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Standard enthalpy of formation of sodium paratungstate $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O(s)$

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Abstract

The standard enthalpy of decomposition of $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O(s)$ at 298.15 K was measured using the method of three-step calorimetry in a Calvet twin-vessel microcalorimeter. The standard enthalpy of formation of $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O(s)$ at 298.15 K was first obtained as $-(21898.2\pm 10.8)$ kJ mol^{-1}.

Keywords: Sodium paratungstate; Enthalpy of formation; Calorimetry; Thermal decomposition

1. Introduction

Sodium paratungstate, $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O$, can easily crystallize from the acidic solution of Na_2WO_4. The thermodynamic properties of $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O$ are of great significance in understanding the aqueous chemistry of isopolytungstates [1,2]. However, there is not been any thermodynamic report about sodium paratungstate in the literature so far.

The thermal behavior of sodium paratungstate has been reported previously [3]. The thermal decomposition involves six steps. The first four steps include dehydration, taking place at about 331, 353, 403 and 588 K, respectively. The fifth step is the phase change of the intermediate appearing at about 691 K. The sixth step finishes at about 733 K and forms the mixture of $4Na_2W_2O_7$ and $Na_2W_4O_{13}$. In the present work, the standard enthalpy of decomposition of $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O(s)$ at 298.15 K was measured using the method of three-step calorimetry in a Calvet twin-vessel microcalorimeter. The standard enthalpy of formation of $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O(s)$ at 298.15 K was first obtained from the experimental result and literature data.

2. Experimental

The synthesis of a sample of sodium paratungstate has been reported previously [3]. The chemical and thermogravimetric analyses gave the composition of $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O$. The sample was ground in an agate mortar and that of 200 mesh was used for measurements.

A Calvet twin-vessel microcalorimeter HT-1000(Setaram, France) was employed. Before the experiment, the sensitivity and temperature scales of the calorimeter were calibrated carefully [4]. The aluminum crucibles, with mass of 0.20–0.25 g in the form of cylinder of 6 mm diameter and 10 mm in

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Table 1
Thermodynamic cycle for calculation of $\Delta_r H_m^0$ for the decomposition of sodium paratungstate

(1)	$Na_{10}H_2W_{12}O_{42}{\cdot}27H_2O$(s, 298.15 K)=$Na_{10}H_2W_{12}O_{42}{\cdot}3H_2O$(s, 441.8 K)+$24H_2O$(g, 441.8 K)
(2)	$Na_{10}H_2W_{12}O_{42}{\cdot}3H_2O$(s, 298.15 K)=$Na_{10}H_2W_{12}O_{42}{\cdot}3H_2O$(s, 441.8 K)
(3)	$24H_2O$(g, 298.15 K)=$24H_2O$(g, 441.8 K)
(4)	$Na_{10}H_2W_{12}O_{42}{\cdot}3H_2O$(s, 298.15 K)=$5Na_2O{\cdot}12WO_3$(s, 614.1 K)+$4H_2O$(g, 614.1 K)
(5)	$5Na_2O{\cdot}12WO_3$(s, 298.15 K)=$5Na_2O{\cdot}12WO_3$(s, 614.1 K)
(6)	$4H_2O$(g, 298.15 K)=$4H_2O$(g, 614.1 K)
(7)	$5Na_2O{\cdot}12WO_3$(s, 298.15 K)=$4Na_2W_2O_7$ (s, 755.8 K)+$Na_2W_4O_{13}$(s, 755.8 K)
(8)	$4Na_2W_2O_7$ (s, 298.15 K)+$Na_2W_4O_{13}$(s, 298.15 K)=$4Na_2W_2O_7$ (s, 755.8 K)+$Na_2W_4O_{13}$(s, 755.8 K)
(1)−(2)−(3)+(4)−(5)−(6)+(7)−(8):	
(9)	$Na_{10}H_2W_{12}O_{42}{\cdot}27H_2O$(s, 298.15 K)=$4Na_2W_2O_7$ (s, 298.15 K)+$Na_2W_4O_{13}$(s, 298.15 K)+$28H_2O$(g, 298.15 K)

