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Numerical Description of Melting/Solidification Temperature of Oxide Nuclear Fuels

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Abstract: The article continues the search for a general law that describes the physical properties of a solid body, represented as a complex compound, through the physical properties of its elements. For a set of mixtures of metal oxides (actinide oxides), their melting or solidification temperatures were described in terms of the atomic weighted sum of the melting/solidification temperatures of these metals and molecular oxygen, multiplied by a variable which depending on the crystal structure and properties of melt of the compound and on the atomic numbers of the elements that make up the compound.

Keywords: thorium–uranium dioxide; thorium–plutonium dioxide; uranium–plutonium dioxide; actinide oxides; melting; solidification

1. Introduction

In previous articles [1,2], formulas were obtained for the thermal conductivity of some nuclear materials depending on the atomically weighted thermal conductivities of the elements that make up these materials. It turned out that there are temperature intervals in which the thermal conductivity of a complex compound is equal to the atomically weighted sum of the thermal conductivities of its elements, multiplied by a variable that depends only on the mole fractions of the elements in the compound and on their atomic numbers. This led us to the idea that any physical quantity can be expressed in this way. In this work, we study the dependence of the melting/solidification temperature of a mixture of actinide oxides on their concentration in a material sample.

The problem of applying the formulas used in this and the previous two works is to find in the literature the corresponding physical quantities of the elements of a complex compound. If our assumption is correct, then we must conclude that in the study of the physical properties of a complex compound, we need complete information about all the elements of this compound. The last nuance is completely ignored in most studies of condensed matter.

2. Phenomenology

Consider a complex compound with the chemical formula $A_kB_lC_n$... Suppose we want to find a law according to which some physical quantity L changes with a change in chemical parameters: $L = L(k, l, n,\ldots)$. Whatever the phase state of the complex compound, when measuring any L, we are dealing with a change in the internal energy of the complex compound. The kinetic and potential parts of the internal energy of any compound are additive quantities. Therefore, we can assume that L can be represented as: $L = (kL_A+lL_B+nL_C+\ldots, k, l, n,\ldots)$, where L_i is the corresponding physical quantity of the element of the complex compound. The electronic structure of a compound determines its physical properties. The electronic structure is completely determined by the atomic numbers of the elements of the compound. Therefore we can write: $L = (kL_A+lL_B+nL_C+\ldots, k, l, n,\ldots, A, B, C,\ldots)$, where $A, B, C, \ldots$ atomic numbers or electric charges of the atomic nuclei of elements. In accordance with the previous results [1,2], we can conclude that the following mathematical construction can describe any L:

$$\frac{1}{L}=\frac{\Theta}{(k\cdot L_A+l\cdot L_B+n\cdot L_C+\ldots)}\cdot\left[\frac{1}{k\cdot A}+\frac{1}{l\cdot B}+\ldots+\frac{h}{n\cdot C}\right], \qquad (1)$$

where *C* is the most electronegative element in the compound, and *h* is a fitting parameter, a rational number that depends on the phase state and structure of the complex compound. Θ is a constant rational number, probably changing from the nature of *L*.

We assume that the real physical law describing *L* in terms of L_i cannot be obtained in exact form due to mathematical difficulties in solving condensed matter physics problems, since we need to solve the many-body problem with about 10^{23} bodies (Avogadro's number). But we can semi-empirically approach the exact resolution in some approximation. In the case when, in a some range of values of internal variables: irradiation doses D_{in} from the own sources of the complex compound, density of defects ρ_{def}, concentration of impurities C_{im}, etc., as well as in a wide range of external parameters: temperature *T*, irradiation doses D_{ex} from external sources, pressure *p*, static fields *E* and *H*, etc., the value of *L* can be written in the next manner: $L = (kL_A+lL_B+nL_C+\ldots)\cdot\Xi(k, l, n,\ldots, A, B, C,\ldots)$ or with indication of all variables:

