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FREE ENERGY OF FORMATION OF U_3O_7 IN THE TEMPERATURE RANGE 25 TO 400°C

C. Pescatore

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October 1988

NUCLEAR WASTE AND MATERIALS TECHNOLOGY DIVISION
DEPARTMENT OF NUCLEAR ENERGY
BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.
UPTON, LONG ISLAND, NEW YORK 11973

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SUMMARY

A temperature dependent expression for the free energy of formation of U_3O_7 from its constitutive elements is obtained utilizing basic thermodynamic data gathered from the literature. Similar expressions for the enthalpy and entropy of formation are also obtained.

1. INTRODUCTION

Uranium oxidation is an important concern during storage of both uranium metal and UO_2 . In an oxic environment UO_2 would oxidize into a generic oxide UO_{2+x} with $0 \leq x \leq 1$. Oxidation of UO_2 reactor fuel into U_3O_8 , i.e., into $\text{UO}_{2.67}$, is accompanied by a large enough volume change to impair the cladding integrity [Knoll, 1987]. Also, the leaching behavior of irradiated UO_2 could change depending on its degree of oxidation into higher oxides [DOE, 1988]. It is likely that, under the NNWSI Project's tuff repository conditions for high level waste, irradiated UO_2 will be oxidized to at least U_3O_7 by the time leaching takes place [DOE, 1988].

A review of thermochemical data of the U-O system, as of 1963, has been provided by Rand and Kubaschewski [Rand, 1963]. It still constitutes a standard reference in the field. A more recent review is available in the Gmelin Handbuch [Gmelin, 1977]. The JANAF Tables do not address uranium and its compounds [JANAF, 1985]. The NBS tables of chemical thermodynamic properties report basic thermodynamic data at 25°C and 1 atm. [NBS, 1982]. In particular, correlations between temperature and the free energy and the enthalpy of formation of the oxides UO_2 , U_3O_8 , and UO_3 from α -uranium are available in the temperature range 298.15 to 935°K [USBM, 1954] and are tabulated in standard handbooks of physical chemistry [CRC, 1980]. The free energy of formation of U_4O_9 can be inferred from Rand and Kubaschewski [Rand, 1963]. These correlations are reported in Table 1.

No general expression for the free energy of formation of U_3O_7 as a function of temperature is available. One such correlation is obtained hereby from basic thermodynamic data gathered from the literature. In the process of obtaining an expression for the ΔG_f of U_3O_7 , similar expressions for the entropy and the enthalpy of formation are also obtained.

Table 1. Free energies of formation of UO_2 , U_4O_9 , U_3O_8 and UO_3 in the temperature range (258.16°, 935° K).

Free energy expression (cal/mol U):					
$\Delta G_f = A + B T + C T \log T + \alpha \cdot 10^{-3} T^2 + \beta \cdot 10^5 T^{-1}$					
Reaction	A	B	C	α	β
$\text{U} + \text{O}_2 = \text{UO}_2 (\text{c})$	-262,880	+100.54	-19.92	+3.70	+2.13
$4\text{U} + 9/2 \text{O}_2 = \text{U}_4\text{O}_9$	-268,837	+53.16	-2.87	----	----
$3\text{U} + 4 \text{O}_2 = \text{U}_3\text{O}_8 (\text{c})$	-287,790	+100.6	-18.86	+3.56	+1.73
$\text{U} + 3/2 \text{O}_2 = \text{UO}_3 (\text{hex})$	-294,090	+114.94	-18.33	+3.49	+1.53

2. THERMODYNAMIC DATA BASE

The oxide phases known collectively as U_3O_7 constitute the least understood region of the U-O phase diagram and lie in the composition range from $\text{UO}_{2.3}$ to $\text{UO}_{2.4}$ [Gmelin, 1977].

U_3O_7 phases appear in four modifications variously denoted according to the length ratio of their crystalline axes: $\alpha\text{-U}_3\text{O}_7$ (tetragonal or pseudocubic), $c/a = 0.99$; $\beta\text{-U}_3\text{O}_7$ (tetragonal), $1.01 \leq c/a \leq 1.02$; $\gamma\text{-U}_3\text{O}_7$ (tetragonal), $1.027 \leq c/a \leq 1.032$; $\delta\text{-U}_3\text{O}_7$ (rhombohedral), $a/b = 1.007$. Alternative identification of the latter phases is as follows:

The reported thermochemical properties of these phases (mostly α -, β -, and γ -phases) are very close to one another. Sometimes the reported data make no distinction among phases. In what follows, we have tried to use thermochemical data for the α -phase as consistently as possible.

