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Original Article

A study on heat capacity of oxide and nitride nuclear fuels by using Einstein-Debye approximation

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ABSTRACT

Knowledge on fuel enthalpy and its temperature derivative, the heat capacity, are important quantities in determination of fuel behavior in normal reactor operation and reactor transients. The aim of this study is to compare the heat capacity of oxide and nitrite fuels by using Einstein-Debye approximation. A simple analytical expression was performed to calculate the heat capacity of fuels. To test the validity and reliability, the calculated formulas were compared to published results for various nuclear fuels including UO_2, ThO_2, PuO_2 and UN. Calculated formulas yielded results in consistent with literature.

1. Introduction

The accurate calculation of thermodynamic properties of nuclear fuels remains as one of the most important problems in nuclear physics and material sciences [1–9]. The use of safe nuclear fuels with proper nuclear reactor design is essential factor to prevent tragic accidents.

The thermodynamic properties of nuclear fuels have been the subject of many theoretical [4–29] and experimental [30–40] investigations. The thermodynamic coefficients (such as heat capacity and thermal expansion) characterize the thermal change in heat generating materials [41].

Determination of heat capacity is required to compute the thermal conductivity by the thermal diffusivity of material [42] and the enthalpy of nuclear fuel. Thermal conductivity is a safety parameter permitting fuel temperature calculations in normal reactor operation conditions [32]. In addition, the determination of heat capacity is necessary to predict fuel behavior in reactor transients. Large heat capacity refers the amounts of stored energy, and potential temperature increase for low thermal conductivity material [43].

The first method to calculate heat capacity was developed by Einstein [44], where all acoustic waves have the same phase velocity. Then, Debye [45], where all optical branches have the same frequency, obtained the well-known T^3 law for the specific heat at low temperatures. Various models, varying in accuracy and computational effort, have been developed to date. There have been many computational schemes, which allow the determination of thermodynamic properties of material by splitting the acoustic and optic contributions to thermodynamic functions [10,46–53]. The authors Sobolev [11] and Sobolev and Lemehov [13] developed some useful equations for the heat capacity, the thermal expansion coefficient, the bulk modulus and the thermal conductivity of dioxides. Mamedov [10] presented an analytical approximation to the heat capacity of nuclear fuels of UO_2 and PuO_2 using the combined Einstein–Debye model as an application of established formula for Debye functions. The calculation results are in agreement with the experimental data. Fink [4] reviewed and analyzed the experimental data to obtain consistent equations for the thermophysical properties of solid and liquid UO_2. Kuosaki et al. [9] evaluated the physicochemical properties of mixed oxide fuel (MOX) using the Molecular dynamics methods. In most of these models, there are some limitations in applicability of it: for instance, all temperature range etc. Unlike Einstein model and Debye model, The Einstein–Debye model considers all contributions from both acoustic and optical parts of the phonon spectrum [10,41].

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Nomenclature

UO_2	Uranium Dioxide
PuO_2	Plutonium Dioxide
ThO_2	Thorium Dioxide
UN	Uranium Mononitride
MOX	Mixed Oxide Fuel
C_V	Heat capacity at constant volume
C_P	Heat capacity at constant pressure
k_B	The Boltzmann constant
N_A	The Avogadro number
θ_D	Debye temperature
θ_E	Einstein temperature
A_0	Constant in Eq. (2)
T	Temperature
T_m	Melting temperature
$L_V(x_D)$	Isochoric heat function
$A(x_E)$	Einstein function
$D_n(\beta,x_D)$	The n-dimensional Debye function
$F_m(n)$	The binomial coefficient
n	Variable used in Eqs. (8) and (9)
m	Variable used in Eqs. (8) and (9)
s	The number of atoms
β	Variable used in Eq. (7)

The objective of this work is to use an analytical approach to calculate the temperature dependences of isobaric heat capacity of nuclear fuels in the framework of the Einstein-Debye model with wide ranges of temperature. Because the proposed model are more advantages in speedier calculation of the results and it is an analytical expression, it can be used to investigate other similar nuclear fuels.

