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Vaporization study on lanthanum–uranium and cerium–uranium alloys by mass-spectrometric method

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Abstract

The partial vapor pressures of La(g) and U(g) over La_xU_{1-x} alloys ($x = 0.01$, 0.02, 0.05, 0.20, 0.99) and Ce(g) and U(g) over Ce_xU_{1-x} alloys ($x = 0.01$, 0.02, 0.04, 0.10, 0.20, 0.97, 0.99) were measured with a time-of-flight mass-spectrometer equipped with a tungsten Knudsen cell over the temperature range between 1619 and 1886 K. The thermodynamic activities of lanthanum or cerium and uranium in the liquid alloys were calculated from the ion intensity ratios of two components (lanthanum or cerium and uranium) in the alloys using the equation derived by Belton and Fruehan. These systems were found to exist as the two phases in the wide compositional range and to exhibit positive deviations from ideal behavior. The Gibbs free energy of formation was calculated from the thermodynamic activity values. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

A molten salt electrorefining process has been adapted to separate the transuranium elements (TRU) from other fission products, mainly composed of rare earth elements. In this process, some rare earth elements are considered to be recovered together with uranium and TRU, since rare earth elements are chemically similar to uranium and TRU. The thermodynamic properties of uranium, TRU and rare earth elements are important to estimate separation efficiency among U, TRU and rare earth elements. However, only limited research has been reported on the solubility of rare earth-uranium systems [1]. This study has indicated that there exists a large miscibility gap between uranium and rare earth elements. In both the cerium–uranium and neodymium–uranium systems, a monotectics was reported to existed in the U–rich compositional region [1].

In this study, lanthanum (the light rare earth element, the number of 4f electrons of which is less than 8, and one of the main components of the fission products) and cerium (the light rare earth element and a possible stand-in for neptunium which is one of the main TRU elements) were selected among rare earth elements. The vapor pressures over the lanthanum–uranium and cerium–uranium systems were measured by mass-spectrometry in an attempt to derive the thermodynamic activities and the thermodynamic properties for the estimation of the thermodynamic stability of the rare earth-uranium systems.

2. Experimental

The metals used as starting materials for the preparation of the alloys were 99.9% pure lanthanum and cerium, and 99.98% pure uranium. The samples of La_xU_{1-x} alloys ($x = 0.01$, 0.02, 0.05, 0.20, 0.99) and Ce_xU_{1-x} alloys ($x = 0.01$, 0.02, 0.04, 0.10, 0.20, 0.97, 0.99) were prepared by mixing the respective pure

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metals in a desired proportion and melting them in a tungsten Knudsen cell installed in a mass-spectrometer. Oxygen contents in the lanthanum, cerium and uranium metals were determined to be in the range of 200–1500 ppm in mass by the mass-spectrometric evolved-gas analysis.

The vapor pressures of the alloys were determined with a time-of-flight mass-spectrometer (CVC model MA-2) equipped with a tungsten Knudsen cell, contained in a tungsten holder. The sample was heated in the tungsten holder by electron bombardment. The temperature was determined with a Leeds and Northrup disappearing-filament optical pyrometer, of which error was estimated to be within 10 K by comparison with the melting point of platinum metal and emf values of a Pt/Pt − 13% Rh thermocouple. The observation for the temperature measurement was made through an orifice of the Knudsen cell. The Knudsen cell had a 7 mm internal diameter, 7 mm in internal height and the diameter of the effusion orifice was 0.5 mm. The electron energy used to ionize the gaseous species was 12 eV. The absolute pressure of each gas species was determined by comparing the intensity of its ionic current with that of silver vapor over a pure silver metal [2]. The values of atomic ionization cross section of silver, lanthanum, cerium and uranium were taken from the table by Mann [3]. The relative multiplier gain was calculated by assuming inverse proportionality to the square root of the mass of the vaporizing species [4].

