# Vaporization behaviour and Gibbs' energy of formation of UTeO$_5$ and UTe$_3$O$_9$ by transpiration
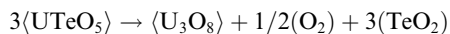
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## Abstract

Vapour pressures of UTeO$_5$ and UTe$_3$O$_9$ were determined by a transpiration technique employing their incongruent vaporization represented by the reactions:

$$3\langle UTeO_5 \rangle \rightarrow \langle U_3O_8 \rangle + 1/2(O_2) + 3(TeO_2)$$

and

$$\langle UTe_3O_9 \rangle \rightarrow \langle UTeO_5 \rangle + 2(TeO_2).$$

Standard Gibbs energies of formation of UTeO$_5$ and UTe$_3$O$_9$ were derived from the vapour pressures of TeO$_2$ measured in the temperature ranges of 1107–1217 and 947–1011 K, respectively, and could be represented by the equations

$$\Delta_f G^\circ \langle UTeO_5 \rangle / kJ/mol(\pm 0.72) = -1614.17 + 0.450\,T \quad (1107 \leqslant T/K \leqslant 1217)$$

and

$$\Delta_f G^\circ \langle UTe_3O_9 \rangle / kJ/mol(\pm 1.31) = -2313.12 + 0.868\,T \quad (947 \leqslant T/K \leqslant 1011)$$

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## 1. Introduction

UTeO$_5$ and UTe$_3$O$_9$ are the only two oxygen-rich ternary compounds reported in the UO$_2$–TeO$_2$–O subsection of the phase diagram of U–Te–O system. Their crystallographic structure and synthesis were investigated by solution [1,2] and solid state reaction [3] routes. An extensive and systematic study on the preparation, characterization and thermal stability of the above compounds in the environments of oxygen, argon and argon-8% hydrogen was completed recently in this laboratory and the results are being published separately [4]. UTeO$_5$ having orthorhombic structure and UTe$_3$O$_9$ with simple cubic lattice have unit cell volumes of 0.42531 and 1.4703 nm$^3$, respectively compared to 0.16351 nm$^3$ of CaF$_2$ type face centred cubic UO$_2$. The mechanical stress caused by dimensional incompatibility of these compounds with the UO$_2$ fuel matrix may result in disintegration of the fuel pellets and hence affect the fuel performance. The present study was undertaken to assess whether the above compounds would be thermodynamically stable in the fuel environment of a UO$_2$ based operating nuclear reactor where Te is a major fission product [5]. A literature survey revealed that there is no report on thermochemical data of these compounds.

## 2. Experimental

### 2.1. Preparation and characterization

The compounds UTeO$_5$ and UTe$_3$O$_9$ were prepared by heating, in air, thoroughly ground mixtures of UO$_2$

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and $TeO_2$ in the ratio 1:1 and 1:3 contained in a ceramic boat for about 8 h at 1023 and 900 K, respectively. $UO_2$ was prepared by reduction of nuclear grade $U_3O_8$ in $Ar–H_2$ at 1023 K. $TeO_2$ (Aldrich) was of better than 99.95% purity. The mixtures were heated at 2 K/min to the required minimum temperature followed by isothermal heating for 8 h. The mixtures maintained at these temperatures were withdrawn intermittently from the furnace and reheated three times after repeated grinding. The heat treatment conditions for the preparation of the compounds from the mixtures of oxides were optimized based on TG and XRD observations made in [4].

The X-ray patterns of the compounds were recorded with the Philips X-ray powder diffractometer (Model No. P.W.1729/40) with the nickel filter and graphite monochromator. The X-ray pattern for 1:1 mixture (heated) showed diffraction lines characteristic of $UTeO_5$ as given in JPCD file (25–1276) while those pertaining to $UO_2$ or $TeO_2$ were absent, implying that $UO_2$ and $TeO_2$ in the mixture were completely used up in the formation of $UTeO_5$ below 1023 K. In the case of a 1:3 mixture of $UO_2$ and $TeO_2$, the product obtained by heating had XRD pattern with the lines of $UTe_3O_9$ as given in JPCD file (25–999) and those due to $UTeO_5$, $TeO_2$ and $UO_2$ were totally absent.

