Thermodynamic properties of hyperstoichiometric urania in the UO_2–$UO_{2.25}$ solid solution range

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Received 26 October 2001; accepted 28 January 2002

Abstract

Experimental data by Nakamura and Fujino [J. Nucl. Mater. 149 (1987) 80] on the x–T–$p(O_2)$ relations for hyperstoichiometric urania between 773 and 1373 K have been used for the assessment of thermodynamic properties of the UO_2–$UO_{2.25}$ solid solution series. The relative partial thermodynamic functions of UO_2 and $UO_{2.25}$ in the UO_2–O_2 and UO_2–$UO_{2.25}$ systems have been calculated using the Gibbs–Duhem equation. The results enable one to determine activity–composition relations and other thermodynamic mixing properties of UO_{2+x} and thermodynamic properties of the $UO_{2.25}$ end-member. The UO_2 activity and its entropic contribution have positive deviations from the mole fraction of the UO_2 end-member in the entire stability range of urania except the near stoichiometric region. A peculiar property of urania are non-zero values of these functions at the second end-member composition. Beyond the near stoichiometric region, the entropy of mixing of UO_{2+x} is approximately half of that of an ideal one-site solid solution, and the enthalpy of mixing is positive. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Uranium dioxide is the base component of the natural mineral uraninite and of fuel for nuclear power stations. Its composition can have both an excess and deficiency of oxygen relative to stoichiometric UO_2. The relationships between composition and oxygen partial pressure $p(O_2)$ of hyperstoichiometric UO_{2+x} were studied by many investigators. The number of experimental determinations of the x–T–$p(O_2)$ relations exceeds 2000 [1,2]. The x–T–$p(O_2)$ relations were used for assessment of the relative partial thermodynamic functions of oxygen, $\Delta\overline{G}(O_2)$, $\Delta\overline{S}(O_2)$ and $\Delta\overline{H}(O_2)$, for statistic thermodynamic modelling and for characterisation of defects in the structure [3–5]. They were also used for the calculation of thermodynamic properties of the reaction $UO_2 + 0.5xO_2 = UO_{2+x}$ [6,7]. Lindemer and Bessmann [1] have carried out the thermodynamic analysis of the available x–T–$p(O_2)$ data considering urania as a solid

solution between UO_2 and a more oxygen-rich uranium oxide with O/U ratios above 2. They conclude that UO_{2+x} may be regarded as an ideal solid solution of the series UO_2–U_4O_9 and UO_2–U_3O_7 at lower- and higher-oxygen activities, respectively.

In general, the available x–T–$p(O_2)$ data enable one to obtain the full thermodynamic description of the UO_{2+x} solid solution series including the assessment of their real thermodynamic mixing properties, in particular activity–composition relations, which are necessary for thermodynamic calculations of the phase equilibria involving urania. With the compositional dependence of the relative partial functions of oxygen in UO_{2+x}, $\Delta\overline{\Phi}(O_2)$, we can use the Gibbs–Duhem equation for evaluating those functions of the second component, UO_2, in the UO_2–O_2 system. With the latter $\Delta\overline{\Phi}(UO_2)$–composition relations, we can use the same approach for evaluating relative partial functions, $\Delta\overline{\Phi}(UO_{2+b})$, of the second end-member in the UO_2–UO_{2+b} solid solution series. This will be demonstrated for the experimental x–T–$p(O_2)$ data by Nakamura and Fujino [2]. These researchers have carried out 636 measurements of the partial pressure $p(O_2)$ of UO_{2+x} with $0.003 < x < 0.23$ at

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773–1373 K using the solid state emf technique. Their investigation differs from other analogous studies by larger quantities of experimental data in broader compositional and temperature ranges. The comparison with data of other studies ([2], Fig. 8) has shown that the derived x–T–$p(O_2)$ relations reproduce quite well the available experimental data in the studied temperature and composition ranges constituting the upper limit data with the highest x values at given $p(O_2)$. The extrapolation of the derived x–T–$p(O_2)$ relations to higher temperatures is in agreement with high-temperature data [8] which enables the applicability of the derived x–T–$p(O_2)$ relations up to 1673 K. The dependence of the relative partial thermodynamic properties of O_2 on the UO_{2+x} composition calculated by Nakamura and Fujino [2] is used in this paper for an assessment of the thermodynamic mixing properties of the hyperstoichiometric urania solid solution.

2. Relative partial thermodynamic functions

According to Nakamura and Fujino [2], the relative partial functions $\Delta\overline{\Phi}(O_2)$ of oxygen in UO_{2+x} with $0.003 < x < 0.23$ at temperatures from 773 up to 1373 K are described by the equations

$$\Delta\overline{G}(O_2) = \Delta\overline{H}(O_2) - T\Delta\overline{S}(O_2), \tag{1}$$

$$\Delta\overline{S}(O_2) = \Delta\overline{S_0} + \Delta\overline{C}_p(O_2)\ln T, \tag{2}$$

$$\Delta\overline{H}(O_2) = \Delta\overline{H}_0 + \Delta\overline{C}_p(O_2)T, \tag{3}$$

