ELSEVIER

Thermochimica Acta 371 (2001) 7–11

thermochimica acta

www.elsevier.com/locate/tca

Thermodynamic properties of $Na_2W_2O_7$(s) and $Na_2W_4O_{13}$(s) in the temperature range 298.15–1000 K

Shijun Liu[a,*], Qiyuan Chen[b], Pingmin Zhang[b]

[a]Department of Chemistry, Xiangtan University, Xiangtan, Hunan 411105, PR China
[b]Department of Chemistry, Central South University of Technology, Changsha, Hunan 410083, PR China

Received 24 November 1998; received in revised form 15 June 2000; accepted 15 November 2000

Abstract

The enthalpy increments $\Delta_{273.15\,\mathrm{K}}^{T}H_{\mathrm{m}}^{0}$ of $Na_2W_2O_7$(s) and $Na_2W_4O_{13}$(s) were measured in the temperature range 273–979 K by the drop method using a high temperature Calvet HT-1000 calorimeter. The results can be represented by the polynomial equations:

$$\Delta_{273.15\,\mathrm{K}}^{T}H_{\mathrm{m}}^{0}(\mathrm{Na_2W_2O_7}) = -71,006 + 211.12T + 10.720 \times 10^{-2}T^2 + 2.566 \times 10^{6}T^{-1}$$

$$\Delta_{273.15\,\mathrm{K}}^{T}H_{\mathrm{m}}^{0}(\mathrm{Na_2W_4O_{13}}) = -136,568 + 388.97T + 6.643 \times 10^{-2}T^2 + 6.950 \times 10^{6}T^{-1}$$

The expressions of the heat capacity against temperature for these two compounds were obtained from the differentiation of the above equations. By combining these results with data from the literature, smoothed thermodynamic functions have been calculated for $Na_2W_2O_7$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Sodium ditungstate; Sodium tetratungstate; Enthalpy increment; Heat capacity

1. Introduction

Sodium ditungstate $Na_2W_2O_7$(s) and sodium tetratungstate $Na_2W_4O_{13}$(s) are stable compounds in the phase diagram [1] of ($Na_2WO_4 + WO_3$). The former has the normal melting temperature which was reported to be 1004 [2] and 1019 K [1]. The latter has the peritectic melting temperature which was reported to be 1057 [3] and 1108 K [1]. The structure of $Na_2W_2O_7$ consists of $(W_2O_7)^{2-}$ chains containing WO_6 octahedra and WO_4 tetrahedra [4]. The structure of $Na_2W_4O_{13}$ is formed by layers of the $((W_4O_{13})^{2-})_\infty$ anion group constructed from WO_6 octahedra by sharing corners and edges [5]. Both compounds have important uses, such as the preparation of tungsten bronze and ceramic materials [1–6]. In the hot corrosion of metals and ceramic materials containing tungsten, We may react with Na under favorable oxygen-potential environments forming tungstates including $Na_2W_2O_7$(s) and $Na_2W_4O_{13}$ [7]. Therefore, the thermodynamic properties of both compounds are necessary for their further research and applications.

At 298.15 K, the standard enthalpies of formation of $Na_2W_2O_7$(s) and $Na_2W_4O_{13}$(s), the heat capacity and the standard entropy of $Na_2W_2O_7$(s) have been reported [8]. The thermochemistry of Na_2O–WO_3 system at 1065–1239 K was studied using emf method [7]. The calorimetric investigation of both compounds at high temperature has not been reported. The present

---

[*] Corresponding author.
E-mail address: sjliu@chemt.chem.nagoya-u.ac.jp (S. Liu).

PII: S0040-6031(00)00761-9

paper represents the experimental results of the enthalpy increment and the derived molar heat capacity for $Na_2W_2O_7$(s) and $Na_2W_4O_{13}$(s) in the temperature range from 273 to 979 K. Based on these results, the smoothed thermodynamic properties of $Na_2W_2O_7$(s) in the temperature range from 298.15 to 1000 K have been calculated.

