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Systematic Thermodynamics of Magnéli-Phase and Other Transition Metal Oxides

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Both the molar enthalpies of formation and the absolute entropies of eight transition metal oxides are found to correlate very strongly with their formula unit volumes at room temperature. The metals are Ti, V, Cr, Nb, Mo, Ce, Pr, and Tb. In particular, the thermodynamic values of additive entities (such as TiO_2 in Ti_nO_{2n-1}) in Magnéli phases (that is, recombination phases based on rebuilding after shear) are very close to those of the entity as a pure compound. Thus, reliable values of these thermodynamic properties can readily be predicted for unmeasured or even unsynthesized examples, and literature values can be checked. These assertions are checked against published results for which incomplete data is available. The contributions of the disordered regions which form between the added entities is tentatively estimated.

Introduction

The oxides and chalcogenides (O, S, Se, Te, Po) of transition metals are materials of significant theoretical and industrial interest, for their structural, physical, tribological, electrical, magnetic, optical, and catalytic properties. Partly because of the variable valencies of the parent metal, they can form extended series of compounds, of which the mixed-valence Magnéli phases are important representatives. The Magnéli phases (formed from oxides of Ti, V, Nb, Mo, W, and mixtures thereof) may be described as recombination phases based on rebuilding after shear,[1] corresponding to sequences of chemical formulas such as TiO_2 (rutile) yielding Ti_nO_{2n-1}. The superstructures formed display recurrent shear planes wherein there is edge-sharing, rather than vertex-sharing, among MO_6 octahedra. Consequently, there is added disorder in such superstructures as compared with standard idealized crystallographic phases.

Considerable effort[2] has been devoted over an extended period to the measurement of thermodynamic quantities of materials such as these, but results tend to be presented as isolated sequences of values. Furthermore, measured results are now seldom added since they are both difficult and tedious to determine; it is therefore both appropriate and important that predictive methods are developed to supplement published values. Theoretical methods (quantum mechanical and semiempirical) are expensive, requiring both computational resources and expertise in their application. Instead, empirical additive procedures are widely and reliably used, and require little specialist knowledge.

We have earlier[3a] classified additive procedures as being of order from *zero* to *fourth*: *zero* order methods depend only on the nature of the material under consideration (such as the Dulong−Petit rule of constant atomic heat capacity being applicable to elements); *first* order are molecular-based relations (such as dependence of entropy on formula volume); *second* order involves additivity of atomic properties (such as formula volume being a sum of constituent ion volumes); *third* order involves additivity of local linkages (such as a molecular energy being the sum of the energies of the constituent bonds); while *fourth* order involves additivity of group properties (on identifying the properties of groups, such as alcohols, esters, and so on). A feature of these additivities is that the number of descriptive parameters required increases rapidly with the order of the method.

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(3) (a) Glasser, L.; Jenkins, H. D. B. *Chem. Soc. Rev.* **2005**, *34*(10), 866–874. (b) Glasser, L.; Jenkins, H. D. B. *Inorg. Chem.* **2008**, *47*(2), 6195–6202 (extensive lists of applications of VBT by ourselves and others may be found in refs 7 and 8, respectively, of this publication).

It is the principal purpose of the present communication to show that intimate relationships exist among the thermodynamic properties of these materials through the simple first order method of close linear dependence on molar volume. These insights are extensions of much recent work[3] which has demonstrated that molar volume is a strong correlating parameter for the thermodynamics of both inorganic and organic condensed-phase materials, largely independent of structural details of the materials. The results will be compared with those of a fourth order method (the Simple Salt Approximation,[4] SSA) which requires knowledge of the values of the properties of the supposed constituents of the materials. It will be found that, where sufficient data are available to apply SSA, the methods are complementary.

