$^{235}$ [1].

Fig. 2.7b
Yield-mass curve for slow-neutron fission of Pu$^{239}$ [1].
When a neutron is absorbed by a fissionable nucleus, two reactions can occur depending on the energy of the neutrons. For example, when a neutron is captured by a $^{235}U$ nucleus, the reactions which can occur are

$$92U^{235} + n^1 \rightarrow 92U^{236^*} + 2.5 n^1 + \text{energy}$$

When the neutron is absorbed by the $^{235}U$ nucleus, it forms an excited $^{236}U$ nucleus, which exists in this form for a short time. The $^{236}U$, in $10^{-4}$ seconds, may either fission or rid itself of its excess energy by giving off a $\gamma$-ray. As far as the fission process is concerned, the latter process is of no interest. The fission fragments can be of a lot having mass numbers between 70 and 160. The mass distribution of the fission products is shown most conveniently in the form of a Fission Yield Curve in which the percentage yields of the different products are plotted against mass number. A typical yield curve, due to Katchoff (11) for the fission of $^{235}U$ by thermal neutrons and by 14-MeV neutrons and curves for thermal fission of $^{239}Pu$ are shown in Fig. 2.7. Each curve shows two peaks corresponding to the light and heavy groups of products. In the case of $^{235}U$, the maximum lies near mass numbers 95 and 135. As can be seen from the diagram, the yields vary from about $10^{-5}\%$ to about 7% which is such a large range that a logarithmic scale is used for the ordinate of the yield curve.

The fission fragments have too many neutrons for stability and most of them decay by electron emission. This makes the core highly radioactive and thus prevents addition of fuel as a regular operational procedure. Most of the fission products have high
absorption cross-sections (i.e. have a high probability of absorbing neutrons) for neutrons and this upsets the neutron economy. Those products which have high absorption cross-section for neutrons and high yields are said to "poison" the core. The main poisons are Xenon and Samarium. The cross-section and yields of the two are:

\[
\begin{align*}
\text{Xe}^{135} : \sigma_a &= 2.72 \times 10^6 \text{ barns, yield : 6.3}\% \\
\text{Sm}^{149} : \sigma_a &= 4.08 \times 10^4 \text{ barns, yield : 1.4}\%
\end{align*}
\]

These two are so important that they are taken into account when a core is designed.

One of the factors which limits the burn-up of the fuel which can be achieved is the formation of fission products which causes a continual change in the composition of the fuel. The fission products can form discrete compounds, go into solution or remain as elements when they are formed. In the former two situations, the new species formed frequently result in occupying a different volume from their precursors. This is reflected in the dimensional change of the fuel, although the effect is much contributed to by the formation of voids within the fuel. Gaseous fission products together with the coalescence of point defects from the lattice supersaturated with Frenkel defects are the main cause of the voids.

The mechanical properties of the fuel are affected by the mechanical properties of the fission product compounds. Many of the intermetallic compounds are brittle but can act to reduce creep if they are distributed along the grain boundaries. Some compounds have low melting points and can lead to centre melting and expedite creep in the fuel if the former are present in sufficient quantities.

Studies of ceramic fuels (14) - (20) have shown inclusions observed in the fuels to be fission product aggregates. In some of
the cases above, the inclusions were found to be resistant to acids (14) and etching solutions (15). Uranium carbide pins which had been irradiated in the NRU reactor to a burn-up of 20,000 MWd/tonne (6.94 x 10^{20}) (fission/cm^3 of UC) were used to study the behaviour of fission products in uranium (14). Electron microprobe analysis of the particles detected ruthenium, rhodium and palladium in the approximate ratio of 1:0.28:0.12 which compared favourably with the fission yield ratio of 1:0.24:0.19, therefore suggesting a similar precipitation behaviour of the three fission products.

In the UC fuels, no Mo nor Tc was detected in contrast with the findings when UO_2 was used. The free energy of formation of Mo_2C (-12.2 Kcal/g.atom of C at 298°K) is larger than that of UC (-23.4 Kcal/g.atom of C at 298°K) (21) but smaller than that of UO_2 (-10.6 Kcal/g.atom of C at 298°K) (21). From the above figures, it is suggested that in UC fuels, the elements molybdenum and technicium exist as carbides and so are dissolved in the acid whilst in the UO_2 fuel, because oxides of these metallic fission products are far less thermodynamically stable than UC, they remain in their elemental forms and hence are found in the inclusions. Phase studies of UC-Mo system (22) also confirmed the fact that Mo cannot be in solution (below 1800°C) in the fuel (UC). Oi (14) observed in UC studies that Ru precipitation increased with temperature indicating that the precipitation behaviour of ruthenium particles could give some information on the thermal history of UC fuel elements.

The transition metals Mo, Tc, Ru, Rh and Pd are present in oxide fuels in the form of a single phase alloy (23) - (25), (15), (17). They are generally white spherical inclusions. Bramman et al (15) extracted these inclusions from the burnt oxide fuel of initial
TABLE II

Quantitative analysis of the mechanically- and chemically- extracted inclusions (15)

<table>
<thead>
<tr>
<th>Element</th>
<th>Spectral Line Used</th>
<th>Concentration (w/o)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mechanically Extracted</td>
<td>Chemically Extracted</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>1st order Lα₁</td>
<td>43.3</td>
<td>43.5</td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>1st order Lα₁</td>
<td>33.6</td>
<td>35.5</td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>1st order Lα₁</td>
<td>15.7</td>
<td>17.7</td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>3rd order Lα₁</td>
<td>7.4</td>
<td>3.3</td>
<td></td>
</tr>
</tbody>
</table>
TABLE III

Lattice Spacing in Mo-Rh Alloys (26)

<table>
<thead>
<tr>
<th>a/o</th>
<th>Lattice Spacing (Å)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>c</td>
</tr>
<tr>
<td>0</td>
<td>2.7003</td>
<td>4.2730</td>
</tr>
<tr>
<td>0.99</td>
<td>2.7014</td>
<td>4.2752</td>
</tr>
<tr>
<td>1.07</td>
<td>2.7012</td>
<td>4.2746</td>
</tr>
<tr>
<td>2.32</td>
<td>2.7024</td>
<td>4.2773</td>
</tr>
<tr>
<td>3.07</td>
<td>2.7033</td>
<td>4.2793</td>
</tr>
</tbody>
</table>
composition, $U_{0.85 \text{Pu}_{0.15}O_2}$, which had been irradiated in the Dounreay Fast Reactor to 8 - 8.5 a/o burn-up. The composition of the mechanically extracted inclusions was Mo 39.0 w/o, Tc 4.2 w/o, Ru 30.4 w/o and Rh 6.7 w/o and this alloy had a hexagonal structure with $a_0 = 2.73 \pm 0.02 \text{Å}$ and $c_0 = 4.444 \pm 0.040 \text{Å}$. A synthetic alloy was prepared containing the same quantities of Mo, Tc, Ru and Rh by Bramman (15) and after heat treatments, the composition of the synthetic alloy, after analysis, revealed one similar to that found for the inclusions. The results obtained are shown in Table II and are compared with the mechanically extracted inclusions. Despite the low value for rhodium, the composition of the two alloys are very similar. Some rhodium was lost during the preparation of the synthetic alloy and hence the low value for rhodium. However, x-ray diffraction patterns indicated the presence of only a single-phase hexagonal structure with cell size $a_0 = 2.761 \pm 0.002 \text{Å}$ and $c_0 = 4.439 \pm 0.005 \text{Å}$, whilst a microprobe analysis showed signs of a second phase (5% volume) that had a composition close to Mo<sub>5</sub>RuTc. The alloy melted between 1800 and 1900°C and the hexagonal alloy had the same structure as Mo-Rh alloys with a hexagonal close packed ε-phase (12). This structure extends from 45 to 82% Rh and the lattice parameters accurate to ± 0.002 Å were as given in Table III.

The chemical inactivity of the inclusions was very pronounced, resisting acid and etching solution attacks. Davies, Boyle, Hanson and Weidenbawn (27) had to use fusion with NaOH-Na₂O₂ at 600°C to get a soluble material. The chemical inactivity, however, permitted the extraction of these inclusions from irradiated fuel to be achieved by chemical dissolution of the fuel matrix. X-ray examination showed these particles to be single phase and to have a hexagonal structure with $a_0 = 2.756 \pm 0.001 \text{Å}, c_0 = 4.426 \pm 0.002 \text{Å}$. An estimate of the composition gave:

$$\text{Mo:Ru:Tc:Rh} = 3:3:1:1$$
Some palladium was also found in these chemically extracted inclusions. A refined analysis (of limited accuracy because of the nature of the specimen) gave the composition as 41.0\% Mo, 31.9\% Ru, 14.9\% Tc, 7.1\% Rh and 2.0\% Pd.

In mechanically extracted inclusions, a second metallic phase adjacent to the Mo-Tc-Ru-Rh-Pd alloy was found. This phase contained U and Pu and had a composition of 25.4\% U, 13.5\% Pu, 38.4\% Pd, 11.9\% Rh and 2.5\% Ru. X-ray diffraction showed this phase to have a fcc structure with a lattice parameter of 4.127 \pm 0.002 Å.

Three types of inclusions have been reported (17). Jeffrey examined 26 inclusions from 4.6\% burn-up UO₂ fuel with Zircalloy cladding and reported that 18 had molybdenum as major constituent, with no barium but rhodium, ruthenium, technitium and neodymium, and sometimes tellerium and palladium were present in this type of inclusion. Both Mo and Ba were found in four of the inclusions together with Rh, Ru and Tc in appreciable amounts and with Ce, Nd, Zr and Strontium as minor constituents. The remainder contained Ba, Ce, Nd, Zr and Sr but no Mo, Ru, Tc or Rh. In the matrix UO₂, Jeffrey detected Nd, Ce, Pr, La and Zr. Though none of the inclusions was large enough for accurate quantitative analysis, relative proportions of fission product elements averaged over all inclusions was quoted (17) giving:

\[ \text{Mo:Ru:Tc:Rh:Ba} = 8.3:3.6:2.5:1:1.7 \]

The proportions quoted showed good agreement with ratios calculated from fission product yield data (Mo:Ru:Tc:Rh:Ba = 8.1:3.6:2.0:1.0:1.9) and also those quoted for the first three elements by Bradbury et al (16). This would suggest that these non-fission products segregate completely into the inclusions. Other results also confirm this fact.

Obviously, fission products play an important role in the life of the nuclear fuel and so the necessity of understanding fuel-fission
<table>
<thead>
<tr>
<th>Property</th>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U</td>
</tr>
<tr>
<td>Atomic number</td>
<td>92</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>238.03</td>
</tr>
<tr>
<td>Distance of closest approach (Å)</td>
<td>3.052 (γ)</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>α-orthorhombic</td>
</tr>
<tr>
<td>Lattice constants (Å)</td>
<td>γ-bcc</td>
</tr>
<tr>
<td>Valence electrons</td>
<td>5f³ 6d 7s²</td>
</tr>
<tr>
<td>Chemical valence</td>
<td>3, 4, 5, 6</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1133°C</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td></td>
</tr>
<tr>
<td>Ionization Potential (V)</td>
<td>8.3</td>
</tr>
<tr>
<td>Density at 20°C (g/cc)</td>
<td>19.05</td>
</tr>
</tbody>
</table>
Fig. 2.8 U-rich end of the U-Pd System (71)
Fig. 2.9 The U-rich end of the U-Rh system (85)
product phase equilibria is quite high.

2.4 Review of Related Phase Diagrams

2.4.1 General

There has been quite an appreciable amount of investigation on the three elements and the binary systems which are involved in the present work. Evidence indicates that the U-Rh system is well established over the complete range of composition while there are still some question marks over some positions of the other two systems, U-Pd and Pd-Rh. In order that an appreciation of the present ternary system be envisaged, the binary systems and some other ternary systems will be reviewed in this section.

The two metals, Pd and Rh resemble each other in a great number of ways. This is to be expected since they are next to each other in the periodic table. However they differ fundamentally from the third metal, U. Unlike Pd and Rh, U is allotropic and this is reflected in the form of the phase diagrams at the U-ends of the two systems (Figs. 2.8 and 2.9). The difference in sizes between U and the other two elements is also reflected in the restricted solid solubilities of the metals in the respective binary systems while the "similar sizes" of Pd and Rh are largely responsible for the complete solid solubility of the metals in each other at higher temperatures. The distance of closest approach for U is taken as $3.052 \text{Å}$ (the value for $\gamma$-U) as compared to $2.7511 \text{Å}$ and $2.6902 \text{Å}$ for Pd and Rh respectively (77). Despite the similarities between Pd and Rh, the two dissolve in uranium to different degrees as can be seen in the subsequent subsections. Table IV summarises the properties of the three elements.
FIG. 2:10 The phase diagram of U-Pd due to Catterall et al. (71).
Fig. 2.11 Lattice parameter of the δ-solid solution in the U-Pd system as a function of uranium concentration.
2.4.2 The Uranium-Palladium System

This system was first investigated in 1956 by Catterall, Grogan and Pleasance (71) by means of metallographic, x-ray and thermal analysis. They found that palladium dissolves up to 38wt.% (22at.%) uranium, forming the δ-solid solution, UPd$_3$. The diagram shown in Fig. 2.10 is due to Catterall and coworkers (71) and differs from the tentative diagram of Park (72). In addition to UPd$_3$, Park reported the existence of two compounds, UPd and U$_3$Pd$_7$, which are stable to room temperature. This is at variance with Catterall's results which report two different compounds, U$_5$Pd$_6$ and UPd.

According to Catterall et al. (71) in this system, the liquidus shows a maximum at approximately 1640°C which corresponds to UPd$_3$ formation, a minimum at 1305°C and 72wt.%Pd and a eutectic between U and UPd at about 1000°C. The two compounds, U$_5$Pd$_6$ and UPd form by peritectic reactions from UPd$_3$ at 1110°C and U$_5$Pd$_6$ at 1050°C respectively. Two decomposition reactions were also observed viz:

$$2U_5Pd_6 \rightarrow 9UPd + UPd_3 \text{ at } 980°C$$
and
$$3UPd \rightarrow 2U + UPd_3 \text{ at } 970°C.$$  

Palladium was found to depress the $\gamma \rightarrow \beta$ uranium transformation to 756°C leaving the $\beta \rightarrow \alpha$ transformation unaffected. The solubility of palladium in uranium (unlike the opposite end) is very small, < 0.3at.% in both α- and β-phases. In γ-uranium however, the extent of solubility was much greater, rising from less than 1.1% at 760°C to 5% at 998°C. These values agree quite well with those of Park (72) who reports a solubility limit of 4% at 995°C.

The variation of lattice parameter with composition was measured by Catterall (73) (Fig. 2.11). The almost-straight line observed between 0 and 22.3%U supported his earlier finding (70) that U dissolved in palladium to a similar extent. According to reference (73), the change in slope of the curve was believed to be due to a weakening
Fig. 2.12 Partial Phase Diagram of the Pd-U System (75)
of the cohesive forces existing in the alloy (10%) at the point where the palladium d-band is completely filled. Other physical measurements made on the δ-solid solution by Catterall (73) showed some features which were difficult to explain on the basis of single-phase alloys. Montgomery and Pells (74) made some low temperature specific heat measurements which showed that some of the alloys in this region were two phase.

Upon this information, Pells (75) re-examined this part of the phase diagram in 1963. The results indicated that the δ-solid solution had a limit at 16.5%U at 1300°C but breaks down eutectically at 13.5%U and 694 ± 2°C to give two compounds Pd₁₁U₂ and Pd₁₁U₂. The phase diagram due to Pells is shown in Fig. 2.12. The compound U₂Pd₁₇ which is reported is placed at a composition which should have the formula U₂Pd₁₅. The two compounds are reported to be non-cubic. In addition to these two compounds are the compounds UPd₅ and UPd₄ which, unlike the former two, have significant range of homogeneity. UPd₅ is reported to have a non-cubic structure and is formed at 8.8%U and 1440°C by a peritectic reaction. UPd₄ is similarly formed by a peritectic reaction at 21%U and 1525°C and has an ordered structure of the Cu₃Au type. It extends from 19.2%U to 20.8%U; variation of lattice parameter with composition for alloys within this region and annealed at 850°C is shown below (75).

<table>
<thead>
<tr>
<th>Uranium a/o</th>
<th>Lattice parameter Å (75)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.3</td>
<td>4.061 ± 0.001</td>
</tr>
<tr>
<td>20.0</td>
<td>4.063 ± 0.001</td>
</tr>
<tr>
<td>20.8</td>
<td>4.068 ± 0.001</td>
</tr>
</tbody>
</table>

These results show a negative deviation from Vegard's Law.

Above 20.8%U appears the compound UPd₃. This is the only compound which is agreed on by all the three groups of workers. The compound
Fig. 2.13 The U-Pd system employing data from references 71, 75 and 156.
UPd$_3$ is reported by Catterall et al. (71) and Heal and Williams (76) to be of the hexagonal TiNi$_3$(DO$_{24}$) type of structure. The former reported that the parameters of UPd$_3$ in two-phase alloys containing excess uranium differed from those in alloys containing excess palladium - see the table below:

<table>
<thead>
<tr>
<th>Specimen (Ref 71)</th>
<th>Lattice Parameters (Å)</th>
<th>c/a ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>c</td>
</tr>
<tr>
<td>Quenched from 975°C * Saturated with U.</td>
<td>5.76(9)</td>
<td>9.64(1)</td>
</tr>
<tr>
<td>Quenched from 1180°C * Saturated with Pd</td>
<td>5.76(3)</td>
<td>9.52(6)</td>
</tr>
</tbody>
</table>

However, the parameters given by Heal and Williams (76) were $a' = 5.769 \pm 0.001$ Å, $c = 9.640 \pm 0.001$ Å, $c/a = 1.671$ at 75.05 a/o Pd.

The Fig. 2.13 is due to the combination of the results obtained by Catterall et al. (71) and Pells (75). The partial diagram of the system above 25 a/o U determined by Catterall et al. is preferred to that by Park and Buzzard (72) because the former represents a more comprehensive investigation and is better documented. However, a comparison of the invariant reactions for the U-Pd system is shown in the table below:
<table>
<thead>
<tr>
<th></th>
<th>According to (72)</th>
<th>According to (71)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eutectic</td>
<td>996°C, 26.3 a/o Pd</td>
<td>998°C, 37.4 a/o Pd</td>
</tr>
<tr>
<td>UPd eutectoid</td>
<td>950°C</td>
<td>970°C</td>
</tr>
<tr>
<td>(γ-U) eutectoid</td>
<td>738°C</td>
<td>756°C</td>
</tr>
<tr>
<td>β ↔ α</td>
<td>642°C</td>
<td>665°C</td>
</tr>
<tr>
<td>Solubility in γ-U at eutectic</td>
<td>2.2 - 4.4 a/o Pd</td>
<td>5.0 a/o Pd</td>
</tr>
</tbody>
</table>

In Fig. 2.13, the 'erroneously placed' compound, U$_2$Pd$_{17}$ is left as Pells reports it.

Pennell (78) did not report that there was no evidence of the existence of the compound UPd$_5$ in studies that he carried out on Uranium-Rare Earth-Pt metal systems. However, Sailer and Rough (79) have reported that UPd$_5$ was definitely known. The appearance of this compound is controversial where Pells (75) and Sailer and Rough (79) have said UPd$_5$ definitely exists. Pennell (78), Park and Buzzard (72) and Catterall et al. (71) failed to show any evidence of the appearance of the compound. Owing to this controversy, this work will attempt to re-establish the Pd-rich end of the system.

2.4.3 The Uranium-Rhodium System

Until 1967, no complete diagram with supporting data had appeared in any published literature. Yorke (82) reported solubilities of 9 ± 1 a/o Rh at 885°C and 8.5 ± 1 a/o Rh at 850°C. He determined a partial diagram from 0 - 30 a/o Rh. Dwight (80), (81) and coworkers (83)
Fig. 2.14 The U-rich end of the U-Rh system\cite{85}.

Fig. 2.15 The complete U-Rh system \cite{85}.
Fig. 2.14 shows the phase diagram determined by Dwight. The diagram shows the existence of two compounds, $U_2Rh$ and $URh$. He also reported the compound $URh_3$. Both Dwight (83) and Yorke (82) reported a maximum solubility of Rh in $\gamma$-U to be about 9 a/o Rh. In both cases, conventional methods of phase diagram determination were employed.

In 1968, Park (85) established a complete phase diagram of the present system. He also employed the conventional techniques, thermal analysis, metallographic examination and x-ray diffraction. Unlike Dwight, Park did not have any evidence of the two compounds - $URh$ and $URh_2$. His diagram was characterised by four compounds viz., $U_4Rh_3$, $U_3Rh_4$ and $U_3Rh_5$ all of which were formed by peritectic reactions and $URh_3$ which is a congruently melting compound. On the uranium rich end, there seems to be some quite good agreement among the three workers; there is a depression of the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ transition temperatures, a maximum solubility of approximately 9 a/o Rh at about 865°C, and a eutectic horizontal at about 865°C. Park reported a maximum solubility of rhodium in $\gamma$-uranium to be near 8 a/o Rh, in $\beta$-uranium to be 1.5 a/o and in $\alpha$-uranium to be about 0.2 a/o Rh. The solid solubility of uranium in rhodium is about 3 a/o U (85).

Earlier work on this system by Park and quoted by Chiswick (84) indicated that $URh$ was present and that it was formed peritectically. This is in agreement with the work of Dwight (83) and Yorke (82).

Naraine and Bell (86) studying the thermodynamic and phase behaviour in the U-Rh-C system confirmed the existence of $URh$ and $U_2Rh$. They employed standard metallographic and electron probe microanalytical techniques to observe the specimen and made thermodynamic measurements on the alloys with a two-compartment galvanic cell using a single crystal of $CaF_2$ as electrolyte. Their results showed that
the system was characterised by five compounds, \(\text{URh}_3\), \(\text{U}_3\text{Rh}_5\), \(\text{U}_3\text{Rh}_4\), \(\text{URh}\) and \(\text{U}_2\text{Rh}\). This is obviously at variance with the results of Park (85) who reported of only four compounds, \(\text{URh}_3\), \(\text{U}_3\text{Rh}_5\), \(\text{U}_3\text{Rh}_4\) and \(\text{U}_4\text{Rh}_3\). The results of Naraine and Bell (86) at the U-rich end are preferred since they are strengthened by the thermodynamic evidence of the existence of the compounds \(\text{URh}\) and \(\text{U}_2\text{Rh}\).

In general, there is quite a good agreement in the behaviour of the liquidus which falls from the melting point of uranium (1133°C (89)) to about 860°C and 25 a/o Rh and rises to 1700°C at 75 a/o Rh (\(\text{URh}_3\) composition), falls again to the eutectic temperature of 1400°C and finally rises to the melting point of rhodium. \(\text{URh}_3\) has been proved beyond doubt to exist.

It is the only congruently-melting compound and has the highest melting point (except for pure Rh). It is reported to have a \(\text{Cu}_3\text{Au}\) type (L12) structure with a lattice parameter of 3.992 Å (85), (87), (88). This compound reacts with rhodium to form a eutectic mixture near 87 a/o rhodium at 1395°C.

The following data have been used to construct a complete diagram (Fig. 2.15).

(a) Invariant Reactions

(i) At 1395°C and 87 a/o Rh, \(\text{L} \leftrightarrow \text{Rh} + \text{URh}_3\); eutectic reaction

(ii) At 1550°C, \(\text{L} + \text{URh}_3 \rightarrow \text{U}_3\text{Rh}_5\); peritectic reaction

(iii) At 1450°C, \(\text{L} + \text{U}_3\text{Rh}_5 \rightarrow \text{U}_3\text{Rh}_4\); peritectic reaction

(iv) At 1155°C, \(\text{L} + \text{U}_3\text{Rh}_4 \rightarrow \text{URh}\); peritectic reaction

(v) At 865°C and 25 a/o Rh, \(\text{L} \leftrightarrow \gamma\text{U} + \text{URh}\); eutectic reaction

(vi) At 685°C and 6 a/o Rh, \(\gamma\text{U} \rightarrow \beta\text{U} + \text{U}_2\text{Rh}\); eutectoid reaction

(vii) At 625°C and 0.6 a/o Rh, \(\beta\text{U} \leftrightarrow \alpha\text{U} + \text{U}_2\text{Rh}\); eutectoid reaction

(viii) At 720°C and 33 a/o Rh, \(\gamma\text{U} + \text{URh} \rightarrow \text{U}_2\text{Rh}\); peritectoid reaction

(b) Congruently-Melting Compound

(i) 1700°C and 75 a/o Pd, \(\text{URh}_3\)

These data have been obtained from references (83), (85) and (86).
Fig. 2.16 Lattice parameter variation in Pt-metal alloys at high temperatures.
Fig. 2.17 Miscibility gaps of the alloys of fcc Pt metals at lower temperatures
2.4.4 The Palladium-Rhodium System

The first investigation of this system was carried out by Tamman and Rocha (89) in 1931. They examined alloys metallographically in the as-cast and after annealing forms at 1200°C and this indicated that the system consisted of a continuous series of solid solutions with the liquidus rising from the melting point of Pd to that of Rh. Elliott (90) cites the work of Rudnitskii et al. (91) in 1955 which indicates a solid-state immiscibility at low temperatures determined by emf studies. According to Elliott, the results of Ref. (91) indicate that the Rh-rich solid solution was based on a low temperature allotropic form which was stable below 1030°C.