$$L(D_{in},\rho_{def},C_{im},\ldots,T,D_{ex},p,E,H,\ldots)=(k\cdot L_A(D_{in},\rho_{def},C_{im},\ldots,T,D_{ex},p,E,H,\ldots)+$$
$$+l\cdot L_B(D_{in},\rho_{def},C_{im},\ldots,T,D_{ex},p,E,H,\ldots)+n\cdot L_C(D_{in},\rho_{def},C_{im},\ldots,T,D_{ex},p,E,H,\ldots)+\ldots)\cdot\Xi, \quad (2)$$

where Ξ is a variable that does not depend on internal and external parameters, but depends on the mole fractions of the elements of the compound and on the atomic numbers. Then we assert that (2) coincides with the general law or maximally close to it. In the latter case, Ξ is equal to square brackets of (1), where *h* is a constant in these ranges of external and internal parameters. The change in *L* due to the electronic, phonon and thermal radiative contributions is hidden in the L_i of all elements of the compound!

3. Application to the melting/solidification temperatures of a compounds

For three samples of mixtures of actinide oxides: UO_2–ThO_2, PuO_2–ThO_2 and UO_2–PuO_2 we used (1) where *L* is the temperature of solidification $T_{solidus}$ or melting point $T_{melting}$ of the mixture. The internal parameter here, on which the phase transition temperature depends, is the mole fraction of thorium dioxide in the first two mixtures and the mole fraction of plutonium dioxide in the last mixture. We do not distinguish between a ternary and a mixed system when using (1) for mixtures of actinide oxides. The temperature of solidification $T_{solidus}$ and melting point $T_{melting}$ of mixtures of actinide oxides coincide within the limits of experimental errors. We choose a specific temperature from the two only for reasons of better statistics.

Relative errors of comparison of experiment and calculation by formula (1) are calculated as follows:

$$\delta=\left|\frac{T^{\exp}-T^{theory}}{T^{\exp}}\right|\cdot 100\%. \qquad (2')$$

For $U_{1-x}Th_xO_2$ formula (1) is as follows:

$$\frac{1}{T_{solidus\,(U,Th)O_2}(x)}=\frac{1}{((1-x)\cdot T_{melting\,U}+x\cdot T_{melting\,Th}+T_{melting\,O_2})}\cdot\left[\frac{1}{(1-x)\cdot U}+\frac{1}{x\cdot Th}+\frac{h(x)}{2\cdot O}\right], \qquad (3)$$

where the melting temperatures of pure elements are taken from [3]: $T_{meltingU}$ = 1407 ± 2 *K*, $T_{meltingTh}$ = 2020 ± 10 *K* and from [4]: $T_{meltingO_2}$ = 54.37 *K*. The solidification and melting temperatures for a pure element are the same. Atomic numbers in (3): *U* = 92, *Th* = 90, *O* = 8. The experimental solidus temperatures of the $U_{1-x}Th_xO_2$ (or $(U,Th)O_2$) system are taken from [5]. The solidification temperature of the system is the temperature at which the last melting zone of the mixture solidifies. The fitting parameter *h* changes with *x*, and the result of fitting according to (3) is shown in Table 1.

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From Table 1 we see that at the molar fraction of thorium dioxide $x \in [0.6, 0.8]$, the structural (fitting) parameter h is constant 7.8 and formula (3) describes $T_{solidus}^{\exp}$ with an accuracy of 0.5%. That is, the solidus temperature of the mixture $U_{1-x}Th_xO_2$ can be described by formula (2) at $x \in [0.6, 0.8]$:

$$\frac{1}{T_{solidus(U,Th)O_2}(x)} = \frac{1}{((1-x)\cdot T_{melting\,U} + x\cdot T_{melting\,Th} + T_{melting\,O_2})}\cdot\left[\frac{1}{(1-x)\cdot 92}+\frac{1}{x\cdot 90}+\frac{78/10}{16}\right]. \qquad (3')$$

At the same time, at $x \in [0.2, 0.6]$, the parameter h changes with a step 4/10 per $\Delta x = 0.2$. In this case, h can be written in (3) for this interval x as: $h = 2\cdot x + 66/10$.

Table 1. Comparison of the experimental solidification temperature (red color) of the UO_2–ThO_2 mixture (taken from [5]) with that obtained by formula (3) (blue color) with the corresponding fitting parameter h.

