Thermochemistry of Sodium Tungstate, Silver Tungstate and Tungstic Acid

BY ROBERT L. GRAHAM AND LOREN G. HEPLER

The heat of solution of Na_2WO_4 has been measured and the standard heat of solution calculated to be -1.6 kcal./mole. Because this heat of solution is very different from that calculated from previously reported heats of formation, we have measured the heat of reaction of crystalline tungstic acid (H_2WO_4) with excess aqueous sodium hydroxide and have found the standard heat of this reaction to be -13.7 kcal./mole H_2WO_4. The heats of solution of Ag_2WO_4 and $AgNO_3$ in aqueous NH_3 and the heat of solution of $AgNO_3$ in water have been measured and the standard heats found to be -12.39, -8.12 and 5.42 kcal./mole, respectively. Our heats of reaction and solution have been used to calculate the heats of formation of WO_4^-(aq), Na_2WO_4(c) and Ag_2WO_4(c) to be -266.6, -379.6 and -230.7 kcal./mole, respectively. The thermodynamics of solution of Ag_2WO_4 is discussed in terms of polytungstate formation.

Our earlier work[1] on the thermochemistry of MoO_4^-(aq) and Na_2MoO_4(c) showed that the heats of formation of these substances as tabulated by the Bureau of Standards[2] are in considerable error. These incorrect heats of formation are based on the results of calorimetric work done by Pissarjewsky,[3] Pechard[4] and Mixter.[5] Because the heats of formation given by the Bureau of Standards[2] for WO_4^-(aq) and Na_2WO_4(c) are based on similar calorimetric work of Pissarjewsky[3] and Mixter[6] and because the heat of solution of sodium tungstate calculated from tabulated heats of formation[2] ($+14$ kcal./mole) seemed unreasonable in comparison with the directly determined heat of solution of sodium molybdate[1] (-2.4 kcal./mole), we decided to determine this heat of solution directly and also to investigate the heats of formation of WO_4^-(aq) and Na_2WO_4(c).

Pan[7] recently reported the results of his investigations of the silver–silver tungstate electrode. From the temperature coefficient of the standard potential of this electrode and the standard potential at 25°, Pan has calculated the free energy, heat and entropy of solution of silver tungstate. Pan's calculated heats of solution of silver chromate[8] and silver molybdate[9] are in excellent agreement with the calorimetrically determined heats reported by Smith, Pitzer and Latimer[10] and Muldrow and Hepler.[11] Nevertheless, we felt it desirable to investigate silver tungstate calorimetrically because of the great tendency of tungstate ions to form more complicated species.

Experimental

Our solution calorimeter has been described in detail.[1,12] Some minor improvements in our operation of the calorimeter have been made and several determinations of the heat of solution of KCl in water have been carried out. Our heats of solution of KCl are in good agreement with the results of earlier investigators and will be reported in detail in a subsequent paper. All of our calorimetric measure-

ments have been carried out using 950 ml. of solution in the calorimeter and all of the calorimetric measurements reported in this paper were carried out at $25.0 \pm 0.2°$.

Materials.—The $AgNO_3$ was Mallinckrodt analytical reagent and was analyzed by titration with $KSCN$[13] and by electrolysis[14] and was found to contain $100.0 \pm 0.1\%$ of the theoretical amount of silver.

The Na_2WO_4 used was Fisher Certified Reagent. After the material was dried at 110°, it was analyzed by precipitating most of the tungsten in a weighed sample as tungstic acid (H_2WO_4) with concentrated HCl and then precipitating the rest of the tungsten with cinchonine according to Lambie's procedure.[15] The Na_2WO_4 was found to be 99.9% pure on the basis of its WO_3 content.

