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Vaporization behaviour of (Pu,Am)N

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Abstract

An unusual vaporization behaviour of plutonium and americium from a reactor grade PuN sample was found in a Knudsen cell effusion mass spectrometric analysis, where initially the mass-239 signal was much lower than the thermodynamic expectation while the mass-241 signal was significantly large. The observation was adequately explained with a thermodynamic model of $(Pu,Am)N_{1-x}$. The analysis was based on a working hypothesis that the Gibbs free energy of formation of AmN is not so different from those of UN, PuN and LaN. The agreement of the calculation and observation supported this hypothesis. The second-law enthalpy of formation of AmN was estimated to be -294 kJ mol^{-1} at 1600 K from the measured vapour pressure of Am over the PuN sample.

Keywords: Americium nitride; Plutonium nitride; Vapour pressure; Free energy of formation; Enthalpy of formation

1. Introduction

Americium is a common impurity in plutonium, since ^{241}Am is the daughter of the isotope ^{241}Pu. Besides, americium, which is of long-term concern in nuclear waste disposal, may be intentionally added to uranium–plutonium fuels for nuclear "incineration" [1]. Therefore knowledge on the americium behaviour in the fuels is pertinent for the future development of nuclear technology. Americium has a special position in the actinide series with its very stable $5f^77s^2$ configuration in the gaseous ground state. The result is a much higher vapour pressure of americium than of the neighbouring elements in the periodic table.

This high vapour pressure of americium is a potential problem in manufacturing fuels regardless of their chemical forms. It may also affect the performance of americium-added fuels. For instance, Ohmichi et al. [2,3] have observed a significant loss of americium during (U,Pu)C fabrication by carbothermic reduction. This is readily explained by a lower thermodynamic stability of Am_2C_3 [4]. The evaporated americium contaminates the apparatus in the fabrication line. On the other hand, the process could be utilized for removing γ-emitting ^{241}Am from plutonium for easier handling at later manufacturing stages [5].

For intentionally adding americium to the fuel, this evaporative loss should be minimized. For nuclear "incineration", the oxides [6], nitrides [7] and alloys [8] have been proposed as candidate fuel forms. This study deals with the americium vaporization behaviour from (Pu,Am)N. The properties of AmN are mostly undefined; only its crystal structure and lattice constant are known. The NaCl-type crystal structure is the same as that of the other mononitrides of the actinides and lanthanides and its lattice parameter of 0.4995 ± 0.0005 nm [9–12] is slightly larger than that of PuN and close to that of GdN.

Recently we have measured the plutonium vapour pressure over PuN and (U,Pu)N by a Knudsen cell effusion mass spectrometric analysis [13]. The raw material was a reactor grade plutonium which originally contained 75.2% ^{239}Pu and 3.4% ^{241}Pu, the balance being the other plutonium isotopes. The Am content had increased to 1.3 at.% owing to the decay of ^{241}Pu by the time of the measurements. The PuN sample was fabricated by carbothermic reduction of PuO_2 in flowing N_2–8%H_2 at 1850 K. The sample contained 500 and 600 ppm of oxygen and carbon respectively.

A significantly large ion signal of mass 241 was noted in the initial heating run, during which the signal of mass 239 was anomalously low. Eventually the mass-241 signal subsided and the mass-239 signal reached a level which is in accord with the expectation from the thermodynamic properties of PuN in the literature. The ion signals were recorded after the initial heating

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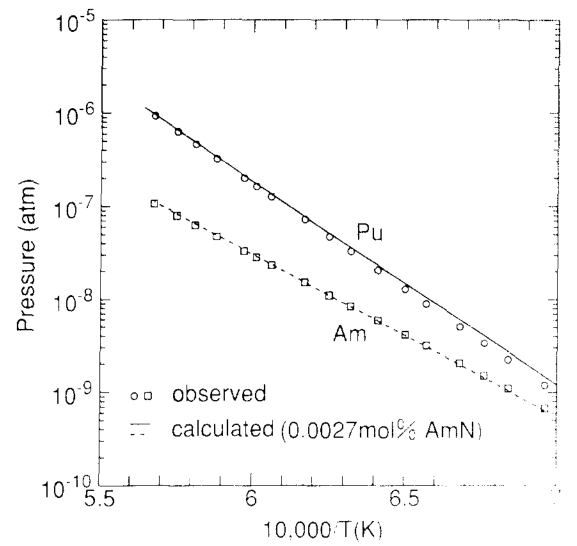

Fig. 1. Observed partial pressures of Pu and Am over a reactor grade PuN sample (open symbols). The measurements were made after the mass-241 signal had subsided (see text). The calculation assumes an AmN content of 0.0027 mol.%.

run where significantly large signals of mass 241 and anomalously low signals of mass 239 were observed. This is because the mass-241 signal was regarded as nothing but an undesired interference in measuring the Pu vapour pressure. Fig. 1 shows the partial pressures of Pu and Am (open symbols) which were obtained in a subsequent cooling run after the initial burst of the mass-241 signal had subsided.

