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## Note

# ENTHALPY INCREMENTS OF $BaZrO_3$ AND $SrZrO_3$—A REPLY TO THE COMMENTS OF CORDFUNKE AND KONINGS

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In a recent paper [1], Cordfunke and Konings raised doubts over the reliability of our calorimetric results on the enthalpy increments of $BaZrO_3$ and $SrZrO_3$ [2]. Our response to the comments follows.

$BaZrO_3$

Our measurements were carried out in the temperature range 1000–1700 K; Cordfunke and Konings' measurements covered the range 400–775 K. In the 1000–1700 K range, the extrapolated values of Cordfunke and Konings are 2–3.5% higher than our values, whereas in the temperature range

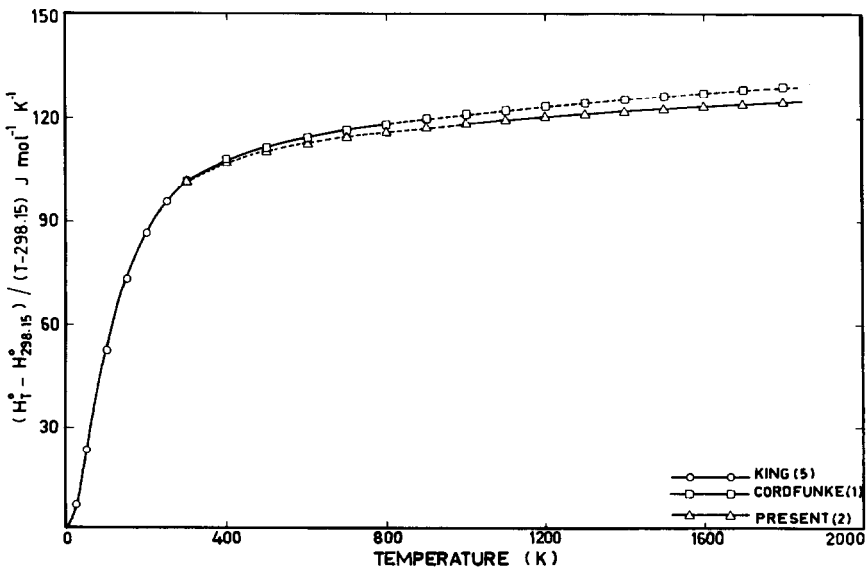


Fig. 1. Reduced enthalpy increment of $BaZrO_3$.

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400–775 K our extrapolated values are only 0.5–1.5% lower than those of Cordfunke and Konings, see Fig. 1.

Cordfunke and Konings also remarked that we did not give the accuracy of our measurements. In an earlier paper [3], we reported our studies on $ThO_2$ and Au in which our results were compared with the assessed values: the accuracy of our results was $\pm 3\%$. Our values and those of Cordfunke and Konings fall within this error band.

## $SrZrO_3$

Cordfunke and Konings [1] also remarked that our values for $SrZrO_3$ are significantly lower than those of Fomichev et al. [4].

In their paper, Fomichev et al. gave the following equation as representing the 'fit' of their measured values

$$H_T^{\ominus} - H_{298.15}^{\ominus} = 147.072T - 2.077 \times 10^{-3}T^2 + 4.148 \times 10^6 T^{-2} - 57277 \text{ (J mol}^{-1}\text{)} \quad (1)$$

