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# MODELING SUB- AND SUPER-AMBIENT HEAT CAPACITIES OF THE GROUP IVA COMPOUNDS DESPITE THE LANTHANIDE CONTRACTION

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## Abstract

This paper is concerned with the estimation of heat capacities in the IVA 3d-transition element compounds using especially Zr and Hf compounds as examples. Most prediction schemes routinely tacitly assume that volumes and masses trend 'in parallel'. However, the lanthanide contraction here ensures for ZrX/HfX systems – and generally elsewhere – that this is not so in this portion of the periodic table. Available methods such as Latimer's, Volumetric Priority, Komada-Westrum, Grimvall's, and Sommers' are compared on IVA elements and compounds. Only the Sommers approach has volumetric input. It provides the best prediction.

**Keywords**: $C_p$, $C_v$, entropies, group IVA element compounds, Hf, Zr

## Introduction

Beyond the morphology of heat capacity trends [1], resolution of the internal degrees of freedom in condensed phase materials continues to be an important aspect of the interpretation and indeed for the procurement even of values of heat-capacities through the delineation of the lattice heat-capacity contribution [2]. In the absence of experimental data the need is even more pronounced since the lattice heat capacity and lattice entropy data may need to be estimated to approximate even the gross contributions. After a brief review of the cruder available methods [3, 4], including the 'unadulterated' Latimer method [5], Grimvall's modifications of it, and the Sommers' enhancement, some aspects of the Komada/Westrum model [2] are enumerated and evaluated for extent data on group IVA element oxides – especially for the values on $ZrO_2$ and $HfO_2$ which differ in the cationic masses by a factor of 1.96 and yet show a volumetric difference of only about 0.16 per cent in their respective unit cell volumes. The discussion is based on more modern replication by Shaviv *et al.* [6] of older heat-capacity measurements of $ZrO_2$ [7] and $HfO_2$ [8] and interpretation by Grimvall [9]. The very recent papers of Atake [10,11] with automated equilibrium, adiabatic heat capacity covering both cryogenic and super-ambient regions, as

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well as the older data of Nevitt [12] are also considered. The nitrides and other Ti, Zr, Hf compounds are reviewed [13].

The earliest data on the Group IVA dioxides (Kelley [7] and Todd [8]) extended only down to about 55 K and the Komada/Westrum approach [2] can be used to compare the cryogenic extrapolation with the more arbitrary approach of Kelley and Todd who used rigid spline curves to extend heat capacities to zero K. The comparison of the sub-ambient data of Shaviv *et al.* with higher temperature data [14–16] extend to beyond 1000 K and the overlap shows excellent agreement.

The excellence of the fits achieved are shown graphically in a series of figures. The comparison of the Komada/Westrum fits is also depicted to temperatures as high as the Lord, Alberg, and Andrews [17] approximation for anharmonic oscillations (in place of the harmonic oscillations of the Komada-Westrum approach) presently permits.

In this era of increasing thermodynamic data shortages, the ability to estimate unmeasured values for thermodynamic properties is a very relevant aspect of science. Our interest in lanthanide and transition series of compounds has emphasized consideration of the relevance of volume on the thermophysical properties.

## A comment on experimentation

The comparison of the cryogenic data of our definitive measurement paper [6] with other measurements has been expanded to take into account the new values of Atake [10, 11] made to provide a firm basis for the thermodynamics of doping in yttria based zirconia ($ZrO_2$) presented at the Calorimetry Conference [10] and submitted to J. Chem. Thermodyn. [11]. The scatter of the four $ZrO_2$ curves – as is too often so – seems excessive in comparison with the several authors' typically seen claims for standard deviation; but since both our samples have been measured in the same calorimeter and are modern values by automated equilibrium adiabatic on high purity samples, we will use them to define the difference increment.