2. Method

The temperature dependences of the heat capacities in the constant-volume and −pressure based on the Einstein-Debye approach are given by [41,52,53], as follows:

$$C_V(T) = 3N_A k_B M(x_D,\ x_E) \tag{1}$$

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

Where, k_B is the Boltzmann constant, $x_D = \theta_D/T$, where, θ_D is the Debye temperature, $x_E = \theta_E/T$, where, θ_E is the Einstein temperature, T is the absolute temperature, N_A is the Avogadro number, $A_0 = 5.1x10^{-3} J^{-1}$K.mol, T_m is the melting temperature, and $M(x_D,\ x_E)$ is defined as

$$M(x_D,\ x_E) = L_V(x_D) + (s-1)A(x_E) \tag{3}$$

Here, s is the number of atoms in one crystalline lattice point and the isochoric heat function $L_V(x_D)$ is defined by Refs. [49,53].

$$L_V(x_D) = \frac{n}{x_D^n} \int_0^{x_D} \frac{t^{n+1} e^t}{(e^t-1)^2} dt \tag{4}$$

and the Einstein function $A(x_E)$ is given by the relation [53]:

$$A(x_E) = x_E^2 \frac{e^{x_E}}{(e^{x_E}-1)^2} \tag{5}$$

$L_V(x_D)$ is expressed through the n-dimensional Debye functions as:

$$L_V(x_D) = \frac{n}{n+1} x_D [D_{n+1}(1,x_D) + D_{n+1}(2,x_D)] \tag{6}$$

The $D_n(\beta,x_D)$ in Eq. (6) is defined as n-dimensional Debye functions given by

$$D_n(\beta,x_D) = \frac{n}{x_D^n} \int_0^{x_D} \frac{t^n}{(e^t-1)^\beta} dt \tag{7}$$

β is an integer (here, $\beta = 2$). The accurate solution for n-dimensional Debye functions is of prime importance in the computation of the heat capacity of materials (C_V and C_P). We proposed a new general formula for the n-dimensional integer Debye functions defined as [54]:

$$D_n(\beta,x_D) = \frac{n}{x_D^n} \lim_{N\to\infty} \sum_{m=0}^{N} (-1)^m F_m(-\beta) H_{nm}(\beta,x_D) \tag{8}$$

Where

$$H_{nm}(\beta,x_D) = \frac{n!}{(m+\beta)} \left[1 - e^{-x_D(m+\beta)} \sum_{K=0}^{n} \frac{x_D^K (m+\beta)^K}{K!} \right]. \tag{9}$$

Where n is integer, $F_m(n) = n!/[m!(n-m)!]$ is the binomial coefficient. In eqs. (8) and (9), m(=0) and N (=200) are lower and upper limit of sum symbol, respectively.

3. Results and discussion

In this study, an analytical method was proposed for calculation of the C_P heat capacity of nuclear fuels UO_2, ThO_2, PuO_2 and UN by using the Einstein−Debye model. A computer program was constructed for the evaluation of the heat capacity by the use of Mathematica 8.0 programming language. The calculation results were compared with previously published theoretical [4,5,9,13,15,19,20,23,28,29] and the experimental data [17,18,21,22,24–27,30]. Results in this study are in consistent with literature as shown in Figs. 1–4. In addition, it was given the error bar (with %5) in the Figures for easy comparison.

In Fig. 1, the temperature dependence of the heat capacity of UO_2 obtained between temperatures 300–1500 K is shown together with the data of previous investigations [4,5,19,23–25]. Especially, at the high-temperature, there is consistency among the compared results. The calculated heat capacity at 1300 K is almost the same as values obtained from other studies: 20.4772 cal/mol.K (this study), 20.4080 cal/mol.K [5], 20.8236 cal/mol.K [23], 20.4245 cal/mol.K [4], 20.9820 cal/mol.K [19], 20.5857 cal/mol.K [24], 20.8645 cal/mol.K [25]. There is also similar curvature between the heat capacity results with previous studies at low temperature.

The computational results versus the results from other investigations [13,15,20–22] for ThO_2 nuclear fuel are shown in Fig. 2.

