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Heat Capacity and Standard Thermodynamic Functions of the Wulfenite $PbMoO_4$ over the Temperature Range of (0 to 320) K

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ABSTRACT: The heat capacity of natural lead molybdate (wulfenite, $PbMoO_4$) has been measured by the method of vacuum adiabatic calorimetry over the temperature range of (4.3 to 80) K, and its thermodynamic functions in the range from (0 to 320) K have been calculated. The obtained standard values are as follows: $C_p^\circ(298.15) = (119.4 \pm 0.13)\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, $S^\circ(298.15) = (161.5 \pm 0.3)\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, and $\Delta H^\circ(298.15) = (23018 \pm 23)\ \mathrm{J \cdot mol^{-1}}$. The experimental data have been compared with the calculated values of the heat capacity obtained previously by different methods. The greatest correspondence of the thermodynamic functions has been obtained when employing the method of interatomic potentials using the computer program LADY.

INTRODUCTION

This study is a continuation of previously published work[1] devoted to determination of thermodynamic properties of natural lead molybdate (wulfenite, $PbMoO_4$). The previous experimental measurements of wulfenite heat capacity by the method of vacuum adiabatic calorimetry have been carried out over the temperature range of (55 to 320) K. The values of wulfenite heat capacity below 55 K have been extrapolated to absolute zero based on the data over the temperature range of (55 to 190) K and have also been calculated by semiempirical methods of quantum-chemical computation and the theory of crystal lattice dynamics. The following thermodynamic functions of wulfenite found on the basis of experimental measurements[2] over the temperature range of (51 to 298) K are known:[3,4] $C_p^\circ(298.15) = 119.7\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ and $S^\circ(298.15) = (166.10 \pm 2.09)\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$. The data on experimental measurements of the wulfenite heat capacity from the temperature of liquid helium to the temperature of liquid nitrogen are given in the present work as well as the revised values of thermodynamic functions of the mineral and comparison of the results of the calculation methods being used.

EXPERIMENTAL PART

A description of the natural wulfenite sample (the deposit Kyzyl-Espe, Kazakhstan) and measuring techniques is given in a previous article.[1] The identification of the sample has been carried out by the methods of X-ray phase analysis, IR spectroscopy, and electron probe microanalysis. The results of electron microprobe analysis are: PbO 59.53 %, MoO_3 37.99 %, WO_3 1.71 %, CaO 0.02 %, Cr_2O_3 0.05 %, CuO 0.03 %, V_2O_5 0.09 %. The tungsten oxide is included as isomorphic admixture in crystal structure of the mineral. The difference between real and ideal molar masses of the mineral is less than 0.13 % and comparable with the accuracy of the measurements. Therefore in the calculation of thermodynamic functions of the mineral the ideal molar mass of wulfenite was taken, and the correction coefficient was not used.

The sample heat capacity was measured in a low-temperature thermophysical unit produced by CJSC "Termis" (Moscow). The unit error while measuring a standard sample of the heat capacity of copper is not more than ± 1.44 % at 5 K, about ± 0.23 % at 40 K, and less than ± 0.11 % in the interval from (80 to 300) K. The weight of the wulfenite sample in a titanium container was 1.7307 g, and measurements of the heat capacity were carried out starting from the temperature of liquid helium of 4.2 K; the magnitude of a temperature stage was 0.3 K in the interval from (4 to 6) K, 0.5 K for the range (6 to 10) K, 1 K for (10 to 20) K, 2 K for (20 to 70) K, and 3 K for the range over 70 K.

The measurements resulted in 154 experimental points in five series (Table 1), the temperature range from (20 to 80) K being measured twice, and the temperature range from (4.2 to 20) K three times.

The experimental points relative scattering from the smoothed values for 95 % of the confidence interval did not exceed ± 2.85 % at (4.3 to 10) K, ± 1.10 % at (10 to 20) K, ± 0.60 % at (20 to 50) K, ± 0.45 % at (50 to 80) K, ± 0.20 % at (80 to 140) K, ± 0.38 % at (140 to 240) K, ± 0.46 % at (240 to 280) K, and ± 0.05 % at (280 to 325) K (Figure 1). The deviations of the experimental values from the smoothed ones at temperatures higher than 80 K were used while calculating uncertainties of the standard entropy and enthalpy.