The simplest of the various volume-based thermodynamic (VBT) relations is the linear relation between entropy and molar volume:

$$S^\circ_{298}/\mathrm{J\,K^{-1}\,mol^{-1}} \approx k(V_\mathrm{m}/\mathrm{nm^3\ formula\ unit^{-1}}) + c \quad (1)$$

where k and c are constants. The relation can equivalently be expressed in terms of density, ρ:

$$S^\circ_{298}/\mathrm{J\,K^{-1}\,mol^{-1}} \approx k'[(M/\mathrm{g\,mol^{-1}})/(\rho/\mathrm{g\,cm^{-3}})] + c \quad (2)$$

where M is the formula mass of the material and k' is a constant related to k:

$$k' = k/602.3 \quad (2a)$$

where the factor 602.3 [$= N_\mathrm{A}/(10^9)^3$] converts between $\mathrm{nm^3}$ per formula unit and $\mathrm{cm^3\,mol^{-1}}$, using the Avogadro constant, N_A.

Other expressions[3] (not invoked in the current paper) relate lattice energies and enthalpies to volume and charge (through an ionic strength factor). Correlation of *formation* enthalpy to volume has not received prior consideration because formation enthalpy depends upon the properties of the constituent elements; these have no absolute basis, so formation enthalpies can only be related (as here) within a group of materials consisting of the same elements in differing proportions.

VBT relations are here explored with reference to sequences of transition metal oxides. Stokłosa and Laskowska have very recently collated much of the enthalpy and volume information for oxides,[5,6] and analyzed the data through their relation to either their atomization enthalpy per oxygen or through "bond lengths" (using the cube-root of the formula volume, V_m, per oxygen as their measure). While their results are valid, some of the quality of the relationships is lost through reliance on (commonly used) empirical formulas, such as $\mathrm{M_{a/b}O}$ (that is, based on the number of metal ions per oxygen ion) rather than on more broadly applicable basis of the stoichiometric chemical formula, $\mathrm{M_aO_b}$, and confused by including peroxides among the oxides. The issue that arises from utilizing empirical chemical formulas such as $\mathrm{Pr_{0.546}O}$ (for $\mathrm{Pr_{12}O_{22}}$) or, similarly, $\mathrm{TbO_{1.72}}$ (for $\mathrm{Tb_7O_{12}}$) is that important chemical relations to congeners, such as $\mathrm{Pr_9O_{16}}$ or $\mathrm{Tb_{11}O_{20}}$, are obscured or even lost, and there is no simple method of conversion of their correlation parameters from the empirical formula sequence to the stoichiometric formula sequence. Furthermore, the analyses of Stokłosa and Laskowska make no reference to the special features of the Magnéli phases of some of the materials with which they deal. The utility of the stoichiometric chemical relations will become clear in what follows.

Thermodynamics and Molar Volumes

Although the thermodynamic information for the oxides is by no means complete, sufficient is available from the standard databases[2] that the present systematic study becomes feasible. For some of the groups under consideration, available data is rather sparse, and these will be dealt with only briefly.

Formula unit volumes are less readily accessible than unit cell volumes and need to be collated from a variety of sources,[7] which may report either crystal structures (too often, even in the primary source, without noting Z, the number of formula units per crystallographic unit cell, V_cell, which then needs to be inferred), or density (which does not require a value for Z, but is subject to greater experimental error). The following formulas are used to generate the required volume results:

$$\begin{aligned} V_\mathrm{m}/\mathrm{cm^3\,mol^{-1}} &= (602.3V_\mathrm{cell}/Z)/\mathrm{nm^3} \\ &= (0.6023V_\mathrm{cell}/Z)/\text{Å}^3 \\ &= M(\mathrm{g\,mol^{-1}})/\rho(\mathrm{g\,cm^{-3}}) \end{aligned} \quad (3)$$

If the molar volume is not listed, it may be calculated from the cell constants, according to the general formula:

$$V_\mathrm{m} = (abc\sqrt{1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma})/Z \quad (4)$$

or, in simplified form (for all except the rhombohedral and triclinic crystal systems)

$$V_\mathrm{m} = abc\sin\eta/Z \quad (5)$$

where η is the unique oblique angle or, if there is no such unique angle, $\eta = 90°$, in which case

$$V_\mathrm{m} = abc/Z \quad (6)$$

Table 1 lists molar volumes and thermochemical data for oxide sequences with an extended range of compositions for the metals Ti, V, Mo, and Pr. (An extended Table S1 appears in the Supporting Information containing data for all of Ti, V, Cr, Nb, Mo, Ce, Pr, and Tb.) The Magnéli phases (indicated by * in Table 1) are represented by the formulas $\mathrm{Ti}_n\mathrm{O}_{2n\text{-}1}$, $\mathrm{V}_n\mathrm{O}_{2n\text{-}1}$, $\mathrm{Nb}_n\mathrm{O}_{2n\text{-}1}$, and $\mathrm{Mo}_n\mathrm{O}_{3n\text{-}1}$. The tabulated data are analyzed in the Figures which follow.