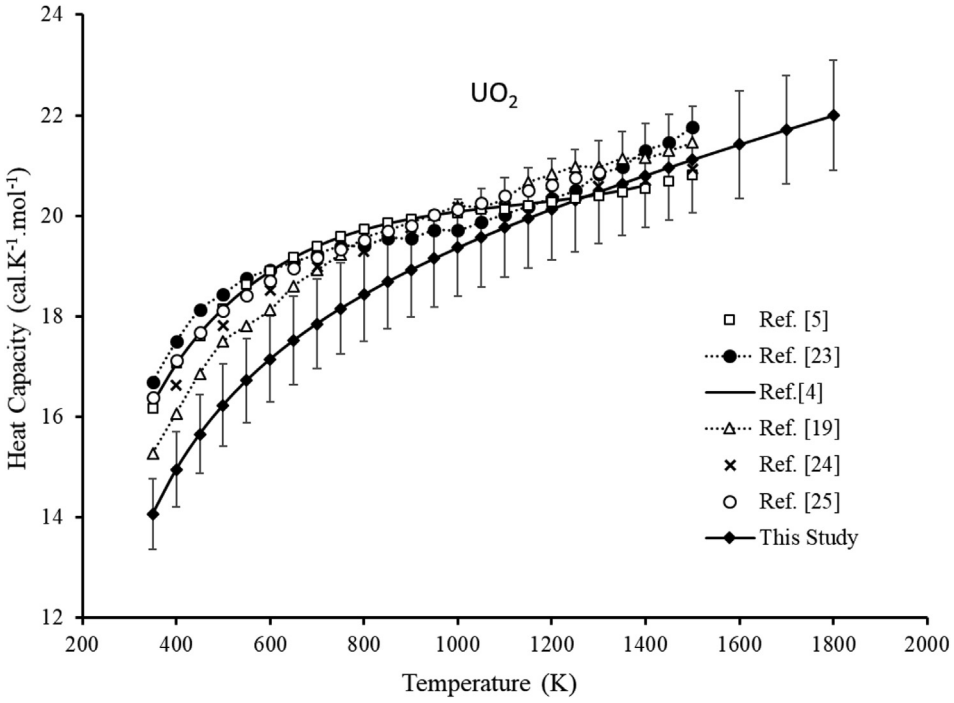

Fig. 1. The temperature dependence of C_P heat capacity (cal/mol.K) of UO_2, $\theta_D = 377$ K [56], $\theta_E = 535.8$ K and.$T_m = 3138$ [57]

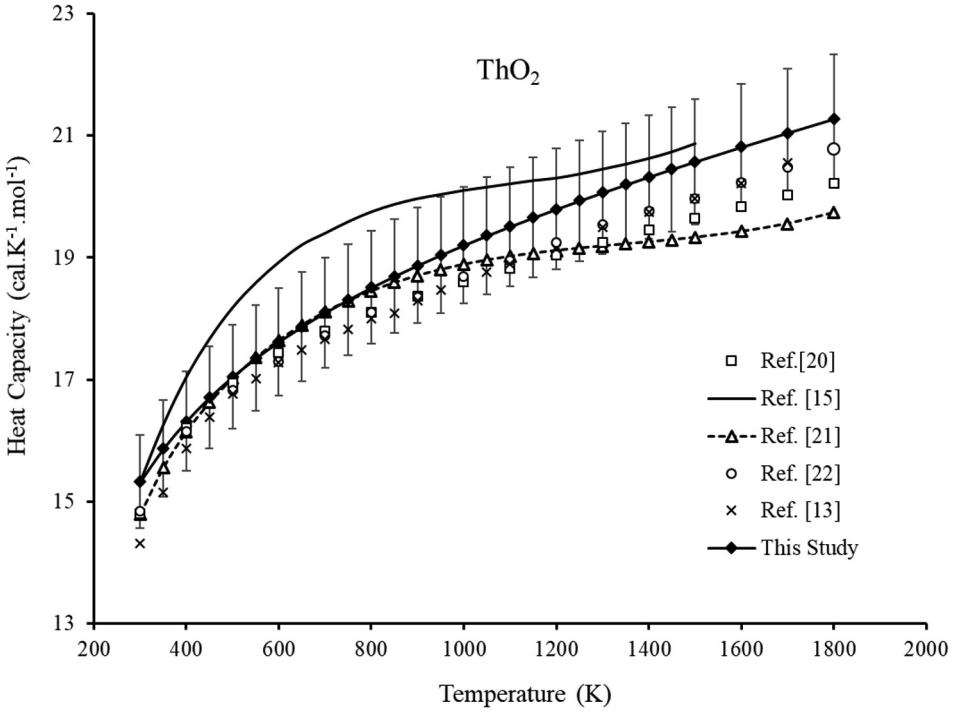

Fig. 2. The temperature dependence of C_P heat capacity (cal/mol.K) of ThO_2.$\theta_D = 393$ K [56], $\theta_E = 153$ K [58] and $T_m = 3923$[59]

