

High-temperature thermal functions and the thermochemistry of zinc tungstate ^a

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Combination of low-temperature heat capacities with results from drop calorimetry has yieldedⁱ a provisional set of thermal functions for ZnWO₄(c) up to 1200 K. These high-temperature thermal functions permit an analysis of the thermochemistry of zinc tungstate and the selection of the value $-(294.6 \pm 0.3)$ kcal_{th} mol⁻¹ for the standard enthalpy of formation at 298.15 K.

1. Introduction

The thermochemistry of many transition metal tungstates has been reviewed by Urosov *et al.*;⁽¹⁾ however, in most instances the paucity of data concerning the thermal functions of these materials has severely hindered accurate analysis or comparison of enthalpies of formation at 298.15 K. This problem is particularly serious for situations involving analysis of high-temperature equilibrium data, since these cases require accurate values for the entropy. The recently determined values for the thermal functions of ZnWO₄^(2, 3) from 5 to 550 K permit an accurate analysis of the thermochemistry of this compound.

2. Thermal functions

From drop-calorimetric measurements of Zharkova and Rezhukhina,⁽⁴⁾ and heat-capacity measurements,⁽³⁾ it was possible to generate a provisional set of high-temperature thermal functions for ZnWO₄. These functions, presented in table 1, are based on 298.15 K as the standard temperature; thus, they are a more convenient set of functions for use in equilibrium calculations involving ZnWO₄ as one reactant.

The only published thermal functions of comparable range for a tungstate of the NiWO₄-type are those given by JANAF⁽⁵⁾ (31 March 1967) for MgWO₄. These

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TABLE 1. High-temperature thermal functions of zinc tungstate
($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

$\frac{T}{\text{K}}$	C_p $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$\{S^\circ(T) - S^\circ(0)\}$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$\{H^\circ(T) - H^\circ(298.15 \text{ K})\}$ $\text{cal}_{\text{th}} \text{mol}^{-1}$	$-\{G^\circ(T) - H^\circ(298.15 \text{ K})\}/T$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$
300	27.38	28.51	50.586	28.34
400	30.83	36.90	2976.3	29.46
500	32.85	44.02	6169.4	31.68
600	34.06	50.12	9519.8	34.26
700	34.85	55.44	12968	36.91
800	35.45	60.13	16484	39.53
900	35.97	64.34	20055	42.05
1000	36.44	68.15	23677	44.48
1100	36.86	71.65	27342	46.79
1200	37.26	74.87	31048	49.00

latter functions, however, were extrapolated without benefit of drop-calorimetric data above 300 K, and neglected entirely the transition between 1373 and 1573 K reported by Dunning and Megaw.⁽⁶⁾

Due partly to the small number of results from drop calorimetry (only four points) and partly to the relatively high curvature of the ZnWO_4 heat capacity, even in the high-temperature region, it was found impossible to joint the low-temperature and high-temperature data smoothly by simple graphical means of the type suggested by Shomate.⁽⁷⁾ An attempt at such a plot of the quantity:

$$\{H^\circ(T) - H^\circ(298.15 \text{ K}) - C_p(298.15 \text{ K})(T - 298.15 \text{ K})\}T/(T - 298.15 \text{ K})^2,$$

against T (which should yield a straight line), seemed to indicate either that the implicit representation of C_p in the form $a + 2bT - c/T^2$ was inadequate in this temperature region, or that the drop-calorimetric results and the lower-temperature results are badly discordant. It was assumed for the purposes of this analysis that the former explanation of the non-linearity is correct.

To avoid the difficulties described above, the heat capacity was extrapolated directly, using adjacent drop-calorimetric enthalpy determinations to obtain average heat capacity values in the high-temperature region. Comparison of $\{H^\circ(T) - H^\circ(T^*)\}$ obtained from this extrapolation with values measured by Zharkova and Rezukhina⁽⁴⁾ is given in table 2. Although the agreement obtained is reasonable, further measurements—through melting if possible—would be desirable.