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Table 1. Experimental Values of the Molar Heat Capacity of Wulfenite from $T = 4.3$ to 81.6 K ($M = 367.1376\ \mathrm{g\cdot mol^{-1}}$)

T	C_p
K	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$
Series 1	
4.339	0.05780
4.718	0.08003
5.112	0.09725
5.351	0.1176
5.573	0.1367
5.802	0.1452
6.030	0.1638
6.346	0.1949
6.757	0.2417
7.170	0.2997
7.595	0.3661
8.020	0.4553
8.448	0.5479
8.881	0.6583
9.317	0.7830
9.751	0.9322
10.18	1.090
10.85	1.388
11.74	1.823
12.64	2.325
13.55	2.902
14.47	3.594
15.41	4.302
16.35	5.029
17.30	5.868
18.25	6.768
19.20	7.706
20.16	8.622
21.61	10.10
23.56	12.09
Series 2	
4.370	0.06698
4.731	0.07860
5.100	0.09620
5.345	0.1174
5.580	0.1328
5.815	0.1505
6.056	0.1647
6.385	0.1969
6.807	0.2454
7.229	0.3078
7.657	0.3786
8.089	0.4660
8.524	0.5635
8.960	0.6785
9.398	0.8039
9.837	0.9549
10.50	1.231
11.39	1.637
12.28	2.113
13.19	2.652
14.10	3.283
15.03	4.010
15.96	4.756
16.91	5.517
17.86	6.417
18.81	7.341
19.77	8.250
21.21	9.721
23.15	11.65
25.13[a]	13.23
27.11	15.85
29.07	18.04
31.08	19.93
33.08	21.91
35.08	23.91
37.08	25.87
Series 3	
36.01	24.78
38.03	26.70
40.02	28.65
42.02	30.57
44.02	32.25
46.02	33.87
48.02	35.42
50.01	37.04
52.01	38.78
54.00	40.43
56.00	41.94
58.00	43.07
60.00	44.68
62.00	46.22
64.00	47.64
66.01	48.91
68.01	50.16
70.02	51.39
72.53	53.05
75.55	54.92
78.57	56.76
81.61	58.59
Series 4	
4.372	0.06993
4.730	0.07844
5.096	0.09543
5.342	0.1172
5.578	0.1326
5.817	0.1481
6.060	0.1669
6.396	0.1997
6.819	0.2486
7.249	0.3106
7.682	0.3831

Table 1. Continued

T	C_p
K	$J \cdot mol^{-1} \cdot K^{-1}$
8.117	0.4716
8.556	0.5709
8.996	0.6835
9.436	0.8195
9.878	0.9763
10.54	1.249
11.43	1.656
12.32	2.145
13.24	2.719
14.16	3.358
15.09	4.041
16.03	4.802
16.98	5.547
17.92	6.465
18.88	7.414
19.84	8.325
21.29	9.780
23.23	11.73
25.19	13.85
27.20[a]	14.89
29.18	18.01
31.13	20.06
33.13	21.97
35.13	23.92
37.12	25.86
39.11	27.82
Series 5	
21.23	9.727
23.09	11.60
25.07	13.69
27.05	15.81
29.05	17.91
31.04	20.01
33.06	21.92
35.07	23.90
37.07	25.82
39.07	27.82
41.07	29.64
43.06	31.42
45.06	33.11
47.05	34.70
49.05	36.30
51.05	37.96
53.04	39.73
55.03	41.32
57.03	42.55
59.03	43.86
61.03	45.45
63.03	46.95
65.03	48.30
67.04	49.59
69.04	50.78
71.55	52.48
74.56	54.33
77.59	56.17
80.63	58.02

[a] These points are not included into the data set for smoothing.

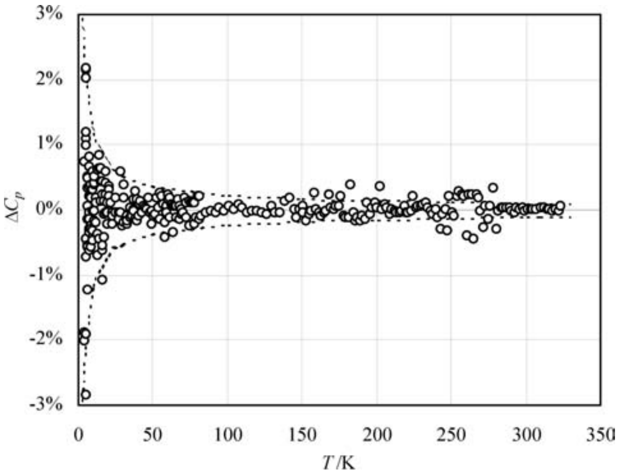

Figure 1. Percentage deviations of experimental values of wulfenite heat capacity from the fitting polynomials $\Delta C_p = (C_{p,\text{exp}} - C_{p,\text{fit}})/C_{p,\text{fit}}$. Dotted lines indicate the corridor of uncertainties including 95 % of the experimental data.