$$
\begin{aligned}
\Delta\overline{C}_p(O_2),\ J\,K^{-1}\,mol^{-1} =\ & -43.4642 - 52.171\ln x \\
& - 11.4939(\ln x)^2 \\
& - 1.5896(\ln x)^3,
\end{aligned} \tag{4}
$$

$$
\begin{aligned}
\Delta\overline{S_0}(O_2),\ J\,K^{-1}\,mol^{-1} =\ & -93.807 + 122.155\ln x \\
& + 22.533(\ln x)^2 \\
& + 5.951(\ln x)^3,
\end{aligned} \tag{5}
$$

$$
\begin{aligned}
\Delta\overline{H}_0(O_2),\ kJ\,mol^{-1} =\ & 373.411 + 120.606\ln x \\
& + 4.4304(\ln x)^2 \\
& + 1506.367(\ln x)^{-1} \\
& + 1050.900(\ln x)^{-2}.
\end{aligned} \tag{6}
$$

This representation of $\Delta\overline{S}(O_2)$ and $\Delta\overline{H}(O_2)$ is based on the assumption that $\Delta\overline{C}_p(O_2)$ for each composition x is independent of T. The dependence of $\Delta\overline{G}(O_2) = RT \ln a(O_2)$ on x and T is shown in Fig. 1.

If the compositional dependence of the relative thermodynamic partial function $\Delta\overline{\Phi}(A)$ for a component
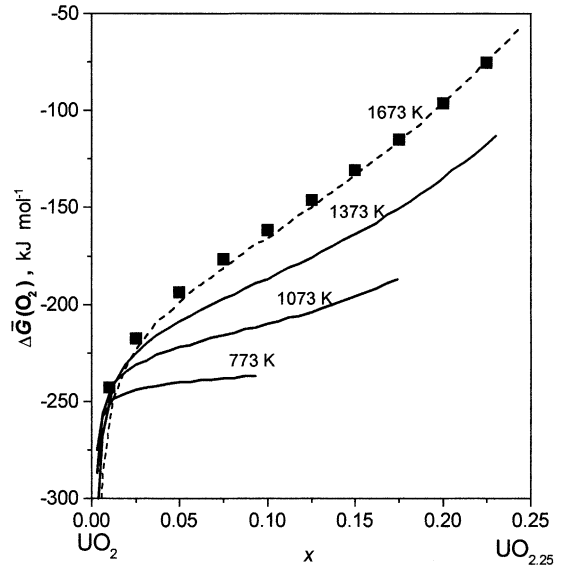

Fig. 1. Relative partial Gibbs energy of oxygen, $\Delta\overline{G}(O_2)$ in UO_{2+x} according to Nakamura and Fujino [2] (—), the extrapolation of these data (– – –) and the experimental data of Haggemark and Broli [8] at 1673 K (■).

A in a binary system is known ($\Phi = H$, S, G, C_p), that for another component B can be determined using the Gibbs–Duhem equation

$$\Delta\overline{\Phi}(B) = \Delta\overline{\Phi_0}(B) - \int_{N_0}^{N} \frac{1-N}{N}\, d\Delta\overline{\Phi}(A), \tag{7}$$

where N is the mole fraction of the component B, $\Delta\overline{\Phi_0}(B)$ is the value of $\Delta\overline{\Phi}(B)$ in the phase of the N_0 composition.

UO_{2+x} may be considered as a urania phase of variable composition $U_{1-N}O_2$ of the binary system UO_2–O_2 with the mole fraction N of the component O_2 being equal to $x/(2+x)$. Taking into account that $\Delta\overline{\Phi_0}(UO_2) = 0$ at $x = 0$, we derive

$$\Delta\overline{\Phi}(UO_2) = -\frac{1}{2}\int_{x=0}^{x} x\, d\Delta\overline{\Phi}(O_2). \tag{8}$$

$\Delta\overline{C}_p(O_2)$, $\Delta\overline{S_0}(O_2)$ and $\Delta\overline{H}_0(O_2)$ expressed in Eqs. (1)–(4) as functions of $\ln x$ can also be expressed with sufficient accuracy by means of a polynomial of the type

$$\Delta\overline{\Phi}_0(O_2) = \sum_i \mathbf{a}_{\Phi,i} x^{n_i}, \tag{9}$$

where $\mathbf{a}_{\Phi,i}$ are coefficients of this polynomial, n_i are exponents and $n_1 = 0$. Then the relative partial thermodynamic functions $\Delta\overline{\Phi}(O_2)$ are expressed by

$$\Delta\overline{\Phi}(O_2) = \sum_i \mathbf{a}^*_{\Phi,i} x^{n_i}, \tag{10}$$

where $\mathbf{a}^*_{\Phi,i}$ are determined by coefficients $\mathbf{a}_{\Phi,i}$ for $\Delta\overline{\Phi}_0(O_2)$ using relations given in Table 1. Coefficients $\mathbf{a}_{\Phi,i}$ given in Table 2 were calculated using values of $\Delta\overline{G}(O_2)$ for stable UO_{2+x} at 773–1373 K with composition and temperature steps being equal to 0.05 and 100 K, respectively. The standard deviation of such representation of $\Delta\overline{G}(O_2)$ from the analytical expression of Nakamura and Fujino [2] is 47 J mol^{-1}.