Later it was considered that the above observation can be used as a basis for the estimation of thermodynamic properties of AmN. The analysis of the vaporization behaviour is described below.

2. Analysis

A high nitrogen partial pressure during the reaction to form the nitride would have suppressed the evaporative loss of americium. The situation is different in the vapour pressure measurements where the PuN sample was heated in vacuum.

Fig. 2 shows the partial pressures of plutonium and nitrogen over PuN_{1-x} at 1473 K which were calculated by the model in Ref. [14]. If the sample is very pure and stoichiometric PuN, it will first become depleted of nitrogen until the congruent vaporizing composition is reached. Congruency is attained when $p(Pu)/p(N_2) = 2(239)^{1/2}/(28)^{1/2} = 5.84$. A pure AmN sample is expected to show a similar behaviour for the following reason. The ratio $p(Am)/p(Pu)$ of metal vapour pressures of AmN and PuN at a given nitrogen partial pressure $p(N_2)$ should be roughly the same as $p^\circ(Am)/p^\circ(Pu)$ of elemental Am and Pu in vacuum, as long as the Gibbs free energies of formation of the nitrides, $\Delta G_f^\circ(MN)$, are not so different from each other. The vapour pressure $p(M)$ over a metal nitride MN is given by

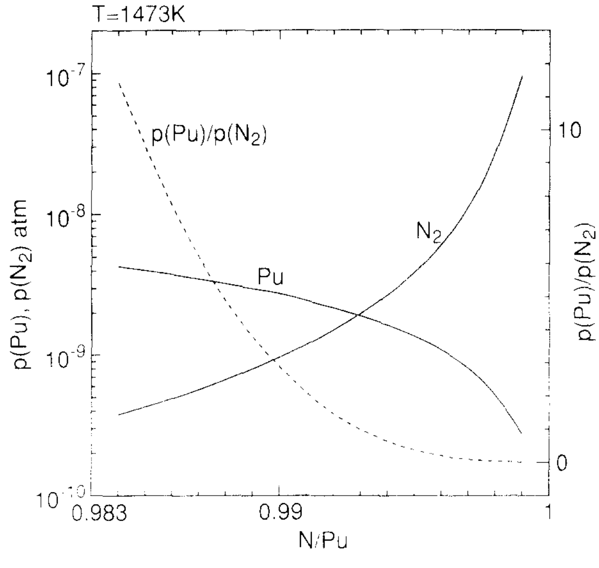

Fig. 2. Partial pressures of Pu and N_2 over PuN as a function of composition N/Pu at 1473 K by the model in Ref. [14].

$$\langle MN \rangle = (M) + \tfrac{1}{2}(N_2) \qquad (1)$$

$$RT \ln a(M) = RT \ln\left(\frac{p(M)}{p^\circ(M)}\right) = \Delta G_f^\circ(MN) - \tfrac{1}{2}RT \ln p(N_2) \qquad (2)$$

Therefore one can predict that the congruent vaporization of AmN, $p(Am)/p(N_2) \approx 5.87$, is realized at a higher $p(N_2)$ than that of PuN, since $p^\circ(Am) \gg p^\circ(Pu)$. The following analysis was made in order to verify this prediction and to compare it with the experimental observation.

