

## THE THERMODYNAMIC PROPERTIES OF $\beta$ - $\text{UO}_3$ AND $\gamma$ - $\text{UO}_3$ \*

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### ABSTRACT

Heat capacities of carefully characterized samples of  $\beta$ - $\text{UO}_3$  and  $\gamma$ - $\text{UO}_3$  have been measured from 5 to 350 K using an adiabatic calorimeter, and from 350 to 700 K by enthalpy increment drop calorimetry. Values for the thermodynamic properties at 298.15 K,  $C_p^\ominus(T)$ ,  $S^\ominus(T)$ ,  $\{H^\ominus(T) - H^\ominus(0)\}$  and  $-\{G^\ominus(T) - H^\ominus(0)\}/T$ , are for  $\beta$ - $\text{UO}_3$ : 81.34 J K<sup>-1</sup> mol<sup>-1</sup>, 96.32 J K<sup>-1</sup> mol<sup>-1</sup>, 14682 J mol<sup>-1</sup>, and 47.062 J K<sup>-1</sup> mol<sup>-1</sup>, respectively, and for  $\gamma$ - $\text{UO}_3$ : 81.67 J K<sup>-1</sup> mol<sup>-1</sup>, 96.11 J K<sup>-1</sup> mol<sup>-1</sup>, 14585 J mol<sup>-1</sup>, and 47.179 J K<sup>-1</sup> mol<sup>-1</sup>, respectively.

### INTRODUCTION

At least six crystalline  $\text{UO}_3$  phases as well as an amorphous form of oxides of this composition are known. A tentative phase diagram of this complicated system was presented by Cordfunke and Aling [1] in 1965. The relatively meager X-ray, infrared, and Raman spectroscopic data then available have been supplemented subsequently. The uniqueness of the  $\text{UO}_3$  structure, in that the uranyl bond is present without the influence of other cations, has occasioned the comparison of the spectral features with those of other uranyl systems [2,3].

That the generally accepted hexagonal structure of  $\alpha$ - $\text{UO}_3$  [4] is incorrect has been demonstrated by neutron diffraction [5]. The results have led to the conclusion that  $\alpha$ - $\text{UO}_3$  is an imperfectly crystalline form of an orthorhombic modification of the oxide, in which twinning occurs on so small a scale that an average X-ray pattern is obtained. The structure of the orthorhombic cell

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is, however, unknown. The complexity of the  $\alpha$ - $\text{UO}_3$  structure has also been shown by Siegel and Hoekstra [6], who used both spectroscopic and X-ray methods. The structure of  $\beta$ - $\text{UO}_3$  has been examined by Debets [7] and that of  $\gamma$ - $\text{UO}_3$  by Engmann and de Wolff [8], by Siegel and Hoekstra [9], and by Loopstra et al. [10]. In both structures, uranium atoms having six- and sevenfold coordination with oxygen atoms occur; however, the atomic arrangement in  $\gamma$ - $\text{UO}_3$  is markedly different from that in  $\beta$ - $\text{UO}_3$ . In the latter, the uranium atoms possess six- and sevenfold coordination with the oxygen atoms. In  $\gamma$ - $\text{UO}_3$  the structure is made up of parallel chains of edge-fused uranium octahedra, cross-linked by uranium dodecahedra. The structure of  $\epsilon$ - $\text{UO}_3$  (with a triclinic unit cell with eight molecules in the cell [11]) is complex but unknown. Only cubic  $\delta$ - $\text{UO}_3$  contains a unique kind of uranium atom, at least if the simple proposed structure [12] is correct. In addition to these phases, all of which can be prepared at atmospheric pressure [13], a more dense orthorhombic polymorph  $\zeta$ - $\text{UO}_3$  has been obtained in the 15–60 kbar pressure interval [14].

In contrast, rather few studies on the chemical thermodynamics of this interesting system have appeared. Wartime studies of a yellow sample of  $\text{UO}_3$ , presumed to be  $\gamma$ - $\text{UO}_3$ , over the cryogenic [15] and elevated [16] temperature regions have been reported. Beketov and Vlasov [17] showed that the thermal stability of these phases increases in the sequence amorphous  $\text{UO}_3$ ,  $\beta$ - $\text{UO}_3$ ,  $\alpha$ - $\text{UO}_3$ , and  $\gamma$ - $\text{UO}_3$  and, in agreement with these observations, Cordfunke and Aling [1] demonstrated that  $\gamma$ - $\text{UO}_3$  is obtained as the ultimate phase upon prolonged heating of  $\alpha$ - or  $\beta$ - $\text{UO}_3$ .

A concise summary of the cryogenic thermophysics of  $\alpha$ -,  $\beta$ -, and  $\gamma$ - $\text{UO}_3$  from the present research has been made by Westrum [18], and values of the standard enthalpies of formation of  $\beta$ - $\text{UO}_3$  and  $\gamma$ - $\text{UO}_3$  have been published by Cordfunke et al. [19]. This determination has been selected as a key value by CODATA [20]. In the present presentation of the cryogenic heat capacities, the data for  $\beta$ - $\text{UO}_3$  and  $\gamma$ - $\text{UO}_3$  are combined with their standard enthalpies of formation and with higher-temperature enthalpy values on identical samples to provide more quantitative conclusions regarding the relative stabilities of these phases.

