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Letter

"Understanding reactions with O_2 for ^{90}Sr measurements by ICP-MS with collision reaction cell" by Favre et al. [Int. J. Mass Spectrom. 265 (2007) 15–22]

In this 2007 paper by Favre and co-workers, studies were made of Sr and Zr interactions with O_2 by ICP-MS in a collision reaction cell in which the ions produced had about a millisecond residence time. From the observed distribution of ZrO^+, $ZrO_2{}^+$, and SrO^+ they produced thermochemical values for these ions that are consistent with previously published values. Experimental measures of $SrO_2{}^+$ ion concentrations were too small for meaningful analysis. However, DFT theoretical calculations were made for all four ions and values were supportive for the three experimental measures. As a result the value calculated for $\Delta H_{f298K}(SrO_2{}^+)$, 853 kJ mol^{-1} was accepted and presented as a first measure of its value. The paper implied that no other information was available in the literature with which to compare. Unfortunately, the authors overlooked the relevant previous work by J.M. Dyke and coworkers [1,2] and by Schofield [3], which indicates that although still slightly uncertain, that this value should be more in the range of 496 ± 45 kJ mol^{-1}. This 357 kJ mol^{-1} discrepancy is very significant and if true would have significant implications not only for strontium but for the indicated trends of its fellow alkaline earth elements in the periodic table.

This thermochemical value for $SrO_2{}^+$ is only critically dependent on two values that remain somewhat uncertain, the ionization potential of SrO_2, considered to be 569 ± 30 kJ mol^{-1} and the strength of the initial bond of the neutral molecule OSr–O, which is taken as 332 ± 30 kJ mol^{-1}. Other values involved are all very reliably determined. Consequently, a discrepancy of this magnitude would have to be absorbed by these values, the ionizing potential increasing and/or the bond strength decreasing. Either of these possibilities seems to be out of the question and inconsistent with periodic table trends.

This note is to bring this inconsistency to the attention of the authors and potential users of the data. The only reasonable conclusion appears to be that there is an error in the DFT calculations for this molecule. It would seem at the present time that the prior values have to be considered the more reliable and this later value concerning $SrO_2{}^+$ cannot be accepted.

References

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