■ DISCUSSION OF THE RESULTS

Calculation of Thermodynamic Functions of Wulfenite. For a mathematical description of the temperature dependence of the wulfenite heat capacity we used a spline-approximation[5] of the experimental values by a third-power polynomial $C_p = a_0 + a_1T + a_2T^2 + a_3T^3$. A cubic spline is the simplest function, providing twice continuous differentiation of the heat capacity required for the determination of thermodynamic functions.[6] Below 5 K the heat capacity values were extrapolated in accordance with the Debye law $C_p/J \cdot mol^{-1} \cdot K^{-1} = a(T/K)^3$, where coefficient a was $7.564 \cdot 10^{-4}$ $J \cdot mol^{-1} \cdot K^{-4}$.

The polynomial coefficients were calculated from experimental data by using the least-squares method; the values of the correlation coefficient for each equation were not less than 0.995. The function value on the boundaries of the temperature range increased no more than 3 to 4 times. No fewer than 3 to 4 points overlapped the experimental points in the areas of the change of polynomials. The values of coefficients of the heat capacity polynomials in the corresponding temperature intervals are given in Table 2.

On the basis of the coefficients found for the heat capacity polynomials the tabulated values of wulfenite thermodynamic functions have been calculated. They are given in Table 3. Over 100 K the heat capacity values coincide with the values calculated previously, but they differ for the integral functions, enthalpy and entropy, which have been calculated based on the extrapolated values; therefore these values are given in the table for the whole interval.

Table 2. Heat Capacity Polynomial Quotients a_n for Wulfenite from T = (5 to 120) K at Different Temperature Ranges ΔT

experimental range, ΔT/K	smoothing range, ΔT/K	polynomial quotients $C_p = a_0 + a_1T + a_2T^2 + a_3T^3$			
		a_0	a_1	a_2	a_3
4.34 to 6.4	5 to 6	0.44623	−0.24665	$4.5022 \cdot 10^{-2}$	$-1.9594 \cdot 10^{-3}$
5.8 to 8.1	6 to 8	0.19726	$-2.5976 \cdot 10^{-2}$	$-8.0698 \cdot 10^{-3}$	$1.9035 \cdot 10^{-3}$
7.6 to 10.5	8 to 10	−2.8645	1.0313	−0.12866	$6.4372 \cdot 10^{-3}$
9.75 to 15.1	10 to 14	0.94040	−0.35189	$3.4087 \cdot 10^{-2}$	$1.9322 \cdot 10^{-4}$
13.2 to 21.3	14 to 20	3.9003	−1.0467	$8.8902 \cdot 10^{-2}$	$-1.2558 \cdot 10^{-3}$
19.2 to 31.13	20 to 30	1.8654	−0.64796	$6.5763 \cdot 10^{-2}$	$-8.4102 \cdot 10^{-4}$
27 to 42	30 to 40	−25.612	2.2082	$-3.2760 \cdot 10^{-2}$	$2.8651 \cdot 10^{-4}$
38 to 49	40 to 47	−94.065	6.4949	−0.11845	$8.1973 \cdot 10^{-4}$
44 to 56	47 to 55	169.26	−9.6451	0.21023	$-1.4036 \cdot 10^{-3}$
52 to 62	55 to 60	−733.71	39.572	−0.68302	$3.9946 \cdot 10^{-3}$
57 to 66	60 to 65	846.22	−40.8985	0.68238	$-3.7236 \cdot 10^{-3}$
64 to 72.5	65 to 70	8.4102	0.75862	$-4.4882 \cdot 10^{-3}$	$3.4601 \cdot 10^{-5}$
68 to 82.9	70 to 80	7.8453	0.45568	$4.5559 \cdot 10^{-3}$	$-3.1085 \cdot 10^{-5}$
78.4 to 126.2	80 to 120	−15.768	1.3008	$-5.6413 \cdot 10^{-3}$	$1.0416 \cdot 10^{-5}$