## EXPERIMENTAL

### *Preparation of the $\text{UO}_3$ samples*

Brick red  $\beta$ - $\text{UO}_3$  was prepared by heating uranyl nitrate hexahydrate (after drying first at 390 K) very rapidly to 725 K in platinum crucibles. Sufficiently crystalline  $\beta$ - $\text{UO}_3$  (i.e. with crystallite sizes  $\sim 60$  nm [21]) was thereby obtained. The sample had an average crystallite size of 58 nm, measured on the (040) reflection of the X-ray pattern [7]; the absence of  $\gamma$ - $\text{UO}_3$  was also established from the X-ray pattern.

TABLE 1

Molar mass and mass fraction for  $\beta$ - $\text{UO}_3$  and  $\gamma$ - $\text{UO}_3$ 

| Compound                 | $M$<br>( $\text{g mol}^{-1}$ ) | $10^2 w(\text{U})$ |       |
|--------------------------|--------------------------------|--------------------|-------|
|                          |                                | Obs.               | Calc. |
| $\beta$ - $\text{UO}_3$  | 286.03                         | $83.12 \pm 0.02$   | 83.22 |
| $\gamma$ - $\text{UO}_3$ | 286.03                         | $83.17 \pm 0.02$   | 83.22 |

Yellow  $\gamma$ - $\text{UO}_3$  was prepared by heating uranyl nitrate first at 470 K until dry; thereafter it was powdered and heated very slowly to about 770 K to give a  $\gamma$ - $\text{UO}_3$  sample free from the  $\beta$ -phase as established by X-ray diffraction.

These  $\text{UO}_3$  samples prepared at ECN had the isotopic distribution of natural uranium. The samples were handled in a glove box and characterized by X-ray diffraction and by chemical analysis. The uranium content was determined by automatic potentiometric titration [22]; the results are given in Table 1.

#### *Low-temperature heat capacity measurements*

Heat capacity data over the 5–350 K range were made in the University of Michigan's Mark II adiabatic cryostat by the usual intermittent heating technique [23]. All determinations of mass, potential current, time, and temperature were ultimately referenced to calibrations made by the National Bureau of Standards. Calorimeter W-42 was used with samples of  $\beta$ - $\text{UO}_3$  ( $\sim 141$  g) and  $\gamma$ - $\text{UO}_3$  ( $\sim 272$  g) and pressures of about 15 kPa of helium to provide thermal equilibration.

#### *High-temperature enthalpy measurements*

These drop calorimetric determinations were made at the Netherlands Energy Research Foundation ECN in an isothermal diphenylether calorimeter as described by Cordfunke et al. [24]. The calorimeter was immersed in a well-stirred water bath which maintained the solid diphenylether in equilibrium with its liquid ( $T_m = 300.06$  K). The specimen was encapsulated in spherical silica ampules which were about  $4.2 \text{ cm}^3$  in volume and weighed about 1.4 g empty. They contained about 6.78 g of  $\beta$ - $\text{UO}_3$  and about 9.84 g of  $\gamma$ - $\text{UO}_3$ , respectively. The samples are heated to the desired temperature in a furnace which is separated from the calorimeter by means of a copper diaphragm in order to avoid heat leakage into the calorimeter. The whole apparatus (calorimeter and furnace) is operated under an argon pressure of about 13 kPa. When the temperature has reached a constant value, the sample is dropped into the calorimeter. Heat from the specimen melts the