## A selection of approaches

### *The Latimer scheme*

The oldest and still perhaps the most popular is the Latimer scheme [5]. Like so many other schemes in which the prime variables are masses and volumes, it is recognized that both are relevant variables; yet, it is customary in virtually all of such schemes to assume that masses and volumes are in some sense proportionate. Grimvall has analyzed the Latimer approach [9] and concludes that 'it is shown from lattice dynamical theory that Latimer's functional dependence correctly expresses the explicit mass dependence of the entropy at high temperatures' with the caveat 'the size of an ion is assumed to scale with the mass'.

### *Volumetric priority scheme*

Many years ago, Grønvold and Westrum [18, 19] demonstrated that although certain of the heavier elements did often follow a Latimer logarithmic trend with the cation mass, the bulk of the chalcogenide compounds of the 3d, 4d, and 5d transition metals revealed an essential constancy for all except the extreme elements of each row rather than dependence on cationic mass. Moreover, the lanthanide (4f) element chalcogenides were perpendicular to the Latimer trend prediction. Chemists, of course, invoke the familiar lanthanide contraction and conclude that volume can be selected as an also dominant variable. Hence the volumetric priority scheme [20] was developed and used successfully essentially as an empirical interpolation device as a function of temperature between two 'reference' compounds showing essentially diamagnetic behavior, e.g., LaX and GdX.

### *Komada-Westrum theory*

In a recent development, the Komada/Westrum theory [2], which has a Debye-like single parameter ($\theta_{KW}$), is evaluated after a number of atomic, molecular, and crystallographic (vibrational) parameters are specified. The theory is based on a simplification of a Born-von Kármán [21] type of vibrational analysis and a harmonic oscillator theory, but can be adjusted, if necessary, for anharmonic oscillations by the Lord *et al.* [17] approximation and pushed to higher temperatures. In a recent study of $Ln_2S_3$ compounds the empirical volumetric priority and the theoretical Komada/Westrum approach gave the same results – within experimental error – on the resolution of Schottky effects and other internal degrees of freedom [22].

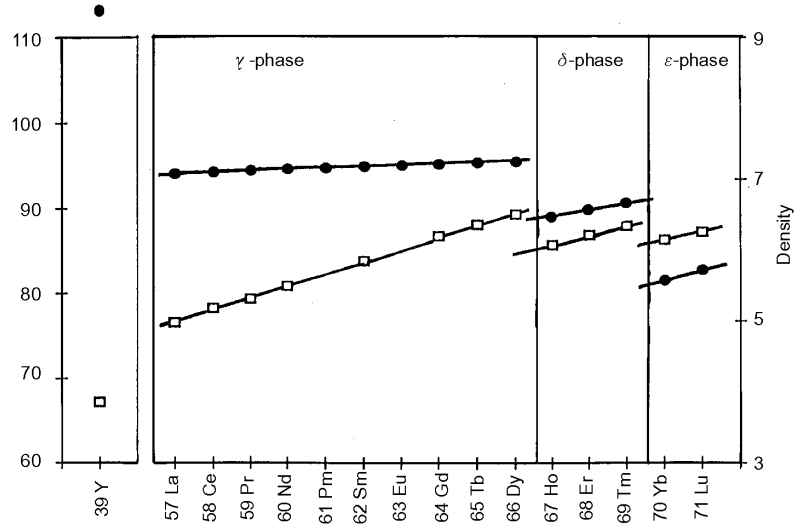


**Fig. 1** $\theta_{KW}$ *vs.* atomic number for the three phases of lanthanide sesquisulfides ($Ln_2S_3$) at 298.15 K (•) together with the densities (□) [23]

We have recently made application of the Komada-Westrum theory [2] and noted that after resolution and subtraction of the internal degrees of freedom of isostructural sequences of γ-, β-, and ε-phase lanthanide sesquisulfides [23] the residual purely lattice vibrations could be modeled (fitted) as lattice-heat-capacity contributions and their $\theta_{KW}$'s plotted as a function of temperature. The resultant values behave smoothly and are nearly linear with temperature as the anharmonicity was largely eliminated and the dependence on atomic number of the lanthanide was very smooth, the trends across changes in phase were consistent – but not predictable [20] as shown in Fig. 1.