Crystalline tungstic acid (H_2WO_4) was prepared by adding $0.05\ M\ Na_2WO_4$ solution dropwise to vigorously stirred $6\ M\ HNO_3$. The desired product precipitated immediately and was washed several times with $1\ M\ HNO_3$. Each time the precipitate was washed it was allowed to stand overnight in contact with the wash solution. Finally, the precipitated H_2WO_4 was washed twice with $0.1\ M\ HNO_3$, filtered and dried over NaOH and P_2O_5 in a vacuum desiccator. After the material had dried for several days it was analyzed in the same fashion as Na_2WO_4 and found to be 99.4% pure on the basis of WO_3 content. Another analysis of the same material after it had dried for a month indicated a purity of 99.8%. This H_2WO_4 dissolved rapidly and completely in dilute NaOH at room temperature to give a clear solution.

Silver tungstate was precipitated at room temperature from $0.05\ M\ Na_2WO_4$ solution by dropwise addition of $0.1\ M\ AgNO_3$ while the tungstate solution was vigorously stirred. Enough $AgNO_3$ was added to precipitate two-thirds of the tungstate and then the precipitated Ag_2WO_4 was washed several times with $0.001\ M\ AgNO_3$. The product was collected on a glass filter and dried over P_2O_5 in an opaque vacuum desiccator. A satisfactory procedure for determination of Ag in Ag_2WO_4 was developed which entailed dissolving Ag_2WO_4 in aqueous NH_3 containing NH_4^--NO_3. The silver was then electroplated on platinum[14] and dissolved in HNO_3. The resulting solution was boiled gently to remove oxides of nitrogen and the silver content determined by titration with $KSCN$.[13] This analytical procedure was tested on solutions containing known amounts of $AgNO_3$ and Na_2WO_4 and was found to give satisfactory results. Two preparations of Ag_2WO_4 were analyzed and found to be 99.7 and 99.8% pure on the basis of silver content. All of our work with silver compounds was carried out in rooms faintly lit by red bulbs.

Several unsuccessful attempts were made to prepare tungstic oxide (WO_3) that would dissolve readily and completely in aqueous NaOH at room temperature to give a clear solution.

Results and Discussion

The heat of solution of Na_2WO_4(c) was measured at several concentrations. Small concentrations of NaOH or NH_4OH (0.005–$0.01\ M$) were present in all of the solutions to repress hydrolysis of WO_4^-(aq). Results of these experiments are given

(1) R. L. Graham and L. G. Hepler, THIS JOURNAL, **78**, 4846 (1956).

(2) "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952.

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

(4) E. Pechard, Ann. chim. phys., **28**, 537 (1893).

(5) W. G. Mixter, Am. J. Sci., **29**, 488 (1910).

(6) W. G. Mixter, ibid., **26**, 125 (1908).

(7) K. Pan, J. Chinese Chem. Soc., **1**, 26 (1954).

(8) K. Pan, ibid., **1**, 1 (1954).

(9) K. Pan, ibid., **1**, 16 (1954).

(10) W. V. Smith. K. S. Pitzer and W. M. Latimer, THIS JOURNAL, **59**, 2642 (1937).

(11) C. N. Muldrow and L. G. Hepler, ibid., **78**, 5989 (1956).

(12) C. N. Muldrow and L. G. Hepler, ibid., **79**, 4045 (1957).

(13) I. M. Kolthoff and J. J. Lingane, ibid., **57**, 2126 (1935).

(14) W. L. Miller, Ind. Eng. Chem., Anal. Ed., **8**, 431 (1935).

(15) D. A. Lambie, Analyst, **64**, 489 (1935).

in Table I. We have extrapolated to infinite dilution in order to obtain the standard heat of solution $\Delta H^0 = -1.6 \pm 0.1$ kcal./mole. This extrapolation was based on the assumption that the heats of dilution of Na_2WO_4 and Na_2SO_4 are the same in dilute solution. This heat of solution of Na_2WO_4 seems very reasonable in comparison with our previously determined heat of solution of Na_2MoO_4[1] (-2.4 kcal./mole) and is in marked disagreement (nearly 16 kcal./mole) with that calculated from the heats of formation based on the work of Pissarjewsky[3] and Mixter.[6]