TABLE 2

Low-temperature heat capacity data for uranium trioxide phases

| $T$<br>(K)        | $C_p$<br>( $J K^{-1}$<br>$mol^{-1}$ ) | $T$<br>(K)       | $C_p$<br>( $J K^{-1}$<br>$mol^{-1}$ ) | $T$<br>(K)        | $C_p$<br>( $J K^{-1}$<br>$mol^{-1}$ ) | $T$<br>(K)       | $C_p$<br>( $J K^{-1}$<br>$mol^{-1}$ ) |
|-------------------|---------------------------------------|------------------|---------------------------------------|-------------------|---------------------------------------|------------------|---------------------------------------|
| $\beta$ - $UO_3$  |                                       |                  |                                       |                   |                                       |                  |                                       |
| <i>Series I</i>   |                                       | <i>Series II</i> |                                       | <i>Series III</i> |                                       |                  |                                       |
| 86.57             | 34.560                                | 5.59             | 0.042                                 | 41.20             | 13.230                                | 280.37           | 79.24                                 |
| 95.12             | 38.020                                | 6.58             | 0.084                                 | 45.66             | 15.347                                | 290.92           | 80.46                                 |
| 114.07            | 45.032                                | 7.41             | 0.159                                 | 50.65             | 17.769                                | 301.59           | 81.67                                 |
| 123.75            | 48.396                                | 8.34             | 0.301                                 | 56.22             | 20.418                                | 312.39           | 82.89                                 |
| 133.28            | 51.426                                | 9.44             | 0.473                                 | 61.69             | 23.091                                | 323.18           | 83.97                                 |
| 142.73            | 54.200                                | 10.61            | 0.741                                 | 66.55             | 25.401                                | 333.80           | 84.98                                 |
| 152.28            | 56.773                                | 11.79            | 0.979                                 | 67.58             | 25.882                                | 335.11           | 85.19                                 |
| 162.14            | 59.245                                | 13.07            | 1.343                                 | 74.35             | 28.962 <sup>a</sup>                   | 345.49           | 86.32                                 |
| 172.12            | 61.643                                | 14.47            | 1.799                                 | 81.28             | 32.162                                |                  |                                       |
| 182.17            | 63.85                                 | 16.03            | 2.356                                 | 89.19             | 35.669                                |                  |                                       |
| 192.29            | 65.90                                 | 17.71            | 2.987                                 | 99.88             | 39.836                                |                  |                                       |
| 202.61            | 67.82                                 | 19.58            | 3.682                                 | 109.89            | 43.585                                |                  |                                       |
| 212.94            | 69.71                                 | 21.80            | 4.527                                 |                   |                                       |                  |                                       |
| 223.11            | 71.42                                 | 24.39            | 5.565                                 |                   |                                       |                  |                                       |
| 233.28            | 72.97                                 | 27.18            | 6.749                                 |                   |                                       |                  |                                       |
| 243.42            | 74.43                                 | 30.20            | 8.083                                 |                   |                                       |                  |                                       |
| 253.38            | 75.94                                 | 33.52            | 9.623                                 |                   |                                       |                  |                                       |
| 263.45            | 77.28                                 | 37.16            | 11.339                                |                   |                                       |                  |                                       |
| $\gamma$ - $UO_3$ |                                       |                  |                                       |                   |                                       |                  |                                       |
| <i>Series I</i>   |                                       | <i>Series II</i> |                                       | <i>Series III</i> |                                       |                  |                                       |
| 146.48            | 54.463                                | 79.79            | 31.033                                | 5.24              | 0.0820                                | 46.13            | 15.928 <sup>b</sup>                   |
| 157.17            | 57.266                                | 84.09            | 32.941                                | 5.98              | 0.0967                                | 51.13            | 18.138                                |
| 166.96            | 59.722                                | 90.36            | 35.577                                | 6.75              | 0.1544                                | 56.67            | 20.610                                |
| 176.18            | 61.865                                | 97.37            | 38.258                                | 7.70              | 0.2565                                | 62.91            | 23.535                                |
| 185.32            | 63.85                                 | 104.77           | 41.041                                | 8.68              | 0.4803                                | 69.73            | 26.573                                |
| 194.75            | 65.73                                 | 113.33           | 44.124                                | 9.75              | 0.7657                                | 76.44            | 29.518 <sup>b</sup>                   |
| 204.34            | 67.61                                 | 122.52           | 47.246                                | 10.96             | 1.0309                                | 83.25            | 32.572                                |
| 213.97            | 69.33                                 | 131.48           | 50.133                                | 12.31             | 1.3594                                |                  |                                       |
| 223.70            | 71.00                                 | 140.32           | 52.785                                | 13.76             | 1.8138                                |                  |                                       |
| 233.47            | 72.63                                 |                  |                                       | 15.25             | 2.3087                                | <i>Series IV</i> |                                       |
| 243.17            | 74.10                                 |                  |                                       | 16.75             | 2.8493                                | 259.61           | 76.38                                 |
| 252.98            | 75.60                                 |                  |                                       | 18.38             | 3.4589                                | 267.10           | 77.66                                 |
| 262.72            | 76.90                                 |                  |                                       | 20.22             | 4.1802                                | 275.97           | 78.83                                 |
| 282.04            | 79.58                                 |                  |                                       | 22.34             | 5.0501                                | 285.97           | 80.17                                 |
| 291.47            | 80.92 <sup>b</sup>                    |                  |                                       | 24.75             | 6.0902                                | 296.03           | 81.34                                 |
| 300.94            | 81.84 <sup>b</sup>                    |                  |                                       | 27.42             | 7.280                                 | 306.43           | 82.63                                 |
| 310.53            | 83.26 <sup>b</sup>                    |                  |                                       | 30.34             | 8.598                                 | 317.29           | 83.89                                 |
| 320.11            | 84.18 <sup>b</sup>                    |                  |                                       | 33.55             | 10.088                                | 328.37           | 84.64                                 |
| 329.73            | 84.81 <sup>b</sup>                    |                  |                                       | 37.35             | 11.837                                | 339.57           | 85.35                                 |
| 339.57            | 85.35 <sup>b</sup>                    |                  |                                       | 41.62             | 13.807                                | 347.36           | 85.77                                 |

<sup>a</sup> These runs were not used in integration because of poor shield control.<sup>b</sup> These runs were not used in curve fitting and integration because of inexplicably irregular drifts.

diphenylether that is in equilibrium with the liquid ether in a closed vacuum system. The resulting volume increment is determined by mercury displacement. The ratio of heat input to mass of mercury making up the volume change is a constant for the apparatus ( $79.977 \pm 0.063 \text{ J g}^{-1}$ ) and is obtained by calibration with  $\alpha\text{-SiO}_2$  and compared with the National Bureau of Standards standard reference material (No. 720) synthetic sapphire,  $\text{Al}_2\text{O}_3$ . Our results with sapphire all agree within 0.2% with the data given by NBS. Corrections were made for the small difference between the calorimeter temperature ( $300.06 \pm 0.01$ ) K and the standard reference temperature, 298.15 K, using  $C_p$  values at 298.15 K. Temperature measurements were made with calibrated Pt-(Pt + 10 mass% Rh) thermocouples to within  $\pm 0.5$  K.

