ESTIMATIONS OF HEAT CAPACITIES FOR ACTINIDE DIOXIDE: UO$_2$, NpO$_2$, ThO$_2$, AND PuO$_2$

E. ESER[1*], H. KOC[2], M. GOKBULUT[3], and G. GURSOY[4]

[1]Department of Physics, Polatlı Faculty of Arts and Sciences, Gazi University, Polatlı, Ankara, Turkey
[2]Department of Electricity and Energy, Vocational School, Muş Alparslan University, Muş, Turkey
[3]Department of Physics, Faculty of Arts and Sciences, Gaziosmanpaşa University, Tokat, Turkey
[4]Department of Medical Services and Technical, Vocational School of Health Services, Ahi Evran University, Kırşehir, Turkey
[*]Corresponding author. E-mail : eserphy@gmail.com

The evaluation of thermal properties of actinide oxide fuels is a problem of high importance for the development of new generation reactors. In the present study, an expression obtained for n-dimensional Debye functions is used to derive a simple analytical expression for the specific heat capacity of nuclear fuels. To test the validity and reliability of this expression, the analytical expression is applied to UO$_2$, NpO$_2$, ThO$_2$, and PuO$_2$. It is seen that the formula was in agreement with the experimental and theoretical results reported in the literature.

KEYWORDS : Nuclear Fuels, Minor Actinide, Temperature Dependence, Uranium Dioxide, Debye Functions

1. INTRODUCTION

The minor actinide (MA: Np, Am, Cm) oxides, which affect the properties of nuclear fuels, are produced from uranium and plutonium fuel materials in nuclear reactors by decay and neutron capture (Minato et al., 2009; Sobolev, 2009; Kurosaki et al., 2011, 2004, 2005). The MA compounds containing mixed oxide fuels are candidates for advanced nuclear fuels for fast breeder reactors, transmutation systems including critical reactors, and accelerator-driven systems (ADS) (Kurosaki et al., 2004; Aizawa, 2002; Wakabayashi, 2002; Ait Abderrahim et al., 2001). Therefore, it is important to determine the properties of MA oxides such as their specific heat capacity, which is one of the most decisive thermal properties and it determines the thermal behavior in heat generating materials.

However, because of the difficulties related to the high radiation fields (Sobolev, 2009; Kurosaki et al., 2004), knowledge about the properties of these oxides is very scarce, and is also limited to only a few properties: specific heat capacity, thermal expansion, thermal conductivity, etc. (Minato et al., 2009; Sobolev, 2009; Kurosaki et al., 2004; Sobolev and Lemehov, 2006). In this manner, a lot of theoretical (Sobolev, 2005, 2009; Sobolev and Lemehov, 2006; Kurosaki et al., 2004; Koç et al., 2011; Terentyev, 2007; Li et al., 2002; Minamoto et al., 2009; Carbajo et al., 2001; Fink, 2000; Bakker et al., 1997) and experimental (Minato et al., 2009; Chollet et al., 2012; Benes et al., 2011; Yamashita et al., 1997; Serizawa et al., 2001;

Serizawa and Arai, 2000; Nishi et al., 2008; Ruello et al., 2005; Agarwal et al., 2003; Ho Kang et al., 2002) studies have been made to determinate the thermophysical properties of MAs.

Kurosaki et al. (2004) calculated the thermophysical properties of minor actinide dioxides using the molecular dynamics (MD) model. Fink (2000) has reviewed the experimental data related to UO$_2$ to obtain consistent equations for its thermodynamic properties. Carboja et al. (2001) studied the thermophysical properties of UO$_2$ and MOX fuels. Minato et al. (2009) measured the lattice parameters and thermal expansion of MA compounds by using high-temperature X-ray diffractometry and the specific heat capacity by drop calorimetry. Serizawa and Arai(2000) calculated the Debye temperature and the Gruneisen constant from the temperature dependence of the Debye temperature for some actinide dioxides. Sobolev (2005) obtained an equation of state (EOS) for actinide dioxide fuels using a combination of macroscopic and microscopic approaches. The model was first tested with a calculation of the specific heat and the coefficient of thermal expansion of various nuclear fuels.

