Reprint from

"THERMODYNAMICS OF NUCLEAR MATERIALS 1974"

VOL.II

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 1975

TERNARY PHASE EQUILIBRIA IN THE SYSTEMS ACTINIDE-TRANSITION METAL-CARBON AND ACTINIDE-TRANSITION METAL-NITROGEN

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Abstract

TERNARY PHASE EQUILIBRIA IN THE SYSTEMS ACTINIDE-TRANSITION METAL-CARBON AND ACTINIDE-TRANSITION METAL-NITROGEN.

Isothermal sections in the ternary phase diagrams of actinide-transition metal-carbon and actinide-transition metal-nitrogen systems are compiled on the basis of new phase studies, using thermodynamic data of carbides and nitrides, and considering the structure and lattice parameters of binary compounds. The lack of experimental results is compensated by estimating the solution behaviour and the phase stabilities. Phase diagrams are given for the systems: Th-(U or Pu)-C, U-(Th or Pu)-N, (Th or U or Pu)-Y-C, (Th or U or Pu)-Ce-C, (Th or U or Pu)-Y-N, (Th or U or Pu)-Ce-N, U-(La or Ce or Pr or Nd)-N, (Th or U or Pu)-Ti-C, (Th or U or Pu)-Zr-C, (Th or U or Pu)-Nb-C, (Th or U or Pu)-Mo-C, U-(Ti or Zr or Hf or Mo)-N, (Th or Pu)-Zr-N, (Th or U or Pu)-Cr-N and (Th or U or Pu)-(Ru or Rh or Pd)-C. Of particular interest is the occurrence of ternary carbides and nitrides.

1. INTRODUCTION

The reaction behaviour of multicomponent systems containing actinide carbides and nitrides is of great interest for many problems in nuclear technology. Of particular importance in this context are ternary systems involving the transition metals, which are the most frequently occurring fission products, the main constituents of the cladding and structural materials, and potential alloying elements.

The clearest way of surveying the reaction behaviour for specific combinations of elements at high temperatures is to extract information from the appropriate phase diagrams. New experimental work was carried out with the actinide elements thorium, uranium and plutonium. The thermodynamic data of the carbides and nitrides, including some estimations, and, furthermore, structural and lattice parameters of these, as well as the valence states of the actinide elements, form the bases for an evaluation of ternary phase equilibria and of some stability criteria of ternary compounds.

Since thorium, uranium and plutonium are the most important actinide elements in nuclear technology, and since for these three actinide elements details of only the binary carbide and nitride systems are known at present, the evaluation of ternary phase diagrams was restricted to these elements. The binary carbide and nitride systems of the actinides which were considered when preparing the ternary sections are given in Figs 1 and 2; information was drawn from the following sources: Th-C [1]; U-C [2]; Pu-C [3]; Th-N [4,5]; U-N [12]; Pu-N [3].[1]

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[1] The figures are all to be found at the end of this paper on pages 220-262.

The Gibbs energies of formation of the carbides and nitrides required for calculations and estimations were only rough values in some cases; therefore the estimated and calculated tie lines must be taken as a first approximation (for thermodynamic data see Refs [3] and [6] for the actinide carbides and nitrides, Refs [7] and [8] for the rare-earth carbides and nitrides, Ref. [9] for the IVA to VIA transition metal carbides, and Ref. [8] for the IVA to VIA transition metal nitrides).

It should be pointed out that this work is not a review of the existing data concerning the constitution of ternary carbide and nitride systems, but is the application of new experimental work, thermodynamic data and theoretical estimations for the construction of phase diagrams. Therefore the entire original literature on the constitution of ternary actinide-transition metal-carbon and actinide-transition metal-nitrogen systems is not fully cited in this work. The references [3, 6] and [9] to [15] give reviews of part of the above-mentioned topics, and were taken into account, just as were the three books on the constitution of binary alloys [16-18].

2. TERNARY PHASE EQUILIBRIA

2.1. Actinide-actinide-carbon systems

The systems consisting of two actinide elements and carbon are characterized by a complete miscibility in the monocarbide, sesquicarbide and dicarbide sections at temperatures at which the corresponding isotypic binary compounds exist. Tentative isothermal sections for the Th-U-C system at 1800°C and for the Th-Pu-C and U-Pu-C systems at 1600°C are given in Fig. 3. No tie lines are drawn in the temperature sections. Calculations which were made on the assumption of ideal solution behaviour [19] in the $(U, Pu)C + (U, Pu)_2C_3$ diphase region show satisfying agreement with experimental results. Details in the Th-Pu-C and U-Pu-C systems are reviewed in Ref. [3] and are given for the Th-U-C system in Refs [15] and [20]. Experimental results in the metal-rich part of the Th-Np-C system [21] confirm complete miscibility in the monocarbide section.

2.2. Actinide-actinide-nitrogen systems

It can be accepted that all the actinide mononitrides are mutually miscible, although this is experimentally confirmed only for ThN-UN and UN-PuN. Using thermodynamic data and estimated interaction parameters, ternary phase equilibria were calculated for the Th-U-N and U-Pu-N systems. Figure 4 shows isothermal sections at 1000°C calculated with the specified interaction parameters and the Gibbs energies of formation:

$^{f}\Delta G^{0}_{UN}$ (cal/mol) = -73 200 + 22.5 T

$^{f}\Delta G^{0}_{ThN}$(cal/mol) = -76 000 + 18.5 T + 2.2 $\times 10^{-20}$ T^{6}

$^{f}\Delta G^{0}_{U_2N_{3+X}}$(cal/mol) ...... see Ref. [8]

$^{f}\Delta G^{0}_{ThN \rightarrow ThN_{1,33}}$ (cal/mol) = -12 100 + 5.4 T

$^{f}\Delta G^{0}_{PuN}$ (cal/mol) = -70 600 + 22.1 T (cf. Ref. [8])

The interaction parameters are estimated for the nitride systems from the lattice parameter differences in connection with a correlation to the carbides, and for the metal systems from the binary phase diagrams (for details see Ref. [8]). Neither a solubility of plutonium in U_2N_3, or of thorium in U_2N_3, or uranium in Th_3N_4 have been considered. Only the invariant points of the three phase equilibria have been calculated for various nitrogen pressures in the nitrogen-rich part of the phase diagrams. α-U_2N_3 and β-U_2N_3 coexist at 1000°C and 1 atm N_2. At 0.1 atm N_2 only β-U_2N_3 occurs [22]. The phase equilibria in the U-Th-N system between metals and mononitrides, investigated experimentally (Ref. [23]), show excellent agreement with the equilibria of the calculated section in Fig. 4. Phase relations in the U-Pu-N system and a description of these in terms of their dependence on various interaction parameters were recently discussed [24].

2.3. Actinide-rare earth-carbon systems

The individual actinide and rare-earth metals show behaviour different to that of carbon. Whereas the light elements of the actinide series (e. g. thorium and uranium) form stable monocarbides and less stable sesquicarbides or dicarbides, the opposite behaviour is observed with the heavier actinide elements (e. g. plutonium and americium). Like the actinide elements in which the trivalent state predominates (plutonium, americium; cf. Ref. [25]), the rare earths form stable sesquicarbides and dicarbides. Only the rare-earth metals with small atomic radii form monocarbides (scandium and yttrium) or subcarbides (samarium to lutetium). The dicarbides of the actinides and rare earths exist with a face-centred cubic high-temperature modification and a tetragonal low-temperature modification. One can accept for the actinide-rare earth-carbon systems with stable monocarbides (ThC, UC) in the high carbon section high-temperature cubic dicarbide solid solutions and two phase equilibria between the rare-earth dicarbides and actinide monocarbides. One can also accept for systems with stable sesquicarbides (Pu_2C_3, Am_2C_3) high-temperature cubic dicarbide solid solutions and solid solutions of the sesquicarbides. Whereas complete solid solutions exist between actinide monocarbides and YC_{1-x}, lanthanide monocarbides (lanthanum, cerium, praseodymium and neodymium) can be stabilized to only some extent by solution in the actinide monocarbides [26, 27].

Typical phase equilibria at 1600°C in these systems are given by tentative ternary sections in Fig. 5 for the Th-Y-C, U-Y-C and Pu-Y-C systems and in Fig. 6 for the Th-Ce-C, U-Ce-C and Pu-Ce-C systems.

Whereas for the cerium-containing systems, experimental data concerning the solution behaviour are available (Th-Ce-C [28], U-Ce-C and Pu-Ce-C [26, 27]) information on yttrium-containing systems are scarce. Preliminary high-temperature X-ray investigations [29] confirm the assumption of a complete solid solution between ThC_{1-x} and YC_{1-x}. At temperatures higher than 1500°C a complete dicarbide solid solution should exist, and a sesquicarbide solid solution could also be obtained at high pressure [30]. Similar to the U-Y-C system [31], extended homogeneity regions of ternary carbides probably exist in the Pu-Y-C-system.

2.4. Actinide-rare earth-nitrogen systems

The experimental work in thorium and uranium-containing ternary nitride systems established the existence of complete solid solutions between ThN and YN, LaN, CeN, PrN and NdN [32], as well as between UN and YN, LaN, CeN, PrN and NdN [33, 34]. Solid solutions between PuN and these rare-earth nitrides are very probable. Figures 7 and 8 show, respectively, tentative isothermal sections of the (Th, U, Pu)-Y-N and (Th, U, Pu)-Ce-N systems. The tie lines in these sections are estimated. However, those of the sections for the U-La-N, U-Ce-N, U-Pr-N and U-Nd-N systems given in Fig. 9 are calculated with the assumption of a regular solution model, with estimated interaction parameters [8]. In agreement with our experimental results the calculation of the decomposition temperature of (U, La)N with ϵ = 8400 cal/mol is about 1700°C. For the calculation the following Gibbs energies of formation were used (cf. Ref. [8]):

$${}^{f}\Delta G^{0}_{UN}\ (\mathrm{cal/mol}) = -73\,200 + 22.5\ T$$

$${}^{f}\Delta G^{0}_{LaN}\ (\mathrm{cal/mol}) = -72\,100 + 25.0\ T$$

$${}^{f}\Delta G^{0}_{CeN}\ (\mathrm{cal/mol}) = -78\,000 + 25.0\ T$$

$${}^{f}\Delta {}^{0}_{PrN}\ (\mathrm{cal/mol}) = -75\,000 + 25.0\ T$$

$${}^{f}\Delta G^{0}_{NdN}\ (\mathrm{cal/mol}) = -71\,000 + 25.0\ T$$

2.5. Actinide-IVA, VA, VIA transition metal-carbon systems

New experimental results in the Th-Ti-C, Th-Zr-C, Th-Nb-C and Th-Mo-C systems, together with the known phase equilibria of the corresponding uranium systems, of the Pu-Mo-C system and estimated phase diagrams of further plutonium-containing systems are presented in the ternary sections shown in Figs 10 to 13. The constitution of the actinide (Th or U or Pu)-Ti-C systems seems to be very similar (Fig. 10). The stable monocarbides TiC and ZrC are in equilibrium with the actinide metals, as is also shown for the corresponding zirconium-containing systems (Fig. 11). Only UC is obviously able to form mixed carbides with ZrC and NbC. The reason, therefore, seems to lie in the difference in the atomic radii. Figure 12 shows ternary sections in the Th-Nb-C, U-Nb-C and Pu-Nb-C systems and Fig. 13 gives sections for the Th-Mo-C, U-Mo-C and Pu-Mo-C systems (for references concerning the U-Mo-C and Pu-Mo-C systems see [10] and [13], respectively). Two ternary compounds were observed in the Th-Mo-C system, which could not as yet, however, be exactly characterized as to structure and composition.

2.6. Actinide-IVA, VA, VIA transition metal-nitrogen systems

Extended experimental work on uranium-containing systems [32, 35, 36] and some experimental data in the thorium and plutonium-containing systems (ThN-ZrN [31], PuN-ZrN [37], Th_2CrN_3 [38], Pu-Cr-N [39]) have, together with experimental and estimated thermodynamic data, been used for calculating and estimating ternary phase equilibria in these nitride systems. Calculated isothermal sections for U-Ti-N at 2000°C, U-Zr-N at 1000°C, U-Hf-N at 1200 and 1500°C, U-Nb-N at 1000°C and U-Mo-N at 1200°C are given in Fig. 14. The interaction parameters listed for each section and the following Gibbs energies of formation are used for the calculation:

$$^{f}\Delta G^{0}_{TiN}\ (\text{cal/mol}) = -80\,900 + 22.8\ T$$

$$^{f}\Delta G^{0}_{ZrN}\ (\text{cal/mol}) = -97\,900 + 23.1\ T$$

$$^{f}\Delta G^{0}_{HfN}\ (\text{cal/mol}) = -88\,200 + 23.0\ T$$

$$^{f}\Delta G^{0}_{NbN}\ (\text{cal/mol}) = -56\,800 + 20.0\ T$$

For details see Ref. [8].

The calculations result in critical temperatures for the solid solutions of about 4000°C for UN-TiN, 800°C for UN-ZrN, 1300°C for UN-HfN and 2600°C for UN-NbN. These temperatures, as well as the solubility limits, agree well with our experimental results. Thorium and plutonium-containing systems are only presented for Th-Zr-N and Pu-Zr-N (Fig. 15) because the existence of complex nitrides in other systems has not been confirmed as yet. Isothermal sections for thorium, uranium and plutonium are given for the nitride systems with chromium in Fig. 16. Whereas throrium and uranium form complex nitrides [35, 38], no ternary compounds could be found for plutonium [39].

2.7. Actinide-platinum metal-carbon systems

Figures 17, 18 and 19 show ternary sections for the following systems: Th-Ru-C (1200°C) [40], U-Ru-C (1300°C) [41], Pu-Ru-C (1200°C) [42], Th-Rh-C (1200°C) [40], U-Rh-C (1300°C) [43], Pu-Rh-C (1200°C) [42], Th-Pd-C (1100°C) [44], U-Pd-C (1300°C) [44] and Pu-Pd-C (1200°C) [42]. These have resulted from our group's experimental work. The work of Haines and Potter [26] has been considered for obtaining data concerning the existence of three phase equilibria: $PuC_{1-x} + Pu_2C_3 + PuRu$, $Pu_2C_3 + PuRh_2 + PuRh_3C_{1-x}$, and $PuC_{1-x} + Pu_2C_3 + PuPd_3$.

The actinide carbides are not in equilibrium with the platinum metals. Partly ternary complex carbides, partly intermetallic compounds and free carbon are formed during the reaction of binary carbides with platinum metals. The tendency to form ternary carbides decreases from ruthenium to rhodium and palladium. The occurrence of ternary phases is discussed in the next section.

3. TERNARY ACTINIDE-TRANSITION METAL CARBIDES AND NITRIDES

Ternary carbides and nitrides exist as mixed phases of binary compounds and as complex compounds with a structure of their own. Mixed and complex phases are known with two non-metallic components and one metallic component (i.e. carbonitrides) as well as with two metallic components and one non-metallic component. Here only the latter case — with metals from the transition metal series — is described. The ternary carbides and nitrides are listed in Fig. 20. Many of the systems containing thorium or plutonium together with the other actinides (with the exception of uranium) have not yet been investigated. Preliminary results in the carbide systems with thorium indicate the existence of ternary phases with rhenium, osmium, iridium and platinum.

The uranium compounds are the most thoroughly investigated up to now. One can distinguish between four different groups of ternary carbides (Fig. 21):

(i) the cubic mixed carbides of the third, fourth and fifth group;
(ii) the orthorhombic carbides with the transition metals of the sixth and seventh group (and also vanadium);
(iii) the tetragonal complex carbides with the iron-group metals;
(iv) the tetragonal complex carbides with the platinum metals.

Ternary nitrides are observed which are isostructural or similar in structure with transition metals of lower group numbers. Thus, orthorhombic complex nitrides exist with VA transition metals, isostructural with the carbides with VIA and Group VII transition metals. The complex nitrides with chromium and manganese (for structural details see Ref. [38]) are closely related to the complex carbides with the platinum metals (for structural details see Ref. [45]). In Fig. 22, the transition is shown from the face-centred cubic mixed phase to the orthorhombic cell of U_2CrN_3 (or — with some non-metal positions vacant — to U_2OsC_{2+x}) and to the tetragonal cell of U_2RuC_2.