## RESULTS

### *Low-temperature data*

The heat capacity data for both the samples given in Table 2 are based on a gram formula mass of 286.03 on the basis of 1961 international atomic weights [25] and presented in chronological sequence to permit deduction of the approximate temperature increments employed in the measurements from the differences in the adjacent mean temperature. The data have been adjusted for curvature (i.e., for the finite temperature increments used in the determination of the heat capacity). The data are also shown graphically in Fig. 1. The experimental heat capacities were curve-fitted to polynomials in reduced temperature by the method of least-squares, and then integrated by computer to yield the values of the thermal functions at regular temperature intervals presented in Table 3 for both phases. The uncertainty in the thermodynamic functions in this table is considered to be less than 0.1% from 100 to 350 K. Additional digits beyond those significant are occasionally given to facilitate interpolation and differentiation.

Values of the entropy and enthalpy increments below 5 K were obtained from plots of  $C_p/T$  vs.  $T^2$ . For both compounds, the magnitudes of these extrapolations are only minute fractions of the totals at 298.15 K. No attempt was made in the process of extrapolation to adjust for contributions due to isotopic mixing or nuclear spin; hence, the values tabulated are practical thermal functions for use in ordinary thermochemical calculations. It was assumed that the zero point entropies were zero and that for reasons discussed below no magnetic contribution is appropriate. As a test of the measurements (and integration procedures), several determinations over about 60-K ranges of temperature were made as indicated in Table 4. The enthalpy increment measured directly (fourth column) is compared with that obtained from heat capacity measurements in Table 2.

TABLE 3

Thermodynamic functions for uranium trioxide phases

| $T$<br>(K)        | $C_p$<br>( $J K^{-1}$<br>$mol^{-1}$ ) | $S^\ominus(T) - S_m^\ominus(0)$<br>( $J K^{-1} mol^{-1}$ ) | $H^\ominus(T) - H^\ominus(0)$<br>( $J mol^{-1}$ ) | $-[G^\ominus(T) - H^\ominus(0)]/T$<br>( $J K^{-1} mol^{-1}$ ) |
|-------------------|---------------------------------------|--|---|---|
| $\beta$ - $UO_3$  |                                       |  |   |   |
| 5                 | 0.025                                 | 0.008  | 0.033   | 0.004   |
| 10                | 0.590                                 | 0.138  | 1.125   | 0.025   |
| 15                | 1.975                                 | 0.611  | 7.184   | 0.134   |
| 20                | 3.824                                 | 1.431  | 21.669  | 0.351   |
| 25                | 5.828                                 | 2.498  | 45.719  | 0.669   |
| 30                | 8.008                                 | 3.749  | 80.25   | 1.075   |
| 35                | 10.309                                | 5.155  | 126.02  | 1.556   |
| 40                | 12.665                                | 6.686  | 183.43  | 2.100   |
| 45                | 15.037                                | 8.314  | 252.67  | 2.699   |
| 50                | 17.435                                | 10.025   | 333.84  | 3.347   |
| 60                | 22.263                                | 13.627   | 532.33  | 4.757   |
| 70                | 27.037                                | 17.422   | 779.1   | 6.293   |
| 80                | 31.627                                | 21.334   | 1072.4  | 7.929   |
| 90                | 35.936                                | 25.309   | 1410.4  | 9.640   |
| 100               | 39.940                                | 29.305   | 1790.3  | 11.406  |
| 110               | 43.656                                | 33.288   | 2208.3  | 13.213  |
| 120               | 47.112                                | 37.238   | 2662.3  | 15.050  |
| 130               | 50.350                                | 41.137   | 3149.7  | 16.908  |
| 140               | 53.371                                | 44.982   | 3668.5  | 18.778  |
| 150               | 56.183                                | 48.760   | 4216.6  | 20.652  |
| 160               | 58.781                                | 52.472   | 4791.5  | 22.522  |
| 170               | 61.170                                | 56.107   | 5391.5  | 24.393  |
| 180               | 63.39                                 | 59.668   | 6014.5  | 26.255  |
| 190               | 65.40                                 | 63.149   | 6658.4  | 28.104  |
| 200               | 67.32                                 | 66.551   | 7322.4  | 29.941  |
| 210               | 69.16                                 | 69.881   | 8004.8  | 31.388  |
| 220               | 70.88                                 | 73.141   | 8704.8  | 33.572  |
| 230               | 72.51                                 | 76.325   | 9421.9  | 35.363  |
| 240               | 74.06                                 | 79.446   | 10155.0   | 37.133  |
| 250               | 75.44                                 | 82.496   | 10902.2   | 38.886  |
| 260               | 76.78                                 | 85.483   | 11663.7   | 40.622  |
| 270               | 77.99                                 | 88.404   | 12437.4   | 42.338  |
| 280               | 79.20                                 | 91.261   | 13223.5   | 44.032  |
| 290               | 80.37                                 | 94.061   | 14021.4   | 45.710  |
| 300               | 81.55                                 | 96.805   | 14831.0   | 47.367  |
| 325               | 84.14                                 | 103.437  | 16902.5   | 51.430  |
| 350               | 86.65                                 | 109.767  | 19038.5   | 55.371  |
| 273.15            | 78.37                                 | 89.33  | 12682   | 42.873  |
| 298.15            | 81.34                                 | 96.32  | 14682   | 47.062  |
| $\gamma$ - $UO_3$ |                                       |  |   |   |
| 5                 | 0.067                                 | 0.021  | 0.084   | 0.004   |
| 10                | 0.828                                 | 0.213  | 1.674   | 0.046   |
| 15                | 2.226                                 | 0.787  | 8.962   | 0.188   |
| 20                | 4.092                                 | 1.674  | 24.644  | 0.444   |

