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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 WO_3(c) with excess OH^-(aq) have been made at 85°C. Similar measurements have been made with MoO_3(c) at both 85 and 25°C, to permit estimation of $\Delta H° = -13.4$ kcal mol^{-1} for the reaction $WO_3(c)+2OH^-(aq) = WO_4^{2-}(aq)+H_2O(liq)$ at 25°C. Combination of this $\Delta H°$ with $\Delta H_f°$ for WO_3(c) leads to $\Delta H_f° = -256.5$ kcal mol^{-1} for WO_4^{2-}(aq). We also obtain $\Delta H_f° = -269.5$ kcal mol^{-1} for H_2WO_4(c). Both of these values are discussed in relation to several earlier investigations.

INTRODUCTION

In 1952 the NBS Circ. 500[1] listed $\Delta H_f° = -279.6$ kcal mol^{-1} for H_2WO_4(c) and $\Delta H_f° = -266.6$ kcal mol^{-1} for WO_4^{2-}(aq), along with related $\Delta H_f°$ values for various tungstates. All of these values were largely based on the results of Huttig and Kurre[2] and Pissarjewsky[3]. Because it was subsequently shown[4] 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 WO_4^{2-}(aq) and H_2WO_4(c) and thence the tabulated properties of several tungstates.

More recently, the NBS Tech. Note 270-4[5] has listed $\Delta H_f° = -270.5$ kcal mol^{-1} for H_2WO_4(c) and $\Delta H_f° = -257.1$ kcal mol^{-1} for WO_4^{2-}(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" WO_3(c) prepared by high temperature dehydration of H_2WO_4(c) does not dissolve in aqueous base at room temperature. But by prolonged dehydration of H_2WO_4(c) at 250°C Spitsyn and Patsukova[6] prepared WO_3(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

$$WO_3(c)+2OH^-(aq) = WO_4^{2-}(aq)+H_2O(liq) \qquad (1)$$

led to $\Delta H_1 = -13.80$ kcal mol^{-1}. They[6] also measured the enthalpy of reaction of

H_2WO_4(c) with the same NaOH solution, as represented by

$$H_2WO_4(c)+2OH^-(aq) = WO_4^{2-}(aq)+2H_2O(liq) \tag{2}$$

and found $\Delta H_2 = -13.05$ kcal mol^{-1}. Combination of these results with $\Delta H_f^\circ = -201.45$ kcal mol^{-1} for WO_3(c) from NBS Tech. Note 270-4[5] and $\Delta H_f^\circ = -68.315$ kcal mol^{-1} for H_2O(liq) from NBS Tech. Note 270-3[7] leads to $\Delta H_f^\circ = -270.52$ kcal mol^{-1} for H_2WO_4(c), as listed in NBS Tech Note 270-4[5].

The NBS Tech. Note 270-4[5] ΔH_f° values correspond to $\Delta H_1^\circ = -14.0$ kcal mol^{-1} and to $\Delta H_2^\circ = -13.3$ kcal mol^{-1}. These values, which refer to infinitely dilute solutions, are 0.2 kcal mol^{-1} more exothermic than the corresponding enthalpies reported by Spitsyn and Patsukova[6], whose results apply to 0.84 M OH^-(aq) and 0.013 M WO_4^{2-}(aq). This difference is in the right direction for a correction of the measured enthalpies[6] to the desired standard state quantities. Graham and Hepler[8] have measured the enthalpy of reaction (2) in dilute solution and have reported $\Delta H_2^\circ = -13.7$ kcal mol^{-1}, which might be preferable to $\Delta H_2^\circ = -13.3$ kcal mol^{-1} above. In any case, the NBS Tech. Note 270-4[5] ΔH_f° values are consistent with a ΔH_2° that is intermediate between the experimental results of Spitsyn and Patsukova[6] and Graham and Hepler[8].

It is possible that the WO_3(c) prepared and used by Spitsyn and Patsukova[6] had a high surface free energy (and enthalpy) as compared to "standard" WO_3(c). If so, the ΔH_f° values for both H_2WO_4(c) and WO_4^{2-}(aq) should be less negative than the tabulated[5] values that are consistent with the results of Spitsyn and Patsukova[6].

Sherfey and Brenner[9] have carried out electrochemical calorimetric measurements leading to $\Delta H = (-7 \pm 1.5)$ kcal mol^{-1} for the reaction

$$W(c)+2OH^-(aq)+2H_2O(liq) = WO_4^{2-}(aq)+3H_2(g) \tag{3}$$

This ΔH permits us to calculate $\Delta H_f^\circ = -253.6$ kcal mol^{-1} for WO_4^{2-}(aq).

DTA measurements[10] have led to $\Delta H = 8.54$ kcal mol^{-1} (uncertainty maybe as much as ± 2 kcal mol^{-1}) for the reaction

$$H_2WO_4(c) = WO_3(c)+H_2O(g) \tag{4}$$

and thence to $\Delta H_f^\circ = -267.8$ kcal mol^{-1} for H_2WO_4(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 Patsukova[6], which is consistent with the possibility that their WO_3(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 H_2WO_4(c) and WO_4^{2-}(aq).

