

## Note on the enthalpies of formation, from the component oxides, of $\text{CoWO}_4$ and $\text{NiWO}_4$ , determined by high-temperature direct synthesis calorimetry

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### Abstract

The enthalpies of formation, from the constituent oxides, of  $\text{CoWO}_4$  and  $\text{NiWO}_4$  have been determined by direct synthesis calorimetry at  $1473 \pm 2$  K. The following values of  $\Delta H_f^\circ$  at 298 K ( $\text{kJ mol}^{-1}$ ) are reported:  $\text{CoWO}_4$ ,  $-60.8 \pm 2.6$ ;  $\text{NiWO}_4$ ,  $-47.3 \pm 2.7$ . The results are compared with the data available in the literature. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Cobalt and nickel tungstates; Enthalpy of formation; High-temperature direct synthesis calorimetry

The thermochemistry of mixed oxide systems is of considerable importance in inorganic chemistry, in the earth sciences, and in material sciences. For many years, for most mixed oxide systems, the only calorimetric method used to obtain enthalpies of formation was the solution calorimetry in aqueous solvents, an indirect method. However, due to the difficulties associated with dissolving many oxides in aqueous solvents near room temperature, calorimetric determination of enthalpies of formation of mixed oxide phases by this method were usually very difficult. The development of high-temperature oxide-melt solution calorimetry by the senior author of this paper in the 1960s [1] represented a remarkable improvement in the calorimetry of mixed oxide systems. It opened wide possibilities in determining the heats of formation of many refractory mixed oxide phases and

in determining the energy changes associated with various physicochemical processes occurring in these systems (cf. [2,3]).

Recently, we have added another calorimetric method, high-temperature direct synthesis calorimetry, to mixed oxide research. We have successfully determined new values for the enthalpies of formation, from the component oxides, of  $\text{MeWO}_4$  ( $\text{Me} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ) by direct synthesis calorimetry at  $1473 \pm 2$  K [4,5]. The cations involved in these tungstates were all divalent. Therefore, we inferred that the high-temperature direct synthesis method might also work for tungstates containing other divalent cations such as Co, Ni, Cu, and Zn.

In this note, our investigation of tungstate thermochemistry is expanded to  $\text{CoWO}_4$ ,  $\text{NiWO}_4$ ,  $\text{CuWO}_4$  and  $\text{ZnWO}_4$ . However, our experiments on  $\text{CuWO}_4$  and on  $\text{ZnWO}_4$  were not successful. For the former, the synthesis product,  $\text{CuWO}_4$ , melted at our calori-

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meter temperature of  $1473 \pm 2$  K. In fact, it flowed out of the unsealed Pt capsule, which contained the powdered mixture of CuO and  $\text{WO}_3$ . Hence, it was impossible to collect the reaction product to carry out a subsequent heat content measurement. For  $\text{ZnWO}_4$ , the vapor pressure seemed to be too high at the calorimeter temperature. This resulted in substantial mass losses both in the synthesis reactions and in the heat content measurements. Therefore, in this note we report only on the values of the enthalpies of formation, from the component oxides, of  $\text{CoWO}_4$  and  $\text{NiWO}_4$ .

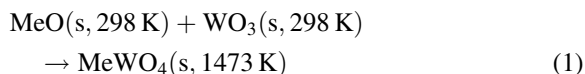
The experiments were all carried out at  $1473 \pm 2$  K in a single-unit differential microcalorimeter, which was described earlier in some detail [6]. All experiments were conducted in air. The actual synthesis reactions were carried out in pure alumina ( $\text{Al}_2\text{O}_3$ ) crucibles.

Calibration of the calorimeter was achieved by dropping pieces of 4 mm diameter pellets of high purity platinum of known mass at room temperature into the calorimeter at  $1473 \pm 2$  K. The enthalpy of pure platinum at this temperature,  $34\,106 \text{ J mol}^{-1}$ , was taken from Hultgren et al. [7]. The calibrations were reproducible within  $\pm 1\%$ .

The CoO powder ( $-325$  mesh) used for the experiments was 99.5% pure (metal basis) and was purchased from CERAC (Milwaukee, WI). The NiO and  $\text{WO}_3$  powders were purchased from Alfa Aesar (Ward Hill, MA) and were all puratronic grade powders with metallic purity of 99.998%. However, the company provided no information about the particle sizes of these two oxides. All the starting materials were examined by X-ray powder diffraction (XRD) before the experiments. The XRD patterns for the three oxides were in perfect agreement with their ASTM standard files. In CoO and NiO, Co and Ni are both divalent cations. However, it is possible that they may change their valence at high temperatures in the presence of oxygen. To make sure that this would not happen in our experiments, we carried out a firing test before we prepared the samples. We fired the CoO and NiO powders in air in a platinum crucible at our calorimeter temperature of 1473 K for 12 h. The masses of these two oxide powders were weighed before and after the firing. We found essentially no change in mass, which suggested that Co and Ni in these oxides remained divalent.  $\text{WO}_3$  was also fired at 1473 K for 12 h before we prepared the samples.

