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Equilibrium distributions of actinides and lanthanides in molten chloride salt and liquid zinc binary phase system

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Abstract

As one of the basic investigations on the group partitioning of actinides and lanthanides by the pyrochemical reductive extraction system, their distribution behavior in a binary phase system of molten chloride and liquid zinc was studied at 873 and 1073 K. Generally speaking, actinides were a little more easily reduced and extracted from the salt phase into the metal phase than lanthanides. However, the separation factors which were the differences in the distribution coefficient between actinides and lanthanides were not so large even at the lower temperature at which those were larger and the group partitioning of these elements seemed less attractive in this system. The present results were much the same as those in the LiF–BeF_2/Zn system and the effect of the selection of the salt phase on the separation factors were hardly observed. For some details, the thermodynamic quantities of actinides and lanthanides in the system were calculated from the equilibrium distributions and discussed. © 1997 Elsevier Science B.V.

1. Introduction

Pyrochemical processing of the nuclear materials using molten salt and liquid metal as solvent is expected for advanced nuclear chemical processing. This is because pyrochemical processing, especially on the comparison with the aqueous processing, has high radiation resistance, compactness and less waste generation. Thus, extensive studies on pyrochemical systems are seen, for example, for the development of molten salt breeder reactors [1] and of metallic fuel fast breeder reactors [2]. Selective extraction of radionuclides in a binary phase system of molten salt and liquid metal has a remarkable attraction because it provides quite satisfactory separation performance in the partitioning of the nuclides. Thus, various extractions in binary phase systems have been studied and proposed for the recovery of nuclear materials and useful elements [3,4].

As a typical study on pyrochemical processing, the experiment by Ferris et al. at ORNL is well known. They investigated the reductive extraction of actinides and fission products in a LiF–BeF_2/Bi system [5,6] and, in their experiments, they measured the equilibrium distributions of several elements to show the technical feasibility of its application for separation. Present authors also measured the equilibrium distributions [7–14] and extraction kinetics [15] in such systems as of LiF–BeF_2 and Bi. In these past studies, the equilibrium distributions of actinides and lanthanides were determined as a function of salt phase composition, metal phase composition and temperature. The mechanism of the reductive extraction was studied in some details and the related thermodynamic quantities were determined. As a result, it has been shown that actinides are more easily reduced and extracted into the metal phase than lanthanides and that different solvent metals give quite different separation factors between actinides and lanthanides [14]. Following these studies, the reductive extraction behaviors of actinides and lanthanides

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have been studied in the binary phase system of molten LiCl–KCl and Zn in the present study. Thermodynamic quantities of the solute elements are determined from the experimental results and discussed.

2. Experimental

All the reagents used were of reagent grade, obtained from Nacalai Tesque. The 1:1 mixture of LiCl and KCl was prepared by melting known amounts of LiCl and KCl and dried up under vacuum before the experiment. The radioactive tracers of ^{239}Np and ^{233}Pa were produced by thermal neutron irradiation of U and Th metals and those of lanthanides were produced by irradiation of the metals. In some runs, ^{239}Pu was also used, which was separated from irradiated UO_2.

The experimental apparatus and procedures employed in the present study were much the same as in the previous ones [7–15]. In the experiment, 2 mol of LiCl–KCl mixture, 2 mol of Zn and small amounts (less than 100 mg each) of radioactive solute metals were loaded in an alumina crucible. After drying at 450 K in vacuum, the system was heated to a given temperature under an inert gas atmosphere. The distribution of the solute elements was controlled by the incremental addition of a Li–Zn alloy as a reductant. After every addition of the reductant, the system was gas-sparged for a few hours to attain equilibrium and then small portions of both phases were sucked into a stainless steel tube as samples. All the samples were weighed and their radioactivities were determined by γ-spectrometry. The radioactivity of ^{239}Pu was measured by α-spectormetry. They were carefully treated to avoid cross contamination. The Li concentration in the metal phase sample was determined by atomic absorption spectrophotometry after dissolving it completely. Experiments were performed at 873 and 1073 K.