TABLE 1

Enthalpy data of Fomichev et al. [4] for $SrZrO_3$

| $T$ (K) | $H_T^{\ominus} - H_{298.15}^{\ominus}$ (J mol$^{-1}$) | | | |
|---|---|---|---|---|
| | As in ref. 4 | | From eqns. | |
| | Measured | From fit | (1) | (2) |
| 562 | 31880 | 31802 | 24735 | 32102 |
| 677 | 46847 | 47166 | 41348 | 47466 |
| 772 | 59670 | 60098 | 55032 | 60398 |
| 871 | 73075 | 73709 | 69252 | 74009 |
| 979 | 88572 | 88652 | 84720 | 88953 |
| 1072 | 101860 | 101566 | 98001 | 101867 |
| 1180 | 116697 | 116591 | 113379 | 116891 |
| 1276 | 129105 | 129959 | 127008 | 130256 |
| 1379 | 144862 | 144293 | 141588 | 144594 |
| 1485 | 160238 | 159438 | 156545 | 159338 |
| 1572 | 170171 | 171126 | 168789 | 171426 |
| 1673 | 185791 | 185140 | 182963 | 185440 |
| 1778 | 199733 | 199684 | 197652 | 199984 |
| 1882 | 213490 | 214061 | 212157 | 214360 |
| 1975 | 227819 | 226888 | 225090 | 227189 |
| 2080 | 240755 | 241341 | 239648 | 241641 |
| 2161 | 254708 | 255209 | 253608 | 255509 |
| 2318 | 274555 | 273965 | 272477 | 274265 |

We believe that there is a printing error in the third term and that it should read $T^{-1}$. Hence the corrected equation is

$$H_T^{\ominus} - H_{298.15}^{\ominus} = 147.072T - 2.077 \times 10^{-3}T^2 + 4.148 \times 10^6 T^{-1} - 57277 \text{ (J mol}^{-1}\text{)} \quad (2)$$

In Table 1, columns 2 and 3 give the measured and fitted values of Fomichev et al. as reported in the table of their paper. Column 4 gives the value computed by eqn. (1) given in their paper. It can be seen that their fit equation does not correlate with their reported fitted values. Column 5 gives the values computed using the corrected eqn. (2).

The reduced enthalpy increment values derived from the above equation are plotted along with our data and the low temperature data of King and Weller [5] in Fig. 2. It can be seen that the difference is greatest at 900 K (2.5%) and decreases at lower and higher temperatures. At 1700 K the difference is only 0.7%. Hence, the argument that our values are significantly lower is untenable. The two sets of data are in agreement within the error band of our measurements. The data of Levitskii et al. [6] are much lower.

Cordfunke and Konings reported that the values of Fomichev et al. join smoothly with the low temperature values of King and Weller. We find that the reduced enthalpy increment value obtained at 300 K from the equation reported by Fomichev et al. is 261.80 J $K^{-1}$ $mol^{-1}$, which is far higher than the $C_{p_{298.15}}$ of King and Weller, namely 103.386 J $K^{-1}$ $mol^{-1}$.

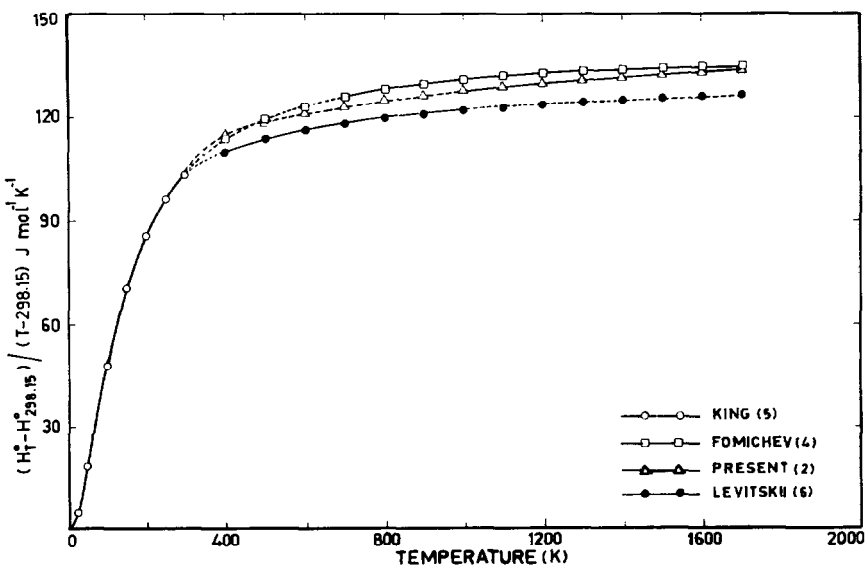


Fig. 2. Reduced enthalpy increment of $SrZrO_3$.

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