

ENTHALPY OF FORMATION OF AQUEOUS TUNGSTATE ION AND OF CRYSTALLINE TUNGSTIC ACID (H_2WO_4)

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ABSTRACT

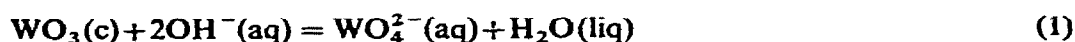
Calorimetric measurements of the enthalpy of reaction of $\text{WO}_3(\text{c})$ with excess $\text{OH}^-(\text{aq})$ have been made at 85°C . Similar measurements have been made with $\text{MoO}_3(\text{c})$ at both 85 and 25°C , to permit estimation of $\Delta H^\circ = -13.4 \text{ kcal mol}^{-1}$ for the reaction $\text{WO}_3(\text{c}) + 2\text{OH}^-(\text{aq}) = \text{WO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{liq})$ at 25°C . Combination of this ΔH° with ΔH_f° for $\text{WO}_3(\text{c})$ leads to $\Delta H_f^\circ = -256.5 \text{ kcal mol}^{-1}$ for $\text{WO}_4^{2-}(\text{aq})$. We also obtain $\Delta H_f^\circ = -269.5 \text{ kcal mol}^{-1}$ for $\text{H}_2\text{WO}_4(\text{c})$. Both of these values are discussed in relation to several earlier investigations.

INTRODUCTION

In 1952 the NBS Circ. 500¹ listed $\Delta H_f^\circ = -279.6 \text{ kcal mol}^{-1}$ for $\text{H}_2\text{WO}_4(\text{c})$ and $\Delta H_f^\circ = -266.6 \text{ kcal mol}^{-1}$ for $\text{WO}_4^{2-}(\text{aq})$, along with related ΔH_f° values for various tungstates. All of these values were largely based on the results of Huttig and Kurre² and Pissarjewsky³. Because it was subsequently shown⁴ that the results of these investigators^{2,3} for similar compounds of molybdenum were in error, it is reasonable to wonder about the reliability of their results for $\text{WO}_4^{2-}(\text{aq})$ and $\text{H}_2\text{WO}_4(\text{c})$ and thence the tabulated properties of several tungstates.

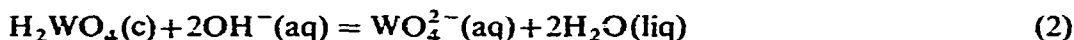
More recently, the NBS Tech. Note 270-4⁵ has listed $\Delta H_f^\circ = -270.5 \text{ kcal mol}^{-1}$ for $\text{H}_2\text{WO}_4(\text{c})$ and $\Delta H_f^\circ = -257.1 \text{ kcal mol}^{-1}$ for $\text{WO}_4^{2-}(\text{aq})$, with no references as to sources of experimental results leading to these values. We can account for these tabulated quantities as follows.

It has long been known that "ordinary" $\text{WO}_3(\text{c})$ prepared by high temperature dehydration of $\text{H}_2\text{WO}_4(\text{c})$ does not dissolve in aqueous base at room temperature. But by prolonged dehydration of $\text{H}_2\text{WO}_4(\text{c})$ at 250°C Spitsyn and Patsukova⁶ prepared $\text{WO}_3(\text{c})$ that would dissolve rapidly and completely in 0.84 M NaOH at 25°C . Their calorimetric measurements at 25°C on this reaction, which we represent by



led to $\Delta H_1 = -13.80 \text{ kcal mol}^{-1}$. They⁶ also measured the enthalpy of reaction of

$\text{H}_2\text{WO}_4(\text{c})$ with the same NaOH solution, as represented by

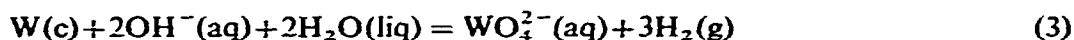


and found $\Delta H_2 = -13.05 \text{ kcal mol}^{-1}$. Combination of these results with $\Delta H_f^\circ = -201.45 \text{ kcal mol}^{-1}$ for $\text{WO}_3(\text{c})$ from NBS Tech. Note 270-4⁵ and $\Delta H_f^\circ = -68.315 \text{ kcal mol}^{-1}$ for $\text{H}_2\text{O}(\text{liq})$ from NBS Tech. Note 270-3⁷ leads to $\Delta H_f^\circ = -270.52 \text{ kcal mol}^{-1}$ for $\text{H}_2\text{WO}_4(\text{c})$, as listed in NBS Tech Note 270-4⁵.