3. Results and discussion

3.1. Mechanism of equilibrium distributions

According to our previous studies [7–14], the equilibrium distribution of a solute element M is given by

$$\mathrm{Li}_{m-n}\mathrm{MCl}_m + n\mathrm{Li} + x\mathrm{Zn} = \mathrm{MZn}_x + m\mathrm{LiCl}, \qquad (1)$$

where $\mathrm{Li}_{m-n}\mathrm{MCl}_m$ and MZn_x represent complex compounds in the salt phase and intermetallic compounds in the metal phase, respectively. The formation of these compounds has been inferred from the dependence of the equilibrium distributions on the salt and metal phase compositions.

By taking Eq. (1), the $D_{\mathrm{M}}/D_{\mathrm{Li}}^n$ value which is defined as the extractability value of each element [11] is represented by

$$\begin{aligned}\log(D_{\mathrm{M}}/D_{\mathrm{Li}}^n) &= -(2.3RT)^{-1}[\Delta G_f^{\circ}(\mathrm{MZn}_x) \\ &\quad + m\Delta G_f^{\circ}(\mathrm{LiCl}) - \Delta G_f^{\circ}(\mathrm{Li}_{m-n}\mathrm{MCl}_m)] \\ &\quad + x\log \mathrm{X}_{\mathrm{Zn}} - (m-n)\log \mathrm{X}_{\mathrm{LiCl}} - \log\gamma_{\mathrm{MZn}_x} \\ &\quad - m\log\gamma_{\mathrm{LiCl}} + \log\gamma_{\mathrm{Li}_{m-n}\mathrm{MCl}_m} + n\log\gamma_{\mathrm{Li}} \\ &\quad + x\log\gamma_{\mathrm{Zn}}, \qquad (2)\end{aligned}$$

where the distribution coefficients D_{M} and D_{Li} are defined as

$$D_{\mathrm{M}} = X_{\mathrm{M(metal)}}/X_{\mathrm{M(salt)}}, \qquad (3)$$

$$D_{\mathrm{Li}} = X_{\mathrm{Li(metal)}}/X_{\mathrm{Li(salt)}}. \qquad (4)$$

The terms in the right hand side in Eq. (2) are constant at a given temperature and composition and then the logarithm of D_{M} is proportional to that of D_{Li} with a slope of n:

$$\log D_{\mathrm{M}} = n\log D_{\mathrm{Li}} + \log K'_{\mathrm{M}}, \qquad (5)$$

where K'_{M} is a constant. By plotting the observed $\log D_{\mathrm{M}}$ values against the $\log D_{\mathrm{Li}}$, the valency of the solute element in the salt phase and the extractability value in $\log(D_{\mathrm{M}}/D_{\mathrm{Li}}^n)$ are obtained from the slope and intercept, respectively.

3.2. Observed distribution behaviors of solutes

As a typical example, the observed distribution coefficients of La are plotted as a function of those of Li in Fig. 1. Curves represent the least squares fitting of the data to Eq. (5) in which the slope of 3 is assumed. The agreements are satisfactorily good and this means that La is present as trivalent species in the salt phase, as observed in the

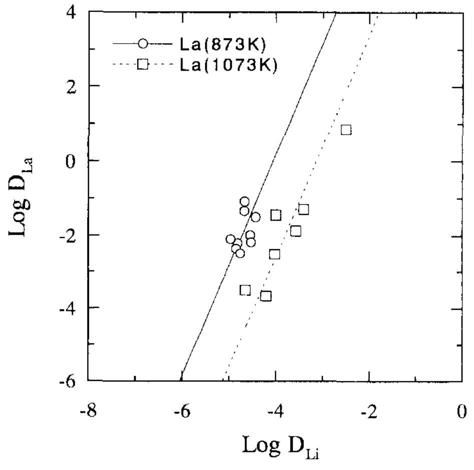

Fig. 1. Distribution coefficient of La as a function of that of Li in the LiCl–KCl/Zn system.

