

Thermodynamics of the uranium-platinum metals systems

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Abstract - A critical assessment is given of the thermodynamics of the uranium-platinum metals systems. It also includes the Gibbs energies of formation of URu₃, U₃Ru₅, URu₃Co_{0.7}, U₂RuC₂, URh₃, UOs₂, UIr₃ and UIr₂ which were determined in this laboratory using solid galvanic cells with CaF₂ single crystal electrolyte between 900 and 1200 K. For this purpose, the isothermal sections of the ternary U-Ru-F, U-Rh-F, U-Os-F and U-Ir-F systems were investigated in preceding experiments. The experimental thermodynamic results of the intermetallic phases and the platinum metal rich solid solution regions are discussed in the light of the semi-empirical cohesion energy model developed by Miedema.

INTRODUCTION

The electromotive force (emf) method is commonly applied for direct measurements of thermodynamic activities and Gibbs energies of formation of alloys and intermetallic compounds at high temperatures. For this purpose, solid ion conducting electrolytes are mostly used in second kind galvanic cells. In the case of an anion conducting electrolyte, e.g. ZrO₂, ThO₂, CaF₂, a single-phase alloy or coexisting phases MII_q and MII_p of an M-II system are equilibrated with an auxiliary electrolyte MX_i (i = 1, m) of which the cation M is identical with the more electropositive component of the M-II alloy; the anion X is identical with the mobile component of the electrolyte:



The unknown chemical potential μ''_X of the component X in the test electrode MX_m, MII_q, MII_p is related to the chemical potential μ'_X of the component X in the reference electrode M, MX₁ by measurement of the electromotive force E of the galvanic cell and application of the Gibbs-Duhem equation

$$\mu''_X - \mu'_X = \mu'_M - \mu''_M = n \cdot F \cdot E$$

where n is the valency and F is the Faraday number. The Gibbs energies of formation of intermetallic phases can be calculated on this experimental basis.

The thermodynamics of alloys and intermetallic phases of the platinum metals II with other transition metals M plays a dominant role in their reaction behaviour as well as in the basic understanding of their cohesion energies. A number of models were developed in the past by Engel and Brewer, Miedema, Colinet and by Bennet and Watson for the interpretation of these in part very stable phases which can react by explosion if intimately powdered mixtures are heated. The Gibbs energy - vs. - concentration curves of the M-II systems are in general asymmetric with a minimum towards the platinum metal side. Therefore, the ordered AuCu₃ type phases MII₃ and the Laves phases MII₂ are of greater interest. In this paper, the thermodynamics of the alloys and intermetallic phases of the platinum metals with uranium is critically reviewed. The phase diagrams of the platinum metal rich regions of these systems are illustrated in Fig. 1.

A significant requirement for the thermodynamic investigation of metallic systems by second kind solid galvanic cells with fluorine ion electrolytes is knowledge of the phase diagrams of the respective ternary fluoride systems. The metallic phases can be in equilibrium with the binary fluorides of one of the binary systems or with ternary fluorides of the system. Two solid fluorides, UF₃ and UF₄, exist in the binary uranium-fluorine system above 420 °C. In the ternary U-Ru-F and U-Os-F systems, URu₃-Ru and UOs₂-Os are in equilibrium with UF₃ (Fig. 2). Therefore, the half-cells UF₃-URu₃-Ru and UF₃-UOs₂-Os are required for measurements of the Gibbs energies of formation of URu₃ and UOs₂. In the ternary U-Rh-F and U-Ir-F systems, URh₃-Rh and UIr₃-Ir are in equilibrium with UF₄ (Fig. 2). Therefore, the half-cells UF₄-URh₃-Rh and UF₄-UIr₃-Ir are necessary for determinations of the Gibbs energies of formation of URh₃ and UIr₃. The equilibria of URu₃ and UOs₂ with UF₃ and of URh₃ and UIr₃ with UF₄ imply the higher thermodynamic stability of the latter intermetallic compounds. The different behaviour can be also inferred from the ternary U-(Rh,Os,Ir,Pt)-C systems, where equi-

