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Standard enthalpy of formation of paratungstate B ion $H_2W_{12}O_{42}{}^{10-}$(aq)

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Abstract

The enthalpy of sodium paratungstate $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O$(s) dissolved in solution of 1.0 mol dm^{-3} $LiClO_4$ was measured at 298.15 K using a Calvet twin-vessel microcalorimeter. The standard enthalpy of formation of paratungstate B ion, $H_2W_{12}O_{42}{}^{10-}$(aq), was calculated on the basis of the experimental results. Combining this with values from the literature led to $\Delta_f H_m^0$ ($H_2W_{12}O_{42}{}^{10-}$, aq, 298.15 K)=$-$(11653.5±10.9) kJ mol^{-1}.

Keywords: Standard enthalpy of formation; Paratungstate B ion; Calorimetry

1. Introduction

The crystallization of solid ammonium paratungstate (APT) from the solution containing paratungstate B ion, $H_2W_{12}O_{42}{}^{10-}$(aq), is an essential intermediate purification step in the overall extraction process of tungsten from its ores. A knowledge of the thermodynamic property of $H_2W_{12}O_{42}{}^{10-}$(aq) is therefore desirable for understanding and controlling this crystallization. The thermodynamic study on paratungstate B ion has been reported by Arnek [1] and Cruywagen et al. [2]. They determined the standard enthalpy of reaction for the formation of $H_2W_{12}O_{42}{}^{10-}$(aq) from $WO_4{}^{2-}$ ion at 298.15 K using titration calorimetry. The standard enthalpy of formation of $H_2W_{12}O_{42}{}^{10-}$(aq) could be obtained from their results. These determinations are indirect because three reactions were assumed in the model of Arnek [1] and four in the model of Cruywagen et al. [2]. Moreover, in the acidic solution of $WO_4{}^{2-}$, the formation of $H_2W_{12}O_{42}{}^{10-}$(aq) is too slow [3,4] to be measured by the titration calorimetry. In the present work, the standard enthalpy of formation of $H_2W_{12}O_{42}{}^{10-}$ (aq) was directly determined at 298.15 K by measuring the enthalpy of solution $\Delta_{sol}H_m$ of sodium paratungstate $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O$(s) in solution of 1.0 mol dm^{-3} $LiClO_4$ using a Calvet twin-vessel microcalorimeter.

2. Experimental

The synthesis of sodium paratungstate has been reported previously [5]. The chemical and thermogravimetric analysis 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 calorimetric measurements. Prior to experiment, the sample was

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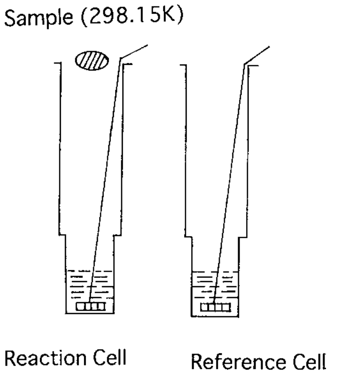

Fig. 1. The scheme of the cells for the dissolving reaction of the sample.

pressed into pellets and kept at reference temperature 298.15 K for 5 h. The solution of 1.0 mol dm^{-3} $LiClO_4$ was prepared by dissolving crystal of $LiClO_4 \cdot 2H_2O$ (A.R.) in distilled water.

A Calvet twin-vessel microcalorimeter HT-1000 (Setaram, France) was employed. Before experiments, the sensitivity and temperature scales of the calorimeter were calibrated carefully [6]. The scheme of the cells for the dissolving reaction of the sample was shown in Fig. 1. Equal volume of solvent was introduced into the reaction cell and reference cell, respectively. The glass clubs, which were hanged by silk yarn (0.2 mm diameter), were used to stir solution by pulling simultaneously silk yarn. This method of stirring was proved to be reliable for the dissolving of the sample and for the stability of the baseline. A pellet of weighed sample at reference temperature was dropped into the reaction cell after the heat-flow baseline had become steady. The reference temperature equals that of the calorimeter. The calorimetric results were collected simultaneously by a computer.