In this study, the analytical expression presented in Mamedov et al. (2009) with the Debye approximation is used to derive a simple analytical expression for the specific heat capacities of nuclear fuels. To test the validity and reliability of this expression, it is applied to UO$_2$, NpO$_2$, ThO$_2$, and PuO$_2$ nuclear fuels.

2. METHODS

The constant-volume and –pressure heat capacities in the Debye approximation are respectively defined as (Nernst and Lindemann, 1911; Debye, 1912; Ghatak et al, 2009; Passler, 2008):

$$C_V(T) = 3n_A R B_3(2, x_D) \tag{1}$$

$$C_P(T) = \frac{T_m}{2A_0 T}\{1 - [1 - 4A_0(T/T_m)C_V(T)]^{1/2}\}. \tag{2}$$

Where R is the gas constant, T is the absolute temperature, n_A is the number of atoms in a molecule of the material, $A_0 = 5.1 x 10^{-3}$ J^{-1} $Kmol$, and T_m is the melting temperature. If the square root in Equation 2 expands conveniently into a Taylor series expansion, the resultant equation is:

$$C_P(T) = C_V(T) + A_0[C_V(T)]^2 \frac{T}{T_m}. \tag{3}$$

In Equations 1-3, $B_n (\beta, x_D)$ is the n-dimensional second kind Debye integral, which is defined as (Sobolev, 2005; Koç et al., 2011):

$$B_n(\beta, x_D) = \frac{n}{n+1} x_D [D_{n+1}(\beta - 1, x_D) + D_{n+1}(\beta, x_D)] \tag{4}$$

and $x_D = \theta_D/T$, where θ_D is the Debye temperature and $D_n (\beta, x_D)$ is the generalized n-dimensional Debye function, which is given as (Mamedov et al., 2009; Guseinov and Mamedov, 2007):

$$D_n(\beta, x_D) = \frac{n}{x_D^n} \int_0^{x_D} \frac{x^n}{(e^x-1)^\beta} dx. \tag{5}$$

It can be seen from Equations 1 and 2 that the choice of reliable formulas for the evaluation of n-dimensional Debye functions is of prime importance in the accurate calculation of C_V and C_P heat capacities for nuclear fuels.

So far, Dubinov and Dubinova (2008) obtained the exact explicit integral-free expressions for the integral Debye functions and an integral-free expression for the heat capacity of the n-dimensional crystals. Sonmezoglu (2008) found an analytical relation for the thermodynamic functions calculated in terms of the Debye temperature using incomplete gamma functions. Further, Guseinov and Mamedov (2007) have derived an analytical expression

for the evaluation of integer and non-integer n-dimensional Debye functions.

The analytical expression suggested for the calculation of the n-dimensional Debye function in the previous article is as follows (Mamedov et al., 2009):

$$D_n(\beta, x_D) = \frac{n}{x_D^n} \lim_{N\to\infty} \sum_{l=0}^N (-1)^l F_l(-\beta) H_{nl}(\beta, x_D). \tag{6}$$

Here, $F_m(n) = n!/([m!(n - m)!])$ is the binomial coefficient and $H_{nl}(\beta, x_D)$ is defined as (Mamedov et al., 2009):

$$H_{nl}(\beta, x_D) = n! \left[1 - e^{-x_D w} \left(\sum_{k=0}^n \frac{(x_D w)^k}{k!}\right)\right] w^{-(n+1)} \tag{7}$$

A detailed derivation of the formulas mentioned above can be found in a previous report by the current authors (Mamedov et al., 2009). Substituting Equation 1 into Equations 3 and 4, the simply-structured formula for the specific heat capacity C_P and the thermal expansion can be obtained as follows:

$$C_P(T) = 3n_A R B_n(2, x_D) \left\{1 + 3n_A A_0 R \left(\frac{T}{T_m}\right) B_n(2, x_D)\right\}, \tag{8}$$

For the oxides considered in this article, the values of Debye temperature and the melting temperature used in the calculations are presented in Table 1.