Carbon is able to stabilize ternary actinide-platinum metal carbides [46] with perovskite structure. Actinides (and other transition metals) with a predominant tetravalent or pentavalent state that can be observed as components in ordered Cu_3Au-type phases with rhodium form perovskite carbides with ruthenium (Fig. 23). Actinides (and other transition metals) with a predominant trivalent state that can be observed as components in ordered Cu_3Au-type phases with palladium form perovskite carbides with rhodium (Fig. 24). Tetravalent metals and palladium form MPd_4 compounds with a "defect Cu_3Au-lattice". Metals with trivalent and tetravalent states, such as cerium or plutonium show homogeneous regions between MPd_4 and MPd_3 or between MRh_3 and MRh_3C. Taking into account the above-mentioned observations, the following perovskite carbides should exist: $PaRu_3C$ ($a \simeq 4.15$ Å); $NpRu_3C$ ($a \simeq 4.13$ Å), $AmRh_3C$ ($a \simeq 4.19$ Å) and $CmRh_3C$ ($a \simeq 4.19$ Å). The existence of the compounds $AmRu_3C$ ($a \simeq 4.16$ Å) and $CmRu_3C$ ($a \simeq 4.16$ Å) is possible.

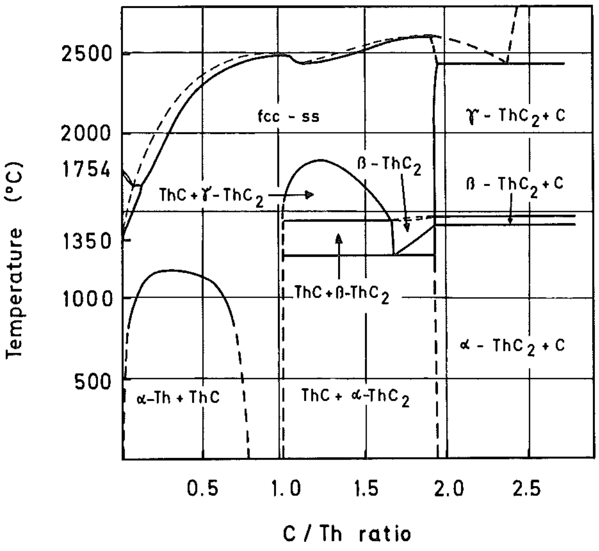
4. DISCUSSION

The thermodynamic information reflected by phase diagrams is only qualitative but is very reliable. An important characteristic feature is consideration of solutions: neglecting these is one of the most frequent errors made when estimating ternary phase equilibria from thermodynamic data of binary phases. Up to now, unfortunately, no well-established method exists for calculating phase diagrams without many assumptions.

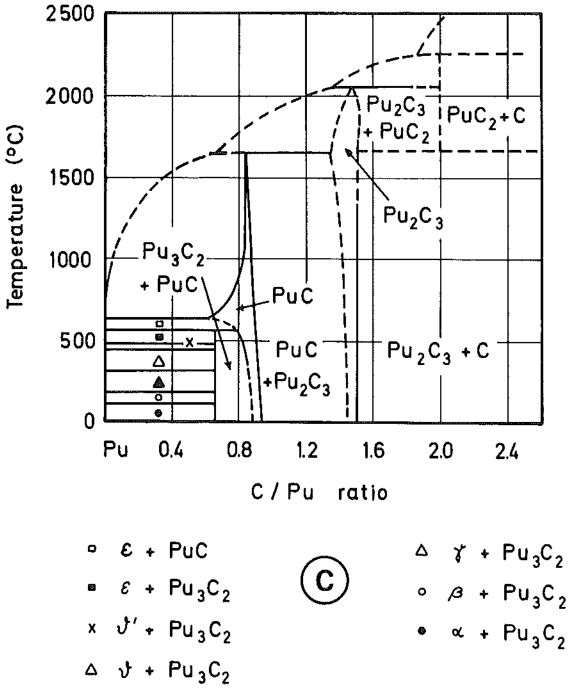
Therefore, the experimental investigation of phase equilibria under given conditions still remains the most reliable method of obtaining information on the reaction behaviour in a system. However, it is very valuable to make calculations and estimations, both to extend and to generalize phase equilibria, and to get an approximate impression of the phase behaviour in unknown systems.

The phase diagrams presented in this work are, in most cases, based on experimental work. Estimated and calculated equilibria are characterized by broken lines and have to be considered as tentative equilibria. Their verification needs, however, only a few, controlled experiments. The solution behaviour is of particular importance for defining the phase equilibria in multicomponent systems of transition metal carbides and nitrides. The occurrence of complete solubility between monocarbides, cubic dicarbides and mononitrides is indicated schematically in Fig. 25. Experimental data existing in combinations with thorium, uranium and plutonium, similarities in the electronic structure and in the lattice parameter differences are the bases for the estimation of this miscibility behaviour (UC_2-LaC_2, -CeC_2; cf. Ref. [47]).

Not all the transition metals could be considered in the scope of this work. Typical representatives and systems with experimental results available were discussed. The complex compounds, for instance, probably control the phase equilibria in systems with the iron-group metals, but there are not sufficient data for a discussion of these systems. As actinide carbides and nitrides are of interest in nuclear technology, however, more data concerning the constitutions of multicomponent systems will certainly be available in the near future.


Temperature (°C)
2500
2000
1754
1350
1000
500
fcc - ss
γ - ThC$_2$ + C
β - ThC$_2$
β - ThC$_2$ + C
ThC + γ - ThC$_2$
ThC + β - ThC$_2$
α - ThC$_2$ + C
α-Th + ThC
ThC + α-ThC$_2$
0.5
1.0
1.5
2.0
2.5
C / Th ratio

Ⓐ


Temperature (°C)
2500
2000
1500
1000
500
0
Pu$_2$C$_3$ + PuC$_2$
PuC$_2$+C
Pu$_2$C$_3$
Pu$_3$C$_2$ + PuC
PuC
PuC + Pu$_2$C$_3$
Pu$_2$C$_3$ + C
x
Pu
0.4
0.8
1.2
1.6
2.0
2.4
C / Pu ratio
□ ε + PuC
■ ε + Pu$_3$C$_2$
x ϑ' + Pu$_3$C$_2$
△ ϑ + Pu$_3$C$_2$
▲ γ + Pu$_3$C$_2$
○ β + Pu$_3$C$_2$
● α + Pu$_3$C$_2$

Ⓒ

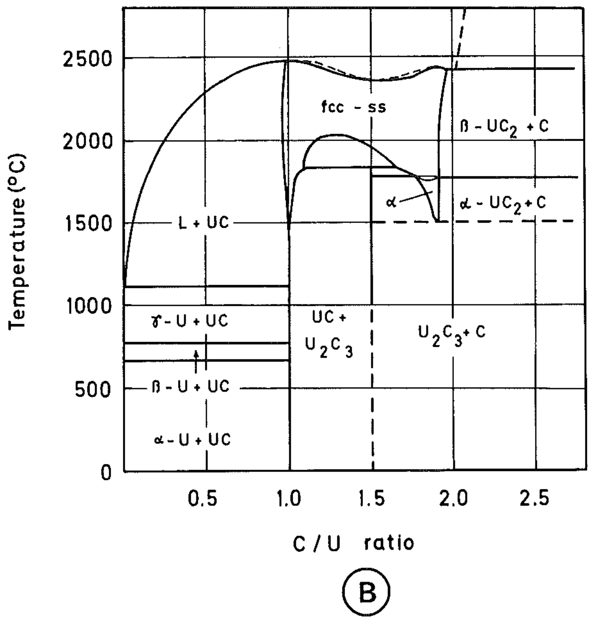
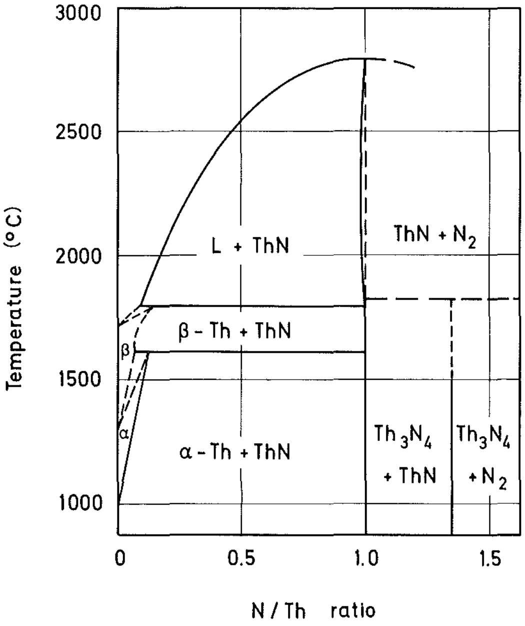
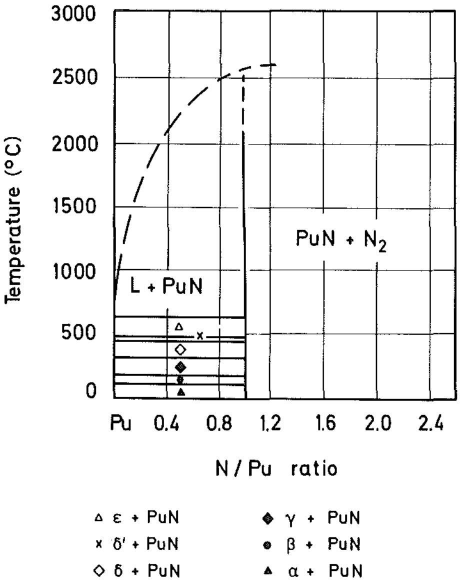


FIG.1. Phase diagrams of binary actinide-carbon systems.


3000
2500
2000
1500
1000
Temperature (°C)
L + ThN
ThN + N2
β - Th + ThN
β
α
α - Th + ThN
Th3N4 + ThN
Th3N4 + N2
0
0.5
1.0
1.5
N / Th ratio

Ⓐ


3000
2500
2000
1500
1000
500
0
Temperature (°C)
PuN + N2
L + PuN
Pu
0.4
0.8
1.2
1.6
2.0
2.4
N / Pu ratio
△ ε + PuN
× δ' + PuN
◇ δ + PuN
◆ γ + PuN
● β + PuN
▲ α + PuN

Ⓒ

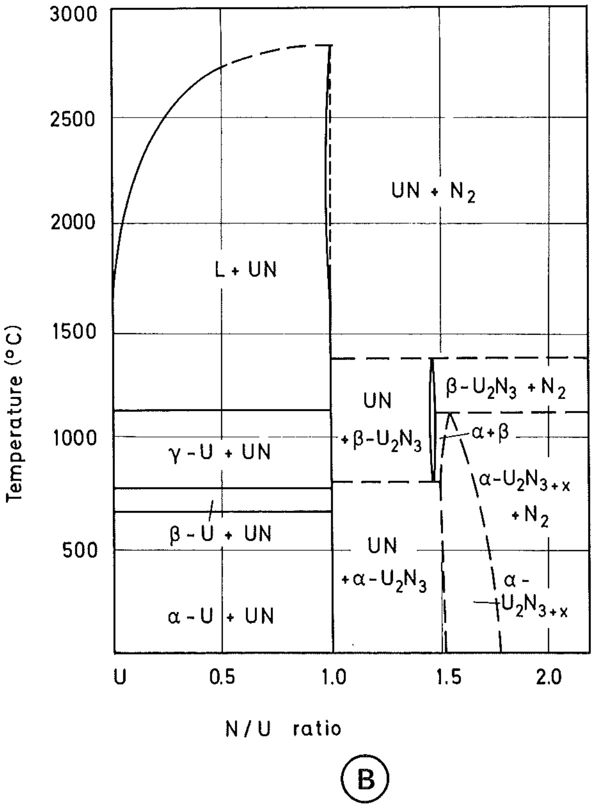


FIG.2. Phase diagrams of binary actinide-nitrogen systems.

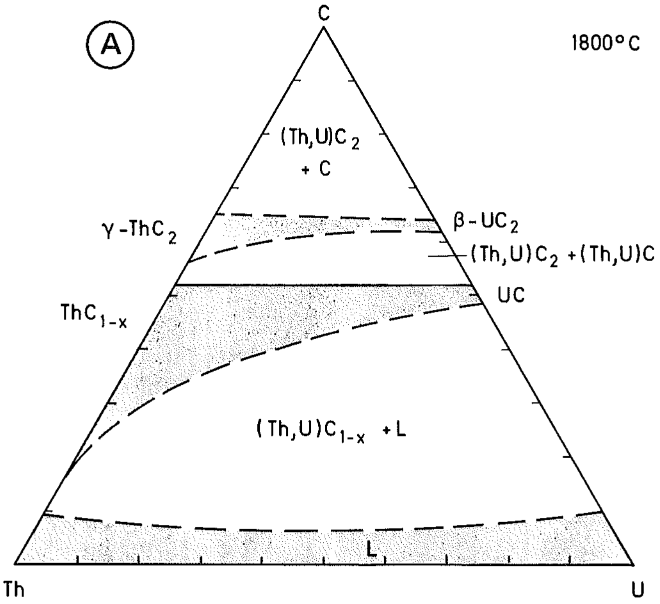
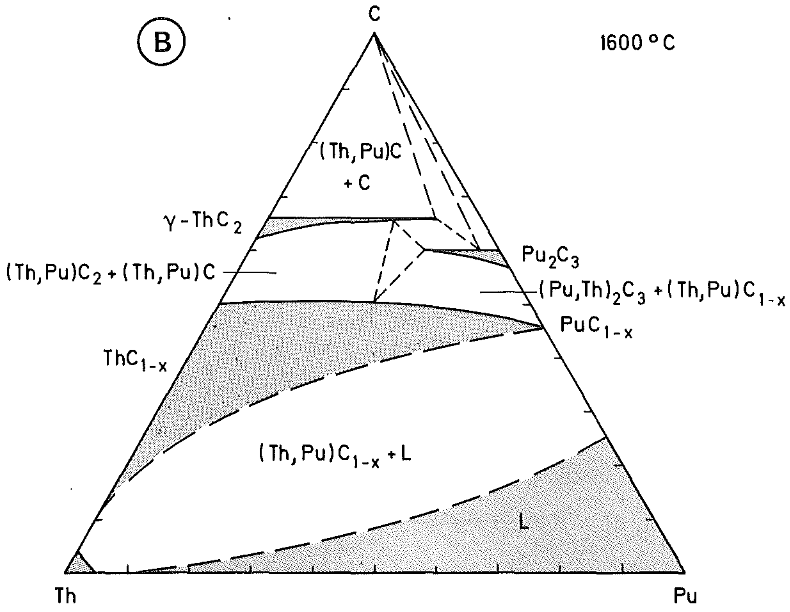
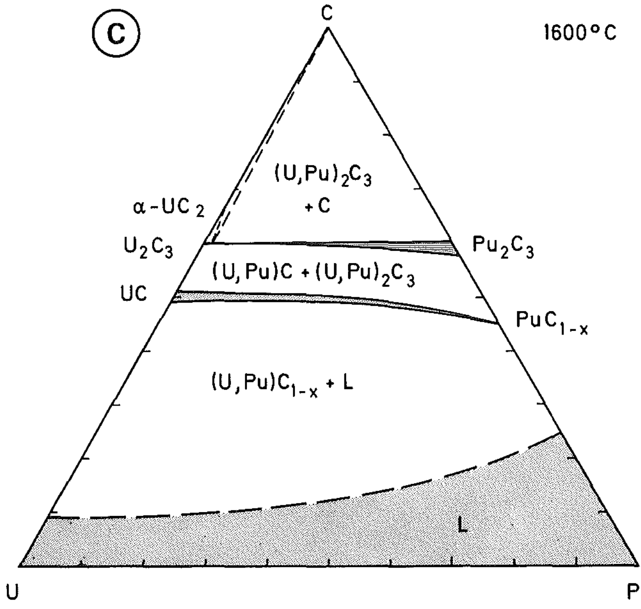


FIG.3. Tentative isothermal sections in the Th-U-C (1800°C), Th-Pu-C (1600°C) and U-Pu-C (1600°C) systems.