The calorimetric samples were prepared by mixing powders of CoO and NiO with  $\text{WO}_3$  in the appropriate stoichiometric proportions. The mixed powders were then ground in an alumina mortar to ensure good mixing and to reduce the size of the particles. The particle size of CoO powder was originally  $-325$  mesh. We believe that during the grinding process, the particle size of this powder should remain unchanged, or possibly become even finer. For the other two oxide powders, the final particle sizes after the grinding were probably comparable to the size of the CoO powder. The mixed powders were pressed into 4-mm-diameter pellets. Because it was difficult to make thick pellets of the powders, several thin pellets with thickness of about 0.5–1 mm were made for each single sample. Since the pellets were usually quite fragile, they were placed in cylindrical platinum capsules. These capsules were prepared from 0.05-mm-thick pure platinum foil; they were closed at both ends but were not sealed by welding. A typical platinum capsule weighed around 100 mg, while the average mass of sample weighed about 230 mg. The capsuled pellets were dried overnight at about 463 K before use.

The enthalpy of formation, from the component oxides, of the compound  $\text{MeWO}_4$  is obtained from the difference between the two sets of measurements. In the first set, the following reaction takes place in the calorimeter:



Here Me stands for Co or Ni.

The products of reaction (1) are then re-used in a subsequent set of measurements to determine the corresponding heat contents:



No matter whether a heat of reaction (the first set) or a heat content (the second set) is measured, a single measurement takes about 1 h to finish. This is the time from dropping the sample into the calorimeter to when a final steady baseline is again obtained in the calorimeter.

From Eqs. (1) and (2), we have

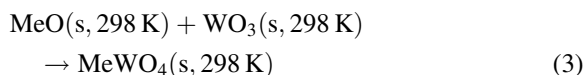


Table 1

Observed heats of reaction, average heat contents at 1473 K, and calculated enthalpies of formation from the component oxides ( $\Delta H_f$ ) and from the elements ( $\Delta H_f^\circ$ ). All data are in  $\text{kJ mol}^{-1}$ <sup>a</sup>

Compound	$\Delta H(1)$	$\Delta H(2) = H_{1473}^\circ - H_{298}^\circ$	$\Delta H_f$	$\Delta H_f^{\circ b}$
CoWO <sub>4</sub>	122.01 ± 1.32 (4)	182.76 ± 2.11 (4)	−60.8 ± 2.6	−1141.6 ± 2.7
NiWO <sub>4</sub>	128.32 ± 2.12 (6)	175.66 ± 1.55 (6)	−47.3 ± 2.7	−1130.0 ± 2.7

<sup>a</sup> Numbers in parentheses indicate numbers of experiments averaged.

<sup>b</sup> The values of  $\Delta H_f^\circ$  for CoO, NiO and WO<sub>3</sub> (−237.9 ± 0.65, −239.3 ± 0.2 and −842.9 ± 0.4  $\text{kJ mol}^{-1}$ ) that were used to calculate the standard enthalpies of formation of CoWO<sub>4</sub> and NiWO<sub>4</sub> were all taken from Robie and Hemingway [8].

And the enthalpy of formation from the component oxides at 298 K is given by

$$\Delta H_f = \Delta H(1) - \Delta H(2) \quad (4)$$

where  $\Delta H(1)$  and  $\Delta H(2)$  are the observed enthalpy changes per mole for Eqs. (1) and (2), respectively.

Table 1 summarizes the experimental results obtained for CoWO<sub>4</sub> and NiWO<sub>4</sub>. The reported values of  $\Delta H(1)$  and  $\Delta H(2)$  are averages of 4–6 individual determinations with standard deviations  $\delta_1$  and  $\delta_2$ , respectively. If the standard deviation for the calibration is  $\delta_3$ , the overall uncertainty in the reported enthalpy of formation is calculated from

$$\delta = \sqrt{\delta_1^2 + \delta_2^2 + \delta_3^2}$$

After the measurements, all the samples were examined by XRD. The XRD patterns of our samples of CoWO<sub>4</sub> and NiWO<sub>4</sub> showed clear and sharp reflections, which were in perfect agreement with the ASTM standard files for these two compounds. Since there was no evidence for any unreacted oxides in

these two samples, the reactions between CoO or NiO and WO<sub>3</sub> were considered complete.

Based on our measured enthalpies of formation from the component oxides and the known values of the standard enthalpies of formation of CoO, NiO and WO<sub>3</sub>, the enthalpies of formation from the elements, i.e., the standard enthalpies of formation of CoWO<sub>4</sub> and NiWO<sub>4</sub>, were calculated and are listed in Table 1.

In Table 2, we compare our results with the corresponding values given by Kubaschewski [9], the values determined in 1969 by Navrotsky and Kleppa [10], and the value for NiWO<sub>4</sub> listed in a National Bureau of Standards Handbook edited by Wagman et al. [11]. It will be seen from Table 2 that our new values of the enthalpies of formation from the component oxides for both CoWO<sub>4</sub> and NiWO<sub>4</sub> are in very good agreement with the values given by Kubaschewski and by Navrotsky and Kleppa. This means that the high-temperature direct synthesis calorimetry clearly works for these two compounds.