3. RESULTS AND DISCUSSION

In the present study, the C_P heat capacity of UO$_2$, NpO$_2$, ThO$_2$, and PuO$_2$ nuclear fuels have been calculated using Equation 7. The heat capacity of UO$_2$, NpO$_2$, ThO$_2$, and PuO$_2$ are shown in Figs.1-4, together with those of the literature (Carbajo et al., 2001; Sobolev and Lemehov, 2006; Sobolev, 2009; Fink, 1982, 2000; MATPRO, 1993; Kruger and Savage, 1968; Agarwal et al., 2003; Kurosaki et al., 2001; Fredrickson and Chasanov, 1970; SGTE, 1996; MALT, 1992; Hiernaut et al., 1993; Southard, 1941; Barin, 1995; Yamashita et al., 1997; Nishi et al., 2008; Serizawa, 2000, 2001; Bakker et al., 1997).

The calculated heat capacities of UO$_2$ nuclear fuel in comparison with the data available in the literature are seen in Fig. 1 (Carbajo et al., 2001; Fink, 2000; MALT, 1992; Fredrickson and Chasanov, 1970; SGTE, 1996; Hi-

Table 1. Debye Temperature and the Melting Temperature for Actinide Dioxides

Material	$\theta_D(K)$	$T_m(K)$
UO$_2$	377 (Willis, 1963)	3138 (Latta et al., 1970)
NpO$_2$	435 (Serizawa et al., 1999)	2820 (Richter and Sari, 1987)
ThO$_2$	393 (Willis, 1963)	2820 (Loeven et al., 2000)
PuO$_2$	415 (Roof, 1960)	2663 (Golovnin, 2000)

ernaut et al., 1993). It can be seen from Fig.1 that a good agreement is achieved for UO₂. Especially, the results obtained are in agreement with the results of Carbajo et al. (2001), Fink (2000), Fredrickson and Chasanov (1970), SGTE (1996), Hiernaut et al. (1993). The harmony between the results increases at high temperatures. For example, at 750 K, the calculated result is 80.795 J/K. mol and the results of the other studies are 82.00 J/K.

mol (Carbajo et al., 2001), 80.985 J/K.mol (Fredrickson, 1970), 80.531 J/K.mol (SGTE, 1996), and 81.496 J/K. mol (Fink, 2000).

The heat capacity of NpO₂ is shown in Fig. 2. The values obtained from the literature (Sobolev, 2009; Yamashita et al., 1997; Serizawa and Arai, 2000; Serizawa et al., 2001; Nishi et al., 2008; Barin, 1995) are also included in Fig. 2. The heat capacity data for NpO₂ increases significantly
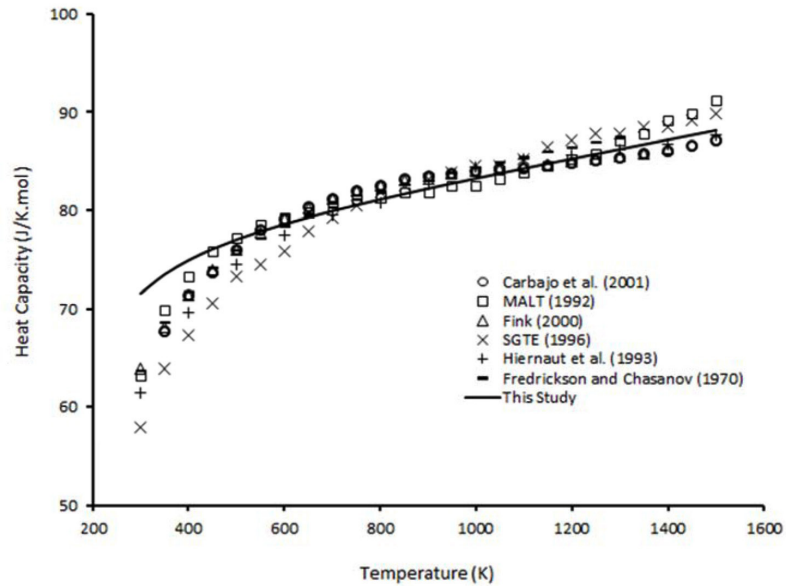