The NBS Tech. Note 270-4⁵ ΔH_f° values correspond to $\Delta H_f^\circ = -14.0 \text{ kcal mol}^{-1}$ and to $\Delta H_2^\circ = -13.3 \text{ kcal mol}^{-1}$. These values, which refer to infinitely dilute solutions, are $0.2 \text{ kcal mol}^{-1}$ more exothermic than the corresponding enthalpies reported by Spitsyn and Patsukova⁶, whose results apply to $0.84 \text{ M OH}^-(\text{aq})$ and $0.013 \text{ M WO}_4^{2-}(\text{aq})$. This difference is in the right direction for a correction of the measured enthalpies⁶ to the desired standard state quantities. Graham and Hepler⁸ have measured the enthalpy of reaction (2) in dilute solution and have reported $\Delta H_2^\circ = -13.7 \text{ kcal mol}^{-1}$, which might be preferable to $\Delta H_2^\circ = -13.3 \text{ kcal mol}^{-1}$ above. In any case, the NBS Tech. Note 270-4⁵ ΔH_f° values are consistent with a ΔH_2° that is intermediate between the experimental results of Spitsyn and Patsukova⁶ and Graham and Hepler⁸.

It is possible that the $\text{WO}_3(\text{c})$ prepared and used by Spitsyn and Patsukova⁶ had a high surface free energy (and enthalpy) as compared to "standard" $\text{WO}_3(\text{c})$. If so, the ΔH_f° values for both $\text{H}_2\text{WO}_4(\text{c})$ and $\text{WO}_4^{2-}(\text{aq})$ should be less negative than the tabulated⁵ values that are consistent with the results of Spitsyn and Patsukova⁶.

Sherfey and Brenner⁹ have carried out electrochemical calorimetric measurements leading to $\Delta H = (-7 \pm 1.5) \text{ kcal mol}^{-1}$ for the reaction



This ΔH permits us to calculate $\Delta H_f^\circ = -253.6 \text{ kcal mol}^{-1}$ for $\text{WO}_4^{2-}(\text{aq})$.

DTA measurements¹⁰ have led to $\Delta H = 8.54 \text{ kcal mol}^{-1}$ (uncertainty maybe as much as $\pm 2 \text{ kcal mol}^{-1}$) for the reaction



and thence to $\Delta H_f^\circ = -267.8 \text{ kcal mol}^{-1}$ for $\text{H}_2\text{WO}_4(\text{c})$.

Both of the ΔH_f° values in the two paragraphs above are less negative than the corresponding values that are based on the results of Spitsyn and Patsukova⁶, which is consistent with the possibility that their $\text{WO}_3(\text{c})$ had a high surface free energy. Unfortunately, the results cited in the two paragraphs above are not sufficiently accurate to settle this question or to give us satisfactory ΔH_f° values for $\text{H}_2\text{WO}_4(\text{c})$ and $\text{WO}_4^{2-}(\text{aq})$.

Because the ΔH_f° values for $\text{WO}_4^{2-}(\text{aq})$ and $\text{H}_2\text{WO}_4(\text{c})$ are of fundamental importance in connection with a considerable number of calorimetric investigations of the thermodynamic properties of many compounds of tungsten (for examples, see refs. 8, 11-14), we have undertaken the measurements described here to obtain new ΔH_f° values.

EXPERIMENTAL

All calorimetric measurements were made with an LKB precision calorimetry system. Measurements at $25.00 \pm 0.05^\circ\text{C}$ were made with the standard 100-ml LKB glass reaction calorimeter, using glass ampoules to contain the solid sample to be dissolved in the calorimetric solution. Similar measurements at $85.00 \pm 0.05^\circ\text{C}$ were made with a stainless-steel bomb calorimeter identical to that described by Olofsson et al.¹⁵ Small heat effects associated with ampoule breaking were determined by means of separate experiments. All ΔH values are reported in terms of the defined calorie (1 cal = 4.1840 J).

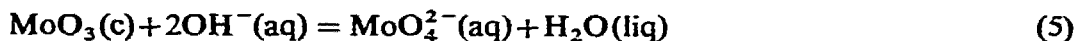
Molybdenum trioxide was prepared for calorimetric measurements by heating Fisher (purified) MoO_3 to about 600°C for 18 h. Different samples of $\text{WO}_3(\text{c})$ were prepared by heating Fisher (purified) "tungstic anhydride" to 200, 300, and 400°C for 24 h. All of these $\text{WO}_3(\text{c})$ samples dissolved readily at 85°C but would not dissolve at 25°C .