In a preliminary paper, Raub (92) cited results of his unpublished work which indicated that a miscibility gap existed at low temperatures in this system. In 1959, Raub, Beeskow and Menzel (93) presented a complete diagram of this system. The system was characterised by a continuous series of solid solution at high temperatures and a miscibility gap at low temperatures. The critical temperature was reported to be 845°C. The miscibility gap is slightly asymmetrical. The results of Raub et al. (93) disproved the allotropy of rhodium proposed by Ref. (91) and the diagram of Raub et al. is preferred because the method used was conventional and also the results agree quite well with others (92), (94). Alloys of the fcc platinum metals with one another indicated a continuous series of solid solution at high temperatures and wide miscibility gaps at low temperatures (93), (95) and (96). Fig. 2.16 shows the lattice constants of these alloys after high temperature annealing (92). As the figure shows, all the "curves" have continuous slope which nearly obeys Vegard's law thus confirming the fact that there is unbroken miscibility in all the binary alloys of the fcc platinum metals with one another at high temperatures. Fig. 2.17 also shows the
Table V

Difference in the melting points of the f.c.c. platinum metals and critical temperature of miscibility gap (92)

<table>
<thead>
<tr>
<th>System</th>
<th>Difference in the melting points in °C</th>
<th>Critical temperature of the miscibility gap in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-Pd</td>
<td>406</td>
<td>830</td>
</tr>
<tr>
<td>Rh-Ir</td>
<td>494</td>
<td>unknown</td>
</tr>
<tr>
<td>Rh-Pt</td>
<td>190</td>
<td>unknown</td>
</tr>
<tr>
<td>Pd-Ir</td>
<td>900</td>
<td>1476</td>
</tr>
<tr>
<td>Pd-Pt</td>
<td>216</td>
<td>unknown</td>
</tr>
<tr>
<td>Ir-Pt</td>
<td>684</td>
<td>975</td>
</tr>
</tbody>
</table>
existence of wide miscibility gaps in the Pd-Ir (95), Pd-Rh (93) and Pt-Ir (96) alloys. As can be seen from the diagram, there are considerable differences in the critical temperature of the different binary systems. By considering some properties of these metals, it was observed (92) that a correlation exists between the differences in melting points of the pure metals and the critical point (Table V). In the Pd-Ir system, for example, the difference in the melting points of the metals involved is 900°C - the biggest difference and the system has the highest critical temperature, 1476°C; whereas in systems with small melting point difference, no miscibility gaps have been seen yet. There is therefore, some indication that the larger the melting point difference, the higher the critical temperature.

A further confirmation of the miscibility gap in the Rh-Pd system can be seen from the work of Myles (94). Myles measured the activities of Pd-Rh alloys from vapour pressure measurement, and found the plot of activity versus composition curve to exhibit large positive deviations from Raoult's law, which is indicative of miscibility gap formation.

2.4.5 Other Related Systems

One of the binary systems in the present study, Pd-Rh, has a miscibility gap, and might be widened or narrowed on addition of the third element, U. Bancroft (99) was the first to consider the effect of third elements, followed by Timmermans (100) who suggested that the critical point of a binary system is mostly lowered when there is no great difference between the miscibilities of the added substance with each of the binary components, while it is raised by the addition of a substance that mixes more readily with one of the components that with the other. In 1943, Prigogine (101) set out the thermodynamic conditions in which a third element will raise or lower the critical
Fig. 2.18 The complete ternary Au-Cu-Ni system (97)
Fig. 2.19 Experimentally determined miscibility gaps in the Au-Cu-Ni system (97)
point, Tc, of a regular binary solution. These conditions were later (1951) reiterated by Meijering (44), (45) who supplied the fundamental basis to the rule due to Timmermans (100). Two ternary systems which show the effects of raised or lowered critical points in the system will be briefly reviewed in the next two subsections. These two systems are (i) Au-Cu-Ni in which Tc rises, and (ii) Au-Pd-Pt in which Tc is lowered.

(a) The Au-Cu-Ni System

This system has been investigated by Raub and Engel (97). They used alloys prepared from 99.9% Cu, Au and Carbonyl Ni, by melting them under hydrogen and argon. Owing to difficulties encountered in bringing the alloys to equilibrium, long periods of time were needed for annealing. The alloys were, therefore, homogenised at very high temperatures, severely deformed and then annealed at the required temperatures for long periods. In general, powder specimens were examined with Cu Kα radiation either by back-reflection photographs or by Debye-Scherrer photographs using the Straumanis asymmetric film mounting, or whenever possible, small rod specimens were employed for examination.

The results of Raub and Engel are shown in Figs. 2.18 and 2.19. Fig. 2.18 shows a ternary critical point in the system which is located at 20 a/o Au, 60 a/o Ni and 970°C and Fig. 2.19 shows the boundaries or limits of the miscibility gap. In addition, Fig. 2.19 shows tie lines in the two phase region for isothermal sections at 400°C, 700°C and 900°C. The directions of the tie lines clearly indicate that Cu dissolves more in gold than nickel, though in the binaries there are complete solubilities in both Cu-Au and Cu-Ni systems. The rule of Timmermans (100) which is mentioned above is satisfied here, since the binary critical temperature is raised from 845°C (in the Au-Ni system) to 970°C (in the Au-Cu-Ni system).
Fig 2.20  Graphically Determined Isothermal Sections of the Au-Cu-Ni Miscibility Gap (98).
Meijering (102) has also calculated this system. His results agreed very well with those of Raub and Engel (97). He (102) assigned energy parameters to the three binary systems and calculated the phase boundaries and tie lines at 500°C. The results indicated, just as Raub and Engel's (Fig. 2.19) did, that there was a decrease in the solubility of Au in Ni upon addition of Cu and, more importantly, that Cu dissolves more in Au than in Ni.

Tarby et al. (98), in 1978, determined the phase diagram of the Au-Cu-Ni system. Information synthesised from the binary system, Au-Cu, Au-Ni and Cu-Ni by a computer program employing a least square technique (103) was used. The characterisation of the binary systems was extended to the Au-Cu-Ni system. Iso-free energy of mixing curves and isoactivity lines were determined for this system. From the activity data, ends of tie lines were established, and therefore, the miscibility gap was also determined. Fig 2.20 shows the resulting isothermal sections of the Au-Cu-Ni miscibility gap. This compares very well with that obtained by Raub and Engel (98).

(b) The Au-Pd-Pt System

This system was first investigated by Nemilov (28) and coworkers (29) in 1943 and 1947 respectively. However, a more detailed account of this system was given by Raub and Worwag (30) whose work is particularly important.

The most interesting feature is a wide miscibility gap which widens with decreasing temperature. The presence of this gap, obviously, confirms the existence of the miscibility gap reported to have been found in the Au-Pt system (31) - (33). The evidence refutes the existence of a peritectic reaction in the Au-Pt system as has been reported by other investigators (31). This is so because of the fact that lattice parameter measurements obtained at a particular temperature indicated that there is a complete ternary solid solution at that temperature which
Fig. 2.21 Lattice parameter variation in the Au-Pd-Pt system

Fig. 2.22 The Au-Pd-Pt system
would otherwise not exist if a peritectic reaction occurred in the system. This lattice parameter data is reproduced in Fig. 2.21, while the complete system is shown in Fig. 2.22.

So far as the present work is concerned, the shape of the miscibility gap in the ternary system (Au-Pd-Pt) is quite interesting. The miscibility gap in the binary Au-Pt system narrows on addition of Pd and this is a feature which can be seen in the present system. There is no ternary critical point in the system which further supports the results that the gap narrows as Pd is added.

2.5 Review of Methods

The methods used to establish phase diagrams are quite varied. They involve first the preparation of an ingot of the alloy under investigation, homogenising the cast alloy, heat treating the homogenised alloy at the required temperature and then using different methods e.g. metallography, thermal analysis, etc. to determine the crystal structure and number of phases.

It is the aim of this section to summarise the equipment and procedure that have been used for the component binary systems and related systems and establish some of their advantages and disadvantages.

2.5.1 X-ray Analysis

X-ray examination of the alloys was carried out on polycrystalline aggregates and only in the case of Park (72) was a single crystal used. The latter method is seldom employed for equilibrium diagram work. Most of the alloys were examined by the Debye Scherrer method using Phillips 11.46-cm or 9-cm camera with mainly Cu Kα and Co Kα radiations. Powders for x-ray examination were obtained by either crushing the ingots into smaller bits and guiding the bits into fine powders in the case of brittle alloys or filing in the cases of tough materials. In the case of the U-Pd system by Pells (75) in particular, powders were made by filing the annealed alloys under carbon tetrachloride, possibly,
to avoid oxidation and hence explosions. Iron was then removed by magnet from the filings and the latter wrapped up in tantalum foil and sealed in out-gassed silica tubes under vacuum. They were then strain relieved at the annealing temperatures and water quenched and subsequently placed in 0.5 mm capillary tubes for mounting.

Park (85) obtained lattice parameter measurements using a diffractometer. He preferred powder to lump specimen though. Single crystal rotation photographs together with powder methods were used to fix some of the structures of the compounds. In all cases, the lattice parameters were obtained by extrapolating to $\Theta = 90^0$, using the Nelson-Riley function.

2.5.2 Metallographic Examination

Specimens for metallographic examination were, as usual, mounted in thermosetting plastic materials and then rough ground on a series of silicon carbide papers, the final paper being mainly 600 grit. Samples were mostly ground under water. The mounted specimens were then polished on Selyt or broadcloth lap with a suspension of diamond dust in paraffin (85). For the U-Rh and U-Ru alloys, solution A was used for etching, the composition of solution A being as follows:

Solution A: 5 parts orthophosphoric acid
8 parts ethylene glycol
8 parts ethyl alcohol

Solution A was used mainly to electroetch the U-rich alloys with a power input of $\sim 30$ Vdc and 10 A.cm$^{-2}$. Some of the U-rich alloys were however electroetched in 10% chromic acid solution at 5 Vdc and 1 A.cm$^{-2}$. Two etchants were used for alloys in the middle of the system (U-Rh). They were

(i) 60% perchloric acid in water at 10 Vdc and 1 A.cm$^{-2}$
and (ii) 60% nitric acid.
At the rhodium-rich end a 5% NaCN solution at 10 V ac and 10 A cm\(^{-2}\) was used as an etchant. However, the author of the U-Rh system (85) did not mention the etching times.

For the Pd-rich end of the system U-Pd, Pells (75) reports that all specimens prepared in the range 0 - 25 a/o U were etched in concentrated HNO\(_3\). He did not mention etching times. However, he reported that the concentrated HNO\(_3\) produced only slight colour difference on the surface and that the specimens were best examined by means of phase contrast.

Catterall et al. (71) who investigated the whole range of the U-Pd system used the following solution for the uranium-rich alloys:

(i) 50% nitric acid in water
and (ii) a mixture of 20% HNO\(_3\) and 10% HCl in water or (iii) steam.

Etching times were reported to be of the order of a few seconds. For the palladium-rich alloys, a hydrochloric acid reagent was used. This required one or two minutes to work. The difficulties encountered in etching these alloys were occasionally overcome by using a mixture of equal parts of 20% KCN and 20% (NH\(_4\))\(_2\)SO\(_4\) (ammonium sulphate).

2.5.3 Other Methods

(a) Thermal Analysis

This method was used mainly to determine transformation temperatures of uranium, eutectic arrests and some of the liquidus points. In all cases, platinum/platinum-rhodium thermocouples were used for the temperature measurements. Pells (75) does not give details of this analysis although he reports that it was done. The major difference in the work of Catterall and Park is the type of furnace used. While the former used a high frequency induction furnace first used by Adcock (108), the latter used a furnace with a molybdenum wire resistance heating element described by Heal and Williams (109). In all cases, the thermal
analysis crucibles were made from Beryllia powder. Rates of cooling employed were 3°C/min (85) and 10°C/min at 1400°C (71). The thermal analysis data were derived from recordings of time versus temperature as the samples went through a heating cycle.

(b) Electrical resistivity measurements

Pells (75) and Catterall (73) employed this method to confirm their findings in the palladium-rich regions of the U-Pd system. Their results differed considerably, although the procedures employed were quite similar. Both workers used strips of alloy for the measurement (8 x 0.5 x 1 cm³ (75) and and 1 mm² x 1.5 cm (73)). Pells used cast specimens and annealed them at 850°C for 50 hours and cut out the rods with the above given dimensions by spark erosion. The surfaces were slightly rubbed on 600-grade silicon-carbide paper, sealed in evacuated silica capsules and heat-treated to produce the resistivity measurements. In both cases the resistivity measurements were carried out at 20°C.

The methods described above are used quite extensively in phase equilibria determinations. However, they each have their advantages and disadvantages.

The main advantage of the x-ray analysis is that one can obtain more information from its results than the others - for example, information with regard to structure, amount of phases and lattice parameter. This is why it is used quite extensively. The main problem associated with this mode of analysis is line broadening which is encountered when the sample is strained and the lattice is distorted.

Metallographic analysis is used mainly for identification of phases and also for estimating relative amounts of phases. It cannot, in its own right, provide information on the structure of the alloy.

Despite their shortcomings, the present work will use both methods of analysis. The liquid phase will not be treated because of time constraints. This means that thermal analysis will not be used although it has been discussed.
2.6 Thermodynamic Aspects of Phase Diagram

2.6.1 Introduction

It was mentioned at the end of 2.1 that thermodynamics can be applied to phase equilibria and that this has proved to be a useful check on experimental data. It has also allowed regions difficult to determine experimentally to be calculated. The method of calculating phase diagrams from thermodynamic data has a long history. In 1908, Van Laar (39) calculated several binary phase diagrams using mostly the symmetrical parabola for the enthalpy of mixing combining it with Gibbs entropy of mixing.

\[ H = ax(1 - x) \]  

\[ S = -R(x \ln x + (1 - x) \ln(1 - x)) \]  

yielding

\[ G = ax(1 - x) + RT(x \ln x + (1 - x) \ln(1 - x)) \]  

as the Gibbs free energy equation.

Since then, quite a number of workers have similarly calculated metallic (36), (40), (41) and other systems (37).

Later Kubaschewski and Chart (1) and others (43) have used thermodynamic data to determine the range of stable phases in equilibrium. Meijering (44), (45) has made a very thorough analysis of the thermodynamic properties and phase diagrams of ternary regular alloys and Hardy (46) investigated, from a statistical mechanics point of view, the phase section from pure iron to NiAl in which a miscibility gap separates the disordered iron-rich phase from an ordered Ni-Al rich phase. A complete review of the thermodynamic calculation of phase diagrams can be found in a paper by Ansara (47).

In the last two decades, computer-based methods have been employed in calculating phase diagrams. This has been promoted strongly by L. Kaufman, and a resume of his work is published in reference (48) and these methods are now applied throughout the world.
It is therefore the aim of this section to review thermodynamic aspects of phase diagram and also to show how phase diagrams can be calculated.

2.6.2 Basic Thermodynamic Consideration

Thermodynamics is a broad scientific discipline, the essence of which is the development of useful quantitative mathematical relationships between the measurable properties of the system. The development of these relationships is based on observational and experimental evidence as to the nature of system and their reactions. The relationships are expressed in terms of quantities which may be designated as "state variables and state properties".

These thermodynamic relationships indicate how stable one phase is in comparison with another phase at a certain temperature e.g. the solid phase of a pure metal with a certain lattice structure compared with the melt. In order to make this comparison, a temperature dependent function is employed. This function, the Gibbs energy, $G$, is composed of the enthalpy $H(T)$ and the entropy $S(T)$.

$$G(T) = H(T) - T.S(T) \quad (5a)$$

The comparison is made by determining $G(T)$ for every phase at every temperature. The stability criterion is, the more negative the function $G$ of a certain phase is, the more stable is that phase.

From measurements of specific heat, $C_p(T)$ at constant pressure, the Gibbs Energy, $G(T)$ can be obtained. This is so since the two entities, $H(T)$ and $S(T)$ which make up $G(T)$ are related to the specific heat as follows:

$$dH = C_p(T) \quad (6a)$$

$$dS = \frac{C_p(T)}{T} \ dT \quad (6b)$$
Equations (6a) and (6b) can be integrated yielding

\[ H(T) = H(0) + \int_0^T C_p(\theta)d\theta \]  

(7a)

and

\[ S(T) = S(0) + \int_0^T \frac{C_p(\theta)}{\theta} d\theta \]  

(7b)

respectively. When these are substituted into equation (5a), we obtain

\[ G(T) = H(0) - T \cdot S(0) - \int_0^T \left[ \frac{T}{\theta} - 1 \right] C_p(\theta)d\theta \]  

(8)

Therefore, if the entities \( H(0), S(0) \) and \( C_p(T) \) are known, the free energy can be determined. Unfortunately, at times, it is quite difficult to obtain \( C_p(T) \) by direct measurements in which case, suitable estimates have to be obtained by extrapolation and/or interpolation of the measurements (49). These procedures require the use of physical models (35), (54) which contribute to the \( C_p(T) \) curve. These effects are connected with the energy absorptions of the atoms (lattice vibrations and thermal expansion), of the free electrons, and for iron and its alloys of the localised energy state of the 3d electrons (magnetic effects).

It is often desirable to have some idea of the meanings of \( H(T) \) and \( S(T) \) when phase stabilities are being considered qualitatively. For this matter, \( H(0) \) can be taken as the cohesion energy of the atoms at \( T = 0 \) which makes it obvious that \( H(0) \) is the more favourable, i.e. more negative, the stronger the atoms are bounded (34). As the temperature is increased, the atomic bonds are weakened and accordingly more unfavourable states of the atoms and electrons are occupied and thermal energy is absorbed. The contribution of \( H(T) \) to thermodynamic stability becomes less as the temperature increases.
Fig. 2.23 Free energy-composition curves in the Hf-Ta system.
Fig. 2.24 Resultant temperature-composition diagram from data from Fig. 2.23 \((51)\)
The entropy can be conceived as a measure of the uncertainty of our knowledge about the state of the phase (34). This uncertainty increases as the number of ways in which a phase can be composed as different states of atoms and electrons increases. According to the Nernst heat theorem (which was later modified by Planck (34)), at $T = 0$, $S(0) = 0$. As can be seen from equation (7b), entropy increases as the temperature increases, therefore the entropy term contributes more to the free energy or thermodynamic stability as the temperature increases. In fact, the influence of the entropy actually predominates according to equation 8 allowing $G(T)$ to assume more negative values with increasing temperature.

2.6.3 Free Energy - Composition Relations

The usual temperature versus composition diagram is a graphical representation of the most stable states of a condensed solution at a given temperature and at a constant pressure. With these conditions, these states correspond to a minimum of the Gibbs energy of the solution. Therefore, it is possible to determine the limits of composition over which any phase, or a combination of phases is stable, if the Gibbs free energies of all possible phases in a system can be calculated at a given temperature, pressure being constant, as a function of composition. A repetition of this analysis for a number of temperatures will enable the phase boundaries of a system to be drawn to produce a temperature-composition diagram. Kaufman (51) has determined a number of binary phase diagrams by this method. He employed the very important fact that the basis for equilibrium is the competition between phases and calculated or determined the free energy curves for all likely competing phases. Fig. 2.23 shows that results obtained by Kaufman when he computed the free energy composition relations in the hafnium-tantalum system. Fig. 2.24 is the resultant temperature-composition diagram. Referring to Fig. 2.23 at $1200^{\circ}$K the $\beta$(bcc) and $\varepsilon$(hexagonal close packed)
phases are more stable than the α(fcc) and L(liquid) phases since their free energies ($-G^\beta$ and $G^e$) lie below the free energies of the fcc and liquid phases ($G^\alpha$ and $G^L$).

2.6.4 Thermodynamic Definition of Binary Equilibrium

The Gibbs free energy of a binary solution of A and B atoms can be calculated from free energies of pure A and pure B. This is given by the equation

$$G^\phi = (1 - x)G^\alpha_A + G^\beta_B + RT(xlnx + (1 - x)ln(1 - x) + EG^\phi$$  \hspace{1cm} (9)

This is similar to equation 5 which was used by Van Laar (39) to calculate binary phase diagrams.

The first two terms of equation 9 represents the contributions of the pure components A and B (the Gibbs energy of A and B) and are added accordingly, to their weights given by $(1 - x)$ and $x$, where $x$ is the atomic fraction of metal B. The entropy of mixing is represented by the third term and corresponds to a random distribution of A and B atoms onto the lattice sites. The last term, $EG^\phi$ which corrects any deviation between the first three terms and the true value of $G^\phi$ is the excess Gibbs energy. This term may be determined in the same way as $G^\phi$ itself and is equal to zero if the solution is ideal. (As will be explained later, there are several models and empirical equations which can be used to describe this term. But for the sake of simplicity and brevity, the definition of equilibrium in both binary and ternary systems will be explained in terms of the regular solution model.)

According to Kaufman (48), in the regular solution approximation

$$E_G^\phi = Mx (1 - x)$$  \hspace{1cm} (10)

where $M$ is an interaction parameter equivalent to "a" in equation (3).

At a temperature $T_0$, if there is no decomposition, two phases, $\phi = \alpha, \beta$ are in metastable equilibrium with each other and the condition is given by
\[ \Delta G^{\alpha+\beta}(x, T_0) = G^\beta(x, T_0) - G^\alpha(x, T_0) \]  

(11)

In accordance with the Gibbs phase rule, the allotropic \( \alpha/\beta \) transition line \( T_0 = T_0(x) \) for binary alloys can be deduced from the above expression. On the other hand, if decomposition occurs, the most favourable, i.e. most negative Gibbs energies are obtained by the common tangent at the two Gibbs energy curves, \( G^\alpha \) and \( G^\beta \) - tangency rule. The partial molar free energies of components A and B in the A-B binary are defined as

\[ \bar{G}^\phi_A = G^\phi - x \frac{dG^\phi}{dx} \]  

(12a)

\[ \bar{G}^\phi_B = G^\phi + (1 - x) \frac{dG^\phi}{dx} \]  

(12b)

For the case of the regular solution, equations (12a) and (12b) reduce to

\[ \bar{G}^\phi_A = G^\phi_A + R T \ln(1 - x) + x^2 M \]  

(13a)

\[ \bar{G}^\phi_B = G^\phi_B + R T \ln x + (1 - x)^2 M \]  

(13b)

When \( M \) is positive, a miscibility gap forms below a temperature \( T_C \) and the phase decomposes into two phases having compositions \( x_{\alpha_1} \) and \( x_{\alpha_2} \) as defined by equations 14a and 14b.

\[ \bar{G}^\phi_A \bigg|_{x_{\alpha_1}} = G^\phi_A \bigg|_{x_{\alpha_2}} \]  

(14a)

and \( \bar{G}^\phi_B \bigg|_{x_{\alpha_1}} = G^\phi_B \bigg|_{x_{\alpha_2}} \)  

(14b)

For the regular solution case,

\[ RT \ln(1 - x_{\alpha_1}) + x_{\alpha_1}^2 M = RT \ln(1 - x_{\alpha_2}) + x_{\alpha_2}^2 M \]  

(15a)

\[ RT nx_{\alpha_1} + (1 - x_{\alpha_1})^2 M = RT nx_{\alpha_2} + (1 - x_{\alpha_2})^2 M \]  

(15b)
Considering equations (15a) and (15b), a symmetrical miscibility gap can result since
\[ x_\beta = 1 - x_\alpha \quad (16) \]
and \((M/RT) = \ln \left( \frac{1 - x_\alpha}{x_\alpha} \right) \cdot (1 - 2x_\alpha) \) \(^{-1} \) \( (17) \)

In this case, the critical temperature \(T_c\) coincides with \(x = 0.5\) and
\[ \Delta G_A^\phi = \frac{\partial G_B^\phi}{\partial x} = \frac{\partial^2 G_A^\phi}{\partial x^2} = \frac{\partial^2 G_B^\phi}{\partial x^2} = 0 \quad (18) \]
and so \( M = 2RT_c \) \( (19) \)

Equation (18) shows here that in order that miscibility gap is formed in a system, \( M \) should have positive values (38).