As seen in Fig. 2, the agreement between calculations and the data in Refs. [13,22] is very good than studies in Refs. [15,20]. In addition, the agreement between our results and those of Ref. [22] is high, especially in temperature range 300–1000 K. The maximum deviation of heat capacity with the values in Refs. [13,22] is about 6.6% at 300 K. The deviation with Refs. [15,20,21] are about 7.3% (at 1800 K) [21], 7.6% (at 650 K) [15], and 7.4% (at 600 K) [20]. We can say that the agreement and stability of the method for ThO_2 are satisfactory as UO_2. The heat capacity of ThO_2 is about 1.8 cal/mol.K (this value for PuO_2 and UN is 1.56 and 3.05 cal/mol.K, respectively) higher than those of UO_2 at 300 K.

The calculated results for the heat capacity of PuO_2 is shown in Fig. 3 in comparison with literature data [5,9,19,26–29]. The agreement between the literature [5,9,19,26–29] with this work is

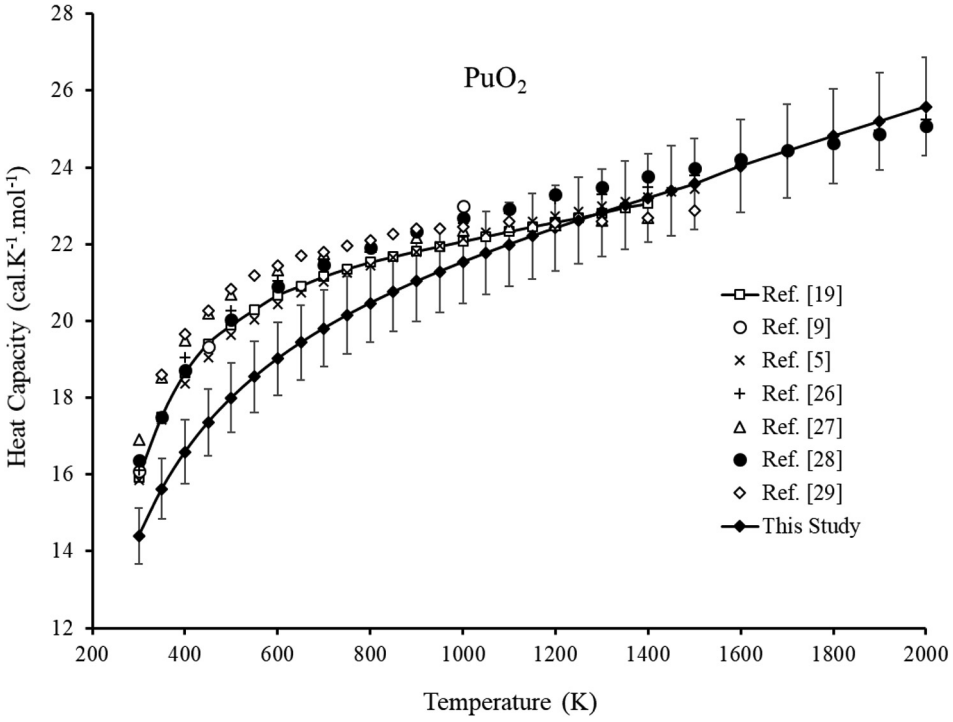

Fig. 3. The temperature dependence of C_P heat capacity (cal/mol.K) of PuO_2, $\theta_D = 415$ K [60], $\theta_E = 571$ K [20] and $T_m = 2663$ [33]

