

Thermal stability and vapour pressure studies on $UTe_3O_9(s)$ and $UTeO_5(s)$

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Abstract

UTe_3O_9 and $UTeO_5$ were prepared by the solid state reaction route and characterized by X-ray diffraction and thermal methods. Thermal and X-ray studies indicated that UTe_3O_9 and $UTeO_5$ vaporize incongruently according to the reactions: $UTe_3O_9(s) \rightarrow UTeO_5(s) + 2TeO_2(g)$; $3UTeO_5(s) \rightarrow U_3O_8(s) + 3TeO_2(g) + \frac{1}{2}O_2(g)$. Vapour pressures of $TeO_2(g)$ over the mixture of $UTe_3O_9(s) + UTeO_5(s)$ in the temperature range 888–948 K and $UTeO_5(s) + U_3O_8(s)$ in the temperature range 1063–1155 K were measured by employing the Knudsen effusion mass loss technique. From the partial pressures of $TeO_2(g)$ measured, the standard Gibbs energy of formation (ΔG_f^0) of $UTe_3O_9(s)$ and $UTeO_5(s)$ were obtained which could be represented by the following relations: $\Delta G_f^0 UTe_3O_9(s) \pm 30 \text{ kJ/mol} = -2318 + 0.7981T \text{ (K)}$ (888–948 K); $\Delta G_f^0 UTeO_5(s) \pm 25 \text{ kJ/mol} = -1616 + 0.4006T \text{ (K)}$ (1063–1155 K). The kinetics of decomposition of UTe_3O_9 and $UTeO_5$ under isothermal heating conditions in flowing air were studied to determine the reaction mechanisms, rate constants and activation energies. © 1998 Elsevier Science B.V.

1. Introduction

Tellurium is one of the highly corrosive fission products, and the study of its interaction with oxide nuclear fuel matrix, clad components and other fission products has become important in nuclear technology [1,2]. Various compounds of tellurium with uranium [3–5], oxides of transition metals [6,7], actinides [8–10] and rare earths [11–13] have been characterized. Vapour pressures of $TeO_2(g)$ over $ThTe_2O_6$ and $CeTe_2O_6$ have been recently reported by us [14,15].

The compounds UTe_3O_9 and $UTeO_5$ are likely to form only under adverse oxidizing conditions in the reactor in the event of sudden ingress of air. The powder XRD patterns of these compounds are reported in the literature [8]. So far only a single value of enthalpy of formation of $UTeO_5(s)$ at 298 K was reported recently [16]. However, no thermochemical and kinetic data are available on other

compounds in the ternary system of U–Te–O. The present work deals with X-ray, thermochemical and kinetic studies carried out on two compounds in the U–Te–O system. The thermodynamic quantities such as the enthalpy of vaporization and the standard Gibbs free energy of formation, were derived from the vapour pressure data of $TeO_2(g)$ over these compounds using the Knudsen effusion mass loss technique.

2. Experimental

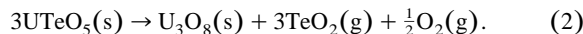
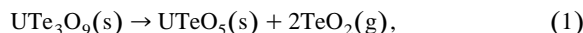
2.1. Preparation and characterization of the compounds

The compounds UTe_3O_9 and $UTeO_5$ were prepared by heating the mixtures of UO_3 and TeO_2 in the respective molar ratios in air at 903 and 973 K for 5 h. The formation of the compounds was confirmed by recording X-ray diffraction powder pattern on a DIANO X-ray diffractometer using nickel filtered $Cu K\alpha$ ($\lambda = 0.15418 \text{ nm}$) radiation. The observed X-ray data are in good agreement with the values reported in the literature [8].

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2.2. TG and DTA experiments

The thermal behaviour of UTe_3O_9 and $UTeO_5$ compounds was studied by TG and DTA experiments in flowing dry air up to 1300 K under non-isothermal conditions at the rate of 5 K/min, in a SINKU-RICO (ULVAC) thermoanalyzer provided with an infrared gold image heating furnace. A sample size of 30 mg was used in this experiment.