TABLE I
HEAT OF SOLUTION OF Na_2WO_4

Moles $Na_2WO_4/950$ ml. soln.	$-\Delta H$ (kcal./mole Na_2WO_4)	Moles $Na_2WO_4/950$ ml. soln.	$-\Delta H$ (kcal./mole Na_2WO_4)
0.01985	1.36	0.04128	1.42
.02286	1.40	.04235	1.28
.02792	1.39	.04622	1.34
.03396	1.35	.05665	1.35
.03560	1.32	.09084	1.35

In order to resolve this discrepancy we measured the heat of reaction of crystalline tungstic acid (H_2WO_4) with a small excess of dilute NaOH. The results of these experiments are given in Table II. We have extrapolated to infinite dilution, again assuming that the heat of dilution of Na_2WO_4 is the same as that of Na_2SO_4 in dilute solution, to obtain $\Delta H_1^0 = -13.7 \pm 0.2$ kcal./mole H_2WO_4 where the calorimetric reaction is given by equation 1. This heat is in good agreement with that reported by Pissarjewsky[3] for the same reaction.
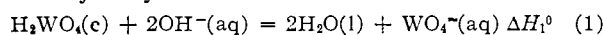
$$H_2WO_4(c) + 2OH^-(aq) = 2H_2O(l) + WO_4^-(aq) \quad \Delta H_1^0 \quad (1)$$

TABLE II
HEAT OF SOLUTION OF $H_2WO_4(c)$ IN NaOH(aq)

Moles $H_2WO_4/950$ ml. soln.	ΔH_1 (kcal./mole H_2WO_4)
0.006920	-13.57
0.01255	-13.55

From our heat of reaction 1 and the heats of formation of H_2O, OH^-(aq) and $H_2WO_4(c)$ given by the Bureau of Standards,[2] we calculate the standard heat of formation of WO_4^-(aq) to be -266.6 kcal./mole which is in good agreement with the value given by the Bureau of Standards[2] based on the work of Pissarjewsky.[3] The only questionable quantity involved in this calculation is the heat of formation of $H_2WO_4(c)$ which is based on Huttig and Kurre's[16] investigation of the temperature coefficient of the partial pressure of H_2O over H_2WO_4. The results of our earlier calorimetric work on $H_2MoO_4(c)$[1] lead us to suspect that the heat of formation of $H_2WO_4(c)$ may be in error by at least as much as 3 or 4 kcal./mole. It would be desirable to eliminate this uncertainty by determining the heat of reaction of $WO_3(c)$ with OH^-(aq), but, as indicated in the experimental section of this paper, we were unable to prepare pure WO_3 that would react properly in the calorimeter.

We have used our heat of solution of Na_2WO_4 and our heat of formation of $WO_4^=$(aq) with the heat of formation of Na^+(aq)[2] to calculate the heat of formation of $Na_2WO_4(c)$ to be -379.6 kcal./mole.

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

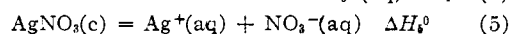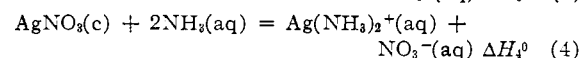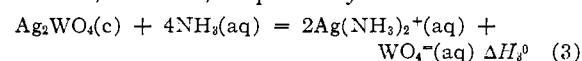Even allowing for an uncertainty of several kcal./mole in the heat of formation of $H_2WO_4(c)$ and $WO_4^=$(aq), our heat of formation of $Na_2WO_4(c)$ is more reliable than that based on Mixter's work[6] (-295 kcal./mole).

The heat of solution of Ag_2WO_4 as indicated in equation 2 cannot be calorimetrically determined directly because silver tungstate is only very

$$Ag_2WO_4(c) = 2Ag^+(aq) + WO_4^-(aq) \quad \Delta H_2^0 \quad (2)$$
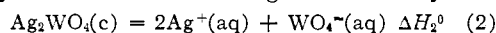
slightly soluble. The desired heat of solution can conceivably be calculated from the results of calorimetric determinations of the heat of precipitation of Ag_2WO_4. However, because of the great tendency of tungstate ions to condense to more complicated species we might expect that values of ΔH_2^0 calculated from heats of precipitation based on the assumption that simple tungstate ions are reacting with silver ions to form stoichiometric Ag_2WO_4 would be in error. The results of several calorimetric investigations of the heat of precipitation confirmed this expectation by giving very erratic results for ΔH_2^0.[17] It is interesting to note that Muldrow and Hepler[11] were able to determine the heat of solution of Ag_2MoO_4 satisfactorily from heat of precipitation measurements.