Kaufman (51) has illustrated the important role played by \( \Delta G_A^{\alpha\rightarrow\beta} \) and \( \Delta G_B^{\alpha\rightarrow\beta} \) in controlling the phase stability. As pointed out earlier (equation (11)),
\[ \Delta G^{\alpha\rightarrow\beta} = G_B^\beta - G_A^\alpha \]

Combining equations (9), (10) and (11), we obtain
\[ \Delta G_A^{\alpha\rightarrow\beta} = x_\beta^2 M_\beta - x_\alpha^2 M_\alpha - RT \ln \left( \frac{(1 - x_\alpha)(1 - x_\beta)}{x_\alpha x_\beta} \right) \quad (19a) \]
and \[ \Delta G_B^{\alpha\rightarrow\beta} = (1 - x_\beta)^2 M_\beta - (1 - x_\alpha)^2 M_\alpha - RT \ln \left( \frac{x_\alpha}{x_\beta} \right) \quad (19b) \]
where \( x_\alpha \) is the composition of the \( \alpha/\alpha+\beta \) boundary and \( x_\beta \) is the composition of the \( \alpha+\beta/\beta \) boundary. Using equation (19b), a series of \( x_\alpha \) and \( x_\beta \) would be allowed at different temperatures which when plotted will yield the typical \( T-x \) curves (phase diagrams).

2.6.5 Ternary Systems

The regular solution approximation can also be applied to ternary systems and Meijering (44), (45), (104) found the results to agree very well with those obtained by conventional methods (e.g. x-ray analysis,
The application of the regular solution model to ternary systems along the lines suggested by Meijering can be represented by the following equation.

\[
G^\phi = zG_A^\phi + xG_B^\phi + yG_C^\phi + RT (z \ln z + x \ln x + y \ln y) + xz E_{G_{AB}}
+ yz E_{G_{AC}} + xy E_{G_{BC}} \tag{20}
\]

where \( z = (1 - x - y) \), \( x \) and \( y \) are the atomic fraction of components A, B and C respectively; \( E_{G_{AB}}, E_{G_{AC}} \) and \( E_{G_{BC}} \) and the interaction parameter for the phase \( \phi \); and \( \phi \) refers to a solution phase.

Equation (20) is a ternary form of equation (9). When \( z = 0 \), it reduces to equation (9) which defines the thermodynamic equilibrium of a binary alloy.

The partial Gibbs energies of A, B and C in the phase are

\[
\bar{G}_A^\phi = G^\phi - x \frac{\delta G^\phi}{\delta x} - y \frac{\delta G^\phi}{\delta y}
= G_A^\phi + RT \ln z + x^2 E_{G_{AB}} + y^2 E_{G_{AC}} + xy \Delta E_{G^\phi} \tag{21}
\]

\[
\bar{G}_B^\phi = G^\phi - (1 - x) \frac{\delta G^\phi}{\delta x} - y \frac{\delta G^\phi}{\delta x}
= G_B^\phi + RT \ln x + (1 - x)^2 E_{G_{AB}} + y^2 E_{G_{AC}} - y(1 - x) \Delta E_{G^\phi} \tag{22}
\]

Similarly,

\[
\bar{G}_C^\phi = G_C^\phi + RT \ln y + x^2 E_{G_{AB}} + (1 - y)^2 E_{G_{AC}} - x(1 - y) \Delta E_{G^\phi} \tag{23}
\]

where \( E_{G^\phi} = E_{G_{AB}} + E_{G_{AC}} - E_{G_{BC}} \tag{24} \)

The above equations (21 - 23) are the ternary forms of equations (12a) and (12b). Equating the partial molar free energies across a two-phase field in a ternary system is the same thing as applying a tangent plane to the free-energy surfaces of two phases which results
in the generation of the lines from the points of contact on phases 1 and 2. This condition can be represented mathematically by the following equations which are the ternary forms of equations (19a) and (19b)

\[ \Delta G_A^{1\rightarrow 2} + RT \ln(z_2/z_1) + \left( E_{AB}^\phi \cdot x_2^2 - E_{AB}^\phi \cdot x_1^2 \right) \]

\[ + \left( E_{AC}^\phi \cdot y_2^2 - E_{AC}^\phi \cdot y_1^2 \right) + \left( \Delta E_{AB}^\phi \cdot x_2 y_2 - \Delta E_{AB}^\phi \cdot x_1 y_1 \right) = 0 \quad (25) \]

\[ \Delta G_B^{1\rightarrow 2} + RT \ln(x_2/x_1) + \left( E_{AB}^\phi \cdot y_2(1 - x_2) - \Delta E_{AB}^\phi \cdot y_1(1 - x_1) \right) = 0 \quad (26) \]

and \[ \Delta G_C^{1\rightarrow 2} + RT \ln(y_2/y_1) + \left( E_{AB}^\phi \cdot x_2^2 - E_{AB}^\phi \cdot x_1^2 \right) \]

\[ + \left( E_{AC}^\phi \cdot (1 - y_2)^2 - E_{AC}^\phi \cdot (1 - y_1)^2 \right) \]

\[ - \left( \Delta E_{AB}^\phi \cdot x_2(1 - y_2) - \Delta E_{AB}^\phi \cdot x_1(1 - x_1) \right) = 0 \quad (27) \]

To define the locus of points along which \( G_1^\phi = G_2^\phi \) the ternary form of equation (11) is employed. This is given by equation (28).

\[ \Delta G^{1\rightarrow 2} (x_0, y_0, T) = G^\phi (x_0, y_0, T) - G_1^\phi (x_0, y_0, T) \quad (28) \]

This curve, as for the case of binary equilibrium, lies in the two-phase region.

Meijering (104), as stated earlier, successfully employed this technique to establish the ternary system Cr-Cu-Ni at 930°C. This agreed quite well with an experimentally determined isothermal section of the system. The method was crude and so satisfactory quantitative results were not expected. However, in its crudest form, the thermodynamic calculation of the system agreed quite well with the experimentally observed one.

Instead of equation (9), the enthalpy of mixing

\[ \Delta G_{\text{mix}} = axy + bxz + cyz + RT (x_0 n x + y_0 n y + z_0 n z) \quad (29) \]

was used. In this equation, \( a, b \) and \( c \) are the binary interaction parameters of the systems Ni-Cr, Cr-Cu and Cu-Ni respectively. These
Fig. 2.25 Calculated isothermal section of the system Au-Cu-Ni at 930°C (45).

Fig. 2.26 Calculated isothermal section in the Cr-Cu-Ni system at 930°C (104).
were estimated and used in equation (29) to determine $\Delta G_{\text{mix}}$. An isothermal section of the ternary system Au-Cu-Ni and 1200°K was similarly determined (45). Figs. (2.25) and (2.26) show the diagrams obtained for the systems Au-Cu-Ni and Cr-Cu-Ni respectively. In the former, the lines were also calculated which indicated that Cu was more soluble in Au than in Ni and also that a ternary critical point existed in the system.

The above obviously indicates how powerful a tool the regular solution model is. However, there are quite a number of systems for which the regular approximation is too much of a simplification. In this case the "subregular" approximation can be used. The model is used in a work by Dinsdale at the NPL (152). Equation (20) is similar to that employed in the NPL formation which is used for the present work. The main difference is that the excess free energies $E_{GAB}$, $E_{GAC}$ and $E_{GBC}$ depend on the compositions in the NPL "set up" while the regular solution model assumes constant values. The NPL form is discussed in Chapter 5 where the thermodynamic calculations are carried out.

2.6.6 Lattice Stability

In considering the Gibbs energy-composition relationship, a general equation was quoted (reproduced below):

$$G^\phi = (1 - x) G_A^\phi + x G_B^\phi + RT (x \ln x + (1 - x) \ln (1 - x)) + E_{G^\phi}$$

This equation, as explained earlier on, can be thought of as being composed of three parts viz:

(a) weighted components of the pure metals $(1 - x)G_A^\phi$ and $G_B^\phi$

(b) the ideal entropy term, $RT (x \ln x + (1 - x) \ln (1 - x))$

and (c) the excess Gibbs energy, $E_{G^\phi}$
The quantities $G_A^\phi$ and $G_B^\phi$ are almost impossible to calculate absolutely. One of the phases will, in effect, have to be assigned a zero value and the others measured or estimated bearing that in mind. In this case, as has been pointed out (48), the relative stability parameters (as they are called) are very important. The lattice stability parameters, $\Delta G^{\alpha+\beta}$ can be obtained in several ways, although not very accurately. (Equation (11) defines this parameter (i.e. $\Delta G^{\alpha+\beta} = G^\beta - G^\alpha$.)

Lomer (50) has put forward some suggestions as to the way the lattice stability parameter should be calculated. His method is, in effect, obtaining quantitative information on lattice stability from first principle calculations. The formal path for the fundamental calculation of the lattice stability consists of six stages, namely:

1. Assume structure -
2. Evaluate self consistent fields for the component-free atoms -
3. Superpose these potentials to get band structure, and use the resulting wave function to get self-consistent solution for solid -
4. Evaluate correlation energy correction
5. Evaluate total energy -
6. Repeat for all suspected rival structures.

However, this procedure is seldom followed. The usual practice has been to investigate a particular term in the energy expression presuming that it varies rapidly as a function of some structural parameter (51). The effects considered above are usually based on or depend on the outer electrons or details of the Fermi surfaces (e.g. Hume-Rothery rules,
TABLE VI

Enthalpy differences between the α, β and ε forms of various metals computed by pseudopotential method (49),(52),(53)

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Delta H^{\beta+\varepsilon}$ (cal-g-atom$^{-1}$)</th>
<th>$\Delta H^{\alpha+\beta}$ (cal-g-atom$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>-1700</td>
<td>2325</td>
<td>49</td>
</tr>
<tr>
<td>Al</td>
<td>-3200</td>
<td>1170</td>
<td>52</td>
</tr>
<tr>
<td>Mg</td>
<td>-1345</td>
<td>-715</td>
<td>52</td>
</tr>
<tr>
<td>Na</td>
<td>-119</td>
<td>-13</td>
<td>52</td>
</tr>
<tr>
<td>Na</td>
<td>117</td>
<td>-36</td>
<td>53</td>
</tr>
<tr>
<td>Li</td>
<td>-66</td>
<td>-32</td>
<td>53</td>
</tr>
<tr>
<td>K</td>
<td>-46</td>
<td>-13</td>
<td>53</td>
</tr>
</tbody>
</table>
magnetic structures etc.) The distortion of structures or their local stability is usually manageable in this way, but comparisons between distinct structures are less trustworthy because it rests to quite an appreciable extent on assumptions of rigid atomic cores (51).

The problem of computing the stability of various structures of pure metals has been solved with variable success by applying method of pseudopotentials (55), (56), (57). The method has great capabilities of providing relevant information on the enthalpy differences between principal crystal forms at 0°K. Table VI summarises the results obtained by Pick (53) and Harrison (49), (52) who employed the method of pseudopotentials to compute the relative energies of bcc (β), hcp (ε) and fcc (α) forms of Na, Mg, Al and Zn. Harrison's results indicate that the ε form of Zn is less stable than the α-form, something which has not been observed. The value obtained for Na is in relatively good agreement with Pick's who had done similar calculations. The latter's result for Li is in agreement with what has been observed so far of the ε and α-forms at low temperature although that for K indicates stability for the hcp form, contrary to observation. This method of calculating lattice stability is not very reliable and in Harrison's words, "this may change with improved pseudopotentials" (55).

High Pressure studies (58) of metals together with atmospheric pressure thermodynamic and volumetric data can be used in a very simple manner to describe lattice stability of the various forms of polymorphs of metals. The lattice stability $\Delta G^{\alpha\rightarrow\beta}$ is usually present in the form

$$\Delta G^{\alpha\rightarrow\beta} = \Delta H^{\alpha\rightarrow\beta} - T_0 \Delta S^{\alpha\rightarrow\beta} + 23.9P (\Delta V^{\alpha\rightarrow\beta})$$

(30)
Fig. 2.27 Observed P-T diagram for Bi

![Observed diagram for bismuth](image)

Fig. 2.28 Calculated P-T diagram for Bi using equations (32) to (36)

![Computed phase diagram for bismuth](image)
A basic assumption for this form of description is that the enthalpy, the entropy and volume differences between polymorphs are treated as being constants. Kaufman (58) using such a first approximation, derived the lattice stability of the five polymorphs of Bi from observed volume changes and solid/liquid equilibria. The equations are

\[ \Delta G_{B_i}^{1\rightarrow L} = 2160 - 4.8 T + 23.9 P (0.98) \text{ cal/g-atom} \]  
\[ \Delta G_{B_i}^{1\rightarrow II} = 945 - 0.2 T - 23.9 P (0.98) \text{ cal/g-atom} \]  
\[ \Delta G_{B_i}^{II\rightarrow III} = 505 - 0.3 T - 23.9 P (0.64) \]  
\[ \Delta G_{B_i}^{III\rightarrow IV} = 545 - 1.2T \]  
\[ \Delta G_{B_i}^{IV\rightarrow V} = 365 - 0.3 T - 23.9 P (0.25) \]

The Clapeyron equation which is given by

\[ \left(\frac{dT}{dP}\right)^{\alpha\rightarrow \beta}_{T_0} = \left(\frac{\Delta V}{\Delta S}\right)^{\alpha\rightarrow \beta}_{T_0} = \tilde{T}_0 \left(\frac{\Delta V}{\Delta H}\right)^{\alpha\rightarrow \beta} \]

can then be used to plot P-T diagrams. Fig. 2.27 shows the observed diagram due to Klement and Jayarman (59) who carried out high pressure equilibria studies of Bi and Fig. 2.28 shows that due to Kaufman (58) employing equations (32) - (36). The latter reported that the error between the two diagrams is within 5 a/o. These first approximations (which presuppose volume and entropy changes that are independent of pressure and temperature) are good enough to generate good diagrams.

Similar lines were used by Holden (60) to produce similar equations for U. A first approximation permitted a simplified representation of the relative stability of the orthorhombic (\(\alpha\)), tetragonal (\(\beta\)) and bcc (\(\gamma\)) phases on the basis of thermodynamic and volumetric data. The equations are:
TABLE VII

LATTICE STABILITY OF VARIOUS STRUCTURES OF GERMANIUM FREE ENERGY DIFFERENCES (cal-g-atom⁻¹)

\[ \Delta G^{\tau_c \to \beta_c} = 300 - 0.30 T - 23.9 (-0.08 + 1.65 \times 10^{-3}P) \]  \hspace{1cm} (39)

\[ \Delta G^{\tau_c \to \delta_c} = 250 + G(\theta/T) - G(\theta/T) - 23.9P (-0.08 + 1.65 \times 10^{-3}P) \]  \hspace{1cm} (40)

where \( \theta_c = 570^\circ K \) and \( \tau_c = 600^\circ K \)

\[ \Delta G^{\delta \to \tau_c} = 30 + 3.30 T - 23.9 P \ (1.30) \] for \( T \geq 400^\circ K \)  \hspace{1cm} (41)

\[ \Delta G^{\delta \to \delta_c} = 500 + G(\theta/T) - G(\theta/T) \ 23.9 P \ (1.30) \]  \hspace{1cm} (42)

where \( \theta_\delta = 340^\circ K \) and \( \tau_c = 600^\circ K \)

\[ G^{\delta \to L} = 8830 - 7.30 T - 23.9 \ (1.00) \]  \hspace{1cm} (43)

where \( P \) is in Kilobars and \( T \) is in degrees kelvin.

\( \tau \) represents a body-centred tetragonal (white tin) structure,
\( \beta_c \) represents a complex body-centred cubic structure with 16 atoms per unit cell,
\( \tau_c \) represents a complex body-centred tetragonal structure with 12 atoms per unit cell,
\( \delta \) represents the diamond cubic structure,
and \( L \) represents the liquid phase.
\[
\Delta G^\alpha_\gamma = 714 - 0.76 T + 23.9 P \quad (0.142)
\]
\[
\text{cal/g-atom}
\]
\[
\Delta G^\beta_\gamma = 1166 - 1.2 T + 23.9 P \quad (0.095)
\]
\[
\text{cal/g-atom}
\]

Equation (30) which gives a very simple description of phase equilibria has very limited applicability for example in areas where volume and entropy changes are not constant, and also in the third law regimes where \( \Delta S \to 0 \). A typical example of such a case is seen from the calculation of the lattice stabilities of various forms of Germanium by Bates et al (61). Table VII shows the results which indicate that the free energy differences between forms of Ge which are seen at higher temperatures have the typical temperature and pressure dependency (equations (40) and (41)). However, for the description of free energy differences between the \( \delta \) and \( \tau_c \) forms which occur at low temperatures where third law restrictions apply, Debye functions are used.

The first term of the RHS of equation (3C) which has so far been considered constant, can also be treated as a variable depending on temperature. This is the most complex form that the lattice stability form can assume. Kaufman and coworkers (62)-(64) have given such a description to the lattice stability of crystal forms of iron. As such, enthalpy together with entropy and volumes changes are all dependent on temperature and the last two of the different forms of iron is due to the magnetic phenomena characteristic of iron. Tauer and Weiss (65) have also developed similar descriptions of the relative stabilities of the different forms of Mn.

In such descriptions, the heat capacity of a form of iron is expressed in terms of
(a) lattice contributions
(b) electronic contributions
and (c) magnetic contributions
as
\[
C_p^\phi(T) = C_v(\theta^\phi/T) (1 + 10^{-nT}) + \gamma T C_p^\mu(T) \tag{44}
\]
which when integrated yields the following equation
\[
G^\phi(T) = H_0^\phi + G^\phi(\theta^\phi/T) + G^\phi_C(\theta^\phi,T) + G^\phi_M(T) - \frac{1}{2}\gamma^\phi T^2 \tag{45}
\]
where
- \(\theta^\phi\) is the Debye temperature of form of iron
- \(\gamma^\phi\) is the electronic specific-heat coefficient
- \(C_p^\mu\) is the magnetic contribution to the heat capacity
- \(H_0^\phi\) is the enthalpy at 0°K, based on \(H_0 = 0\)
- \(G(\theta/T)\) is the vibrational free energy
- \(G^\phi_0(\theta^\phi/T)\) is the \((C_p-C_v)\) correction term
and \(G^\phi_M(T)\) is the magnetic free energy

Finally, a simple way of describing the lattice stability of crystal forms is one employed by Kaufman (48). In this approach, he assumed temperature independent enthalpies and entropies of transformation for pure metallic non-magnetic elements:
\[
\Delta G^\psi+\phi = \Delta H^\psi+\phi - T \Delta S^\psi+\phi \tag{same as equation (11)}
\]
and has the form of the characteristic straight-line equation \(y = mx + c\).
Since the predominant equation in the above above equation stems from differences in the phonon spectra of \(\psi\) and \(\phi\) which is nearly linear in \(T\) for \(T > \theta_D\) (164), the equation is valid or applicable above the Debye temperature. A \(T^2\) term which is contributed by the difference in the electronic specific heat of \(\psi\) and \(\phi\) and the anharmonic contributions to \(C\) (i.e. \(C_p - C_v\)) is absent here because, in most
cases, this contributes less than 10% of the linear contribution. 
\( \Delta H_{\psi \rightarrow \phi} \) can be taken as the heat of transformation if \( \psi \) and \( \phi \) are stable phases. If \( \phi \) is taken as the liquid phase, then by assuming Richard's rule (66) which states that the entropy of melting of a stable close-packed structure 1st coordination (8) - (12) is \( \approx 2.0 \text{ cal. (mol.}^0\text{K})^{-1} \), 
\( \Delta H_{\psi \rightarrow L} \) can be obtained directly from the melting point \( (T_0^\psi) \) i.e.

\[
\Delta H_{\psi \rightarrow L} = \frac{T_0^\psi}{T_0} \Delta S_f^{\psi \rightarrow L} = 2 \frac{T_0^\psi}{T_0}
\]  

(46)

However, this method of assigning 2.0 cal. (mol.\(^0\text{K})^{-1} \) to \( \Delta S_f \) can cause considerable discrepancies in the relative values of \( \Delta S_f \) of the stable forms, irrespective of their structures (67). Miodownik's (67) work on structural entropy has improved the method of estimating \( \Delta S_f \). In fact, he shows that the application of Richard's rule can affect the phase equilibria treatment by Kaufman and also that the treatment can be extended to the third law regimes. Using the method developed by Ardell (151) for calculating the melting point and entropies of fusion for low temperature allotropes, he showed that some of the values of \( \Delta S_f \) that Kaufman used were unlikely to be correct. He also used a Bernal model for a liquid and arrived at a simple equation which can be used to estimate a zero point entropy, \( \Delta S_f^O \)

\[
\Delta S_f^O = K(\ln Z'_{\text{liq}} - \ln Z'_{\text{solid}})
\]  

(47)

where \( k \) is a constant and \( Z' \) are coordination numbers. Kaufman's (48) simple treatment was used since there were not enough \( \Delta S_f \) values.

In dealing with solid state transformation Kaufman plotted observed and/or estimated values of \( \Delta H^{\alpha \rightarrow \beta} \) and \( \Delta S^{\alpha \rightarrow \beta} \) against group numbers. A best-fit curve through the points enabled unknown values to be estimated. His plots only included groups 4 to 10; however, Micheals et al. (68) and Chan et al. (69) in collaboration with
Fig 2.29 Enthalpy ($\Delta H$) and Entropy ($\Delta S$) differences between fcc and bcc crystal structures of pure metals as a function of Group Number (68).

Fig 2.30 Enthalpy ($\Delta H$) and Entropy ($\Delta S$) differences between bcc and hcp structures of pure metals as a function of Group Number (68).
Aaronson, have extended these plots to include groups 1, 2 and 3. Their results are shown in Figs. 2.29 and 2.30 and include the rare-earth elements which have been assigned the group number 3.5. With this simple treatment and assuming a regular approximation, Chan et al. were able to fit, to quite a reasonable extent, some binary phase diagrams involving the actinide elements (69). (However, they conclude that the Kaufman approach can be improved by incorporating in the regular solution constant the effects of difference in size and valence, i.e. the Hume-Rothery factors. In other words, the regular approximation is too simple to account for some of the systems and therefore, a subregular approach should be employed.)

2.6.7 Procedures for estimating thermochemical data of pure metals and alloys

As was pointed out earlier, Kaufman's approach to calculating phase diagrams relies heavily on availability of thermodynamic data. This, together with the fact that knowledge of phase relationships and thermodynamic properties is required to deal effectively with possible materials problems in the nuclear industry, makes it necessary that ways of estimating thermochemical data should be explored. In exploring ways of estimating such data, a number of predictive models have been used - the major ones being

(a) the Engel-Brewer theory (70),
(b) the model of Miedema, de Boer and Boom (113), (114), and (c) the model of Watson and Bennett (115) - (117).

The models have been used quite extensively to predict or estimate thermodynamic data for properties of alloys and pure metal phases where data are not available and hence, helps greatly to understand and predict phase diagrams.
(a) Engel-Brewer Theory

Brewer (70), (118) - (122) has published several papers on the stabilities of transition metal alloys. He applied a valence-bond model to metals which is essentially Pauling's theory (125). Another important contribution to this theory is the development of the correlation between electronic configuration and crystal structure of normal metals by Hume-Rothery (123), which was later extended to transition metals by Engel (124). The contribution by Engel was summarised by Brewer (70) as follows:

1. Stability or bonding energy depends on average number of unpaired electrons per atom available for bonding.

2. The contribution that d-electrons make to bonding increases with atomic number while that of s or p decreases with atomic number.