2. Experimental

2.1. Sample preparation and characterization

The reagent grade $Na_2WO_4{\cdot}2H_2O$ was purified by twice recrystallization from distilled water, and then dried at 523 K for 24 h to obtain pure Na_2WO_4. No impurity lines were found in the powder X-ray pattern of Na_2WO_4. Tungsten trioxide was spectroscopically pure reagent. ($Na_2WO_4 + WO_3$) was mixed thoroughly in an agate mortar. The mixture was melted in a platinum crucible at 1023 K for 10 min, then quenched in air to obtain [6] $Na_2W_2O_7$(s). ($Na_2WO_4 + 3WO_3$) was mixed thoroughly in an agate mortar. The mixture was enclosed in a platinum crucible at 943 K for 30 h, then cooled to room temperature at the rate of 20–30 $\mathrm{K\,h^{-1}}$ to obtain $Na_2W_4O_{13}$(s) [6]. The products were ground in an agate mortar and were kept in a desiccator.

The XRD analysis of the samples was performed on a D500 X-ray diffraction analyzer (Siemens, Germany). The XRD patterns of the samples agreed with no that reported previously [6] and that in JCPDS for $Na_2W_2O_7$ (No 32–1186) and $Na_2W_4O_{13}$ (No 27–1425). Chemical and spectrographic analyses of the samples gave the results shown in the Table 1. The results showed that the constituent elements were in the required stoichiometry.

2.2. Calorimetric technique

A high temperature microcalorimeter HT-1000 (Setaram, France) was used to determine the enthalpy increments of samples [9]. The temperature scale of the calorimeter was calibrated by a Pt (Pt + 10 mass% Rh) thermocouple and by determining the melting temperatures of In, Pb, Zn and Al. The sensitivity of the calorimeter was calibrated by determining the enthalpy increments of α-Al_2O_3 (99.95 mass%, obtained from Refractory Factory of Shanghai, PR China), in the form of cylinders of 4 mm diameter and 2–5 mm long. The enthalpy increments of the samples were determined by dropping the sample from a constant temperature to the isothermal zone of the calorimeter.

The dried sample (0.2–0.3 g) was enclosed in a platinum crucible (with mass of 0.48150 g and a form of cylinder of 5 mm diameter and 7 mm long). The crucible was sealed in a glass tube (10 mm diameter and 150 mm long) which had been flushed with purified argon. The tube was kept at the constant temperature in a thermostatic container. The crucible was dropped quickly from the tube into the isothermal zone of the calorimeter when the baseline of the calorimeter reached a steady state. The enthalpy increments of the empty crucible were measured separately at the same condition. With the same method, the enthalpy increments of standard material, α-Al_2O_3 powder (obtained from Shimadzu, Japan, originally used for DTA standard material) was measured to check the precision and accuracy of the method. At least three drops experiments were done at each temperature for each sample, and the uncertainty is the standard deviation of the mean.

The general constant temperature was 313.2 K, hence $\Delta_{313.2\mathrm{K}}^{T}H_{\mathrm{m}}^{0}$ was directly obtained. The measurement carried out at 502.6 K was also done from the constant temperature 273.15 K, therefore, $\Delta_{273.15\,\mathrm{K}}^{313.2\,\mathrm{K}}H_{\mathrm{m}}^{0} = \Delta_{273.15\,\mathrm{K}}^{502.6\,\mathrm{K}}H_{\mathrm{m}}^{0} - \Delta_{313.2\,\mathrm{K}}^{502.6\,\mathrm{K}}H_{\mathrm{m}}^{0}$, was indirectly obtained. The final result was presented by

$$\Delta_{273.15\,\mathrm{K}}^{T}H_{\mathrm{m}}^{0} = \Delta_{313.2\,\mathrm{K}}^{T}H_{\mathrm{m}}^{0} + \Delta_{273.15\,\mathrm{K}}^{313.2\,\mathrm{K}}H_{\mathrm{m}}^{0} \qquad (1)$$

Table 1
Chemical compositions of $Na_2W_2O_7$ and $Na_2W_4O_{13}$

Compound	WO_3 content (mass%)	Na_2O content (mass%)	Mole ratio (WO_3/Na_2O)
$Na_2W_2O_7$	88.19 ± 0.06	11.78 ± 0.09	2.001
$Na_2W_4O_{13}$	93.71 ± 0.05	6.27 ± 0.08	3.995

To confirm the transition temperature of the samples, the HT-1000 calorimeter was operated in the scanning mode at a heating rate of 3.3 mK s^{-1} for the samples enclosed in the platinum crucible.