Based on the non-isothermal data, four temperatures were chosen to carry out kinetic studies under isothermal heating conditions on both the compounds. A sample size of 20 mg was used in all the isothermal experiments. The samples were loaded in an alumina cup and heated at the rate of 20 K/min in flowing air to the desired temperature and the mass loss thereafter was followed with respect to time.

2.3. Vapour pressure measurements

Vapour pressures were measured using Cahn microbalance by the Knudsen effusion technique. A boron nitride cell, with a knife edge orifice of ~ 1.0 mm diameter at the centre of the lid, was used as Knudsen cell. Detailed experimental procedure and the nature of calibration were reported in our earlier studies [14,15]. The microbalance was calibrated by measuring the vapour pressures of $Te_2(g)$ over $Te(s)$, and the data were used to calculate the actual Claussing factor [17]. In the temperature range of the present study, the contribution of $Te(g)$ monomer pressure

over $Te(s)$ is negligible and the total pressure is only attributed to $Te_2(g)$ [18]. The vapour pressures of $TeO_2(g)$ over $TeO_2(s)$ were measured using the above cell and the data were compared with the reported data [19]. The good agreement indicated the reliability of experimental measurement using the Knudsen cell.

The vapour pressures of $TeO_2(g)$ over $UTe_3O_9(s)$ and $UTeO_5(s)$ were measured respectively in the temperature ranges 888–948 K and 1063–1155 K. After the completion of the first experiment, the sample was heated at 1000 K for constant weight. Further the sample temperature was raised to 1060 K to record the mass loss measurements due to the decomposition of $UTeO_5(s)$ up to 1155 K. Three runs were carried out to generate the vapour pressure data.

3. Results and discussion

3.1. Kinetic studies

The decomposition of $UTe_3O_9(s)$ under non-isothermal heating conditions, as shown in the thermogram in Fig. 1, proceeded in two stages according to reactions 1 and 2 and the percentage mass loss as read from the figure for each reaction matched according to Eqs. (1) and (2).

X-ray diffraction patterns of the intermediate and that of the final product in each run were identified as $UTeO_5$ and U_3O_8 respectively. Isothermal studies were carried out to derive kinetic parameters and mechanism of decomposition. For UTe_3O_9 , the temperatures chosen are 1088, 1103, 1118 and 1133 K, and for $UTeO_5$, they are 1258, 1273, 1288 and 1307 K. The mass loss at the respective