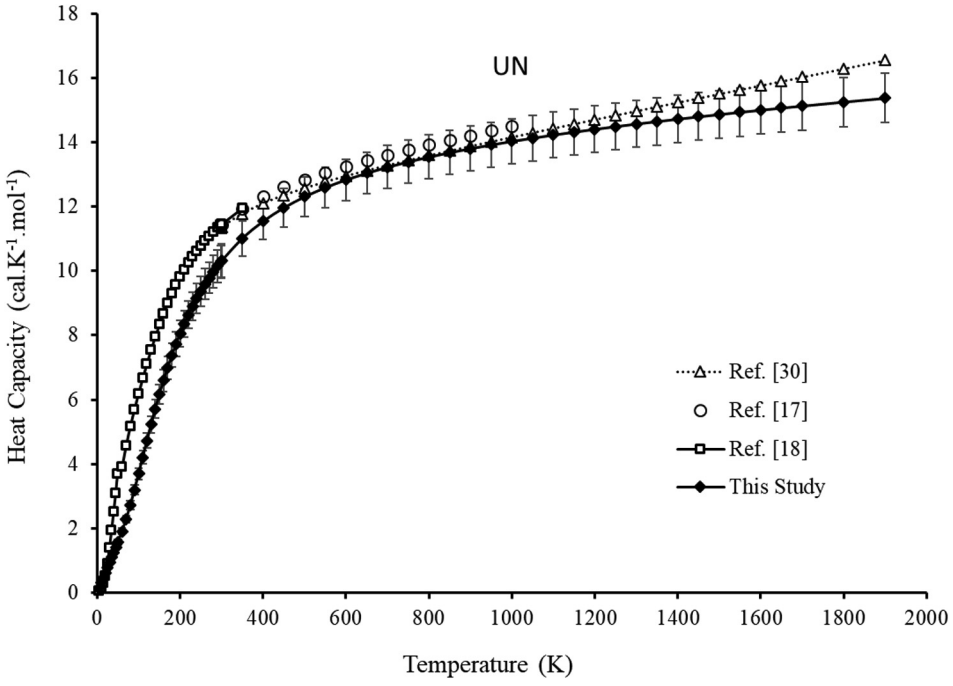

Fig. 4. The temperature dependence of C_P heat capacity (cal/mol.K) of UN. $\theta_D = 325$ [60], $\theta_E = 534$ K; and $T_m = 3123$ K [61]

noteworthy above 1000 K temperature. For instance, at 1200 K, the calculations in this study (22.4182 cal/mol.K) is close to values from previous studies including 22.7289 cal/mol.K [5], 22.5664 cal/mol.K [19], 23.1724 cal/mol.K [26], 22.4887 cal/mol.K [27], 23.2935 cal/mol.K [28], 22.5504 cal/mol.K [29]. The highest deviation between the calculated and literature results is at 350 K [29] and equals to 18.9%. There can be many reasons for this deviation. Other effects, the Schottky and the excited terms on heat capacity should also be considered. Kato et al. [55] showed that were important in heat capacity evaluation of PuO_2.

A comparison of the heat capacity obtained in this study with the literature data [17,18,30] for UN is shown in Fig. 4 as heat capacity against the temperature. The results indicate an agreement with the data given by Refs. [17,18,30]. The data shown in Fig. 4 revealed small deviations in the temperature region above 1600 K. The highest deviation is about 7.7% at 1900 K.

Calculated heat capacity values in this study were in consistent with the literature data [4,5,9,13,15,17–30]. However, the results for some fuels at low temperatures did not yielded a reasonable consistency. Nevertheless, low temperatures are insignificant when compared to average reactor core temperatures in the nuclear reactor. It is important that reported results are in agreement with the reactor core temperatures. Finally, we can say that the presented method in this work shows significant accuracy. In addition, tested method is more generic and free of any restrictions on its application to analyze the thermodynamic properties of nuclear fuels. Our results could be used as a theoretical method for experimental studies of nuclear fuels.

4. Conclusion

In this work, the heat capacities of UO_2, ThO_2, PuO_2 and UN nuclear fuels were investigated by a novel method based on the Einstein-Debye model. The heat capacity of nuclear fuels mentioned above were compared. It was observed that the stability of the method is generally acceptable for the used nuclear fuels, and the obtained method can use in calculating the thermodynamic properties of nuclear fuels.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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