Sample	$T_{solidus}^{\exp}, K$	h	$T_{solidus}^{theory}, K$	$\delta,\%$
UO_2	3126±55	73/10	3128	0.1
$U_{0.95}Th_{0.05}O_2$	3098±54	40/10	3085	0.4
$U_{0.8}Th_{0.2}O_2$	3157±69	70/10	3126	1.0
$U_{0.6}Th_{0.4}O_2$	3341±53	74/10	3357	0.5
$U_{0.4}Th_{0.6}O_2$	3447±59	78/10	3431	0.5
$U_{0.2}Th_{0.8}O_2$	3529±91	78/10	3512	0.5
$U_{0.05}Th_{0.95}O_2$	3584±67	55/10	3568	0.4
ThO_2	3624±86	90/10	3616	0.2

For $Pu_{1-x}Th_xO_2$ formula (1) is as follows:

$$\frac{1}{T_{solidus(Pu,Th)O_2}(x)} = \frac{1}{((1-x)\cdot T_{melting\,Pu} + x\cdot T_{melting\,Th} + T_{melting\,O_2})}\cdot\left[\frac{1}{(1-x)\cdot Pu}+\frac{1}{x\cdot Th}+\frac{h(x)}{2\cdot O}\right], \qquad (4)$$

where the melting temperatures of pure elements are taken from [3]: $T_{meltingPu}$ = 913 ± 2 K, $T_{meltingTh}$ = 2020 ± 10 K and from [4]: $T_{meltingO_2}$ = 54.37 K. The solidification and melting temperatures for a pure element are the same. Atomic numbers in (4): Pu = 94, Th = 90, O = 8. The experimental temperatures of solidus of the $Pu_{1-x}Th_xO_2$ (or $(Pu,Th)O_2$ system) are taken from [6]. The fitting parameter h changes with x, and the result of fitting the experiment according to formula (4) is shown in Table 2. For $Pu_{0.30}Th_{0.70}O_2$, there is no solidification temperature $T_{solidus}^{\exp}$ in [6]. We obtained it by linear interpolation of temperature between the nearest points on the graph in fig. 2 from [6].

From Table 2 we see that at $x \in [0.46, 0.92]$ h changes symmetrically. We approximated it by the parabolic law for this interval x: $h = -13.26\cdot x^2 + 18.295\cdot x + 1.09$.

Table 2. Comparison of the experimental solidification temperature (red color) of the PuO_2–ThO_2 mixture (taken from [6]) with that obtained by formula (4) (blue color) with the corresponding fitting parameter h.

Sample	$T_{solidus}^{\exp}, K$	h	$T_{solidus}^{theory}, K$	$\delta,\%$
PuO_2	3050±55	49/10	3053	0.1
$Pu_{0.95}Th_{0.05}O_2$	3008±45	17/10	3011	0.1

$Pu_{0.85}Th_{0.15}O_2$	3050±49	46/10	3030	0.6
$Pu_{0.54}Th_{0.46}O_2$	3208±55	67/10	3192	0.5
$Pu_{0.30}Th_{0.70}O_2$	3395±50	74/10	3391	0.1
$Pu_{0.08}Th_{0.92}O_2$	3551±68	67/10	3522	0.8
$Pu_{0.03}Th_{0.97}O_2$	3592±67	32/10	3606	0.4
ThO_2	3624±86	90/10	3616	0.2

For $U_{1-x}Pu_xO_2$ formula (1) is as follows:

$$\frac{1}{T_{melting\,(U,Pu)O_2}(x)}=\frac{1}{((1-x)\cdot T_{melting\,U}+x\cdot T_{melting\,Pu}+T_{melting\,O_2})}\cdot\left[\frac{1}{(1-x)\cdot U}+\frac{1}{x\cdot Pu}+\frac{h(x)}{2\cdot O}\right], \qquad (5)$$

where the melting temperatures of pure elements are taken from [3]: $T_{meltingU}$ = 1407 ± 2 K, $T_{meltingPu}$ = 913 ± 2 K and from [4]: $T_{meltingO_2}$ = 54.37 K. Atomic numbers in (5): Pu = 94, U = 92, O = 8. The experimental temperatures of the melting points of $U_{1-x}Pu_xO_2$ (or $(U,Pu)O_2$ system) are taken from [7]. The melting point of the system is the temperature at which the first solid zone appears in the melt. The fitting parameter h changes with x, and the result of fitting the experiment according to formula (5) is shown in Table 3. For $U_{0.40}Pu_{0.60}O_2$, there is no temperature $T^{\exp}_{melting}$ in [7]. We got it by linear interpolation of the temperature between the nearest points on the phase diagram in Fig. 3 from [7].