height, were used as containers. There was a hole of 0.5 mm diameter in the cup of the crucible for the release of $H_2O(g)$ so that the calorimetry was made in isobaric conditions. First, the sample with mass of 0.15–0.25 g was placed in the crucible and kept at the reference temperature, 298.15 K. Then the crucible was dropped from the reference temperature into the isothermal zone of the calorimeter after the heat-flow baseline had become steady. Calorimetric data were collected simultaneously by a computer. The enthalpy increments of the empty crucible from reference temperature to reaction temperature were measured with the same condition.

In order to measure the standard enthalpy of reaction $\Delta_r H_m^0$ for the following reaction at 298.15 K:

$$\begin{aligned}&Na_{10}H_2W_{12}O_{42}\cdot 27H_2O(s)\\&\quad = 4Na_2W_2O_7(s) + Na_2W_4O_{13}(s)\\&\qquad + 28H_2O(g)\end{aligned} \tag{1}$$

the method of three-step calorimetry was used. The sample of $Na_{10}H_2W_{12}O_{42}{\cdot}27H_2O(s)$ was first measured at 441.8 K, and the reaction [3] is:

$$\begin{aligned}&Na_{10}H_2W_{12}O_{42}\cdot 27H_2O(s)\\&\quad = Na_{10}H_2W_{12}O_{42}\cdot 3H_2O(s) + 24H_2O(g)\end{aligned} \tag{2}$$

The product of reaction (2), $Na_{10}H_2W_{12}O_{42}{\cdot}3H_2O(s)$, was then measured at 614.1 K, and the reaction [3] is:

$$\begin{aligned}&Na_{10}H_2W_{12}O_{42}\cdot 3H_2O(s)\\&\quad = 5Na_2O\cdot 12WO_3(s) + 4H_2O(g)\end{aligned} \tag{3}$$

The product of reaction (3), $5Na_2O{\cdot}12WO_3(s)$, was finally measured at 755.8 K, the reaction can be expressed as [3]:

$$\begin{aligned}&5Na_2O\cdot 12WO_3(s)\\&\quad = 4Na_2W_2O_7(s) + Na_2W_4O_{13}(s)\end{aligned} \tag{4}$$

The XRD showed that the final calorimetric product was a mixture of $Na_2W_2O_7$ and $Na_2W_4O_{13}$.

The thermodynamic cycle for the calculation of $\Delta_r H_m^0$ is listed in Table 1.

Therefore,

$$\begin{aligned}\Delta_r H_m^0 \equiv \Delta H_9 &= \Delta H_1 - \Delta H_2 - \Delta H_3 + \Delta H_4\\&\quad - \Delta H_5 - \Delta H_6 + \Delta H_7 - \Delta H_8\end{aligned} \tag{5}$$

where: ΔH_3, ΔH_6 and ΔH_8 were calculated from the reference data [5,6] listed in Table 2; ΔH_1, ΔH_2, ΔH_4, ΔH_5 and ΔH_7 were measured using an HT-1000 calorimeter.

ΔH_2 and ΔH_5 are the enthalpy increments of the samples, and the time of determination of both enthalpies was about 60 min. ΔH_1, ΔH_4 and ΔH_7 are the enthalpy changes of non-isothermal decomposition for the samples. The measurement time was about 150 min for ΔH_1 and ΔH_4, and about 60 min for ΔH_7, respectively.

3. Results and discussion

The results calculated from Table 2 are: ΔH_3=117.4 kJ mol^{-1}, ΔH_6=45.0 kJ mol^{-1} and ΔH_8=665.0 kJ mol^{-1}. The experimental results are listed in Table 3.

From the calculated and experimental results, it could be obtained that $\Delta_r H_m^0$=(1349.4±4.9) kJ mol^{-1} for the reaction (1).

