- (1) Iandelli, Aldo, and Ferro, Ricardo, Ann. chim. (Rome), <u>42</u>, 598-606 (1952).
- Maskrey, J. T., and Frost, B.R.T., "The System Uranium-Lead" (AERE M/R 1027), J. Inst. Metals, 811, 171-180 (December, 1953).

URANIUM-GOLD



The Constitutional Diagram

The uranium-gold system has been studied by $Buzzard^{(1)}$. The diagram shown was constructed from data obtained by thermal, microscopic, and X-ray analyses.

The uranium-rich eutectic is reported to occur at 1105 C and 10.5 a/o gold. The gold-rich eutectic is reported to occur at 87.5 a/o gold and 852 C. (1)

Two compounds were identified by Buzzard, although the structures have not been determined. The compounds appear to be delta (U_2Au_3) and epsilon (UAu_3) .⁽¹⁾

The solubility of uranium in gold appears to be between 0.2 and 0.3 a/o at 852 C, while the solubility of gold in uranium is approximately 6 a/o at 1105 C. (1)

Additions of gold lower the transformation temperatures of uranium to 738 and 647 C, as shown in the diagram⁽¹⁾.</sup>

Data from the United Kingdom do not agree well with this diagram. The National Physical Laboratory reports that as many as six compounds may be present in the system. ⁽²⁾ The completeness of the diagram by Buzzard and the apparent agreement of data obtained by X-ray diffraction, thermal analysis, and metallographic examination lend strong support to the diagram shown.

Crystallography

No information is available on the crystal structure of the compounds in the uraniumgold system.

- Buzzard, R. W., and Park, J. J., "The Gold-Uranium System", J. Natl. Bur. Standards, <u>53</u>, 291 (1954).
- (2) National Physical Laboratory, "Note on Some Alloys of Gold and Uranium", AERE X/M 100 (1952).

URANIUM-HOLMIUM

Uranium and holmium exhibit an immiscibility gap in the liquid state. Solubility of holmium in liquid uranium is reported to increase from 0.025 w/o at 1150 C to 0.075 w/o at 1250 C. (1)

Crystallography

Nothing is known concerning the possibility of compounds in this system.

Reference

(1) Wilhelm, H. A., "Nuclear Fuels Newsletter", WASH-704 (December, 1957). Classified.

URANIUM-HYDROGEN



The Constitutional Diagram

The uranium-hydrogen system has received considerable study. Diagrams illustrating the solubility of hydrogen in uranium at 1-atm pressure and at high pressure have been determined and are shown. (1) Work done since the diagrams were developed has shown that the diagrams are useful; the data are reproducible by the original techniques.

The data were determined by an absorption technique. In this process a sample of uranium rod, dry abraded under argon, is introduced into a gasometric apparatus which is evacuated and then filled with a measured amount of hydrogen. The amount of hydrogen absorbed is calculated from pressure changes in a known volume. The precision of the method is ± 0.2 ppm for a 25-g sample⁽¹⁾.

Mattraw⁽²⁾ reports a solubility of 3.0 ppm at 295 C and $100-\mu$ pressure. These data disagree with those of Mallett⁽¹⁾ by a factor of 250. However, it is probable that Mattraw had not observed true interstitial solution of hydrogen, but rather chemisorption on the surface of his finely divided sample. Samples of small surface-to-mass ratio do not show the anomalous high hydrogen pickup.⁽¹⁾

Many people have contributed to the present knowledge of UH_3 , the only hydride in this system. It has been shown that UH_3 exists in two crystallographic forms.^(3,4) Delta UH_3 (called "alpha" UH_3 by Mulford), the more recently discovered form, has been produced by reacting uranium powder with hydrogen gas at 25 to minus 80 C⁽³⁾, by reacting massive uranium with hydrogen gas at minus 40 C, and by electrolysis of a solution of $HClO_4$ or Na_2CO_3 , where uranium is used as the cathode⁽⁴⁾. Mulford suggests that delta is metastable. The yield of delta increases as the temperature of formation is decreased.⁽³⁾

Once formed, delta does not decompose during annealing at 100 C but does decompose at 250 C. No attempt was made to show the delta phase in the diagram because epsilon ("beta" UH_3) is the phase commonly observed.