3. Results and discussion

3.1. Vapor pressure

The temperature dependence of vapor pressure of U(g) over pure metal U obtained in this study was in good agreement with that over pure metal reported previously [5–7]. The enthalpy of formation at 298 K was calculated by the second and the third law treatments. The second law enthalpy of formation at the median temperature of the measurements (ΔH_θ^0) was obtained directly from the slope of the logarithmic plot of the vapor pressure of U(g) versus inverse temperature and the difference between the heat content at the median temperature (H_θ) and that at the standard state (H_{298}):

$$\Delta_f H_{298}^0 = \Delta H_\theta^0 + (H_\theta - H_{298})_l - (H_\theta - H_{298})_g, \tag{1}$$

where $(H_\theta - H_{298})_l$ is the heat content difference of liquid uranium metal and $(H_\theta - H_{298})_g$ is that of uranium gas, both values of which have been assessed by Barin [8] and Hultgren [9]. The second law enthalpy of formation ($\Delta_f H_{298}^0$) was obtained to be 516.3 ± 19.1 kJ mol^{-1} for uranium in this study. The third law enthalpy was calculated as the averaged value of the standard enthalpies derived from each individual experimental data point with the relation

$$-(R \ln P_U + \Delta\text{fef})T = \Delta_f H_{298}^0, \tag{2}$$

where Δfef is the change in the free energy function. The free energy function has been assessed by Barin [8] and Hultgren [9]. The third law treatment includes smaller error than the second law treatment, as the third law value can be calculated from each data point. The third law enthalpy was obtained to be 530.7 ± 5.1 kJ mol^{-1} for uranium in this study, which was in good agreement with the literature values within the error (540.5 ± 8.4 kJ mol^{-1} [5], 529.2 ± 4.2 kJ mol^{-1} [6] and 539.7 ± 3.4 kJ mol^{-1} [7]). The enthalpies of formation for the lanthanum and cerium have been reported by the authors in preceding papers [10,11].

The experimental values of the ion intensity ratio for the liquid Ln–U alloys (Ln = La and Ce) are given in Figs. 1 and 2, respectively, as a function of reciprocal temperature. Since the ratio of the ion intensities of $La_{0.20}U_{0.80}$ is seen to be the same as those of $La_{0.05}U_{0.95}$, two phases are thought to coexist in these compositional

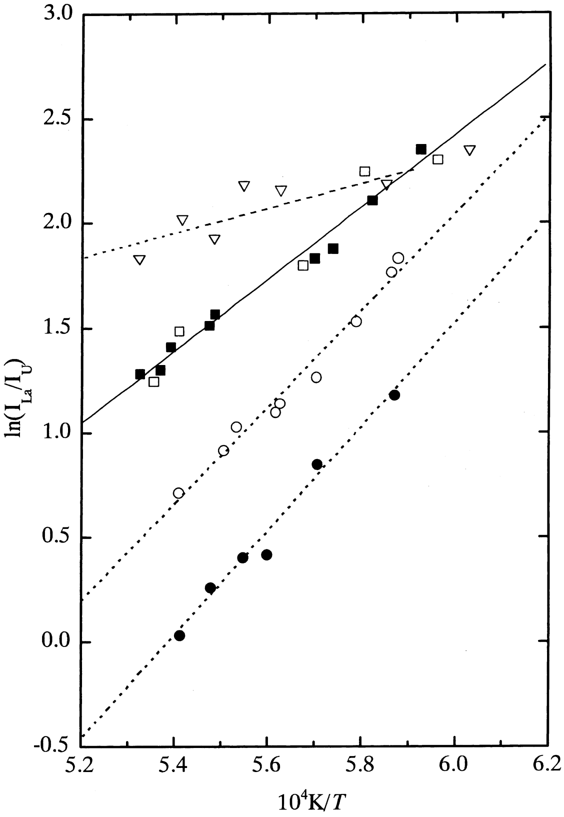

Fig. 1. Experimental intensity ratios for La–U system. (▽) $La_{0.99}U_{0.01}$, (■) $La_{0.20}U_{0.80}$, (□) $La_{0.05}U_{0.95}$, (○) $La_{0.02}U_{0.98}$, (●) $La_{0.01}U_{0.99}$.