## 2.2. Measurement of vapour pressure

The vapour pressure over the above compounds was measured by the transpiration technique employing an automatically recording transpiration apparatus [6]. The method consists of measuring the mass loss of the sample per unit volume of the carrier gas swept over at different temperatures.The flow rate of the carrier gas is so adjusted that the equilibrium between the vapour and the condensed phase is virtually undisturbed.This condition is deduced from the plot of mass loss per unit volume of the carrier gas swept versus the flow rate. The apparent vapour pressure $p$ in pascals is calculated using the equation

$$p(TeO_2)/Pa = (W/V_c)(RT_c/M) = 15.63(W/V), \qquad (1)$$

where $T_c$ is the ambient temperature in K at which the gas is collected, $M$ is the molecular weight of the vapour species, $R$ is the gas constant in $cm^3$ atm $K^{-1}$ $mol^{-1}$, $W$ is the mass loss in mg of the sample and $V_c$ is the volume in litre of the carrier gas swept over the sample. In the present case, $T_c = 300 \pm 0.5$ K, the major vaporizing species being $TeO_2(g)$, $M = 159.6$, and $R = 82.06$ $cm^3$ atm $K^{-1}$ $mol^{-1}$. The four quantities measured experimentally are $T_c$, $W$, $V_c$ and $T$, where $T$ represents the temperature at which the condensed phase is in equilibrium with the vapour.

The automatic recording transpiration apparatus used in this study was calibrated for mass employing the standard weights of 10, 100 and 1000 mg supplied by Sartorius–Werke GmbH, Germany. The temperature measuring chromel–alumel thermocouple located close to the sample under investigation was calibrated at the melting points of pure In, Cd, Zn, Sb and Ag employing the 'drop method' described in Ref. [7]. The drop method specially developed for the in situ calibration of the thermocouple fixed in the apparatus consists in suspending the pure samples of the calibrants, tied and supported by thin steel wire from the central suspension wire of the TG balance, with the sample and the thermocouple bead placed in the same plane, closest to each other but out of contact.

The TG chart paper recording the temperature and the mass of the samples simultaneously showed a sudden change in the mass when the sample melted and dropped down spontaneously under gravity. The corresponding temperature on the chart was marked as the melting temperature of the calibrant. Thus were the thermocouple and the chart paper calibrated. The temperature read from the chart was within ±1 K of the temperature deciphered potentiometrically with ice cold junction as the reference.

The flow rate was calibrated using the 'soap film' technique described elsewhere [8]. The soap film technique employs a burette without stopcock, held in a vertical configuration with the narrow end fused to a soap solution reservoir at the bottom. The reservoir has two inlets at different heights and opposite to each other. The higher inlet is designed to let in the carrier gas into the reservoir and the lower one provided with a rubber pro-pippette is meant to raise the level of the soap solution so as to reach the higher inlet port to enable bubble formation. The carrier gas flowing through the transpiration apparatus was let through soap solution and carried a soap bubble into the burette. The time period for the travel of the bubble between two graduation marks on the burette i.e. 0 and 50 ml was noted. This exercise was repeated three times before and after the traspiration run and an average of the two sets was taken as the flow rate.The volume of the gas passed over the sample was calculated from the flow rate of the gas and the total time for which the gas was passed over the sample. The flow rate was controlled employing the capillary flowmeter described in Ref. [8].