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Table 1. Literature-Based Thermodynamic Data for the Oxides of Ti, V, Mo, and Pr[a]

	V_m / cm^3 mol^{-1}	$S°$/ J K^{-1}mol^{-1}	$\Delta_fH°$ / kJ mol^{-1}	$\Delta_fG°$ / kJ mol^{-1}
TiO_2	18.89	50.3	−944.7	−889.4
*$Ti_{20}O_{39}$	(371)[b]	1015.4	−18533.0	−17460.4
*$Ti_{10}O_{19}$	(183)[b]	505.5	−9085.9	−8564.2
*Ti_9O_{17}	164.28	454.4	−8141.2	−7674.6
*Ti_8O_{15}	146.15	403.2	−7196.5	−6784.9
*Ti_7O_{13}	126.94	351.9	−6251.5[c]	−5894.9
*Ti_6O_{11}	108.02	300.5	−5306.5	−5004.9
*Ti_5O_9	88.98	249.0	−4360.9	−4114.2
*Ti_4O_7	70.12	198.7	−3404.5	−3213.2
Ti_3O_5	52.76	129.4	−2459.1	−2317.4
Ti_2O_3	32.06	77.2	−1520.9	−1433.9
TiO	12.91	34.8	−542.7	−513.3
Ti_3O_2		105.5	−1085.4	−1028.3
V_2O_5	54.2	130.5	−1551.0	−1418.6
V_6O_{13}		335.0	−4456.0	−4103.2
VO_2	19.1	51.8	−713.6	−658.7
V_2O_4	38.2	103.5	−1427.2	−1317.4
*V_8O_{15}	137.1	401.7	−5522.5	−5110.0
*V_7O_{13}	119.6	351.5	−4808.2	−4451.2
*V_6O_{11}	101.5	322.2	−4094.0	−3798.6
*V_5O_9	83.9	258.6	−3378.2	−3134.1
*V_4O_7	69.9	218.0	−2640.0	−2454.2
*V_3O_5		163.0	−1933.0	−1801.1
*V_2O_3	30.8	98.1	−1218.8	−1137.9
$VO_{1.24}$ (= $V_{13}O_{16}$?)		39.3	−523.4	−488.0
VO	11.6	39.0	−431.8	−403.6
MoO_2	19.8	46.5	−587.9	−532.1
*Mo_8O_{23}	262.2	590.8	−5817.0	−5221.9
MoO_3	30.7	77.7	−744.6	−667.5
*Mo_4O_{11}	134.2	290.0	−2807.0	−2523.1
*Mo_9O_{26}	296.9	694.0	−6531.0	−5866.5
PrO_2	25.4	79.9	−974.4	−915.0
Pr_2O_3	47.8	158.0	−1809.6	−1720.9
Pr_6O_{11} (=$PrO_{1.833}$)	147.4	482.0	−5638.4	−5313.6
Pr_7O_{12} (=$PrO_{1.72}$)	176.4	559.4	−6677.7	−6323.3
$Pr_{12}O_{22}$	295.0	959.0	−12829.1	−12178.1

[a] Molar volumes, V_m; absolute entropies, $S°$, formation enthalpies, $\Delta_fH°$; and calculated Gibbs formation energies, $\Delta_fG°$, at 298 K. Those oxides of Ti, V, and Mo which form Magnéli phases are labelled by *. [b] Estimated formula unit volumes, based upon that of the closest congener, Ti_9O_{17}, using the formula (cf. Table 2): $V_m = V_m(Ti_9O_{17}) + 18.8\Delta n$ cm^3 mol^{-1}. [c] The values of absolute entropy and enthalpy of formation are obtained from Waldner P.; Eriksson, G. *Calphad* **1999**, *23*(2), 189−218. Waldner and Eriksson's reported enthalpy of formation, Δ_fH, of Ti_7O_{13} (−3 415 kJ mol^{-1}) is inconsistent with the values of its neighboring congeners. Instead, the temperature-dependent Gibbs energy value of Hashimoto and Abe (http://www.nims.jp/cmsc/pst/database/o-elem/oti/oti_can.TDB) has been used, together with the absolute entropy of Waldner and Eriksson, to evaluate Δ_fH at 298 K.