Crystallography

Uranium hydride has been shown to exist in two forms. Data for both delta and epsilon are given in the tabulation along with data for epsilon ("beta") UD_3 .

The data for delta UH₃ are from Mulford⁽³⁾. Caillat⁽⁴⁾ has confirmed this information. He reports that $a = 4.161 \pm 0.002$ A and density is 11.1 g/cm³.

The data for epsilon UH_3 and epsilon UD_3 are from Rundle. (5,6) These compounds were studied by X-ray, although the structure was resolved through neutron-diffraction studies of epsilon UD_3 . The epsilon UH_3 reported by Rundle was prepared under a pressure of 1800 psi at 500 to 600 C. (6) Hydride prepared at lower pressures yielded lattice constants of a = 6.32 ± 0.001 A. Slightly higher values were obtained in earlier work(7,8).

The hydrogen atoms in epsilon UH₃ are reported to lie in distorted tetrahedra, equidistant from four uranium atoms with uranium-hydrogen distances of 2.32 A. There are two types of structures, each with 12 nearest hydrogen atoms at this distance. The proposed space group is Pm3n, with parameters for 24 (k) of $y = 0.155 \pm 0.02$ and $Z = 0.31 \pm 0.02$. These values are sufficiently close to y = 0.156 and Z = 0.313 to put each hydrogen atom equidistant from four uranium atoms. The structure gives satisfactory agreement between calculated and observed intensities.⁽⁵⁾

The structure of epsilon UH_3 is unique and is not entirely understood, but it is reported that no metallic uranium-uranium bonds of importance are present in the structure. The hydride is assumed to be held together by uranium-hydrogen interactions. Rundle suggests that these interactions may be described in terms of delocalized covalent bonds.⁽⁶⁾

The work of Gibb(9) may be of general interest.

		Unit Cell					
		Dimensions,	Number of	Dens g/c	ity, m ³	Space	
Phase	Type	A	Molecules	X-Ray	Other	Group	Remarks
Delta ("alpha") UH ₃	Cubic	$a = 4.160 \pm 0.001$	2			Pm3n	
Epsilon (''beta'') UH ₃	Cubic	a = 6.6310 ± 0.0008	8	10.92	10.95	Pm3n	
Epsilon (''beta'') UD ₃	Cubic	a = 6.620 ± 0.002	8	11.11		Pm3n	

- Mallett, M. W., and Trzeciak, M. J., "Hydrogen Uranium Relationships", Trans. ASM, 50 (1958).
- (2) Mattraw, H. C., J. Phys. Chem., 59, 93 (1955).
- (3) Mulford, R.N.R., Ellinger, F. H., and Zachariasen, W. H. (AECU-2700), J. Am. Chem. Soc., <u>76</u>, 297-298 (1954).
- (4) Caillat, R., Coriou, H., and Perio, P., "A New Form of the Hydride of Uranium", Compt. rend., <u>237</u>, 812-13 (October 12, 1953).
- (5) Rundle, R. E., "The Hydrogen Positions in Uranium Hydride by Neutron Diffraction", (AECD-3111), J. Am. Chem. Soc., 73, 4172-4 (1951).
- (6) Rundle, R. E., "The Structure of Uranium Hydride and Deuteride", J. Am. Chem. Soc., <u>69</u> (7), 1719-23 (1947).
- (7) Katz, J. J., and Rabinowitch, Eugene, "The Chemistry of Uranium, Part I", 180-213 (1951).
- (8) Zachariasen, W. H., unpublished information (1943).
- (9) Gibb, Thomas, Jr., et al., "Metal-Hydrogen Systems III. The Uranium-Hydrogen System", J. Am. Chem. Soc., <u>74</u> (12), 6203-07 (1952).