$UTeO_5$ did not gain mass during dynamic heating in oxygen upto 1198 K implying that no oxidation of the compound occurred. The compound started losing mass in oxygen above 1198 K and in argon above 1173 K. The higher initiation temperature of mass loss in oxygen suggested oxygen dependence of the process. The residue after partial vaporization contained a mixture of $U_3O_8$ and $UTeO_5$ and the vapour turned solid was identified by XRD as $TeO_2$. So the only reaction $UTeO_5$ undergoes in oxygen environment is loss of $TeO_2$ in vapour

form accompanied with the evolution of $O_2$ and is represented by reaction (2):

$$3\langle UTeO_5 \rangle = \langle U_3O_8 \rangle + 3(TeO_2) + 1/2(O_2). \tag{2}$$

$UTe_3O_9$ also did not show any mass gain when heated dynamically in TG in oxygen upto 1023 K and hence underwent no oxidation. It started losing mass in oxygen as well as in argon at and above the same temperature i.e. 1023 K suggesting oxygen-independence of the vaporization process. The partial vaporization of $TeO_2$ from $UTe_3O_9$ left a residue containing $UTeO_5$ and $UTe_3O_9$ and a condensate containing $TeO_2$, as identified by XRD. So $UTe_3O_9$ undergoes incongruent vaporization reaction only, in oxygen environment as represented by the reaction (3).

$$\langle UTe_3O_9 \rangle = \langle UTeO_5 \rangle + 2(TeO_2). \tag{3}$$
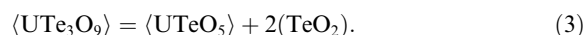
The transpiration measurements are based on the incogruent vaporization of $UTeO_5$ and $UTe_3O_9$ [4] according to the reactions (2) and (3), respectively. Ref. [9] reveals that at $p_{O2} = 1.01$ Pa, $TeO_2(g)$, $TeO(g)$, $(TeO)_2(g)$ and $(TeO_2)_2(g)$ are the various tellurium bearing species in the vapour phase over pure $\langle TeO_2 \rangle$, the partial pressures decreasing in the order: $p_{TeO2(g)} > p_{TeO(g)} > p_{(TeO)2(g)} > p_{(TeO2)2(g)}$. At $p_{O2} = 101325$ Pa i.e., the experimental oxygen pressure, the $TeO(g)$ and $(TeO)_2(g)$ will not be formed, so the only vapour species present during the transpiration would be $TeO_2(g)$ and $(TeO_2)_2(g)$. At $T = 889$ K, $p_{TeO2(g)}/p_{(TeO2)2(g)} \approx 100$ meaning thereby that the vapour phase will consist of 99% $TeO_2(g)$ and 1% of $(TeO_2)_2(g)$. Hence the vapour phase is assumed to be predominantly $TeO_2(g)$.

The uranium–oxygen phase diagram shows that $U_3O_8$ is the stable phase [10,11] in the temperature range of measurement of the partial vapour pressure of $TeO_2$ over $UTeO_5$. The occurrence of $U_3O_8$ in reaction (2), as identified by XRD, is also consistent with the phase diagram of the U–O system.

The vapour pressure of $(TeO_2)$ over $\langle UTeO_5 \rangle$ and $\langle UTe_3O_9 \rangle$ was measured in one atmosphere of flowing oxygen.

The mass loss from the sample of $UTeO_5$ as $TeO_2$ and $O_2$ per unit volume of oxygen was measured as a function of flow rate at 1182 K. It was found to remain constant in the range of flow rates between 3.3 and 3.6 l/h, indicating the saturation of the carrier gas by the vapour. Measurements at different temperatures were carried out using a flow rate of 3.5 l/h. The mass losses were apportioned in the mass ratio of $3TeO_2$: $1/2O_2$ i.e. 96.77% of the mass loss was attributed to $(TeO_2)$ and 3.23% due to $O_2$. The pressures of $(TeO_2)$ were calculated from the corresponding losses as presented in Table 1.

Similar experiments carried out with $\langle UTe_3O_9 \rangle$ as a function of flow rate at 989 K established that the carrier gas was saturated with $TeO_2$ vapour in the flow rate between 3.5 and 3.8 l/h. A flow rate of about 3.7 l/h was