Substitution of Eq. (10) for Eq. (8) allows us to express the dependence of $\Delta\overline{\Phi}(UO_2)$ on x. Using Eqs. (1)–(3) and Eqs. (8) and (9) we obtain general equations for the relative partial functions

$$\Delta\overline{\Phi}(UO_2) = -\frac{1}{2}\sum_i \mathbf{a}^*_{\Phi,i}\frac{n_i}{n_i+1}x^{n_i+1}. \tag{11}$$

Now applying the Gibbs–Duhem equation to UO_{2+x} as to a solid solution of the UO_2–UO_{2+b} series and substituting both $N = x/b$ and $\Delta\overline{\Phi}(UO_2)$ according to Eq. (11) we can determine the relative partial functions for the UO_{2+b} end-member

$$\Delta\overline{\Phi}(UO_{2+b}) = \Delta\overline{\Phi}_0(UO_{2+b})$$
$$+ \frac{1}{2}\sum_i \mathbf{a}^*_{\Phi,i}\left[\frac{n_i}{n_i+1}\left(x_0^{n_i+1} - x^{n_i+1}\right) - b(x_0^{n_i} - x^{n_i})\right], \tag{12}$$

Table 1
Expressions for the parameters $\overline{\Phi}$ and $\mathbf{a}^*_{\Phi,i}$

$\overline{\Phi}$	$\mathbf{a}^*_{\Phi,i}$
$\overline{C}_p$	$\mathbf{a}_{C,i}$
$\overline{S}$	$\mathbf{a}_{S,i} + \mathbf{a}_{C,i}\ln T$
$\overline{H}$	$\mathbf{a}_{H,i} + \mathbf{a}_{C,i}T$
$\overline{G}$	$\mathbf{a}_{H,i} - \mathbf{a}_{S,i}T + \mathbf{a}_{C,i}T(1 - \ln T)$

Table 2
Coefficients $\mathbf{a}_{\Phi,i}$ of Eq. (10) for evaluation of thermodynamic functions of O_2 in urania UO_{2+x} ($\mathbf{a}_{C,i}$ and $\mathbf{a}_{S,i}$ in J K^{-1} mol^{-1}, $\mathbf{a}_{H,i}$ in kJ mol^{-1})

i	n_i	$\mathbf{a}_{C,i}$	$\mathbf{a}_{S,i}$	$\mathbf{a}_{H,i}$
1	0	−43.4642	−93.807	373.411
2	1	13.9859	380.076	−3981.508
3	2	0	0	4006.248
4	1/2	−313.072	−726.702	5822.553
5	−1/2	6.5004	−32.324	16.8036
6	1/3	277.138	512.063	−4321.283
7	−1/3	12.532	−82.589	−111.7484
σ^a		0.01	0.1	0.1

[a] Standard deviation from assessments of $\Delta\overline{\Phi}$ in the paper by Nakamura and Fujino [2].

where $\Delta\overline{\Phi}_0(UO_{2+b})$ is the value of this relative partial function at $x = x_0$.

According to the graphical representation in the paper by Nakamura and Fujino [2] the limits in composition of urania in the equilibria $UO_{2+x} + U_4O_{9-y}$ between 673 and 1440 K can be expressed by the equation

$$x_0 = -8.2655 - 1.4974 \times 10^{-2}T$$
$$+ 2.28752 \times 10^{-6}T^2 + 0.66781T^{1/2}. \tag{13}$$

The relative partial functions of the UO_2 end-member allow us to calculate its activity in the UO_{2+x} solid solution series

$$a(UO_2) = \exp(\Delta\overline{G}(UO_2)/RT). \tag{14}$$

It is then also possible to separate the entropic contribution, $a_S(UO_2)$, and the enthalpic contribution, $a_H(UO_2)$, to the activity of UO_2

$$a_S(UO_2) = \exp(-\Delta\overline{S}(UO_2)/R), \tag{15}$$

$$a_H(UO_2) = \exp(\Delta\overline{H}(UO_2)/RT). \tag{16}$$

There are a number of uranium oxides with U/O > 2 which can be considered as potential end-members of the UO_{2+x} solid solution series. According to the experimental data of Roberts and Walter [7], the association of UO_{2+x} with $x < 0.25$ and U_4O_{9-y} is stable below 1396 K, urania with $x = 0.245$ is in equilibrium with U_4O_9 and $UO_{2.6}$ at 1396 K, and urania with $x \approx 0.25$ is in equilibrium with $UO_{2.6}$ at higher temperatures up to 1673 K. Budnikov et al. [9] found that heating of $UO_{2.666}$ in air led to the formation of two-phase associations, $UO_{2.25} + UO_{2.6}$ at 1773 K and $UO_{2.25} + UO_{3.6}$ at 2973 K. The constant composition of urania in association both with $UO_{2.6}$ and $UO_{3.6}$ in the broad temperature range can be considered as an evidence that $UO_{2.25}$ is the composition limit of urania being the second end-member of this solid solution series. It contradicts the proposed U–O phase diagrams (for instance [10]) where urania in equilibrium with $UO_{2.6}$ has the composition $x > 0.25$. However, the acceptance of $UO_{2.25}$ as a solid solution end-member enables us to explain the mismatch noted in [10] between the phase boundary and oxygen isobars for UO_{2+x} and $UO_{2+x} + UO_{2.6}$ in the x–T diagram at temperatures above 1400 K. The abrupt change of $p(O_2)$ at $x \approx 0.25$ which is characteristic of near end-member compositions as is seen by the example of UO_{2-x} and UO_{2+x} with $x \approx 0$ can be responsible for this mismatch.