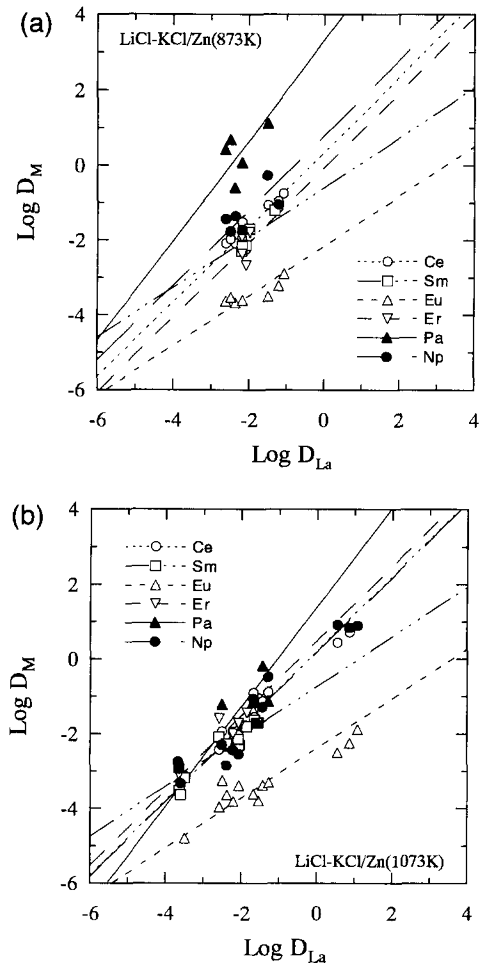

Fig. 2. Distribution coefficients of lanthanides and actinides as a function of that of La in the LiCl–LiCl–KCl/Zn system at (a) 873 K and (b) 1073 K.

fluoride system [8]. The extractability value in $\log(D_M/D_{Li}^n)$ has thus been determined for La. The distribution coefficients of some other elements are plotted against those of La in Fig. 2 and different correlations may be recognized due to different valences in the salt phase. In Fig. 2 curves with the slopes of 4/3, 1 and 2/3 are drawn for tetra-, tri- and divalent elements, respectively, by following the observations in similar systems [5–10]. All the distribution data have been analyzed by using Eq. (5) and the extractability values have been determined as summarized in Table 1.

Fig. 3 shows the atomic number dependence of the obtained extractability values at 873 and 1073 K. It can be seen that actinides of Pa, Np and Pu are more extractable than lanthanides. This is important since such differences may be applied to the group partitioning of actinides and lanthanides. However, the separation factors which are the differences in the distribution coefficient between actinides

Table 1
Extractability values in $\log(D_M/D_{Li}^n)$ of lanthanides and actinides from molten LiCl–KCl into liquid Zn

Element	n	m	$\log(D_M/D_{Li}^n)$ at:	
			873 K	1073 K
La	3	3	12.16 ± 0.18	9.37 ± 0.43
Ce	3	3	12.49 ± 0.17	9.58 ± 0.43
Pr				
Nd	3	3	11.9 ± 0.21	9.38 ± 0.49
Pm				
Sm	2	2	7.52 ± 0.16	5.52 ± 0.29
Eu	2	2	5.97 ± 0.15	3.87 ± 0.30
Gd	3	3	11.93 ± 0.22	9.13 ± 0.44
Tb	3	3	11.57 ± 0.37	
Dy	3	3		10.16 ± 0.43
Ho				
Er	3	3	12.10 ± 0.27	9.85 ± 0.44
Tm	3	3	12.02 ± 0.26	9.95 ± 0.44
Yb	2	2	7.33 ± 0.23	5.24 ± 0.29
Pa	4	6	19.53 ± 0.37	13.88 ± 0.66
Np	3	3	12.95 ± 0.25	9.55 ± 0.44
Pu	3	3	12.84 ± 0.24	

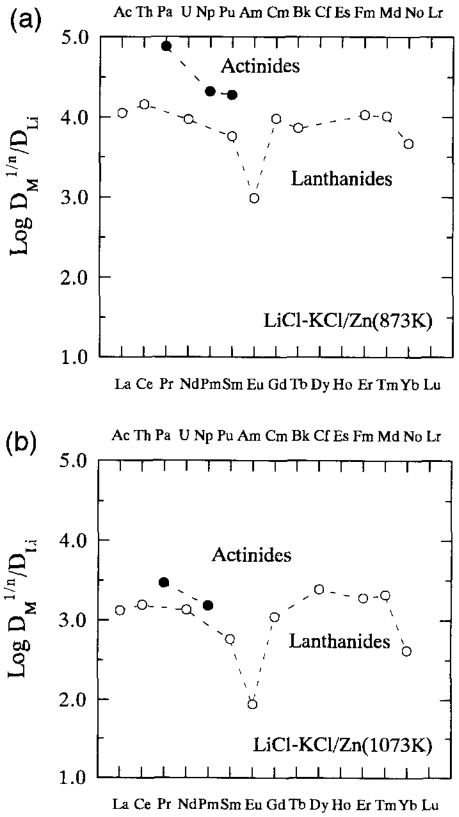

Fig. 3. Atomic number dependence of measured extractability in the LiCl–KCl/Zn system at (a) 873 K and (b) 1073 K.