At the highest temperature given in table 1 (1200 K), the heat capacity exceeds the harmonic limit ($18R$) by approximately 4 per cent; this is considered a reasonable deviation for heat capacities at nearly $0.8T_m$. (T_m for ZnWO_4 has been reported.^(8, 9)) A similar deviation from the harmonic limit is found for $\text{WO}_3(\text{c})$ at $0.8T_m$. (Compare JANAF,⁽⁵⁾ 30 September 1966.) The presence of a small transition below melting such as that observed by Yakovleva and Rezukhina⁽¹⁰⁾ for CoWO_4 ($\Delta H_t = 445 \text{ cal}_{\text{th}} \text{mol}^{-1}$ at about 986 K) is not necessarily excluded by the apparent agreement obtained in this work.†

† Throughout this paper $\text{cal}_{\text{th}} = 4.184 \text{ J}$.

TABLE 2. Comparison of enthalpy increments for zinc tungstate
(cal_{th} = 4.184 J)

T K	$H^\circ(T) - H^\circ(293.2 \text{ K})^a$ cal _{th} mol ⁻¹	$H^\circ(T) - H^\circ(298.15 \text{ K})^b$ cal _{th} mol ⁻¹	$H^\circ(T) - H^\circ(298.15 \text{ K})^c$ cal _{th} mol ⁻¹	$\Delta(\Delta H)$ cal _{th} mol ⁻¹
750.5	14724	14860	14735	125
905.4	20190	20326	20247	79
1009.3	23955	24091	24012	79
1095.6	27118	27254	27178	76

^a Data of Zharkova and Rezukhina⁽⁴⁾ converted to molar basis.

^b Data of Zharkova and Rezukhina⁽⁴⁾ molar data adjusted to 298.15 K as base temperature, using the cryogenic C_p results obtained by Lyon and Westrum.⁽³⁾

^c Enthalpy function computed from extrapolated C_p as described in text.

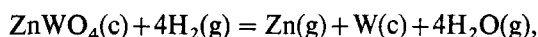
^d Difference: $\{H^\circ(T) - H^\circ(298.15 \text{ K})\}_{\text{expt}} - \{H^\circ(T) - H^\circ(298.15 \text{ K})\}_{\text{calc.}}$

3. Thermochemistry

The availability of thermal functions for ZnWO₄ enables tests for concordance in the previously published thermochemical data. Accordingly, the equilibrium data of Zharkova *et al.*,⁽¹¹⁾ and the more recent solution calorimetric data of Navrotsky and Kleppa⁽¹²⁾ were reduced by standard methods of analysis for comparison at 298.15 K.

EQUILIBRIUM DATA

The equilibrium data of Zharkova *et al.*,⁽¹¹⁾ for the reaction:



were subjected to both second- and third-law analyses. For the second-law analysis, $\ln K_p$ for the reaction was curve-fitted by least squares to the form:

$$\ln K_p = A + B/T + C \ln T.$$

From the slope calculated at the midpoint of the range of measurements, the enthalpy of reaction was computed, which was subsequently reduced to 298.15 K and combined with other thermochemical data to yield the standard enthalpy of formation ΔH_f° of ZnWO₄. The details of this calculation, and the subsidiary data used, are given in table 3.

The third-law analysis of these equilibrium data was carried out using $-\{G^\circ(T) - H^\circ(298.15 \text{ K})\}/T$ for the various reactants, curve-fitted to the form:

$$-\{G^\circ(T) - H^\circ(298.15 \text{ K})\}/T = A + B/T + C/T^2 + D \ln T.$$

The results of this analysis are shown in table 4.

SOLUTION-CALORIMETRIC DATA

The direct calorimetric data of Navrotsky and Kleppa⁽¹²⁾ required little more than reduction to 298.15 K *via* the relevant enthalpy increments. A description of the thermochemical system involved and these results are presented in table 5.

TABLE 3. Second-law analysis of the data of Zharkova *et al.*⁽¹¹⁾
 (cal_{th} = 4.184 J)