URANIUM-INDIUM

A compound, UIn_3 , has been identified. (1,2) Solubilities of uranium in liquid indium have been reported(3) as given below:

Temperature, C	600	650	700	750	800	850	900
Solubility, w/o	0.08	0.10	0.15	0.25	0,45	0.70	1.05

Crystallography

An intermetallic compound, UIn₃, has been reported.^(1,2) Data for UIn₃ are summarized below⁽²⁾. Iandelli⁽¹⁾ reports the same structure, but gives a slightly lower lattice constant, a = 4.588 A. He has studied the following UX₃-type compounds: UIn₃, UGa₃, UTl₃, USi₃, UGe₃, and UPb₃.

Unit Cell							
774		Dimensions,	Number of	Den g/c	sity,	Space	
Phase	<u>1ype</u>	A	Molecules	<u>x-Ray</u>	Others	Group	Remarks
UIn3	Fcc	a = 4.6013	1			Pm3m	L12-type structure, iso- morphous with UGa ₃ ,
32							US1 ₃ , UGe ₃ , UPb ₃ , USn ₃ , and UAl ₃

- (1) Iandelli, Aldo, and Ferro, Ricardo, Ann. chim. (Rome), <u>42</u>, 598-60 (1952).
- Maskrey, J. T., and Frost, B.R.T., "The System Uranium-Lead" (AERE M/R-1027), J. Inst. Metals, 81, 171-180 (December, 1953).
- (3) Hayes, E. E., and Gordon, P., J. Met. and Cer., TID-65, 130-41 (July, 1948). Classified.

URANIUM-IRIDIUM

The solubility of iridium in uranium at 890 C is reported⁽¹⁾ to be about 3 a/o. A compound, UIr₂, has been identified.

Crystallography

An intermetallic compound, UIr_2 , has been reported⁽²⁾. It has the C15, $MgCu_2$ structure.

		Unit Cell					
		Dimensions,	Number of	Density, g/cm ³	Space	n 1	
Phase	Type	A	Molecules	X-Ray Other	Group	Remarks	
UIr ₂	Fcc	a = 7.509	8	19.62	Fd3m	C15, MgCu ₂ structure	

References

- (1) Park, J. J., private communication (October, 1956).
- (2) Heal, T. J., and Williams, G. I., "Compounds of Uranium With the Transition Metals of the Second and Third Long Periods", Acta Cryst., <u>8</u>, 494 (1955).

URANIUM-IRON



The Constitutional Diagram

The uranium-iron diagram has been determined independently by Kaufmann⁽¹⁾ and by Grogan⁽²⁾ and has been studied by Foote⁽³⁾. The diagram shown is Kaufmann's. The liquidus points and the isotherms reported by Grogan vary slightly from those of this diagram; otherwise, the two diagrams are identical.

Grogan⁽²⁾ reports some details of the uranium-rich alloys. Solubilities of iron in uranium taken from this work are tabulated below.

Phase	Temperature	Solubility, w/o		
Alpha	660 C	Nil		
	Alpha-beta isotherm	<0.02 iron		
Beta	Alpha-beta isotherm	<0.02 iron		
	Beta-gamma isotherm	0.1 iron		
Gamma	Beta-gamma isotherm	0.2 iron		
	U ₆ Fe peritectic	0.35 iron		

The solubility in the gamma region depicted in the accompanying diagram $^{(1)}$ agrees well with the data above.

Crystallography

The structure of U₆Fe has been determined by Baenziger⁽⁴⁾ and is isomorphous with U₆Mn, U₆Co, and U₆Ni. The observed unit-cell volume for U₆Fe (557 A³) is quite close to the volume calculated by assuming additivity of atomic volumes (547 A³).

The data tabulated for UFe₂ are from the work of $Grogan^{(2)}$. Kaufmann⁽¹⁾ has reported a slightly higher value for the lattice, a = 7.050 A. Similar data have been reported by Baenziger⁽⁴⁾ and Brook⁽⁵⁾, indicating that UFe₂, UMn₂, and UCo₂ are isomorphous and are the Cl5-type MgCu₂ structure. The compound UNi₂ is reported to have the Cl4-type MgZn₂ structure. Ternary alloys involving all of these phases are described in the section devoted to ternary alloys.