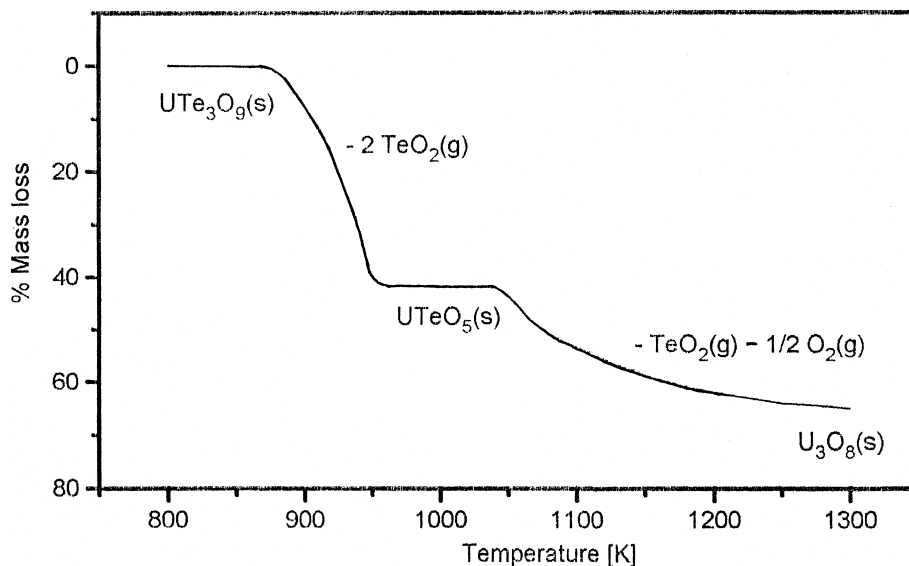


Fig. 1. Thermogram for the decomposition of $UTe_3O_9(s)$ under non-isothermal heating conditions in air at the rate of 5 K/min.

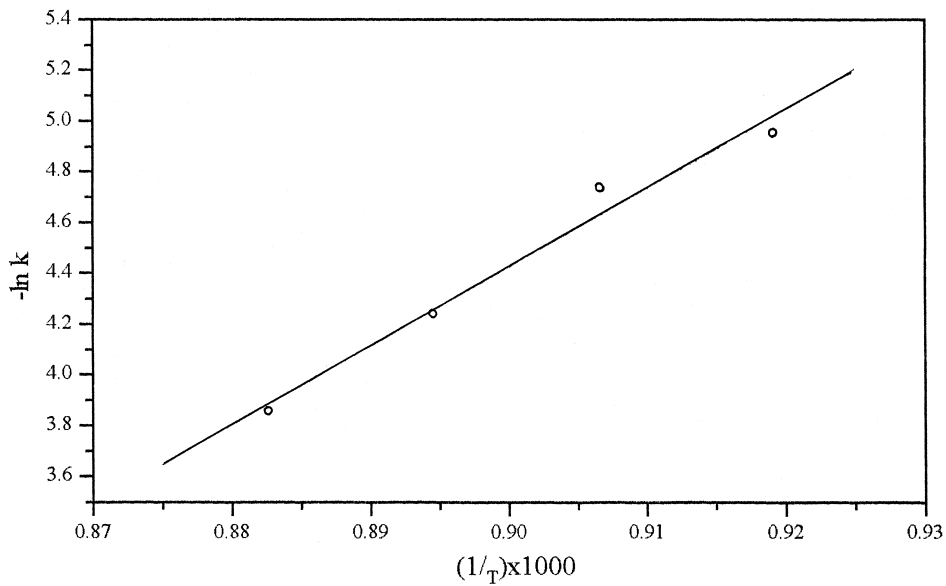


Fig. 2. Arrhenius plot of $-\ln k$ vs. $1/T$ (K) for the decomposition of $UTe_3O_9(s)$.

temperatures was measured with respect to time, and the fraction decomposed α was calculated using the relation

$$\alpha = (W_t - W_0)/(W_f - W_0), \quad (3)$$

where W_0 , W_t and W_f are respectively the weights at initial stage, any time t and the completion of the reaction. The α values were fit into various kinetic expressions as reported

[20] and the correct model corresponding to the best linear fit was obtained for the following phase boundary controlled rate equation

$$g(\alpha) = 1 - (1 - \alpha)^n = kt/r_0, \quad (4)$$

where $g(\alpha)$ is a function of α , k the rate constant and n the dimensional symmetry. The data gave best linear fits