B
C
1600 °C
(Th,Pu)C + C
γ-ThC$_2$
Pu$_2$C$_3$
(Th,Pu)C$_2$ + (Th,Pu)C
(Pu,Th)$_2$C$_3$ + (Th,Pu)C$_{1-x}$
PuC$_{1-x}$
ThC$_{1-x}$
(Th,Pu)C$_{1-x}$ + L
L
Th
Pu


C
C
1600°C
(U,Pu)$_2$C$_3$ + C
α-UC$_2$
U$_2$C$_3$
Pu$_2$C$_3$
(U,Pu)C + (U,Pu)$_2$C$_3$
UC
PuC$_{1-x}$
(U,Pu)C$_{1-x}$ + L
L
U
Pu

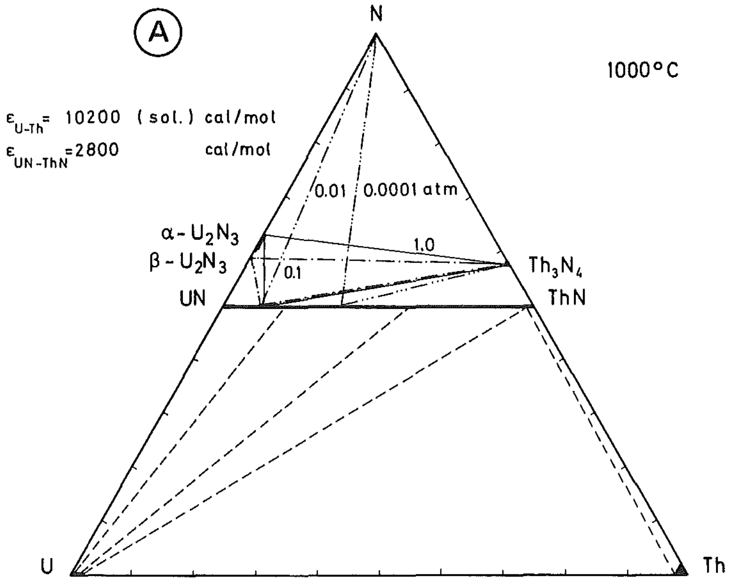
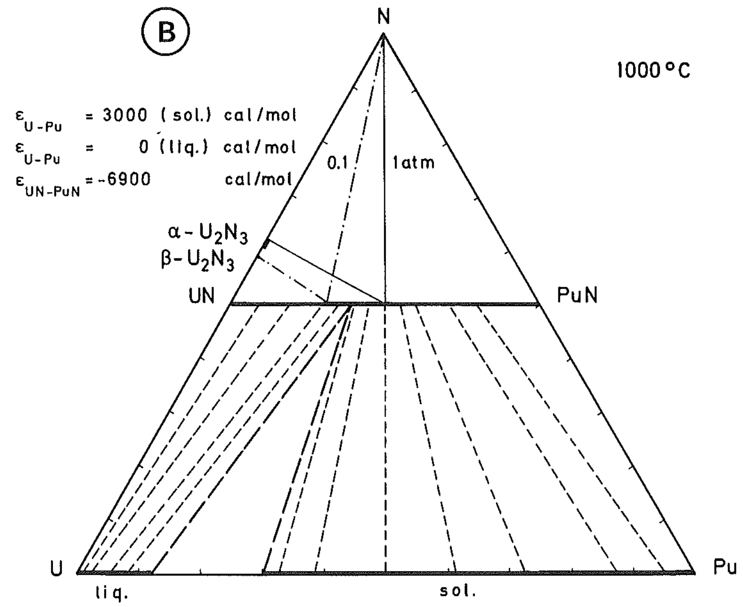


FIG.4. Calculated isothermal sections in the Th-U-N and U-Pu-N systems at 1000°C.


Ⓑ
N
1000 °C
ε U-Pu = 3000 (sol.) cal/mol
ε U-Pu = 0 (liq.) cal/mol
ε UN-PuN = -6900 cal/mol
0.1
1atm
α-U2N3
β-U2N3
UN
PuN
U
Pu
liq.
sol.

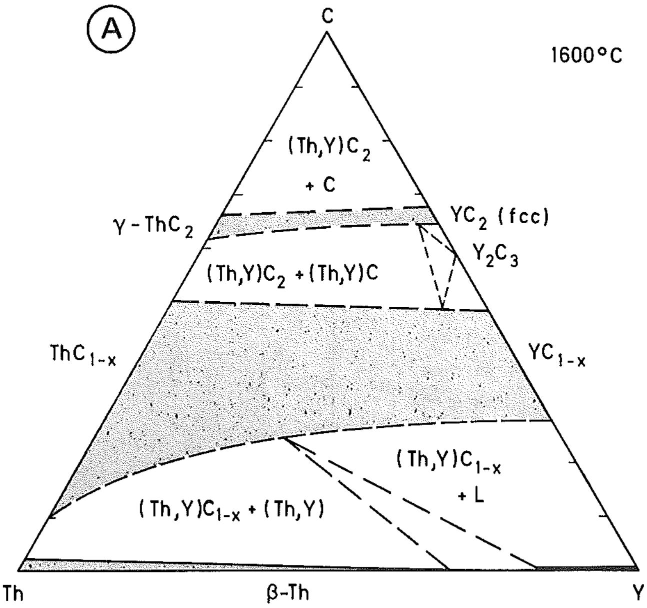
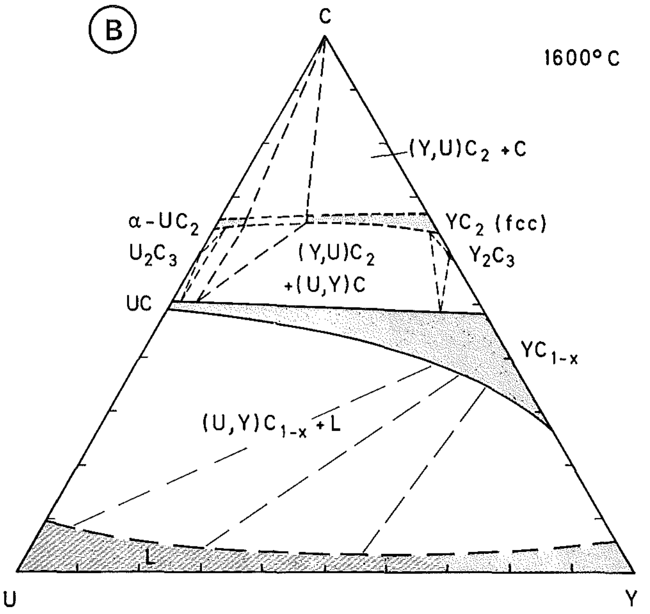
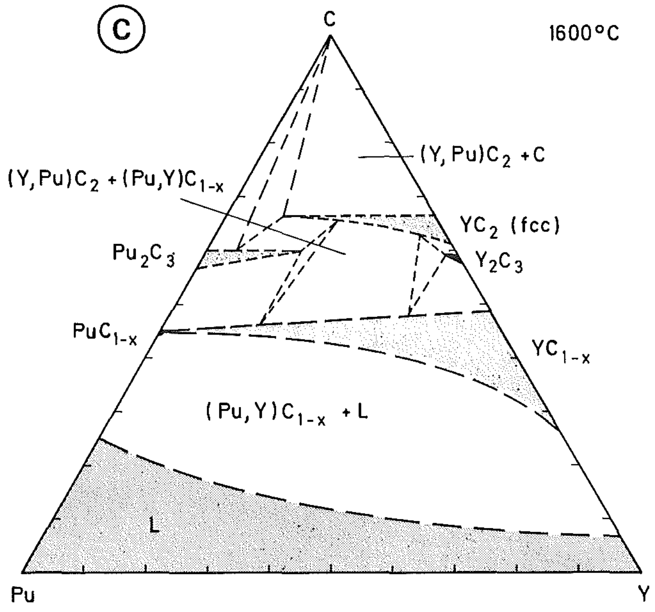


FIG.5. Tentative isothermal sections in the Th-Y-C, U-Y-C and Pu-Y-C systems at 1600°C.


B
C
1600° C
(Y,U)C_2 + C
α-UC_2
U_2C_3
YC_2 (fcc)
Y_2C_3
(Y,U)C_2
+(U,Y)C
UC
YC_{1-x}
(U,Y)C_{1-x} + L
L
U
Y


C
C
1600°C
(Y, Pu)C_2 +C
(Y,Pu)C_2 + (Pu,Y)C_{1-x}
YC_2 (fcc)
Pu_2C_3
Y_2C_3
PuC_{1-x}
YC_{1-x}
(Pu,Y)C_{1-x} + L
L
Pu
Y

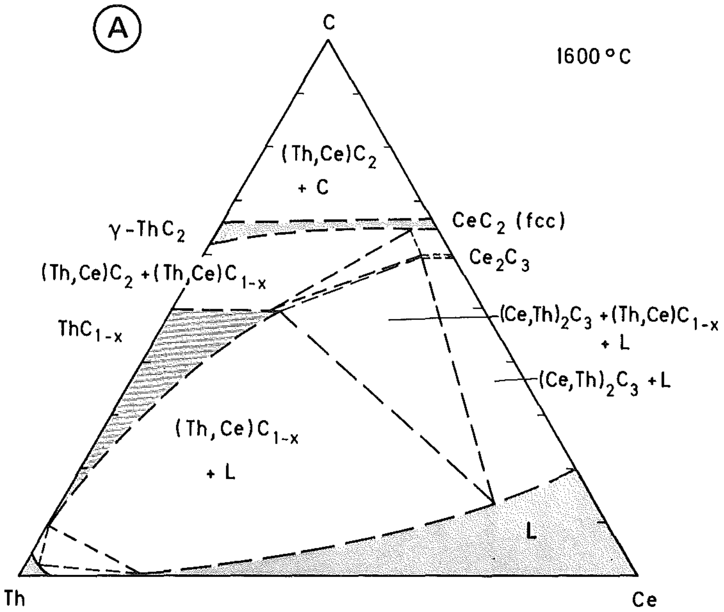
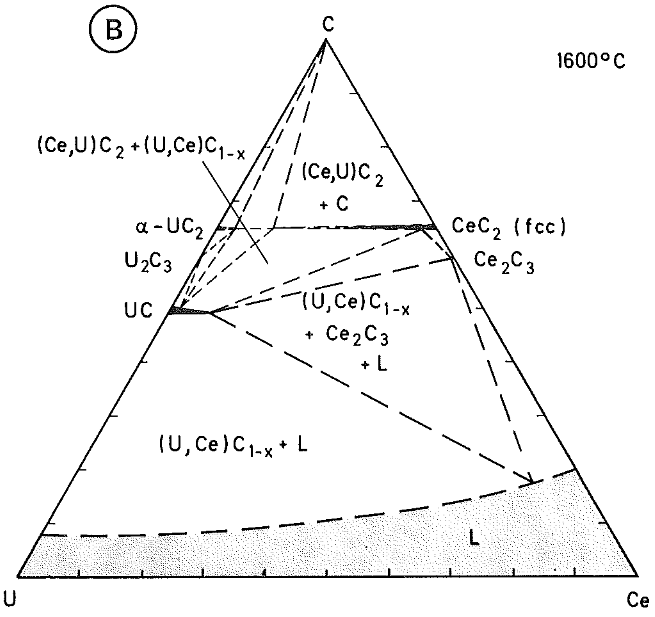
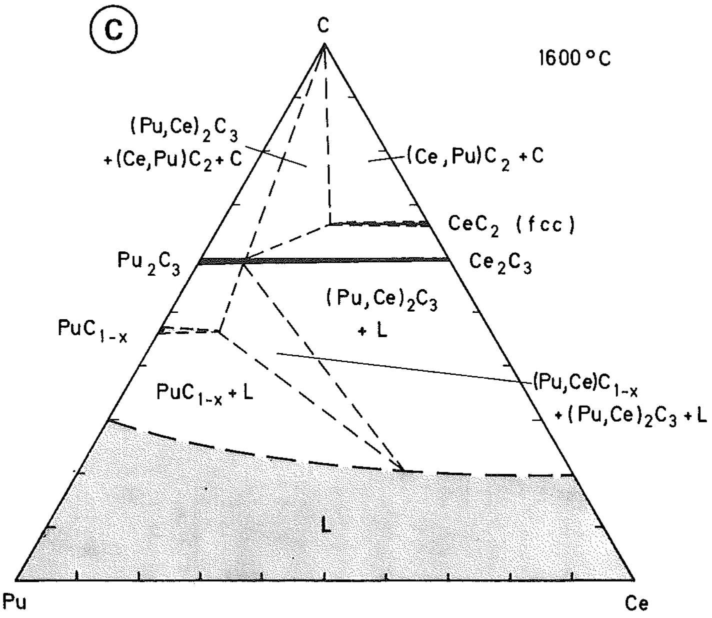


FIG.6. Tentative isothermal sections in the Th-Ce-C, U-Ce-C and Pu-Ce-C systems at 1600°C.


B
C
1600°C
$(Ce,U)C_2 + (U,Ce)C_{1-x}$
$(Ce,U)C_2$ + C
α-UC_2
CeC_2 (fcc)
U_2C_3
Ce_2C_3
UC
$(U,Ce)C_{1-x}$ + Ce_2C_3 + L
$(U,Ce)C_{1-x}$ + L
L
U
Ce


C
C
1600 °C
$(Pu,Ce)_2C_3$ + $(Ce,Pu)C_2$ + C
$(Ce,Pu)C_2$ + C
CeC_2 (fcc)
Pu_2C_3
Ce_2C_3
$(Pu,Ce)_2C_3$ + L
PuC_{1-x}
$(Pu,Ce)C_{1-x}$ + $(Pu,Ce)_2C_3$ + L
PuC_{1-x} + L
L
Pu
Ce

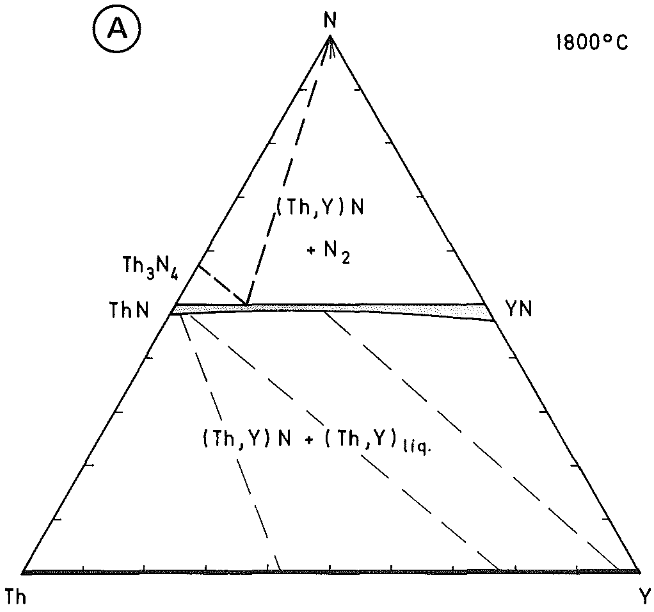
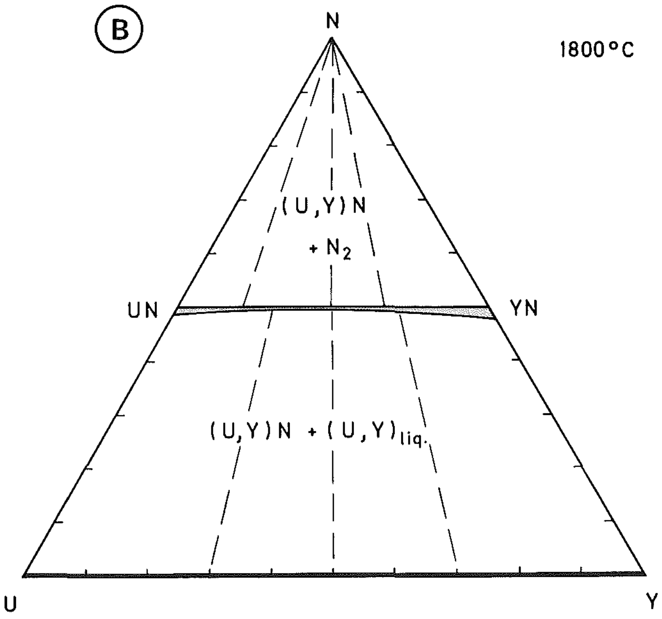
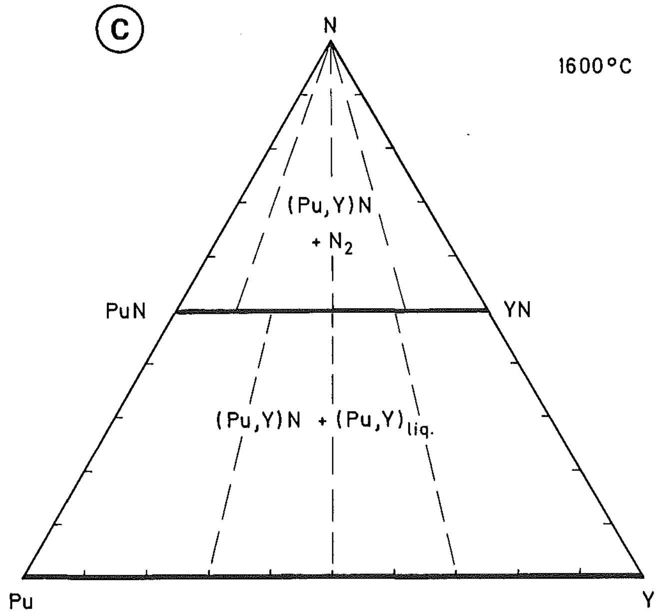


FIG.7. Tentative isothermal sections in the Th-Y-N (1800°C), U-Y-N (1800°C) and Pu-Y-N (1600°C) systems.