Typical $\theta_{KW}$ *vs. T* plots for the group IVA compounds based upon $C_V'$s are displayed in Fig. 2.

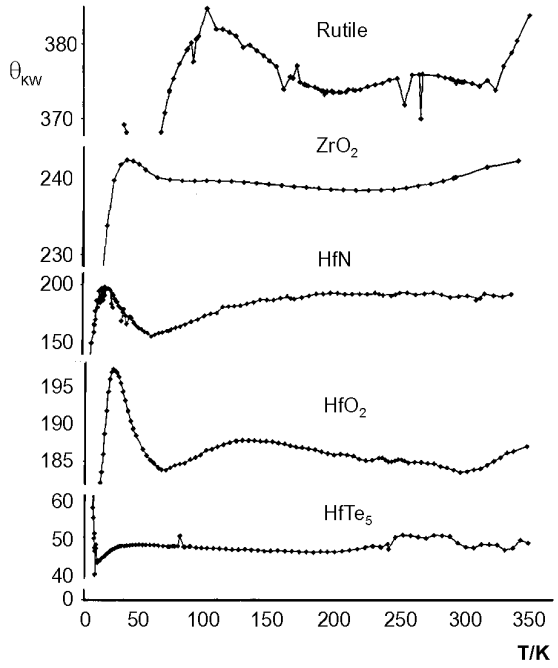


**Fig. 2** Characteristic plots of $\theta_{KW}$ *vs.* temperature for the compounds indicated

## *Grimvall's approach*

Grimvall, too, has developed his own theory for lattice heat capacity/entropy extrapolations [24] and applied it to the Zr /Hf systems [25]. It is based on the selection of an entropy $\theta_D$ (called $\theta_S$) at a super-ambient temperature.

## *Sommers' approach*

Yet another theory based on the same Zr/Hf systems [13] seems to be far more effective. For those of us dealing with group IVA transition elements, lanthanide series, etc., the volume change is a very relevant concept and possibly often the pre-

dominant variable. In this scheme, estimates of the standard state entropies, $S^o_m$, based upon the molar cation mass and molar volumes (referred to that of elemental Ti) or its compounds are applicable to those series which have substantially reached their equipartition limit, as have the elements; anharmoncity effects are ignored:

$$S^o(\text{HfN, 298.15 K})/R = S^o(\text{ZrN, 298.15 K})/R + \ln(M_{Hf}V_{HF}/M_{Zr}V_{Zr}) \quad (1)$$

where the $V'$s are those of the ions. For the nitrides and carbides, the heat capacities at 298.15 K average only about 75 to 80% of their equipartition limits at the reference temperature. For these, an adjustment using the ratio of the Debye characteristic temperatures (i.e., $\theta'_D$s) may be added to the right side of Eq. (1).

$$\ln(\theta_{D,ZrN} / \theta_{D,HfN}) \quad (2)$$

## Results and discussion

### *$ZrO_2$ and $HfO_2$*

We should recognize at the outset that although compounds like the monoclinic modifications of $ZrO_2$ and $HfO_2$ are indeed isostructural, there may be important distinctions in the atomic arrangements which has hitherto escaped our purview – and apparently that of others, since for example, the transition to another modification of $HfO_2$ takes place at a much higher temperature than that for $ZrO_2$. Moreover, defects are special structural features which play a much more significant role for oxides than, say, for tellurides. But we can at least hope for a 'generic' solution. For convenience in arranging the data and results in these systems, we will use Table 1 to store needed relevant data and some results.