Fig. 2 shows the $a(UO_2)$–x and $a_S(UO_2)$–x relations for UO_{2+x} as a phase of the system UO_2–O_2. It will be noted that these assessments do not depend on the choice of the second solid solution end-member. UO_{2+x} as a solid solution of the UO_2–$UO_{2.25}$ series clearly deviates from the Raoult rule. It is especially noteworthy

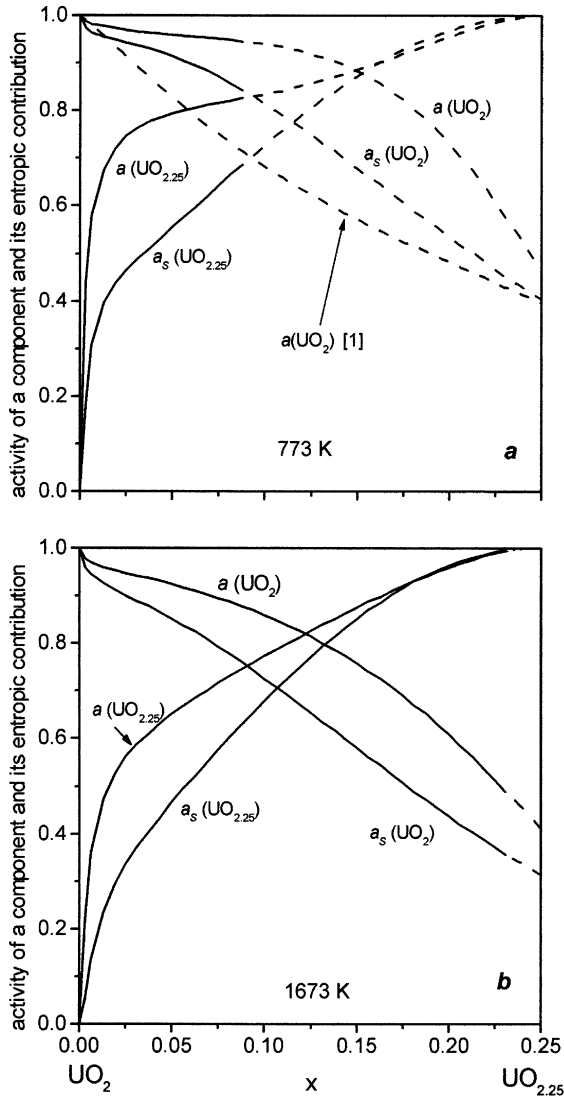Fig. 2. Activities $a(UO_2)$, $a(UO_{2.25})$ and their entropic contributions in UO_{2+x} at 773 K (a) and 1673 K (b). The Lindemer and Bessmann [1] estimations of $a(UO_2)$ are reduced to the UO_2–$UO_{2.25}$ system.

that $a(UO_2)$ and $a_S(UO_2)$ differ from zero at $x = 0.25$. This is not surprising because all uranium oxides including UO_{2+x} and richer in oxygen like $UO_{2.666}$ have non-zero values of $a(UO_2)$, where the latter is determined by the equilibrium constant $K = a(UO_2)p(O_2)$ of the reaction $UO_{2+y} = UO_2 + 0.5O_2$ at $a(UO_{2+y}) = 1$. In the system U–O_2, $a(UO_2)$ equals unity for stoichiometric urania, decreases in all non-stoichiometric compounds with increasing or decreasing U/O ratio and is zero only in pure uranium and oxygen. Such activity–

composition relations must be common to all binary M–O systems with non-stoichiometric compounds as exemplified by the Fe–O system [11]. A non-zero activity of a component in the standard state of the second component was found in some other binary solid solutions, for instance in Fe_3O_4–$ZnFe_2O_4$ [12,13] and Fe_3O_4–$CoFe_2O_4$ [14]. These solid solutions cannot be described by existing thermodynamic models of solutions and must be referred to a special type.

The enthalpic contribution $a_H(UO_2)$ increases with increasing x from unity at $x = 0$ up to 1.35 at x near 0.2 and then decreases. $a(UO_{2.25})$ and $a_S(UO_{2.25})$ change from 0 at $x = 0$ up to 1 at $x = 1$.