Thermodynamic Correlations for the Oxides

There is an extensive literature[8] on the thermodynamics and structures of titanium oxides, in both Magnéli and other phases. Figure 1 displays both the room temperature (298 K) standard formation enthalpies and absolute entropies of materials with increasing proportions of metal, from TiO_2 to Ti_3O_2; the corresponding data are reported in Table 1. Materials of formulas Ti_nO_{2n-1} ($n \geq 4$) are generally regarded as Magnéli phases.

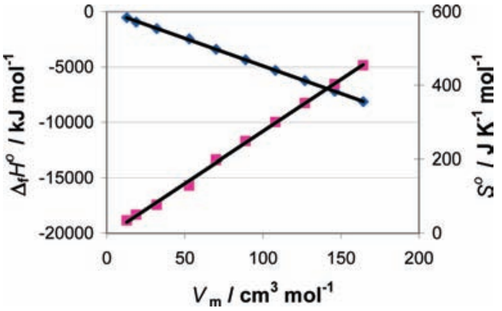

Figure 1. Entropy (squares) and formation enthalpy (diamonds) of titanium oxides versus molar volume. The linear correlation for the formation enthalpy has the formula: $\Delta_fH° = -49.9\ (\pm0.3)\ V_m + 84\ (\pm28)$ with $R^2 = 0.999$, while that for absolute entropy has the formula: $S° = 2.81\ (\pm0.04)\ V_m - 6\ (\pm4)$ with $R^2 = 0.998$. The estimated standard deviations listed for the linear correlations have been determined using de Levie's Excel macro, LS1.[9] (Note: Slight differences between the constants here quoted and those obtained plotting data directly from Table 1 may arise because of truncation of the data listed in the table.).

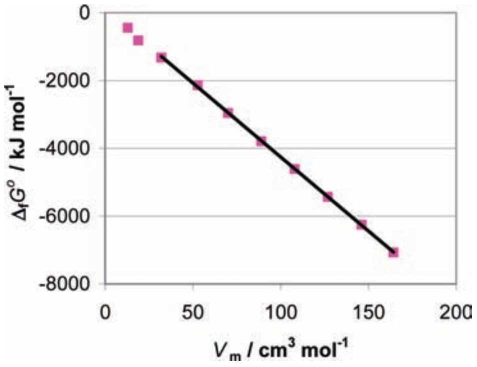

Figure 2. Gibbs formation energies of titanium oxides versus molar volume. The linear correlation for the Magnéli phases has the formula: $\Delta_fG° = -47.4\ (\pm0.3)\ V_m + 119\ (\pm28)$ with $R^2 = 0.999$.

The Gibbs energies of formation are plotted in Figure 2, and a linear correlation obtained for the Magnéli phase materials alone since the earlier oxides are somewhat aberrant.

As may be seen from Figures 1 and 2, the thermodynamic values vary in a highly systematic fashion across the whole composition range, largely independent of any structural details. The entropy slope (2.81 J K^{-1} cm^{-3}) should be compared with our generic value[10] of 2.26 J K^{-1} cm^{-3} for ionic solids as a group. Plots (not shown) of the formula unit volume, formation enthalpy, absolute entropy, and formation Gibbs energy against the number, n, of TiO_2 groups yield the values given in Table 2.