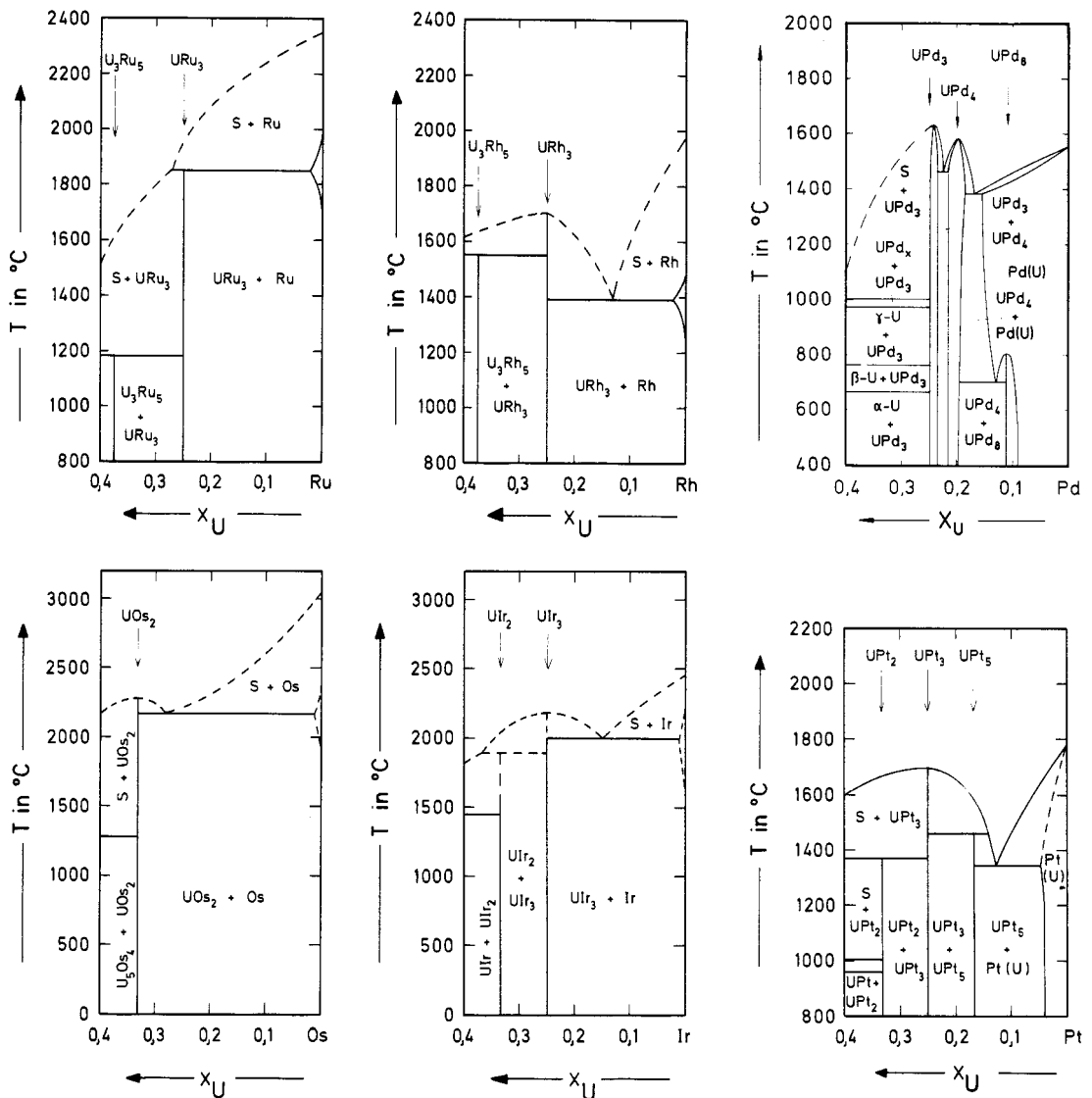


Fig. 1. Phase diagrams of the platinum metal rich regions of the systems with uranium, S = liquid

librium exists between carbon and the intermetallic phases URh₃, UIr₂, UIr₃, UPt₃ and UPt₅, whereas an equilibrium between carbon and UOs₂ is not observed due to the lesser thermodynamic stability of this intermetallic phase (ref. 1).

THE URANIUM-RUTHENIUM SYSTEM

The constitution of the U-Ru system was investigated by Park (ref. 2). It is characterized by five intermetallic phases: URu melts congruently in an approximately equimolar composition, U₂Ru, U₃Ru₄, U₃Ru₅ and URu₃ are formed peritectically. The last of these is the only solid compound above 1300 °C and crystallizes in the cubic AuCu₃ type structure (ref. 3). The ruthenium rich part of the phase diagram is represented in Fig. 1. The phase diagram of the ternary U-Ru-C system was established at 1300 °C (ref. 4). It is characterized by the tetragonal compound U₂RuC₂ (ref. 5) and by the cubic phase URu₃C_x (CaTiO₃ type) by filling the octahedral voids of the AuCu₃ type structure with carbon up to $x=0.7$ at 1300 °C (ref. 4).