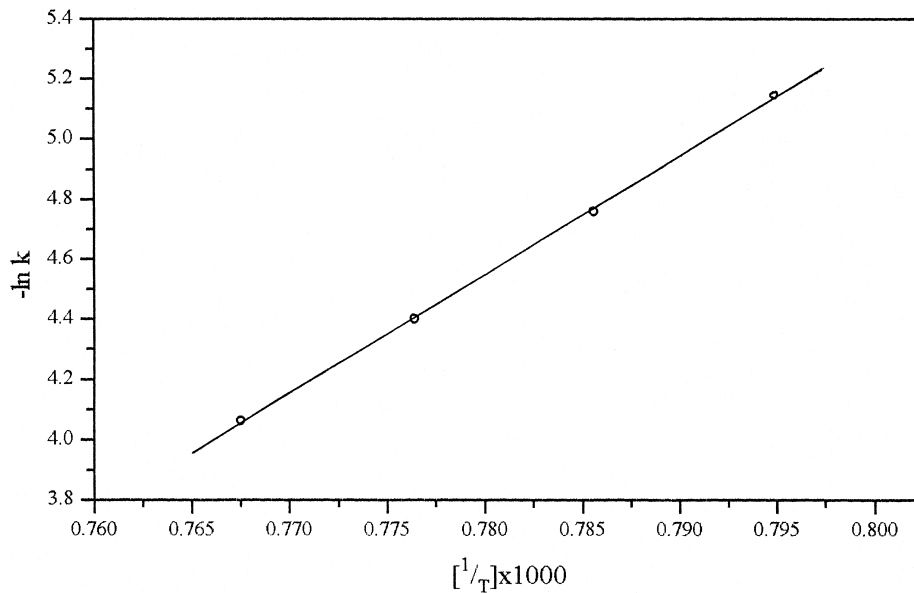


Fig. 3. Arrhenius plot of $-\ln k$ vs. $1/T$ (K) for the decomposition of $UTeO_5(s)$.

Table 1

Rate constants for the decomposition of UTe_3O_9 at different temperatures with the Arrhenius rate expression $\alpha = kt$

Temperature (K)	$-\ln k$
1088	4.9533
1103	4.7399
1118	4.2405
1133	3.8547

for Eq. (4) with $n = 1$ for the one-dimensional symmetry and the rate equation becomes

$$g(\alpha) = \alpha = kt. \quad (5)$$

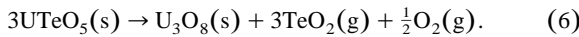
The activation energies were derived from the slopes of the linear plots between $-\ln k$ and $1/T$ (K) at various temperatures as shown in Figs. 2 and 3 respectively, for UTe_3O_9 and $UTeO_5$. The rate constants are given in Tables 1 and 2. The slopes when used in the Arrhenius equation gave an activation energy of 265 ± 5 and 331 ± 5 kJ/mole respectively for the UTe_3O_9 and $UTeO_5$ compounds.

3.2. Vapour pressure measurements

Though the vapour pressures over $UTeO_5$ were measured in the second experiment as indicated in Eqs. (1) and (2), its Gibbs energy calculations are discussed here prior to that of UTe_3O_9 , as these data are required for the calculation of energy of formation of UTe_3O_9 .

3.2.1. $UTeO_5$

From the non-isothermal studies on $UTeO_5$ (s) by TG and DTA techniques, it is observed that the compound decomposes and vaporizes incongruently with the loss of TeO_2 (g) according to the relation



The equilibrium pressures measured over $UTeO_5$ (s) + U_3O_8 (s) were due to the combined loss of TeO_2 (g) and $\frac{1}{2}O_2$ (g) as seen in reaction (6). The oxygen pressures derived from the emf studies [21] were used for the calculation of the partial pressures of oxygen and subsequently

Table 2

Rate constants for the decomposition of $UTeO_5$ at different isothermal temperatures, with the Arrhenius rate expression $\alpha = kt$

Temperature (K)	$-\ln k$
1258	5.1465
1273	4.7572
1288	4.3998
1307	4.0611

Table 3

Gibbs energy of formation of $UTeO_5$ at different temperatures

Temperature (K)	$p(TeO_2)$ (Pa)	$p^0(TeO_2)$ (Pa)	$\Delta G_f^0 UTeO_5$ (kJ/mol)
1063	0.989	50.792	-1189.9
1076	1.473	78.802	-1184.6
1088	1.992	102.629	-1179.6
1099	2.558	130.090	-1175.2
1108	2.748	157.388	-1172.9
1113	3.722	174.726	-1169.1
1124	5.086	219.168	-1164.0
1138	6.388	290.596	-1159.1
1155	7.715	405.565	-1153.9