3. The concentration of s and p electrons determines the structure. The bcc structure occurs with 1.5 (or less) electrons per atom (this corresponds to the d^{n-1}s electronic configuration, where n = number of valance electrons). The hcp structure occurs between ~1.75 - 2.25 sp electrons/atom (i.e. d^{n-2}sp configuration) and the ccp structure occurs around 3 sp electrons/atom (d^{n-3}sp^2 configuration). The diamond or ZnO and ZnS structures occur with 4 sp electrons/atom.

4. The electronic distribution (number of s, p, d, f electrons) in metal phases is close to the gaseous distribution with the number of unpaired d electrons higher if neighbouring atoms have unpaired d electrons available for bonding.
Fig. 2.31 Potential energies of $d^{10}$ and $d^{7.5}sp^{1.5}$ configurations of Pd as a function of internuclear distance.
Carbon and nitrogen additions supply additional electrons to the transition metals of the third to fifth groups to allow them to take on the very stable electronic structure of the sixth group.

The Engel-Brewer theory has been applied to palladium. The ground state of a gaseous Pd-atom is $d^{10}$. If the average distance, $r$, between the nuclei of the atoms is decreased, the form of the interaction potential is a shallow curve (Fig. 2.31) and only weak Van der Waals forces are experienced. However, if the electronic configuration is changed to $d^{7.5}sp^{1.5}$ configuration by exciting the atoms the potential follows a deep curve as $r$ is reduced, in other words, this configuration is the most stable and will be stabilised as $r \to 0$ (Fig. 2.31). To excite the gaseous atoms from the electronic configuration of $d^{10}$ to $d^{7.5}sp^{1.5}$, an amount of energy equivalent to 586 KJ.mol$^{-1}$ will have to be supplied - the promotion energy. As the internuclear distance is reduced, the energy of states of the $d^{7.5}sp^{1.5}$ configuration falls below that of $d^{10}$ and the cohesion of Pd is due to five bonding electrons per atoms. The net enthalpy of sublimation is the bonding enthalpy, $\Delta H_b$ of Pd atoms in the $d^{7.5}sp^{1.5}$ configuration of 963 kcal due to the five electrons minus the promotion energy of the $d^{7.5}sp^{1.5}$ state of Pd. $\Delta H^*_\text{Sub}$ are known fairly well and can even be predicted if the promotion energy for the elements is known from spectroscopic studies. $\Delta H_b$, enthalpy of bonding can be estimated. Alloys are treated similarly.

(b). The Cellular Model of Miedema and Coworkers

In a series of papers, Miedema and coworkers (113), (114), (126) - (129) have shown that a relatively simple atomic model can be used to account for the heat of formation of transition and
non-transition metals, their solid and liquid alloys and intermetallic compounds. This method describes the energy effects of alloy formation in terms of Wigner-Seitz cells of the component elements.

Two contributions (114) are responsible for the energy effects; the first arises from the fact that the boundary conditions between dissimilar cells change to different effects. There is a discontinuity in the density of electrons \(n_{WS}\) at the boundary and this discontinuity \(\Delta n_{WS}\) will have to be smoothed out since the original densities at the cell boundary of the pure metals correspond to an energy minimum for each of them. The removal of the discontinuity leads to a positive contribution (which to a first approximation, was found to be proportional to \(\Delta n_{WS}\)^2 to the energy alloying (126).

The second contribution arises due to the chemical potential \(\phi^*\) for electrons in the two types of pure metal cells. Charge transfer results in a negative contribution to the heat of formation. This, to a first approximation, is found to be proportional to \((\Delta\phi^*)^2\).

These two portions add up to give
\[
\Delta H \sim (-Pe(\Delta\phi^*) + Q (\Delta_{WS})^2)
\]
with \(\Delta H\) - enthalpy of formation/g-atom of alloy,
\(e\) - the elementary charge,
\(P + Q\) - constants for a given group of alloys systems.

However, careful analysis (126) indicated that the energy term, rather than being simply proportional to \((\Delta n_{WS})^2\), is actually proportional to \((\Delta n_{WS})^{\frac{1}{3}}\) since it contains a factor \(n^{-\frac{4}{3}}\) in front of \((\Delta n_{WS})^2\) in equation (49). Therefore, the equation becomes
\[
\Delta H \sim (-Pe(\Delta\phi^*) + Q_0 (\Delta_{WS}^{\frac{1}{3}})^2) \quad (49)
\]
In considering non-transitional metals, Miedema et al. (126) added a term, \(-R\) which represents a large contribution. This term, \(R\) arises from a more effective d-p hybridisation energy (relative to the pure
d-metal) that is gained when a d-type transition metal acquires a p-electron type neighbouring atom. Thus, the equation (49) becomes:

\[ \Delta H \sim (-P_e(\Delta \phi^*) + Q_o \left( \Delta n_{WS}^{\frac{1}{3}} \right)^2 - R) \]  

(50)

The equation for the prediction of \( \Delta H \) becomes complete when the total area of contact surface between dissimilar atoms is taken into account. The concept "surface concentration" is, therefore, introduced (126) to account for this effect. The surface concentrations of atoms A and B are related to their molar volumes, \( V_A \) and \( V_B \) by the relations,

\[ C_A^s = \frac{C_A V_A}{(C_A V_A + C_B V_B)} \]  

(51)

\[ C_B^s = \frac{C_B V_B}{(C_A V_A + C_B V_B)} \]  

(52)

(where \( C_A \) and \( C_B \) are atomic concentrations of A + B respectively). In a regular solution or solid solution, \( \Delta H \) will contain the product \( C_A^s C_B^s \) in this concentration dependence effect. However, for ordered compounds, owing to the fact that the area of contact between dissimilar cells is larger than the statistical value, the contraction dependence is different from that of the solid solution. The difference can be derived empirically and is given by a simple analytical expression.

\[ f(C_A^s, C_B^s)_{\text{ordered}} = C_A^s C_B^s \left( 1 + 8 \left( C_A^s C_B^s \right)^2 \right) \]  

(53)

Another factor, \( g(C_A, C_B) \) which is a function of the atomic concentration completes the terms required to combine to give a prediction of \( \Delta H \) for transition metals. \( \Delta H \) is, therefore, given by

\[ \frac{\Delta H}{N_o} = f(C_A^s, C_B^s, g(C_A, C_B)(-P_e(\Delta \phi^*)^2 + Q_o(\Delta n_{WS}^{\frac{1}{3}})^2) \]  

(54)

where

\[ g(C_A, C_B) = 2(C_A^2 V_A^3 + C_B^2 V_B^3) / (V_A^3 + V_B^3) \]
Table VIII

Enthalpies of formation of some transition metal compounds (155)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Estimated $\Delta H$ (298.15 K) (kJ mol$^{-1}$) [Miedema]</th>
<th>Experimental $\Delta H$ (298.15 K) (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr $\text{Ru}_2$</td>
<td>-230</td>
<td>-180 ± 3</td>
</tr>
<tr>
<td>Zr $\text{Tr}_3$</td>
<td>-310</td>
<td>-360 ± 38</td>
</tr>
<tr>
<td>Hf $\text{Tr}_3$</td>
<td>-272</td>
<td>-393 ± 42</td>
</tr>
<tr>
<td>U $\text{Ru}_3$</td>
<td>-146</td>
<td>-151 ± 1</td>
</tr>
<tr>
<td>U$\text{Rh}_3$</td>
<td>-159</td>
<td>-218</td>
</tr>
<tr>
<td>U$\text{Pd}_3$</td>
<td>-251</td>
<td>-550 ± 33</td>
</tr>
<tr>
<td>U$\text{Ir}_3$</td>
<td>-213</td>
<td>-418 ± 42</td>
</tr>
</tbody>
</table>
Table VIII compares values of the enthalpy of formation using the predictive model of Miedema and coworkers and experimental values. The table groups the compounds under different values of \( (\Delta \phi^*/\Delta n_{WS}^{1/3}) \). This is because the accuracy of the \( \Delta H \) values is related to \( (\Delta \phi^*/\Delta n_{WS}^{1/3}) \). A list of \( \Delta \phi^* \) and \( \Delta n_{WS}^{1/3} \) values (127) has been compiled for predicting the \( \Delta H \) values.

The two procedures discussed in this section are both used to predict \( \Delta H \) of solutions and compounds. However, they are difficult to reconcile with each other. The model of Miedema for example, explains that alloys of Y, Hf and Zr with Rh or Pd have high stabilities just as does the model of Engel-Brewer, but whereas in Miedema's model, charge (negative) is transferred from the electropositive metals, Y and Zr to the Rh and Pd atoms which, in effect, reduces the number of Y and Zr Al-electrons to fill the Rh and Pd d-levels, the Engel-Brewer model (118) (70) suggests that the number of d-electrons in Y and Zr atoms is increased whilst that of Rh and Pd is reduced.

The models discussed above generally only give an overall value for \( \Delta H \) which is equivalent to a rather simple model - the Regular solution model. These estimates are then used as data or starting material for calculating the free energy curves of phases. From the free energy curves phase boundaries are determined. It is therefore necessary that in the next section some of these models which are actually models which consider the interaction between the various elements involved are reviewed.

2.6.8 Interaction Models

In order that equation (20) can be used to estimate the free energy of an alloy, the term \( E_G^{\phi} \), excess energy should be estimated. To do this, a number of interaction models have been used. These models have been, or may be used to predict the thermochemical properties of mixing and phase diagrams of multicomponent systems.
(a) the Regular Solution Model,

(b) the Quasi-Chemical Approximation

and (c) the Surrounded-Atom Model.

(a) The Regular Solution Model

The regular solution theory was originally developed by Hildebrand (130) (131). It describes a substitutional solution in which every atom is surrounded by Z nearest neighbours, and assumes that Z is the same whatever central atom is considered and that the mean composition is similar to the rest of the solution. No ordering is assumed in the solution and hence the entropy of mixing is ideal. The excess energy for a multi-component system is $\Delta G^E$,

$$\Delta G^E = \Delta H = \sum \lambda_{ij} x_i x_j$$

(55)

where $\lambda_{ij} = 2N_0 (\frac{1}{2} e_{ii} + \frac{1}{2} e_{jj} - e_{ij}) =$ the interaction in the binary energies of formation of solution i-j the different pairs involved.

This model has been widely used to calculate phase diagrams in binary and ternary systems and has been used to estimate thermodynamic properties of binary alloys. Meijering (44), (45) has carried out an extensive work on calculation of phase diagram with this model. His results on the Cu-Ni-Cr system are in excellent agreement with the experimental results (104). Kaufman has estimated isothermal sections at 1800 and 300K for the Mo-W-Os, Zr-Ta-W, Re-W-Ta and Re-Hf-Mo (48).

(b) The Quasi-Chemical (Model) Approximation

In this approximation, the basic assumptions are that every atom has Z nearest neighbours but, unlike the regular solution model, the competitive action of different types of atom towards a central atom is taken into account. The distribution of the components is calculated using a mass-action-like expression (132). In a multi-component system, the most probable number $n_{ij}$ for a pair i-j is
\[ n_{ij}^2 = \left(n_i - \sum_{k=m}^{k=m} \delta_{ik} n_{ik}\right) \left(n_j - \sum_{k=m}^{k=m} \delta_{jk} n_{jk}\right) \times \exp\left(-2\lambda_{ij}/zRT\right) \] (56)

in which the variables \( \delta_{ik} \) and \( \delta_{il} \) assume the values 0 or 1 depending on whether \( i \) is equal to or different from \( k \) and \( l \) and \( m \) is the number of components in the system. The excess Gibbs energy is given by the following expression.

\[ \Delta G^E = \sum_{i=m}^{k=m-1} (zRT/2)x_i \ln \left(\frac{n_i - \sum_{k=m}^{k=m} \delta_{ik} n_{ik}}{nx_i^2}\right) \] (57)

where \( l = 1 \) and the enthalpy of mixing can be shown to be equal to

\[ \Delta G^E = \sum_{i=m-1}^{j=m} \sum_{i=1}^{j=i+1} \lambda_{ij} \left(n_{ij}/n\right) \] (58)

Hagemark (133) has applied this model to describe the thermodynamic properties of liquid ternary solutions and Stringfellow (134), (135) has applied the model to calculate phase diagrams of In-Ga-As, In-As-Sb, Ge-Si-Sn and Ge-Si-Pb. The agreement of the calculated and experimental measurements is excellent.

(c) The Surrounded Atom Model

The basic assumption of this model (also known as the "central atom theory") is to consider an atom in the field of force of its \( Z \) nearest neighbours as the basic entity. This concept was the classical hypothesis: separation of degrees of freedom, quasi-lattice structure for the liquid alloys and absence of long range interaction to describe the configuration of the solution. The classical statistical treatments of Bragg and Williams or of Guggenheim for which, in both cases, the functions are directly related to the partition function of the solution, can be used to derive the thermodynamic functions of mixing. In this model when treating the excess free energy, it is necessary to consider the influence of the degrees
of freedom of vibration which are taken into account in the form of Einstein oscillators. It must, however, be born in mind that the potential energy, like the characteristic temperature of such atoms, is a function of the composition of the surroundings. The regular and quasi-chemical approximation are obtained, if a linear relationship expressing the potential energy with respect to the composition, is taken into account by the two statistical treatments mentioned above. However, if a parabolic relationship is used to express the energy and the characteristic temperature, and if a random solution is considered, it can be shown (136) that the enthalpy of mixing can be expressed by the following equation

\[ \Delta H = x_A x_B (\Delta H_A^\infty) x_B + \Delta H_B^\infty x_A^A + x_A x_C (\Delta H_A^\infty x_C^C + \Delta H_C^\infty x_A^A) + x_B x_C (\Delta H_B^\infty x_C^C + \Delta H_C^\infty x_B^B) + (x_A x_B x_C / 3z - 1) + (\Delta H_A^\infty + \Delta H_B^\infty + \Delta H_C^\infty + \Delta H_A^\infty + \Delta H_B^\infty + \Delta H_C^\infty) \] (59)

where the term \( \Delta H_{ij} \) represents the partial heat of solution of i in the dilute binary solution i-j.

This model was developed simultaneously by Mathieu and coworkers (137), (138) and Lupis and coworkers (140). The model can be generalized to a multicomponent system, and in this case, any excess function can be expressed by

\[ x = \sum_{i=m-1}^{m} \sum_{j=i+1}^{m} x_i x_j (x_i^\infty x_j^\infty + x_j^\infty x_i^\infty) + \sum_{k=m}^{m-1} x_{k+1} (3z - 1) \sum_{i=1}^{k} x_i^\infty \] (60)

(d) **Empirical Equations**

The models which have been described above, when combined with assumptions of the bond energies of the atoms, as an approach to the
thermodynamic function has proved to be very powerful. However, except for the parabolic relationship which is obtained in equation 60, the regular solution and quasi-chemical approximation lead to symmetrical thermodynamic functions of mixing with respect to composition. This behaviour, according to experimental results, is shown by only few systems and, therefore, this has led to the development of empirical models to interpolate the thermodynamic properties in multi-component systems from experimental information for the limiting binary systems.

Representation of thermodynamic properties of mixing of solutions (when data exist) by power series (141) - (146) has been employed to quite an extent. The general form for the excess Gibbs energy can be expressed by the following relation:

\[ \Delta G^e = \sum_{ij} x_i x_j a_{ij} + \sum_{ijk} x_i x_j x_k a_{ijk} + \sum_{ijkl} x_i x_j x_k x_l a_{ijkl} + \ldots \]  

where the summation \( \sum_{ij} x_i x_j a_{ij} \) is given by the following

\[ \sum_{ij} x_i x_j a_{ij} = \sum_i x_i \sum_j x_j a_{ij} \]

and \( a_{ij} = a_{ji} \), whilst \( a_{ii} = a_{jj} = 0 \).

In some cases, the binary coefficients are known if experimental data are available. The higher coefficients are then circulated usually, by the least square methods. Hasebe and Taiji (147) and Counsell et al. (148) have used this equation to calculate isothermal sections of Cu-Fe-Ni and Cr-Fe-Ni (148), (147) and Fe-Cu-Mn (147) systems and obtained excellent agreement with experiment. Gaye and Lupis (150) have also used the equation to calculate the isothermal section at 793K for the Bi-Pb-Zn system. The NPL formation which the present author proposes to employ has such a power series.
CHAPTER THREE

EXPERIMENTAL METHODS

3.1 Materials Used

The uranium used in the preparation of the alloys was supplied by the United Kingdom Atomic Energy Commission at Harwell, Didcot. The purity of the uranium was 99.95 a/o. The impurities (in ppm by weight: were as follows:

- Fe, 7;
- Mn, 5;
- Al, 7;
- Mg, =0;
- Cr, 12;
- O, H and N ~100.

They (uranium samples) were received in the form of buttons which were cleaned to remove superficial oxides before melting.

The palladium used was obtained from Johnson Matthey and Co. Ltd. through UKAEA, Harwell. The purity of the palladium was more than 99.99 w/o. Spectrographic analysis carried out by Johnson Matthey and Co. Ltd. gave the following approximate impurity content in ppm by weight:

- Na, 3;
- Fe, 2;
- Si, 2;
- Cu and Mg, 1 each.

The palladium was obtained in the form of rods of different diameters.

Rhodium was similarly obtained (i.e. from Johnson Matthey and Co. Ltd. through UKAEA). Its purity was 99.99 w/o with the main impurities being Fe, Ir, Pd and Pt. This was obtained as powder which had been compressed into pellets for subsequent melting.

3.2 Alloy Preparation

The alloys which weighed between 3.0 g and 7.5 g were prepared by the direct melting of the elements under a Zr-gettered argon atmosphere in an arc furnace using a non-consumable tungsten electrode (Fig. 3.1). Prior to weighing, the uranium was cleaned by making the metal one of the electrodes in a cell whose electrolyte was made up of H₃PO₄, H₂SO₄ and H₂O in the proportion 1:2:2 to ensure that the black oxide layer which formed on the surface of U-metal was removed. A Stanton balance was used to weigh all the alloy constituents.
Fig. 3.1 The Argon arc-melting furnace
Fig. 3.2 The hearth of the Argon arc-melting furnace
The water-cooled hearth (Fig. 3.2) had two depressions: in one was placed a piece of Zr for gettering and in the other was placed the alloy mixture. After placing the alloy mixture and the Zr getter in the depressions in the copper hearth, the furnace was closed, its atmosphere evacuated, purged four times with argon and finally, back filled with the same gas to a pressure of 280 torr. The zirconium button was first melted to getter the atmosphere and this was done by holding the molten zirconium button in that state for about one minute. Extreme care was taken during the initial stage of the melting of the charge so as not to lose an appreciable amount of the elements. Since palladium was the most volatile and spluttered badly, care was taken to insure minimum loss by melting it slowly before melting the whole charge. The alloys were all weighed after melting to find out how much had been lost as a result of the melting process. Some of the weights have been shown in a table (Table VII).

The ingots were all in the form of buttons and were broken into smaller pieces in a steel percussion mortar. However, the alloys richer in the noble metals (i.e. Pd and Rh) were quite tough and could not be broken up in the steel percussion mortar. These alloys were therefore cut into small portions by a Servomet Spark Machine. After cutting up the specimen, they were smeared in paraffin and hence had to be cleaned in an ultrasonic bath. The spark eroder cuts the samples by producing a rapid series of spark discharges of controlled energy between the tool (a tinned copper wire) and the work (ingot). The sparks erode the ingot by melting a small crater of metal and vaporising or ejecting the liquid into paraffin which contains both specimen and tinned copper wire. The rate of removal of the specimen from the vicinity of the wire depends on the energy and frequency of the discharges. Low energies were used for the cutting up of the alloys since this produced fine finishes.
TABLE VIII

<table>
<thead>
<tr>
<th>Code</th>
<th>U (g)</th>
<th>Pd (g)</th>
<th>Rh (g)</th>
<th>Total Weight (g)</th>
<th>Weight after melting (g)</th>
<th>Weight loss (g)</th>
<th>Percent weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>2.122</td>
<td>3.559</td>
<td>0.236</td>
<td>5.917</td>
<td>5.807</td>
<td>0.110</td>
<td>1.89</td>
</tr>
<tr>
<td>G2</td>
<td>2.091</td>
<td>3.274</td>
<td>0.454</td>
<td>5.819</td>
<td>5.609</td>
<td>0.210</td>
<td>3.74</td>
</tr>
<tr>
<td>G3</td>
<td>2.633</td>
<td>3.822</td>
<td>0.857</td>
<td>7.312</td>
<td>7.163</td>
<td>0.149</td>
<td>2.08</td>
</tr>
<tr>
<td>G4</td>
<td>2.359</td>
<td>3.167</td>
<td>1.025</td>
<td>6.551</td>
<td>6.429</td>
<td>0.122</td>
<td>1.90</td>
</tr>
<tr>
<td>G5</td>
<td>2.579</td>
<td>2.747</td>
<td>1.542</td>
<td>6.868</td>
<td>6.672</td>
<td>0.196</td>
<td>2.94</td>
</tr>
<tr>
<td>G6</td>
<td>2.018</td>
<td>1.642</td>
<td>1.505</td>
<td>5.165</td>
<td>5.150</td>
<td>0.015</td>
<td>0.29</td>
</tr>
<tr>
<td>G7</td>
<td>1.932</td>
<td>1.155</td>
<td>1.822</td>
<td>4.909</td>
<td>4.894</td>
<td>0.015</td>
<td>0.31</td>
</tr>
<tr>
<td>G8</td>
<td>1.870</td>
<td>0.729</td>
<td>2.004</td>
<td>4.603</td>
<td>4.594</td>
<td>0.009</td>
<td>0.21</td>
</tr>
<tr>
<td>G9</td>
<td>1.806</td>
<td>0.335</td>
<td>2.147</td>
<td>4.288</td>
<td>4.284</td>
<td>0.004</td>
<td>0.01</td>
</tr>
</tbody>
</table>

a) Table showing weight of metals, weight after melting, weight loss and percent weight loss after melting.

<table>
<thead>
<tr>
<th>Code</th>
<th>Nominal Composition</th>
<th>a/oU</th>
<th>a/o Pd</th>
<th>a/o Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>(20, 75, 5)</td>
<td>19.96 (20.44)</td>
<td>74.90 (74.30)</td>
<td>5.14 (5.26)</td>
</tr>
<tr>
<td>G2</td>
<td>(20, 70, 10)</td>
<td>19.98 (20.92)</td>
<td>69.98 (68.57)</td>
<td>10.04 (10.51)</td>
</tr>
<tr>
<td>G3</td>
<td>(20, 65, 15)</td>
<td>20.00 (20.52)</td>
<td>64.94 (64.03)</td>
<td>15.06 (15.45)</td>
</tr>
<tr>
<td>G4</td>
<td>(20, 60, 20)</td>
<td>19.97 (20.44)</td>
<td>59.96 (54.02)</td>
<td>20.47 (20.54)</td>
</tr>
<tr>
<td>G5</td>
<td>(21, 50, 29)</td>
<td>20.98 (21.76)</td>
<td>50.00 (48.15)</td>
<td>29.02 (30.09)</td>
</tr>
<tr>
<td>G6</td>
<td>(22, 40, 38)</td>
<td>22.00 (22.08)</td>
<td>40.95 (39.83)</td>
<td>37.95 (39.09)</td>
</tr>
<tr>
<td>G7</td>
<td>(22, 30, 48)</td>
<td>22.13 (22.22)</td>
<td>28.60 (29.32)</td>
<td>48.27 (48.46)</td>
</tr>
<tr>
<td>G8</td>
<td>(23, 20, 57)</td>
<td>22.99 (23.04)</td>
<td>20.04 (19.85)</td>
<td>56.97 (57.11)</td>
</tr>
<tr>
<td>G9</td>
<td>(24, 10, 66)</td>
<td>24.02 (24.04)</td>
<td>9.96 (9.86)</td>
<td>66.02 (66.10)</td>
</tr>
</tbody>
</table>

b) Table showing the nominal composition (in atomic percent), the actual percentage based on the weights of each metal and the atomic percentage of the alloys if the worse case is considered i.e. if all the weight lost was due to loss of palladium only (the most volatile of the three in brackets).
Fig. 3.3 The apparatus for encapsulation of specimens
However, using low energies required longer times and so the cut specimens were covered with more paraffin which increased the cleaning times. The cleaning times ranged between 3 to 5 hours.

Lump specimens, after cleaning, were dried and placed in a Tantalum tube for encapsulation. The Ta-tube was, in turn, placed in silica tube which was evacuated to $10^{-5}$ torr. The evacuated tube is then flushed twice with research grade argon and finally filled with the same gas to a pressure of 150 mm Hg, gettered with Zr and sealed. Fig. 3.3 shows the arrangement for encapsulation.