Table 3. Molar Thermodynamic Functions of Wulfenite from T = (5 to 320) K (M = 367.1376 g·mol^{-1})

T	$C_{p,m}$	$\Delta_0^T S_m^\circ$	$\Delta_0^T H_m^\circ/T$	Φ_m°
K	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}
5	0.0945	0.0315	0.0236	0.0079
10	1.020	0.289	0.2219	0.0668
15	3.964	1.193	0.9245	0.2689
20	8.481	2.925	2.225	0.6997
25	13.63	5.362	3.984	1.378
30	18.91	8.316	6.033	2.283
35	23.83	11.60	8.225	3.376
40	28.64	15.10	10.48	4.621
45	33.05	18.73	12.75	5.986
50	37.12	22.42	14.98	7.445
55	41.18	26.16	17.18	8.976
60	44.54	29.88	19.32	10.56
65	48.27	33.60	21.41	12.19
70	51.39	37.29	23.44	13.85
75	54.53	40.94	25.41	15.54
80	57.54	44.56	27.32	17.24
85	60.44	48.14	29.18	18.95
90	63.20	51.67	31.00	20.67
95	65.83	55.16	32.76	22.39
100	68.32	58.60	34.48	24.12
110	72.93	65.33	37.77	27.56
120	77.09	71.86	40.87	30.98
130	81.01	78.18	43.81	34.37
140	84.57	84.32	46.60	37.72
150	87.87	90.27	49.24	41.03
160	90.97	96.04	51.75	44.29
170	93.67	101.6	54.14	47.49
180	96.24	107.1	56.41	50.65
190	98.68	112.3	58.57	53.76
200	101.0	117.5	60.63	56.82
210	103.1	122.4	62.60	59.83
220	105.0	127.3	64.49	62.78
230	107.0	132.0	66.29	65.69
240	109.1	136.6	68.03	68.55
250	111.2	141.1	69.72	71.36
260	113.4	145.5	71.35	74.13
270	116.3	149.8	72.96	76.85
273.15	117.9	151.2	73.47	77.70
273.44	118.2	151.3	73.51	77.78
280	117.2	154.1	74.54	79.53
290	118.4	158.2	76.03	82.17
298.15	**119.4 ± 0.13**	**161.5 ± 0.3**	**77.20 ± 0.08**	**84.30 ± 0.22**
300	119.6	162.2	77.46	84.77
310	120.8	166.2	78.84	87.34
320	121.6	170.0	80.17	89.86

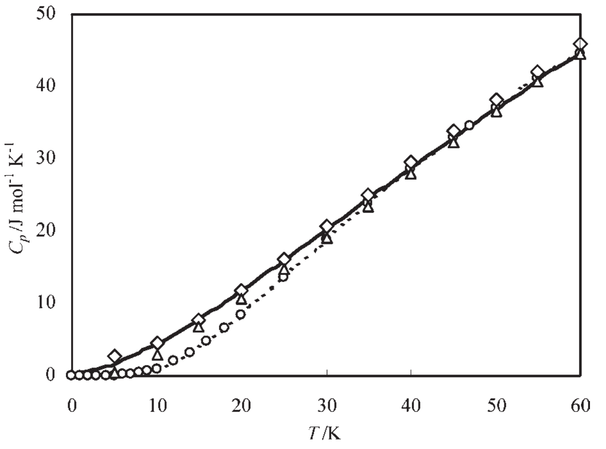

Figure 2. Experimental and calculated dependences of the heat capacity of wulfenite. ○ and dotted lines, fitted experimental data; solid curve, extrapolation data from previous work;[1] ◇, MNDO calculation; △, LADY calculation.

Table 4. Comparison of the Experimental and Calculated Standard Thermodynamic Functions of Wulfenite at T = 298.15 K

	$C_{p,\mathrm{m}}$	$\Delta_0^T S_\mathrm{m}^\circ$	$\Delta_0^T H_\mathrm{m}^\circ$	Φ_m°
	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
this work	**119.4 ± 0.13**	**161.5 ± 0.3**	**23018 ± 23**	**84.30 ± 0.22**
Bissengaliyeva et al.[1]	119.41 ± 0.13	168.33 ± 2.06	23095 ± 50	90.86 ± 1.31
Weller and Kelley[2]	119.70	166.11 ± 2.09		
MOPAC MNDO	114.7	168.8	23048	89.32
LADY IAP	118.8	165.4	23196	87.64

The uncertainties of thermodynamic functions for the measured substance were evaluated in the temperature range of (0 to 298.15) K by summing up the absolute values of relative uncertainties in the heat capacity measurement calculated for the corresponding temperature intervals (the pitch was not more than 5 K). The uncertainties evaluated by the equations describing the boundaries of the 95 % confidence interval were used for the calculation. The uncertainty value of the reduced Gibbs energy Φ has been calculated as the sum of relative uncertainties of entropy and enthalpy.