The literature on the structures[11] and thermodynamics[12] of vanadium oxides, both Magnéli and other phases, is considerable. Horiuchi, et al.,[13] developed a systematic description of the Magnéli phases ($2 \leq n \leq 7$) based on addition of

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Table 2. Linear Correlations (and Their Estimated Standard Deviations[9]) of Molar Volume (V_m), Formation Enthalpy ($\Delta_f H$), Absolute Entropy ($S°$), and Formation Gibbs Energy ($\Delta_f G$), and Corresponding Increments Per Basic Structural Unit (TiO_2, VO_2, or MoO_3) of Transition Metal Oxide Phases at 298 K[a]

	V_m/cm^3 mol^{-1}	$\Delta_f H°$/kJ mol^{-1}	$S°$/J K^{-1} mol^{-1}	$\Delta_f G°$/kJ mol^{-1}
Ti_nO_{2n-1}		$-49.9(\pm0.3)\ V_m + 84(\pm28)$	$2.81(\pm0.04)\ V_m - 6(\pm4)$	$-47.4(\pm0.3)\ V_m + 119(\pm28)$
	$\Delta\ V_m/n = 18.8(\pm0.1)$	$\Delta(\Delta_f H)/n = -945.3(\pm0.3)$	$\Delta S°/n = 51.8(\pm0.5)$	$\Delta(\Delta_f G)/n = -890.5(\pm0.4)$
TiO_2 (rutile)	18.89	−944.7	50.3	−889.4
Magnéli V_nO_{2n-1}		$-40.4(\pm0.7)\ V_m + 49(\pm54)$	$2.93(\pm0.07)\ V_m + 8(\pm6)$	
non-Magnéli V_nO_{2n-1}		$-37.5(\pm1.4)\ V_m + 376(\pm145)$	$3.00(\pm0.19)\ V_m - 29(\pm20)$	
V_nO_{2n-1}	$\Delta\ V_m/n = 17.8(\pm0.3)$	$\Delta(\Delta_f H)/n = -723.8(\pm3.3)$	$\Delta S°/n = 52.9(\pm2)$	$\Delta(\Delta_f G)/n = -664.6(\pm17)$
$V_2O_4/2$	19.1	−713.6	51.8	−659.2
MoO_3		$-21.7(\pm0.5)\ V_m - 71(\pm87)$	$2.29(\pm0.06)\ V_m - 1(\pm11)$	
	$\Delta\ V_m/n = 33.8(\pm0.8)$	$\Delta(\Delta_f H)/n = -734.8(\pm10)$	$\Delta S°/n = 77.6(\pm2)$	$\Delta(\Delta_f G)/n = -659.7(\pm8)$
MoO_3	30.7	−745.1	77.7	−668.0
Pr−O (no systematic chemical formula)		$-43.4(\pm2.3)\ V_m + 415(\pm386)$	$3.24(\pm0.04)\ V_m + 1(\pm6)$	
PrO_2	25.4	−974.4	79.9	−915

[a] Data for the Pr−O system, with no systematic chemical formula, is included.

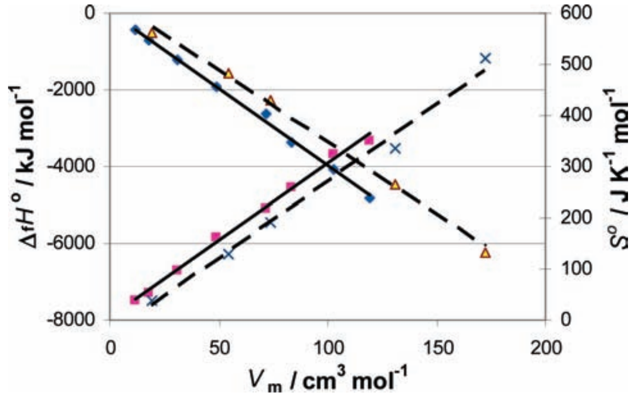

Figure 3. Entropy (squares and crosses) and formation enthalpy (diamonds and triangles) of vanadium oxides versus molar volumes. The linear correlation (full lines) for the formation enthalpy of the Magnéli phases (diamonds) has the formula: $\Delta_f H° = -40.4\ (\pm0.7)\ V_m + 49\ (\pm54)$ with $R^2 = 0.997$, while that for absolute entropy (squares) has the formula: $S° = 2.93\ (\pm0.07)\ V_m + 8\ (\pm6)$ with $R^2 = 0.996$. For the non-Magnéli phases (broken lines), the formation enthalpy (triangles) has the formula: $\Delta_f H° = -37.5\ (\pm1.4)\ V_m + 376\ (\pm145)$ with $R^2 = 0.996$, while that for absolute entropy (crosses) has the formula: $S° = 3.00\ (\pm0.19)\ V_m - 29\ (\pm20)$ with $R^2 = 0.989$.

successive VO_2 groups, while Kuwamoto, Otsuka, and Sato[14] extended the sequence to V_9O_{17}.