		Unit Cell						
		Dimensions,	Number of	Density, g/cm ³		Space		
Phase	Type	A	Molecules	X-Ray	Other	Group	Remarks	
Delta (U6Fe)	Bc tetrag- onal	$a = 10.31 \pm 0.04$ c = 5.24 \pm 0.02	4	17.7		I4/mcm, I42, or I4c2	Isomorphous with U6Mn, U6Co, U6Ni	
Epsilon (UFe ₂)	Fcc	a = 7.042	8	13.21		Fd3m	C15-type, MgCu ₂ structure iso- morphous with UA1 ₂	

References

- Gordon, P., Kaufmann, A. R., "The Alloy Systems Uranium-Aluminum and Uranium-Iron" (AECD-2683), J. Metals, <u>2</u>(1), 182 (1950).
- (2) Grogan, J. D., "The Uranium-Iron System", J. Inst. Metals, 77, 571-580 (1950).
- (3) Foote, Frank, unpublished information (1945).
- (4) Baenziger, N. C., Rundle, R. E., Snow, A. I., and Wilson, A. S., "Compounds of Uranium with the Transition Metals of the First Long Period" (AECD-2598), Acta Cryst., 3, 34-40 (1950).
- (5) Brook, G. B., Williams, G. I., and Smith, E. M., "Pseudo-Binary Phase Sections Between Laves Phases in Ternary Alloys of Uranium", J. Inst. Metals, <u>83</u>, 271 (1954-1955).

URANIUM-LANTHANUM

Uranium and lanthanum show little miscibility in the liquid state.(1,2) The solubility of lanthanum in liquid uranium is reported to be 0.75 w/o at 1150 C and 0.90 w/o at 1250 C, while uranium solubility in lanthanum is given as 0.3 w/o at 1000 C and 1.0 w/o at 1250 C.(1)

Crystallography

Data concerning the possibility of compounds in this system are not available.

References

(1) Wilhelm, H. A., "Nuclear Fuels Newsletter", WASH-704 (December, 1957). Classified.

(2) National Physical Laboratory, United Kingdom, unpublished information (1949-1950).

URANIUM-LEAD



The Constitutional Diagram

The major features of the uranium-lead system are agreed upon by all investigators. The diagram shown is from Teitel⁽¹⁾. The results of Maskrey and $Frost^{(2)}$ differ only in that the compound delta (UPb) is shown to melt congruently at 1280 C and no region of immiscibility is shown above 1280 C. The interpretation of Maskrey and $Frost^{(2)}$ is based on thermal analyses, while Teitel⁽¹⁾ depicts the immiscibility gap on the basis of chemical analyses of liquated alloy samples. Separated layers formed by liquation analyzed 41 to 43 w/o uranium and 97.4 to 98.5 w/o uranium. It is difficult to account for such a large difference in composition unless a region of immiscibility exists.

The compounds UPb and UPb₃ are pyrophoric and are therefore difficult to study. The compound UPb is reported to be more pyrophoric than is $UPb_3^{(2)}$.

The solubility of lead in uranium is quite low, and lead additions have little effect on the phase transformations in uranium. The uranium-rich eutectic is reported to occur at 99.6 w/o uranium.

The solubility of uranium in lead has been determined by Teitel(5), who quotes solubilities of 0.002, 0.046, 0.26, and 0.59 w/o at 416, 612, 806, and 1000 C, respectively.

Crystallography

The structure of UPb has been reported by Teitel⁽⁵⁾. Numerous determinations of the structure of UPb₃ have been made, and parameters of 4.73 $A^{(4)}$, 4.795 $A^{(3)}$, and 4.7934 $A^{(2)}$ have been reported. The structure in the tabulation is from Maskrey and Frost⁽²⁾, but the parameter is from Teitel⁽⁵⁾.

Phase	Туре	Dimensions,	Number of Molecules	Dens g/cr X-Ray	ity, m ³ Other	Space Group	Remarks
Delta (UPb)	Bc tetrag- onal	a = 11.04 c = 10.60	48	13.7			
Epsilon (UPb ₃)	Simple cubic	a = 4.791	1	12.98		Pm3m	L12, AuCu ₃ ordered structure iso- morphous with UA13, UGa3, UIn3, USi3, UGe3, and USn3.