and lanthanides are not so large even at the lower temperature at which those are larger and, from a technological point of view, the group partitioning of these elements seems less attractive in this system. In our previous study [14], the separation factors have been studied in the systems of LiF–BeF_2/Bi, LiF–BeF_2/Sn, LiF–BeF_2/Cd and LiF–BeF_2/Zn and a systematic difference in the separation factors has been observed in different systems; the separation factor is the highest in the Bi system and it decreases in the order of the Sn, Zn and Cd systems. The present results are much the same as those in the LiF–BeF_2/Zn system and no apparent difference in the separation factors has been observed due to different salt phases. The importance of the alloying energies in the metal phase on the separation factors has been confirmed.

3.3. Thermodynamic considerations

For some details, the thermodynamic quantities are evaluated from the obtained extractability data. Eq. (2) is used to calculate the standard Gibbs free energy of formation of intermetallic compounds, $\Delta G_f^o(MZn_x)$. Also, we can calculate the $\Delta H_f^o(MZn_x)$ and $\Delta S_f^o(MZn_x)$ values from the temperature dependence of the $\Delta G_f^o(MZn_x)$ by using the following equation:

$$\Delta G_f^o(MZn_x) = \Delta H_f^o(MZn_x) - T\Delta S_f^o(MZn_x). \qquad (6)$$

In the present system, each solute is present in a low concentration (less than 1 mol%) and, by assuming that $Li_{m-n}MCl_m$ and MZn_x do not interact with the solvent, the values γ_{MZn_x} and $\gamma_{Li_{m-n}MCl_m}$ are approximately estimated to be unity. The γ_{LiCl} is taken from the literature [16] and the γ_{Li} in Zn is given by Eq. (7) [17]:

$$\log \gamma_{Li(Zn)} = 0.78 - 2346/T. \qquad (7)$$

The other thermodynamic data of $\Delta G_f^o(MCl_n)$ are taken from the literatures [18–20] and, referring to the case of Th [9], the $\Delta G_f^o(Li_2MCl_6)$ value of Pa are estimated by

$$\Delta G_f^o(Li_2MCl_6) = \Delta G_f^o(MCl_4) + 2\Delta G_f^o(LiCl) - 10\,(\text{kcal/mol}). \qquad (8)$$

Table 2 summarizes the evaluated free energy of formation, enthalpy and entropy of formation of intermetallic compounds MZn_x. For comparison, the literature values of some lanthanides [21] and actinides [22] are also shown in Table 2.

Rather good agreements are found for the $\Delta G_f^o(MZn_x)$ values of lanthanides between the present results and the literature ones [21]. As for the $\Delta H_f^o(MZn_x)$ and $\Delta S_f^o(MZn_x)$ values, however, some differences may be recognized to be present. One of the reasons for those differences are attributed to the large uncertainties in the present values, which come from such scatters in the measured extractability values. As shown in Fig. 1, the values are much scattered especially at 1073 K and, by considering this, further confirmation may be needed for the differences in the $\Delta H_f^o(MZn_x)$ and $\Delta S_f^o(MZn_x)$ values. Similar differences may also be found for actinides. In this case, however, apparent differences are recognized to

Table 2
Thermodynamic quantities of intermetallic compounds of lanthanides and actinides in liquid Zn