Figure 3 displays both the room temperature (298 K) standard formation enthalpies and absolute entropies of materials with increasing proportions of metal, from V_2O_5 to VO, while the data are reported in Table 1.

As may be seen from Figure 3, the thermodynamic values of the vanadium oxide Magnéli phases vary in a very systematic fashion across the whole composition range, largely independent of any structural details, while the values for the non-Magnéli phases differ slightly. The entropy slope for the non-Magnéli phases (2.93 J K^{-1} cm^{-3}) should be compared with our generic value[10] of 2.26 J K^{-1} cm^{-3} for ionic solids as a group. Plots (not shown) of the formula unit volume, formation enthalpy, absolute entropy and Gibbs formation energy against the number, *n*, of VO_2 groups yield the values given in Table 2.

Data for the molybdenum oxides, which is much sparser, is plotted in Figure 4. Again, we see that satisfactory linear correlations occur, within the range of the limited data set. Plots (not shown) of the formula unit volume, formation enthalpy, absolute entropy and Gibbs formation energy against the number, *n*, of MoO_3 groups yield the values given in Table 2.

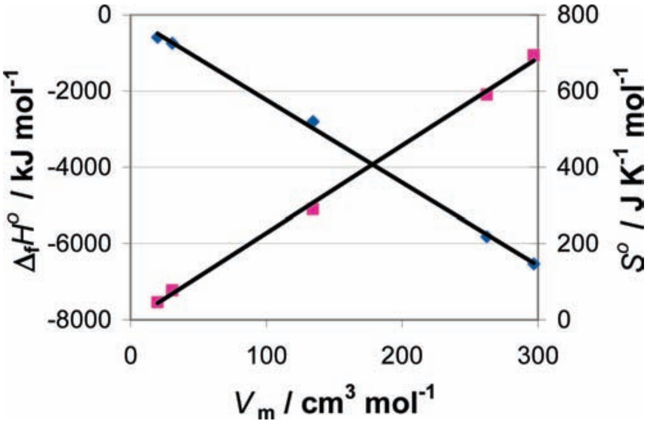

Figure 4. Entropy (squares) and formation enthalpy (diamonds) of molybdenum oxides versus molar volume. The linear correlation for the formation enthalpy has the formula: $\Delta_f H° = -21.7\ (\pm0.5)\ V_m - 71\ (\pm87)$ with $R^2 = 0.998$, while that for absolute entropy has the formula: $S° = 2.29\ (\pm0.06)\ V_m - 1\ (\pm11)$ with $R^2 = 0.998$. A linear correlation (not shown) of Gibbs formation energy versus molar volume has the formula: $\Delta_f G° = -19.5\ (\pm0.4)\ V_m - 66\ (\pm78)$ with $R^2 = 0.999$.

Rare-Earth Oxides[15]

The three rare earth elements cerium, praseodymium, and terbium have large series of oxides; these are, however, not Magnéli phases. Praseodymium has the most extensive published series, and we plot the corresponding data in Figure 5 and list the correlation parameters in Table 2. Data for Ce[16] and Tb,[15] together with that for Cr[17] (another non-Magnéli system) are relegated to the Supporting Information since they provide the same basic information as for praseodymium.

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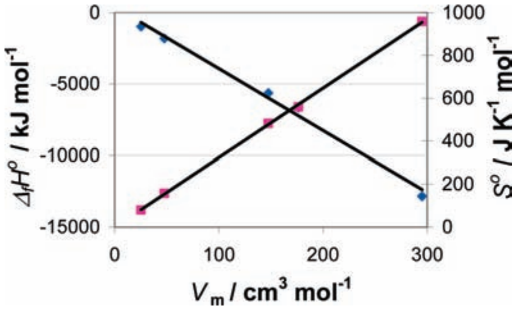

Figure 5. Entropy (squares) and formation enthalpy (diamonds) of praseodymium oxides versus molar volumes. The linear correlation for the formation enthalpy has the formula: $\Delta_f H^\circ = -43.4\ (\pm 2.3)\ V_m + 415\ (\pm 386)$ with $R^2 = 0.992$, while that for absolute entropy has the formula: $S^\circ = 3.24\ (\pm 0.04)\ V_m - 1\ (\pm 6)$ with $R^2 = 0.999$.