B
N
1800 °C
(U,Y)N
+ N_2
UN
YN
(U,Y)N + $(U,Y)_{liq.}$
U
Y


C
N
1600 °C
(Pu,Y)N
+ N_2
PuN
YN
(Pu,Y)N + $(Pu,Y)_{liq.}$
Pu
Y

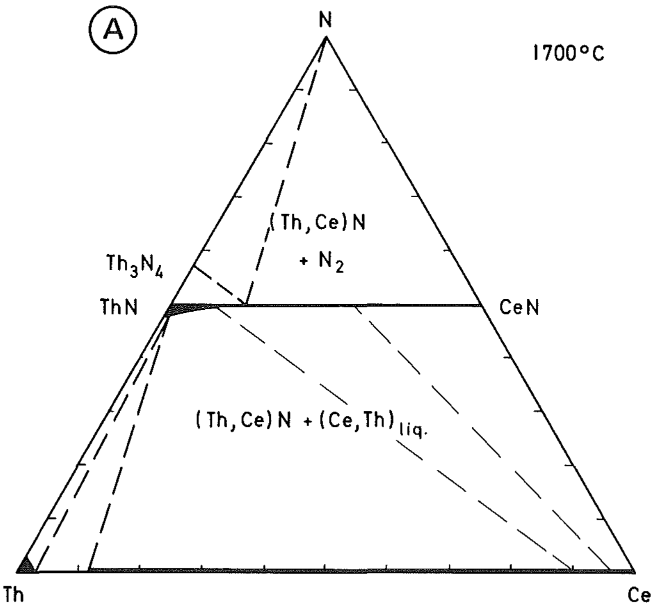
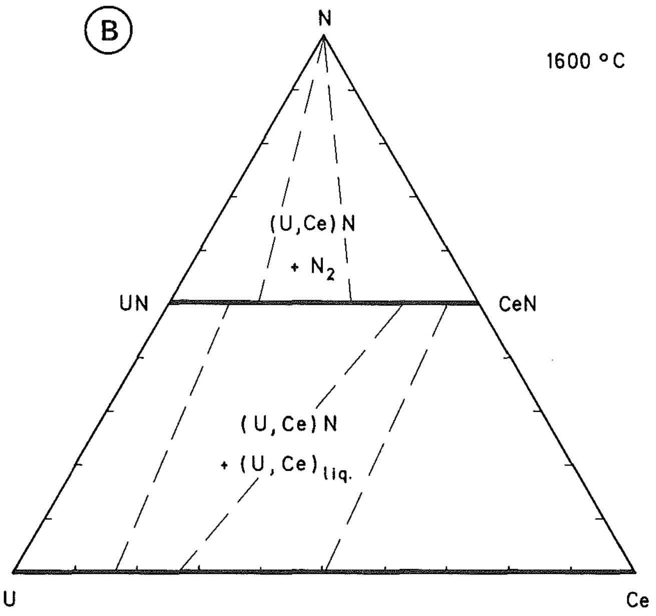
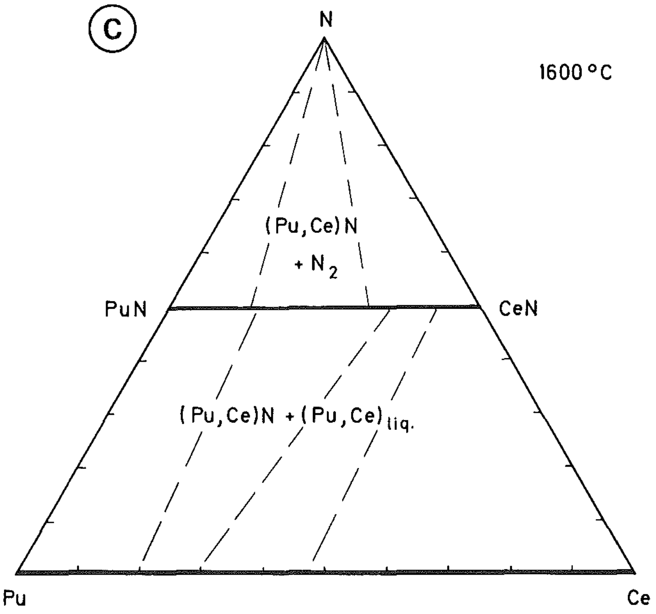
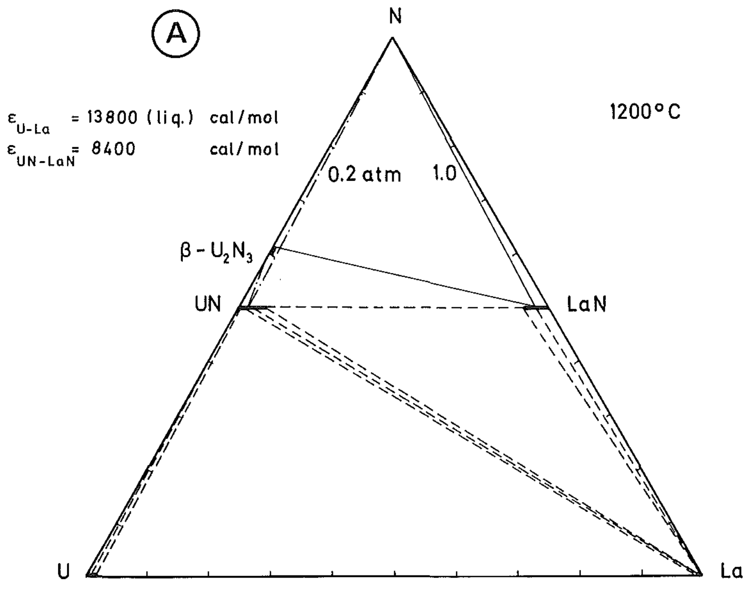
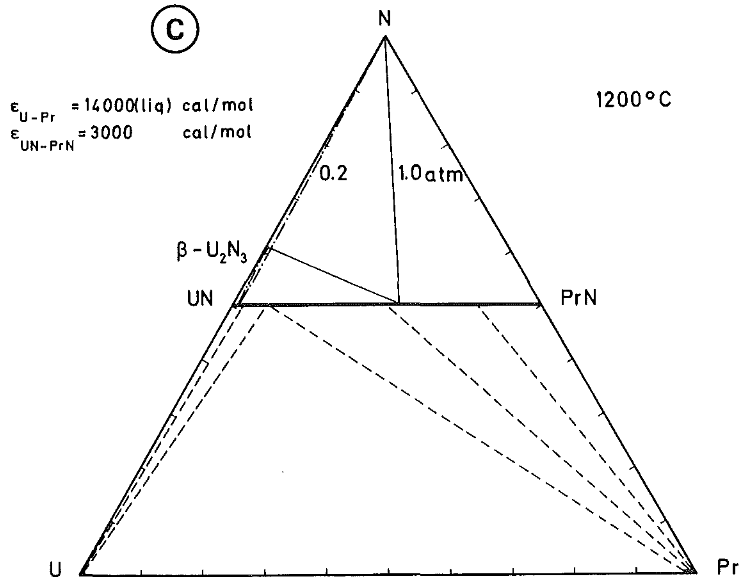


FIG.8. Tentative isothermal sections in the Th-Ce-N (1700°C), U-Ce-N (1600°C) and Pu-Ce-N (1600°C) systems.


B
N
1600 °C
(U,Ce) N
+ N₂
UN
CeN
(U, Ce) N
+ (U, Ce) liq.
U
Ce


C
N
1600 °C
(Pu,Ce) N
+ N₂
PuN
CeN
(Pu,Ce)N + (Pu,Ce) liq.
Pu
Ce


A
N
ε U-La = 13800 (liq.) cal/mol
ε UN-LaN = 8400 cal/mol
1200°C
0.2 atm
1.0
β-U2N3
UN
LaN
U
La


C
N
ε U-Pr = 14000(liq) cal/mol
ε UN-PrN = 3000 cal/mol
1200°C
0.2
1.0atm
β-U2N3
UN
PrN
U
Pr

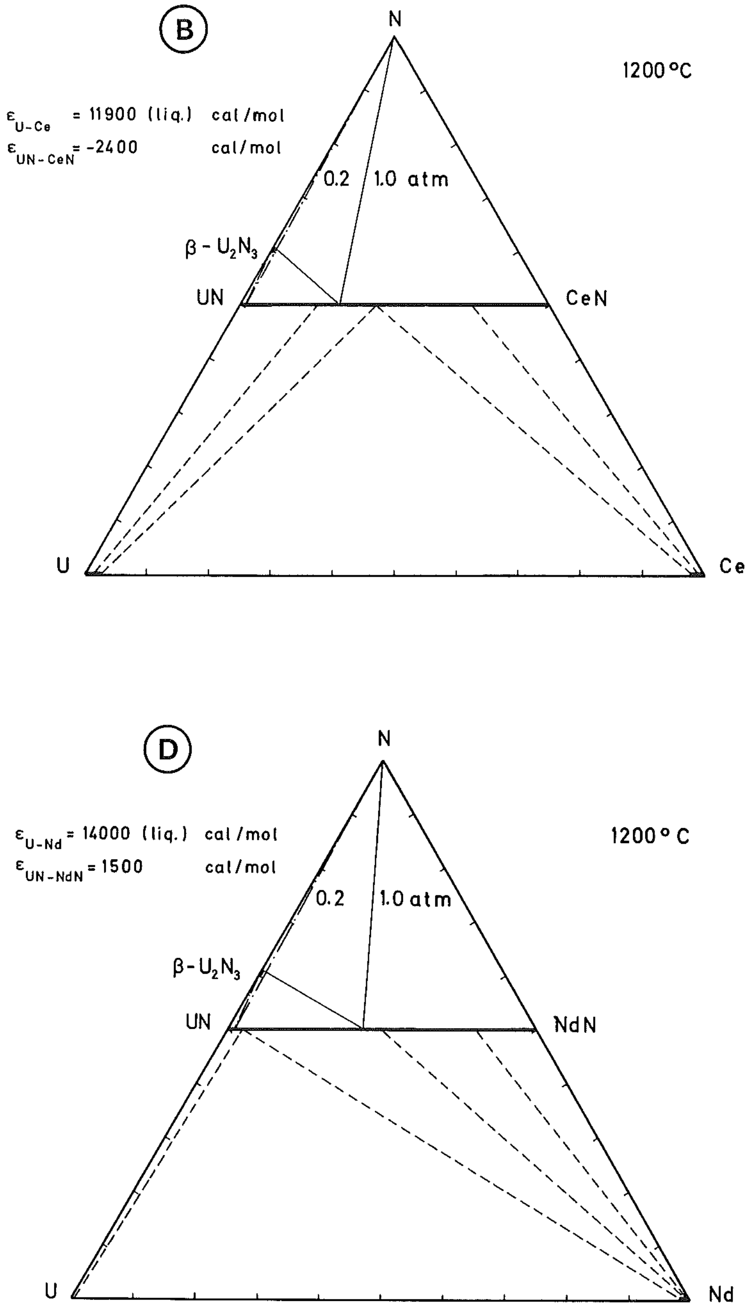


FIG.9. Calculated isothermal sections in the U-La-N, U-Ce-N, U-Pr-N and U-Nd-N systems at 1200°C.

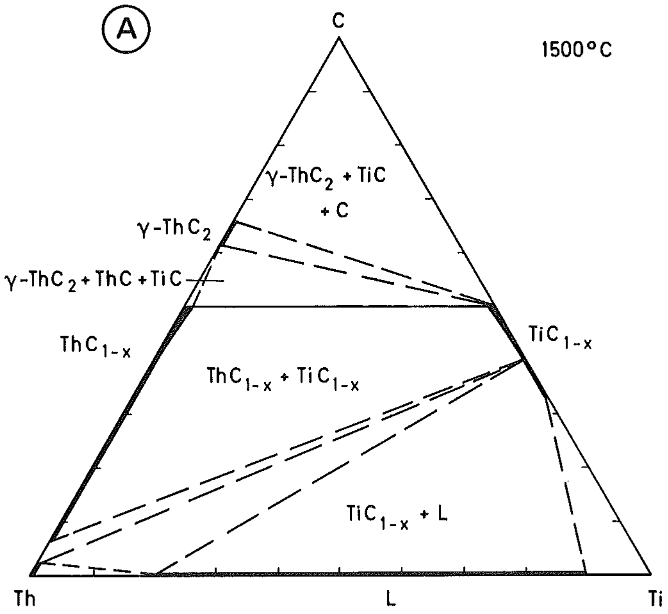
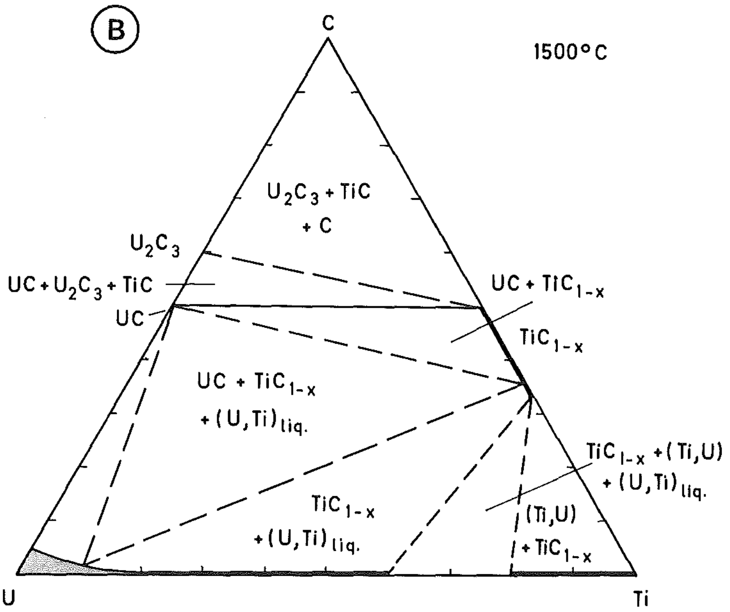
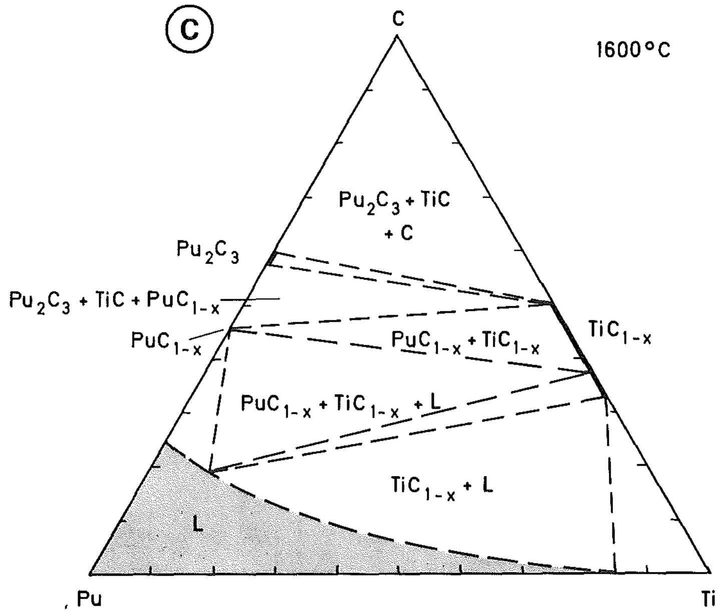


FIG.10. Isothermal sections in the Th-Ti-C (1500°C), U-Ti-C (1500°C) and Pu-Ti-C (1600°C) systems (tentative) at the temperatures indicated.