We also had attempted to measure $\Delta_r H_m^0$ of reaction (1) by using the methods of one-step and two-step

Table 2
Heat capacity values used in the present work

Substance	$C_{P,m}$ (J K^{-1} mol^{-1})	Reference
H_2O(g)	$34.376+7.841\times10^{-3}(T/K)-0.423\times10^{6}(T/K)^{-2}$	[5]
$Na_2W_2O_7$(s)	$211.12+10.720\times10^{-2}(T/K)-2.566\times10^{6}(T/K)^{-2}$	[6]
$Na_2W_4O_{13}$(s)	$388.97+13.286\times10^{-2}(T/K)-6.950\times10^{6}(T/K)^{-2}$	[6]

Table 3
Experimental results of the enthalpy change (kJ mol^{-1})for the reactions listed in Table 1 (p^0=101.325 kPa. Molar mass of $Na_{10}H_2W_{12}O_{42}\cdot27H_2O$, $Na_{10}H_2W_{12}O_{42}\cdot3H_2O$ and $5Na_2O\cdot12WO_3$ are 3596.5, 3164.1 and 3092.1 g mol^{-1}, respectively. Uncertainty is the standard deviation of the mean)

No.	ΔH_1	ΔH_2	ΔH_4	ΔH_5	ΔH_7
1	1552.9	263.6	700.7	461.5	655.8
2	1556.1	268.3	698.5	460.9	645.0
3	1556.0	253.3	699.4	464.5	650.3
4	1559.4	266.4	703.6	468.0	639.3
5	1558.0	261.6	696.1	467.1	
Mean	1556.5±1.1	262.6±2.6	699.7±1.2	464.4±1.4	647.6±3.5

calorimetry. The result for one-step calorimetry (at 786.6 K) was (1096.9±25.0) kJ mol^{-1} (11 runs) and that for two-step calorimetry (at 594.0 and 786.6 K) was (1344.5±5.2) kJ mol^{-1} (5 runs). When the method of one-step calorimetry was used, the temperature of measurement was much higher than that of dehydration of $Na_{10}H_2W_{12}O_{42}\cdot27H_2O$(s). A large amount of H_2O(g) evolved and was released quickly from the calorimeter; hence, the temperature of released H_2O(g) must be lower than that of measurement. The result was, therefore, lower than what it should be. The result obtained from the method of two-step calorimetry was also unreliable because of this reason.

Thus, for the decomposition in which gas was released in multistage step, the enthalpy change should be separately measured at the end temperature of each step. According to the mechanism [3] of decomposition of $Na_{10}H_2W_{12}O_{42}\cdot27H_2O$(s), the dehydration of the first three steps takes place in a near-temperature range. If the enthalpy change of these three steps was separately measured at the end temperature of each step, the error will be enhanced. Therefore, it was suitable to measure enthalpy change of the first three steps, i.e. ΔH_1, at the end temperature of the third dehydration. The enthalpy change of the fourth step, i.e. ΔH_4, was measured in the second step of calorimetry. There are no changes in mass during the fifth and sixth steps of the decomposition; hence, the enthalpy change of these two steps, i.e. ΔH_7, could be measured in the third step of calorimetry. Hence, the method of three-step calorimetry is reliable for the determination of $\Delta_r H_m^0$ based on the reaction (1). From the result obtained by this method, the following value is recommended:

$$\Delta_r H_m^0 = (1349.4 \pm 4.9)\,\mathrm{kJ\,mol^{-1}}$$

Combining this with the values of standard enthalpies of formation, namely −(2405.0±2.0) kJ mol^{-1} for $Na_2W_2O_7$(s) [7], −(4157.6±5.2) kJ mol^{-1} for $Na_2W_4O_{13}$(s) [7], and −(241.83±0.04) kJ mol^{-1} for H_2O(g) [8], the standard enthalpy of formation of $Na_{10}H_2W_{12}O_{42}\cdot27H_2O$(s) at 298.15 K can be obtained as:

$$\Delta_f H_m^0(Na_{10}H_2W_{12}O_{42}\cdot 27H_2O, s, 298.15\,K) = -(21898.2 \pm 10.8)\,\mathrm{kJ\,mol^{-1}}.$$

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