The enthalpy of solution of KCl(s) in water (10.00 cm^3) to form about $KCl \cdot 1120\ H_2O$ was measured at T=(298.15±0.5) K to check the accuracy of the calorimetric method. The results are listed in Table 1. The mean value of seven experimental runs was (17.48±0.12) kJ mol^{-1}, which was in good agreement with the value 17.503 kJ mol^{-1} from the literature [7]. The accuracy of the calorimeter is therefore reliable.

Table 1
Results of enthalpy of solution for KCl(s) in 10.00 cm^3 H_2O at 298.15 K (molar mass of KCl is 74.555 g mol^{-1})

No.	W_{KCl}/g	Q_p/J	$\Delta_{sol}H_m$/(J mol^{-1})
1	0.04023	9.563	17722
2	0.03370	7.956	17601
3	0.03650	8.599	17565
4	0.03782	8.994	17730
5	0.03796	8.974	17625
6	0.03401	7.851	17211
7	0.03857	8.749	16912
Average			17479±115

In order to determine $\Delta_f H^0_m$ ($H_2W_{12}O_{42}{}^{10-}$, aq, 298.15 K), the reaction at 298.15 K:

$$\begin{aligned} Na_{10}H_2W_{12}O_{42} \cdot 27H_2O(s) + nH_2O \\ = 10Na^+(aq) + H_2W_{12}O_{42}{}^{10-}(aq) \\ + 27H_2O(l) \end{aligned} \quad (1)$$

was used. During the aging of the aqueous solution of $Na_{10}H_2W_{12}O_{42} \cdot 27H_2O(s)$, paratungstate B ion ($H_2W_{12}O_{42}{}^{10-}$) would be slowly converted to paratungstate A ($W_7O_{24}{}^{6-}$), while such conversion could be prevented in the presence of Li^+ ion [3]. Therefore, the enthalpy of solution $\Delta_{sol}H_m$ for the reaction (1) could be measured, using a HT-1000 calorimeter when a given mass of $Na_{10}H_2W_{12}O_{42} \cdot 27H_2O(s)$ is completely dissolved in the solution of 1.0 mol dm^{-3} $LiClO_4$. By making measurements with various mass of $Na_{10}H_2W_{12}O_{42} \cdot 27H_2O(s)$, $\Delta_{sol}H^0_m$ could be obtained by extrapolation to infinite dilution of $H_2W_{12}O_{42}{}^{10-}$(aq). The time of each measurement was about 40 min.

3. Results and discussion

The experimental results for the solution of $Na_{10}H_2W_{12}O_{42} \cdot 27H_2O(s)$ in 10.00 cm^3 solution of 1.0 mol dm^{-3} $LiClO_4$ are listed in Table 2.

The standard enthalpy $\Delta_{sol}H^0_m$ for the reaction (1) was calculated by fitting values of $\Delta_{sol}H_m$ from Table 1 to a linear function of m_{SPTB}, where m_{SPTB} denotes mol dm^{-3},

$$\Delta_{sol}H_m = (124.2 \pm 0.2) + (897.3 \pm 51.3) \times m_{SPTB} \quad (2)$$

so that $\Delta_{sol}H^0_m$=(124.2±0.2) kJ mol^{-1}. The extent of fit is shown in Fig. 2.