The heat capacity and enthalpy of URu₃ were measured by adiabatic calorimetry between 7 and 345 K and by drop calorimetry between 406 and 890 K (ref. 6). At 298 K, $C_{p,298} = 101.4$ J/K·mol, $S^{\circ}_{298} = 144.5$ J/K·mol for the standard entropy and $H^{\circ}_{298} - H^{\circ}_0 = 21202$ J/mol for the enthalpy.

Gibbs energy of formation measurements on URu₃ and URu₃C_{0.7} were performed for the first time by the electromotive force method with second kind galvanic cells using single crystal

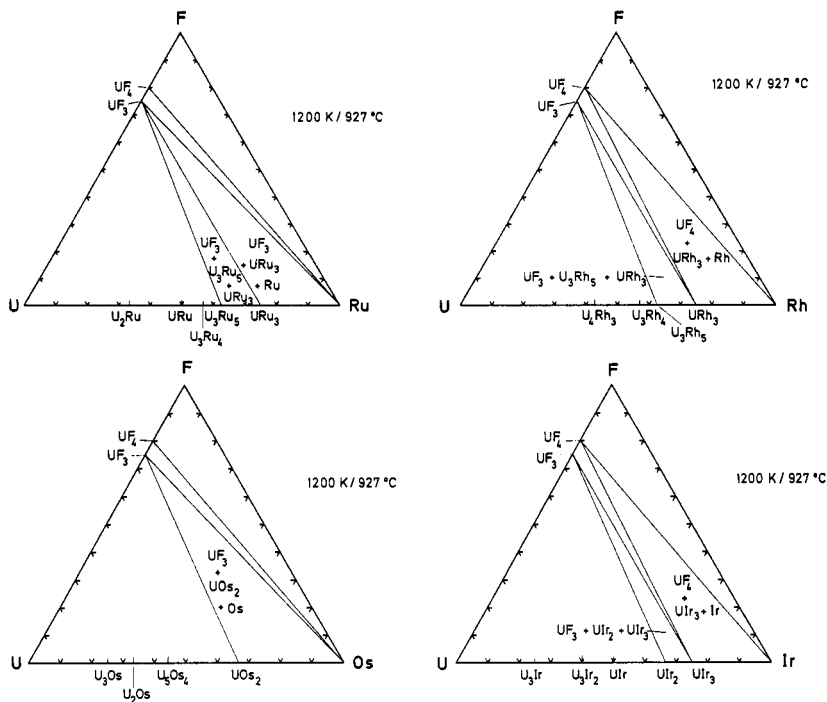
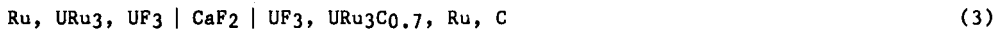
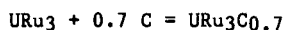
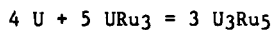
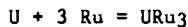


Fig. 2. Isothermal sections of the ternary U-Ru-F, U-Rh-F, U-Os-F and U-Ir-F systems at 927 °C.

CaF₂ electrolyte (ref. 4). Unfortunately, side-reactions between the platinum leads and the electrodes were not recognized. Therefore, amended values of the Gibbs energies of formation of URu₃ and URu₃C were given (ref. 7). The reasons for misleading emf measurements by use of electrodes incompatible with the electrical leads are discussed in ref. 8. The following galvanic cells were used for determinations of the Gibbs energies of formation of the intermetallic phases URu₃ and U₃Ru₅ of the U-Ru system and - in extension of this method to ternary phases - of those of the carbides URu₃C_{0.7} and U₂RuC₂ of the U-Ru-C system (ref. 9):



The overall reactions of cells (1) to (4) are:



The emf's of cells (1) to (4) are given by the equations (E in mV, T in K):

$$E_1 (\pm 14) = (688 \pm 50) - (0.124 \pm 0.047) \cdot T, 950 - 1130 \text{ K}$$

$$E_2 (\pm 7) = (173 \pm 43) + (0.042 \pm 0.040) \cdot T, 960 - 1130 \text{ K}$$

$$E_3 (\pm 3) = - (22.6 \pm 34.3) + (0.1153 \pm 0.0314) \cdot T, 1040 - 1140 \text{ K}$$

$$E_4 (\pm 7) = (655 \pm 30) - (0.107 \pm 0.027) \cdot T, 1020 - 1200 \text{ K}$$

Thermodynamic data of the auxiliary electrolyte UF₃ are not required for calculations of the Gibbs energies of formation of URu₃, U₃Ru₅, URu₃C_{0.7} and U₂RuC₂ using the arrangements of cells (1) to (4):

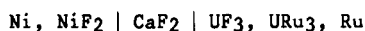
$$\Delta_f G^\circ \langle \text{URu}_3 \rangle = - 199100 + 35.9 \cdot T \pm 4000 \text{ J/mol}, 950 - 1130 \text{ K}$$

$$\Delta_f G^\circ \langle \text{U}_3\text{Ru}_5 \rangle = - 398600 + 43.6 \cdot T \pm 4800 \text{ J/mol}, 960 - 1130 \text{ K}$$

$$\Delta_f G^\circ \langle \text{URu}_3\text{C}_{0.7} \rangle = - 192600 + 2.5 \cdot T \pm 4100 \text{ J/mol}, 1040 - 1140 \text{ K}$$

$$\Delta_f G^\circ \langle \text{U}_2\text{RuC}_2 \rangle = - 380200 + 52.5 \cdot T \pm 3600 \text{ J/mol}, 1020 - 1200 \text{ K}$$

The Gibbs energy of formation of URu₃ (ref. 7, 9) fits well with that in ref. 10, where a different reference electrode was used in the galvanic cell:



The cell reaction



gives, by use of the Gibbs energies of formation of NiF₂ and UF₃,

$$\Delta_f G^\circ < \text{URu}_3 > = -178500 + 16.3 \cdot T \text{ J/mol, } 1090 - 1180 \text{ K}$$

A third law evaluation of the heat of formation of URu₃ based on the emf measurements in ref. 7 and 9 and on the Gibbs energy functions of URu₃ (ref. 6), U (ref. 11) and Ru (ref. 11) yields

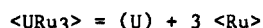
$$\Delta_f H^\circ_{298} < \text{URu}_3 > = - (154 \pm 4) \text{ kJ/mol}$$

The third law enthalpy of formation of URu₃ calculated by ref. 10 on the basis of their experimental results gives

$$\Delta_f H^\circ_{298} < \text{URu}_3 > = - (150.8 \pm 0.3) \text{ kJ/mol}$$

However, the given error seems to be too low due to the inaccuracy of the Gibbs energies of formation of UF₃ and NiF₂ used in their cell.

In an earlier paper, the Gibbs energy of formation of URu₃ was determined by mass spectrometry and a U-233 target collection apparatus between 1680 and 2100 K according to the reaction



which gives, by use of the enthalpy and entropy of vapourization of uranium, ref. 12,

$$\Delta_f G^\circ < \text{URu}_3 > = -79500 + 35.2 \cdot T \text{ J/mol, } 1680 - 2100 \text{ K}$$

A third law enthalpy of formation of URu₃ with estimated Gibbs energy function data yields

$$\Delta_f H^\circ_{298} < \text{URu}_3 > = - (49 \pm 22) \text{ kJ/mol}$$

This value is too positive compared to the emf results and thermodynamic model predictions.

THE URANIUM-RHODIUM SYSTEM

The U-Rh system is characterized by four intermetallic compounds: U₄Rh₃, U₃Rh₄ and U₃Rh₅ which are formed peritectically, and URh₃ with a congruent melting point. This phase crystallizes in the cubic AuCu₃ type structure (ref. 13). The maximum solubility of uranium in rhodium is below 1 at.% U at 1373 K. A phase diagram of the system is given by Park (ref. 14). The rhodium rich part is represented in Fig. 1.

The heat capacity and enthalpy of URh₃ were measured by adiabatic calorimetry between 7 and 345 K and by drop calorimetry between 424 and 842 K (ref. 6). At 298 K, C_{p,298} = 103.0 J/K·mol, S°₂₉₈ = 152.2 J/K·mol for the standard entropy and H°₂₉₈ - H°₀ = 21942 J/mol for the enthalpy.