Substoichiometric PuN–AmN solid solutions $(Pu, Am)N_{1-x}$ were treated by a sublattice formalism [14] wherein plutonium and americium atoms are on the metal sublattice and the nitrogen atom and its vacancy (V) on the non-metal sublattice of the NaCl-type structure. The excess free energy of mixing is given as a function of site occupation fractions Y_{Mi} and Y_{Nj} on the metal and non-metal sublattices respectively:

$$\Delta^E G = \sum_{i=1}^{2} Y_{Mi} L_{Ni} Y_{N1} Y_{N2} + \sum_{j=1}^{2} Y_{Nj} L_{Mj} Y_{M1} Y_{M2} \qquad (3)$$

where the Ls are interaction parameters. It is also assumed that

$$Y_{N1} + Y_{N2} = 1 \qquad (4)$$

$$Y_{M1} + Y_{M2} = 1 \qquad (5)$$

Table 1 gives the pertinent parameters. In the table PuV and AmV denote hypothetical species which have the structure of a mononitride with the vacant nitrogen sublattice. $\Delta G_f^\circ(AmN)$ is estimated by assuming

Table 1
Parameters for the equilibrium calculation

Species	ΔG_f° (J mol^{-1})
Pu (g)	$331873-92.108T$
Am (g)	$248006-107.552T$
PuN	$-296691+84.366T$
PuV	$-4770+5.690T$
AmN	$-297659+92.054T$
AmV	0
Pair	**L (J mol^{-1})**
PuV–PuN	$-60800+46.4T$
AmV–AmN	0
PuN–AmN	0
PuV–AmV	0

$\Delta H_{f,298}(\text{AmN}) = \Delta H_{f,298}(\text{PuN})$ and $\Delta C_p(\text{AmN}) = \Delta C_p(\text{UN})$ to 923 K. $\Delta G_f^\circ(\text{AmN})$ in the table is a working equation in the total absence of thermodynamic data on AmN. Its appropriateness is discussed later. The parameters for PuN_{1-x} were obtained from a previous study of $(\text{U,Pu})\text{N}_{1-x}$ [14]. The thermodynamic properties of gaseous americium were taken from Ref. [15]. The equilibria were calculated with the Gibbs free-energy minimizer ChemSage [16]. No particular efforts were made to fit the parameters to the experimental observation, but the latter was well reproduced by the calculation.

3. Results and discussion

3.1. Vaporization behaviour of (Pu,Am)N

In Fig. 1 the solid and broken lines are the calculated partial pressures of Pu and Am respectively which were estimated at the N/(Pu + Am) atom ratios where congruency of the PuN component is attained. The calculation agrees well with the observation but assumes that the AmN concentration is 0.0027 mol.%, which is much lower than that originally contained in the sample.

The initial burst of americium vapour and the resulting depletion of americium can be understood as follows. In the analysis shown in Fig. 3 a nearly stoichiometric $(\text{Pu}_{0.99}\text{Am}_{0.01})\text{N}$ sample is assumed to be kept at a given temperature, say 1473 K, for a sufficiently long time. An underlying physical fact is that the diffusion coefficient of the nitrogen atom in the nitride is much larger than those of actinide metal atoms. Then the sample will experience three stages.

Stage I: $N/(Pu+Am) > 0.9976$ at 1473 K

Nitrogen is preferentially lost from the surface. With a small loss of nitrogen the ratio N/(Pu + Am) reaches a point where congruent vaporization of the AmN component occurs.

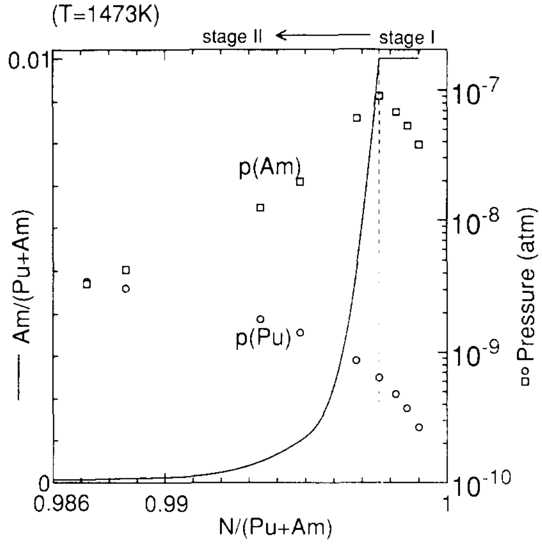

Fig. 3. Predicted change in composition (solid curve) and partial pressures (open symbols) when $(\text{Pu}_{0.99}\text{Am}_{0.01})\text{N}$ is kept at 1473 K for a sufficiently long time. The change in partial pressures upon heating to higher temperatures is shown in Fig. 4.

Stage II: $0.9976 > N/(Pu+Am) > 0.9855$ at 1473 K

Americium and nitrogen vs. plutonium are preferentially lost. The solid curve in Fig. 3 represents the compositions where congruency of the AmN component is realized. A faster solid state diffusion of nitrogen can quickly adjust the surface concentration to restore the congruency at each new americium content. The vapour pressure p(Pu) increases with decreasing nitrogen content, while p(Am) decreases owing to surface depletion of the AmN component.