Table 1
Vaporization data and Gibbs energy of formation for $UTeO_5$

| Temperature (K) | $W/V_c$ [a] (mg/l) | $p_{TeO2}$ (Pa) | $p°_{TeO2}$ (Pa) | $\Delta_f G°_{\langle UTeO5 \rangle}$ (kJ/mol) |
|---|---|---|---|---|
| 1107 | 0.041 | 0.64 | 204.66 | −1117 |
| 1122 | 0.074 | 1.16 | 290.64 | −1110 |
| 1132 | 0.100 | 1.56 | 365.31 | −1105 |
| 1141 | 0.147 | 2.30 | 447.24 | −1100 |
| 1152 | 0.213 | 3.33 | 570.28 | −1095 |
| 1166 | 0.310 | 4.84 | 771.87 | −1090 |
| 1175 | 0.431 | 6.74 | 934.11 | −1085 |
| 1182 | 0.469 | 7.33 | 1081.35 | −1083 |
| 1196 | 0.719 | 11.24 | 1441.68 | −1077 |
| 1209 | 1.080 | 16.88 | 1871.81 | −1071 |
| 1215 | 1.295 | 20.24 | 2107.55 | −1068 |
| 1217 | 1.444 | 22.57 | 2191.99 | −1066 |

[a] Mass loss due to $TeO_2$ after the correction for oxygen loss.

employed for the determination of the temperature coefficient of the vapour pressure over $\langle UTe_3O_9 \rangle$.

## 3. Results and discussion

The values of vapour pressure of $TeO_2$ over $UTeO_5$ at different temperatures are listed in Table 1 and the plot of ln $p(TeO_2)$ versus 1/T is shown in Fig. 1. The corresponding linear least squares equation for the tabulated data can be expressed as

$$\ln(p(TeO_2)/Pa)(\pm 0.06) = -42625.8/T + 38.12$$
$$(1107 \leqslant T/K \leqslant 1217). \tag{4}$$

The values of vapour pressure over $\langle UTe_3O_9 \rangle$ at different temperatures are listed in Table 2 and the plot of ln $p(TeO_2)$ versus 1/T is shown in Fig. 2. The corresponding linear least squares equation for the data can be expressed as

$$\ln(p(TeO_2)/Pa)(\pm 0.06) = -33412.7/T + 35.51$$
$$(947 \leqslant T/K \leqslant 1011). \tag{5}$$

### 3.1. Standard Gibbs energy of formation of $\langle UTeO_5 \rangle$

The standard Gibbs energy of formation of $\langle UTeO_5 \rangle$ can be expressed in terms of partial pressure of $(TeO_2)$ over the mixture of $\langle UTeO_5 \rangle$ and $\langle U_3O_8 \rangle$ by the equation

$$3\Delta_f G°\langle UTeO_5 \rangle = \Delta_f G°\langle U_3O_8 \rangle + 3\Delta_f G°(TeO_2)$$
$$+ 3RT \ln p(TeO_2) + 1/2(RT \ln pO_2). \tag{6}$$

As the oxygen pressure is fixed at 1 atm. the last term in the equation becomes zero. Alernatively, the Gibbs energy of formation can also be expressed in terms of partial pressures of the Tellurium bearing species above the compound and pure $\langle TeO_2 \rangle$ and Gibbs energies of
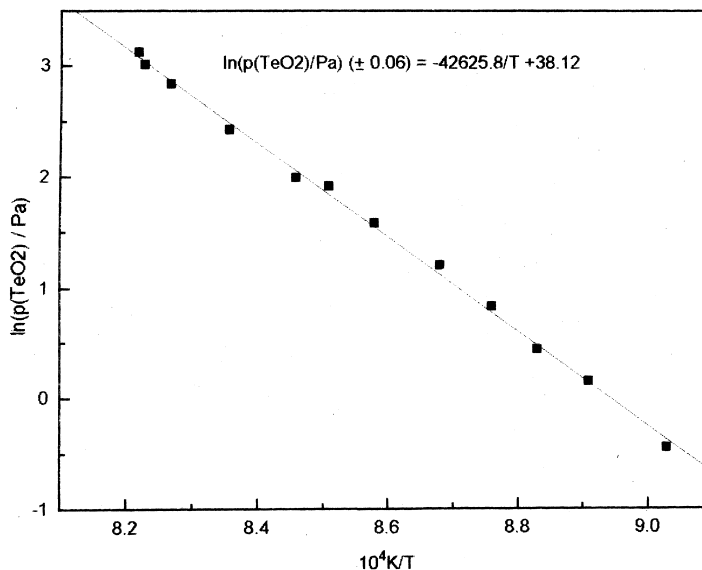
Fig. 1. $\ln(p(TeO_2)/$ Pa) versus $10^4$ K/T plot for $UTeO_5$.