B
C
1500°C
U_2C_3 + TiC + C
U_2C_3
UC + U_2C_3 + TiC
UC
UC + TiC_{1-x}
TiC_{1-x}
UC + TiC_{1-x} + $(U,Ti)_{liq.}$
TiC_{1-x} + (Ti,U) + $(U,Ti)_{liq.}$
TiC_{1-x} + $(U,Ti)_{liq.}$
(Ti,U) + TiC_{1-x}
U
Ti


C
C
1600°C
Pu_2C_3 + TiC + C
Pu_2C_3
Pu_2C_3 + TiC + PuC_{1-x}
PuC_{1-x}
PuC_{1-x} + TiC_{1-x}
TiC_{1-x}
PuC_{1-x} + TiC_{1-x} + L
TiC_{1-x} + L
L
Pu
Ti

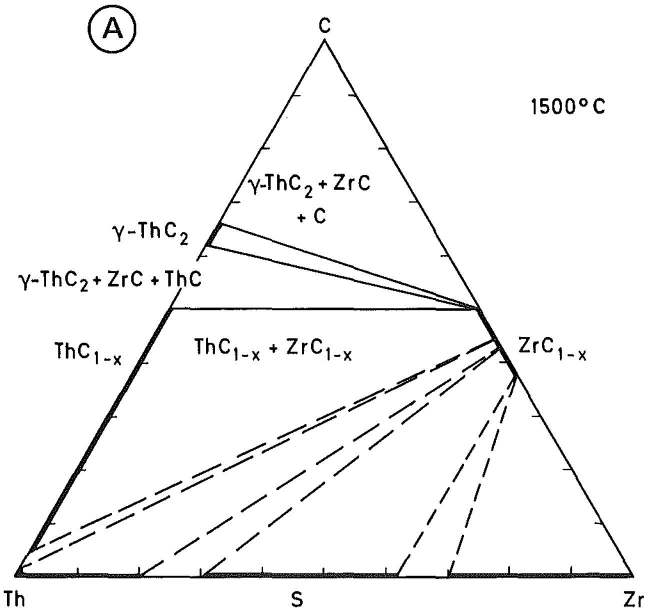
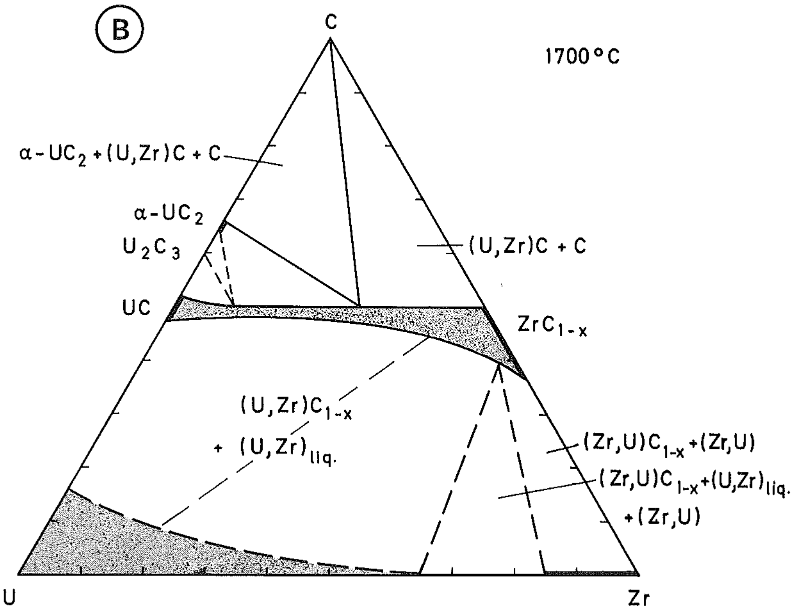
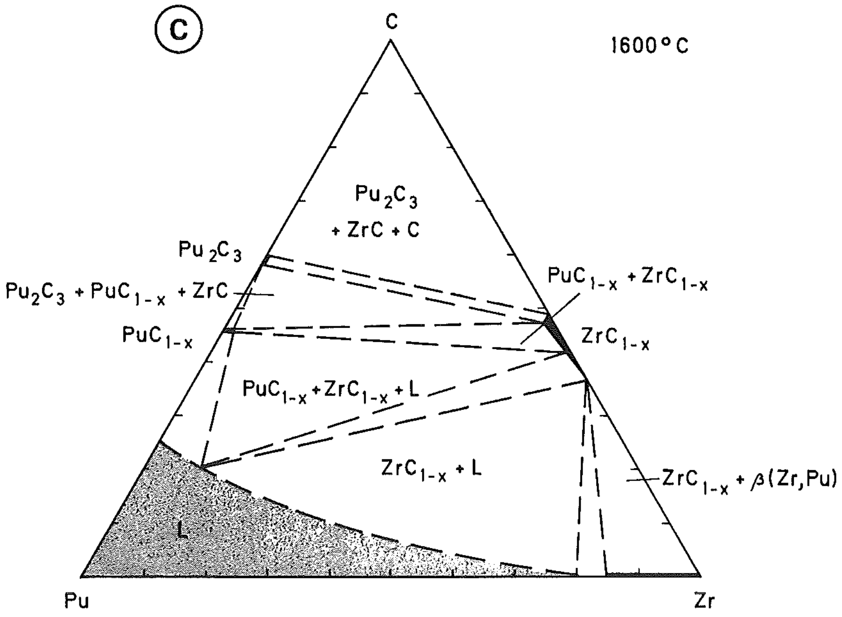


FIG.11. Isothermal sections in the Th-Zr-C (1500°C), U-Zr-C (1700°C) and Pu-Zr-C (1600°C) systems (tentative) at the temperatures indicated.


B
C
1700°C
α-UC_2 + (U,Zr)C + C
α-UC_2
U_2C_3
UC
(U,Zr)C + C
ZrC_{1-x}
$(U,Zr)C_{1-x}$
+ $(U,Zr)_{liq.}$
$(Zr,U)C_{1-x}$ + (Zr,U)
$(Zr,U)C_{1-x}$ + $(U,Zr)_{liq.}$
+ (Zr,U)
U
Zr


C
C
1600°C
Pu_2C_3
+ ZrC + C
Pu_2C_3
Pu_2C_3 + PuC_{1-x} + ZrC
PuC_{1-x} + ZrC_{1-x}
PuC_{1-x}
ZrC_{1-x}
PuC_{1-x} + ZrC_{1-x} + L
ZrC_{1-x} + L
ZrC_{1-x} + β(Zr,Pu)
L
Pu
Zr

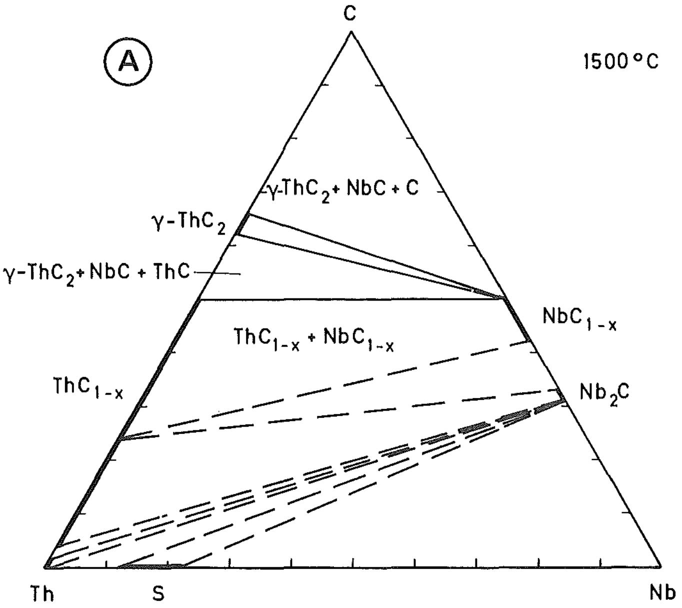
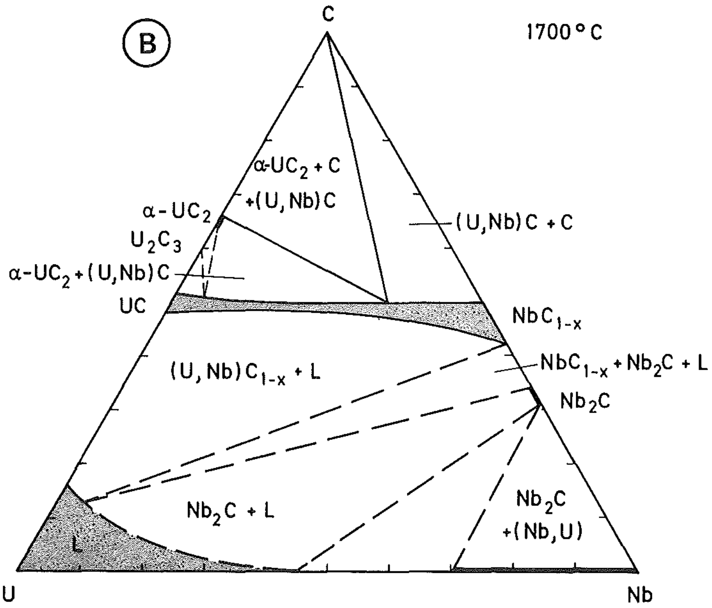
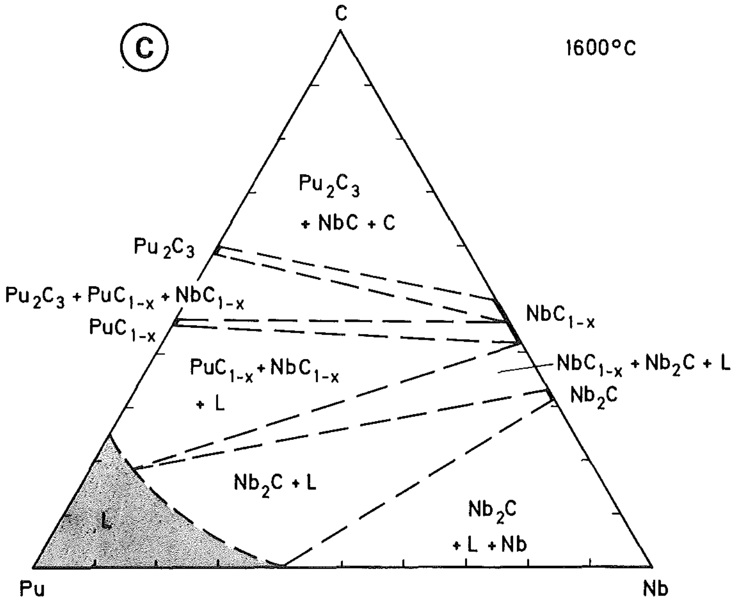


FIG.12. Isothermal sections in the Th-Nb-C (1500°C), U-Nb-C (1700°C) and Pu-Nb-C (1600°C) systems (tentative) at the temperatures indicated.


B
C
1700 °C
α-UC$_2$ + C +(U, Nb) C
α-UC$_2$
U$_2$C$_3$
α-UC$_2$ + (U, Nb) C
UC
(U, Nb) C + C
NbC$_{1-x}$
(U, Nb) C$_{1-x}$ + L
NbC$_{1-x}$ + Nb$_2$C + L
Nb$_2$C
Nb$_2$C + L
Nb$_2$C +(Nb, U)
L
U
Nb


C
C
1600°C
Pu$_2$C$_3$ + NbC + C
Pu$_2$C$_3$
Pu$_2$C$_3$ + PuC$_{1-x}$ + NbC$_{1-x}$
PuC$_{1-x}$
NbC$_{1-x}$
PuC$_{1-x}$ + NbC$_{1-x}$ + L
NbC$_{1-x}$ + Nb$_2$C + L
Nb$_2$C
Nb$_2$C + L
Nb$_2$C + L + Nb
L
Pu
Nb

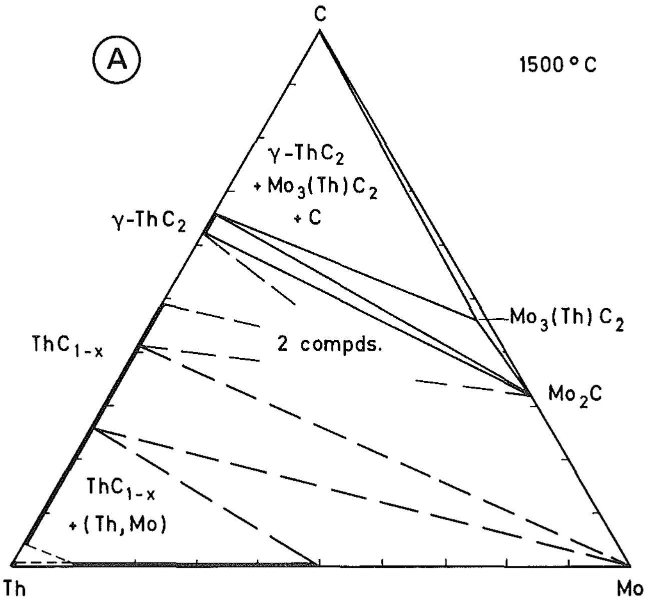
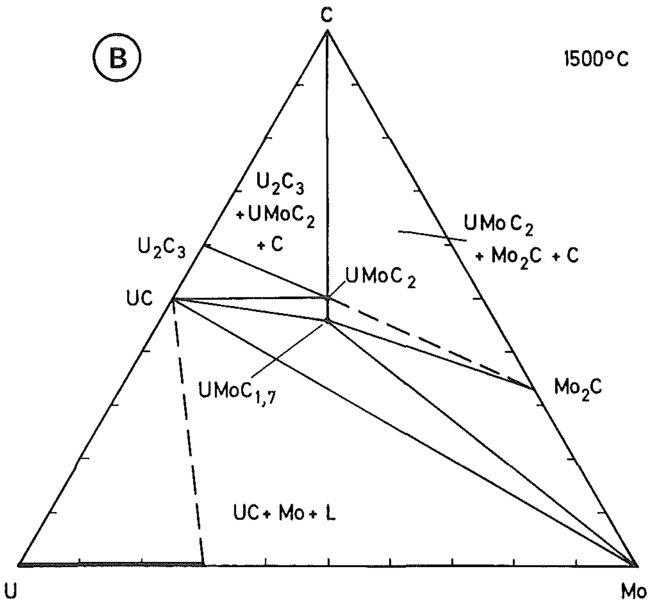
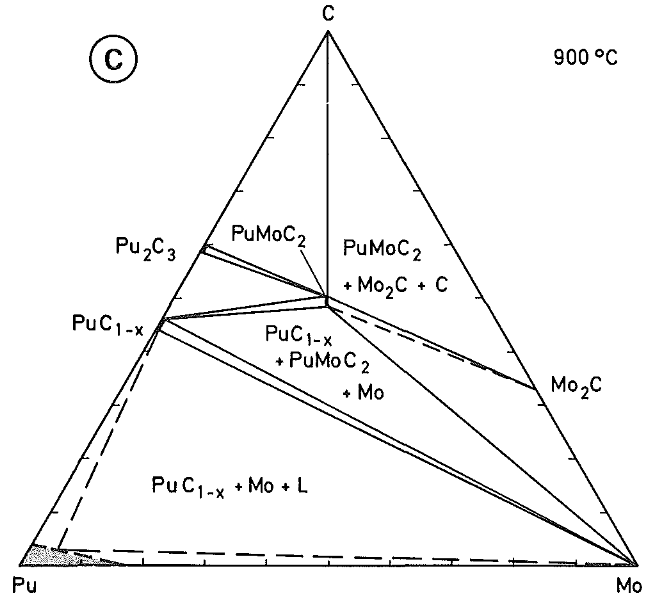


FIG.13. Isothermal sections in the Th-Mo-C (1500°C), U-Mo-C (1500°C) and Pu-Mo-C (900°C) systems.