The heat of solution of Ag_2WO_4 as in equation 2 can be calculated from the heat of solution of Ag_2WO_4 and $AgNO_3$ in aqueous NH_3 and the heat of solution of $AgNO_3$ in water as indicated by equations 3, 4 and 5, respectively. We see that ΔH_2^0

$$Ag_2WO_4(c) + 4NH_3(aq) = 2Ag(NH_3)_2^+(aq) + WO_4^-(aq) \quad \Delta H_3^0 \quad (3)$$

$$AgNO_3(c) + 2NH_3(aq) = Ag(NH_3)_2^+(aq) + NO_3^-(aq) \quad \Delta H_4^0 \quad (4)$$

$$AgNO_3(c) = Ag^+(aq) + NO_3^-(aq) \quad \Delta H_5^0 \quad (5)$$

$= \Delta H_3^0 + 2(\Delta H_5^0 - \Delta H_4^0)$ and that the value of ΔH_2^0 so obtained should not be in error due to polytungstate formation because analysis of the Ag_2WO_4 we dissolved showed it to be of satisfactory composition and the solution in which it was dissolved was sufficiently alkaline that we could be sure tungsten was present as simple tungstate ions.

Results of our investigations of heats of reactions 3, 4 and 5 are given in Tables III, IV and V. We have extrapolated to infinite dilution graphically and with the aid of heats of dilution calculated from heats of formation tabulated by the Bureau of Standards.[2] We have obtained $\Delta H_3^0 = -12.39 \pm 0.16$ kcal./mole Ag_2WO_4, $\Delta H_4^0 = -8.12 \pm 0.07$ kcal./mole $AgNO_3$ and $\Delta H_5^0 = +5.42 \pm 0.05$ kcal./mole $AgNO_3$. We calculate $\Delta H_2^0 = +14.7 \pm 0.2$ kcal./mole Ag_2WO_4. This heat of solution has been used with our heat of formation of WO_4^-(aq) and the heat of formation of Ag^+(aq)[2] to calculate the heat of formation of $Ag_2WO_4(c)$ to be -230.7 kcal./mole.

Pan's data on the silver–silver tungstate electrode lead to $\Delta H_2^0 = +12.11$ kcal./mole Ag_2WO_4.[7] This heat differs from our calorimetric heat in the direction that would be expected if his tungstate solutions and/or silver tungstate electrodes contained more than negligible amounts of poly-

(17) Details of these experiments and our interpretation of them are given in the Ph.D. Dissertation of R. L. Graham, University of Virginia, 1958.

TABLE III

HEAT OF SOLUTION OF Ag_2WO_4 IN 0.16 M NH_3

Moles Ag_2WO_4/950 ml. soln.	ΔH_3 (kcal./mole Ag_2WO_4)
0.004435	−12.22
.009520	−12.28
.010013	−12.30
.012845	−12.11

TABLE IV

HEAT OF SOLUTION OF $AgNO_3$ IN 0.16 M NH_3

Moles $AgNO_3$/950 ml. soln.	ΔH_4 (kcal./mole $AgNO_3$)
0.003492	−8.08
.003694	−8.09
.009345	−8.08
.019239	−8.06
.047520	−8.04

TABLE V

HEAT OF SOLUTION OF $AgNO_3$

Moles $AgNO_3$/950 ml. soln.	ΔH_5 (kcal./mole $AgNO_3$)
0.004010	+5.45
.004501	+5.44
.009998	+5.47
.010707	+5.46
.031557	+5.45
.062937	+5.46

tungstates. We believe that our value for the heat of solution of $AgWO_4$ (14.7 kcal./mole) is better than Pan's value.[7]