3. Results and discussion

The results of the scanning mode of the calorimeter showed the endothermic step occurred at 1005 K (peak temperature) for $Na_2W_2O_7$ and 1059 K (peak temperature) for $Na_2W_4O_{13}$. The former corresponds to the congruent melting temperature of $Na_2W_2O_7$(s), which is in agreement with the value of 1004 K reported by Nolte and Kordes [2]. The latter corresponds to the incongruent melting temperature of $Na_2W_4O_{13}$(s), which is comparable to the value of 1057 K reported by Hoermann [3]. There is no phase transition below these temperatures for $Na_2W_2O_7$(s) and $Na_2W_4O_{13}$(s). Both temperatures are lower than the values reported by Chang and Sachdev [1].

The experimental enthalpy increments of the α-Al_2O_3 powder in this work are compared in Table 2 with NBS values [10]. The results showed the good precision and accuracy of the calorimetric determination.

The experimental enthalpy increments for $Na_2W_2O_7$(s) and $Na_2W_4O_{13}$(s) are given in Tables 3 and 4, respectively. We previously reported the experimental enthalpy increments of $Na_2W_2O_7$(s) in a letter [11]. The results in the letter which are different from the results of the present paper and are incorrect were obtained before temperature scales of the calorimeter were calibrated. The results (in the temperature range 273–979 K) listed in Tables 2–4 can be expressed by the following polynomial equations, respectively:

$$\Delta^{T}_{273.15\,\mathrm{K}} H^{0}_{\mathrm{m}}(\alpha\text{-Al}_2\text{O}_3) = -43,975 + 111.64T + 8.693 \times 10^{-3}T^2 + 3.525 \times 10^{6}T^{-1} \tag{2}$$

$$\Delta^{T}_{273.15\,\mathrm{K}} H^{0}_{\mathrm{m}}(\text{Na}_2\text{W}_2\text{O}_7) = -71,006 + 211.12T + 10.720 \times 10^{-2}T^2 + 2.566 \times 10^{6}T^{-1} \tag{3}$$

$$\Delta^{T}_{273.15\,\mathrm{K}} H^{0}_{\mathrm{m}}(\text{Na}_2\text{W}_4\text{O}_{13}) = -136,568 + 388.97T + 6.643 \times 10^{-2}T^2 + 6.950 \times 10^{6}T^{-1} \tag{4}$$

Table 2
Results of enthalpy increments for α-Al_2O_3 powder (M = 101.9613 g mol^{-1})

T (K)	$\Delta^{T}_{273.15\,\mathrm{K}} H^{0}_{\mathrm{m}}$ (J mol^{-1})		
	Experimental	Calculated	NBS value [10]
313.2	3148	3100	3113
342.1	5605 ± 42	5541	5567
381.2	9116 ± 34	9095	9111
421.5	13028 ± 24	12991	12988
462.1	17099 ± 12	17100	17082
502.6	21310 ± 37	21347	21320
543.1	25689 ± 36	25713	25687
583.6	30105 ± 64	30181	30161
624.3	34744 ± 71	34758	34750
664.6	39251 ± 80	39367	39371
705.2	44084 ± 39	44077	44094
745.4	48911 ± 61	48803	48831
786.0	53671 ± 37	53631	53667
826.7	58553 ± 291	58525	58564
877.7	64824 ± 252	64727	64761
928.1	70889 ± 135	70926	70946
978.8	77160 ± 209	77230	77224

Table 3
Results of enthalpy increments for $Na_2W_2O_7$(s) (M = 525.68 g mol^{-1})