B
1500°C
C
U_2C_3 + $UMoC_2$ + C
$UMoC_2$ + Mo_2C + C
U_2C_3
UC
$UMoC_2$
$UMoC_{1,7}$
Mo_2C
UC + Mo + L
U
Mo


C
900 °C
C
Pu_2C_3
$PuMoC_2$
$PuMoC_2$ + Mo_2C + C
PuC_{1-x}
PuC_{1-x} + $PuMoC_2$ + Mo
Mo_2C
PuC_{1-x} + Mo + L
Pu
Mo

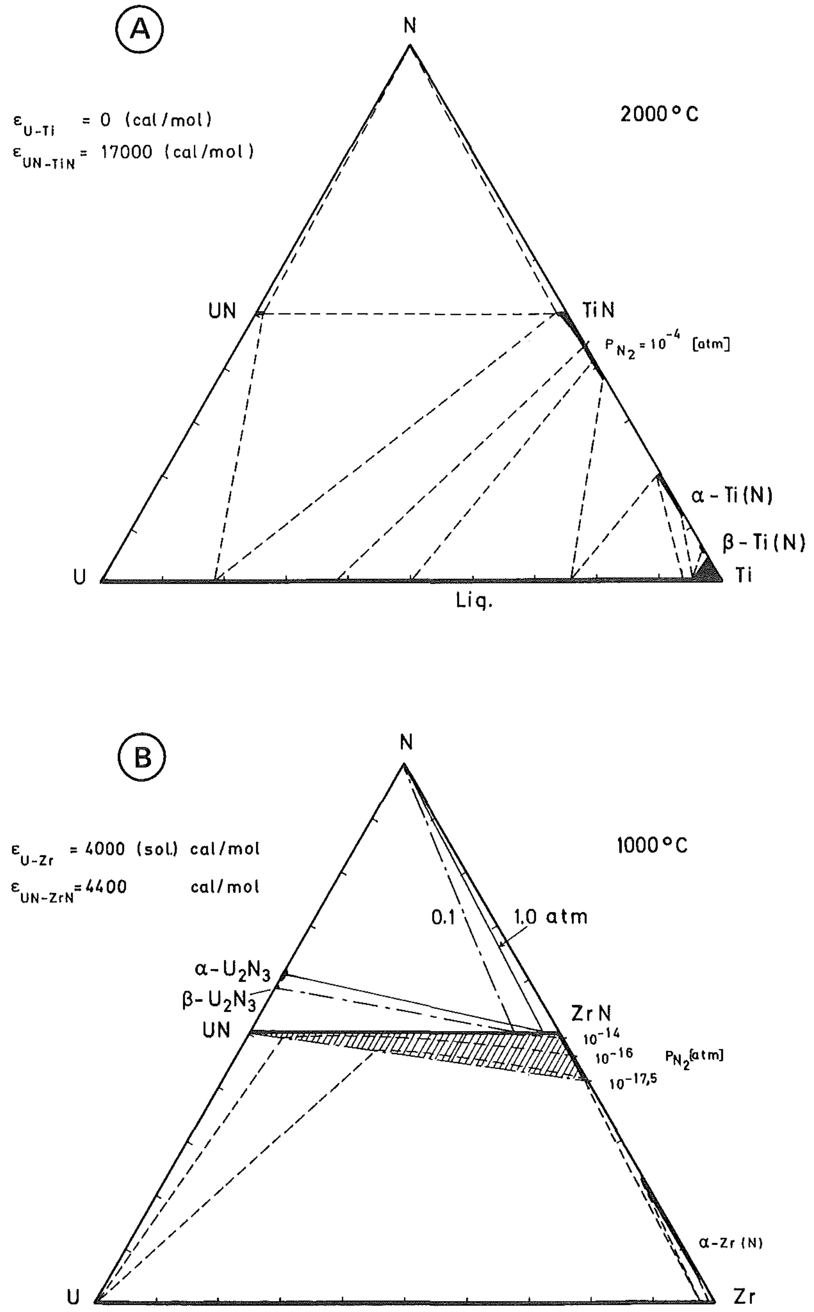
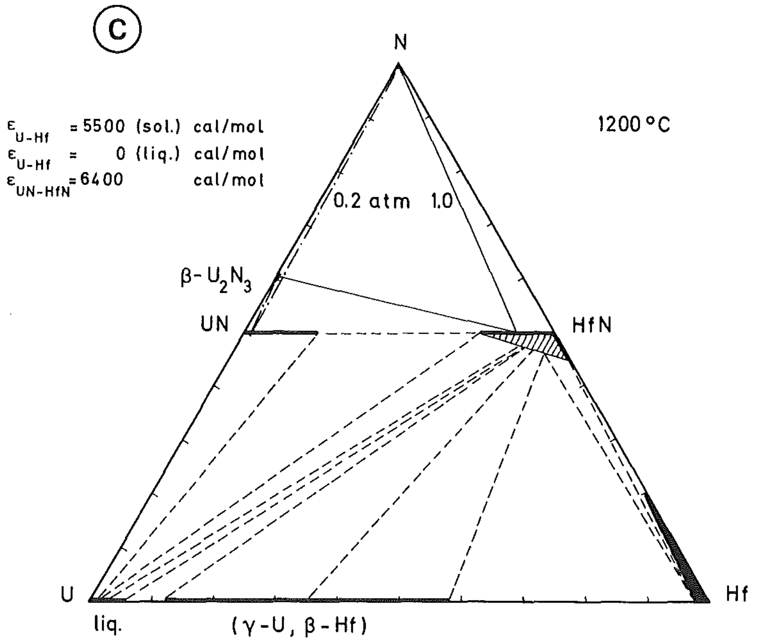
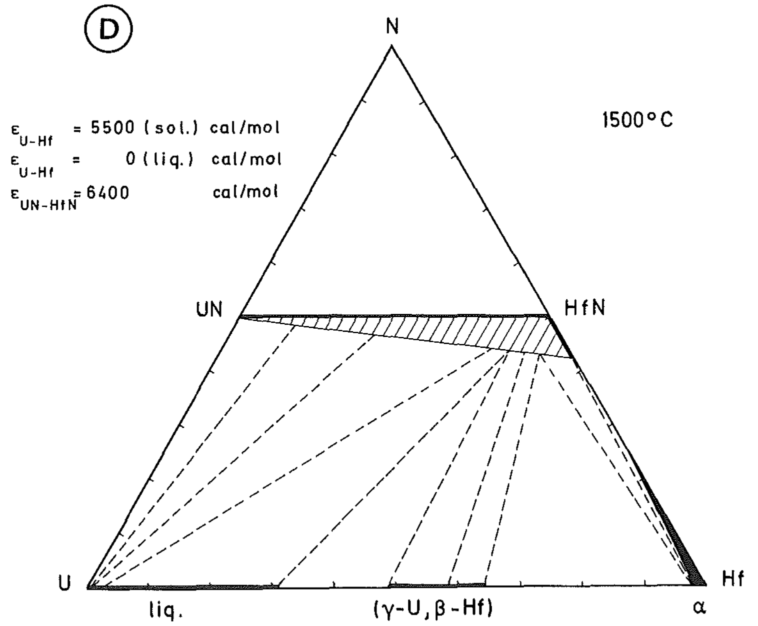


FIG.14. Calculated isothermal sections in the U-Ti-N (2000°C), U-Zr-N (1000°C), U-Hf-N (1200 and 1500°C), U-Nb-N (1000°C) and U-Mo-N (1200°C) systems.


C
N
ε_{U-Hf} = 5500 (sol.) cal/mol
ε_{U-Hf} = 0 (liq.) cal/mol
ε_{UN-HfN} = 6400 cal/mol
1200 °C
0.2 atm
1.0
β-U_2N_3
UN
HfN
U
Hf
liq.
(γ-U, β-Hf)


D
N
ε_{U-Hf} = 5500 (sol.) cal/mol
ε_{U-Hf} = 0 (liq.) cal/mol
ε_{UN-HfN} = 6400 cal/mol
1500 °C
UN
HfN
U
Hf
liq.
(γ-U, β-Hf)
α

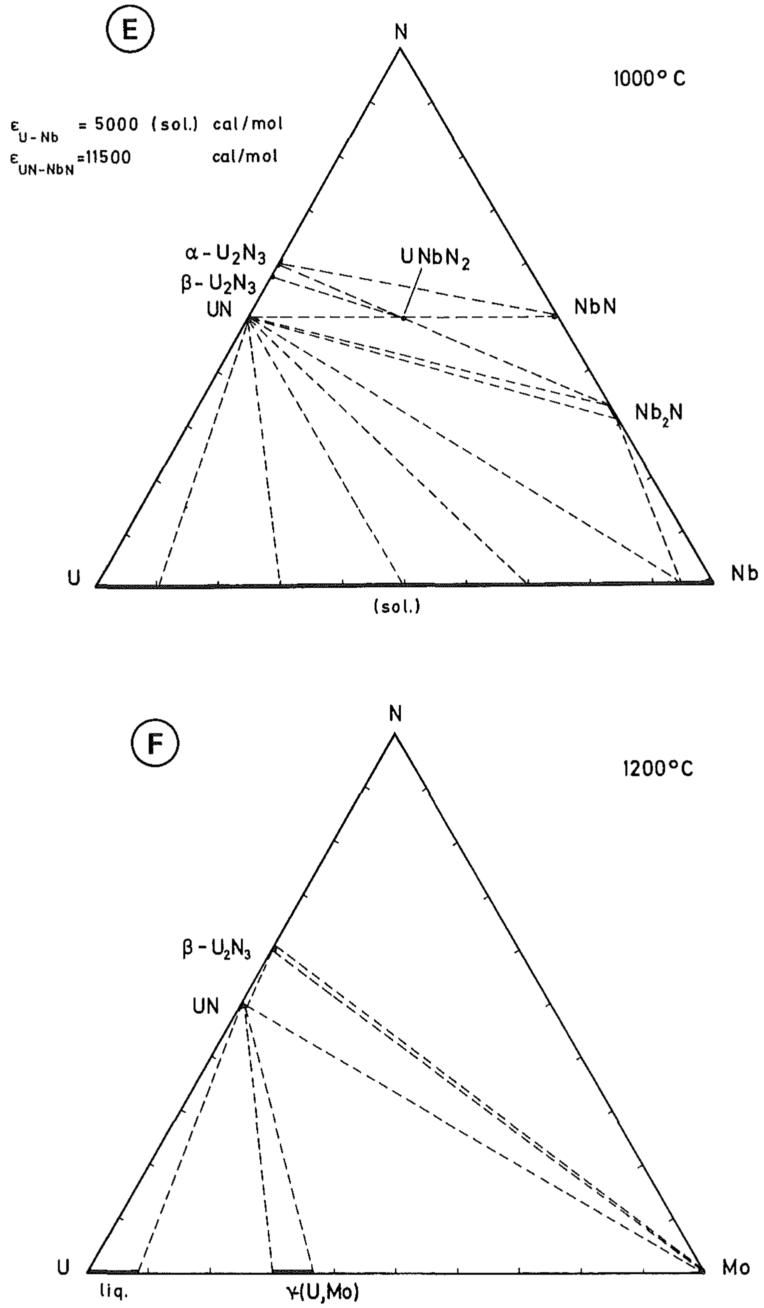


Fig. 14. Continued.

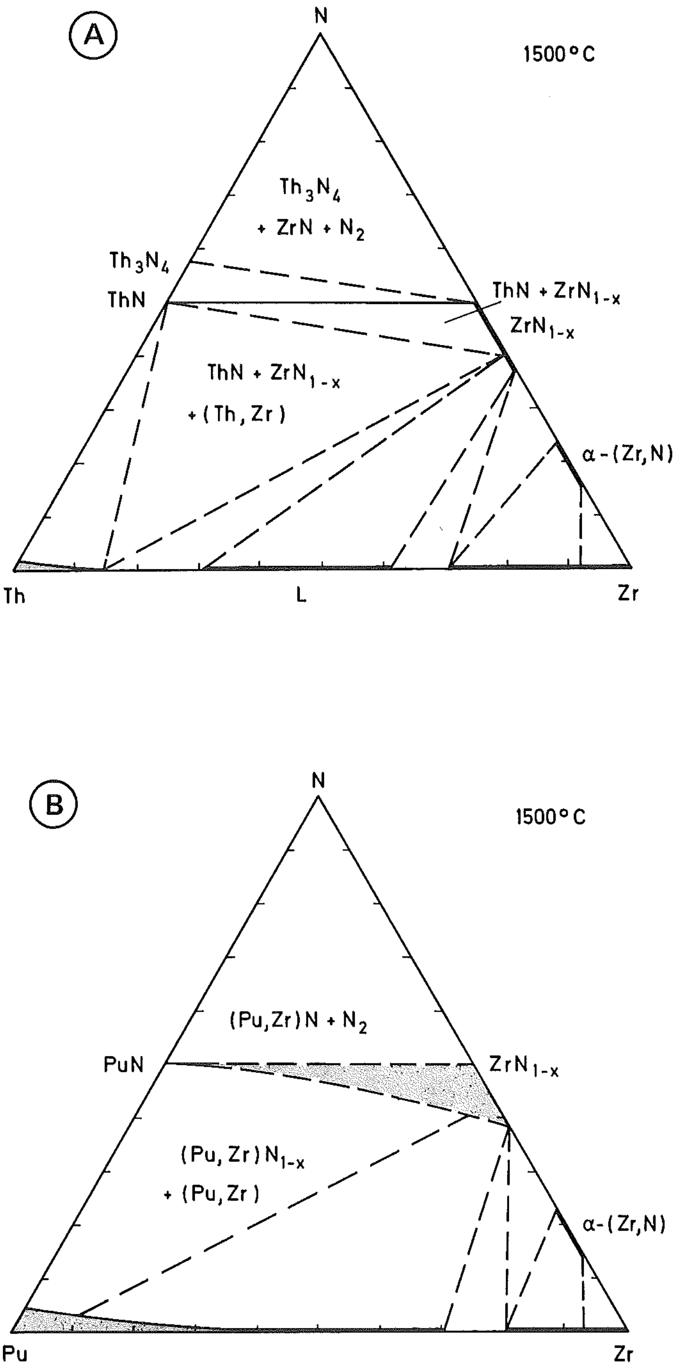


FIG.15. Tentative isothermal sections in the Th-Zr-N and Pu-Zr-N systems at 1500°C.

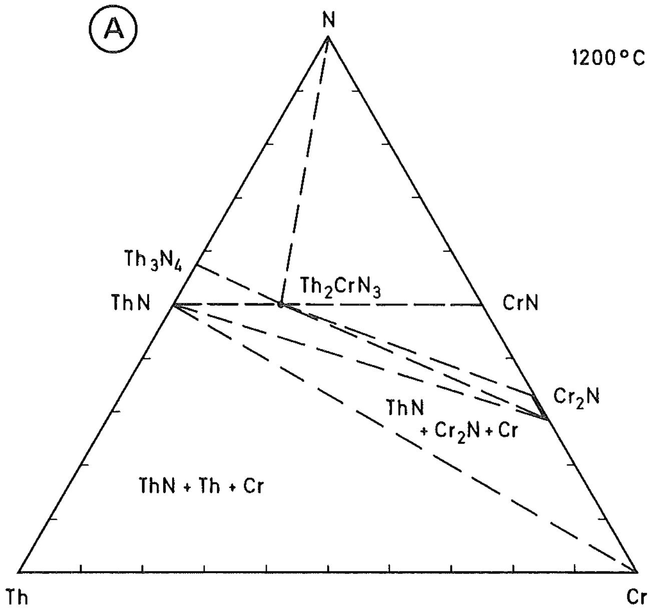
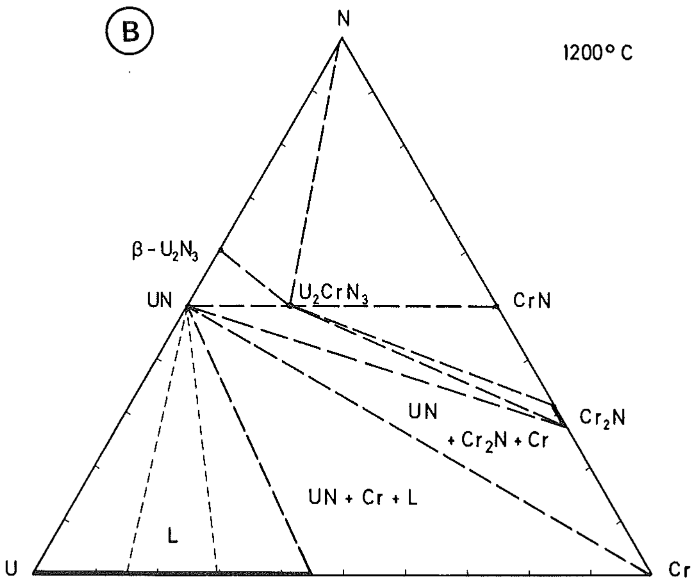
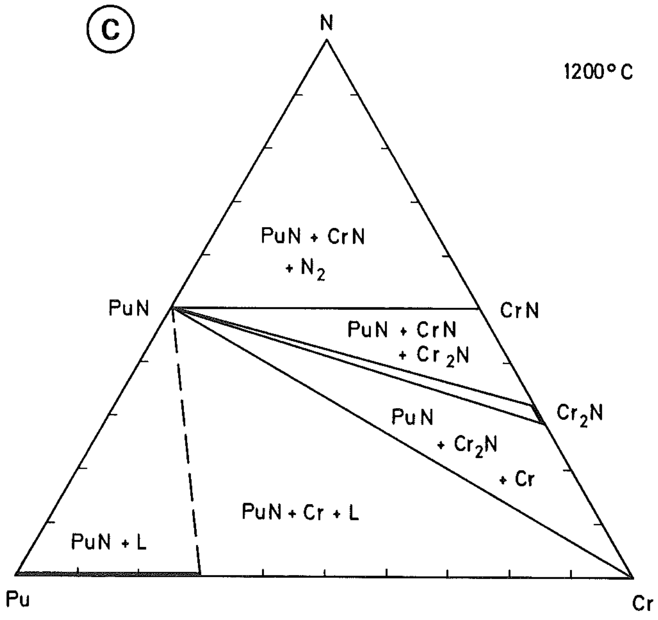


FIG.16. Tentative isothermal sections in the Th-Cr-N, U-Cr-N and Pu-Cr-N systems at 1200°C.