Element	$\Delta G_f^o(MZn_x)$ at 873 K (kcal mol^{-1})	$\Delta G_f^o(MZn_x)$ at 1073 K (kcal mol^{-1})	$\Delta H_f^o(MZn_x)$ (kcal mol^{-1})	$\Delta S_f^o(MZn_x)$ (cal K^{-1} mol^{-1})	Note
La	−35.72	−31.86	−52.54	−19.27	[21]
	−38.56 ± 0.72	−31.23 ± 2.11	−70.55 ± 9.98	−36.64 ± 11.46	
Ce	−34.92	−30.07	−56.11	−24.27	[21]
	−32.97 ± 0.68	−24.60 ± 2.11	−69.53 ± 9.90	−41.88 ± 11.36	
Pr	−34.87	−30.44	−54.19	−22.13	[21]
Nd	−26.89 ± 0.84	−19.91 ± 2.40	−57.36 ± 11.41	−34.90 ± 13.11	
Pm					
Sm	−43.24 ± 0.64	−36.89 ± 1.42	−70.96 ± 7.09	−31.75 ± 8.15	
Eu	−42.16 ± 0.60	−33.90 ± 1.47	−78.20 ± 7.18	−41.28 ± 8.25	
Gd	−28.97 ± 0.88	−22.95 ± 2.16	−55.23 ± 10.53	−30.08 ± 12.10	
Tb	−26.18 ± 1.48				
Dy		−7.82 ± 2.11			
Ho					
Er	−15.74 ± 1.08	−10.10 ± 2.16	−40.35 ± 11.05	−28.19 ± 12.71	
Tm	−13.85 ± 1.04	−8.88 ± 2.16	−35.54 ± 10.94	−24.85 ± 12.59	
Yb	−46.29 ± 0.92	−40.38 ± 1.42	−72.09 ± 7.92	−29.55 ± 9.14	
Pa	23.98 ± 1.48	41.24 ± 3.24	−51.34 ± 16.20	−86.28 ± 18.63	
Np	0.59 ± 1.00	10.29 ± 2.16	−41.75 ± 10.83	−48.50 ± 12.46	
		−19.4			[22]
Pu	−12.28 ± 0.96				
	−23.28	−18.66	−43.45	−23.1	[22]

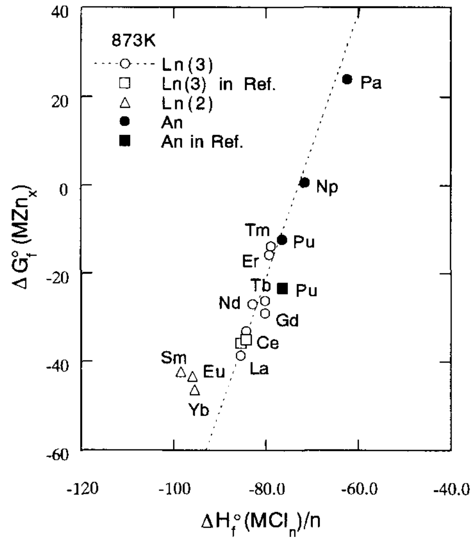

Fig. 4. $\Delta G_f^\circ(\mathrm{MZn}_x)$ versus $\Delta H_f^\circ(\mathrm{MCl}_n)/n$. The curve is drawn as an aid for the eye.

be present even in the $\Delta G_f^\circ(\mathrm{MZn}_x)$ values and then the confirmation is also suggested.

Because of the smaller differences between the present values and the literature ones, the $\Delta G_f^\circ(\mathrm{MZn}_x)$ values may be used for further considerations. Fig. 4 shows the correlation of the $\Delta G_f^\circ(\mathrm{MZn}_x)$ values with the normalized standard enthalpy change $\Delta H_f^\circ(\mathrm{MCl}_n)/n$ of the chloride complex compounds. The $\Delta H_f^\circ(\mathrm{MCl}_n)/n$ values directly reflect the ionic bonding strength between the metal cation and chloride anion in the salt phase and, by comparing both values, some information may be obtained for the nature of the intermetallic compounds MZn_x in the metal phase. As shown in Fig. 4, a good correlation has been observed between both values for trivalent lanthanides. This indicates that the intermetallic interaction between the lanthanides and zinc is of a similar type of bonding as of the cation–anion bonding, i.e., ionic bonding in the salt phase. In addition, it is interesting to note that a similar correlation is also obtained for actinides with no large gap between actinides and lanthanides. Of course, this is of the fact that the differences in the extractability values between actinides and lanthanides are not so large in the present liquid zinc system. On the contrary, in the liquid bismuth system in which the higher separation factors between both group elements have been observed[14], the stronger interaction is attained for actinides than lanthanides.