**Table 1** Selected experimental data on HfX and ZrX compounds at 298 K

| | $S^o/R$ | $\Delta S^o/R$ |
|---|---|---|
| $ZrO_2$ | 6.04 | 0.75 |
| $HfO_2$ | 6.79 | |
| ZrN[a] | 4.67 | 0.72 |
| HfN | 5.39 | |
| $ZrTe_5$ | 31.96 | 1.03 |
| $HfTe_5$ | 32.99 | |

[a] cf. also Table 2

Experimental data [6] on monoclinic $ZrO_2$ and $HfO_2$ $S^o/R$ at 298.15 K show values of 6.04 and 6.79 so that the increment between the two compounds is 0.75. None of the schemes mentioned seems appropriate in explaining the increment; however, the essential correctness of the values are confirmed by their magnitudes and by Fig. 3.

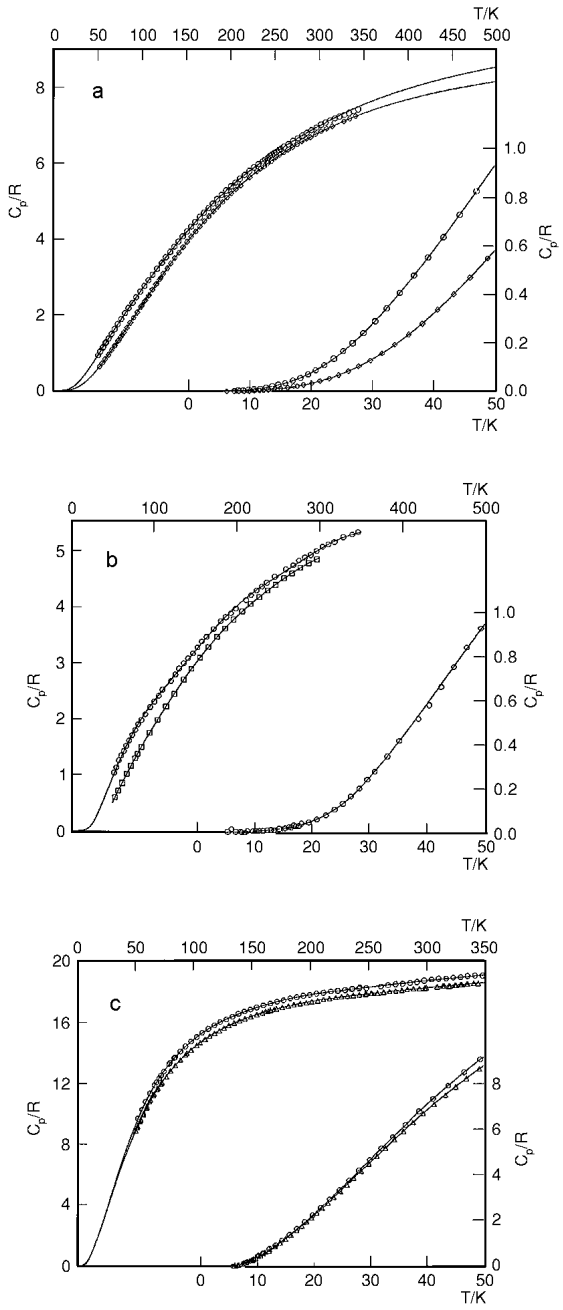


**Fig. 3** $C_P$ values for $ZrO_2$ and $HfO_2$ to 500 K [6] for comparison and to show the smooth fits to higher temperature data (a). Parts (b) and (c) are for IVA nitrides [13] and pentatellurides [27]