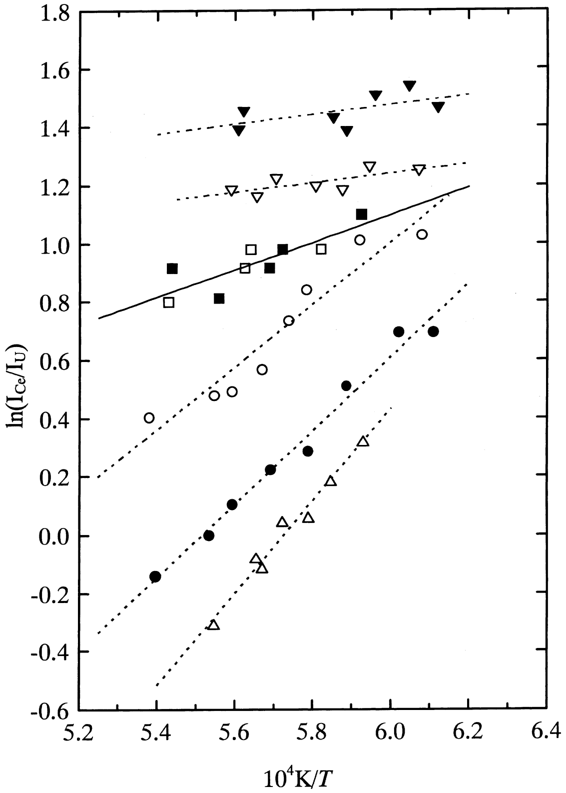

Fig. 2. Experimental intensity ratios for Ce–U system. (▼) $Ce_{0.99}U_{0.01}$, (▽) $Ce_{0.97}U_{0.03}$, (□) $Ce_{0.20}U_{0.80}$, (■) $Ce_{0.10}U_{0.90}$, (○) $Ce_{0.04}U_{0.96}$, (●) $Ce_{0.02}U_{0.98}$, (△) $Ce_{0.01}U_{0.99}$.

and temperature ranges. Transition temperatures from the two-phase coexistent region to a single phase region were obtained from the intersection points between the solid line and the dotted line shown in Figs. 1 and 2. The phase diagrams of the La–U and Ce–U systems are shown using the solubility limits, thus obtained, in Figs. 3 and 4 together with that reported by Haefling and Daane [1]. In these figures these Ln–U (Ln = La and Ce) systems are seen to have a large miscibility gap at high temperatures, such as from $x_{La} = 0.04$ to 0.99 for La_xU_{1-x} and from $x_{Ce} = 0.05$ to 0.95 for Ce_xU_{1-x}, both at 1773 K.

3.2. Thermodynamic quantities

3.2.1. Thermodynamic activities

The thermodynamic activities of the components can be calculated from the ion intensities using the following equation derived by Belton and Fruehan [12];

$$\ln(\gamma_i) = -\int_{x_i=1}^{x_i=x_i} x_j \mathrm{d}\left[\ln\left(\frac{I_j}{I_i}\right) - \ln\left(\frac{x_j}{x_i}\right)\right], \qquad (3)$$

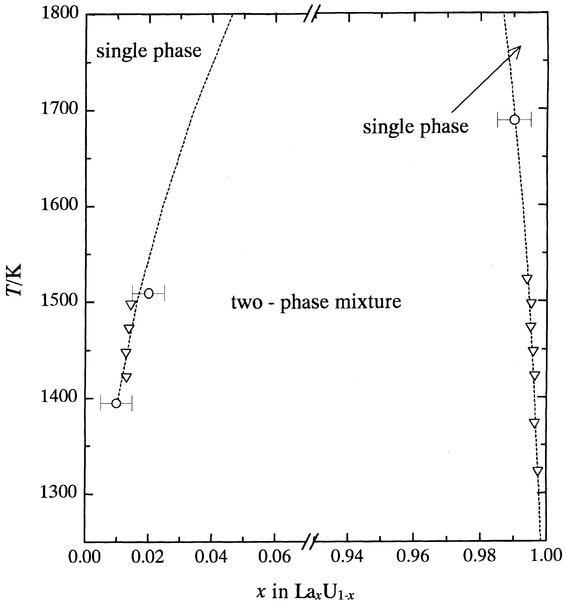

Fig. 3. The phase diagram of the La–U system. (▽) Haefling and Danne [1], (○) This study.

where γ_i, I_i, and x_i are the thermodynamic activity coefficient, ion intensity and mole fraction of component i, respectively.