formation of the other phases co-existing in equilibrium vaporisation reaction as given by the equation

$$3\, \Delta_f G°\langle UTeO_5 \rangle = \Delta_f G°\langle U_3O_8 \rangle + 3\, \Delta_f G°\langle TeO_2 \rangle \\ + 3RT\, \ln[p(TeO_2)/p°(TeO_2)]. \quad (7)$$

The ratio, $p(TeO_2)/p°(TeO_2)$, in the last term of the above equation represents the activity of $TeO_2$ in solid $UTeO_5$ in the temperature range 1107–1217 K, beyond the melting point (1006 K) of $TeO_2$. The choice of $p°(TeO_2)$ as the vapour pressure of metastable pure solid $TeO_2$ at $T >$ m.pt. of $TeO_2$ is consistent with the definition [12] of the activity function, $a_i$, as $a_i^\alpha = p_i^\alpha/P_i^\alpha$, wherein $\alpha$ refers to solid or liquid phase in which the activity of the $i$th solute is being considered. In the present case, $\alpha$ is solid. Consistent with this, the $\Delta_f G°$ in the second term of the right-hand side of the Eq. (7) refers to the metastable solid $TeO_2$.

The data for $\Delta_f G°\langle U_3O_8 \rangle$ and $\Delta_f G°\langle TeO_2 \rangle$, taken from the recent compilation of Cordfunke and Konings [13] alongwith the values for $\ln[p(TeO_2)/p°(TeO_2)]$ from Table 1 were used in Eq. (7). The vapour pressure of

Table 2
Vaporisation data and Gibbs' energy of formation for $UTe_3O_9$.

| Temperature (K) | $W/V_c$ (mg/l) | $p_{TeO_2}$ (Pa) | $p°_{TeO_2}$ (Pa) | $\Delta_f G°_{(UTe3O9)}$ (kJ/mol) |
|---|---|---|---|---|
| 947 | 0.086 | 1.34 | 2.43 | −1492 |
| 958 | 0.127 | 1.99 | 3.46 | −1482 |
| 969 | 0.189 | 2.95 | 4.88 | −1472 |
| 976 | 0.270 | 4.22 | 6.05 | −1464 |
| 991 | 0.374 | 5.85 | 9.49 | −1454 |
| 1002 | 0.536 | 8.38 | 13.10 | −1445 |
| 1011 | 0.770 | 12.03 | 16.95 | −1435 |

($TeO_2$) over solid $TeO_2$ i.e. $p°(TeO_2)$and the free energy of formation of solid $TeO_2$ were linear least square fitted, extrapolated to the said temperature range and used to derive the Gibbs energy of formation of $\langle UTeO_5 \rangle$. The data for the vapour pressure of ($TeO_2$) over pure solid $TeO_2$ taken from the measurements [7] in the same set-up of our laboratory and expressed as

$$\ln(p°(TeO_2)/Pa)(\pm 0.04) = -29088.5/T + 31.52 \\ (911 < T/K < 989) \quad (8)$$

was extrapolated over the range 1107–1217 K and used in the calculations. $\Delta_f G°\langle UTeO_5 \rangle$ derived from the Eq. (7) could be expressed by the equation

$$\Delta_f G°\langle UTeO_5 \rangle/kJ/mol(\pm 0.72) = -1614.17 + 0.450\, T \\ (1107 \leqslant T/K \leqslant 1217). \quad (9)$$

### 3.2. Standard Gibbs energy of formation of $\langle UTe_3O_9 \rangle$

The Gibbs energy of formation for the compound $\langle UTe_3O_9 \rangle$ can be expressed as a function of temperature by means of equations in terms of the partial pressure of ($TeO_2$) over a mixture of $\langle UTe_3O_9 \rangle$ and $\langle UTeO_5 \rangle$ by the equation

$$\Delta_f G°\langle UTe_3O_9 \rangle = \Delta_f G°\langle UTeO_5 \rangle + 2\Delta_f G°(TeO_2) \\ + 2RT\, \ln\, p(TeO_2). \quad (10)$$