For x-ray analysis, powder specimens were obtained by filing off some of the lump specimen if the latter was very tough. Any steel particles from the diamond saw were removed with a magnet. The above mentioned procedure for production of powder specimens was used after attempts to make the lump specimens brittle by cooling it with liquid nitrogen below its ductile-to-brittle transition temperature had failed. Most of the powder specimens obtained by filing had to be strain relieved to produce sharper lines.

If the metal was brittle enough, powder specimens were simply obtained by grinding bits of the alloy in an agate mortar. In order to obtain fine and sharp lines on the Debye-Scherrer films, the specimens were ground so as to pass through a wire-mesh sieve. This method of sieving had to be carefully carried out because of the possibility of separating hard second phases through the sieve. This will introduce serious errors in determining the amount of phases present and hence care had to be taken in carrying out this operation. The technique employed to prevent such physical separation of the phases, was to grind a small piece of sample, sieve it and the portion retained on the sieve returned to the mortar for regrinding. The process was repeated until all the samples had passed through the sieve thus ensuring that no particular phase had been sieved preferentially.
3.3 Heat Treatment

Homogenisation treatment, with the object of rendering the composition uniform throughout the samples was carried out on the as-cast samples. This treatment was carried out on portions of most alloys so as not to lose all the alloy of a given composition should an accident occur. Large portions of a given alloy were inserted into a high silica glass tubing under an argon atmosphere as protection against oxidation and sealed. The capsules (sample + glass tubing) were loaded on to a ceramic boat and placed in a furnace 750°C for 3 weeks. Metallographic analysis revealed that this temperature was not high enough to relieve homogenisation and this necessitated the upgrading of the temperature to 1000°C. The steps taken were similar to that described above, except that the samples were placed in a tantalum tube before inserting into the silica tubing. The soaking times of the samples ranged from 0 - 20 days depending on the composition. In all cases, the capsules were furnace cooled.

The second type of heat treatment of the alloy was carried out at particular temperatures (1050°C, 1150°C and 1250°C) in order to bring the sample to equilibrium at the said temperatures, followed by quenching to retain the equilibrium state. The samples were, again, placed in tantalum tubes, which were in turn placed in the silica glass tubing, flushed twice with argon and sealed. The resultant capsules were loaded on to ceramic boats and placed in the furnace with a thermocouple within ½" of the capsule. The soaking times were:

(a) 15 - 20 days at 1050°C
(b) 10 - 15 days at 1150°C
(c) 3 - 7 days at 1250°C
Fig. 3.4 Multipurpose holder (with specimen)

Steel ring
Conducting resin
Specimen
Non-conducting resin
Persnex disc
3.4 Alloy Characterisation

The alloys were characterised by the following methods:

(a) Metallography

(b) X-ray analysis

and (c) Electron microprobe analysis

X-ray analysis was used more than any of the other methods with electron microprobe analysis being least employed. Some difficulties were encountered in the metallographic and electron microprobe techniques. However, these problems were reduced to quite appreciable degrees by various methods.

3.4.1 Metallography

Samples were mounted in a compound multi-purpose holder. This was made up of a perspex disc with a hole in the middle into which a steel ring fits. The specimen was placed on top of the ring and contact between the two secured by use of a conducting resin (Fig. 3.4). The steel ring afforded a back contact to enable electro-etching to be performed and also, a hole in the ring to allow the specimen to be polished or ground by an automatic polisher/grinder. Another advantage of the multi-purpose holder is that it allowed the specimen to be etched cathodically and also to be used directly for microprobe analysis owing to the contact between the specimen and the steel ring.

The specimens were ground and polished on a 69-1000 Automatic Miniment Grinder/Polisher. This instrument was used to grind the specimen on a series of silicon carbide papers, the final paper being the 600 grit. Water was used as lubricant.

The samples were polished on a series of nap-free pads impregnated with diamond dust (0.5 μ) and 0.1 μ) respectively, and lubricated with Automet lapping oil. They were finally polished on a nylon cloth impregnated with 0.5 μ Al₂O₃ using water as a lubricant. The samples were washed, dried and examined under the microscope.
Fig. 3.5 Cathodic Etching Machine
Samples which were devoid of surface scratches were etched and re-examined. Three etching techniques were used, viz. chemical etching, electro-etching and cathodic etching in which the sample is made one of the electrodes (cathode) in an evacuated chamber. The technique used depended on the composition of the alloy.

Palladium-rich alloys were etched with one of the following two reagents:

(i) $\text{H}_2\text{SO}_4$, $\text{H}_3\text{PO}_4$ and $\text{HNO}_3$ mixture in the ratio 1:1:1

(ii) Aqua regia ($\text{HCl}$ and $\text{HNO}_3$ in the ratio 3:1)

Etching times were of the order of a few minutes. These alloys were considerably difficult to attack.

Rhodium-rich alloys and alloys with Rh-Pd in 1:1 ratio were electro-etched in a solution of the same composition as (i) above, with a power input of about $30 \text{ V Ac}$ and $0.4 \text{ A/cm}^2$. These etching times were again, of the order of a few minutes. This method produced only slight colour differences and the specimens were best examined by means of phase contrast.

Specimens consisting of the compound phases URh$_3$, UPd$_4$ and UPd$_3$ were etched by a third method – cathodic etching.

The equipment for this method consists of a hollow glass cylinder, $I$ (10 cm in diameter) as a closed chamber with two electrodes at the ends which ensure the production and flow of ions used in the etching process. Fig. 3.5 is a picture of the equipment. The specimen "sits" on the cathode and is actually part of this electrode. The glass cylinder is placed over the cathode, $F$ and with a top brass cover, $K$, this makes a closed chamber. The anode is made of tungsten and has a disc, $B$ at its end which spreads the ion beam uniformly in the chamber. The cathode, $F$ is situated at the bottom of the chamber. An insulating cap, $E$ is slotted onto $F$ and then the specimen holder, $D$ (with the specimen on it) is slid on to the brass tip of the cathode $F$. The
Fig 3.6 Circuit diagram of the plasma (cathodic) etching machine
 protector, H is then screwed on to the specimen holder insulating the whole of the cathode, thus preventing the ion beam from "straying". This allows the ion beam to be concentrated on the exposed sample. A pump is connected to the base of the chamber to evacuate it.

The procedure includes "loading" the sample holder with the sample and securing the former on to the cathode. The glass cylinder is then placed over the cathode and the brass cover placed on top of the latter. The space is evacuated to about 0.01 torr, flushed with argon gas and evacuated again. This procedure is repeated 3-4 times and the chamber is filled with argon to about 60 μ pressure. By means of a variac, a voltage drop of between 1000 V and 3500 V is created between the two electrodes. The current and voltage which can be varied by either using the variac or changing the gas (argon) pressure were recorded on an ammeter, J and voltmeter, G respectively. The etching times ranged between some few minutes to several minutes (5 - 50 minutes).

This method was employed by Haines (108) for similar alloys with an appreciable amount of success. The circuit diagram for the system is shown in Fig. 3.6. This differs from the one employed by Haines (108) by the presence of the extra auxiliary circuit, A. The auxiliary circuit makes the system safer as it ensures that the primary circuit is always broken whenever the dial on the variac is not at 0 V (zero voltage) at the beginning of each etching period which can, otherwise, prove to be dangerous.

3.4.2 X-ray Analysis

X-ray diffraction patterns were obtained from many of the as-cast and annealed specimens. Three methods were employed, namely the Debye-Scherrer, Guinier and diffractometer methods.

Samples were sealed in 0.5 mm capillary tubes and mounted on a 19 cm Debye-Scherrer camera employing the unsymmetrical, or Straumanis,
method of film loading. The samples were then irradiated using Cu $K_\alpha$ radiation ($Cu\ K_\alpha = 1.54056\ \AA$, $Cu\ K_\alpha_2 = 1.54439\ \AA$) (109). The radiation was Ni-filtered. Apart from the nickel filter placed in front of the collimator, a Ni foil was mounted concentric with the film to reduce the intense background on the high-angle end of the film.

The concentrically placed Ni foil served its purpose in some cases but not in others. Occasionally, an added disadvantage was that the lines on the films appeared very faintly after about 3 - 4 hours of irradiation. A Co $K_\alpha$ source was therefore used in an attempt to reduce the background radiation but this did not improve the quality much. Most the samples were therefore irradiated with a Cu $K_\alpha$ source.

A further attempt was made to combat the background fluorescence which was intense at the high-angle end of the films by using the Guinier method. The XDC-700 G-H camera was used. Powder specimens which had been strain relieved were smeared on double-sided sellotape which was then stuck on to a rectangular specimen holder. The radiation used was, again, Cu $K_\alpha$. The advantages of this method were that either lines from the high-angle end or low-angle end only could be received on the film which was also concentrically placed in the cylindrical camera. This thus avoided the high-angle lines and therefore the intense background fluorescence associated with it. The lines obtained were sharp and, like the Debye-Scherrer method, they were measured on a vernier scale and using the Nelson-Riley function, accurate lattice parameters were obtained from the line position data. Use was made of a programme on a Texas (TI59) Instrument developed to calculate $\sin \theta$, $\sin^2 \theta$, $h^2 + k^2 + l^2$ and "a" values from the line position data. The programme originally developed by Miodownik was
quick and very reliable. The programme required & - inputs but the present author modified it to accept the raw line positional data as input.

In order to estimate, and in some cases, determine the relative amounts of different phases in samples, the diffractometer was used. The samples used were, again, in powder form. The specimens for the diffractometer were made in the same way as those for the Guinier method. Cu Kα radiation was used as the x-ray source. In two phase alloys, the 111 and 311 lines were scanned. The relative areas under the peaks were measured and the relative amounts of the phases determined from the areas. In this case copper was used as standard to obtain accurate line positions to check on lattice parameters. In some cases both Cu Kα and Co Kα (Co Kα₁ = 1.788965 Å, Co Kα₂ = 1.792850 Å) radiations were used to scan the whole 2θ-range to check lattice parameter values.

3.4.3 Electron Microprobe Analysis

Microprobe analysis was carried out on some of the specimens using a JEOL JXA 50A microscope,

(i) to confirm the composition of single phase alloys and (ii) to determine compositions of phases in multiphase alloys.

This equipment has the conventional vertical column layout, with specimen stage controls at the bottom of column together with an optical microscope and a Bragg spectrometer on either side of it. The detector, Si(Li) is located at the rear of the column. The electrons in the microprobe were obtained, from a tungsten filament electron gun held at an accelerating voltage of 25 kv. At this voltage, the sums of the atom fractions of the component elements were found to vary very much from 1. The voltage was, therefore, reduced to 15 kV where quite reasonable results were obtained. The electron beam was accelerated
and focused by electromagnetic lenses to a fine beam capable of 1 μm
resolution. The electrons excite the characteristic x-rays of the
elements present in the sample provided the incident beam is of
sufficient energy. The intensities of the x-ray lines from the
specimen are compared with those from standard samples (pure metals
in the case of Pd and Rh and UPd$_3$ in the case of uranium). Two wave-
length dispersive spectrometers were used to analyse the characteristic
x-rays. The signal from the spectrometer is fed to a pulse height
analyser and then to a scalar and digital print linked to a teletype
tape.

The characteristic radiation used to detect each element is
shown below:

<table>
<thead>
<tr>
<th>Element</th>
<th>Radiation</th>
<th>Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>M$_\alpha$</td>
<td>Quartz</td>
</tr>
<tr>
<td>Pd</td>
<td>L$_\alpha$</td>
<td>Quartz</td>
</tr>
<tr>
<td>Rh</td>
<td>L$_\alpha$</td>
<td>Quartz</td>
</tr>
</tbody>
</table>

A programme was used to calculate the concentration of the elements
from the peak to background counts taking account of changes in
specimen current. In this programme, the peaks of the different
elements were deconvoluted before the calculation was made. This
solved, to some extent, the problem of the overlapping of the three
peaks (U M$_\alpha$, Pd L$_\alpha$ and Rh L$_\alpha$ lines). The programme was also corrected
for fluorescence, atomic number effects and absorption. The final
results were accurate to ± 2 a/o.

3.5 Phases Detected

The phases in the system were mainly detected by x-ray analysis
and then confirmed by either metallographic analysis or by electron
microprobe analysis. A qualitative analysis was usually obtained on the phases by using the Debye-Scherrer method. A photograph was taken of each sample and this was compared to photographs of the pure compounds and solid solutions. Another photograph was taken making sure that the lines were sharp so as to obtain a lattice parameter measurement from it. The following phases were found in the system:

(i) $\text{UPd}_4(\text{Rh})$, $\alpha_1$ - a solution of rhodium in the compound $\text{UPd}_4$. This has the structure of $\text{UPd}_4$ i.e. $\text{Li}_2$ (fcc).

(ii) $\text{UPd}_3(\text{Rh})$, $\varepsilon$ - a solution of rhodium in the compound $\text{UPd}_3$. This has the hexagonal (D024) close-packed structure of $\text{UPd}_3$.

(iii) $\text{URh}_3(\text{Pd})$, $\alpha_2$ - a solution of Pd in $\text{URh}_3$. The x-ray structure of this phase is also face centred cubic $\text{Li}_2$.

(iv) $\text{Rh}(\text{Pd},\text{U})$ or $\text{Pd}(\text{Rh},\text{U})$ ($\delta'$ or $\delta$) is a solution of U and Pd in rhodium or uranium rhodium in palladium. This has a face centred structure like the $\delta$-solution in the system U-Pd.

(v) A solution of Pd in a compound involving U and Rh ($\varepsilon'$). This has a non-cubic structure.
4.1 Results from the different analytical procedures

4.1.1 X-ray analysis

Debye-Scherrer powder photographs were taken of the alloys. The lattice parameter measurements obtained by this method for alloys having compositions lying along the line joining URh$_3$ and UPd$_4$ are shown in Table IX. The error for the lattice parameters so obtained was ± 0.002 Å except for alloys with high noble-metal content where errors ranged between ± 0.002 and ± 0.004 Å. Lattice parameter versus composition curves were also plotted. (These have been shown in the appropriate sub-sections of this chapter and chapter 5.) The variation across the α$_2$ single phase region in particular, was almost linear, thus obeying Vegard's law (Fig. 4.1). A maximum was seen at a point $X_{\text{UPd}_4} = 0.85$, where $X_{\text{UPd}_4}$ is the mole fraction of UPd$_4$. To check on the accuracy of the lattice parameter of the alloys in general (obtained from the Debye-Scherrer method), and of the alloys showing high lattice parameter (maximum in Fig. 4.1) in particular, the Guinier method was employed. Comparison between the results produced from these two methods is shown in Table X. The values obtained by the Guinier method were slightly lower than those obtained by the other method, although the same variation was shown by both methods. The lower values from the Guinier method are not surprising since the programme used to compute the values was designed to calculate the average of the lattice parameter from the individual lines.

The variation of lattice parameter with composition of alloys 2 a/o U away from the Pd-Rh base line at 1250°C is also shown in Fig. 4.2. The almost linear variation obtained indicates that the
# TABLE IX

**Lattice Parameter Variation across the Pseudobinary Section URh₃ - UPd₄**

<table>
<thead>
<tr>
<th>Nominal Composition(%)</th>
<th>Lattice Parameter (a, \text{(A)})</th>
<th>Microprobe Results(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>U</td>
</tr>
<tr>
<td>20 80 0 1 4.063</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>20 75 5 1 4.070</td>
<td></td>
<td>21.0</td>
</tr>
<tr>
<td>20 70 10 1 4.078</td>
<td></td>
<td>20.2</td>
</tr>
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<td>20 65 15 1 4.067</td>
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<td>21.1</td>
</tr>
<tr>
<td>20 60 22 1 4.064</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>21 50 29 1 4.047</td>
<td></td>
<td>19.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.9</td>
</tr>
<tr>
<td>22 40 38 2 4.029</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>22 30 48 2 4.018</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>23 20 57 2 4.009</td>
<td></td>
<td>22.8</td>
</tr>
<tr>
<td>24 0 66 2 3.998</td>
<td></td>
<td>22.9</td>
</tr>
<tr>
<td>25 0 75 2 3.991</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>
Fig 4.1 Lattice Parameter variation across the Quasi-binary System URh₂-UPd₄.
Fig. 4.2 Lattice Parameter of Ternary Alloys

\[ U_{0.02}(Pd_xRh_{1-x})^{0.98} \]

![Graph showing lattice parameter (a) vs. relative atomic fraction (x).](image)

- Cullity (109)
- Catterall (71)
- Present work
(a) Microstructure of alloy 14 (27/63/10) (x 1K); cathodic etching; bright: $\varepsilon$, dark: $\alpha_1$ at 1250°C

(b) A magnified photograph of alloy 13 (5K) to show the two phases more clearly
(c) Alloy 7 (22/30/48) (x 1K); $\alpha_2$ single phase at 1150°C

(d) Alloy 1 (20/75/5), (x 1K); $\alpha_1$ single phase at 1150°C
(e) Alloy 30 (22.5/5/72.5) (x 1K); dark: $\alpha_2$, bright: $\delta$; 1250°C

(f) Alloy 32 (12.5/5/82.5) (x 1K); dark: $\alpha_2$, bright: $\delta$; 1250°C
(g) Alloy 29 (5/47.5/47.5) (x 0.5K); dark : \( \delta' \); bright : \( \delta \); 1050\(^\circ\)C chemical etching
region is occupied by a single phase (the Pd-Rh solid solution).
Similar results have been used to establish the different phase fields
of the ternary system.

4.1.2 Metallographic Analysis

Microscopic examinations were carried out on the samples in both
as-cast and annealed conditions and were examined after polishing and
etching as described in section 3.4.1. Typical microstructures of
some phases in the ternary system are shown in Fig. 4.3 Figs. 4.4a
and 4.4b show typical photographs of successfully etched alloys by two
different etching procedures. The results show that chemical etching
(using etchants described in section 3.4.1) was not very successful
on alloys with high uranium content, they were quite successful when
employed on noble-metal rich alloys. Figs. 4.4c and 4.4d are the
results of etching the same alloys by using a mixture of acids and
cathodic etching respectively.

4.1.3 Electron Microprobe Analysis

Results from the electron microprobe analysis indicated that the
actual compositions (obtained from the weights of the metals used)
were quite close to the compositions of the alloys obtained from this
analysis. They showed that there was a maximum of about 1.1 a/o
shift between the composition obtained from this analysis and the
composition obtained by weighing the elements. This is very good in
the sense that the error was well within that incurred in using the
electron microprobe (2 a/o): the nominal composition and the EPMA
results for some single and two phase alloys are shown in Table XI.
These results were used to determine the phase boundaries of two phase
fields. An important application of this analysis was to ensure that
the elements were uniformly distributed in the alloys. Fig. 4.5 is
a microscan of U across alloy 19 showing a uniform distribution of the
element in the alloy. Similar scans for the other two elements showed
Fig. 4.4a Cathodic etching of alloy 30 (22.5/5/72.5) (x 1K)

Fig. 4.4b Chemical etching of alloy 35 (10/30/70) (x 1.5K)
Fig. 4.4c Chemical etching of alloy 30 (22.5/5/72.5)

Fig. 4.4d Cathodic etching of alloy 35 (10/20/70)
Fig. 4.5 Microscan of U across alloy 19
TABLE X

COMPARISON BETWEEN THE RESULTS OF LATTICE PARAMETER
MEASUREMENT OBTAINED BY TWO DIFFERENT X-RAY METHODS
AT 1250°C

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<tr>
<th>Alloy Composition (%)</th>
<th>Lattice Parameter, Å</th>
<th>Debye Scherrer</th>
<th>Guinier</th>
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that the elements were uniformly distributed i.e. no segregation of the elements occurred.

4.2 Current Binary-Phase Diagrams

In order to make the establishment of the ternary system easier, certain portions of the component binaries were re-examined. This included the Pd-rich and Rh-rich portions of the U-Pd and U-Rh systems respectively and observation of five alloys prepared across the Pd-Rh system. All the binary alloys involved here were examined by x-ray using the Debye-Scherrer method.

4.2.1 U-Pd

Two alloys were prepared in this system, with compositions 17 a/o U and 18 a/o U. These samples had been prepared by Pells (75) and had been reported by him as single phase alloys. X-ray analysis clearly showed these two alloys to be in a two phase field at a temperature of 1150°C. The lattice parameters measured for these alloys indicated the alloys to be of two fcc structures, one with super-lattice lines. The lattice parameters obtained are shown in the table below. They showed that one phase was the δ-solid solution reported by Pells (75) and by Catterall and coworkers (71) and the other phase was the UPd₄ phase which was found by Pells but not by Catterall (71). There was no indication of the existence of a phase with a non-cubic structure.

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<th>Lattice Parameter (Å)</th>
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Electron Microprobe Analysis on Single and Two-Phase Alloys

at 1250°C

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18 a/o U alloy

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</table>

The average density of UPd$_4$ was found to be 12.41 g/cc in distilled water. This is in good agreement with the value of 12.31 g/cc obtained by Terekhov et al. (156).

4.2.2 U-Rh

A few numbers of alloys examined by x-ray analysis confirmed the existing diagram determined by Park (85). Three alloys of compositions 80, 90 and 95 a/o Rh were prepared, heat-treated at 1250°C after homogenising and observed. All of them showed the URh$_3$ pattern and the simple fcc lines of Rh. However, the lattice parameter which was obtained for the Rh-rich solid solution phase (i.e. U in Rh solid solution) was quite high and predicted the Rh/Rh-URh$_3$ boundary to be 2 a/o. This value is very high compared with Park's value of about 0.05 a/o Rh.

80 a/o Rh alloy

<table>
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<td>3.811 (5)</td>
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TABLE XII
Lattice Parameter Measurements in the Pd-Rh System

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</table>

Temp 1 = (i) 800°C in the case of present work
   (ii) 600°C in the case of Raub's work
Temp 2 = (i) 1150°C in the present work
   (ii) 900°C in Raub's work
* alloy was annealed at 800°C
Code numbers apply to alloys in the present work only
**4.2.3 Pd-Rh**

The five alloys prepared in this system were all single phase at 1150°C. At 800°C, alloys 3 and 4 (the 50 a/o and 30 a/o Pd alloys respectively) were found to be two phase. The x-ray films showed two sets of lines and the lattice parameters measured are shown in Table XII. Attempts at annealing the alloys at 500°C were not very successful since the alloys could not attain equilibrium structures even after six weeks. However, the results at 800°C and 1150°C indicated that there is a
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<th>Phases</th>
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<td></td>
</tr>
<tr>
<td>G20</td>
<td>U 16 Pd 80 Rh 4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.045</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G21</td>
<td>U 14 Pd 84 Rh 2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.913</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G22</td>
<td>U 12 Pd 86 Rh 2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.907</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G23</td>
<td>U 22.5 Pd 67.5 Rh 10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.084</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(+ from one line)
Fig. 4.6 Lattice parameter variation with composition in Pd-Rh alloys
Fig. 4.7  NOBLE METAL-RICH END OF U-Pd-Rh SYSTEM at 1250°C

- Single phase alloy
- Two phase alloy
Fig. 4.9 Noble metal rich end of the U-Pd-Rh system at 1050°C
Fig. 4.10 Compositions of ternary alloys prepared
Fig. 4.11a Lattice parameter measurements across the section, $U_{0.1}(\text{Pd}_x\text{Rh}_{1-x})^{0.9}$.
Fig. 4.11b Lattice parameter variation with composition across the $\alpha_2$ phase field at 1250°C

The above diagram also indicates the phase boundaries between the $\alpha_2$ single phase region and various phase regions using the lattice parameter of the $\alpha_2$ phase in the two-phase alloys.
miscibility gap in the system. No attempt was made to find the critical point since this has been reported in the literature and the results have been quite consistent (92). The results at 800°C gave an indication that miscibility gap might be slightly skewed towards rhodium.

In Table XII, the x-ray analysis of the alloys at the two temperatures is displayed. The error bar for the lattice parameter measurements was ±0.003 Å. This value is due to the line broadening in the Debye-Scherrer films of the alloys. Miodownik and Saunders (165) who determined this system using thin films also encountered this line broadening problem. Their results also confirmed the existence of the miscibility gap but the gap was symmetrical in their case. A plot of lattice parameter against composition shows that there is a slight positive deviation from Vegard's law at high temperatures where a complete series of solid solution is observed (Fig. 4.6).