TABLE 3 (continued)

| $T$<br>(K) | $C_p$<br>( $J K^{-1}$<br>$mol^{-1}$ ) | $S^\ominus(T) - S_m^\ominus(0)$<br>( $J K^{-1} mol^{-1}$ ) | $H^\ominus(T) - H^\ominus(0)$<br>( $J mol^{-1}$ ) | $-[G^\ominus(T) - H^\ominus(0)]/T$<br>( $J K^{-1} mol^{-1}$ ) |
|------------|---------------------------------------|--|---|---|
| 25         | 6.201                                 | 2.812  | 50.300  | 0.799   |
| 30         | 8.447                                 | 4.138  | 86.86   | 1.243   |
| 35         | 10.753                                | 5.615  | 134.85  | 1.761   |
| 40         | 13.058                                | 7.201  | 194.39  | 2.339   |
| 45         | 15.347                                | 8.870  | 265.43  | 2.971   |
| 50         | 17.615                                | 10.606   | 347.82  | 3.648   |
| 60         | 22.192                                | 14.221   | 546.85  | 5.104   |
| 70         | 26.732                                | 17.983   | 791.6   | 6.678   |
| 80         | 31.146                                | 21.845   | 1081.1  | 8.330   |
| 90         | 35.355                                | 25.757   | 1413.8  | 10.050  |
| 100        | 39.309                                | 29.690   | 1787.4  | 11.816  |
| 110        | 42.999                                | 33.610   | 2199.1  | 13.619  |
| 120        | 46.438                                | 37.501   | 2646.4  | 15.447  |
| 130        | 49.639                                | 41.346   | 3127.1  | 17.292  |
| 140        | 52.626                                | 45.137   | 3638.4  | 19.146  |
| 150        | 55.413                                | 48.861   | 4179.0  | 21.004  |
| 160        | 58.015                                | 52.522   | 4746.3  | 22.861  |
| 170        | 60.442                                | 56.116   | 5338.8  | 24.711  |
| 180        | 62.701                                | 59.635   | 5954.7  | 26.552  |
| 190        | 64.81                                 | 63.082   | 6592.3  | 28.384  |
| 200        | 66.78                                 | 66.454   | 7250.0  | 30.204  |
| 210        | 68.62                                 | 69.760   | 7927.4  | 32.008  |
| 220        | 70.37                                 | 72.994   | 8622.4  | 33.798  |
| 230        | 72.05                                 | 76.157   | 9334.5  | 35.572  |
| 240        | 73.60                                 | 79.258   | 10062.9   | 37.330  |
| 250        | 75.14                                 | 82.295   | 10806.9   | 39.066  |
| 260        | 76.57                                 | 85.270   | 11565.4   | 40.786  |
| 270        | 77.99                                 | 88.186   | 12338.2   | 42.489  |
| 280        | 79.37                                 | 91.048   | 13125.2   | 44.170  |
| 290        | 80.67                                 | 93.855   | 13925.2   | 45.836  |
| 300        | 81.92                                 | 96.609   | 14738.1   | 47.484  |
| 325        | 84.47                                 | 103.274  | 16819.7   | 51.522  |
| 350        | 85.90                                 | 109.587  | 18950.6   | 55.446  |
| 273.15     | 78.41                                 | 89.03  | 12585   | 43.020  |
| 298.15     | 81.67                                 | 96.11  | 14585   | 47.179  |

### High-temperature enthalpies

The results of the drop calorimetric measurements (shown in Table 5) can be represented over the range of the experimental measurements as a function of temperature by a polynomial expression of the form  $H^\ominus(T) - H^\ominus(298.15 \text{ K}) = aT + bT^2 + cT^{-1} + d$ , the coefficients of which have been obtained by least-squares. The boundary conditions applied were  $H^\ominus(T) -$