T (K)	$\Delta^{T}_{273.15\,\mathrm{K}} H^{0}_{\mathrm{m}}$ (J mol^{-1})	
	Experimental	Calculated
273.15	0	
313.2	8452	8567
342.1	15099 ± 175	14992
381.2	24144 ± 53	23993
421.5	33729 ± 151	33591
462.1	43559 ± 105	43551
502.6	53742 ± 108	53748
543.1	64113 ± 265	64188
583.6	74839 ± 265	74856
624.3	85490 ± 268	85797
664.6	96518 ± 224	96840
705.2	108132 ± 337	108170
745.4	119833 ± 198	119587
786.0	131613 ± 81	131313
826.7	143280 ± 147	143264
877.7	158835 ± 301	158510
928.1	173641 ± 210	173870
978.8	189486 ± 673	189613

Table 4
Results of enthalpy increments for $Na_2W_4O_{13}$(s) ($M = 989.37$ g mol^{-1})

T (K)	$\Delta^{T}_{273.15\,K}H^0_m$ (J mol^{-1})	
	Experimental	Calculated
273.15	0	
313.2	13985	13957
342.1	24590 ± 260	24584
381.2	39599 ± 173	39590
421.5	55850 ± 229	55673
462.1	72573 ± 405	72400
502.6	89488 ± 114	89536
543.1	106967 ± 228	107071
583.6	124943 ± 344	124967
624.3	143131 ± 153	143287
664.6	161643 ± 420	161737
705.2	180234 ± 463	180621
745.4	199358 ± 317	199599
786.0	219497 ± 317	219039
826.7	239068 ± 911	238795
877.7	264334 ± 394	263918
928.1	289043 ± 486	289139
978.8	314587 ± 688	314895

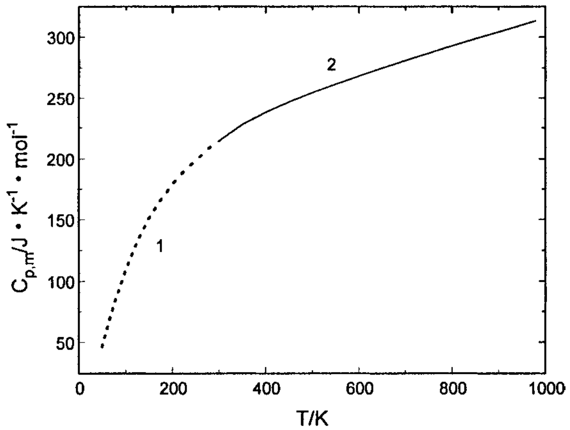

Fig. 1. The molar heat capacity of $Na_2W_2O_7$: (1) Weller and Kelley [12]; (2) present work.

Differentiation of Eqs. (2)–(4) yields the following expressions for the molar heat capacity of α-Al_2O_3, $Na_2W_2O_7$(s) and $Na_2W_4O_{13}$(s), respectively, in the interval 273–979 K:

$$C_{p,m}(\alpha\text{-}Al_2O_3) = 111.64 + 17.386 \times 10^{-3}T - 3.525 \times 10^{6}T^{-2} \qquad (5)$$

$$C_{p,m}(Na_2W_2O_7) = 211.12 + 10.720 \times 10^{-2}T - 2.566 \times 10^{6}T^{-2} \qquad (6)$$

$$C_{p,m}(Na_2W_4O_{13}) = 388.97 + 13.286 \times 10^{-2}T - 6.590 \times 10^{6}T^{-2} \qquad (7)$$

The values of C^0_p (298.15 K) for $Na_2W_2O_7$(s) and $Na_2W_4O_{13}$(s) are 214.2 and 350.4 J mol^{-1} K^{-1}, respectively. The former is in good agreement with the value of 214.9 J mol^{-1} K^{-1} reported by Weller and coworkers [8,12]. Eq. (4) is plotted in Fig. 1 together with the results of Weller and Kelley [12]. Our results smoothly join the low temperature measurements of Weller and Kelley [12] at 298.15 K.