4.3 The U-Pd-Rh System (Noble-metal rich end)

The noble-metal rich end of the system has been investigated at the temperatures 1250°C, 1150°C and 1050°C. Tentative diagrams for the isothermal sections at the above temperatures are shown in Figs. 4.7, 4.8 and 4.9 respectively. Fig. 4.10 shows the nominal compositions of the alloys used in the present investigations. It also shows the chronological order in which the alloys were prepared (e.g. alloys on line AA' were prepared first, followed by alloys on BB' etc.)

Table XIII summarises the results from the lattice parameter determinations. Some of these results are plotted in Figs. 4.11a and 4.11b to obtain the boundaries between one and two phase regions. The plots show positive deviations from Vegard's law. The decrease in lattice parameter of the δ-phase in two phase alloys indicates that the surface of the δ-solution moves towards the Pd-Rh base line with decrease in temperature. It was observed that alloys with high Pd and Rh contents, gave somewhat diffuse lines making it quite difficult to
Fig. 4.12 Micrograph of alloy 16 (24/24/50) (x 0.5K). The main phase is the $\alpha_1$ solid solution whereas the $\varepsilon'$ second phase was found in the grain boundaries. (The $\varepsilon'$-phase is near the centre of the photograph.)
obtain high precision in their lattice parameter determinations. The determination of phase boundaries was supplemented by metallographic and electron microprobe analysis.

No ternary compound was found in this portion of the system. URh₃ was found to be in equilibrium with UPd₄. The solid solution of Rh in UPd₄ was seen to bend towards to U end of the diagram, interrupting the two phase region between URh₃ and UPd₃. Rhodium has a low solubility in UPd₃ which is a very stable compound \( G_f^{\text{UPd}_3} = 76.19 \text{ Kcal.mole}^{-1}, T = 1100^\circ \text{C} \) (161). The solubility of Rh in UPd₃ was determined to be about 6 a/o Rh at 1250°C whilst Pd dissolved to a much greater extent in URh₃ (45 a/o Pd).

4.3.1 Isothermal Section at 1250°C

X-ray diffraction and metallographic analysis were used to determine this section. The section is shown in Fig. 4.7. Electron microprobe analysis was also used to confirm some of the results. The tie lines in the two phase regions were fitted from results obtained by x-ray and electron microprobe analysis. The tie lines are shown as broken lines on the diagram. X-ray analysis of alloys 16 (26/24/50) and 15 (27/43/30) showed very faint lines of a second phase which could not be identified. A micrograph of alloy 16 is shown in Fig. 4.12 and electron microprobe analysis showed that the compositions of the two phases were as follows:

Alloy 16 (26/24/50)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition (a/o)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U</td>
</tr>
<tr>
<td>1</td>
<td>37.2</td>
</tr>
<tr>
<td>2</td>
<td>23.9</td>
</tr>
</tbody>
</table>
The relative amounts of the two phases were in the ratio of about 10:1. These results were used to "fix" the tie line going through alloy 16. A similar result was obtained from alloy 15 (i.e. the Debye-Scherrer film was similar to that of alloy 16) except that the lattice parameter of $\alpha_2$ phase was larger in this alloy than in the case of alloy 16. A summary of the compositions of co-existing phases in two phase alloys at 1250°C obtained by electron microprobe analysis are shown in Table XI. The results indicated that there is equilibrium between the following phases at 1250°C.

$$\alpha_1$$ and $\varepsilon$

$$\alpha_1$$ and $\alpha_2$

$$\alpha_1$$ and $\delta$

$\alpha_2$ and $\delta$

$\alpha_2$ and $\varepsilon'$

The results obtained from the electron microprobe analysis agree quite well with those obtained by x-ray powder photographs. For example, from Fig. 4.7, the mole fraction UPd$_4$ is 0.34 in alloy 16 and this means that the $\alpha_2$ phase (lattice parameter = 4.014 Å) has a composition which lies approximately, halfway between alloys 8 and 7. This agrees quite well with the composition of the $\alpha_2$ phase in that alloy. Very similar processes were used to fix most of the tie lines.
Seven alloys were found to be single, \( \alpha_1 \), ten alloys as \( \delta \)-single solid solution and four \( \alpha_2 \)-single phase solution in the whole of the region of the ternary system investigated at this temperature. Although no alloys were detected as containing three phases, the three phase region \( \alpha_1 + \alpha_2 + \delta \) is fairly well defined.

### 4.3.2 Isothermal Section at 1150°C

The diagram for this section is shown in Fig. 4.8. Most of the alloys investigated at this temperature had very similar results as at the previous temperature (1250°C). The alloys which showed some different characteristics were

(i) alloy 15 in which the unknown \( \epsilon' \) phase still showed very faintly on x-ray powder film together with the \( \alpha_2 \) phase and another phase \( \alpha_1 \). The lattice parameter obtained for the \( \alpha_1 \) and \( \alpha_2 \) phases and the relative amounts were used to fix the boundary between the three-phase field \( (\epsilon' + \alpha_1 + \alpha_2) \) and the two-phase field \( (\alpha_1 + \alpha_2) \). (See Table XIII).

(ii) alloy 35 (10/20/70) in which the \( \alpha_2 \) phase appears as well as the \( \delta \) phase. (At 1250°C, this alloy is a single phase, showing only the solid solution.)

(iii) alloy 12 (24/46/30) which was single phase (\( \alpha_2 \)) at 1250°C, becomes a two phase alloy with the \( \alpha_2 \) solid solution co-existing with the \( \alpha_1 \) solid solution.

(iv) alloy 44 (11/65/24) which shows faint lines of \( \alpha_1 \) phase together with \( \delta \)-lines indicating that the single phase decomposes to \( \delta \) and \( \alpha_1 \) phase.
(v) The lattice parameters of the alloys 31
(17.5/5/77.5), 32 (12.5/5/82.5) and 43
(15/17.5/67.5) decrease appreciably
compared to that at 1250°C.

4.3.3 Isothermal Section at 1050°C

This isothermal section at 1050°C is shown in Fig. 4.9. Most of
the alloys, like at 1150°C, maintained their structures. The most
interesting of the alloys whose structures changed was that of alloy 42
(15/25/60). The powder photograph taken of this alloy showed three sets
of lines. The lattice parameters were measured to be

(i) 4.010 Å
(ii) 3.931 Å
(iii) 3.883 Å

Owing to difficulties encountered, none of the etching methods described
in Chapter 3 could reveal the microstructure of this alloy.

Alloys 29 (5/47.5/47.5) and 39 (2/49/49) showed two phases. The powder
patterns were those of two δ-solutions, δ' (Rh-rich) and δ(Pd-rich)
phases. These results clearly showed that the miscibility gap which
exists in the palladium-rhodium binary system also existed in the ternary
system of U-Pd-Rh and that the miscibility gap in the ternary system
extended to a higher temperature than it is in the binary.

Alloy 22 (12/86/62) was found to be single phase at the two
temperatures (1250°C and 1150°C) but was found to be two phased at 1050°C
by x-ray analysis. The lattice parameter measured indicated
that the second phase was the α1 solid solution. None of the alloys in
the Pd-rich corner of the system showed a non-cubic pattern. The powder
patterns from the x-ray analysis showed lines which belonged to cubic
structures.
The thermodynamic aspects of phase diagrams have been discussed extensively in Section 2.5. The discussion indicated that thermodynamic data can be used to calculate phase diagrams (or conversely thermodynamic data can be estimated from phase diagrams). This makes use of the fact that if the Gibbs energies of all the phases forming a system are known for a given temperature at constant pressure, their composition at equilibrium corresponds to the minimum Gibbs energy $G$ of the system. In order to achieve this, one can either measure the free energies of the alloys experimentally or estimate them from mathematical models. It must be emphasised though that there is a distinction between input parameters which are numerical values based on experimental information either independent thermochemical data or critical features of these diagrams, and models which are purely algebraic equations. The latter process is used in computer calculations. A lot of models have been used to predict the free energy of alloys but the form always takes the shape of equation 9 (which is rewritten as)

$$ G = LS + ID + XS $$

where

- $LS$ = Lattice stability term,
- $ID$ = Ideal entropy term
and
- $XS$ = Excess energy term

It must be mentioned here that in the ternary system models a fourth term is added to equation (62). This term has been called the Ternary Interaction Parameter (TIP) by Dinsdale (152).

The Gibbs energies of all the phases forming the system are then computed for a given temperature at constant pressure and the most stable phase (or phases) is that with minimum free energy (or Gibbs energy), $G$. From the above definition the resulting diagram is hence a function of
the molar fraction of the different components, $i$, in the co-existing phases i.e.

$$G = f(T, x_i)$$

In the computation, equation 63 is readily transformed into

$$T = g(x_i)$$

which is the form in which a phase diagram is plotted.

5.2 Evaluation of Parameters

5.2.1 Determination of Lattice Stability Parameters

The importance of the knowledge of lattice stability in the thermodynamic calculation of phase diagrams has been emphasised by Kaufman (48) and, earlier on, (section 2.6.6) in the present work. The term Lattice Stability is actually the contribution of the free energy of the pure elements to the free energy of the alloy.

The lattice stabilities for the different forms of uranium have been studied and determined by Holden (111) and Hultgren et al. (112). The relative stabilities (111) for the polymorphs of U were determined from high pressures studies to be

$$\Delta G^{\alpha \rightarrow \beta} = 714 - 0.76 T + 23.9 P \ (0.142) \text{ cal.g-atom}^{-1}$$

$$\Delta G^{\beta \rightarrow \gamma} = 116 - 1.12 T + 23.9 P \ (0.142) \text{ cal.g-atom}^{-1}$$

and by Hultgren et al. (112) at atmospheric pressure as

$$\Delta G^{\alpha \rightarrow \beta} = 667 - 0.709 T \text{ cal.g-atom}^{-1}$$

$$\Delta G^{\beta \rightarrow \gamma} = 1137 - 1.09 T \text{ cal.g-atom}^{-1}$$

$$\Delta G^{\beta \rightarrow L} = 2036 - 1.45 T \text{ cal.g-atom}^{-1}$$

However, none of the above forms is fcc, the $\alpha$-form has an end-centred-orthorhombic structure, the $\beta$ has a complex tetragonal structure and the $\gamma$, a bcc structure. Due to the fact that most of the alloys in the system are fcc just as the other two elements, Pd and Rh, it is therefore necessary to determine also the relative stability of the fcc form of U with respect to the liquid form. The fcc form of U has not been reported, not even from high pressure studies of the metal. A method employed by
Fig. 5.1 Extrapolation of the $\delta$-solid solution solidus/liquidus to estimate the melting point of the fcc form of $U,T^X_U$

At Percent Pd

Fig. 5.2 $\Delta H^{\alpha+\beta}$ and $\Delta S^{\alpha+\beta}$ versus Group Number (68)
Table XIV

Lattice stability of the unstable fcc form of U

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^{6\rightarrow L}$</th>
<th>$\Delta S^{6\rightarrow L}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present Work</td>
<td>2300</td>
<td>2.0</td>
</tr>
<tr>
<td>Micheals et al (68)</td>
<td>2786</td>
<td>2.06</td>
</tr>
</tbody>
</table>

The values of Micheals et al were arrived at by reading off the $\Delta H^{\alpha\rightarrow \beta}$ and $\Delta S^{\alpha\rightarrow \beta}$ from fig. 5.2 and applying the relation

\[
\Delta G^{\alpha\rightarrow L} = \Delta G^{\alpha\rightarrow \beta} + \Delta G^{\beta\rightarrow L}
\]
Kaufman (149) to obtain lattice stability parameters was employed. The trajectory of the observed α/L equilibrium (where α = fcc) of the binary system of U and another metal which crystallises in the fcc form (Pd) was used to estimate the "melting point" of the fcc U, \( \bar{T}_U \) (Fig. 5.1). This value was determined as 1150°K i.e.

\[ \bar{T}_U = 1150°K \]

Assuming Richard's rule thus assigning a value of 2 cal(g-atom.°K)\(^{-1}\) to the entropy of fusion, the enthalpy of fusion of fcc U is given as

\[
\Delta H_{u}^{\alpha \rightarrow L} = \bar{T}_U \Delta S_{u}^{\alpha \rightarrow L}
\]

\[ = 1150°K \times 2.0 \text{ cal.g-atom}^{-1}.\text{°K}^{-1} \]

\[ = 2300 \text{ cal.g-atom}^{-1} \]

(since \( \Delta G_{\alpha \rightarrow L}(T=\bar{T}_U) = 0 \))

Substituting the above values into equation 11, the free energy difference between metastable fcc U and liquid U is given by

\[
\Delta G_{\alpha \rightarrow L} = 2300 - 2.0 T
\]

The values for \( \Delta H_{\alpha \rightarrow L} \) and \( \Delta S_{\alpha \rightarrow L} \) above compares favourably with those obtained by Micheals et al. (68) (Table XIV), whose work on the Kaufman approach to binary phase diagram calculation led to the plotting of \( \Delta H \) and \( \Delta S \) against group numbers (Fig. 5.2). In this case, the actinides were assigned group number 3.5 together with the rare earths. From Fig 5.2

\[ \Delta H_{u}^{\alpha \rightarrow \beta} = 750 \text{ g-atom}^{-1} \text{ and } \Delta S_{u}^{\alpha \rightarrow \beta} = 0.6 \text{ cal.g-atom}^{-1}.\text{°K}^{-1} \]

To obtain \( \Delta G_{\alpha \rightarrow L} \), the expression

\[ \Delta G_{U}^{\alpha \rightarrow L} = \Delta G_{U}^{\alpha \rightarrow \beta} + \Delta G_{U}^{\beta \rightarrow L} \]

is used.
TABLE XV
Relative Stabilities of Some Forms of U, Pd and Rh

\[ \Delta G^{\delta \rightarrow L}, \text{cal mol}^{-1} \]

<table>
<thead>
<tr>
<th>Element</th>
<th>( \Delta H )</th>
<th>( \Delta S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>2300</td>
<td>-2.00</td>
</tr>
<tr>
<td>Pd</td>
<td>3640</td>
<td>-2.00</td>
</tr>
<tr>
<td>Rh</td>
<td>4480</td>
<td>-2.00</td>
</tr>
</tbody>
</table>

\[ \Delta G^{\alpha_1 \rightarrow L} \]

<table>
<thead>
<tr>
<th>Element</th>
<th>( \Delta H )</th>
<th>( \Delta S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>2000</td>
<td>0.00</td>
</tr>
<tr>
<td>Pd</td>
<td>4500</td>
<td>0.00</td>
</tr>
<tr>
<td>Rh</td>
<td>2500</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Fig. 5.3 Relationship between free energy and lattice parameter measurement.
From the above

$$\Delta G^{\alpha+\beta} = 750 - 0.6 T$$

and using data on melting of uranium from Hultgren's work, the stability of the bcc ($\beta$) form of uranium with respect to the liquid $G^{\beta+L}$ is given by

$$\Delta G^{\beta+L}_u = 2036 - 1.45 T$$

$$\Delta G^{\alpha+L}_u = 2786 - 2.05 T$$

Similar procedures were used to obtain the lattice stability parameters which are shown in table XV for all the elements in the different structures being considered i.e. fcc ($\delta$), fcc$_{\text{ord}}$ ($\alpha_1$) and liquid (L). The parameters for the $\alpha_1$-forms were estimated assuming that it was a modified form of the $\delta$-form. As such, the $\Delta H$ values were chosen so that they did not differ appreciably from those for the $\delta$-forms. Owing to the crudeness of the method, zero entropy factors were also assigned to ensure that $\alpha_1$ was always unstable with respect to the other two phases (i.e. $\delta$ and L).

In estimating the $\Delta H$'s of the $\alpha_1$ forms of the elements, the x-ray parameter data were employed. The data give some important clues to the forms of the lattice stabilities. On extrapolating the diameter of U atoms $d^U_x$ to $d^U_{100}$ where $x$ is the atom percent U in the alloy, the diameter of the U atom with different valencies is obtained. These values are related to the $\Delta G^0$ and are shown in Fig. 5.3.

5.2.2 Excess Free (Gibbs) Energy

A power series of the Margules type equation was used to represent the excess free energy in the present work. The general equation which is represented as $XS$ is given here as

$$XS = G^F = \Sigma x_ix_j^ia_{ij} + \Sigma x_i x_j x_k^a_{ijk} + \ldots$$

(65)
TABLE XVI

Enthalpies of Solution at Infinite Dilution for Some Transition Metals (174)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Th</th>
<th>U</th>
<th>Pu</th>
<th>Mo</th>
<th>Tc</th>
<th>Ru</th>
<th>Pd</th>
<th>Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th</td>
<td>-</td>
<td>+25</td>
<td>-1</td>
<td>+63</td>
<td>-194</td>
<td>1224</td>
<td>-438</td>
<td>-316</td>
</tr>
<tr>
<td>U</td>
<td>+20</td>
<td>-</td>
<td>+9</td>
<td>+7</td>
<td>-123</td>
<td>-144</td>
<td>-224</td>
<td>-180</td>
</tr>
<tr>
<td>Pu</td>
<td>-1</td>
<td>+8</td>
<td>-</td>
<td>+34</td>
<td>-107</td>
<td>-126</td>
<td>-234</td>
<td>-175</td>
</tr>
<tr>
<td>Mo</td>
<td>+43</td>
<td>+6</td>
<td>+31</td>
<td>-</td>
<td>-44</td>
<td>-58</td>
<td>-57</td>
<td>-60</td>
</tr>
<tr>
<td>Tc</td>
<td>-131</td>
<td>-102</td>
<td>-98</td>
<td>-45</td>
<td>-</td>
<td>+1</td>
<td>+17</td>
<td>+1</td>
</tr>
<tr>
<td>Ru</td>
<td>-149</td>
<td>-118</td>
<td>-224</td>
<td>-57</td>
<td>-1</td>
<td>-</td>
<td>+24</td>
<td>+5</td>
</tr>
<tr>
<td>Pd</td>
<td>-307</td>
<td>-192</td>
<td>-224</td>
<td>-59</td>
<td>+17</td>
<td>+25</td>
<td>-</td>
<td>+8</td>
</tr>
<tr>
<td>Rh</td>
<td>-210</td>
<td>-147</td>
<td>-154</td>
<td>-59</td>
<td>+1</td>
<td>+5</td>
<td>+7</td>
<td>-</td>
</tr>
</tbody>
</table>

NB Units are in KJ.mol\(^{-1}\) and solvents are arranged horizontally.
where $x_i$ is the atomic fraction of the $i^{th}$ component and $a_{ij}$ and $a_{ijk}$ and the interaction parameters in the binary $i$-$j$ system and the ternary $i$-$j$-$k$ system, respectively. These parameters generally depend on temperature and composition, and in this work, empirical expressions of the following form were employed:

$$a_{ij} = a_{ij}^{(0)} + a_{ij}^{(1)} + (x_i - x_j) + a_{ij}^{(2)} (x_i - x_j)^2 + \ldots \quad (66)$$

where $a_{ij}^n = a_{ij}^{n0} + b_{ij}^n T + c_{ij}^n T^2 + d_{ij}^n T^3 + e_{ij}^n T^4 \quad (67)$

and $a_{ijk} = H = \text{constant}$

In the case of the binary system, the subregular approach employed (equation 63) was written in a slightly different but equivalent way:

$$a_{ij}^0 = a_{ij}^{i(j)} x_i + a_{ij}^{j(i)} x_j \quad (68)$$

where $a_{ij}^{i(j)} = a_{ij}^{i(j)} + b_{ij}^{i(j)} T + c_{ij}^{i(j)} T^2 + d_{ij}^{i(j)} T^3 + e_{ij}^{i(j)} T^4$

with $a_{ijk}$ being set to zero (since a binary system was being considered). The advantage that the form of the equation represented by equation (66) has over that in equation (65) is that the former reduces to the regular solution model when $a_{ij}^n = 0$ for all $n \geq 1$. This is not true when the multicomponent form of equation (68) is being considered since for the regular solution, one obtains

$$a_{ij}^0 = (x_i + x_j) a_{ij}^0$$

which is not constant (in contrast to $a_{ij}^{(1)}$ in equation (63) where $a_{ij}^1 = \text{constant} = 0$) except for binaries where, as usual, $x_i + x_j = 1$. However, $a_{ij}^{i(j)}$ and $a_{ij}^{j(i)}$ can easily be obtained from experiments or heats of solutions at infinite dilution plus a "reasonable" entropy factor. The work of Miedema and coworkers (174) has proved very helpful for that matter. Table XVI shows the enthalpies of solution at infinite dilution.
for some transition metals including the elements under consideration in the present work. The values have been arrived at by using equations (51) - (54) and setting the value of \( Q/P \) to 9.4 eV\(^2 \) l (d.u\(^{2/3} \)) for all alloy systems. Although some of the results are debatable, the values serve as good starting points for \( a_i^0(j) \) and \( a_j^1(i) \) which can be transformed into \( a_i^0(j) \) and \( a_j^1(i) \) by setting

\[
a_{ij}^0 = \left( \frac{1}{2} \right) \left( a_{i(j)}^0 + a_{j(i)}^0 \right) \tag{69}
\]

and

\[
a_{ij}^1 = \left( \frac{1}{2} \right) \left( a_{i(j)}^0 - a_{j(i)}^0 \right) \tag{70}
\]

5.2.3 Free (Gibbs) Energy of Formation of Compounds

The thermodynamic properties of the compounds in the uranium systems have been investigated by several workers (153) - (155). In all the investigations the EMF method using solid CaF\(_2\) as electrolyte was employed. Naraine and Bell (86) reported the following values for \( \Delta G_{\text{compd}}^f \) (in cal.mol\(^{-1}\)).

\[
\Delta G_f^0 (\text{URh}_3) = -67500 + 25.8 T \text{ (1000 - 1200 K)} \tag{71}
\]

\[
\Delta G_f^0 (\text{U}_3\text{Rh}_5) = -148910 + 60.23 T \text{ (1000 - 1200 K)} \tag{72}
\]

\[
\Delta G_f^0 (\text{U}_3\text{Rh}_4) = -130900 + 54.02 T \text{ (1000 - 1200 K)} \tag{73}
\]

\[
\Delta G_f^0 (\text{URh}) = -36520 + 16.06 T \text{ (1000 - 1200 K)} \tag{74}
\]

\[
\Delta G_f^0 (\text{U}_2\text{Rh}) = -43520 + 20.48 T \text{ (893 - 978 K)} \tag{75}
\]

The Gibbs energy of formation of URh\(_3\) has also been reported by Holleck and Kleykamp (153) to be

\[
\Delta G_f^0 (\text{URh}_3) = -61370 - 1.1T \text{ (1000 - 1150 K)} \tag{76}
\]

while Schmidt (154) reported the following for the same compound

\[
\Delta G_f^0 (\text{URh}_3) = -101500 + 19.1 T \text{ (1073 - 1773 K)} \tag{77}
\]
Wijenba (155) gives the same compound:

\[
\Delta G_f^0 (\text{URh}_3) = -75326 + 2.2 T \tag{78}
\]

In none of these works was the reference state mentioned. Presumably, for URh\(_3\), \(\gamma\)-U and fcc Pd were used as reference states. Miedema and coworkers (126) have reported that the enthalpy of formation of URh\(_3\) (using equations (51) - (54) is

\[
\Delta H_f^0 (\text{URh}_3) = -9500 \text{ cal.g-atom}^{-1}
\]

The agreement between the enthalpy terms obtained for \(\Delta G_f^0 (\text{URh}_3)\) values is not as poorly correlated as the entropy factors. As such two values of \(\Delta G_f^0 (\text{URh}_3)\) were used in calculating the Rh-rich end of the U-Rh system. A value of 40,000 cal-mol\(^{-1}\) was used basing its choice on the fact that Miedema's \(\Delta H\) value had been the only estimate using a model. And assuming a regular solution model, the URh\(_3\)/liquid, liquidus, and solvus curves were calculated to fit the observed phase diagram. The value for this calculation was

\[
\Delta G_f^0 (\text{URh}_3) = 40,000 + 0.8 T \text{ cal.mol}^{-1} \tag{79}
\]

The second value was arrived at by considering the fact that the observed \(\Delta G_f^0 (\text{URh}_3)\)'s lie reasonably close together - 60,000 and 75,000 cal.mol\(^{-1}\). A value of 62,000 cal.mol\(^{-1}\) (which lies in between these values) was therefore employed and a temperature coefficient of 1.6 T cal.g-atom\(^{-1}\)K\(^{-1}\) was imposed yielding a free energy of formation of

\[
\Delta G_f^0 (\text{URh}_3) = -15500 - 1.6 T \text{ cal.g-atom}^{-1} \tag{80}
\]

A minimum of three compounds has been reported (75) to exist above 1050\(^{\circ}\)C in the U-Pd system between 70% Pd and pure palladium. Out of these three, the present work and work due to Terekhov et al. (156) and Pennell (78) have shown that only two are actually found in the system.
TABLE XVII

Free Energy of Formation, $\Delta G_f^0$ of Uranium Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Free Energy of Formation (cal.g-atom$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UPd$_3$</td>
<td>hcp</td>
<td>-15500 - 1.18 T</td>
</tr>
<tr>
<td>UPd$_3$</td>
<td>fcc</td>
<td>-15240 + 1.70 T</td>
</tr>
<tr>
<td>UPd$_4$</td>
<td>fcc</td>
<td>-11950 + 0.95 T</td>
</tr>
<tr>
<td>URh$_3$</td>
<td>fcc</td>
<td>-15500 - 1.60 T</td>
</tr>
</tbody>
</table>

(126), (153), (154), (161)
The two compounds are UPd$_3$ and UPd$_4$. Both compounds were treated as line compounds in calculating the system initially. But the latter was represented as a solution when the ternary system was being calculated. As a line compound, the free energy of formation of UPd$_4$ was represented by

$$\Delta G_f^0 (\text{UPd}_4) = -59750 + 0.95 T \text{ cal.mol}^{-1}$$

whilst that of UPd$_3$ was represented by the equation

$$\Delta G_f^0 (\text{UPd}_3) = -62000 + 4.72 T \text{ cal.mol}^{-1}$$

Due to the fact that the $\alpha_1$ phase was treated as a solution phase in the ternary system, the $\Delta G_f^0 (\text{UPd}_3)$ had to be slightly adjusted to allow UPd$_3$ to melt at the same temperature as that in the binary system. This is due to the fact that with a totally different formulation, the $\Delta G_f$ of the solution phase is not the same as the value adopted in the line compound formulation thus causing the peritectic reaction to occur at a slightly higher temperature. For the ternary system, this value was adjusted to

$$\Delta G_f^0 (\text{UPd}_3) = -61800 + 4.72 \text{ cal.mol}^{-1}$$

since UPd$_4$ was treated as a solution phase.