3. Integral functions of mixing

Integral functions of mixing Φ^M of the UO_{2+x} solid solutions can be determined using the relative partial functions $\Delta\overline{\Phi}$ of the end-members UO_2 and UO_{2+b}

$$\Phi^M(UO_{2+x}) = (1 - N)\Delta\overline{\Phi}(UO_2) + N\Delta\overline{\Phi}(UO_{2+b}). \quad (17)$$

Substituting by $N = x/b$ and by expressions for $\Delta\overline{\Phi}(UO_2)$ and $\Delta\overline{\Phi}(UO_{2+b})$ according to Eqs. (11) and (12) leads to

$$\Phi^M(UO_{2+x}) = \frac{1}{2}\sum_i \mathbf{a}^*_{\Phi,i}\frac{1}{n_i + 1}x(x^{n_i} - b^{n_i}). \quad (18)$$

The heat capacity $C_p(UO_{2+x})$ of the solid solutions UO_2–$UO_{2.25}$ (Fig. 3) shows a positive deviation from
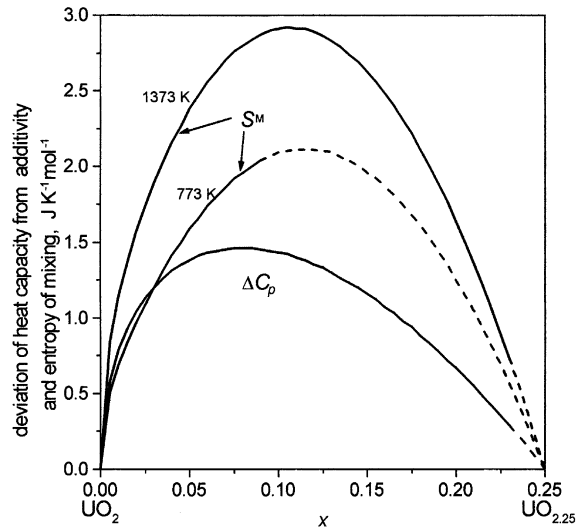

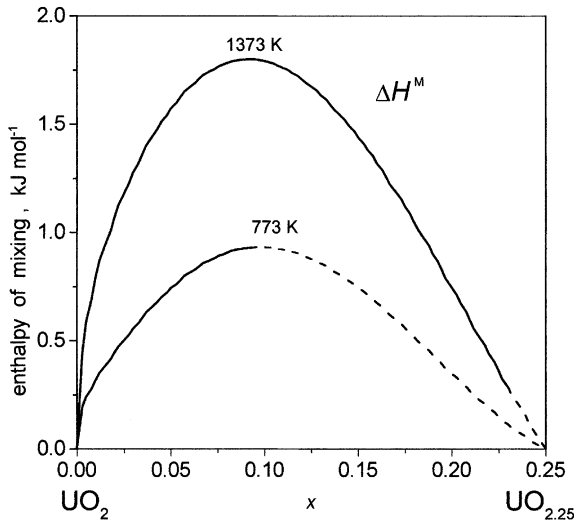Fig. 3. Deviation of C_p from additivity and the entropy of mixing, S^M in the UO_2–$UO_{2.25}$ solid solutions at 773 and 1373 K.

Fig. 4. Enthalpy of mixing, H^M, of the UO_2–$UO_{2.25}$ solid solutions at 773 and 1373 K.

additivity with the maximum displaced to the first end-member. The assumption of $\Delta \overline{C}_p(O_2)$ to be independent of temperature as already accepted by Nakamura and Fujino [2] results in a constant $C_p^M(UO_{2+x})$ at different temperatures. The entropy of mixing $S^M(UO_{2+x})$ is almost symmetric with respect to N at lower temperatures. Non-additivity of $C_p(UO_{2+x})$ results in an increase of $S^M(UO_{2+x})$ with temperature. The enthalpy of mixing $H^M(UO_{2+x})$ is positive and rather small (Fig. 4). Maxima of these functions are displaced to the UO_2 end-member.

4. Thermodynamic mixing parameters

For an analysis of the entropy of mixing S^M and enthalpy of mixing H^M of urania we can use the following relations:

$$S^M = -\alpha R(N \ln N + (1 - N) \ln(1 - N)), \qquad (19)$$

$$H^M = W^H N(1 - N), \qquad (20)$$

where N is the mole fraction of the second component, $UO_{2.25}$, being equal to $4x$. The factor α denotes the ratio of S^M between real and ideal solutions, respectively. The compositional dependence of W^H reflects features of H^M because W^H is a constant in regular solutions and a linear function of composition in subregular solutions.

Fig. 5 shows that α and W^H for UO_{2+x} are non-linear functions of x which depend on temperature. Urania in the near stoichiometric region has very large values of α
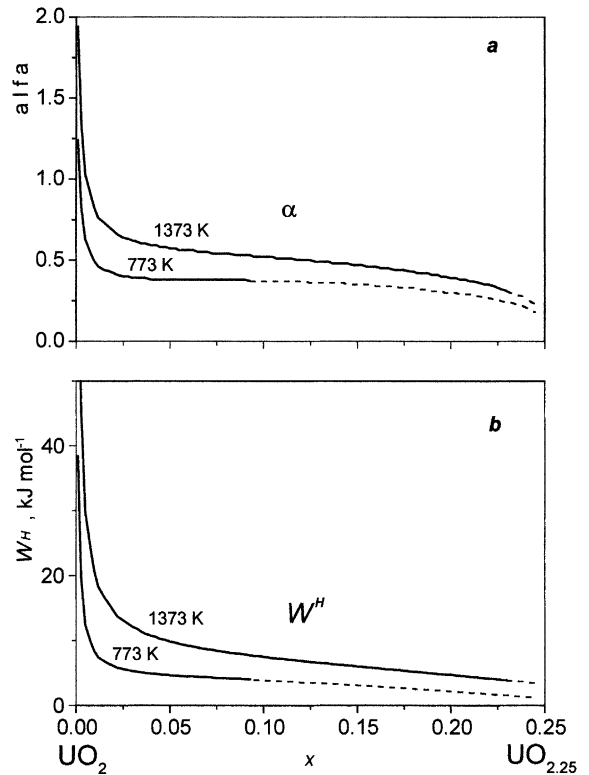