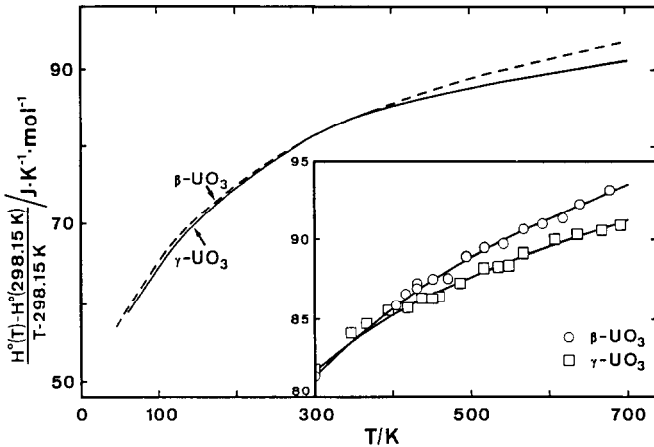


Fig. 1. The reduced and smoothed enthalpy increments of  $\beta$ - $\text{UO}_3$  and  $\gamma$ - $\text{UO}_3$  (insert, experimental values).

$H^\ominus(298.15 \text{ K}) = 0$  and  $C_p(T) = C_p(298.15 \text{ K})$  at  $T = 298.15 \text{ K}$ . The values of  $C_p(298.15 \text{ K})$  are taken from Table 3. The drop calorimetric measurements for  $\beta$ - $\text{UO}_3$  can be represented (298–678 K) by the equation

$$H^\ominus(T) - H^\ominus(298.15 \text{ K}) = 86.170T + (12.4922 \times 10^{-3})T^2 \\ + (10.9151 \times 10^5)T^{-1} - 30463$$

The standard deviation is 0.32%.

For  $\gamma$ - $\text{UO}_3$  we obtain (298–693 K)

$$H^\ominus(T) - H^\ominus(298.15 \text{ K}) = 88.701T + (7.2448 \times 10^{-3})T^2 \\ + (10.0903 \times 10^5)T^{-1} - 30475$$

The standard deviation is 0.35%.

At temperatures below 300 K the differences in  $C_p$  between  $\beta$ - $\text{UO}_3$  and  $\gamma$ - $\text{UO}_3$  are very small; between 300 and 360 K the  $C_p$  value of  $\gamma$ - $\text{UO}_3$  is, judging from the precision with which the values have been measured, even somewhat higher than that of  $\beta$ - $\text{UO}_3$ . Above 360 K the  $C_p$  values of the

TABLE 4

Comparison of enthalpy determinations of  $\gamma$ - $\text{UO}_3$  with smoothed heat capacity curve

| Detn. | $T_1$ (K) | $T_2$ (K) | $H^\ominus(T) - H^\ominus(0)$ (J mol $^{-1}$ ) |        |
|-------|-----------|-----------|--|--------|
|       |           |           | Expt.  | Calc.  |
| A     | 140.93    | 198.18    | 3443.9   | 3443.4 |
| B     | 198.18    | 256.04    | 4138.0   | 4134.6 |



TABLE 5

High-temperature enthalpy increments for uranium trioxide phases

| <i>T</i><br>(K)                           | $H^\ominus(T) - H^\ominus(298.15\text{ K})$<br>(J mol <sup>-1</sup> ) |       | $\delta$<br>(J mol <sup>-1</sup> ) | <i>T</i><br>(K) | $H^\ominus(T) - H^\ominus(298.15\text{ K})$<br>(J mol <sup>-1</sup> ) |       | $\delta$<br>(J mol <sup>-1</sup> ) |
|---|---|-------|------------------------------------|-----------------|---|-------|------------------------------------|
|   | Expt.   | Calc. |                                    |                 | Expt.   | Calc. |                                    |
| <i><math>\beta</math>-UO<sub>3</sub></i>  |   |       |                                    |                 |   |       |                                    |
| 404.9                                     | 9172  | 9171  | 1                                  | 517.9           | 19663   | 19623 | 40                                 |
| 417.2                                     | 10316   | 10278 | 38                                 | 542.7           | 21952   | 21992 | -40                                |
| 432.2                                     | 11701   | 11639 | 62                                 | 568.2           | 24471   | 24453 | 18                                 |
| 432.3                                     | 11678   | 11648 | 30                                 | 593.0           | 26822   | 26869 | -47                                |
| 452.4                                     | 13507   | 13490 | 17                                 | 617.9           | 29199   | 29317 | -118                               |
| 471.6                                     | 15190   | 15268 | -78                                | 640.5           | 31582   | 31558 | 24                                 |
| 494.4                                     | 17461   | 17401 | 60                                 | 678.4           | 35421   | 35353 | 68                                 |
| <i><math>\gamma</math>-UO<sub>3</sub></i> |   |       |                                    |                 |   |       |                                    |
| 347.1                                     | 4118  | 4093  | 25                                 | 516.9           | 19308   | 19263 | 45                                 |
| 366.3                                     | 5773  | 5743  | 30                                 | 536.0           | 21009   | 21033 | -24                                |
| 394.6                                     | 8258  | 8212  | 46                                 | 548.3           | 22108   | 22179 | -71                                |
| 419.6                                     | 10416   | 10425 | -9                                 | 568.6           | 24117   | 24078 | 39                                 |
| 438.6                                     | 12134   | 12124 | 10                                 | 608.4           | 27916   | 27831 | 85                                 |
| 452.5                                     | 13321   | 13376 | -55                                | 636.8           | 30584   | 30533 | 51                                 |
| 460.8                                     | 14068   | 14127 | -59                                | 668.1           | 33499   | 33531 | -32                                |
| 486.3                                     | 16426   | 16449 | -23                                | 693.1           | 35902   | 35940 | -38                                |