TeO_2 (g) by difference. The oxygen pressure is represented by the relation

$$\log p_{O_2} \text{ (kPa)} = -39773/T \text{ (K)} + 23.5. \quad (7)$$

The magnitude of oxygen pressures calculated from Eq. (7) in the temperature range of the present study was found to be too small ($\sim 10^{-10}$ Pa) to contribute significantly to the mass loss recorded. Hence, the total mass loss for reaction (6) was attributed entirely to that of TeO_2 (g) only.

The equilibrium vapour pressures of TeO_2 (g) over U_3O_8 (s) and $UTeO_5$ (s) were calculated at various temperatures by using the rate of mass loss relation (8)

$$p \text{ (Pa)} = (dw/dt)(1/kA)\sqrt{T/M} \times 2.28 \times 10^3, \quad (8)$$

where dw/dt is the rate of mass loss in g/s, A is the area of cross-section of the orifice of the Knudsen cell in cm^2 , T is the temperature in K, M is the molar mass of the vaporizing species and k is the Claussing factor [17].

The measured vapour pressure values of TeO_2 (g) over U_3O_8 (s) and $UTeO_5$ (s) at various temperatures are given in Table 3 and the corresponding least squares fit of $\log p(TeO_2, g)$ against $1/T$ (K) is shown in Fig. 4 and can be represented by the relation

$$\log p(TeO_2, g) \text{ (kPa)} \pm 0.04 = -12273/T \text{ (K)} + 8.56. \quad (9)$$

Table 4

Gibbs energy of formation of UTe_3O_9 at different temperatures

Temperature (K)	$p(TeO_2)$ (Pa)	$p^0(TeO_2)$ (Pa)	$\Delta G_f^0 UTe_3O_9$ (kJ/mol)
888	0.1792	0.4945	-1609.6
894	0.2635	0.4945	-1602.8
906	0.3492	0.8807	-1596.4
917	0.5743	1.2380	-1586.8
924	0.8138	1.5320	-1580.1
930	0.9602	1.8340	-1576.4
935	1.3490	2.1270	-1570.1
942	1.3520	2.6110	-1568.6
948	2.2550	3.1940	-1559.1

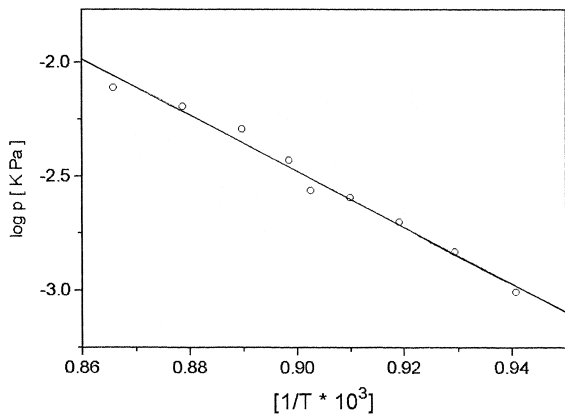


Fig. 4. Temperature dependence of the vapour pressures of $\text{TeO}_2(\text{g})$ over $\text{UTeO}_3(\text{s})$ and $\text{U}_3\text{O}_8(\text{s})$.