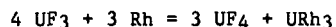
Gibbs energy of formation measurements were made on URh₃ by the emf method using solid electrolyte galvanic cells in the arrangements:



The latter cell (5) gives an emf of

$$E_5 (\pm 1) = (108 \pm 9) - (0.0315 \pm 0.0086) \cdot T, \text{ E in mV, } 900 - 1100 \text{ K}$$

which is based on the cell reaction



This result is illustrated in Fig. 3. The Gibbs energy of formation of URh₃ was calculated by use of the thermodynamic data of the auxiliary electrolytes NiF₂, UF₃ (ref. 10), UF₄ (ref. 10), MnO and UO₂ and resulted in

$$\Delta_f G^\circ < \text{URh}_3 > = -316400 + 9.3 \cdot T \text{ J/mol, } 950 - 1115 \text{ K (ref. 10)}$$

$$\Delta_f G^\circ < \text{URh}_3 > = -316200 + 13.2 \cdot T \text{ J/mol, } 900 - 1320 \text{ K (ref. 15)}$$

$$\Delta_f G^\circ < \text{URh}_3 > = -313700 + 20.6 \cdot T \text{ J/mol, } 900 - 1100 \text{ K (ref. 16)}$$

A third law evaluation of the heat of formation of URh₃ yields (ref. 10)

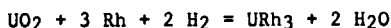
$$\Delta_f H^\circ_{298} < \text{URh}_3 > = - (301.2 \pm 0.2) \text{ kJ/mol}$$

It should be noted that the given error is too low, because it should include the errors of the auxiliary electrolytes NiF₂ and UF₄. A third law evaluation of the heat of formation of URh₃ based on the emf measurements by ref. 16 and on the Gibbs energy functions of URh₃ (ref. 6), U (ref. 11) and Rh (ref. 11) yields

$$\Delta_f H^\circ_{298} < \text{URh}_3 > = - (297 \pm 4) \text{ kJ/mol}$$

The given error includes those of the respective thermodynamic data of the auxiliary electrolytes UF_3 and UF_4 quoted in ref. 10.

The auxiliary electrolyte UF_3 was used in the test electrode UF_3 - URh_3 -Rh of older experiments (ref. 17), which is not in thermodynamic equilibrium according to the phase diagram of the U-Rh-F system in Fig. 2. By these reasons, the Gibbs energies of formation of the uranium richer phases of the U-Rh system measured by ref. 18 are also not correct. Further, the Gibbs energy of formation of URh_3 determined by coupled reduction of UO_2 and by electrochemical oxygen partial pressure measurements of the H_2/H_2O ratio according to the reaction



should be disregarded, due to the very negative entropy of formation (ref. 19); an adjusted value at 1500 K is given in ref. 20: $\Delta_f G^\circ_{1500} <URh_3> = -306$ kJ/mol. The isothermal section of the U-Rh-Pd system was investigated at 1323 K (ref. 21). The observed closed region of immiscibility within the Rh-Pd(U) solid solution was used to calculate the relative partial molar excess Gibbs energy of uranium in rhodium at infinite dilution, which resulted in $x_s \Delta \bar{G}^{\circ}_{U} = -290$ kJ/mol at 1323 K.

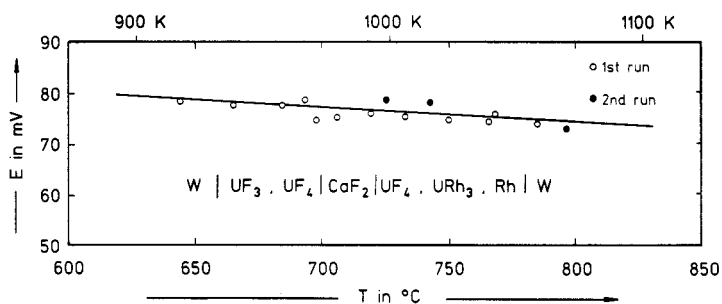


Fig. 3. Electromotive force of the cell $UF_3, UF_4 | CaF_2 | UF_4, URh_3, Rh$ as a function of the temperature.