Because the ΔH_f° values for WO_4^{2-}(aq) and H_2WO_4(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±0.05 °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±0.05 °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 WO_3(c) were prepared by heating Fisher (purified) "tungstic anhydride" to 200, 300, and 400 °C for 24 h. All of these WO_3(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 WO_3(c) that would dissolve rapidly at this temperature. We could, however, make calorimetric measurements on this reaction at 85 °C, at which temperature "standard" WO_3(c) dissolves readily. Then, by making similar measurements with MoO_3(c) at both 25 and 85 °C we could obtain a reliable estimate of $\Delta H_1(25\,°C) - \Delta H_1(85\,°C)$ 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 WO_3(c) were dissolved in 65 ml of 0.055 M NaOH to yield 0.01 M WO_4^{2-}(aq) solution in 0.036 M OH^-(aq). We obtained an average $\Delta H_1(85\,°C) = -12.57$ kcal mol^{-1}, with average deviation 0.24 kcal mol^{-1}.

We have made closely similar measurements on the reaction

$$MoO_3(c) + 2OH^-(aq) = MoO_4^{2-}(aq) + H_2O(liq) \qquad (5)$$

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

The $\Delta H_5(25\,°C)$ above is in good agreement with results of four other investigations[4,11,16] carried out with slightly different conditions.

We now take $\Delta H_1(25\,°C) - \Delta H_1(85\,°C) = \Delta H_5(25\,°C) - \Delta H_5(85\,°C) = -0.75$ kcal mol^{-1} and combine with our $\Delta H_1(85\,°C) = -12.57$ kcal mol^{-1} to obtain $\Delta H_1(25\,°C) = -13.32$ 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:

$\Delta H_1^\circ = -13.4$ kcal mol^{-1}. Finally, combination of this ΔH_1° with ΔH_f° values[5,7] for WO_3(c), OH^-(aq), and H_2O(liq) leads to $\Delta H_f^\circ = -256.5$ kcal mol^{-1} for WO_4^{2-}(aq).

The ΔH_f° given above for WO_4^{2-}(aq) is less negative than the value listed in NBS Tech. Note 270-4[5], which is consistent with the suggestion that the WO_3(c) used by Spitsyn and Patsukova[6] had a surface energy higher than that of standard state WO_3(c).

Combination of $\Delta H_2^\circ = -13.7$ kcal mol^{-1} from Graham and Hepler[8] with the above ΔH_f° for WO_4^{2-}(aq) leads to $\Delta H_f^\circ = -269.5$ kcal mol^{-1} for H_2WO_4(c).

If the ΔH_f° values cited above for WO_4^{2-}(aq) and H_2WO_4(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 270-4[5] and NBS Tech. Note 270-6[18].

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REFERENCES

1 F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, *National Bureau of Standards Circular 500*, U.S. Gov. Printing Office, Washington, D.C., 1952.

2 G. F. Huttig and B. Kurre, *Z. Anorg. Chem.*, 126 (1923) 167.

3 L. Pissarjewsky, *Z. Anorg. Chem.*, 24 (1900) 108.

4 R. L. Graham and L. G. Hepler, *J. Amer. Chem. Soc.*, 78 (1956) 4846.

5 D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm, *National Bureau of Standards Tech. Note 270-4*, U.S. Gov. Printing Office, Washington, D.C., 1969.

6 V. I. Spitsyn and N. N. Patsukova, *Russ. J. Inorg. Chem.*, 10 (1965) 1304.

7 D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm, *National Bureau of Standards Tech. Note 270-3*, U.S. Gov. Printing Office, Washington, D.C., 1968.

8 R. L. Graham and L. G. Hepler, *J. Amer. Chem. Soc.*, 80 (1958) 3538.

9 J. M. Sherfey and A. Brenner, *J. Electrochem. Soc.*, 105 (1958) 665.

10 I. G. Worsley, W. M. Keely and L. G. Hepler, unpublished results, 1968.

11 M. F. Koehler, L. B. Pankratz and R. Barany, *Bureau of Mines Report of Investigations No. 5973*, U.S. Gov. Printing Office, Washington, D.C., 1962.

12 R. Barany, *Bureau of Mines Report of Investigations No. 6143*, U.S. Gov. Printing Office, Washington, D.C., 1962.

13 H. Opperman, G. Stover and G. Kunze, *Z. Anorg. Allg. Chem.*, 387 (1972) 317; 387 (1972) 329.

14 J. Burgess, C. J. W. Fraser, R. D. Peacock and P. Taylor, *J. Fluorine Chem.* 3 (1973/74) 55.

15 G. Olofsson, S. Sunner, M. Efimov and J. Laynez, *J. Chem. Thermodyn.*, 5 (1973) 199.

16 P. A. G. O'Hare and H. R. Hoekstra, *J. Chem. Thermodyn.*, 5 (1973) 851; 6 (1974) 117.

17 V. B. Parker, *Thermal Properties of Aqueous Uni-univalent Electrolytes, NSRDS-NBS 2*, U.S. Gov. Printing Office, Washington, D.C., 1965.

18 V. B. Parker, D. D. Wagman and W. H. Evans, *National Bureau of Standards Tech. Note 270-6*, U.S. Gov. Printing Office, Washington, D.C., 1971.