oxides diverge, resulting in a more pronounced stability of  $\gamma$ -UO<sub>3</sub> vs.  $\beta$ -UO<sub>3</sub>.

### *Thermochemical values*

Combination of the data of the present research with literature data permits the evaluation of the chemical thermodynamics of formation for the phases noted. Utilizing values for the enthalpies of formation at 298.15 K of  $\beta$ -UO<sub>3</sub>,  $-1220.1 \pm 0.8$  [19] and  $\gamma$ -UO<sub>3</sub>,  $-1223.8 \pm 2.0$  kJ mol<sup>-1</sup> [26], the entropies at 298.15 K of uranium,  $50.20 \pm 0.20$  [26], and oxygen gas,  $205.037 \pm 0.033$  J K<sup>-1</sup> mol<sup>-1</sup> [26], we concluded that the standard thermochemical values for the formation process are those given in Table 6.

## DISCUSSION

An impression of the accuracy of the measurements as well as of the deviation of the samples from each other is given in Fig. 1.

There is only one prior determination of the low-temperature heat capacity of UO<sub>3</sub> by Jones et al. [15] (which is believed to be the  $\gamma$ -phase because

TABLE 6  
Thermodynamic properties of  $\beta$ - $\text{UO}_3$  and  $\gamma$ - $\text{UO}_3$

| $T$<br>(K)               | $C_p^\ominus$<br>( $\text{J K}^{-1} \text{ mol}^{-1}$ ) | $S^\ominus$<br>( $\text{J K}^{-1} \text{ mol}^{-1}$ ) | $-[G^\ominus(T) - H^\ominus(298)]/T$<br>( $\text{J K}^{-1} \text{ mol}^{-1}$ ) | $H^\ominus(T) - H^\ominus(298)$<br>( $\text{J mol}^{-1}$ ) | $\Delta_f H^\ominus(T)$<br>( $\text{J mol}^{-1}$ ) | $\Delta_f G^\ominus(T)$<br>( $\text{J mol}^{-1}$ ) |
|--------------------------|---|---|--|--|--|--|
| $\beta$ - $\text{UO}_3$  |   |   |  |  |  |  |
| 298                      | 81.340  | 96.320  | 96.320   | 0  | -1220100   | -1142151   |
| 300                      | 81.537  | 96.824  | 96.324   | 150  | -1220083   | -1141668   |
| 400                      | 89.342  | 121.459   | 99.629   | 8732   | -1218826   | -1115707   |
| 500                      | 94.296  | 141.958   | 106.102  | 17928  | -1217298   | -1090100   |
| 600                      | 98.129  | 159.500   | 113.575  | 27555  | -1215745   | -1064808   |
| 700                      | 101.432   | 174.879   | 121.256  | 37536  | -1214282   | -1039770   |
| 800                      | 104.452   | 188.623   | 128.833  | 47832  | -1212978   | -1014931   |
| 900                      | 107.308   | 201.092   | 136.179  | 58421  | -1211887   | -990243  |
| 1000                     | 110.063   | 212.541   | 143.251  | 69290  | -1213469   | -965500  |
| $\gamma$ - $\text{UO}_3$ |   |   |  |  |  |  |
| 298                      | 81.670  | 96.110  | 96.110   | 0  | -1223800   | -1145788   |
| 300                      | 81.836  | 96.616  | 96.116   | 150  | -1223783   | -1145306   |
| 400                      | 88.190  | 121.130   | 99.412   | 8687   | -1222571   | -1119321   |
| 500                      | 91.910  | 141.237   | 105.829  | 17704  | -1221222   | -1093664   |
| 600                      | 94.592  | 158.241   | 113.183  | 27035  | -1219965   | -1068273   |
| 700                      | 96.784  | 172.992   | 120.696  | 36607  | -1218911   | -1043078   |
| 800                      | 98.716  | 186.044   | 128.065  | 46383  | -1218127   | -1018016   |
| 900                      | 100.496   | 197.775   | 135.169  | 56345  | -1217663   | -993034  |
| 1000                     | 102.182   | 208.451   | 141.972  | 66479  | -1219980   | -967921  |

of its preparation and color). Although the trend of our data is the same, the data of Jones et al. are somewhat higher than those of the present sample, possibly due to poor crystallinity, non-stoichiometry or impurities. These authors report having exposed their finely ground oxide to the atmosphere, and noted that water had been taken up. In the hope of removing this absorbed water, they heated the sample in an oven at 373 K for 3 h immediately before sealing it into the calorimeter. Their data show a small anomaly just below the ice point indicating a free water content of about 0.04 mol%. The sample was subsequently used by Moore and Kelley [16] who reported that the sample as received from Jones et al. contained 1.17% by weight of water which was not removable at 393 K. An analysis made by Moore and Kelley [16] on their final material indicated only 83.02 mass% of uranium compared with the theoretical value of 83.22 mass%. Jones et al. [15] considered that any significant amount of water contained in their sample was bound in such a manner as to give an almost normal heat capacity at the ice point, and made no correction.