The free energy of formation of the fcc form of UPd$_3$ which is metastable at all temperatures and atmospheric pressure was estimated to be

$$\Delta G_f^0 (\text{UPd}_3, \text{fcc}) = -15240 + 1.70 T \text{ cal.g-atom}^{-1}$$

Table XVII summarises the free energies of formation for all the compounds found in the systems.

5.3 Computation of Phase Boundaries

In principle, the computer calculation of the phase boundaries can be divided into two groups. One of them is to search for a set of phases
having the best compositions to minimize the free energy of the entire alloy system. The other is to solve the simultaneous equations concerning the chemical potentials of the components in each phase. The former was employed by Counsell et al. (148), and the latter by Kaufman and Bernstein (48) and Tarby et al. (157). The former method was employed in this work. For the ternary calculations, the "Simplex" method, the steepest descent method developed by Nelder and Mead (158) was used in a package developed by Dinsdale (159). For the binary diagrams, a program originally developed by Saunders (160) and later modified to use the formation of excess free energy employed in the NPL package, was used in performing the calculations.

5.3.1 Calculation of the Phase Boundaries in the Binary Systems

The ranges of temperature considered in these calculations were between 1300°C and 2500°C for the U-Pd and U-Rh systems and 950°C and 2500°C for the Pd-Rh system. In these ranges, uranium exists as liquid and bcc form whilst the other two elements exist as liquid and fcc. The thermodynamic data used in the calculations were taken from assessments made by Miedema and coworkers (126) - (128) for the uranium-palladium and the uranium-rhodium systems, Naraine and Bell (86), Schmidt (154), Holleck and Kleykamp (153), Lorenzelli and Marcon (161) and Wijbenga (155) for the compounds occurring in the two systems. In addition, values for the heats and entropies of fcc → liquid transformation of the pure metals were taken from Kaufman and Bernstein (48) and Hultgren et al. (112). The phase diagrams were constructed by computation using the above mentioned parameters which are described fully in Section 5.2.

The general procedure adopted was that heats and excess entropies of mixing were calculated for the fcc and/or liquid phase alloys in each binary system for the selected temperature and were combined through the equation
Fig. 5.4 The calculated phase diagram of U-Pd showing UPd₄ as a line compound.

Fig. 5.5 The U-Pd system treating UPd₄ as a solution phase.
Fig. 5.6 The calculated phase diagram of U-Rh system using parameters from Park's work (85) and thermodynamic data from the literature.

Fig. 5.7 The diagram of U-Rh system calculated to fit that due to Park as much as possible.
Fig. 5.8 The calculated diagram of the Pd-Rh system at high temperatures.

Octavio et al. [expt.] (169)

Present work [calc.]
to give the excess Gibbs energies of mixing, $\Delta G^E$ for each phase. Each set of $\Delta G^E$ data was fitted to a series of the general form

$$\Delta G^E = x_1 x_2 (x_1 H_1 + x_2 H_2)$$

(85)

(the Kaufman formulation) or

$$\Delta G^E = x_1 x_2 (A + B (x_1 - x_2) + C (x_1 - x_2)^2 + ...$$

(86)

(the NPL formalism) which are equivalent to equations (68) and (66) respectively. These were added to the LS and ID terms of equation (63) to calculate the Gibbs energy of the alloy. With the aid of the tangency program developed by Saunders (160), the phase boundaries were calculated. Some of the thermodynamic data were very poorly established and hence, it necessitated the adjustments to such values until the calculated Gibbs energy curves for the different phases reproduced the phase boundaries which had been observed by conventional methods.

Figs. 5.4 to 5.8 are the computed diagrams of the binary systems. UPd$_4$ is represented as a line compound in the U-Pd system in Fig. 5.4. To fit the diagram as closely as possible to the observed one, the melting point of UPd$_3$ in the U-Pd system was set at $1600^\circ$C. Similarly, the melting point of URh$_3$ was raised to $1788^\circ$C so as to be able to reproduce the peritectic reaction, Fig. 5.6, which occurs at the composition of the compound U$_3$Rh$_5$. Setting the melting point of URh$_3$ at a temperature below $1780^\circ$C produced a eutectic reaction between the compounds URh$_3$ and U$_3$Rh$_5$ as indicated by Fig. 5.6. Fig. 5.8 is the solidus and liquidus calculated for the Pd-Rh system.

5.3.2 Calculation of the Ternary System

The computer program used for calculating the isothermal sections of the U-Pd-Rh system is described elsewhere (159), (162), (163). For the sake of brevity the equations used to represent the solution phases
and compounds and the method of representing the data will be considered here.

The Gibbs energy of transformation for an element from an adopted reference structure to that of the phase under consideration (in this case LS) is stored as the coefficients of a four power series in temperature:

\[ A = A_1 + A_2 T + A_3 T^2 + A_4 T^3 \]  

(87)

Usually \( A_3 \) and \( A_4 \) are set to zero but occasionally the coefficient \( A_2 \) is also set to zero.

The excess energy of formation of binary solution phases were represented by 20 coefficients. The reason for this can be seen from the expansion of equation (86) to fifth terms and the temperature dependency of the coefficients \( A, B, C, D \) and \( E \). For example,

\[ B = b_1 + b_2 T + b_3 T^2 + b_4 T^3 \]

The \( T^2 \) and \( T^3 \) terms are always set to zero so that entropy and heat data obtained from either estimates or experiments can be used. The excess energy of formation of the ternary system is then derived by summing contributions from each binary system using the Margules model. This model, owing to its symmetry and independence of order of elements, is preferred to those designed by Bonnier (164) and Toop (165).

The excess energy \( \Delta G_{\text{ter}} \) due to ternary interactions is expressed as

\[ \Delta G_{\text{ter}} = \sum_{i=1}^{n-2} \sum_{j=i+k}^{n-1} \sum_{k=j+i}^{n} x_i x_j x_k H_{ijk} \]  

(88)

where \( H_{ijk} \) = ternary interaction coefficient (TIP)

Two coefficients are stored in the computer to represent the Gibbs energy of formation of a binary compound from its component elements in their reference phase as a function of temperature. Thus
\[ \Delta G_{\text{bin}}^f = a + bT \]

where \( a \) and \( b \) are the stored coefficients.

The Gibbs energy of formation of line-compounds across ternary phase fields is represented by the equation

\[
\Delta_f G_{\text{LC}} = \frac{x_i}{y} \Delta G_{ij}^f + \frac{x_k}{u} \Delta G_{jk}^f + RT \left( x_i \ln \frac{x_i}{y} + x_k \ln \frac{x_k}{u} \right) \\
- \frac{x_i}{y} (1-y) \ln (1-y)/x_j + \frac{x_k}{u} (1-u) \ln (1-u) x_j \\
+ x_i x_k (a' + b' T) \tag{89}
\]

where \( x_i, x_j \) and \( x_k \) are the mole fractions of component \( i, j \) and \( k \) respectively and \( \Delta G_{ij}^f \) and \( \Delta G_{jk}^f \) represent the Gibbs energy of formation of the binary compounds \( A_yB(1-y) \) and \( C_uB(1-u) \) between compounds lie. The last term is an interaction term which allows for any interaction between the compounds with the coefficient \( a' \) and \( b' \) being entered each time a calculation is initiated. The two coefficients are actually used to improve agreement with any experimental phase diagram information available.

The above mentioned coefficients are all listed in a certain order in a file. Table XVIII shows a format of this file with the necessary coefficients in the required order.

In effect, the calculation for the ternary system involved the collection of data for solution phases obtained from the binaries which were combined together through an expression analogous to equation (68) to yield excess energies. These were combined with data from the pure components to yield the free energies of formation of the solution phases. A similar treatment with compounds yields Gibbs energies of formation of the compounds. The "simplex" method was then used to determine the lowest free energies thereby yielding the phase boundaries.
TABLE XVIII
Format of Input File to NPL Program

UUPDRH
3
UU
PD
RH
2
.25, .76
1
-15450, 1.18, 0
.24, .76
1
-15240, 1.7, 0
1
.25, .75
1
-15500, 1.6, 0
0
3
1
2
4
-42450, -1.0, 0, 0
27550, 0.5, 0, 0
0, 0, 0, 0
0, 0, 0, 0
0, 0, 0, 0
-41000, -1.3, 0, 0
27000, 0.05, 0, 0
0, 0, 0, 0
0, 0, 0, 0
0, 0, 0, 0
-41000, -1.3, 0, 0
75000, 0.05, 0, 0
0, 0, 0, 0
0, 0, 0, 0
0, 0, 0, 0
-40000, -1.1, 0, 0
20000, 0.4, 0, 0
0, 0, 0, 0
0, 0, 0, 0
0, 0, 0, 0
-28000, -0.6, 0, 0
17500, 0.4, 0, 0
0, 0, 0, 0
0, 0, 0, 0
0, 0, 0, 0
-28000, -0.6, 0, 0
27000, 0.4, 0, 0
0, 0, 0, 0
0, 0, 0, 0
0, 0, 0, 0

Title of System
No. of elements
Elements

No. of compound in first system i.e. UU-PD
Composition of compound

ΔG^f of compound expressed as a + b T + c n T

No. of compound in second system, i.e. UU-RH

No. of compound in third system i.e. PD-RH
No. of solutions in Ternary System
Liquid phase
α solid solution phase
UPd_4 (α_1) phase
Excess Gibbs Energy for system 1, UU-PD

L

δ

α_1 (UPd_4)

XS Energy for system 2, UU-RH

L

δ

α_1
### TABLE XVIII (continued)

#### Format of Input File to NPL Program

<table>
<thead>
<tr>
<th>X Energy for system 3, PD-RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4500, 0, 0, 0</td>
</tr>
<tr>
<td>-1500, 0, 0, 0</td>
</tr>
<tr>
<td>0, 0, 0, 0</td>
</tr>
<tr>
<td>0, 0, 0, 0</td>
</tr>
<tr>
<td>+350, 0, 0, 0</td>
</tr>
<tr>
<td>-150, 0, 0, 0</td>
</tr>
<tr>
<td>0, 0, 0, 0</td>
</tr>
<tr>
<td>0, 0, 0, 0</td>
</tr>
<tr>
<td>5000, 0, 0, 0</td>
</tr>
<tr>
<td>0, 0, 0, 0</td>
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<tr>
<td>0, 0, 0, 0</td>
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<tr>
<td>0, 0, 0, 0</td>
</tr>
<tr>
<td>0, 0, 0, 0</td>
</tr>
<tr>
<td>-30000</td>
</tr>
<tr>
<td>-30000</td>
</tr>
<tr>
<td>-75000</td>
</tr>
</tbody>
</table>

No. of Ternary compounds

Ternary Interaction Parameters for solutions

<table>
<thead>
<tr>
<th>No. Lattice Stabilities for the elements of temp. ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>298, 5000</td>
</tr>
<tr>
<td>2296, -2.05, 0, 0</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>298, 5000</td>
</tr>
<tr>
<td>1, 0, 0, 0</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>298, 5000</td>
</tr>
<tr>
<td>2000, 0, 0, 0</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>298, 5000</td>
</tr>
<tr>
<td>3640, -2, 0, 0</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>298, 5000</td>
</tr>
<tr>
<td>1, 0, 0, 0</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>298, 5000</td>
</tr>
<tr>
<td>4500, 0, 0, 0</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>298, 5000</td>
</tr>
<tr>
<td>4480, -2, 0, 0</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>298, 5000</td>
</tr>
<tr>
<td>1, 0, 0, 0</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>298, 5000</td>
</tr>
<tr>
<td>2000, 0, 0, 0</td>
</tr>
</tbody>
</table>
Fig 5.9 Calculated U-Pd-Rh System at 1400°K

Line coeff.=(5500,2)
TIP (δ)= -30000
TIP (α)= -75000
Fig 5-10 Calculated U-Pd-Rh System at 1500K

Line coeff. = 15500.2
TP(Mg) = 30000
TIP(Mg) = 75000

End of M.G.

Rh

U
Fig. 5.11 The calculated system at 1550 K

Line coefficient = (5500, 2), TIP = -30,000 (6)
TIP = -75,000 (α₁)
Figures 5.9 to 5.11 are the calculated isothermal sections of the U-Pd-Rh system at 1400°K, 1500°K and 1550°K respectively. This diagram depicts most of the features obtained in using experimental methods. The miscibility gap is calculated to disappear at 1500°K.
CHAPTER SIX
Discussion

6.1 Introduction

This chapter is divided into two sections viz:

(i) Binary

(ii) The Ternary U-Pd-Rh System

The main features in the binary system are first discussed with the aid of crystallographic information obtained in the present work and thermodynamic data.

This is followed by a discussion on the U-Pd-Rh system as a whole.

6.2 Binary Systems

6.2.1 The U-Pd System

The main purpose of investigating a portion of this system was to ascertain the existence of phases which previous workers had not agreed upon. As discussed in sub-section 2.4.2, previous workers have disagreed on the phases which existed at this end (Pd-rich) of the system (71), (75), (78). Whereas Catterall (71) had reported a δ-solid solution extending from pure Pd to 22 a/o U in this system, Pells (75) disagreed with this result and established an alternative scheme. Four compounds were identified within the same composition range in the system viz. UPd₄, UPd₅, U₂Pd₁₁ and U₂Pd₁₇, the latter two existing at relatively low temperatures. The work of Pennell (78) on the system at 1000°C and above confirmed the existence of UPd₄ but failed to see the compound UPd₅. The results of sub-section 4.2.1 clearly support Pennell's claim that although UPd₄ exists, UPd₅ is absent from this system. Table XIX which is a reproduction of some of the results in sub-section 4.2.1 summarises the results obtained from two alloys which had been prepared in this region and annealed at 1150°C. Both phases existing in equilibrium have face centred cubic structures in the two alloys. The lattice parameters obtained for the different phases clearly indicate that the region is
TABLE XIX
Lattice Parameter of the Equilibrium Phases in Some Pd-Rich U-Pd Alloys

<table>
<thead>
<tr>
<th>Phase present</th>
<th>Lattice Parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alloy 1 (17a/o U)</td>
</tr>
<tr>
<td>α₁</td>
<td>4.059</td>
</tr>
<tr>
<td>δ</td>
<td>4.000</td>
</tr>
</tbody>
</table>

TABLE XX
A record of the relative intensities and θ-values of an x-ray pattern of a 18 a/o alloy (1250°C)

<table>
<thead>
<tr>
<th>Line</th>
<th>Relative Intensity</th>
<th>θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>vw</td>
<td>19.023</td>
</tr>
<tr>
<td>2</td>
<td>w</td>
<td>19.212</td>
</tr>
<tr>
<td>3</td>
<td>w</td>
<td>20.905</td>
</tr>
<tr>
<td>4</td>
<td>s</td>
<td>22.593</td>
</tr>
<tr>
<td>5</td>
<td>w</td>
<td>24.553</td>
</tr>
<tr>
<td>6</td>
<td>w</td>
<td>30.202</td>
</tr>
<tr>
<td>7</td>
<td>s</td>
<td>33.100</td>
</tr>
<tr>
<td>8</td>
<td>s</td>
<td>36.245</td>
</tr>
<tr>
<td>9</td>
<td>ms</td>
<td>38.399</td>
</tr>
<tr>
<td>10</td>
<td>s</td>
<td>40.356</td>
</tr>
<tr>
<td>11</td>
<td>w</td>
<td>50.921</td>
</tr>
<tr>
<td>12</td>
<td>w</td>
<td>57.853</td>
</tr>
</tbody>
</table>
The free energy curve of phase m lies above the tangent touching the curves of phases α and β. A number of factors can cause the curve \( G_{\text{met}} \) to fall below the tangent XY. These factors include cold working, irradiation, quenching etc. In that case the phase m will appear in the system and will be in metastable equilibrium with α or β.
Fig. 6.2  A diagram of the U-Pd system highlighting the differences between the works of Pells (75) and Terekhov et al (156)
two phase in contrast to Pells' single phase. The two phases were identified as

(i) the $\alpha_1$ solid solution
and (ii) the solid solution of U in Pd ($\delta$-solid solution).

The results show that the $\delta$-solid is in equilibrium with the $\alpha_1$ solid solution phase at high temperatures. Owing to the temperatures at which the experiments were carried out, nothing can be deduced concerning the compounds $U_2Pd_{11}$ and $U_2Pd_{17}$.

It should be pointed out however, that when the 18 a/o U alloy was annealed for a few days (2 - 3 days) and quenched very rapidly, the structure was different; x-ray powder patterns indicate a non-cubic structure which could not be identified. This x-ray pattern which kept appearing any time the alloy was annealed for about 2 - 3 days was probably the phase that had been reported by Pells. It is likely that this structure is only obtained as a result of non-equilibrium cooling.

Pells' compound phase, probably, does exist but as metastable phase with a free energy curve quite close to the tangent joining those of the $\delta$-solid solution and the $\alpha_1$ (UPd$_4$) - "compound" phase as shown schematically in Fig. 6.1. Table XX shows a record of the relative intensities and $\theta$-values of the lines from an x-ray pattern of the 18 a/o alloy annealed for 2 days.

It is very interesting to know that some Russian work (156) which had not been reviewed by the present author until after the work reported here was complete also indicates that UPd$_5$ is absent in this system. This work, unlike Pells' findings showed that UPd$_4$ is a congruently melting compound. The former reports of the formation of the compound by a peritectic reaction. Fig. 6.2 is a diagram highlighting the differences between the two works. The area occupied by the UPd$_5$ phase in Pells' diagram for this system is reported (156) as being a two phase field, the equilibrium phase being a UPd$_4$ phase and a $\delta$-solid solution phase.
One interpretation could be that U atoms are located on only six out of the eight vertices where cubes meet contributing only 0.75 (6 x 0.025) U atoms to the unit cell. If each face is assumed to have a Pd atom, that contributes 3 (1 x 6) Pd atom to the cell. This yields the formula $U_{0.75}Pd_{3}$ (or UPd$_4$) per unit cell.

X indicates vacant site.

**TABLE XXI**

**Bonding Properties of Some Transition Metals**

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronic Configuration in gaseous ground state</th>
<th>Electronic Configuration in metallic ground state</th>
<th>No. of bonding d-electrons in solid state</th>
<th>Melting point (K)</th>
<th>Substitution Energy (kJ mole$^{-1}$)</th>
<th>Promotion Enthalpy (kJ mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>$4d^7,5s$</td>
<td>$4d^6,5sp$</td>
<td>4</td>
<td>2583</td>
<td>650.2</td>
<td>301</td>
</tr>
<tr>
<td>Rh</td>
<td>$4d^8,5s$</td>
<td>$4d^{6,5},6sp^{1.5}$</td>
<td>3.5</td>
<td>2239</td>
<td>554.4</td>
<td>464</td>
</tr>
<tr>
<td>Pd</td>
<td>$4d^{10}$</td>
<td>$4d^{7,5},6sp^{1.5}$</td>
<td>2.5</td>
<td>1825</td>
<td>375.7</td>
<td>586</td>
</tr>
<tr>
<td>Os</td>
<td>$5d^6,6s^2$</td>
<td>$5d^6,sp$</td>
<td>4</td>
<td>3318</td>
<td>788.3</td>
<td>293</td>
</tr>
<tr>
<td>Iv</td>
<td>$5d^7,6s^2$</td>
<td>$5d^{6,5},6sp^{1.5}$</td>
<td>3.5</td>
<td>2727</td>
<td>669.9</td>
<td>498</td>
</tr>
<tr>
<td>Pt</td>
<td>$5d^9,6s$</td>
<td>$5d^{7,5},6sp^{1.5}$</td>
<td>2.5</td>
<td>2045</td>
<td>563.6</td>
<td>506</td>
</tr>
<tr>
<td>Ac</td>
<td>$6d^{1,7s^2}$</td>
<td>$6d^2,7s$</td>
<td>2</td>
<td>1323</td>
<td>410.0</td>
<td>110.0</td>
</tr>
<tr>
<td>Th</td>
<td>$5f^{6d^2},6s^2$</td>
<td>$5f^6d^3,7s$</td>
<td>3</td>
<td>2023</td>
<td>597.9</td>
<td>66.5</td>
</tr>
<tr>
<td>U</td>
<td>$5f^{2d},17s^2$</td>
<td>$5f^6d^2,7s$</td>
<td>2</td>
<td>1408</td>
<td>535.6</td>
<td>74.9</td>
</tr>
<tr>
<td>Pu</td>
<td>$5f^{6d^2},9s^2$</td>
<td>$5f^6d^2,7s$</td>
<td>2</td>
<td>918</td>
<td>347.3</td>
<td>178.2</td>
</tr>
</tbody>
</table>
The one compound phase which has since been found to exist in the system, after Catterall had failed to see it, is the UPd\(_4\) phase. Its existence has been confirmed by the results of the present work and by the work of Pells (76) and Terekhov and coworkers (156). The solubility range of this phase is about 3 a/o at about 1400°C (156).

The density of the compound UPd\(_4\) was determined as 12.41 ± 0.02 g/cc and this agrees very well with that reported by Terekhov et al. UPd\(_4\) has an L12 (ordered fcc) lattice which is unusual since most compounds with this type of structure have the formula AB\(_3\) with atomic sites

IA at 0, 0, 0
3B at 0, 1⁄2, 1⁄2; 1⁄2, 0, 1⁄2; 1⁄2, 1⁄2, 0.