References

- (1) Teitel, R. J., "The Lead-Uranium System" (AECD-3173), J. Metals, 4, 397-400 (1952).
- (2) Frost, B.R.T., and Maskrey, J. T., "The System Uranium-Lead" (AERE-M/R 1027)
 J. Inst. Metals, <u>82</u> (1), 171-180 (1953).
- (3) Fitzpatrick, J. M., and Kaufmann, A. R., unpublished information (1950).
- (4) Iandelli, A., and Ferro, R., Ann. chim. (Rome), 42, 598-606 (1952).
- (5) Teitel, R. J., "The Uranium-Lead System", J. Inst. Metals, 85, 409-412 (1956-57).

URANIUM-LUTECIUM

Uranium and lutecium exhibit an immiscibility gap in the liquid state. Solubility of lutecium in liquid uranium is reported to increase from 0.2 w/o at 1150 C to 0.4 w/o at 1250 C. $^{(1)}$

Crystallography

Nothing is known concerning the possibility of compounds in this system.

Reference

(1) Wilhelm, H. A., "Nuclear Fuels Newsletter", WASH-704 (December, 1957). Classified.

URANIUM-MAGNESIUM



The Constitutional Diagram

The magnesium-uranium diagram shown has been worked out by investigators at Ames Laboratory. (1) The immiscibility of the two metals has been cited by others(2,3).

Early work on this system gave evidence of intermetallic phases and thus led to a faulty conception of the system. The later work of Tracy, Chiotti, and Wilhelm(1) provides not only a complete diagram but also an explanation of early erroneous information. It was found that the method of preparation of diffusion and liquation samples was important; if magnesium and uranium were heated together in ordinary crucible materials, uranium carbide or uranium silicide layers, depending on the refractory material, were formed between the uranium and magnesium layers.

Two techniques were found to be especially successful in this work. The first involves heating massive uranium or uranium shavings in molten magnesium in a crucible consisting of 90 w/o magnesium oxide and 10 w/o magnesium fluoride. The other technique consists of melting magnesium and holding it molten in a uranium container. Both methods avoid collection of contaminants at the interface of the two immiscible metals (1).

Diffusion samples prepared by holding magnesium in a uranium crucible for 24 hr at 1015 C showed no evidence of diffusion bands or intermetallic compounds.⁽¹⁾ The work described appears to be quite thorough, since a variety of techniques, including thermal analysis, X-ray studies, microscopic examination and diffusion or liquation tests were utilized.⁽¹⁾

Uranium and magnesium are almost completely immiscible, even at high temperatures. At 1150 C and 3-atm pressure, 0.14 w/o uranium is soluble in magnesium, while only 0.004 w/o magnesium is soluble in uranium. The solubility of uranium in magnesium is reported to decrease to 0.05 w/o at 675 C and to 0.005 w/o at 650 C.(1) In a more recent determination of uranium solubilities in magnesium, values of 0.002 w/o at 650 C and of 0.17 w/o at 1132 C were obtained.(4)

The melting points of magnesium and uranium and the transformation temperatures in uranium are affected very little in these alloys.

Crystallography

There are no compounds in the uranium-magnesium system.

References

- Chiotti, P., Tracy, G. A., and Wilhelm, H. A., "Magnesium-Uranium Alloy System", Trans. AIME, <u>206</u>, 562-67 (1956).
- (2) A.E.R.E., United Kingdom, unpublished information (March, 1947).
- (3) Iandelli, Aldo, and Ferro, Ricardo, Ann. chim. (Rome), 42, 598-600 (1952).
- (4) Wilhelm, H. A., "Nuclear Fuels Newsletter", WASH-704, 2-4 (December, 1957). Classified.

URANIUM-MANGANESE



The Constitutional Diagram

The constitutional diagram of uranium-manganese is shown in the accompanying figure(1). The system has two intermetallic compounds, U_6Mn and UMn_2 . The general characteristics of the system are confirmed by data from the United Kingdom.⁽²⁾ Although some difference in data occurs at the manganese end of the system, there is not enough information