Compared to those reported by Ditmars et al. [10], the deviations of the heat capacity for α-Al_2O_3 calculated using Eq. (5) are 6.73% at 273.15 K, −2.33% at 298.15 K, −1.24% at 313 K, and within 0.5% from 330 to 979 K. These results allow us to estimate that

Table 5
Thermodynamic properties of $Na_2W_2O_7$(s)

T (K)	$\Delta^{T}_{273.15\,K}H^0_m$ (J mol^{-1})	$C_{p,m}$ (J mol^{-1} K^{-1})	S^0_m (J mol^{-1} K^{-1})	$-\Delta_f H^0_m$ (kJ mol^{-1})	$-\Delta_f G^0_m$ (kJ mol^{-1})
298.15	0	214.2	254.4	2405.0	2216.8
300	396	214.8	255.7	2405.0	2215.2
400	23122	238.0	320.9	2408.9	2127.1
500	47775	254.5	375.9	2406.3	2088.4
600	73928	268.3	423.5	2402.5	2025.1
700	101397	280.9	465.9	2397.5	1962.6
800	130091	292.9	504.1	2391.5	1900.8
900	159958	304.4	539.3	2384.6	1839.9
1000	190969	315.8	572.0	2376.8	1779.9

the probable errors in heat capacity for $Na_2W_2O_7$(s) and $Na_2W_4O_{13}$(s) decreased from about 2.5% at 298.15 K to less than 0.5% at $T > 330$ K.

Eqs. (3) and (6) can be extrapolated to 1000 K because the melting temperature of $Na_2W_2O_7$(s) is higher than 1000 K. Combining the standard entropy [8] at 298.15 K, 254.4 J mol^{-1} K^{-1} and the standard enthalpy of formation [8] at 298.15 K, −2405.0 kJ mol^{-1} with Eqs. (3) and (6), the thermodynamic properties of $Na_2W_2O_7$(s) from 298.15 to 1000 K are obtained in Table 5. The thermodynamic properties of Na(s), O_2(g), and W(s) used in the calculations for Table 5 were taken from reference [13]. The thermodynamic properties of $Na_2W_4O_{13}$(s) can not be calculated because the standard entropy of $Na_2W_4O_{13}$(s) has not been determined.

It is interesting that the values of C_p^0 (298.15 K) for Na_2O(s) [13], Na_2WO_4(s) [13], $Na_2W_2O_7$(s) and $Na_2W_4O_{13}$(s) (68.6, 141.8, 214.2 and 350.6 J mol^{-1} K^{-1}, respectively) can be presented by a linear Eq. (8) with correlation coefficient 0.9996. The linear equation of the heat capacity also exists in the compounds $K_2W_nO_{3n+1}$ [9]:

$$C_{p,\mathrm{m}} = 70.6 + (70.3 \times n),$$
$$(n = 0, 1, 2, 4, \text{for}\, Na_2W_nO_{3n+1}(s)\, \text{at}\, 298.15\,K) \qquad (8)$$

Acknowledgements

The authors acknowledge the Ministry of Education of China for financial support (Doctorate Program Fund, 9553305).

References

[1] L.L.Y. Chang, S. Sachdev, J. Am. Ceram. Soc. 58 (1975) 267.
[2] G. Nolte, E. Kordes, Z. Anorg. Allgem. Chem. 371 (1969) 149.
[3] V.F. Hoermann, Z. Anorg. Allgem. Chem. 177 (1928) 145.
[4] K. Okada, H. Morikawa, F. Marumo, S. Iwai, Acta Crystallogr. B31 (1975) 1200.
[5] K. Viswanathan, J. Chem. Soc., Dalton Trans. (1974) 2170.
[6] W. Kondo, T. Manabe, T. Kumagai, T. Mizuta, J. Chem. Soc. Jpn. (1993) 1034.
[7] R.Y. Lin, J.F. Elliott, Metall. Trans. 14A (1983) 1713.
[8] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, R.L. Nuttall, NBS Technical Note 270-8, US Government Printing Office, Washington, 1981.
[9] Q. Chen, S. Liu, P. Zhang, J. Chem. Themodyn. 31 (1999) 513.
[10] P.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, J. Res. Nat. Bur. Stand. 87 (1982) 159.
[11] S. Liu, Q. Chen, P. Zhang, Chin. Chem. Lett. 9 (1998) 495.
[12] W.W. Weller, K.K. Kelley, US Bur. Mines Report No. 6191, 1963.
[13] O. Knacke, O. Kubaschewski, K. Hesselmann, Thermochemical Properties of Inorganic Substances, 2nd Edition, Springer, New York, 1991.