The thermodynamic activity of lanthanum or cerium and uranium obtained in this study are shown in Figs. 5 and 6. These figures indicate that thermodynamic ac-

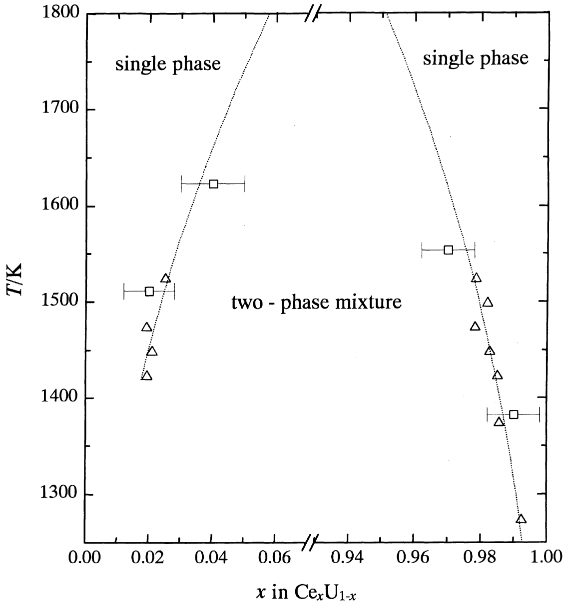

Fig. 4. The phase diagram of the Ce–U system. (△) Haefling and Danne [1], (□) This study.

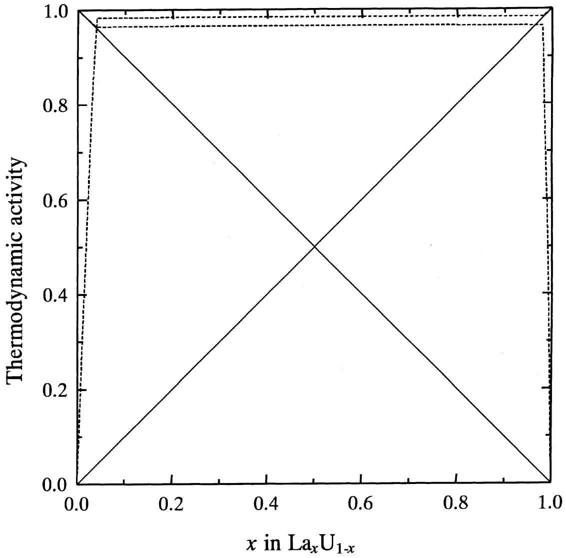

Fig. 5. Thermodynamic activities of La and U in the La–U systems at 1773 K. (- - - -) La–U system and (——) Raoult's law.

tivities of these systems have the positive deviation from Raoult's law, suggesting the presence of a repulsive interaction between Ln and U atoms in the alloys.

3.2.2. Gibbs free energies of formation and the excess free energies

The Gibbs free energy of formation ($\Delta_f G^0$) and the excess free energy (ΔG^{Ex}) of the lanthanum (or cerium)-uranium alloys can be calculated from thermodynamic activities and activity coefficients of the components by using the following Eqs. (4) and (5):

$$\Delta_f G^0 = x_{Ln} RT\ \ln(a_{Ln}) + x_U RT\ \ln(a_U), \tag{4}$$

$$\Delta G^{Ex} = x_{Ln} RT\ \ln(\gamma_{Ln}) + x_U RT\ \ln(\gamma_U), \tag{5}$$

where R is the gas constant and T the absolute temperature. The compositional dependences of the Gibbs free energy of formation and the excess free energy of mixing obtained in this study are shown in Fig. 7. The Gibbs free energies of formation of these alloys show minima in a U-rich compositional region.

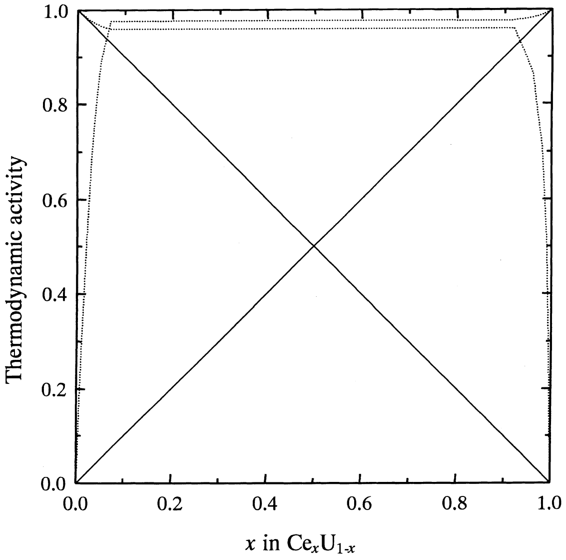

Fig. 6. Thermodynamic activities of Ce and U in the Ce–U systems at 1773 K. (·····) Ce–U system and (——) Raoult's law.