THE URANIUM-PALLADIUM SYSTEM

The earliest results for the U-Pd system refer to the intermetallic phase UPd_3 which crystallizes in the hexagonal $TiNi_3$ type structure (ref. 3). Several phase diagrams were published: Catterall et al. (ref. 22) investigated the entire concentration range and observed an fcc. U_xPd_{1-x} ($x \leq 0.22$) solid solution region, the intermetallic phase UPd_3 with a congruent melting point at 1640 °C and two high temperature phases U_5Pd_6 and UPd . The palladium rich part of the system up to 22 at.% U was further examined by Pells (ref. 23). Two compounds with the compositions U_2Pd_{17} and U_2Pd_{11} were established which transform at 800 and 1030 °C, resp. into the fcc. U_xPd_{1-x} solid solution ($x \leq 0.165$ at 1300 °C). The existence of two peritectic phases, UPd_5 and fcc. UPd_4 (AuCu₃ type), was stated. Terekhov et al. (ref. 24) examined the palladium rich part of the system up to 24 at.% U. They confirmed the fcc. solid solution range up to 15.5 at.% U at 1400 °C. However, they observed only two intermetallic phases in the investigated concentration region, the tetragonal line compound UPd_8 which transforms into the U_xPd_{1-x} solid solution at 800 °C, and fcc. UPd_4 which crystallizes in the AuCu₃ type defect structure, $U_{0.75}Pd_{0.25}Pd_3$, and melts congruently at about 1585 °C. The best assessment that can be made at the moment is a synthesis of Catterall's work in the region $x_{Pd} \leq 0.75$ (ref. 22) and of Terekhov's et al. results in the region $x_{Pd} > 0.75$ (ref. 24). Phase studies at 1050 °C by the present author have yielded the following results (ref. 21): the maximum solubility of uranium in palladium is 15.0 at.% U; UPd_4 has a homogeneity region between 19.1 and 21.6 at.% U; the homogeneity region of UPd_3 is in the 23.3-24.8 at.% range. The palladium rich part of the phase diagram is represented in Fig. 1.

The heat capacity and enthalpy of UPd_3 were measured by adiabatic calorimetry between 1 and 16 K (ref. 25) and between 5 and 350 K (ref. 26) as well as by drop calorimetry between 392 and 875 K. At 298 K, $C_{p,298} = 102.1$ J/K·mol, $S^\circ_{298} = 176.4$ J/K·mol for the standard entropy and $H^\circ_{298} - H^\circ_0 = 23425$ J/mol for the enthalpy. The enthalpy of formation of UPd_3 was measured by fluorine combustion calorimetry (ref. 27), which yielded at 298 K: $\Delta_f H^\circ_{298} <UPd_3> = - (524 \pm 31)$ kJ/mol.

The relative partial molar Gibbs energy of uranium in the Pd(U) solid solution and the Gibbs energy of formation of UPd_4 were determined in the temperature range 1073 - 1473 K by coupled reduction of UO_2 and by electrochemical oxygen partial pressure measurements of the H_2/H_2O ratio (ref. 19, 20). This resulted in the Gibbs energies of formation:

$$\Delta_f G^\circ <U_{0.16}Pd_{0.84}> = -60850 \text{ J/g-at.}, 1073 \text{ K (Pd(U) phase boundary)}$$

$$\Delta_f G^\circ <UPd_4> = -350 \text{ kJ/mol}, 1473 \text{ K}$$

A Gibbs energy of formation result of UPd₃ at 1673 K based on calorimetric measurements was quoted in ref. 27:

$$\Delta_f G^\circ < \text{UPd}_3 > = - 527 \text{ kJ/mol, } 1673 \text{ K}$$

A mass spectrometric investigation of UPd₃ at 1673 K yielded (ref. 28):

$$\Delta_f G^\circ < \text{UPd}_3 > = - 259 \text{ kJ/mol, } 1673 \text{ K}$$

The isothermal section of the U-Rh-Pd system was investigated at 1323 K (ref. 21). The observed closed region of immiscibility within the Rh-Pd(U) solid solution was used to calculate the relative partial molar excess Gibbs energy of uranium in palladium at infinite dilution which resulted in $x^s \Delta \bar{G}^{\infty} \text{U} = - 390 \text{ kJ/mol}$ at 1323 K. Relative partial molar Gibbs energies of uranium at 1173 K on the uranium side of the system are quoted in ref. 29:

$$\Delta \bar{G}^{\infty} < \gamma \text{-U}_{0.98} \text{Pd}_{0.02} > = - 260 \text{ J/mol}$$

$$\Delta \bar{G}^{\infty} < \gamma \text{-U(Pd) - UPd}_3 > = - 450 \text{ J/mol}$$

Selected Gibbs energies of formation of uranium-palladium phases are represented in Fig. 4. The thermodynamics is in part inconsistent with the constitution of the system. Further experimental studies are necessary.