Stage III: $N/(Pu+Am) \approx 0.9855$ at 1473 K

The N/(Pu + Am) ratio reaches a point where the PuN component, which is in great excess, vaporizes congruently. Little change in the composition and partial pressures will occur once this point is reached. If the temperature is raised from this point, p(Pu) and p(Am) will change as shown in Fig. 4. Congruency of the PuN component will be realized with little nitrogen loss as the temperature is raised. The difference between Figs. 1 and 4 lies in the AmN contents.

In the actual vapour pressure measurements, unlike in the model case, the sample was not isothermally annealed. Therefore it is difficult to estimate the degree of surface depletion of the AmN component when congruency of the PuN component is eventually obtained. The depletion should be a function of the temperature history. However, the above discussion on Fig. 3 illustrates the mechanism of the burst of americium vapour and the surface depletion of the AmN component. It should also be noted that the composition

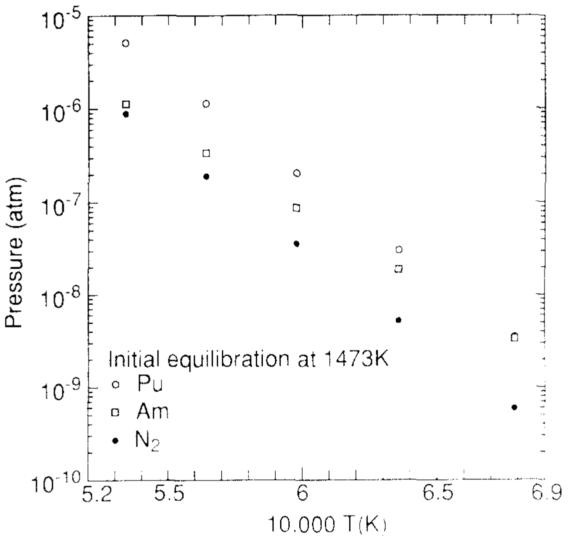

Fig. 4. Arrhenius plot of partial pressures of Pu, Am and N_2 over PuN containing 0.007 mol.% AmN.

for congruency of the PuN component is approximately independent of the AmN concentration when the latter is sufficiently small (compare p(Pu) in Figs. 2 and 3). Actually, p(Pu) in Fig. 1 agrees with that obtained by Kent and Leary [17], who used plutonium of a higher isotopic purity (97.7% ^{239}Pu and 0.07% ^{241}Pu).

3.2. *Enthalpy of formation of AmN*

The above analysis showed the appropriateness of the working equation for ΔG_f°(AmN) in Table 1. With its metallic ground state of f^6ds^2 or f^6dsp and nearly localized f-electrons, americium resembles the lanthanides rather than the lighter actinides in various properties. It is worth noting, however, that ΔG_f° and $\Delta H_{f,298}^\circ$ of LaN [18] are close to those of UN and PuN [19].

The second-law enthalpy of formation of AmN can be directly estimated from the experimental data in Fig. 2 without assuming the surface concentration of AmN in the PuN sample. It is, however, necessary to assume that the surface concentration of the AmN component is constant and that the interaction between the AmN and PuN components is nearly ideal. The value of p(Pu) in Fig. 2 yields $p(N_2)$ by the condition of congruency of the PuN component:

$$\ln p(N_2)\ (\text{atm}) = 13.7409 - \frac{51808}{T} \qquad (6)$$

The observed p(Am) is fitted as

$$\ln p(\text{Am})\ (\text{atm}) = 6.2345 - \frac{39289}{T} \qquad (7)$$

Then the equilibrium constant K_p for the formation of AmN in PuN via

$$(\text{Am}) + \tfrac{1}{2}(N_2) = [\text{AmN}]_{\text{PuN}} \qquad (8)$$

is given by

$$\ln K_p = \ln p(\text{Am}) + \tfrac{1}{2}\ln p(N_2) = -13.1050 + \frac{65193}{T} \qquad (9)$$

The temperature dependence of K_p gives the enthalpy of formation of AmN from gaseous americium and nitrogen as

$$\Delta H_T = -R\,\frac{d(\ln K_p)}{d(1/T)}$$
$$= -542\ \text{kJ mol}^{-1} \qquad (T_{AV} = 1600\ \text{K}) \qquad (10)$$

Combining this value with ΔG_f° of gaseous americium in Table 1, the enthalpy of formation of AmN from N_2 and liquid americium at 1600 K is estimated to be -294 kJ mol^{-1}. For comparison, the standard enthalpies of formation $\Delta H_{f,298}^\circ$ of UN [19], PuN [19] and LaN [18] are -296, -299 and -301 ± 38 kJ mol^{-1} respectively.