Alternatively, the Gibbs energy of formation can also be expressed in terms of partial pressures of the tellurium bearing species above the compound, pure solid $TeO_2$ and the Gibbs energies of formation of the other coexisting phases as follows:

Fig. 2. $\ln(p(TeO_2)/\ Pa)$ versus $10^3$ K/T plot for $UTe_3O_9$.

$$\Delta_f G^\circ \langle UTe_3O_9 \rangle = \Delta_f G^\circ \langle UTeO_5 \rangle + 2\Delta_f G^\circ \langle TeO_2 \rangle$$
$$+ 2RT \ \ln[p(TeO_2)/p^\circ(TeO_2)]. \quad (11)$$

The data used in Eq. (11) were taken from Eq. (9) and [13], respectively. $\Delta_f G^\circ \langle UTe_3O_9 \rangle$ calculated from Eq. (11) could be expressed by the equation
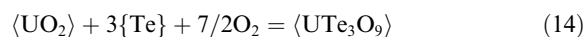
$$\Delta_f G^\circ (UTe_3O_9)/kJ/mol(\pm 1.31) =$$
$$-2313.12 + 0.868 \ T \quad (947 \leqslant T/K \leqslant 1011). \quad (12)$$

### 3.3. Possibility of formation of $\langle UTeO_5 \rangle$ and $\langle UTe_3O_9 \rangle$ in the fuel pin

The oxygen potential at $T = 1000$ K in the environment of irradiated $UO_2$-based fuel with about 10 000 MWD/metric tonne burn up in a nuclear reactor is estimated to be about −450 kJ/mol [14]. At this oxygen potential, tellurium is expected to be in the elemental form [5]. Considering the possiblity of formation of these compounds at a typical fuel temperature of 1000 K by the reaction of oxygen with tellurium and the oxide fuel according to the following schemes:

$$\langle UO_2 \rangle + \{Te\} + 3/2O_2 = \langle UTeO_5 \rangle \quad (13)$$

and

$$\langle UO_2 \rangle + 3\{Te\} + 7/2O_2 = \langle UTe_3O_9 \rangle \quad (14)$$
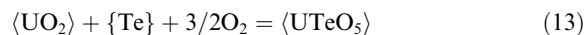
the Gibbs energy changes for the reactions (13) and (14) calculated for an oxygen potential of −450 kJ/mol are +424.67 and +1046.8 kJ/mol, respectively and clearly rule out the possibility of formation of the compounds.

The minimum oxygen partial pressures required for the formation of the two compounds according to the

reactions (13) and (14) at 1000 K are of the order of ∼$10^{-4}$ and ∼$10^{-3}$ Pa, respectively which are too high (about 15 orders of magnitude higher) compared to what would be contributed by a burn-up of 10 000 MWD/ metric tonne [14].

## 4. Conclusion

The Gibbs energy of formation of the compounds $\langle UTeO_5 \rangle$ and $\langle UTe_3O_9 \rangle$ as determined by transpiration technique can be expressed in form of the following equations:

$$\Delta_f G^\circ \langle UTeO_5 \rangle/kJ/mol(\pm 0.72) = -1614.17 + 0.450 \ T$$
$$(1107 \leqslant T/K \leqslant 1217),$$

$$\Delta_f G^\circ \langle UTe_3O_9 \rangle/kJ/mol(\pm 1.31) = -2313.12 + 0.868 \ T$$
$$(947 \leqslant T/K \leqslant 1011).$$

The formation of the compounds $UTeO_5$ and $UTe_3O_9$ in the fuel pin under normal operating conditions is highly unlikely.

The second law heats of formation at the mean temperatures of measurement, for $UTeO_5$ at 1162 K and for $UTe_3O_9$ at 979 K are found to be −1614.17 ± 0.72 and −2313.12 ± 1.31 kJ/mol, respectively.

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