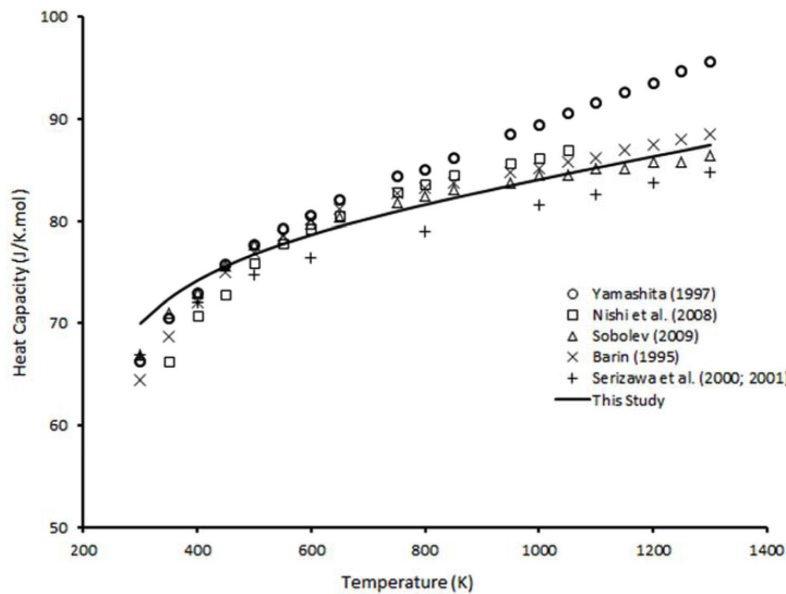Fig. 1. The Temperature Dependence of C_P Heat Capacity of UO₂.

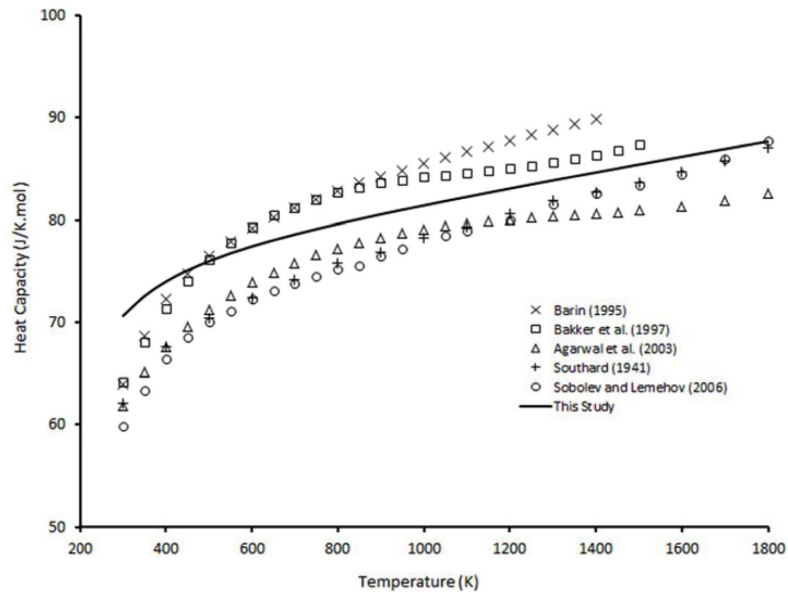Fig. 2. The Temperature Dependence of C_P Heat Capacity of NpO₂.

Fig. 3. The Temperature Dependence of C_P Heat Capacity of ThO_2.

with temperature. The agreement is good at T ≥ 450 K, especially those of Sobolev (2009), Barin (1995), Serizawa et al. (2001), Serizawa and Arai (2000), and Nishi et al. (2008). The remarkable uncertainty is also observed with the results of Yamashita et al. (1997) and, the largest uncertainty is 8.45% at 1300 K. This uncertainty can be an indication of a supplementary anharmonic contribution that was not taken into account in the model. Knowledge about this has previously been reported by Serizawa et al. (2001). Consequently, the agreement and stability of the method for NpO_2, as with UO_2, are satisfactory.