2.1 Specific Heat

U_3O_7 specific heat measurements in the temperature range 100 to 400°C can be found in the literature [Mukaibo, 1962] and are reported hereafter as Table 2.

Table 2. Experimental values of U_3O_7 specific heat in the temperature range 100 to 400°C [Mukaibo, 1962].

T (°C)	T (°K)	C_p (cal/mol/K)
100	373.16	54.2
120	393.16	56.1
140	413.16	57.0
160	433.16	58.1
180	453.16	59.2
200	473.16	60.4
220	493.16	61.3
240	513.16	62.1
260	533.16	63.1
280	553.16	63.8
300	573.16	64.8
320	593.16	65.5
340	613.16	66.3
360	633.16	67.0
380	653.16	67.4
400	673.16	68.0

On combining these data with Westrum's [Westrum, 1962] data point of 51.09 cal/mol/K at room temperature and least-square-fitting all data points to the function:

$$C_p = A + BT + C T^{-2}, \quad (1)$$

one obtains the following values for the coefficients A, B, and C:

$$\begin{aligned} A &= 44.59805, & \sigma &= 4.0355 \\ B &= 3.70675 \cdot 10^{-2}, & \sigma &= 0.5699 \cdot 10^{-2} \\ C &= -4.48384 \cdot 10^{+5}, & \sigma &= 265,594 \end{aligned}$$

where T is expressed in degree Kelvin.

2.2 Standard Enthalpy and Entropy

Both the standard enthalpy (heat content at 25°C), H_{298} , and the standard entropy (entropy content at 25°C), S_{298} , of U_3O_7 are available. From Fitzgibbon [Fitzgibbon, 1967] it is:

$$H_{298} = - 272,800 \quad \text{cal/mol U.}$$

From Westrum [Westrum, 1962]:

$$S_{298} = + 19.73 \quad \text{cal/mol U.}$$

3. MATHEMATICAL EXPRESSIONS FOR ΔH_f , ΔS_f AND ΔG_f AS A FUNCTION OF TEMPERATURE

The reaction of formation of U_3O_7 from its constitutive elements is

or, taking a unit mole of uranium as the reference,

The corresponding values for the enthalpy, entropy and free energy differentials of Reaction (2.a) at a given temperature, denoted ΔH_f , ΔS_f , and ΔG_f , respectively, are obtained by taking the differences:

$$\Delta H_f = \sum H_{\text{products}} - \sum H_{\text{reactants}}, \quad (2.b)$$

etc.

The reference equations to be used in order to obtain the temperature dependence are:

$$\Delta H_f = \Delta H_{298} + \int_{298}^T \Delta C_p dT, \quad (2.c)$$

$$\Delta S_f = \Delta S_{298} + \int_{298}^T (\Delta C_p/T) dT, \quad (2.d)$$

$$\Delta G_f = \Delta H_f - T \Delta S_f \quad (2.e)$$

The basic thermodynamic data needed to express ΔH_f , ΔS_f , and ΔG_f as function of temperature according to Equations (2.c)-(2.e) are summarized in Tables 3 and 4.

Table 3. Standard enthalpies and entropies of reactants and products of Reaction (2.a).

	$-H_{298}$ (cal/mol)	S_{298} (cal/mol/K)	Reference
UO _{2.33}	272,800	19.73	From Section 2.2
U(α)	0	12	[Rand, 1963]
O ₂	0	49.003	[CRC, 1980]

Table 4. Specific heats of reactants and products of Reaction (2.a).

$$C_p = A + B \cdot 10^{-3} T + C \cdot 10^{-5} T^{-2} \quad (\text{cal/mol/K})$$

	A	B	C	T Range	Reference
UO _{2.33}	14.866	12.356	-1.495	298-673 °K	From Section 2.2
U(α)	2.61	8.95	1.17	298-941 °K	[Rand, 1963]
O ₂	8.27	0.258	-1.877		[CRC, 1980]

3.1 Enthalpy of Formation

From Equation (2.c), the enthalpy of formation of U_3O_7 in the temperature range 298-673°K is given by the expression:

$$\Delta H_f = -273,568 - 0.463 \cdot 10^{+5} T^{-1} + 2.608 T + 1.638 \cdot 10^{-3} T^2 \quad (4)$$