Reaction	$\frac{\Delta H_f^\circ}{\text{kcal}_{\text{th}} \text{ mol}^{-1}}$
ZnWO ₄ (c, 1116 K) + 4H ₂ (g, 1116 K) = Zn(g, 1116 K) + W(c, 1116 K) + 4H ₂ O(g, 1116 K)	(81.85 ± 0.5) ^a
ZnWO ₄ (c, 298.15 K) = ZnWO ₄ (c, 1116 K)	(27.93 ± 0.08) ^b
4H ₂ (g, 298.15 K) = 4H ₂ (g, 1116 K)	23.154 ^c
Zn(g, 1116 K) = Zn(g, 298.15 K)	-4.063 ^d
W(c, 1116 K) = W(c, 298.15 K)	-5.135 ^e
4H ₂ O(g, 1116 K) = 4H ₂ O(g, 298.15 K)	-29.505 ^f
Zn(g, 298.15 K) = Zn(c, 298.15 K)	-(31.170 ± 0.10) ^g
4H ₂ O(g, 298.15 K) = 4H ₂ O(l, 298.15 K)	-42.076 ^h
4H ₂ O(l, 298.15 K) = 4H ₂ (g, 298.15 K) + 2O ₂ (g, 298.15 K)	273.260 ⁱ
ZnWO ₄ (c, 298.15 K) = Zn(c, 298.15 K) + W(c, 298.15 K) + 2O ₂ (g, 298.15 K)	(294.3 ± 0.6)

^a Zharkova *et al.*⁽¹¹⁾ 8 points.^b Zharkova and Rezukhina⁽⁴⁾ (see table 1).^c JANAF⁽⁵⁾ (31 March 1961).^d Hultgren *et al.*⁽¹³⁾^e JANAF⁽⁵⁾ (30 June 1966).^f JANAF⁽⁵⁾ (31 March 1961).^g Hultgren *et al.*⁽¹³⁾^h Wagman *et al.*⁽¹⁴⁾ⁱ Wagman *et al.*⁽¹⁵⁾
 TABLE 4. Third-law analysis of the data of Zharkova *et al.*⁽¹¹⁾ for the reaction:
(cal_{th} = 4.184 J)

$\frac{T}{\text{K}}$	$\frac{\Delta G_f^\circ(T)}{\text{kcal}_{\text{th}} \text{ mol}^{-1}}$	$\frac{-\Delta\{G^\circ(T) - H^\circ(298.15 \text{ K})\}/T}{\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}}$	$\frac{\Delta H_f^\circ(298.15 \text{ K})}{\text{kcal}_{\text{th}} \text{ mol}^{-1}}$
1041.15	32.25	65.34	100.28
1075.15	31.42	65.00	101.31
1080.15	31.32	64.96	101.48
1092.15	30.05	64.84	100.86
1118.15	28.75	64.59	100.97
1137.15	28.45	64.41	101.70
1151.15	27.43	64.28	101.43
1191.15	25.50	63.92	101.63

Mean value: (101.21 ± 0.4)^{c, d}

^a The values for the reactants were based on data from the following sources: ZnWO₄(c), table 1; H₂(g), JANAF⁽⁵⁾ (31 March 1961); Zn(g), Hultgren *et al.*⁽¹³⁾; W(c), JANAF⁽⁵⁾ (30 June 1966); H₂O(g), JANAF⁽⁵⁾ (31 March 1961).

^b Calculation of $\Delta H_f^\circ(298.15 \text{ K})$ was based on the equation:

$$\Delta H_f^\circ(298.15 \text{ K}) = \Delta G_f^\circ(T) - T\Delta\{G^\circ(T) - H^\circ(298.15 \text{ K})\}/T.$$

^c The third-law drift, defined as the slope of a plot of $\Delta H_f^\circ(298.15 \text{ K})$ against T , is estimated as $(7 \pm 4) \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$.

^d Combination of this result with the subsidiary thermochemical data given in table 3 yields $-(301.2 \pm 0.6) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ for ΔH_f° of ZnWO₄.

TABLE 5. Analysis of solution-calorimetric data of Navrotsky and Kleppa⁽¹²⁾
{solvent: 3Na₂O·4MoO₃(l)}
(cal_{th} = 4.184 J)

Reactions ^a	$\Delta H_f^\circ(970 \text{ K})$ kcal _{th} mol ⁻¹
ZnO(c) + solvent(l) = solution I(l)	-(3.20 ± 0.06) ^b
WO ₃ (c) + solvent(l) = solution II(l)	(7.24 ± 0.18) ^b
Solution III(l) = ZnWO ₄ (c) + 2 solvent(l)	-(14.11 ± 0.17) ^b
Solution I(l) + solution II(l) = solution III(l)	(0.00) ^c
ZnO(c) + WO ₃ (c) = ZnWO ₄ (c)	-(10.07 ± 0.26)