The heat capacities of ThO_2 obtained in this study are compared with those reported in the literature (Sobolev and Lemehov, 2006; Bakker et al., 1997; Agarwal et al., 2003; Barin, 1995; Southard, 1941) in Fig. 3. The calculations were performed in the temperature range 300 - 1800 K. It can be said that the calculated results moderately agree with the literature results. For example, at 400K the calculated result is 73.986 J/K.mol and the reported results are 72.302 J/K.mol (Barin, 1995), 71.384 J/K.mol (Bakker et al., 1997), 67.584J/K.mol (Agarwal et al., 2003), 66.367 J/K.mol (Sobolev and Lemehov, 2006) and 67.605 J/K.mol (Southard, 1941). The variation between the calculated and literature results for ThO_2 also is remains constant with increasing temperature. The biggest deviation between our calculations and the literature results is at 300K and equals 15.31% (Sobolev and Lemehov, 2006). After 700K, the value of deviation gradually increases with elevating temperature. This behavior could be explained by a supplementary contribution. Therefore, a more detailed analysis is needed to explain this effect.

The computational results of the temperature depend-

ence of the heat capacity are shown in Fig. 4 for PuO_2. The values obtained from the literature (Kurosaki et al., 2001; Carbajo et al., 2001; MATPRO, 1993; Oetting, 1982; SGTE, 1996; Kruger and Savage, 1968; Fink, 1982) are also plotted in Fig. 4. As seen from the figure, the obtained results are roughly in agreement with the relevant literature data on PuO_2 nuclear fuel. The results obtained at high temperatures are more satisfactory than those obtained at low temperatures. The maximum variation in the value is about 19% in the temperature range from 300 to 550 K. The disagreement of specific heat at the medium temperature has also been reported by Sobolev (2005). As Sobolev (2005) pointed out, the difference between the calculated and the experimental heat capacity in this temperature range is still a problem. Some models have been suggested to improve the disagreement (Minamoto et al., 2009; Stan and Cristea, 2004; Latta and Fryxell, 1970).

4. CONCLUSION

In conclusion, using the Debye model we have presented calculations of the heat capacity of nuclear fuels with various temperatures, ranging from low to melting temperatures. This method is completely generic and free of any restrictions on its application to analyze the thermophysical properties of nuclear fuels. It was observed that the agreement with benchmark computational and literature results and stability of the method are satisfactory for nuclear fuels, especially UO_2 and NpO_2. Consequently, by using the Debye approximation, the analytical expression obtained in the present paper can be used in the study of total internal
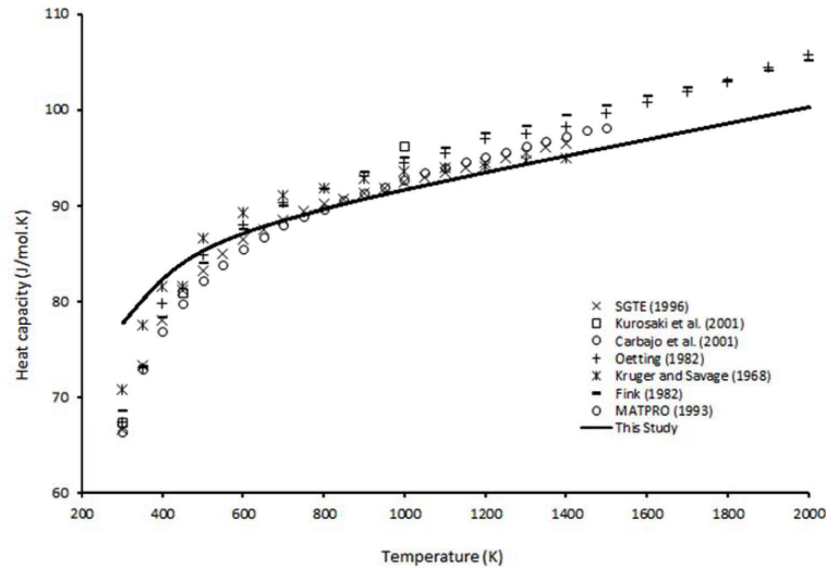
Fig. 4. The Temperature Dependence of C$_P$ Heat Capacity of PuO$_2$.

energy and linear thermal expansion coefficients, especially in the calculation of heat capacity.

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