The standard molar Gibbs energy for reaction (6) is given by the equation

$$\Delta G_r^0 = \Delta G_f^0 \text{U}_3\text{O}_8(\text{s}) + 3\Delta G_f^0 \text{TeO}_2(\text{g}) - 3\Delta G_f^0 \text{UTeO}_5(\text{s}) \quad (10)$$

and ΔG_f^0 for the formation of UTeO_5 can be written as

$$3\Delta G_f^0 \text{UTeO}_5(\text{s}) = \Delta G_f^0 \text{U}_3\text{O}_8(\text{s}) + 3\Delta G_f^0 \text{TeO}_2(\text{g}) - \Delta G_r^0. \quad (11)$$

Also,

$$\Delta G_r^0 = -RT \ln K,$$

where K is the equilibrium constant for reaction (6) and can be represented as

$$k = \left\{ p^3(\text{TeO}_2, \text{g}) a(\text{U}_3\text{O}_8(\text{s})) p^{1/2}(\text{O}_2) \right\} / a^3(\text{UTeO}_5(\text{s})). \quad (12)$$

Since, for the stoichiometric condensed phases in equilibrium with $\text{TeO}_2(\text{g})$, activities of $\text{U}_3\text{O}_8(\text{s})$ and $\text{UTeO}_5(\text{s})$ being unity, the equilibrium constant k can be written as

$$K = p^3(\text{TeO}_2) p^{1/2}(\text{O}_2). \quad (13)$$

By substituting the value of k in Eq. (12), and on rearrangement Eq. (11) becomes

$$\begin{aligned} 3\Delta G_f^0 \text{UTeO}_5(\text{s}) &= \Delta G_f^0 \text{U}_3\text{O}_8(\text{s}) \\ &+ 3\Delta G_f^0 \text{TeO}_2(\text{g}) + 3RT \ln p(\text{TeO}_2) + \frac{1}{2}RT \ln p\text{O}_2. \end{aligned} \quad (14)$$

The value of $\Delta G_f^0 \text{TeO}_2(\text{g})$ used in the present study, is from the equilibrium between $\text{TeO}_2(\text{l})$ and $\text{TeO}_2(\text{g})$ as the temperature range of the present study is above the melting temperature of TeO_2 . Hence Eq. (14) becomes

$$\begin{aligned} 3\Delta G_f^0 \text{UTeO}_5(\text{s}) &= \Delta G_f^0 \text{U}_3\text{O}_8(\text{s}) + 3\Delta G_f^0 \text{TeO}_2(\text{l}) \\ &+ 3RT \ln p(\text{TeO}_2, \text{g}) / p^0(\text{TeO}_2) + \frac{1}{2}RT \ln p\text{O}_2, \end{aligned} \quad (15)$$

where $p^0(\text{TeO}_2)$ is the partial pressure of $\text{TeO}_2(\text{g})$ over liquid TeO_2 and the vapour pressures are taken from the reported data [22]. Also, the free energy formation of $\text{U}_3\text{O}_8(\text{s})$ and $\text{TeO}_2(\text{l})$ are taken from the literature [19], and the pressures of $\text{O}_2(\text{g})$ from emf measurements [21]. Thus

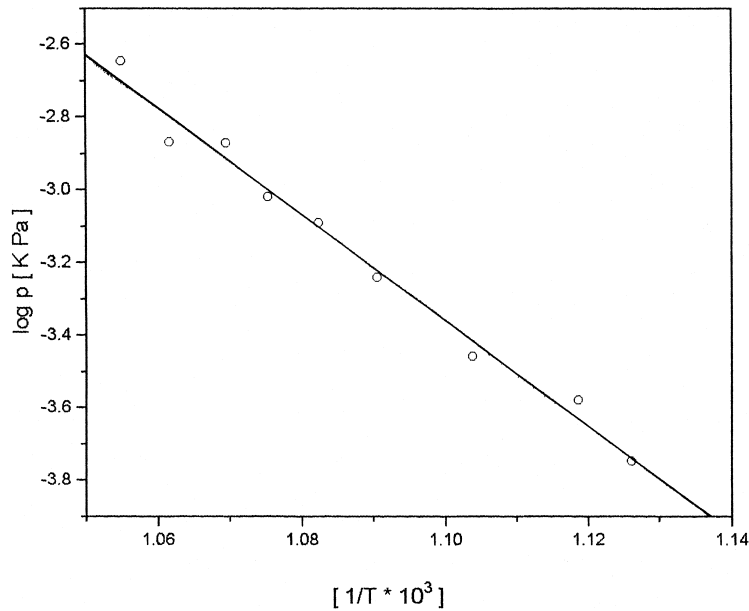


Fig. 5. Temperature dependence of the vapour pressures of $\text{TeO}_2(\text{g})$ over $\text{UTe}_3\text{O}_9(\text{s})$ and $\text{UTeO}_5(\text{s})$.