Unpublished measurements on the susceptibility by the Gouy method [27] indicated both  $\text{UO}_3$  phases to be very weakly paramagnetic, probably due to the presence of different oxygen atom environments of uranium atoms. No anomalies were found between 1.3 and 5 K.

The relative stabilities of  $\beta\text{-UO}_3$  and  $\gamma\text{-UO}_3$  can be seen in Table 6. These are clearly in accord with previous observations of Cordfunke and Aling [1]. The small differences in the  $\Delta G^\ominus$  values as compared with significant differences in structure are interesting and emphasize the need for precise data in correlating phase behavior.

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## REFERENCES

- 1 E.H.P. Cordfunke and P. Aling, *Trans. Faraday Soc.*, 61 (1965) 50.
- 2 S.D. Gabelnick, G.T. Reedy and M.G. Chasanov, *J. Chem. Phys.*, 59 (1973) 6397.
- 3 J.J. Verbist, J. Riga, C. Tenret-Noel, J.J. Pireaux, G. d'Ursel, R. Caudane and E.G. Derouane, *Plutonium 1975 and Other Actinides. Proceedings of the 5th International Conference on Plutonium and Other Actinides. Baden-Baden, 1975*, Elsevier, Oxford, Amsterdam, New York, 1976, p. 409.
- 4 W.H. Zachariasen, *Acta Crystallogr.*, 1 (1948) 265.
- 5 B.O. Loopstra and E.H.P. Cordfunke, *Rec. Trav. Chim. Pays-Bas*, 85 (1966) 135.
- 6 S. Siegel and H.R. Hoekstra, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 497.
- 7 P.C. Debets, *Acta Crystallogr.*, 21 (1966) 589.
- 8 R. Engmann and O.M. de Wolff, *Acta Crystallogr.*, 16 (1963) 993.
- 9 S. Siegel and H.R. Hoekstra, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 455.
- 10 B.O. Loopstra, J.C. Taylor and A.B. Waugh, *J. Solid State Chem.*, 20 (1977) 9.
- 11 L.M. Kovba, L.M. Vidaviskii and E.G. Labut, *Zh. Strukt. Khim.*, 4 (1963) 627.
- 12 E. Wait, *J. Inorg. Nucl. Chem.*, 1 (1955) 309.
- 13 E.H.P. Cordfunke, *The Chemistry of Uranium*, Elsevier, Amsterdam, 1969, p. 86.
- 14 S. Siegel, H.R. Hoekstra and E. Sherry, *Acta Crystallogr.* 20 (1966) 292.
- 15 W.M. Jones, J. Gordon and E.A. Long, *J. Chem. Phys.*, 20 (1952) 695.
- 16 G.E. Moore and K.K. Kelley, *J. Am. Chem. Soc.*, 69 (1947) 2105.
- 17 A.R. Beketov and G.W. Vlasov, *Zh. Prikl. Khim.*, 38 (1965) 2103.
- 18 E.F. Westrum, Jr., in *Thermodynamics: Proceedings of the Symposium on Thermodynamics with Emphasis on Nuclear Materials, 1965, Vol. II, IAEA, Vienna, 1966*, p. 497.
- 19 E.H.P. Cordfunke, W. Ouweltjes and G. Prins, *J. Chem. Thermodyn.*, 7 (1975) 1137.
- 20 CODATA Recommended Key Values for Thermodynamics, *CODATA Bulletin 10*, CODATA, Paris, 1973.
- 21 E.H.P. Cordfunke, *J. Inorg. Nucl. Chem.*, 23 (1961) 285.
- 22 J. Slanina, F. Bakker, C. Lautenbag, W.A. Lingerak and T. Sier, *Mikrochim. Acta*, 1 (1978) 519.
- 23 E.F. Westrum, Jr. and G.T. Furukawa, in J.P. McCullough and D.W. Scott (Eds.), *Experimental Thermodynamics*, Butterworth, London, 1968, p. 133.
- 24 E.H.P. Cordfunke, R.P. Muis and G. Prins, *J. Chem. Thermodyn.*, 11 (1979) 819.
- 25 A.E. Cameron and E. Wichers, *J. Am. Chem. Soc.*, 84 (1962) 4175.
- 26 CODATA Recommended Key Values for Thermodynamics—1977, *CODATA Bulletin 28*, CODATA, Paris, 1978.
- 27 F. de Boer (University of Amsterdam), private communication.