Fig. 5. Compositional dependence of the ratios $\alpha = S^M(UO_{2+x})/S_{id}^M$ (a) and $W^H = H^M(UO_{2+x})/(N(1-N))$ (b) in the UO_2–$UO_{2.25}$ solid solutions.

and W^H which decrease considerably with increasing x. Urania with $x > 0.02$–0.04 has almost linear compositional dependences of α and W^H decreasing weakly with increasing x. Values of α being close to 0.5 show that $S^M(UO_{2+x})$ is about half of S^M of an ideal one-site solid solution. A near linear dependence of W^H on x indicates that $H^M(UO_{2+x})$ can be expressed at constant temperature by an asymmetric Margules model. In particular, it can be expressed by $W^H = 1.96 - 8.01N$ kJ mol^{-1} at 1373 K.

5. Integral thermodynamic properties

The difference between some integral functions of hyperstoichiometric urania, $\Phi(UO_{2+x})$, and that of the compositionally equivalent mechanical mixture of UO_2 and O_2 can be expressed by means of the relative partial functions of UO_2 and O_2

$$\Phi(UO_{2+x}) - \Phi(UO_2) - \frac{x}{2}\Phi(O_2)$$
$$= \Delta\overline{\Phi}(UO_2) + \frac{x}{2}\Delta\overline{\Phi}(O_2). \qquad (21)$$

Substituting $\Delta\overline{\Phi}(O_2)$ and $\Delta\overline{\Phi}(UO_2)$ from Eqs. (10) and (11), we obtain an expression for some integral properties of urania, (UO_{2+x})

$$\Phi(UO_{2+x}) = \Phi(UO_2) + \frac{x}{2}\Phi(O_2) + \sum_i \mathbf{a}^*_{\Phi,i}\frac{1}{n_i+1}x^{n_i+1}. \tag{22}$$

Calculated thermodynamic properties for stable UO_{2+x} in the temperature range from 800 up to 1400 K are given in Table 3. Thermodynamic properties of

Table 3
Thermodynamic properties of UO_{2+x} (C_p and S^0 in $J\,K^{-1}\,mol^{-1}$, $\Delta_f H^0$ and $\Delta_f G^0$ in $kJ\,mol^{-1}$)