**Table 2** Comparison of estimation schemes for prediction of group IVA compounds at 298.15 K

| Input parameters | | | | Measured values | | Output values | |
|---|---|---|---|---|---|---|---|
| Substances | $V^a$ | $\theta_D^b$ | $C_p$ | $S_m^o$ | $\Delta S^o$ | Calc. Sommers [27] | Calc. Grimvall [24] |
| Metals | | | | | | | |
| Ti | 10.63 | – | 3.01 | 3.58 | | Ref. | Ref. |
| Zr | 14.02 | – | 3.11 | 4.57 | 0.72 | 4.50 | 4.35 |
| Hf | 13.48 | – | 3.09 | 5.15 | | 5.13 | 5.20 |
| Nitrides | | | | | | | |
| TiN | 11.73 | 708 | 4.46 | 3.56 | | Ref | Ref. |
| ZrN | 14.44 | 582 | 4.87 | 4.67 | 0.72 | 4.61 | 4.35 |
| HfN | 13.86 | 510 | 5.00 | 5.39 | | 5.37 | 5.20 |
| Carbides | | | | | | | |
| TiC | 12.1 | 808 | 4.06 | 2.91 | | Ref | Ref |
| ZrC | 15.56 | 688 | 4.54 | 3.99 | 0.78 | 3.96 | 3.71 |
| HfC | 15.02 | 582 | 4.51 | 4.77 | | 4.76 | 4.56 |

[a] In $cm^3\ mol^{-1}$ from lattce parameters
[b] $\theta_D$ (i.e., Debye characteristic temperature)

### *ZrN and HfN*

Using our HfN data [13] together with the Todd ZrN data [26] gives an experimental value of $\Delta S^o/R$=0.72. As can be seen in Table 2, the prediction of Grimvall's method is 0.85 whereas that of the Sommers' method is 0.76, an even more accurate prediction. If we extend the methods to cover the pure metals themselves as well as the refractory carbides, again the Sommers' values in Table 2 are seen to be far superior to those of Grimvall's method, whether or not the adjusted equation is employed. Both are far better than the Latimer approach; (negative contributions are customarily assigned in the literature for the anionic volumetric contribution of these refractory compounds.)

### *$ZrTe_5$ and $HfTe_5$*

These 'exotic' metallic compounds with zig/zag heavy atom tellurium chains may seem like a far call for any theory, but since some of us had reported on their heat capacities and other properties earlier, we put it to the test. The $\Delta S^o/R$ increment here is 1.03 on a molal basis and it will be seen to be behaving rather similarly to the simpler, ionic compounds mentioned above. The comparison between Grimvall's and Sommers' predictions are shown in Table 2, together with input data.

The NAPS document listed [27] provides the source codes for the programs used for the evaluation and smoothing of the experimental heat-capacity data of this research as well as the integration of the thermal functions and selection of the values at rounded temperatures for the dioxides, nitrides, and pentatellurides of the IVA elements.

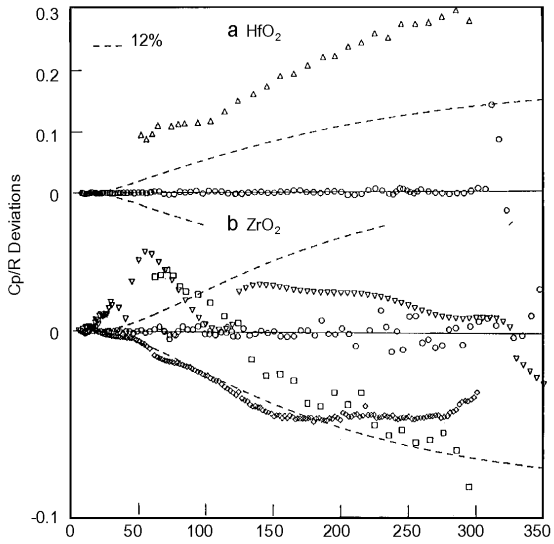


**Fig. 4** Deviation plot for group IVA dioxides. a – For $HfO_2$: Shaviv *et al*. [6], o; Todd [8], △. The dashed lines=±1 per cent. b – For $ZrO_2$: Shaviv *et al*. [6] (o); Kelley *et al*. [7] (□); Nevitt *et al*. [12] (▽); Atake *et al*. [10, 11] (◊)

It provides such details as required for running it successfully and rapidly to fit the entire temperature spectrum of raw data in 15 to 20 seconds on 486 and faster PC's.

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