From Table 3 we see that at the molar fraction of plutonium dioxide $x \in [0.39, 0.46]$, the structural (fitting) parameter h is constant 5.9 and formula (5) describes $T^{\exp}_{melting}$ with an accuracy of 0.7% to 0.03%. That is, the melting temperature of the mixture $U_{1-x}Pu_xO_2$ can be described by formula (2) at $x \in [0.39, 0.46]$:

$$\frac{1}{T_{melting\,(U,Pu)O_2}(x)}=\frac{1}{((1-x)\cdot T_{melting\,U}+x\cdot T_{melting\,Pu}+T_{melting\,O_2})}\cdot\left[\frac{1}{(1-x)\cdot 92}+\frac{1}{x\cdot 94}+\frac{59/10}{16}\right]. \qquad (5')$$

Table 3. Comparison of the experimental solidification temperature (red color) of the UO_2–PuO_2 mixture (taken from [7]) with that obtained by formula (4) (blue color) with the corresponding fitting parameter h.

Sample	$T^{\exp}_{melting}, K$	h	$T^{theory}_{melting}, K$	$\delta,\%$
UO_2	3150±17	73/10	3128	0.7
$U_{0.88}Pu_{0.12}O_2$	3113±25	56/10	3109	0.1
$U_{0.70}Pu_{0.30}O_2$	3073±25	60/10	3083	0.3
$U_{0.61}Pu_{0.39}O_2$	3043±32	59/10	3066	0.7
$U_{0.57}Pu_{0.43}O_2$	3026±25	59/10	3027	0.03
$U_{0.54}Pu_{0.46}O_2$	2996±23	59/10	2995	0.03
$U_{0.40}Pu_{0.60}O_2$	2983±25	55/10	2997	0.5
$U_{0.25}Pu_{0.75}O_2$	2923±25	51/10	2899	0.8
$U_{0.20}Pu_{0.80}O_2$	2963±25	47/10	2950	0.4
$U_{0.10}Pu_{0.90}O_2$	2999±25	35/10	2997	0.07
PuO_2	3016±22	50/10	2994	0.7

4. Dependence of the fitting parameter *h* on the lattice parameters

All three mixtures of actinide oxides have a cubic crystal structure fcc, $Fm\bar{3}m$. By looking at how the lattice parameter *a* changes with *x*, we can probably figure out how *h* depends on *a*. It can be seen from the above tables that *h* increases from minimum values to maximum with increasing *x*, and at the largest *x*, *h* decreases. We observe the same behavior for the difference in lattice parameters for mixtures with close *x* - see Table 4. We can assume that: $h \sim a_{x_2} - a_{x_1}$, where $x_2 > x_1$. But what step should we choose for *x* in order to substitute the corresponding a_x into *h*?

On the other hand, the melting/solidification temperature corresponds to a first-order phase transition, which is accompanied by a change in interatomic distances. It is logical to conclude that we need to take the difference between the atomic distance a_{liq_x} in the liquid (molten) mixture and the lattice parameter of the solid sample for a given *x*: $h \sim a_{liq_x} - a_x$. There are no data on the close order of the atomic structure of melts of mixtures of actinide oxides. Thus, we cannot find out the dependence of *h* on the structural parameters of these nuclear materials at present. It probably has the following form: $h = \varsigma \cdot (a_{liq_x} - a_x)$, where ς is some constant with the unit of measure [m^{-1}].

Table 4. Lattice parameters *a* of mixtures $(U,Th)O_2$ (taken from [5]) and $(Pu,Th)O_2$ (taken from [6]) depending on the molar fraction *x* of ThO_2, and the difference in the lattice parameters of neighboring samples with increasing *x*.