Application of the Correlations

We consider how the correlations here presented may be applied. For this purpose, we note that the formula unit volumes of $Ti_{10}O_{19}$ and of $Ti_{20}O_{39}$ are not available, although their formation enthalpies and absolute entropies have been published (see Table 1).

We may readily estimate their volumes, according to footnote *a* of Table 1:

$$V_m(Ti_{10}O_{19}) = V_m(Ti_9O_{17}) + V_m(TiO_2) = 183\ \text{cm}^3\ \text{mol}^{-1} \quad \text{and}$$

$$V_m(Ti_{20}O_{39}) = V_m(Ti_9O_{17}) + 11xV_m(TiO_2) = 371\ \text{cm}^3\ \text{mol}^{-1}$$

where we have used $V_m(Ti_9O_{17})$ as their closest congener to minimize the resultant extrapolation of the correlation.

Correspondingly, we may use the thermodynamic volume correlations in Table 1 to make the following estimates:

$\Delta_f H^\circ(Ti_{10}O_{19}) = -49.9\ V_m + 84 = -9\,053$ kJ mol^{-1} (with an estimated standard deviation of 83 kJ mol^{-1}). The value reported in Table 1 is $-9\,085.9$ kJ mol^{-1}, which lies well within the predicted range. $S^\circ(Ti_{10}O_{19}) = 2.81\ V_m - 6 = 508.5$ J K^{-1} mol^{-1} (with an estimated standard deviation of 11 J K^{-1} mol^{-1}). The value reported in Table 1 is 505.5 J K^{-1} mol^{-1}, which lies well within the predicted range.

$\Delta_f H^\circ(Ti_{20}O_{39}) = -18\,434$ kJ mol^{-1} (with an estimated standard deviation of 195 kJ mol^{-1}). The value reported in Table 1 is $-18\,533$ kJ mol^{-1}, which lies well within the predicted range. $S^\circ(Ti_{20}O_{39}) = 1\,037$ J K^{-1} mol^{-1} (with an estimated standard deviation of 19 J K^{-1} mol^{-1}). The value reported in Table 1 is 1 015 J K^{-1} mol^{-1}, which also lies well within the predicted range.

As noted earlier, the Simple Salt Approximation[4] can yield equivalent predictions, provided data for congeners is available, as in the current situation. The following results are obtained, using the data in Table 1:

$$\Delta_f H^\circ(Ti_{10}O_{19}) = \Delta_f H^\circ(T_9O_{17}) + \Delta_f H^\circ(TiO_2) = -9085.9\ \text{kJ mol}^{-1}$$

$$S^\circ(Ti_{10}O_{19}) = S^\circ(T_9O_{17}) + S^\circ(TiO_2) = 504.7\ \text{J K}^{-1}\ \text{mol}^{-1}$$

These SSA results match well with the experimental values and also with those of the volume correlations.

$$\Delta_f H^\circ(Ti_{20}O_{39}) = \Delta_f H^\circ(T_9O_{17}) + 11x\Delta_f H^\circ(TiO_2) = -18533\ \text{kJ mol}^{-1}$$

$$S^\circ(Ti_{20}O_{39}) = S^\circ(T_9O_{17}) + 11xS^\circ(TiO_2) = 1008\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(1% difference from reported value)

Further, it is possible to combine the above methods, by addition of a salt value to a correlation value from Table 2, as below:

$$\Delta_f H^\circ(Ti_{10}O_{19}) = \Delta_f H^\circ(T_9O_{17}) + \Delta(\Delta_f H^\circ)(TiO_2)/n = -8141.2 - 945.3 = -9086\ \text{kJ mol}^{-1}$$

$$S^\circ(Ti_{10}O_{19}) = S^\circ(T_9O_{17}) + \Delta S^\circ(TiO_2)/n = 506.2\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta_f H^\circ(Ti_{20}O_{39}) = \Delta_f H^\circ(T_9O_{17}) + 11x\Delta(\Delta_f H^\circ)(TiO_2)/n = -18540\ \text{kJ mol}^{-1}$$

$$S^\circ(Ti_{20}O_{39}) = S^\circ(T_9O_{17}) + 11x\Delta S^\circ(TiO_2)/n = 1024\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(1% difference from reported value)

It is always appropriate to use a number of predictive procedures to check the results against each other.