(cal/mol U)

3.2 Entropy of Formation

In the temperature range 298-673°K, the entropy of formation of U_3O_7 has the following representation:

$$\Delta S_f = -65.015 - 0.2315 \cdot 10^{+5} T^{-2} + 6.006 \log T + 3.726 \cdot 10^{-3} T, \quad (5)$$

(cal/mol U)

3.3 Free Energy of Formation

The resulting free energy of formation of U_3O_7 in the temperature range 298-673°K is:

$$\begin{aligned} \Delta G_f = & -273,568 + 67.623 T \\ & -2.088 \cdot 10^{-3} T^{+2} - 0.2315 \cdot 10^{+5} T^{-1} \\ & -6.006 T \log T \end{aligned} \quad (6)$$

where the units are cal/mol U.

Using the UO_2 and UO_3 data reported in Table 5, the above equation for the free energy of formation of U_3O_7 is compared in Table 6 with predictions based on Equation (7):

$$\Delta G_{f,x} = \Delta G_{f,0} + x (\Delta G_{f,1} - \Delta G_{f,0}), \quad 0 \leq x \leq 1 \quad (7)$$

where $\Delta G_{f,x}$ is the free energy of formation of oxide UO_{2+x} on a per unit mol-uranium basis. Equation (7) is a linear interpolation of the relevant data for UO_2 ($x=0$) and UO_3 ($x=1$) and it has been shown [Pescatore, 1986] to be a good approximation for the free energy of formation of the other intermediate

oxides U_4O_9 and U_3O_8 . As it can be seen, Equation (7) is a good approximation of Equation (6). Thus, Equation (7) provides a method to estimate the ΔG_f of U_3O_7 .

Table 5. Free energies of formation of some uranium oxides as a function of temperature.

Temp. (°C)	Temp. (°K)	UO_2 (kcal/mol U)	U_4O_9 (kcal/mol U)	U_3O_8 (kcal/mol U)	UO_3 (kcal/mol U)
25	298.16	-247.27	-255.10	-268.57	-273.03
50	323.16	-246.16	-253.99	-267.14	-271.45
75	348.16	-245.06	-252.87	-265.73	-269.87
100	373.16	-243.97	-251.75	-264.32	-268.30
125	398.16	-242.88	-250.64	-262.92	-266.75
150	423.16	-241.81	-249.53	-261.54	-265.20
175	448.16	-240.75	-248.42	-260.16	-263.66
200	473.16	-239.69	-247.32	-258.78	-262.12
225	498.16	-238.64	-246.21	-257.42	-260.60
250	523.16	-237.60	-245.11	-256.05	-259.07
275	548.16	-236.56	-244.01	-254.70	-257.56
300	573.16	-235.53	-242.91	-253.35	-256.04
325	598.16	-234.50	-241.81	-252.00	-254.53
350	623.16	-233.48	-240.71	-250.66	-253.03
375	648.16	-232.46	-239.61	-249.32	-251.53
400	673.16	-231.45	-238.52	-247.99	-250.03

Table 6. Values of ΔG_f of U_3O_7 based on the Equation (6) and Equation (7).

$A = \Delta G_f$, from Equation (6)

$B = \Delta G_f$, from Equation (7)

$C = B - A$

Temp. (°C)	Temp. (°K)	A (kcal/mol U)	B (kcal/mol U)	C (kcal/mol U)
25	298.16	-258.1	-255.6	2.33
50	323.16	-256.88	-254.51	2.37
100	373.16	-254.45	-252.07	2.38
150	423.16	-252.06	-249.53	2.53
200	473.16	-249.69	-247.09	2.60
250	523.16	-247.35	-244.69	2.66
300	573.16	-245.03	-242.30	2.73
350	623.16	-242.74	-239.93	2.81

4. CONCLUSIONS

General expressions for the enthalpy, entropy, and free energy of formation of U_3O_7 have been obtained in the temperature range 25 to 400°C from basic thermodynamic data. Under normal conditions, this temperature range encompasses all practical implementations of UO_2 fuel storage and isolation.

A comparison of the ΔG_f of U_3O_7 with the ΔG_f of U_3O_8 and UO_3 (Tables 5 and 6), confirms the metastability of U_3O_7 with respect to these latter oxides.

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