^a Utilizing the thermal functions for ZnWO₄, ZnO, and WO₃ from table 1, Kelley,⁽¹⁶⁾ and JANAF⁽⁸⁾ (30 September 1966) respectively, results in a value of -(9.90 ± 0.3) kcal_{th} mol⁻¹ for $\Delta H_f^\circ(\text{ZnWO}_4, \text{c})$ for formation from the oxides at 298.15 K. $\Delta H_f^\circ(\text{ZnWO}_4, \text{c})$ at 298.15 K is calculated as -(294.6 ± 0.3) kcal_{th} mol⁻¹, based on values at 298.15 K of -83.24 and -201.45 kcal_{th} mol⁻¹ for $\Delta H_f^\circ(\text{ZnO}, \text{c})$ and $\Delta H_f^\circ(\text{WO}_3, \text{c})$ of Wagman *et al.*^(14, 15)

^b Navrotsky and Kleppa.⁽¹²⁾

^c Undetermined, but assumed small because of the rather dilute solutions involved.

4. Discussion

From the summary given in table 6, it is apparent that the second-law analysis of the data of Zharkova *et al.*⁽¹¹⁾ is in exceedingly good accord with the result obtained from the data of Navrotsky and Kleppa,⁽¹²⁾ although the latter result is probably less subject to uncertainty. The third-law analysis of the equilibrium data, however, shows evidence for some thermodynamic inconsistency in this system. The relatively large third-law drift, (7 ± 4) cal_{th} K⁻¹ mol⁻¹, is an indication that either the absolute values of K_p , or one or more of the values of $-\{G^\circ(T) - H^\circ(298.15 \text{ K})\}/T$ are significantly in error. In view of the close agreement of the second-law analysis with the results of direct calorimetry, it is believed that systematic errors in K_p values are the more likely source of the discrepancy in the third-law analysis.

TABLE 6. Summary of enthalpies of formation of zinc tungstate
(cal_{th} = 4.184 J)

$\Delta H_f^\circ(\text{ZnWO}_4, \text{c}, 298.15 \text{ K})$ ^a kcal _{th} mol ⁻¹	$\Delta H_f^\circ(\text{ZnWO}_4, \text{c}, 298.15 \text{ K})$ ^b kcal _{th} mol ⁻¹	References
-(294.6 ± 0.3) ^c	-(9.9 ± 0.3)	Navrotsky and Kleppa ⁽¹²⁾
-(294.3 ± 0.6) ^d	-(9.6 ± 0.6)	Zharkova <i>et al.</i> ⁽¹¹⁾ Second Law
-(301.2 ± 0.6) ^e	-(16.5 ± 0.6)	Zharkova <i>et al.</i> ⁽¹¹⁾ Third Law

^a ΔH_f° from the elements.

^b ΔH_f° for formation from the oxides (ZnO, WO₃).

^c See table 5 for details. Navrotsky and Kleppa⁽¹²⁾ reported only ΔH_f° for formation from the oxides at 970 K.

^d See table 3 for details.

^e See table 4 for details. The third-law drift is estimated as (7 ± 4) cal_{th} K⁻¹ mol⁻¹. Urosov *et al.*⁽¹⁾ have given $S^\circ(\text{ZnWO}_4, 298.15 \text{ K})$ as (31.1 ± 3) cal_{th} K⁻¹ mol⁻¹ based on the equilibrium data. The discrepancy between this result and that determined calorimetrically,⁽⁹⁾ (28.34 ± 0.1) cal_{th} K⁻¹ mol⁻¹, is consistent with the third-law drift.

The value for $\Delta H_f^\circ = -(294.6 \pm 0.3) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ derived from the work of Navrotsky and Kleppa⁽¹²⁾ is selected here as the most reliable value for this quantity. This value may be compared with estimates and approximate calculations given by Wilcox and Bromley,⁽¹⁷⁾ $-(293 \pm 15) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$, Urosov *et al.*,⁽¹⁾ $-296 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$, and Wagman *et al.*,⁽¹⁵⁾ $-293 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$. Using the selected value of ΔH_f° and the value⁽³⁾ of $S^\circ(298.15 \text{ K})$ of $(28.34 \pm 0.1) \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ results in a value of $\Delta G_f^\circ(\text{ZnWO}_4, \text{c}, 298.15 \text{ K}) = -(268.5 \pm 0.4) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$. The entropies of Zn(c), W(c), and O₂(g) were taken from the compilations of Wagman *et al.*^(14, 15)

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