B
N
1200° C
β - U_2N_3
UN
U_2CrN_3
CrN
Cr_2N
UN
+ Cr_2N + Cr
UN + Cr + L
L
U
Cr


C
N
1200° C
PuN + CrN
+ N_2
PuN
CrN
PuN + CrN
+ Cr_2N
Cr_2N
PuN
+ Cr_2N
+ Cr
PuN + Cr + L
PuN + L
Pu
Cr

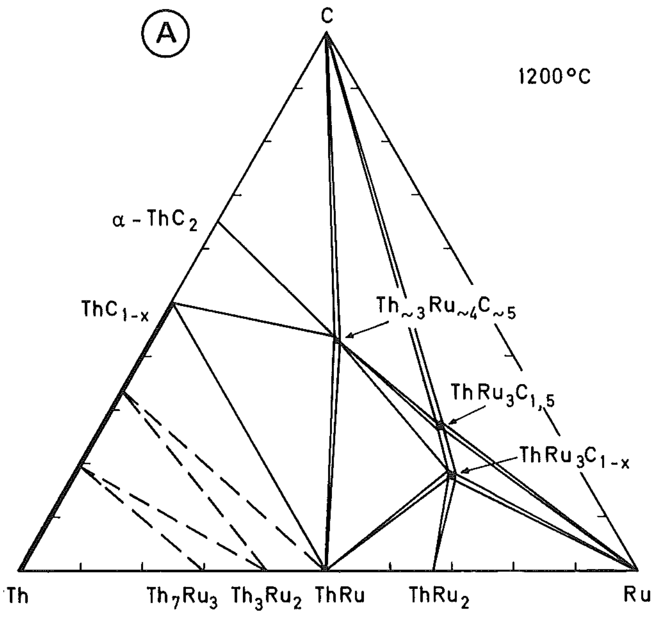
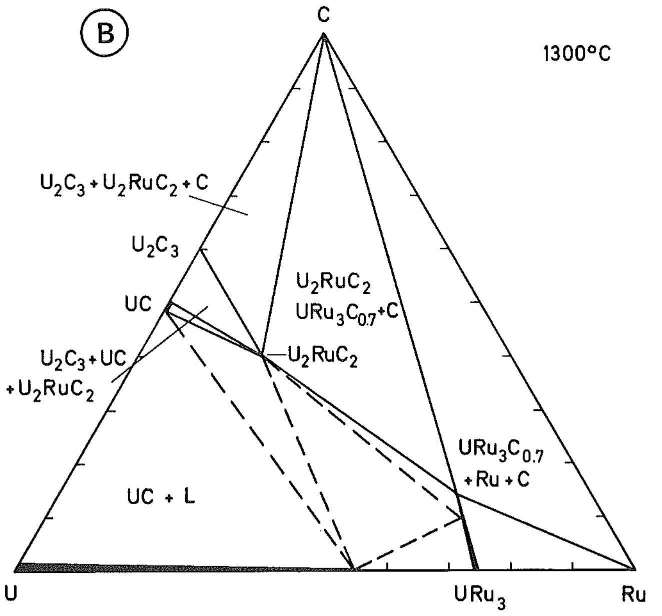
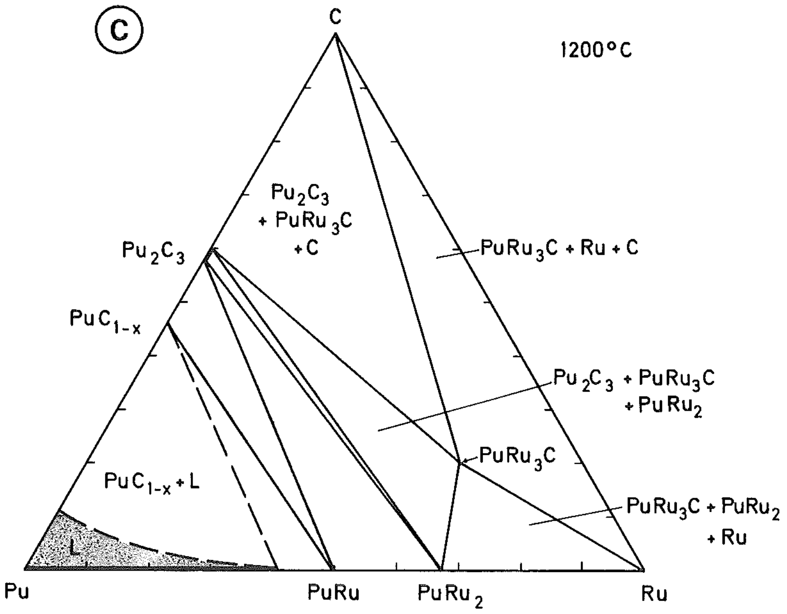


FIG.17. Isothermal sections in the Th-Ru-C (1200°C), U-Ru-C (1300°C), Pu-Ru-C (1200°C) systems.


B
C
1300°C
U₂C₃ + U₂RuC₂ + C
U₂C₃
UC
U₂C₃ + UC + U₂RuC₂
U₂RuC₂ URu₃C₀.₇ + C
U₂RuC₂
URu₃C₀.₇ + Ru + C
UC + L
U
URu₃
Ru


C
C
1200°C
Pu₂C₃ + PuRu₃C + C
Pu₂C₃
PuRu₃C + Ru + C
PuC₁₋ₓ
Pu₂C₃ + PuRu₃C + PuRu₂
PuRu₃C
PuC₁₋ₓ + L
L
PuRu₃C + PuRu₂ + Ru
Pu
PuRu
PuRu₂
Ru

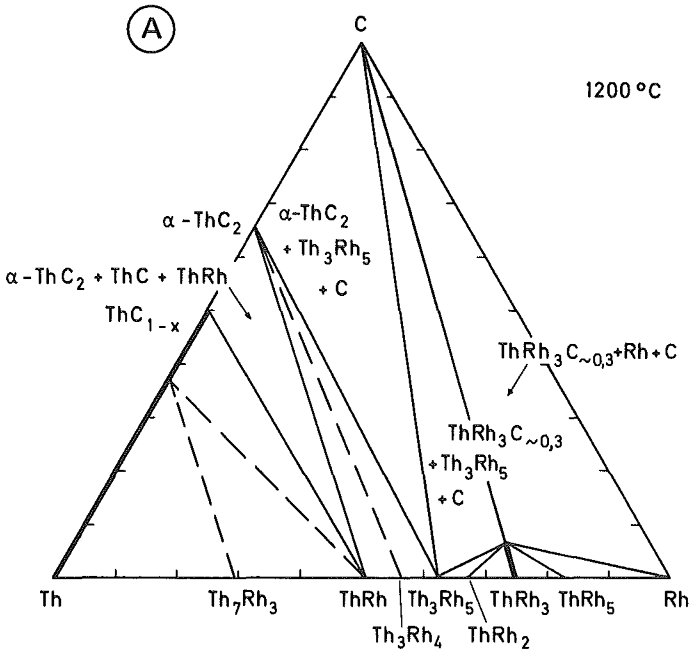
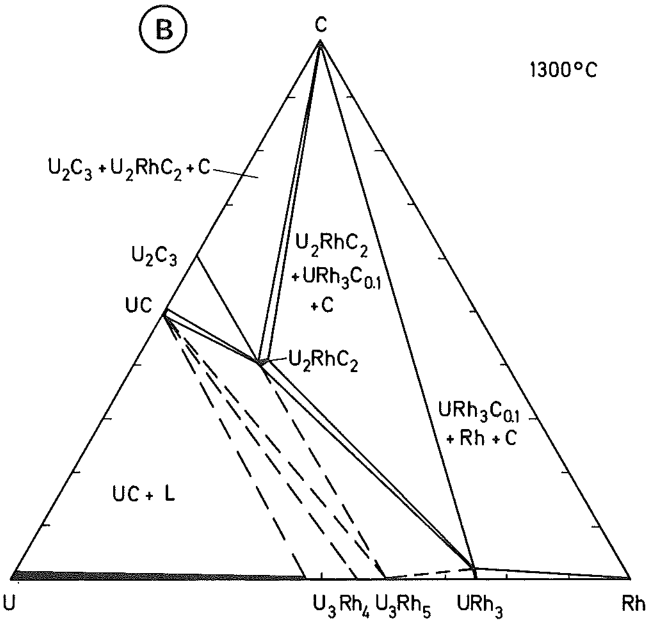
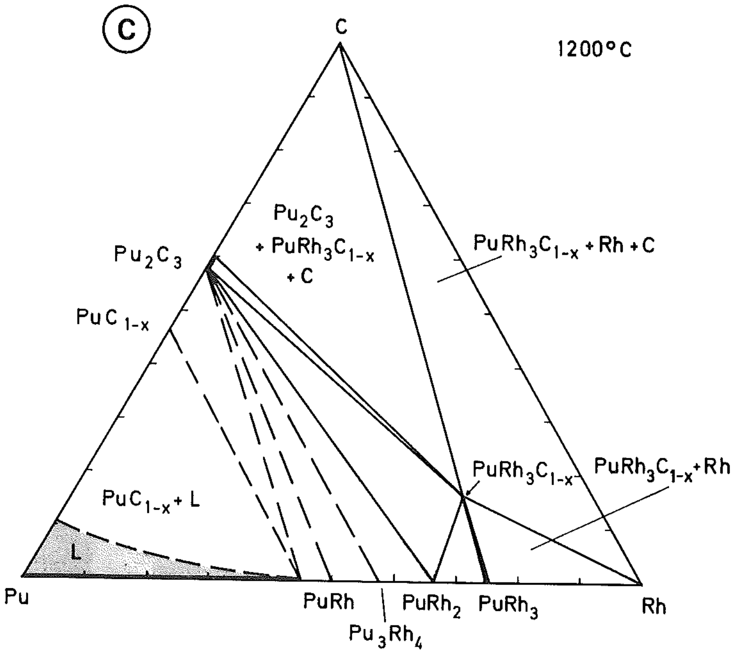


FIG.18. Isothermal sections in the Th-Rh-C (1200°C), U-Rh-C (1300°C), Pu-Rh-C (1200°C) systems.


B
C
1300°C
U₂C₃ + U₂RhC₂ + C
U₂C₃
UC
U₂RhC₂ + URh₃C₀.₁ + C
U₂RhC₂
URh₃C₀.₁ + Rh + C
UC + L
U
U₃Rh₄
U₃Rh₅
URh₃
Rh


C
C
1200°C
Pu₂C₃ + PuRh₃C₁₋ₓ + C
PuRh₃C₁₋ₓ + Rh + C
Pu₂C₃
PuC₁₋ₓ
PuRh₃C₁₋ₓ
PuRh₃C₁₋ₓ + Rh
PuC₁₋ₓ + L
L
Pu
PuRh
Pu₃Rh₄
PuRh₂
PuRh₃
Rh

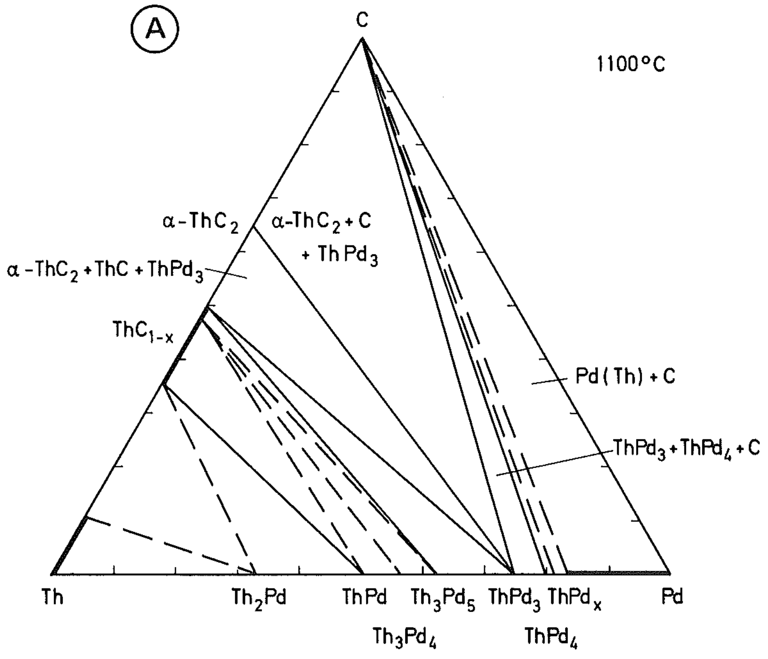
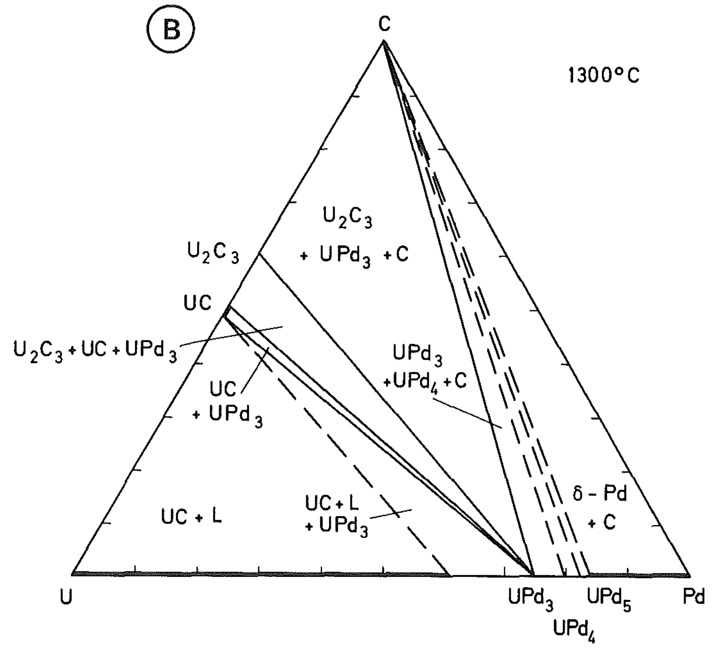
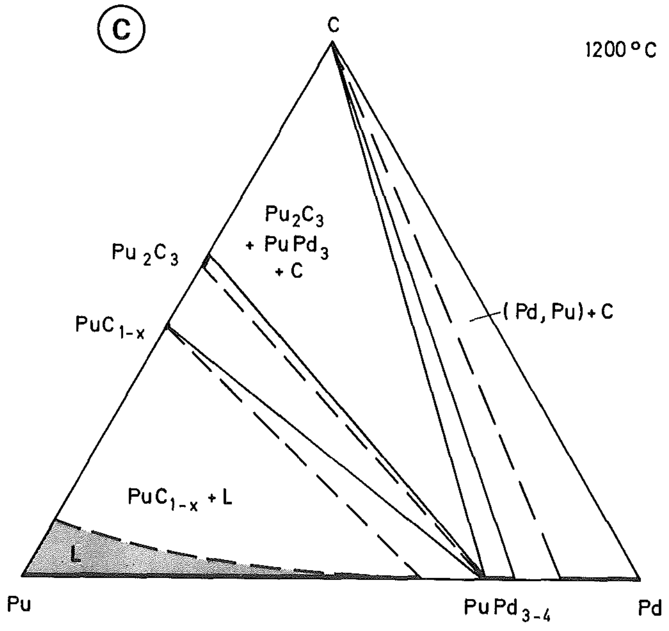


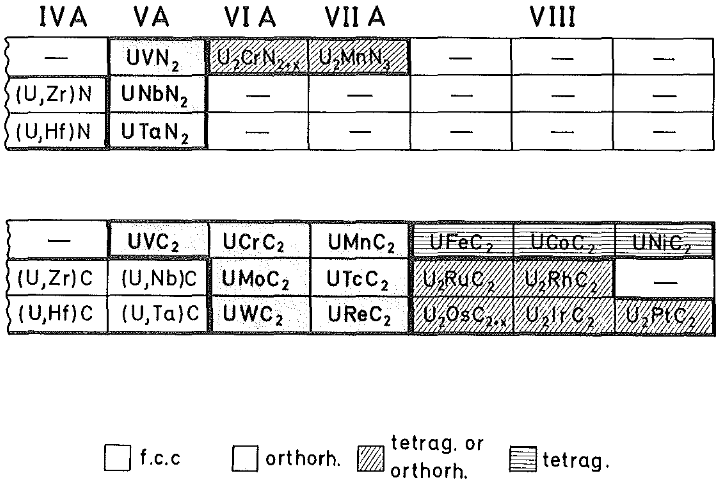
FIG.19. Isothermal sections in the Th-Pd-C (1100°C), U-Pd-C (1300°C), Pu-Pd-C (1200°C) systems.