Table 2
Experimental enthalpy of solution $\Delta_{sol}H_m$ of $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O(s)$ in 10.00 cm^3 solution of 1.0 mol dm^{-3} $LiClO_4$ at 298.15 K (molar mass of $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O$ (SPTB) is 3596.5 g mol^{-1})

No.	W_{SPTB}/g	m_{SPTB}/(mol dm^{-3})	$\Delta_{sol}H_m$/(kJ mol^{-1})
1	0.18343	0.00510	128.8
2	0.15975	0.00444	128.3
3	0.15301	0.00425	127.9
4	0.12592	0.00350	127.4
5	0.11675	0.00325	127.3
6	0.10641	0.00296	126.7
7	0.07005	0.00195	126.0

From reaction (1), we then have

$$\begin{aligned}\Delta_f H_m^0(H_2W_{12}O_{42}{}^{10-}, aq) &= \Delta_{sol}H_m^0 + \Delta_f H_m^0(Na_{10}H_2W_{12}O_{42}\\ &\quad \cdot 27H_2O, s) - 10\Delta_f H_m^0(Na^+, aq)\\ &\quad - 27\Delta_f H_m^0(H_2O, l) \qquad (3)\end{aligned}$$

Combining this value with the standard enthalpies of formation, −(240.30±0.065) kJ mol^{-1} for $Na^+(aq)$ [8], −(285.83±0.04) kJ mol^{-1} for $H_2O(l)$ [8], and −(21898.1±10.8) kJ mol^{-1} for $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O(s)$ from our measurement [9], we could obtain the following value:

$$\begin{aligned}\Delta_f H_m^0(H_2W_{12}O_{42}{}^{10-}, aq,\ 298.15\,K)\\ = -(11653.5 \pm 10.9)\,kJ\,mol^{-1}\end{aligned}$$

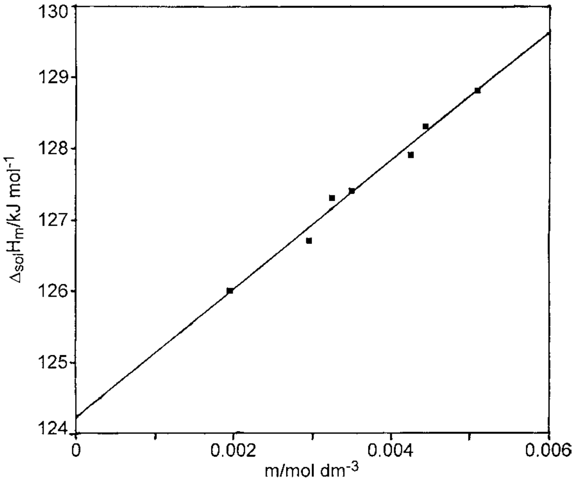

Fig. 2. The curve of $\Delta_{sol}H_m$ against m/mol dm^{-3} for $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O(s)$ dissolving in solution of 1.0 mol dm^{-3} $LiClO_4$ at 298.15 K.

Arnek [1] and Cruywagen et al. [2] determined the standard enthalpy of the reaction

$$\begin{aligned}12WO_4{}^{2-}(aq) + 14H^+(aq)\\ = H_2W_{12}O_{42}{}^{10-}(aq) + 6H_2O(l) \qquad (4)\end{aligned}$$

The results are $\Delta_r H_m^0$ (298.15 K)=−(531±8) kJ mol^{-1} in the medium [1] of 3.0 mol dm^{-3} $NaClO_4$ and −(542±4) kJ mol^{-1} in the medium [2] of 1.0 mol dm^{-3} NaCl, respectively. With data of the standard enthalpies of formation for $WO_4{}^{2-}(aq)$ [10], −1073.2 kJ mol^{-1}, and for $H_2O(l)$ [8], the standard enthalpy of formation of $H_2W_{12}O_{42}{}^{10-}(aq)$ was calculated to be −11694.4 kJ mol^{-1} from the result reported by Arnek [1] and to be −11705.4 kJ mol^{-1} from the result reported by Cruywagen et al. [2]. There is an obvious difference between their values and ours. Since only our result is obtained from the direct measurement method, our result should be recommended as the value of standard enthalpy of formation of $H_2W_{12}O_{42}{}^{10-}(aq)$.

Acknowledgements

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