Comparison of the Experimental and Calculated Thermodynamic Functions of Wulfenite. The heat capacity values extrapolated to absolute zero according to the high-temperature component (constituent) of the heat capacity are overevaluated against the experimental values (Figure 2). It is connected with the fact that the coefficient of structural dimension of wulfenite determined by analogy with the isostructural compound $CaWO_4$ was assumed to be close to 2, although it is seen from the low-temperature measurements that this value equals 3. Thus, it is undesirable to determine the structural dimension of the compound even according to the isostructural compounds since the true dynamics of the lattice can significantly differ for these cases.

The heat capacity values calculated by the semiempirical method MNDO[7] are also somewhat overestimated in the area below 50 K in comparison with the experimental values. A more exact coincidence is shown by the values calculated in the program LADY[8] according to the method of interatomic potentials (IAP) by means of agreement of the experimental and calculated vibration spectra. The values of wulfenite thermodynamic functions obtained by the calculation methods and from the experimental data are compared in Table 4.

Among the calculated values of enthalpy $\Delta_0^T H_\mathrm{m}^\circ$, the value calculated by the MNDO method corresponds to the experiment most of all. The thermodynamic functions $\Delta_0^T S_\mathrm{m}^\circ$ and Φ_m° calculated by means of the vibration states by the method of IAP in program LADY are the closest to the experimental values. Thus, in this particular case the most preferable calculation method is the IAP method, allowing us to coordinate the experimental and calculation vibration states of crystalline substances with a reasonable degree of accuracy.

The value of entropy obtained in this work differs from the literature and calculated values published previously by up to 4.5 %. This is explained by the fact that more previous data on thermodynamic functions of wulfenite are based on one or another method of extrapolation of the heat capacity values to 0 K; in the calculation methods themselves there is also a number of approximations and suppositions effecting the fidelity of the result. The obtained experimental data on the low-temperature heat capacity of wulfenite are the most reliable information reflecting correctly the true character of changing of the inner energy of the substance with a rise in temperature.

CONCLUSION

On the basis of the low-temperature measurements of the wulfenite heat capacity by the method of adiabatic calorimetry the standard values of the mineral thermodynamic functions have been determined. Among the calculation methods being used, the calculation by means of the computer program LADY under the theory of crystal lattice dynamics turned out to be the most accurate.

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REFERENCES

(1) Bissengaliyeva, M. R.; Bespyatov, M. A.; Gogol, D. B. Experimental measurement and calculation of mole heat capacity and thermodynamic functions of wulfenite $PbMoO_4$. *J. Chem. Eng. Data* **2010**, *55* (9), 2974–2979.

(2) Weller, W. W.; Kelly, K. K. Low-temperature heat capacities and entropies at 298.15 K of lead molibdate and lead tungstates. *U.S. Bur. Mines Rept. Inv.* **1964**, no. 6357, 5.

(3) Naumov, G. B.; Ryzhenko, B. N.; Khodakovsky, I. L. *Reference book of thermodynamic values (for geologists)* (in Russian); Atomizdat: Moskva, 1971.

(4) Robie, R.; Hemingway, B. *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar (10^5 Pascals) Pressure and at Higher Temperatures*; U.S. Gov. Printing Office: Washington, DC, 1995.

(5) Iorish, V. S.; Tolmach, I. I. The technique and program of low-temperature heat capacity experimental data proceeding with using approximating spline. *Zh. Fiz. Khim.* **1986**, *60*, 2583–2587 (in Russian).

(6) Titov, V. A.; Chernyavskii, L. I.; Voronin, I. A.; Kornilov, A. N. On the spline approximation of low-temperature calorimetry data. *Russ. J. Phys. Chem.* **2006**, *80* (7), 1025–1028.

(7) http://www.fqs.pl/.

(8) Smirnov, M. B.; Kazimirov, V. Yu. *LADY: Software for Lattice Dynamics Simulations*; Communication of the Joint Institute for Nuclear Research: Dubna, 2001.