4. Conclusions

An unusual vaporization behaviour of plutonium and americium from a PuN sample was adequately explained with a thermodynamic model of (Pu,Am)N_{1-x}. The agreement of the calculated and observed behaviour supports the working hypothesis that the Gibbs free energy of formation of AmN is not so different from those of the nitrides of other lanthanides and lighter actinides. The second-law enthalpy of formation of AmN was estimated to be -294 kJ mol^{-1} at 1600 K from the vapour pressure of Am over the PuN sample. The estimated enthalpy of formation is close to those of UN, PuN and LaN. The estimation, however, is based on a few assumptions. Further study on the vaporization of (Pu,Am)N is planned to clarify the americium behaviour in detail.

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References

[1] L. Koch, Formation and recycling of minor actinides in nuclear power stations, in A.J. Freeman and C. Keller (eds.), *Handbook on the Physics and Chemistry of the Actinides,* Elsevier, Amsterdam, 1986, pp. 457–489.

[2] T. Ohmichi, Y. Suzuki, Y. Arai, T. Sasayama and A. Maeda, *J. Nucl. Mater., 139* (1986) 253.

[3] T. Ohmichi, S. Nomura and A. Maeda, *J. Nucl. Sci. Technol., 22* (1985) 329.

[4] C.E. Holley Jr., M.H. Rand and E.K. Storms, *The Chemical Thermodynamics of Actinide Elements and Compounds Pt. 6; The Actinide Carbides,* International Atomic Energy Agency, Vienna, 1984.

[5] T. Ohmichi, S. Nomura and A. Maeda, *Jpn. Patent H4-58593,* 1992.

[6] M. Salvatores, C. Prunier, Y. Guerin, A. Zaetta and I. Slesarev, *Proc. Int. Conf. and Technol. Expo. on Future Nuclear Systems: Emerging Fuel Cycles and Waste Disposal Options Global '93,* American Nuclear Society, 1993, pp. 548–554.

[7] T. Mukaiyama, H. Takano, T. Takizuka, T. Ogawa, H. Yoshida and Y. Gunji, *Trans. ANS, 84* (1991) 548.

[8] T. Inoue, M. Kurata, L. Koch, J.C. Spirlet, C.T. Walker and C. Sari, *Trans. ANS, 84* (1991) 552.

[9] J.P. Charvillat, U. Benedict, D. Damien, C.H. de Novion, A. Wojakowski and W. Muller, in W. Muller and R. Lindner (eds.), *Transplutonium Elements,* North-Holland, Amsterdam, 1976.

[10] D.A. Damien, R.G. Haire and J.R. Peterson, *Conf-780823-8,* 1978.

[11] V.M. Radchenko, M.A. Ryabinin, A.G. Seleznev, E.B. Shimbarev, L.V. Sudakov, I.I. Kapshukov and B.Ya. Vashiliev, *Radiochimiya,* (2) (1982) 173.

[12] Y. Akimoto, *J. Inorg. Nucl. Chem., 29* (1967) 2650.

[13] Y. Suzuki, A. Maeda, Y. Arai and T. Ohmichi, *J. Nucl. Mater., 188* (1992) 239.

[14] T. Ogawa, *J. Nucl. Mater., 201* (1993) 284.

[15] F.L. Oetting, M.H. Rand and R.J. Ackermann, *The Chemical Thermodynamics of Actinide Elements and Compounds Pt. 1; The Actinide Elements,* International Atomic Energy Agency, Vienna, 1976.

[16] G. Eriksson and K. Hack, *Metall. Trans. B, 21* (1990) 1013.

[17] R.A. Kent and J.A. Leary, *Los Alamos Scientific Laboratory Rep. LA-3902,* 1968.

[18] K.A. Gschneidner Jr. and N. Kippenhan, Thermochemistry of the rare earth carbides, nitrides and sulfides for steelmaking, *Iowa State University Rep. IS-RIC-5,* 1972.

[19] T. Matsui and R.W. Ohse, *High Temp.-High Press., 19* (1987) 1.