4. Conclusions

The vapor pressures of lanthanum (or cerium) and uranium over the lanthanum (or cerium)-uranium system were measured by means of mass-spectrometry. The phase diagrams determined from the vapor pressures indicates that these systems have wide two-phase coexistent regions, $x_{Ln} = 0.04$–0.99 for the lanthanum–ura-

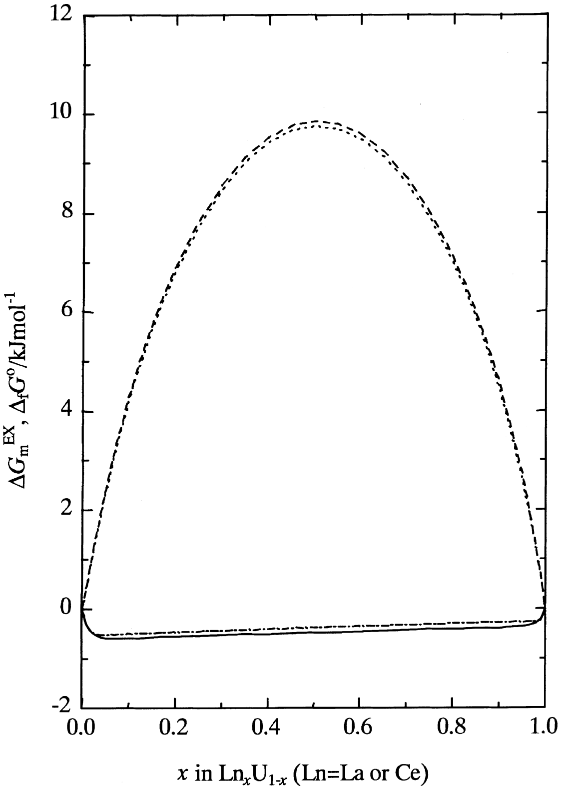

Fig. 7. The Gibbs free energy of formation and excess free energy for Ln–U alloys at 1773 K. La–U system (- - - -)ΔG^{Ex}, (-·-·-·-·-)$\Delta_f G^0$, Ce–U system (·········)ΔG^{Ex}, (——)$\Delta_f G^0$.

nium system and 0.05–0.95 for the cerium–uranium system, respectively, at 1773 K. The thermodynamic activities of the components showed markedly positive deviations from Raoult's law. From the Gibbs free energies of formation calculated from the thermodynamic activities, the alloys in a U-rich compositional region were found to be more stable compared to those with U-poor compositions.

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References

[1] J.F. Haefling, A.H. Daane, Trans. Met. Soc. AIME 215 (1959) 336.
[2] P.C. Marx, E.T. Chang, N.A. Gokcen, High Temp. Sci. 2 (1970) 37.
[3] J.B. Mann, in: K. Ogata, T. Hayakawa (Eds.), Recent Developments in Mass Spectroscopy, University of Tokyo Press, Tokyo, 1970, p. 814.
[4] P. Mahadevan, G.D. Manuson, J.K. Layton, C.E. Carlson, Phys. Rev. 140 (1965) A1407.
[5] A. Pattoret, J. Drowart, S. Smoes, Thermodynamics of Nuclear Materials, IAEA, Vienna, 1967, p. 613.
[6] R.J. Ackermann, E.G. Rauh, J. Phys. Chem. 73 (1969) 769.
[7] M. Kanno, M. Yamawaki, T. Koyama, N. Morioka, J. Nucl. Mater. 154 (1988) 154.
[8] I. Barin, Thermochemical Data for Pure Substances, VCH, Weinheim, Germany, 1989.
[9] R. Hultgren, R.L. Orr, D. Anderson, K.K. Kelley, Selected Values of the Thermodynamic Properties of Metals and Alloys, American Society for Metals, Ohio, 1974.
[10] Y. Shoji, T. Matsui, K. Nakamura, T. Inoue, J. Nucl. Mater. 254 (1998) 9.
[11] Y. Shoji, T. Matsui, K. Nakamura, T. Inoue, J. Nucl. Mater. 247 (1997) 37.
[12] G.R. Belton, R.J. Fruehan, J. Phys. Chem. 71 (1967) 1403.