Pells explained the unusual situation by stating qualitatively that "some uranium sites are vacant or Pd occupies some uranium sites" on such a lattice. A substitution of the values of the lattice parameter and density into the following equation

\[ \rho = \frac{1.66042 \Sigma A}{V'} \]  

(where \( \rho \) = density in g/cc, \( \Sigma A \) = sum of atomic weights of atoms in a unit cell and \( V' = A^3 \) is the volume of the unit atom in Å\(^3\)) yields a \( \Sigma A \) value of 501. If there are 0.75 U atoms and 3 Pd atoms in a unit cell, the \( \Sigma A \) of the unit cell would then be

\[ (0.75 \times 238.03) + (3 \times 106.4) = 500 \]

implying that the compound has a formula U\(_{0.75}\)Pd\(_3\) which is equivalent to UPd\(_4\). With U-atoms located on only 6 out of the 8 vertices of the cell, each cell will have two vacant sites on some of the U-lattice points. (Fig. 6.3). Since most of L12 compounds have the A+B atoms in the ratio of 1:3 e.g. AuCu\(_3\), UPd\(_4\) is referred to as having a "defect" L12 structure. However, in the ternary U-Pd-Rh system, this phase extends continuously to include this 1:3 ratio as seen in Fig. 4.7.
UPd$_4$ has quite a high stability. A qualitative prediction that it is a very stable intermetallic compound can be made using the Engel-Brewer theory (118). This theory which is based on the valence bond model predicts that when the elements U and Pd are combined to form the compound UPd$_4$ there is approximately a gain of 0.2 in the bonding electrons when compared with the elements. The enthalpy of formation of UPd$_4$ can be estimated as follows:

If we assume that all the electrons in the incompletely filled energy levels are spread uniformly over UPd$_4$ and consider the fact that U has a maximum of 6 (f, d and s, p) electrons and Pd a maximum of 10 (d and s, p) electrons, the average electrons per atom value will be

$$(0.2 \times 6\text{ e}) + (0.8 \times 10\text{ e}) = 9.2\text{ e}$$

With this value, one can consider UPd$_4$ as a hypothetical element with this number of electrons per atom. Such an element will therefore have sublimation energy which will be between those of Rh and Pd, and this will be given by

$$\Delta H_{\text{Subl}}(\text{UPd}_4)_{\text{Hypo}} = 0.2 \times \Delta H_{\text{Subl}}(\text{Rh}) + 0.8 \times \Delta H_{\text{Subl}}(\text{Pd})$$  (90)

From Table XXI, this value will be 518.4 kJ.g-atom$^{-1}$. This value can be considered as the hypothetical value for UPd$_4$. The excess enthalpy of the intermetallic compound UPd$_4$ as compared to the elements Pd and U would be

$$\Delta H^0(\text{UPd}_4) = 0.2 \left(\Delta H_{\text{Subl}}(\text{UPd}_4)_{\text{Hypo}} - \Delta H_{\text{Subl}}(\text{U})\right)$$

$$+ 0.8 \left(\Delta H_{\text{Subl}}(\text{UPd}_4)_{\text{Hypo}} - \Delta H_{\text{Subl}}(\text{Pd})\right)$$  (91)

This will then be equal to 555 kJ.mol$^{-1}$or 111 kJ.g-atom$^{-1}$which is comparable to very stable intermetallics like UPd$_3$, HfPd$_3$, ZrPd$_3$, etc.
The δ-solid solution was found to contain less U than Pells had quoted. From the computer calculations, the solubility of U in Pd was less than 22 a/o. This behaviour (i.e. high solubility of U in Pd) is striking because among the platinum metals, it is only in Pd that this high solubility is seen. U dissolves in Pd to the extent of about 16 a/o U and in Pt to about 5 a/o u. The values for the rest are less than 5 a/o.

At the temperatures under consideration, uranium is in the bcc form. So it is not surprising that the platinum metals do not dissolve U to a large extent since they are either of the hcp or fcc forms. One would have thought that the sizes of the atoms could explain the situation but Pt is bigger than Pd yet it is in the latter that U dissolves most. Therefore, the size of the atom is not responsible for the behaviour of U in these metals. As can be seen from Table XXI the ground states of Pd and Pt atoms indicate that there are more d-electrons in these two metals than the rest of the Pt metals. Now, when uranium with its unused 6d orbitals is mixed with any of the Pt metals which have excess of 4d and 5d electrons an extreme decrease in Gibbs energy for any structure would be expected (167). According to Brewer, there are overlaps of the d-orbitals of the atoms of the noble metals with the sharing of the excess d-electrons of the noble metals without violating Paul's Exclusion Principle. Since there are more of excess d-electrons in Pt and Pd, the decrease in Gibbs energy would be greatest, thereby enhancing the dissolution of U in the two metals. The relatively low cohesive enthalpy of Pd compared to Pt is due to the former's d^{10} configuration in the gaseous state. This has resulted in palladium having the lowest sublimation energy and melting point in the series and may explain the large solid solution range in the U-Pd system since alloying entails breaking and making of bonds.
Fig. 6.4 Modelled variation of free energy curves at 1400K in
(a) the U-Pd system

(b) the U-Rh system
6.2.2 The U-Rh System

Unlike the previous system, U-Rh has a very limited δ-solid solution range. The system is quite well documented but the experiments and calculations carried out in this work indicate a slightly higher value for the solubility of U in Rh. The computer calculations of Chapter 5 indicate a maximum solubility of about 3 a/o U in Rh, which at 1400 K is about twice the value quoted by Park. The lattice parameter measurements for ternary alloys in the δ-a₂ (i.e. δ-solid solution and URh₃ compound phase) two phase region also indicate a similar range of solubility (sub-section 5.3.1).

The line compound, URh₃ was calculated to melt at 1788°C using existing and modified thermodynamic data (153), (154). With the existing data, the compound U₃Rh₅ which is usually obtained by the peritectic reaction

\[ \text{L} + \text{URh}_3 \rightleftharpoons \text{U}_3\text{Rh}_5 \]

at 1550°C, melts congruently implying that a eutectic rather than a peritectic reaction is seen (Figs. 5.7 and 5.6).

The equivalent of the solution phase UPd₄ (i.e. URh₄) is not seen in the system at any temperature because the free energy curves had been modelled to reflect as much as possible the experimental results embodied in the equilibrium diagrams. A possible explanation for unstable condition of URh₄ might be due to the fact that the bonding energy is not enough to offset the large promotional energy (464 KJ/mol) of Rh. Applying the Engel-Brewer theory, the bonding energy of URh₄ is estimated to be 300.7 kJ.mol⁻¹ which is not enough to pay off the promotional energy. No other compounds were found in the system between 0 and 25 a/o Rh in contrast to the U-Pd system.

It has been mentioned earlier on that this system has a limited δ-solid solution range. Fig. 6.4 shows the modelled variation of
Fig. 6.5 The Pd-Rh system at lower temperatures.
the free energy of the different phases in the systems with composition at 1400°K. The slopes for solution (2) i.e. the δ-phase in the U-Rh system are not as steep as that found in the U-Pd system, and with the free energy of formation of URh₃ being much lower than the G - for the solution (2), this means that the tangent drawn from the tip of the line AR to the curve of the δ-phase is touched further away from Xₚₐd = 0. Moreover, the fact that the free energy curves of the δ-phase and phase in the U-Pd system are very close makes this more likely so (i.e. tangent touches curve (2) further away from Xₚₐd = 0).

6.2.3 The Pd-Rh System

The essence of investigating this system was to confirm the shape of the miscibility gap. The results, as can be seen from sub-section 4.2.3, indicate clearly that the gap is skewed towards rhodium. The results at 800°C (Table XII) show that two of the five alloys were in a 2-phase field. The composition of the equilibrium phases which existed in the alloy were in agreement with those obtained by Raub, Beeskow and Menzel (93). The Pd-rich phase in alloys 3 and 4 had 31 a/o Rh while the Rh-rich phase had about 80 a/o Rh. The Rh-rich phase in the present work, therefore, had 5 a/o more than Raub and coworkers. But from the two sets of results, the miscibility gap is found to be a good 30 a/o from the Pd-line and 20 a/o from the Rh-line. The 10 a/o difference in these figures is quite appreciable to shift the critical point (845°C (93)) towards rhodium (Fig. 6.5).

The other three alloys were single phase at 800°C. The lattice parameters obtained at 1150°C have been plotted against a/o Rh (Fig. 6.5). Although a straight line is fitted through the points, there is a slight positive deviation which is an indication of the miscibility gap which is formed at lower temperatures. The results agree quite well with those of Raub (92) in which there was a positive deviation of the lattice parameter
Fig. 6.6 The experimentally determined Ir-Pt system

![Ir-Pt diagram]

Fig. 6.7 The computed diagram of Pd-Rh system

![Pd-Rh diagram]
Fig. 6.8 The U-Pd-Rh system

(a) A hypothetical section at 1250°C

(b) The isothermal section at 1250°C
Fig. 6.9 The Fe-Cr-Mo ternary system (175)
variation with composition. The flat-top of the gap is also agreed on by both groups of workers.

The liquidus and solidus of this system is "dotted" in Raub's work and is at variance with that reported here. Fig. 6.7 is the phase diagram of this system at higher temperatures. The calculated diagram shows the solidus and liquidus to be S-shaped (Fig. 6.7). A similar shape is seen in the Ir-Pt (168) system (Fig. 6.6). Ir and Pt are in the same group as Rh and Pd respectively.

6.3 The U-Pd-Rh System

The experimental isothermal sections of the noble-metal rich end of this system have been shown in Figs. 4.7, 4.8 and 4.9. From the knowledge of the three binaries, one would have expected a continuous system, at least at higher temperatures, as the case in the Pd-Rh system. This means that a diagram like the one in Fig. 6.8a should have resulted. However, as can be seen, there is a two phase field in the pseudo-binary system, URh₃-UPd₄. As a result of this, a three phase field involving three fcc structures α₁, α₂ and δ solid solutions must be present. Although there was no direct evidence of this phase field at higher temperatures i.e. 1250°C and 1150°C, the three two phase regions bounding the area were detected (Fig. 6.8b).

6.3.1 α₁ Solution Phase

An interesting feature in the system is the intrusion of the α₁ (UPd₄) phase into the path of the ε UPd₃) phase. This prevents the latter structure from coming into equilibrium with the α₂ phase. This intrusion also gives the α₁ phase field, a "dog feet" shape which is similar to that found about the σ-phase field in the Fe-Cr-Mo system (175). However, in the latter case, the σ-phase field does not intrude into any other's path and also occupies a larger area (see Fig. 6.9). The σ-phase field is seen "bending" and widening to come into equilibrium with the ε-phase in the system.
The model used to predict the free energy curves of UPd$_4$ is too crude to give exact representations for the AG of UPd$_4$ if one considers the fact that UPd$_4$ can be looked on as a line compound, or as an ordered solid solution or as having a defect lattice when only a very simple model for a disordered solid solution was used. This is not helped by the fact that the AG differences between UPd$_3$ and UPd$_4$ are very small - to the order of a few cal.mol$^{-1}$. However, despite all these constraints, the shape of the solid solution phase field is confirmed in the calculation of the system. In the ternary, a negative TIP (-75000 cal.mol$^{-1}$) was imposed on the free energy of the solution phase, implying that all things being equal, the minimum point of the free energy surface will be at (33.33 a/o Rh, 33.33 a/o Pd), the centre of the triangle. However, the estimated lattice stabilities of the pure elements together with the infinite dilution ($H_1$ and $H_2$) values of equation 85 which are then converted to the A- and B-values of equation 86 are such that the $\alpha_1$ phase is unstable at all temperatures in all the systems but around about 80 a/o Pd in the U-Pd system. This means the minimum point will not occur at the ideal point (33 a/o Rh, 33 a/o Pd), but will shift towards the U-end. The overall effect is that this phase field is seen to "move" towards the U-end as shown in Figs. 5.9 - 5.11.

Most L12 compounds have the A + B atoms in the ratio of 1:3 e.g. AuCu$_3$ but UPd$_4$ which has this structure is not in this ratio. It is therefore referred to as "having a 'defect' L12 structure". However, it must be pointed out that in an earlier section in the present work, the compound was shown to have some vacant lattice sites. In the ternary system (U-Pd-Rh), the $\alpha_1$ solution phase extends continuously to include this 1:3 ratio. In order to maintain this L12 structure, it is necessary to have a valency change probably because of size factor or strain energy considerations.
Fig. 6.10 Lattice parameter variation across the quasi-binary system, URh₃–UPd₄.

Kleykamp (1000°C)

Present work (1050°C)

Mole fraction UPd₄, (m/f UPd₄)

Periodic Parameter, Å
Fig. 6.11  0.8 m/f UPd$_4$ alloy (x 0.5K). Main phase is $\alpha_1$, second phase, $\alpha_2$, is seen in grain boundaries.

Fig. 6.12  0.6 m/f UPd$_4$ alloy (x 0.5K). Main phase is $\alpha_2$, and minor phase seen in the grain boundaries is $\alpha_1$. 
Comparison of lattice parameter changes in $A_3B-B_3C$ pseudobinary systems.
The behaviour of this phase in extending towards U is further confirmed by the work of Bramman and coworkers (15). In an attempt to study the behaviour of fission products in ceramic nuclear fuels, Bramman et al. prepared a ternary alloy of U, Pd and Rh with a composition of 45 w/o U, 45 w/o Pd and 10 w/o Rh. It was found to be single phased with a cubic structure and a lattice parameter of 4.080 Å. This alloy is marked on Fig. 4.7 and clearly falls in the α₁ phase field.

6.3.2 The Pseudo-Binary System URh₃-UPd₄

The present results indicate a miscibility gap in this system, the phase in equilibrium being (URh₃ and UPd₄) solution phases. The presence of the miscibility gap contradicts the results obtained by Kleykamp (179) whose x-ray parameter plot (Fig.6.10) was interpreted that "there is an uninterrupted series of solid solution across the system at 1000°C". Five alloys in the present work show two phases and Figs. 6.11 and 6.12 are micrographs of alloys with composition lying inside the two phase region. They clearly show the two phases. Kleykamp's results rely only on an x-ray analysis and it is possible that he missed the second phase in his 0.68 m/f (mole fraction) UPd₄ alloy which is the only alloy in the two phase region.

The alloys between 0.8 m/f UPd₄ and UPd₄ are found to have quite high lattice parameters as shown in Fig. 4.1. Kleykamp's results did not cover this region although the 0.8 m/f UPd₄ alloy shows a high lattice parameter similar to those found in this work. The reason for these unexpected high lattice parameter values will be quite interesting and will have to be looked into. A similar increase in lattice parameter is seen in the pseudo-binary system CePd₃-CeRh₃, where the L12 structure is maintained (Fig. 6.15b).

The above results form an interesting pattern when combined with similar work on Ce-Rh-Pd (171) and Zr-Rh-Pd (171) (Fig. 6.15).
former case, the fcc (L12) structure is maintained right across the
pseudo-binary section, Rh₃Ce-CePd₃ with a marked increased in lattice
parameter as Pd₃Ce is approached. In the corresponding section
involving zirconium alloys on the other hand, the fcc (L12) structure
of Rh₃Zr disappears giving way to the hexagonal (D024) structure of
Pd₃Zr with a suitable intervening two phase region. In the pseudo-
binary (Rh₁₋ₓPdₓ)₃Ce alloy system where there is no change in crystal
structure across the composition range, the cerium atoms are assumed to
have changed their electronic state from 4f⁰ to a 4f⁰.55 configuration
as the cerium atoms change from the four valent state to a valent state
equivalent to 3.45 where the change of slope in lattice parameter versus
composition occurs (Fig. 6.15b). Holland-Moritz et al (172) gave further
evidence for the existence of the 4f electrons in Pd₃Ce using diffuse
neutron scattering. In the zirconium ((Rh₁₋ₓPdₓ)₃Zr) system, there is
a change in crystal structure across the composition range - from a
fcc (L12) phase in the binary alloy Rh₃Zr to a hexagonal (D024) phase
in the binary alloy Pd₃Zr because, unlike the cerium atoms, the
zirconium atoms have a stable configuration 4d² 5s² in the outer shell,
and cannot therefore adjust their valency.

The structure of the phases across this system indicates a change
from one L12 structure to another L12 and then to a D024 (UPd₃) structure.
Some of the lattice spacings of alloys determined in the present study are
shown in Fig. 6.15a to explain the above situation. The figure shows the
variation of lattice spacing as a function of palladium content in the
pseudo-binary section, U(Rh₁₋ₓPdₓ)₃. At about x = 0.8, there is an abrupt
increase in the lattice parameters which corresponds to the
L12 U(PdₓRh₃)₃, α₁ phase similar to the situation in the cerium-palladium-
rhodium systems. Effective diameters which were derived from the lattice
spacings show a corresponding change from 3.210 Å to 3.340 Å which, in
Fig. 6.16  Isothermal section of the ternary U-Pd-Rh system, showing atomic diameters and valencies of Uranium.

Valencies are in brackets
turn, correspond to uranium atoms acting with valencies 5 and 4 respectively. Hence, associated with the maintenance of the $L1_2$ structure is a valency change just as found in the cerium system. The effective diameter, however, reduces to $3.330 \text{ Å}$ at the Pd end. This diameter (Fig.6.16) corresponds to a valency of 5 again which shows that on changing the structure of the $\alpha_2$ (URh$_3$) $L1_2$ to the $\varepsilon$ (UPd$_3$) $DO24$ structure, the valency of U remains the same as found in the zirconium-palladium-rhodium system.

6.4 Summary of Findings

The structures of alloys of uranium and the fission products Pd and Rh have been investigated and tentative isothermal sections have been established by both experiment and calculation. This thesis has established the noble-metal rich ends of U-Pd and U-Rh.

There is only one intermetallic compound between 75 a/o Rh and pure Rh in the U-Rh system, which is URh$_3$. The other binary system, U-Pd, however, has two intermetallic compounds, UPd$_3$ and UPd$_4$, the latter having the same structure as URh$_3$ whilst UPd$_3$ has a hexagonal $DO24$ structure. The UPd$_4$ has a fcc $L1_2$ structure like that normally assumed by A-B compounds in the ratio 1:3. Density measurements indicate that UPd$_4$ has a defect lattice, although this could be further justified. The estimation of $\Delta G^f$(UPd$_4$) shows a high stability for this intermetallic compound and is responsible for its appearance in the U-Pd system. Palladium dissolves uranium to a very large extent in comparing with other platinum metals. This is due to the fact that Pd has more d-electrons which can occupy the empty d-orbitals of uranium. The stable electronic configuration of Pd means that the variable valency exhibited by U is probably responsible for the formation of most intermetallics in the U-Pd system. UPd$_5$ was not detected in the system. The temperatures at which both experiment and calculations were carried out were too high for the $U_2\text{Pd}_{11}$ and $U_2\text{Pd}_{17}$ to be detected.
Fig. 6.13 Lattice parameter variation in ternary U-Pd-Rh alloys with Pd:Rh = 1:1 (2250°C)
The U-Rh system between 75 a/o Rh and Rh was found to be occupied mainly by the two phase field where the metal is in equilibrium with the fcc, L12 intermetallic compound, URh$_3$. The solubility limit of U in Rh was found to be more than Park's - ~ 5 a/o U. The Engel-Brewer theory was used to estimate the $\Delta G^f$(URh$_3$) and was found to be very high and comparable with those of ZrRh$_3$ and HfRh$_3$.

The Pd-Rh system reconciled with that due to Raub et al. (93) in the solid state. However, when the phase boundaries of the two phase field involving the solid and liquid were calculated, it was found to be similar to that in the Ir-Pt system instead of the "dotted" solidus/liquidus that Raub suggested. The calculated diagram agreed very well with the experimentally determined one (93), (160) thus suggesting that the thermodynamics of the system were quite well established.

In the ternary U-Pd-Rh system, the UPd$_4$ solution phase extends to include the 1:3 ratio suggesting that the reason for the UPd$_4$ having a defect lattice might be due to electronic or size factor. Extensive solubility of Pd in URh$_3$ was found but there was only a limited solubility of Rh in UPd$_3$. This low solubility is probably due to the strain induced in the hexagonal structure by the Rh atoms in assisting to transform the D024 structure of UPd$_3$ to the fcc L12 structure of URh$_3$. The $\delta$-solid solution in the U-Pd is found to extend right across the ternary system. The variation of lattice parameter in alloys with Pd and Rh in the ratio of 1:1 is shown in Fig. 6.13. This indicates that there is a continuous solid solution within the 0 a/o U and ~10 a/o U range. A slight positive variation is indicated in the graph to show the existence of a miscibility gap at lower temperatures. The valency of uranium across the pseudo-binary URh$_3$-UPd$_3$ varied between 5.5 and 4 implying that some of the f-electrons in U-atoms are promoted into the d-orbitals in going from the rhodium end to the Pd end. The model used to calculate the equilibrium
between the intermetallics showed that URh$_3$ was in equilibrium with UPd$_4$, which was in turn found to be in equilibrium with UPd$_3$. The miscibility gap in the Pd-Rh system, as theory predicts, increases on U addition. This is in conformity with Timmerman's finding that a miscibility gap will widen if the third element is dissolved to different extents in the two metals.
Phase equilibria for the U-Pd-Rh system at 1050°C, 1150°C and 1250°C have been evaluated both experimentally and by calculation.

In the process of evaluating the ternary, it has been found that the binary system U-Pd is characterised by only two compounds at high temperature between 0 a/o U and 25 a/o U. The compounds are

(i) UPd$_3$ which is a line compound

and (ii) UPd$_4$ which has a range of solubility of about 2 a/o width. The compound, UPd$_5$ is not present as reported earlier on (85). The solubility of uranium in Pd (i.e. δ-solid solution) is not more than 15 a/o at any temperature. UPd$_4$ possesses a "defect" L12 structure with two corners of the unit cell being vacant instead of being occupied by uranium atoms. In the ternary system, this phase extends continuously to include the 3:1 ratio of atoms which is typical of L12 compounds.

A thermodynamic model has been used to explain the anomalous Pd-rich end of the system. The characteristics of this can best be explained through uranium exhibiting a variable valency. At 25 a/o U, it shows valency 4 and valency 5 at 20 a/o. In the liquid state, uranium displays valency 6.

The liquidus and solidus in the Pd-Rh system have been calculated and were found to be similar to that in the Ir-Pt system. The miscibility gap in the rhodium-palladium system increases on addition of uranium and the critical point in the ternary rises well above that found in the binary system.

URh$_3$ does not come into equilibrium with UPd$_3$ because the α$_1$ (UPd$_4$) phase extends in such a direction that makes this impossible. A miscibility gap was found to exist in the pseudo-binary URh$_3$-UPd$_4$ system.
The empty 5d-orbitals of uranium permit the use of paired d-electrons from the Pd and Rh atoms thus ensuring stability. Using the Engel-Brewer theory, the above electronic effects have been shown to be responsible for the high stability of the intermetallics in the U-Pd and U-Rh systems. The d$^{10}$ configuration of Pd is probably responsible for the large extensive δ-solid solution range in the U-Pd system.

A similar explanation is probably responsible for the high stability of intermetallic compounds and alloys of Pu and U with fission products like Rh, Pd and Ru in reactor fuels.
CHAPTEER EIGHT

8.1 Suggestions for Further Work

This study is only a small contribution to much needed information on the fuel/fission product studies necessary to understand the field. Further work could be done in the following ways:

(a) Since it is only the noble-metal rich end of the U-Pd-Rh system that has been established, work could be done on the uranium-rich end to complete work done on this system.

(b) The present work has been done within a small temperature range - 1050°C to 1250°C. To establish a more complete phase diagram, work should be done outside the 1050°C - 1250°C range - especially in the liquid range which this present work has not focussed attention on.

(c) The pseudo-binary system has been established. A more detailed study is required for precise determination of the phase boundaries.

(d) Density measurements were used to determine that UPd₄ has a defect lattice. It is therefore suggested that other methods be used to confirm this.

(e) Thermodynamics data - some from the literature and some estimates from thermodynamic models - have been used to calculate the systems in this thesis. There is an existing controversy over some of these values - especially UPd₃ and URh₃. In fact, most of the values used do not state reference states. It is therefore suggested that these thermodynamic data be measured experimentally using Galvanic cells with CaF₂ electrolyte. Such data could then be used to re-establish the system more accurately, thereby refining the diagrams obtained by calculation.
Intermetallic compounds of uranium with their platinum metals Ru, Rh and Pd are of technological importance because they are formed during fission of nuclear fuel in a reactor. These compounds have been identified as face-centred cubic \((U, Pu) Me_3\) phases \((Me = Ru, Rh\) and Pd\) \((15)\). The importance of \((U, Pu) Me_3\) phases in reactor technology is that considerable Pu enrichment has been found in this phase compared to the U/Pu ratio in mixed oxide fuels. Added to this is the fact that \((U, Pu) Me_3\) compounds have a very high resistance to dissolution in acids which will cause undesirable Pu loss during processing. In the light of the above, other systems in which some of these intermetallics occur should be studied.
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