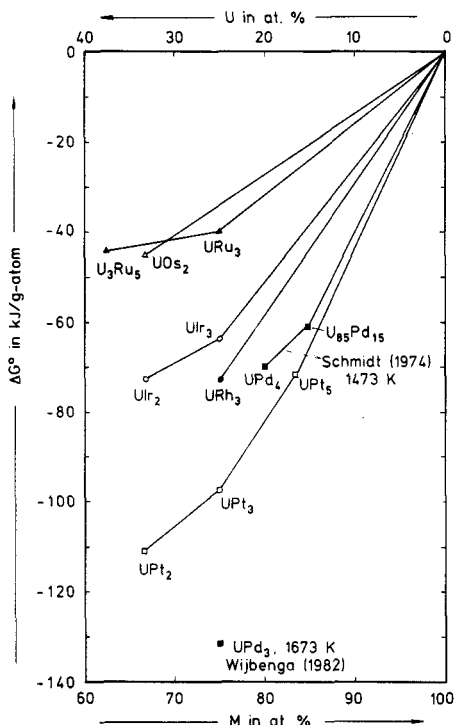


Fig. 4. Gibbs energies of formation of the platinum metal rich phases of uranium (at 1100 K unless otherwise stated).

THE URANIUM-OSMIUM SYSTEM

The constitution of the U-Os system was investigated over the entire composition range by Knapton (ref. 30). It is characterized by four intermetallic phases: U₃Os, U₂Os, U₅Os₄ and UOs₂. The last of these crystallizes in the MgCu₂ type Laves phase structure (ref. 3) and melts congruently. The osmium rich part of the phase diagram is represented in Fig. 1.

Thermodynamic measurements were made by the emf method with a second kind galvanic cell using single crystal CaF₂ electrolyte (ref. 7). The Gibbs energy of formation of UOs₂ was determined between 940 and 1050 K with the cell



according to the cell reaction



The calculation of the emf of cell (6) by the least-squares method

$$E_6 (\pm 10) = (618 \pm 48) - (0.140 \pm 0.058) \cdot T, \text{ E in mV, } 940 - 1050 \text{ K}$$

gives in the Gibbs energy of formation of UOs₂ directly:

$$\Delta_r G^\circ = - 3 \cdot F \cdot E = \Delta_f G^\circ < \text{UOs}_2 >$$

$$\Delta_f G^\circ < \text{UOs}_2 > = - 179000 + 40.6 \cdot T \pm 3000 \text{ J/mol, } 940 - 1050 \text{ K}$$

THE URANIUM-IRIDIUM SYSTEM

The constitution of the U-Ir system was investigated by Park and Mullen (ref. 31). Five intermetallic phases were observed: U_3Ir , U_3Ir_2 , UIr , UIr_2 and UIr_3 . The last of these crystallizes probably in the cubic $AuCu_3$ type structure (ref. 13), UIr_2 in the cubic $MgCu_2$ type Laves phase structure (ref. 3). The iridium rich part of the phase diagram is represented in Fig. 1.

Gibbs energy of formation measurements were made on UIr_3 and UIr_2 by the emf method using solid electrolyte cells in the arrangements (ref. 32):

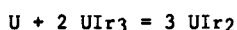
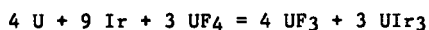


The cells give emf's of

$$E_7 (\pm 5) = (866 \pm 84) + (0.018 \pm 0.078) \cdot T, E \text{ in mV, } 1040 - 1130 \text{ K}$$

$$E_8 (\pm 2) = (535 \pm 11) - (0.032 \pm 0.011) \cdot T, E \text{ in mV, } 940 - 1090 \text{ K}$$

which are based on the cell reactions



The Gibbs energy of formation of UIr_3 was calculated by use of the thermodynamic data of UF_3 and UF_4 (ref. 10) and yielded together with that of UIr_2

$$\Delta_f G^\circ <UIr_3> = -243600 - 9.7 \cdot T \text{ J/mol, } 1040 - 1130 \text{ K}$$

$$\Delta_f G^\circ <UIr_2> = -214000 - 3.4 \cdot T \text{ J/mol, } 940 - 1130 \text{ K}$$