Our heats of reactions 4 and 5 are in good agreement with the heats reported by Smith, Brown and Pitzer,[18] Lange and Martin[19] and Roth.[20] On the basis of our ΔH_4^0 and ΔH_5^0 we calculate the standard heat of formation of $Ag(NH_3)_2^+(aq)$ to be −26.87 kcal./mole and the standard partial molal entropy to be 57.8 cal./deg. mole. For these calculations we have used heats of formation and

(18) W. V. Smith, D. V. Brown and K. S. Pitzer, THIS JOURNAL, 59, 1213 (1937).

(19) E. Lange and W. Martin, Z. physik. Chem., A180, 233 (1937).

(20) W. A. Roth, Z. Elektrochem., 50, 107 (1944).

entropies given by the Bureau of Standards[2] and the equilibrium constant for the dissociation of $Ag(NH_3)_2^+[aq]$ given by Vosburgh and McClure.[21]

We are unable to make a completely reliable calculation of the entropy of solution of Ag_2WO_4 because we do not have a completely reliable free energy of solution of Ag_2WO_4. The best free energy of solution available is that due to Pan,[7] but our calorimetric measurements indicate his results are in error—probably due to the presence of polytungstates. We therefore use Pan's free energy of solution (15.4 kcal./mole) as a lower limit and our heat of solution (ΔH_2^0) to calculate that the entropy of solution is at least as negative as −2.4 cal./deg. mole. On the basis of a comparison with $Ag_2CrO_4^8$ and $Ag_2MoO_4^{9,11}$ we would expect the entropy of solution to be about ten entropy units more negative than the limiting value calculated above. This corresponds to a free energy of solution about 3 kcal./mole more positive than that reported by Pan[7] and seems reasonable in view of the importance of polytungstates in these investigations.

All of the heats of formation of tungsten compounds reported in this paper are based on the heat of formation of $H_2WO_4(c)$. Any change in the accepted value for the heat of formation of this compound will change the heats of formation of $WO_4^=(aq)$, $Na_2WO_4(c)$ and $Ag_2WO_4(c)$ but will not change the heat of solution of Ag_2WO_4 we have calculated from our heats of reaction and solution.

(21) W. C. Vosburgh and K. S. McClure, THIS JOURNAL, 65, 1060 (1943).

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A Spectrophotometric Study of Some Molybdenum Thiocyanate Complexes

BY D. D. PERRIN[1]

Molybdenum(V) forms a series of complexes with thiocyanates in molar hydrochloric acid. For the amber-colored complex used in chemical analysis the Mo:CNS ratio is 1:3. The complex is uncharged and is probably $MoO(CNS)_3$. A yellow complex, of Mo:CNS ratio 1:2, is described, and a colorless 1:1 complex is postulated to explain observed changes in absorbancy with changes in thiocyanate concentration. The three complexes exist in equilibrium with molybdenum(V) and thiocyanate ion. Association constants in 60% acetone–water have been calculated from the absorbancy data.

Reduction of molybdates in acid thiocyanate solutions gives a characteristic amber to orange-red color. This reaction, which is commonly used to estimate low concentrations of molybdenum, requires for maximum color development a hydrogen ion concentration approximately one molar and a high concentration of thiocyanate ion.

A wide range of formulas have been assigned to

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the molybdenum thiocyanate complex which is formed under these conditions.[2-4] Recent work confirms that the complex contains pentavalent molybdenum.[2,4,5] Molybdenum(V), prepared by

(2) C. F. Hiskey and V. W. Meloche, THIS JOURNAL, 62, 1565 (1940), who also review earlier formulations.

(3) A. T. Dick and J. B. Bingley, Nature, 158, 516 (1946).

(4) A. K. Babko, J. Gen. Chem. (U.S.S.R.), 17, 642 (1947).

(5) C. E. Crouthamel and C. E. Johnson, Anal. Chem., 26, 1284 (1954).