Ⓑ
C
1300°C
U_2C_3
UC
U_2C_3 + UC + UPd_3
UC + UPd_3
U_2C_3 + UPd_3 + C
UPd_3 + UPd_4 + C
δ - Pd + C
UC + L
UC + L + UPd_3
U
UPd_3
UPd_5
Pd
UPd_4


Ⓒ
C
1200°C
Pu_2C_3 + $PuPd_3$ + C
Pu_2C_3
PuC_{1-x}
(Pd, Pu) + C
PuC_{1-x} + L
L
Pu
$PuPd_{3-4}$
Pd

	Th	U	Pu
V		UVC_2 UVN_2	
Nb		$UNbN_2$	
Ta		$UTaN_2$	
Cr	Th_2CrN_3	$UCrC_2$ U_2CrN_3	
Mo	2 compds.	$UMoC_2$ $UMoC_{1.7}$	$PuMoC_2$
W		UWC_2 $UWC_{1.7}$ z-(U,W,C)	$PuWC_2$
Mn	Th_2MnN_3	$UMnC_2$ U_2MnN_3	
Tc		$UTcC_2$	$PuTcC_2$
Re	compd.	$UReC_2$ $UReC_{1.7}$	
Fe		$UFeC_2$	$PuFeC_2$ $Pu_3Fe_4C_5$
Ru	$Th_3Ru_4C_5$ $ThRu_3C_{1.5}$ $ThRu_3C$	U_2RuC_2 URu_3C_{1-x}	$PuRu_3C$
Os	compd.	U_2OsC_{2+x}	
Co		$UCoC_2$	
Rh		U_2RhC_2	$PuRh_3C_{1-x}$
Ir	compd.	U_2IrC_2	
Ni	$Th_2Ni_3C_2$ $Th_2Ni_3C_5$	$UNiC_2$ U_2NiC_3	
Pd			
Pt	compd.	U_2PtC_2	

FIG.20. Ternary complex carbides and nitrides of thorium, uranium and plutonium with transition metals.

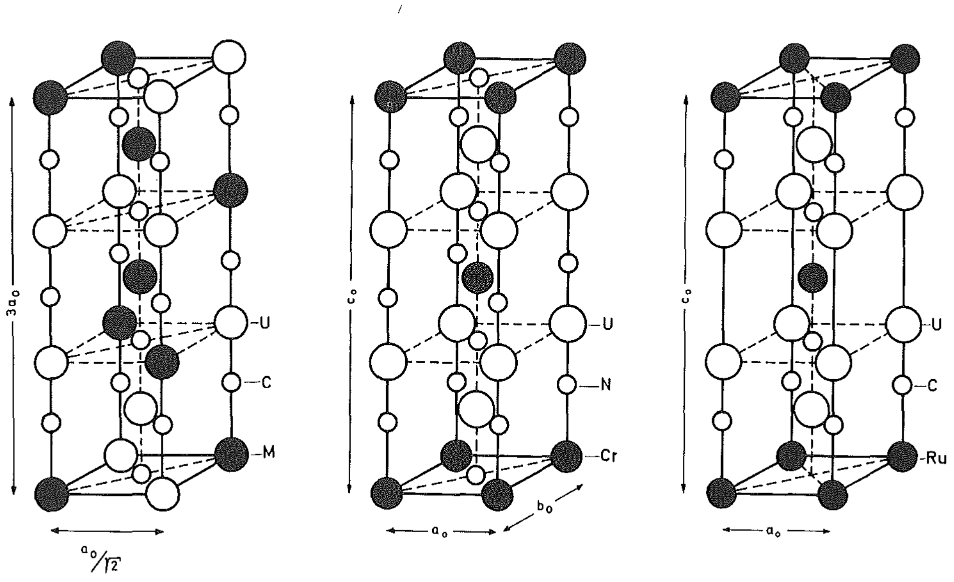


IVA	VA	VI A	VII A	VIII		
—	UVN_2	▨ U_2CrN_{2+x}	▨ U_2MnN_3	—	—	—
(U,Zr)N	$UNbN_2$	—	—	—	—	—
(U,Hf)N	$UTaN_2$	—	—	—	—	—

—	UVC_2	$UCrC_2$	$UMnC_2$	▤ $UFeC_2$	▤ $UCoC_2$	▤ $UNiC_2$
(U,Zr)C	(U,Nb)C	$UMoC_2$	$UTcC_2$	▨ U_2RuC_2	▨ U_2RhC_2	—
(U,Hf)C	(U,Ta)C	UWC_2	$UReC_2$	▨ U_2OsC_{2+x}	▨ U_2IrC_2	▨ U_2PtC_2

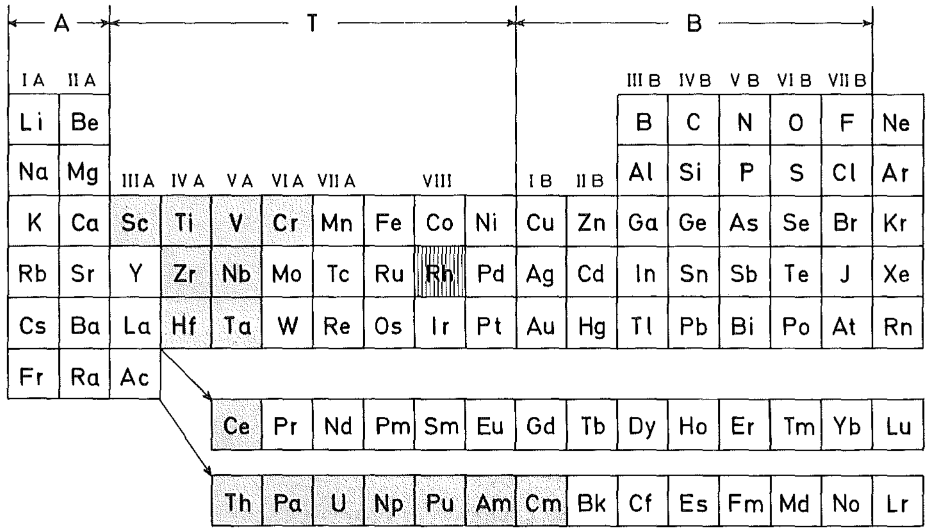
☐ f.c.c ☐ orthorh. ▨ tetrag. or orthorh. ▤ tetrag.

FIG.21. Ternary uranium-transition metal carbides and nitrides.

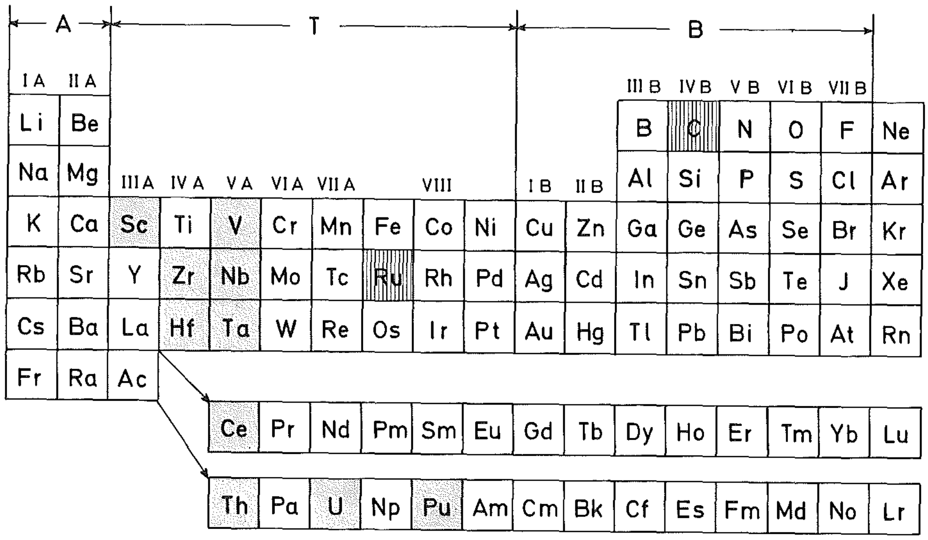


(U,M)C ⟶ $U_2CrN_3 \rightarrow (U_2OsC_{2+x})$ ⟶ U_2RuC_2

FIG.22. Structures of the (U,M)C mixed crystal (U and M are statistically distributed), orthorhombic U_2CrN_3 and tetragonal U_2RuC_2.



▨ MRh_3 (Cu_3Au-type)



▨ MRu_3C_{1-x}

FIG.23. The occurrence of binary MRh_3 phases and ternary MRu_3C_{1-x} carbides.

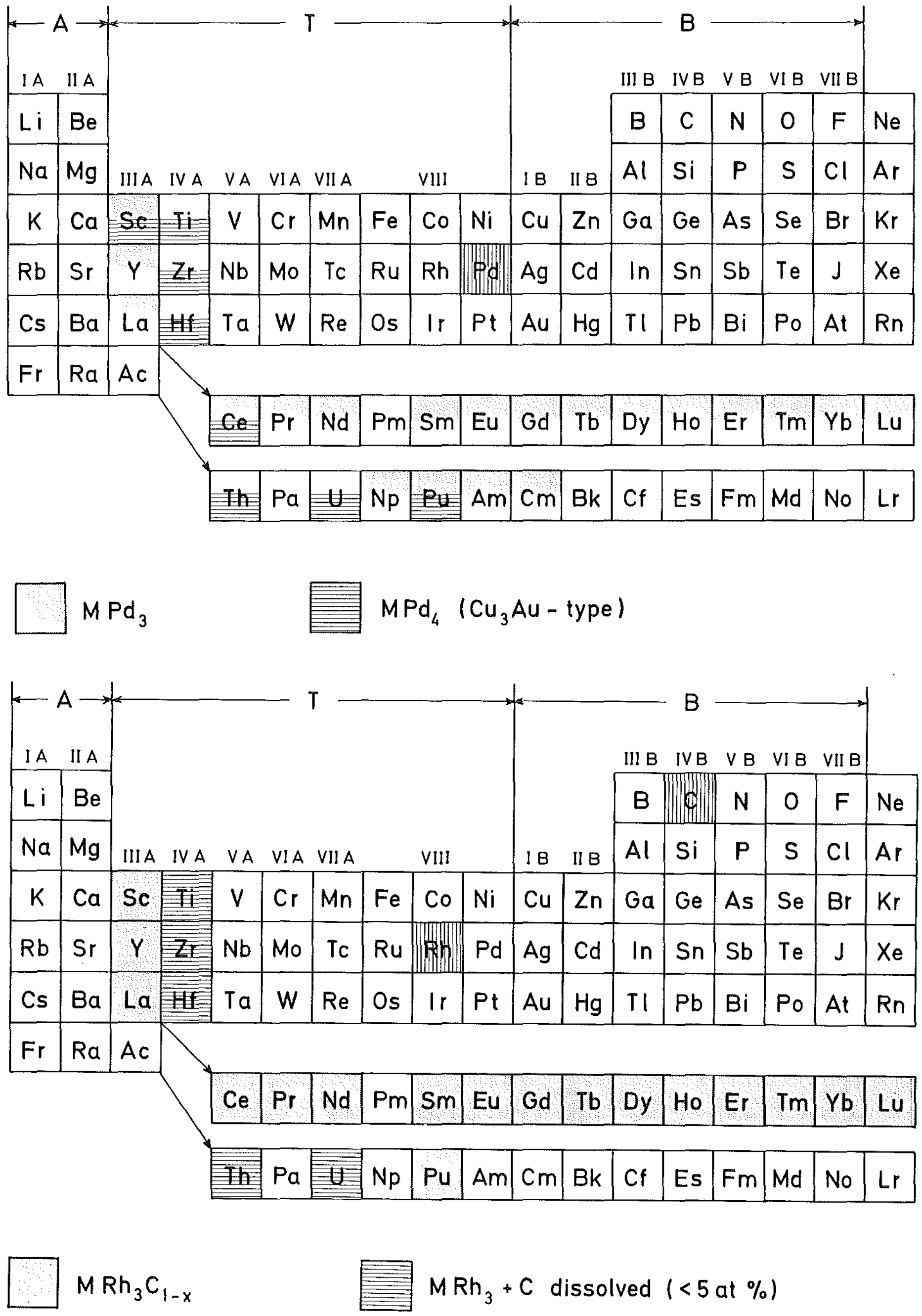


FIG.24. The occurrence of binary MPd_3 and MPd_4 phases and ternary MRh_3C_{1-x} carbides.

Ⓐ

	ThC	PaC	UC	NpC	PuC
ThC	▨	(+)	+	+	+
PaC	(+)	▨	(+)	(+)	(+)
UC	+	(+)	▨	(+)	+
NpC	+	(+)	(+)	▨	(+)
PuC	+	(+)	+	(+)	▨

	YC
ThC	(+)
PaC	(+)
UC	+
NpC	(+)
PuC	(+)

	TiC	ZrC	HfC	VC	NbC	TaC
ThC	–	–	–	–	–	–
PaC	(–)	(–)	(–)	(–)	(–)	(–)
UC	–	+	+	– comp.	+	+
NpC	(–)	(–)	(–)	(–)	(–)	(–)
PuC	–	–	(–)	(–)	(–)	(–)

Ⓑ

	ThC_2	UC_2	PuC_2
ThC_2	▨	+	+
UC_2	+	▨	+
PuC_2	+	+	▨

	YC_2	LaC_2	CeC_2	PrC_2	NdC_2
ThC_2	(+)	(+)	(+)	(+)	(+)
UC_2	+	+	+	(+)	(+)
PuC_2	(+)	(+)	(+)	(+)	(+)

Ⓒ

	ThN	UN	NpN	PuN	AmN
ThN	▨	+	(+)	(+)	(+)
UN	+	▨	(+)	+	(+)
NpN	(+)	(+)	▨	(+)	(+)
PuN	(+)	+	(+)	▨	(+)
AmN	(+)	(+)	(+)	(+)	▨

	YN	LaN	CeN	PrN	NdN
ThN	+	+	+	+	+
UN	+	+	+	+	+
NpN	(+)	(+)	(+)	(+)	(+)
PuN	(+)	(+)	(+)	(+)	(+)
AmN	(+)	(+)	(+)	(+)	(+)

	TiN	ZrN	HfN	VN	NbN	TaN
ThN	–	–	(–)	(–)	(–)	(–)
UN	–	+	+	– comp.	– comp.	– comp.
NpN	(–)	(+)	(+)	(–)	(–)	(–)
PuN	(–)	(+)	(+)	(–)	(–)	(–)
AmN	(–)	(–)	(–)	(–)	(–)	(–)

+	miscible	(+)	not investigated but probably miscible
–	immiscible	(–)	not investigated but probably immiscible

FIG.25. The occurrence of complete miscibility in face-centered cubic (A) monocarbide, (B) dicarbide and (C) mononitride systems of the actinides.

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DISCUSSION

M. KATSURA: This question is addressed to both Mr. Holleck and Mr. Potter. Can the structure of the carbon change the form of the phase diagrams in the regions in which carbon is present?

P.E. POTTER: Yes, this could occur for example in a system such as U-Zr-C, where the composition of the (U, Zr)C phase in equilibrium with carbon and UC_2 would be influenced by the different thermodynamic properties with some departure from the graphite structure.

A.S. PANOV: Mr. Holleck, your paper has to some extent supplied the answer to the question I asked of Mr. Potter at the beginning of this session. Now I should like to ask you whether the phase boundaries of the homogeneity regions shown in your diagram of, for example, $U_y Me_{1-y} C_{1\pm x}$ were obtained experimentally or whether they were derived from estimates.

H. HOLLECK: Most of the extended homogeneity regions are bounded by broken lines. This means, as I pointed out in my paper, that the phase boundaries are estimates. In many cases, however, there is also some experimental evidence for these estimates.

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