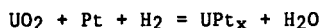
Unfortunately, it was not recognized in previous experiments (ref. 7) that the composition UF_3 - UIr_3 -Ir in the test electrode of the cell was not in thermodynamic equilibrium according to the phase diagram of the U-Ir-F system in Fig. 2. Therefore, the older results (ref. 7) must be disregarded. The Gibbs energy of formation of UIr_3 was further measured by coupled reduction of UO_2 and by electrochemical determination of the oxygen partial pressure of the H_2/H_2O ratio (ref. 19). These results should be disregarded due to the very negative entropy of formation. An adjusted value at 1500 K is cited in ref. 20: $\Delta_f G^\circ_{1500} <UIr_3> = -303 \text{ kJ/mol}$.

The thermodynamic stability of UIr_3 is slightly lower than that of URh_3 (see Fig. 4), which is also reflected by the phase equilibria of the ternary U-Ir-C and U-Rh-C systems (ref. 1): U_2IrC_2 and C are in equilibrium with the relatively more stable phase UIr_2 , whereas U_2RhC_2 and C are in equilibrium with URh_3 .

THE URANIUM-PLATINUM SYSTEM

The phase diagram of the U-Pt system is based on the work of Park and Fickle (ref. 33). Four intermetallic phases were observed: UPt , UPt_2 , UPt_5 , which are formed peritectically, and UPt_3 . This phase crystallizes in the hexagonal $SnNi_3$ type structure (ref. 3) and melts congruently. The maximum solubility of uranium in platinum is 4 at.% U. The platinum rich part of the phase diagram is represented in Fig. 1.

The relative partial molar Gibbs energy of U in the Pt(U) solid solution and the Gibbs energies of formation of UPt_2 , UPt_3 and UPt_5 were determined by coupled reduction of UO_2 and by electrochemical oxygen partial pressure measurements of the H_2/H_2O ratio (ref. 19, 20):



The following results can be derived from the measurements:

$$\Delta_f G^\circ <UPt_2> = -382500 + 45.6 \cdot T \text{ J/mol, } 1470 - 1670 \text{ K}$$

$$\Delta_f G^\circ <UPt_3> = -444500 + 50.7 \cdot T \text{ J/mol, } 970 - 1670 \text{ K}$$

$$\Delta_f G^\circ <UPt_5> = -490400 + 55.3 \cdot T \text{ J/mol, } 970 - 1670 \text{ K}$$

The entropies of formation are unusually negative. The Gibbs energies of formation of these uranium-platinum phases at 1473 K are illustrated in Fig. 4.

THE ENTHALPIES OF FORMATION OF THE INTERMETALLIC URANIUM-PLATINUM METAL PHASES IN THE LIGHT OF THE MIEDEMA MODEL

A number of thermodynamic models have been developed in the past to predict the enthalpy of formation of intermetallic compounds by atomistic considerations. One of the most successful models is that of Miedema et al. (ref. 34) which is based on two coordinates only, the electron density at the boundary of the Wigner-Seitz atomic cell and the chemical potential of the electronic charge. Table 1 compares the predicted enthalpies of formation of intermetallic uranium-

TABLE 1. Enthalpy of formation of uranium-platinum metal phases, in kJ/g-atom, comparison of experiments with the predicted values by Miedema (ref. 34).

phase	$\Delta_f H^\circ$, exptl.	T in K	method	$\Delta_f H^\circ$, calculated
URu ₃	- 38	298	3rd law, emf	- 38
U ₃ Ru ₅	- 50	1100	2nd law, emf	- 51
URh ₃	- 75	298	3rd law, emf	- 48
UPd ₃	- 131	298	calorimetry	- 61
UOs ₂	- 60	1100	2nd law, emf	- 43
UIr ₃	- 61	1100	2nd law, emf	- 51
UIr ₂	- 71	1100	2nd law, emf	- 65
UPt ₅	- 82	1400	coupled reduction	- 46
UPt ₃	- 111	1400	coupled reduction	- 68
UPt ₂	- 128	1400	coupled reduction	- 87

platinum metal phases with the experimental results critically assessed in this paper. As the majority of the experiments is based on emf measurements in a rather narrow temperature range it is hard to decide whether a 2nd law evaluation of the enthalpy of formation of the intermetallic compounds is permitted. Further calorimetric studies are recommended to verify the thermodynamic predictions from precise experimental results.

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