the free energy formation of $UTeO_5$, obtained in the present study, can be represented by the relation

$$\Delta G_f^0 UTeO_5(s) \pm 25 \text{ kJ/mol} = -1615 + 0.4006T \text{ (K)} \text{ (1060–1155 K)}. \quad (16)$$

These values are in close agreement with those obtained by the emf technique as given by the relation

$$\Delta G_f^0 UTeO_5(s, T) \pm 4.6 \text{ kJ/mol} = -1626 + 0.4559T \text{ (K)} \text{ (821–994 K)}. \quad (17)$$

A value of -1606 kJ/mol was reported in the literature for $\Delta H_f, 298.15$ for the compound $UTeO_5(s)$ [16].

3.2.2. UTe_3O_9

Since the decomposition temperatures for $UTe_3O_9(s)$ as seen in Fig. 1 are significantly different for both reactions (1) and (2), and the sample heated to constant weight at 1000 K indicated single phase $UTeO_5(s)$, it was possible to carry out the mass loss measurements for both the compounds using one sample of UTe_3O_9 in a single run. XRD analysis of the partly reacted sample at 925 K indicated the presence of a mixture of $UTe_3O_9(s)$ and $UTeO_5(s)$ while that of $UTeO_5(s)$ at 1075 K showed the presence of $UTeO_5$ and U_3O_8 .

The equilibrium vapour pressures of $TeO_2(g)$ over $UTeO_5(s) + UTe_3O_9(s)$ were calculated at various temperatures by using Eq. (6), and are given in Table 3. The corresponding least squares fit of $\log p(TeO_2)$ against $1/T$, for $UTe_3O_9(s)$ is shown in Fig. 5, which could be represented by the given relation

$$\log p(TeO_2) \text{ (kPa)} \pm 0.04 = -14486/T \text{ (K)} + 12.0 \text{ (888–948 K)}. \quad (18)$$

The standard Gibbs energy of formation for reaction (1) is given by the equation

$$\Delta G_f^0 = \Delta G_f^0 UTeO_5(s) + 2\Delta G_f^0 TeO_2(g) - \Delta G_f^0 UTe_3O_9(s). \quad (19)$$

Rearranging the above equation, the Gibbs energy of formation of $UTe_3O_9(s)$ can be written as

$$\Delta G_f^0 UTe_3O_9(s) = \Delta G_f^0 UTeO_5(s) + 2\Delta G_f^0 TeO_2(g) + 2RT \ln p(TeO_2), \quad (20)$$

$$\Delta G_f^0 UTe_3O_9(s) = \Delta G_f^0 UTeO_5(s) + 2\Delta G_f^0 TeO_2(l) + 2RT \ln (p(TeO_2)/p^0(TeO_2)), \quad (21)$$

where $p^0(TeO_2)$ is the partial pressure of $TeO_2(g)$ over pure $TeO_2(l)$.

Using the data of $p^0(TeO_2, g)$ from our earlier studies [14], the Gibbs energy of formation of $TeO_2(l)$ from the literature data and that of $UTeO_5(s)$ from our current experimental values, the energy of formation of $UTe_3O_9(s)$

were calculated and are given in Table 4 which could be represented by the following relation:

$$\Delta G_f^0 UTe_3O_9(s) \pm 30 \text{ kJ/mol} = -2318 + 0.7981T \text{ (K)} \text{ (888–948 K)}. \quad (22)$$

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