4. Conclusions

The reductive extraction behavior of actinides and lanthanides in a typical binary phase system of molten chloride and liquid zinc was studied and some conclusions were obtained as follows.

(1) In the LiCl–KCl/Zn system, actinides and lanthanides behaved as slightly different groups. The separation factors between both group elements are not so large even at lower temperatures and, from a technological point of view, the group partitioning of these elements seems less attractive in this system. The present results are much the same as those in the $\mathrm{LiF{-}BeF_2/Zn}$ system and no apparent difference in the separation factors has been observed due to different salt phases.

(2) The thermodynamic quantities of actinides and lanthanides in the liquid zinc phase were evaluated from the observed extractabilities, and some regularities were found for the standard Gibbs free energy of formation of the intermetallic compounds in the zinc phase due to their similar ionic nature to the complex compounds in the salt phase. Such regularities might be useful for predicting unknown extractability values.

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References

[1] A.M. Weinberg et al., Nucl. Appl. Technol. 8 (1970) 105.
[2] D.C. Wade, Y.I. Chang, Nucl. Sci. Eng. 100 (1988) 507.
[3] G.A. Jensen, A.M. Platt, G.B. Mellinger, W.J. Bjorklund, Nucl. Technol. 65 (1984) 305.
[4] K. Naito, T. Matsui, Y. Tanaka, J. Nucl. Sci. Technol. 23 (1986) 540.
[5] L.M. Ferris, J.C. Mailen, F.J. Smith, J. Inorg. Nucl. Chem. 32 (1970) 2019.
[6] L.M. Ferris, J.C. Mailen, F.J. Smith, J. Inorg. Nucl. Chem. 33 (1971) 1325.
[7] H. Moriyama, K. Yajima, Y. Tominaga, K. Moritani, J. Oishi, Nucl. Technol. 62 (1983) 133.
[8] H. Moriyama, K. Yajima, N. Nunogane, T. Ohmura, K. Moritani, J. Oishi, J. Nucl. Sci. Technol. 21 (1984) 949.
[9] H. Moriyama, N. Nunogane, J. Oishi, J. Nucl. Sci. Technol. 24 (1987) 120.
[10] J. Oishi, H. Moriyama, K. Moritani, S. Maeda, M. Miyazaki, Y. Asaoka, J. Nucl. Mater. 154 (1988) 163.
[11] H. Moriyama, K. Kinoshita, Y. Ito, J. Nucl. Sci. Technol. 27 (1990) 827.
[12] H. Moriyama, K. Kinoshita, Y. Asaoka, K. Moritani, Y. Ito, J. Nucl. Sci. Technol. 27 (1990) 937.
[13] H. Moriyama, K. Kinoshita, T. Seshimo, Y. Asaoka, K. Moritani, Y. Ito, in: Proc. of 3rd Int. Conf. on Nuclear Fuel

Reprocessing and Waste Management, Vol. 2, Sendai, 1991, p. 639.

[14] H. Moriyama, T. Seshimo, K. Moritani, Y. Ito, T. Mitsugashira, J. Alloys Compounds 213&214 (1994) 354.

[15] H. Moriyama, M. Miyazaki, Y. Asaoka, K. Moritani, J. Oishi, J. Nucl. Mater. 182 (1991) 113.

[16] J. Lumsden, Thermodynamics of Molten Salt Mixtures (Academic Press, London, 1966).

[17] V.A. Lebedev, Selectivity of Liquid Metal Electrodes in Molten Halides (in Russian).

[18] Y.-C. Kim, thesis, Kyoto University (1979).

[19] J.J. Katz, G.T. Seaborg, L.R. Morss, The Chemistry of the Actinide Elements, Vol. 2 (Chapman and Hall, London, 1986).

[20] I. Barin, O. Knacke, O. Kubaschewski, Thermochemical Properties of Inorganic Substances (Springer, Berlin, 1977).

[21] I. Johnson, R.M. Yonco, Metall. Trans. 1 (1970) 905.

[22] P. Chiotti, V.V. Akhachinskij, I. Ansara, M.H. Rand, The Chemical Thermodynamics of Actinide Elements and Compounds, Part 5, The Actinide Binary Alloys (IAEA, Vienna, 1981).