| T (K)	x	C_p	S^0	$\Delta_f H^0$	$\Delta_f G^0$
800	0.003	81.98	48	−1079.9	−945.7
	0.050	84.66	51.07	−1086.6	−954.8
	0.100	86.57	53.57	−1094.1	−964.3
	0.108	86.91	53.99	−1095.7	−966.2
900	0.003	83.47	51.92	−1079.5	−929.3
	0.050	86.16	55.15	−1086.0	−938.7
	0.100	88.08	57.70	−1093.4	−948.4
	0.145	89.69	59.58	−1101.2	−957.9
1000	0.003	84.88	55.20	−1081.7	−912.5
	0.050	87.58	58.57	−1088.0	−922.2
	0.100	89.52	61.18	−1095.3	−932.1
	0.150	91.13	63.08	−1103.1	−941.7
	0.166	91.72	63.66	−1106.3	−945.5
1100	0.003	86.27	58.02	−1085.4	−895.4
	0.050	88.98	61.52	−1091.5	−905.3
	0.100	90.93	64.18	−1098.7	−915.4
	0.150	92.56	66.10	−1106.4	−925.2
	0.180	93.42	66.93	−1111.1	−930.9
1200	0.003	87.64	60.48	−1084.1	−878.1
	0.050	90.36	64.11	−1090.1	−888.4
	0.100	92.32	66.81	−1097.1	−898.7
	0.150	93.96	68.75	−1104.7	−908.7
	0.193	95.10	69.80	−1111.0	−916.2
1300	0.003	89.02	62.68	−1082.7	−861.0
	0.050	91.75	66.42	−1088.4	−871.6
	0.100	93.72	69.17	−1095.4	−882.2
	0.150	95.36	71.12	−1102.9	−892.2
	0.200	96.79	72.38	−1110.8	−901.7
	0.212	97.05	72.55	−1112.3	−903.5
1400	0.003	90.41	64.65	−1081.1	−844.1
	0.050	93.15	68.50	−1086.7	−855.0
	0.100	95.12	71.29	−1093.5	−865.8
	0.150	96.77	73.26	−1101.0	−876.0
	0.200	98.21	74.52	−1108.8	−885.5
	0.242	99.23	75.05	−1115.1	−892.6
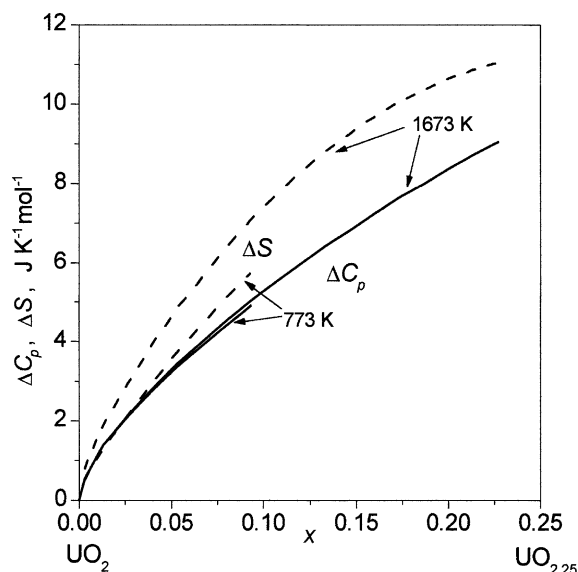
Fig. 6. Difference in heat capacity, ΔC_p, and the difference in entropy, ΔS^0 between non-stoichiometric (UO_{2+x}) and stoichiometric (UO_2) urania at 773 and 1673 K.
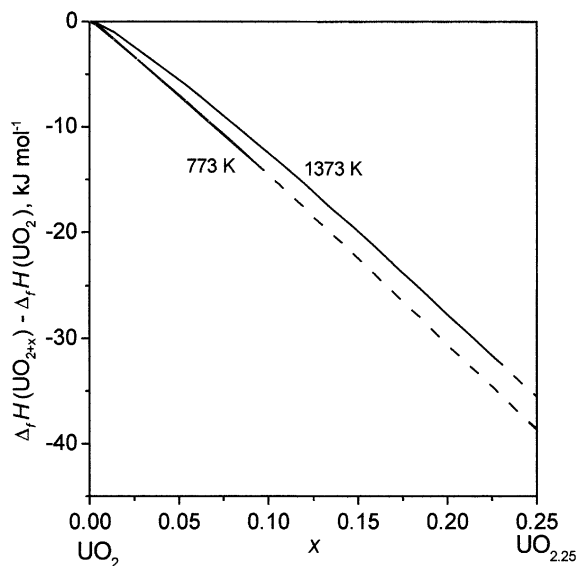

Fig. 7. Difference in enthalpy of formation, $\Delta_f H^0$ between non-stoichiometric (UO_{2+x}) and stoichiometric (UO_2) urania at 773 and 1673 K.

O_2 and UO_2 for these calculations were taken from [15]. The difference between thermodynamic properties of hyperstoichiometric and stoichiometric urania, $\Phi(UO_{2+x}) - \Phi(UO_2)$, where Φ stands for heat capacity
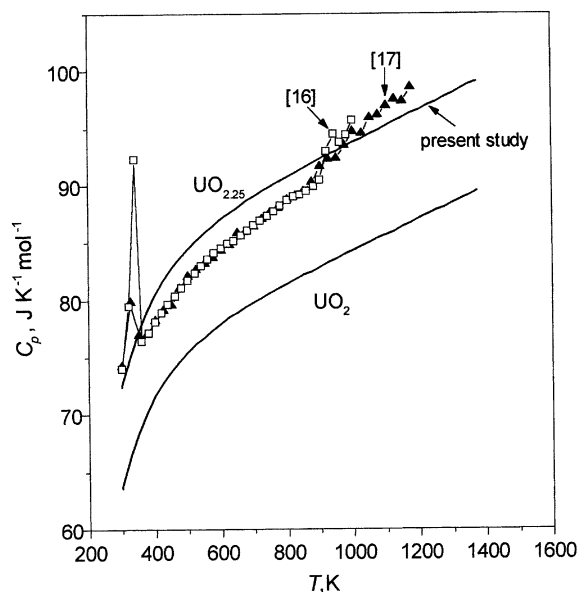
Fig. 8. Temperature dependence of the heat capacity of UO_2 and $UO_{2.25}$.

C_p, entropy S^0 and enthalpy of formation $\Delta_f H^0$ is shown in Figs. 6 and 7, respectively. According to the experimental data [16], the difference between $C_p(UO_{2.254})$ and $C_p(UO_{2.017})$ changes from 6.33 J K^{-1} mol^{-1} at 800 K up to 11.08 J K^{-1} mol^{-1} at 1000 K. Our calculation gives an intermediate value (≈ 8 J K^{-1} mol^{-1}).