Table 2

Comparison of the enthalpies of formation from the component oxides ( $\Delta H_f$ ) and from the elements ( $\Delta H_f^\circ$ ) for CoWO<sub>4</sub> and NiWO<sub>4</sub> reported in the present work with literature values. For readers' reference, a literature value of  $\Delta H_f^\circ$  for FeWO<sub>4</sub> is also listed. All data are in  $\text{kJ mol}^{-1}$ <sup>a</sup>

Compound	$\Delta H_f$	Reference	$\Delta H_f^\circ$	Reference
FeWO <sub>4</sub>	−39.9 ± 4.1*	[8]	−1154.8 ± 4.3	[8]
CoWO <sub>4</sub>	−60.8 ± 2.6	This work	−1141.6 ± 2.7	This work
	−61.9 ± 3.8	[9]	−1142.7 ± 3.9*	[9]
	−60.2 ± 1.1	[10]	−1141.1 ± 1.3*	[10]
NiWO <sub>4</sub>	−47.3 ± 2.7	This work	−1129.5 ± 2.7	This work
	−45.2 ± 2.1	[9]	−1127.4 ± 2.2*	[9]
	−44.2 ± 1.2	[10]	−1126.4 ± 1.3*	[10]
			−1133.4	[11]

<sup>a</sup> Values with asterisk were calculated either based on the listed values of the standard enthalpy of formation ( $\Delta H_f^\circ$ ) in the reference or based on the listed values of the enthalpy of formation from the component oxides ( $\Delta H_f$ ) in the reference using Robie and Hemingway's values of  $\Delta H_f^\circ$  for pertinent oxides [8].

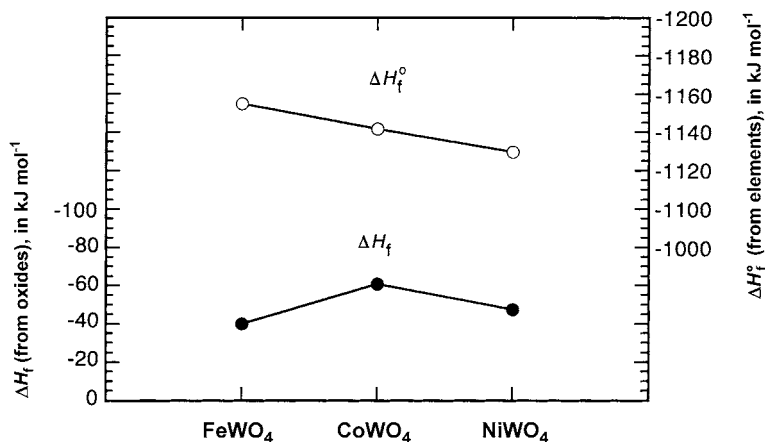


Fig. 1. Standard enthalpies of formation ( $\Delta H_f^o$ ) and enthalpies of formation from the component oxides ( $\Delta H_f$ ) of tungstates of the iron group elements. The value of  $\Delta H_f$  for FeWO<sub>4</sub> ( $-39.9 \pm 4.1 \text{ kJ mol}^{-1}$ ) was calculated based on the value of  $\Delta H_f^o$  for the same compound ( $-1154.8 \pm 4.3 \text{ kJ mol}^{-1}$  [8]). The values of  $\Delta H_f^o$  for CoWO<sub>4</sub> and NiWO<sub>4</sub> ( $-1141.6 \pm 2.7$  and  $-1129.5 \pm 2.7 \text{ kJ mol}^{-1}$ , respectively) were calculated based on the values of  $\Delta H_f$  for these two compounds determined in the present work. Used for these calculations were also the values of  $\Delta H_f^o$  for FeO, CoO, NiO and WO<sub>3</sub> ( $-272.0 \pm 1.1$ ,  $-237.9 \pm 0.65$ ,  $-239.3 \pm 0.2$  and  $-842.9 \pm 0.4 \text{ kJ mol}^{-1}$ , respectively), all taken from [8].

For the readers' reference, the standard enthalpy of formation of FeWO<sub>4</sub>, the mineral ferberite, is also listed in Table 2.

In Fig. 1, the values of both  $\Delta H_f$ , the enthalpy of formation from the oxides, and  $\Delta H_f^o$ , the enthalpy of formation from the elements are plotted for the tungstates of the iron group elements. It is apparent that the standard enthalpy of formation,  $\Delta H_f^o$ , becomes less negative first from FeWO<sub>4</sub> to CoWO<sub>4</sub>, then from CoWO<sub>4</sub> to NiWO<sub>4</sub>. However, the enthalpy of formation from the oxides,  $\Delta H_f$ , changes somewhat differently. It first becomes more negative from FeWO<sub>4</sub> to CoWO<sub>4</sub>, and then less negative from CoWO<sub>4</sub> to NiWO<sub>4</sub>.

### Acknowledgements

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