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Standard Enthalpy of Formation of Monoclinic Ammonium Paratungstate

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Abstract: The enthalpy of reaction for the decomposition of monoclinic ammonium paratungstate, $(NH_4)_{10}H_2W_{12}O_{42}4H_2O(s)$, was measured using a HT-1000 calorimeter. From the experimental results, the standard enthalpy of formation of ammonium paratungstate at 298.15 K is obtained.

Keywords: Standard enthalpy of formation, monoclinic ammonium paratungstate, calorimetry.

Monoclinic ammonium paratungstate, $(NH_4)_{10}H_2W_{12}O_{42}4H_2O(s)$, is an essential intermediate compound in the extraction of tungsten from its ores[1]. The knowledge of the properties of ammonium paratungstate is desirable for controlling its crystallization and its thermal decomposition. However, the study on the thermodynamic properties has not been reported. In the present work, the enthalpy of reaction for the thermal decomposition of ammonium paratungstate was measured, and its standard enthalpy of formation at 298.15 K is obtained.

The sample of monoclinic ammonium paratungstate was prepared according to the literature[1]. The XRD and chemical analysis showed that the sample is $(NH_4)_{10}H_2W_{12}O_{42}4H_2O$.

Up to about 723 K, the thermal decomposition of monoclinic ammonium paratungstate[2] can be expressed as:

$$(NH_4)_{10}H_2W_{12}O_{42}4H_2O\ (s)=12WO_3(s)+\ 10NH_3(g)+\ 10H_2O(g) \qquad (1)$$

The standard enthalpy of reaction $\Delta_r H_m^0$ (298.15 K) for the reaction (1) was measured using three-

steps calorimetry[3] in a HT-1000 calorimeter. The composition of the product of each step calorimetry was determined from the weight loss of the sample and the N content analysis of the product. The thermodynamic cycle for calculation of $\Delta_r H_m^0$ (298.15 K) is listed in **Table 1**.

Hence: $\Delta_r H_m^0$ (298.15 K) = $\Delta H_1 - \Delta H_2 - \Delta H_3 + \Delta H_4 - \Delta H_5 - \Delta H_6 + \Delta H_7 - \Delta H_8$ (2)

In the equation (2), ΔH_3, ΔH_6 and ΔH_8 were calculated from the published dada[4]. ΔH_3 =40.21 kJ · mol^{-1}, ΔH_6 =122.09 kJ · mol^{-1} and ΔH_8 =542.13 kJ · mol^{-1}. ΔH_1, ΔH_2, ΔH_4, ΔH_5 and ΔH_7 were measured using calorimeter. The experimental results are listed in **Table 2**.

Therefore, $\Delta_r H_m^0$ (298.15 K) =(430.1±10.2) kJ • mol^{-1}.

Table 1 Cycle for the calculation of $\Delta_r H_m^0$ (298.15 K) based on the reaction (1)

1) $(NH_4)_{10}H_2W_{12}O_{42}4H_2O$ (s, 298.15K) = $4(NH_4)_2O$ • $12WO_3$ • $2H_2O$(s, 482.4K)+ $2NH_3$(g, 482.4K) + $4H_2O$(g, 482.4K)
2) $4(NH_4)_2O$ • $12WO_3$ • $2H_2O$(s, 298.15K) = $4(NH_4)_2O$ • $12WO_3$ • $2H_2O$(s, 482.4K)
3) $2NH_3$(g, 298.15 K)+ $4H_2O$(g, 298.15K)= $2NH_3$(g, 482.4K)+ $4H_2O$(g, 482.4K)
4) $4(NH_4)_2O$ • $12WO_3$ • $2H_2O$(s, 298.15K) = $(NH_4)_2O$ • $12WO_3$(s, 583.5K)+ $6NH_3$(g, 583.5K) + $5H_2O$(g, 583.5K)
5) $(NH_4)_2O$ • $12WO_3$(s, 298.15 K)= $(NH_4)_2O$ • $12WO_3$(s, 583.5K)
6) $6NH_3$(g, 298.15K)+ $5H_2O$(g, 298.15K)= $6NH_3$(g, 583.5K)+ $5H_2O$(g, 583.5K)
7) $(NH_4)_2O$ • $12WO_3$(s, 298.15K)=$12WO_3$(s,755.3K)+$2NH_3$(g, 755.3K)+H_2O(g, 755.3K)
8) $12WO_3$(s,298.15K)+2 NH_3(g, 298.15K)+ H_2O(g, 298.15K) = $12WO_3$(s, 755.3K)+2 NH_3(g, 755.3K) + H_2O(g, 755.3K)
1) -2) -3) +4) -5) -6) +7) -8):
9) $(NH_4)_{10}H_2W_{12}O_{42}4H_2O$ (s, 298.15K)= $12WO_3$(s, 298.15K)+ $10NH_3$(g, 298.15K)+ $10H_2O$(g, 298.15K)

Table 2 The results of enthalpy (in kJ • mol^{-1}) for the reactions listed in **Table 1**

No.	ΔH_1	ΔH_2	ΔH_4	ΔH_5	ΔH_7
1	641.81	330.89	853.68	378.71	364.19
2	643.91	324.26	814.10	370.88	342.37
3	644.03	325.17	836.52	375.98	356.54
4	642.68	344.13	868.24	365.36	352.18
5	640.05	338.24	842.97	370.26	363.20
6	639.93	336.15		369.35	337.69
7	640.27	328.83		365.33	346.91
8	640.21	320.87			
9	643.28	341.90			
10	640.24	334.22			
Mean	641.7±0.5	331.4±2.0	843.1±9.0	370.8±1.9	351.9±3.8

From the values of the standard enthalpy of formation[4] for WO_3(s), NH_3(g) and H_2O(g), the standard enthalpy of formation at 298.15 K of monoclinic ammonium paratungstate can been obtained:

$\Delta_f H_m^0$ ($(NH_4)_{10}H_2W_{12}O_{42}4H_2O$, s, 298.15 K) = -(13423.7±10.2) kJ • mol^{-1}.

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