The extrapolation of $\Delta\bar{G}(O_2)$ up to $x = 0.25$ and T down to 298.15 K allows to assess the thermodynamic properties of the $UO_{2.25}$ end-member, at standard conditions: $C_{p,298} = 72.3$ J K^{-1} mol^{-1}, $S_{298}^0 = 74.9$ J K^{-1} mol^{-1}, $\Delta_f H_{298}^0 = -1126.1$ kJ mol^{-1} and $\Delta_f G_{298}^0 = -1075.0$ kJ mol^{-1}. The heat capacity of $UO_{2.25}$ in the range 298–1373 K is expressed by

$$C_p = 69.98 + 1.584 \times 10^{-2}T - 1.792 \times 10^6 T^{-2}$$
$$- 3.076 \times 10^2 T^{-0.5} \text{ J K}^{-1}\text{mol}^{-1}. \quad (23)$$

Fig. 8 shows that the thus calculated values for the heat capacity are close to the available experimental data for $UO_{2.25}$ [16,17]. Our assessment of the thermodynamic properties of the virtual end-member can be compared with standard thermodynamic properties of cubic β-$UO_{2.25}$ which is stable above 348 K: $S_{298}^0 = (85.4 \pm 0.2)$ J K^{-1} mol^{-1}, $\Delta_f H_{298}^0 = -(1127.4 \pm 1.7)$ kJ mol^{-1} and $\Delta_f G_{298}^0 = -(1069 \pm 1.7)$ kJ mol^{-1} [18]. Values of $\Delta_f H_{298}^0$ are very close, while values of S_{298}^0 and $\Delta_f G_{298}^0$ differ between cubic β-$UO_{2.25}$ and the $UO_{2.25}$ end-members values calculated from experimental data for the stable UO_{2+x} solid solutions. A better agreement is at higher temperatures where the compositional stability ranges are larger.

6. Conclusions

The x–T–$p(O_2)$ relations for hyperstoichiometric UO_{2+x} have been exploited as a source of thermodynamic information on mixing properties of non-stoichiometric solid solutions in the UO_2–UO_{2+b} series. $UO_{2.25}$ can be accepted as high-oxygen solid solution end-member because high-temperature urania most rich in oxygen has this composition in a broad temperature range.

The x–$p(O_2)$ relationships for UO_{2+x} have been used for the determination of the relative partial functions of UO_2 in the UO_2–O_2 system using the Gibbs–Duhem equation and then for the determination of these functions for $UO_{2.25}$ in the UO_2–$UO_{2.25}$ system. The activity $a(UO_2)$ exceeds the molar fraction of UO_2 in these solid solutions considerably, and has a non-zero value for the $UO_{2.25}$ end-member. The latter behavior is peculiar for spinels of the Fe_3O_4–$CoFe_2O_4$ and Fe_3O_4–$ZnFe_2O_4$ series and all these solid solutions thereof cannot be described by means of regular, subregular or other known solid solution models but must refer to a special type. UO_{2+x} as a solid solution of the UO_2–$UO_{2.25}$ series has a positive deviation of the heat capacity from additivity and a small positive enthalpy of mixing. Its entropy of mixing is approximately equal to half of the entropy of mixing of an ideal one-site solid solution, S_{id}^M. The near stoichiometric urania with very small values of x has very large ratios S^M/S_{id}^M and $H^M/(N(1-N))$ which decrease considerably with increasing x.

References

[1] T.B. Lindemer, T.M. Besmann, J. Nucl. Mater. 130 (1985) 473.
[2] A. Nakamura, T. Fujino, J. Nucl. Mater. 149 (1987) 80.
[3] P. Gerdanian, M. Dodé, J. Chim. Phys. Phys.–Chim. Biol. 62 (1965) 171.

[4] Ya. Saito, J. Nucl. Mater. 51 (1974) 112.

[5] A. Nakamura, T. Fujino, J. Nucl. Mater. 167 (1989) 36.

[6] S. Aronson, J. Belle, J. Chem. Phys. 29 (1958) 151.

[7] L.E.J. Roberts, A.J. Walter, J. Inorg. Nucl. Chem. 22 (1961) 213.

[8] K. Hagemark, M. Broli, J. Inorg. Nucl. Chem. 28 (1966) 2837.

[9] P.P Budnikov, S.G. Trekhsvyatsky, V.I. Kushakovsky, Dokl. Akad. Nauk SSSR 128 (1959) 85.

[10] Y.S. Kim, J. Nucl. Mater. 279 (2000) 173.

[11] V.A. Kurepin, Geochem. Int. 12 (1975) 114.

[12] Y. Tretyakov, Thermodynamics of Ferrites, Khimiya, Leningrad, 1967.

[13] I. Katayama, J. Shibata, M. Aoki, Z. Kozuka, Trans. Japan Inst. Met. 18 (1977) 743.

[14] E. Aukrust, A. Muan, Trans. Met. Soc. AIME 230 (1964) 1395.

[15] R.A. Robie, B.S. Hemingway, Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar pressure and at high temperatures, US Geological Survey Bulletin 2131, 1995.

[16] F. Grønvold, N.J. Kveseth, A. Sveen, J. Tichy, J. Chem. Thermodyn. 2 (1970) 665.

[17] K. Seta, T. Matsui, H. Inaba, K. Naito, J. Nucl. Mater. 110 (1982) 47.

[18] I. Grenthe, J. Fuger, R.J.M. Konings, R.J. Lemire, A.B. Mueller, C. NguyenTrung Cregu, H. Wanner, in: H. Wanner, I. Forest (Eds.), Chemical Thermodynamics, Chemical Thermodynamics of Uranium, vol. 1, North-Holland, Amsterdam, 1992.