Sample	a_x, Å	$a_{x_2} - a_{x_1}$, *pm*	Sample	a_x, Å	$a_{x_2} - a_{x_1}$, *pm*
UO_2	5.4708	–	PuO_2	5.3978	–
$U_{0.95}Th_{0.05}O_2$	5.4775	0.67	$Pu_{0.95}Th_{0.05}O_2$	5.4167	1.89
$U_{0.8}Th_{0.2}O_2$	5.4985	2.1	$Pu_{0.85}Th_{0.15}O_2$	5.4314	1.47
$U_{0.6}Th_{0.4}O_2$	5.5243	2.58	$Pu_{0.54}Th_{0.46}O_2$	5.5093	7.79
$U_{0.4}Th_{0.6}O_2$	5.5501	2.58	$Pu_{0.30}Th_{0.70}O_2$	5.5451	3.58
$U_{0.2}Th_{0.8}O_2$	5.5735	2.34	$Pu_{0.08}Th_{0.92}O_2$	5.5799	3.48
$U_{0.05}Th_{0.95}O_2$	5.5898	1.63	$Pu_{0.03}Th_{0.97}O_2$	5.5937	1.38
ThO_2	5.5971	0.73	ThO_2	5.5971	0.34

5. Conclusions

The possibility of describing the melting/solidification temperature of $U_{1-x}Th_xO_2$ and $U_{1-x}Pu_xO_2$ as the sum of the atomically weighted melting points of the pure elements of these mixtures at $x \in [0.6, 0.8]$ and [0.39, 0.46], respectively, gives confidence that there is a general law that makes it possible to express any physical quantity of a complex compound in terms of the sum of the atomically weighted corresponding physical quantities of the pure elements that make up its composition. This is confirmed by our previous results for the thermal conductivity of nuclear materials [1,2] and the superconducting transition temperature in high-temperature cuprates [8].

The main conclusion of this study is the fact that the study of a complex compound requires complete information about the pure elements of this compound. The last nuance is completely ignored in most studies of condensed matter.

References

1. Kizka, V. Thermal Conductivity of Carbides and Nitrides of Zr, Th and U: Numerical Approach. *Preprints.org* 2023, 2023030403. https://doi.org/10.20944/preprints202303.0403.v1
2. Kizka, V. Thermal Conductivity of ZrO2, ZrSiO4, (U,Zr)SiO4 and UO2: Numerical Approach. *Preprints.org* 2023, 2023020406. https://doi.org/10.20944/preprints202302.0406.v1

3. Rudy J. M. Konings and Ondrej Beneš. The Thermodynamic Properties of the f-Elements and Their Compounds. I. The Lanthanide and Actinide Metals. *Journal of Physical and Chemical Reference Data* 39, 043102 (2010). https://doi.org/10.1063/1.3474238
4. Richard B. Stewart, Richard T Jacobsen, W. Wagner; Thermodynamic Properties of Oxygen from the Triple Point to 300 K with Pressures to 80 MPa. *Journal of Physical and Chemical Reference Data* 1 September 1991; 20 (5): 917–1021. https://doi.org/10.1063/1.555897
5. R. Böhler et al. The solidification behaviour of the UO2–ThO2 system in a laser heating study. *Journal of Alloys and Compounds* **616** (2014) Pages 5-13. https://doi.org/10.1016/j.jallcom.2014.07.055
6. R. Böhler et al. High temperature phase transition of mixed (PuO2 + ThO2) investigated by laser melting. *The Journal of Chemical Thermodynamics* **81** (2015) Pages 245-252. https://doi.org/10.1016/j.jct.2014.10.006
7. Dario Manara et al. The Melting Behaviour of Oxide Nuclear Fuels: Effects of the Oxygen Potential Studied by Laser Heating. *Procedia Chemistry* **7** (2012) Pages 505-512. https://doi.org/10.1016/j.proche.2012.10.077
8. Kizka, V. A. Numerical Approach in Superconductivity: An Advanced Study. *Recent Advances in Mathematical Research and Computer Science* **6** (2022) 56–63. https://doi.org/10.9734/bpi/ramrcs/v6/1634a