RESULTS

We could not make calorimetric measurements leading to the ΔH of reaction (1) at 25°C without getting involved in the uncertain issue of possible high surface energy of specially prepared $\text{WO}_3(\text{c})$ that would dissolve rapidly at this temperature. We could, however, make calorimetric measurements on this reaction at 85°C , at which temperature "standard" $\text{WO}_3(\text{c})$ dissolves readily. Then, by making similar measurements with $\text{MoO}_3(\text{c})$ at both 25 and 85°C we could obtain a reliable estimate of $\Delta H_1(25^\circ\text{C}) - \Delta H_1(85^\circ\text{C})$ that we need for calculation of the desired ΔH_1 at 25°C .

Five calorimetric measurements on reaction (1) have been made at 85°C . In each measurement about 6×10^{-4} mol of $\text{WO}_3(\text{c})$ were dissolved in 65 ml of 0.055 M NaOH to yield 0.01 M $\text{WO}_4^{2-}(\text{aq})$ solution in 0.036 M $\text{OH}^-(\text{aq})$. We obtained an average $\Delta H_1(85^\circ\text{C}) = -12.57 \text{ kcal mol}^{-1}$, with average deviation $0.24 \text{ kcal mol}^{-1}$.

We have made closely similar measurements on the reaction



at both 25 and 85°C . Average values obtained are $\Delta H_5(25^\circ\text{C}) = -18.52 \text{ kcal mol}^{-1}$ (av. dev. = $0.03 \text{ kcal mol}^{-1}$) and $\Delta H_5(85^\circ\text{C}) = -17.77 \text{ kcal mol}^{-1}$ (av. dev. = $0.28 \text{ kcal mol}^{-1}$). Combination of these values gives $\Delta H_5(25^\circ\text{C}) - \Delta H_5(85^\circ\text{C}) = -0.75 \text{ kcal mol}^{-1}$.

The $\Delta H_5(25^\circ\text{C})$ above is in good agreement with results of four other investigations^{4,11,16} carried out with slightly different conditions.

We now take $\Delta H_1(25^\circ\text{C}) - \Delta H_1(85^\circ\text{C}) = \Delta H_5(25^\circ\text{C}) - \Delta H_5(85^\circ\text{C}) = -0.75 \text{ kcal mol}^{-1}$ and combine with our $\Delta H_1(85^\circ\text{C}) = -12.57 \text{ kcal mol}^{-1}$ to obtain $\Delta H_1(25^\circ\text{C}) = -13.32 \text{ kcal mol}^{-1}$. Combination of this value with enthalpies of dilution^{1,17} leads to the desired standard state enthalpy of reaction (1) at 25°C :

$\Delta H_1^\circ = -13.4 \text{ kcal mol}^{-1}$. Finally, combination of this ΔH_1° with ΔH_f° values^{5,7} for $\text{WO}_3(\text{c})$, $\text{OH}^-(\text{aq})$, and $\text{H}_2\text{O}(\text{liq})$ leads to $\Delta H_f^\circ = -256.5 \text{ kcal mol}^{-1}$ for $\text{WO}_4^{2-}(\text{aq})$.

The ΔH_f° given above for $\text{WO}_4^{2-}(\text{aq})$ is less negative than the value listed in NBS Tech. Note 270-4⁵, which is consistent with the suggestion that the $\text{WO}_3(\text{c})$ used by Spitsyn and Patsukova⁶ had a surface energy higher than that of standard state $\text{WO}_3(\text{c})$.

Combination of $\Delta H_2^\circ = -13.7 \text{ kcal mol}^{-1}$ from Graham and Hepler⁸ with the above ΔH_f° for $\text{WO}_4^{2-}(\text{aq})$ leads to $\Delta H_f^\circ = -269.5 \text{ kcal mol}^{-1}$ for $\text{H}_2\text{WO}_4(\text{c})$.

If the ΔH_f° values cited above for $\text{WO}_4^{2-}(\text{aq})$ and $\text{H}_2\text{WO}_4(\text{c})$ are adopted, related changes in enthalpies of formation of various tungstates and other compounds of tungsten should be made. Some of these compounds are discussed in papers already cited^{8,11-14}. Others are listed in NBS Tech. Note 270-4⁵ and NBS Tech. Note 270-6¹⁸.

ACKNOWLEDGMENTS

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