Observations and Conclusions

It is, perhaps, not unexpected that there should be consistent linear trends in the thermodynamic properties of materials formed by successive additions of the same formula unit (e.g., TiO_2 for the Magnéli-phase titanium oxides). However, it is striking that these thermodynamic properties are strongly correlated with molar volume, relatively independent of the details of crystal structure. While the electronic properties can vary widely across such sequences, from metallic conduction to insulation, this has little influence on the relation between their structural and their thermodynamic properties.

The close relation reported above between the values for the pure oxides (TiO_2, $V_2O_4/2$, and MoO_3) and the corresponding incremental values for their respective oxide sequences then demonstrates that an assumption of additivity for these thermodynamic quantities can be considered to be reliable, and used for predictive purposes, as in the applications tested above. The excellent linearity of the correlations between formation enthalpy and molar volume and absolute entropy and molar volume, for the whole range of oxides here considered, also suggests that this additivity can, with little hesitation, be extended to the chalcogenides of the transition metals in general.

The slopes of the correlations listed here should be compared with our generic values,[10] for example the value of 2.26 J K^{-1} cm^{-3} for the entropy correlation for ionic solids as a group. The entropy correlation slopes for these complex oxides are rather larger (even up to 3.62 J K^{-1} cm^{-3} for the terbium oxides), perhaps because of disorder introduced at junctions between the additive groups. Indeed, we may even speculate (following a suggestion by an anonymous referee) on a disorder-based contribution to the thermodynamic values, by calculating the excess between the correlated difference per unit and that of the contributing unit. For example, from Table 2:

$$\Delta S(\mathrm{TiO_2})/n - S(\mathrm{TiO_2}) = 51.8 - 50.3 = 1.5\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

This implies that there is an entropy contribution of 1.5 J K^{-1} mol^{-1} by the disorder for each mole of the parent TiO_2 which is added to form the Magnéli phase. Using the corresponding differences, disorder increases the enthalpy contribution by 0.6 kJ mol^{-1} while the Gibbs energy is stabilized by 1.1 kJ mol^{-1}. Similar values are obtained for the disorder contributions to the phases of V_nO_{2n-1}.

We have here reported enthalpies of formation; that is for reactions of the type

$$a\mathrm{M(s)} + b/2\,\mathrm{O_2(g)}[\rightarrow a\mathrm{M(g)} + b\mathrm{O(g)}] \rightarrow \mathrm{M}_a\mathrm{O}_b\mathrm{(s)}$$

This reaction is written as though proceeding (hypothetically) through an atomization process.

The following reaction, which is the reverse of the second part of the above formation reaction, corresponds to the atomization reaction:

$$\mathrm{M}_a\mathrm{O}_b\mathrm{(s)} \rightarrow a\mathrm{M(g)} + b\mathrm{O(g)}$$

In many ways, atomization enthalpies might be preferred[18] to formation enthalpies since they remove the complication of including half the bond enthalpy of oxygen and the sublimation enthalpies of the metals. However, atomization enthalpies are large quantities, which tends to obscure minor differences between species (as, in particular, may be seen in Figure 2 between the Magnéli and non-Magnéli phases, which is not evident in a plot of atomization enthalpies). For this reason, and for familiarity, we have used formation enthalpies in these discussions.

Supporting Information Available: For all the transition metal oxides considered (Ti, V, Cr, Nb, Mo, Ce, Pr, and Tb), Table S1 lists published molar formula unit volumes, standard absolute entropies, and standard enthalpies of formation, as well as calculated Gibbs energies of formation. Figures S1 to S4, respectively, plot enthalpies of formation and absolute entropies for the oxides of metals omitted from the main text; that is, for Cr, Nb, Ce and Tb. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Spencer, J. N.; Moog, R. S.; Gillespie, R. J. *J. Chem. Educ.* **1996**, *73*, 631–636.