UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Thermodynamic Properties for Berlinite, $AlPO_4$

by

B. S. Hemingway[1], R. A. Robie[1], and K. M. Krupka[2]

Open-file Report 92-510

---

1. U. S. Geological Survey, Reston, VA 22092

2. Battel Pacific Northwest Laboratories, Richland, Washington 99352

Abstract

The heat capacities of berlinite, $AlPO_4$, have been measured by differential scanning calorimetry within the temperature interval of 330 to 1000 K. A λ-shaped heat-capacity anomaly was observed with a peak temperature of about 855.1 K corresponding to the α-β phase change in berlinite. The enthalpy of the phase change is 1694 ± 85 $J{\bullet}mol^{-1}$ based upon the equations for the heat capacity given below. The heat capacity of berlinite may be calculated from the following equations:

$$C_p = 1983.30 - 1.64948T + 7.72x10^{-4}T^2 - 2.93193x10^4T^{-0.5} + 2.0607013x10^7T^{-2}$$

$$C_p = 124.78 + 1.7677x10^{-2}T$$

The first equation is valid from 298.15 to 855.1 K and fits the data in the temperature interval of 298.15 to 810 K to ± 0.55 percent. The second equation is valid from 855.1 to 1000 K and fits the data in the temperature interval of 880 to 1000 K to ± 1.26 percent. Larger deviations occur in the region of the α-β transition, from 810 to 880 K.

The thermodynamic properties of berlinite are given at integral temperatures to 1000 K based upon an enthalpy of formation of -1716.0 ± 3.0 $kJ{\bullet}mol^{-1}$ with red phosphorus as the reference state and an entropy of 90.79 ± 0.42 $J{\bullet}mol^{-1}{\bullet}K^{-1}$, both at 298.15 K.

Introduction

Phosphorus is removed from domestic waste water by precipitation with Ca^{+2}, Fe^{+2}, Fe^{+3}, or Al^{+3} salts (Tomson and Vignona, 1984). Removal of phosphorus from industrial sources of waste may be more cost effective at the source and at superambient temperatures. The thermodynamic properties of berlinite, $AlPO_4$, must be known as a function of temperature to properly evaluate the role of Al^{+3} in these processes. The heat capacities of two samples of berlinite were measured by K. M. Krupka between 330 and 1000 K over a two year period in the middle 1970's. This report presents the results of that study and tabulates the thermodynamic properties of berlinite to 1000 K.

Samples

Two samples of berlinite were used in this study. Most of the measurements were made using a portion of a synthetic sample provided by Marlene Morris of the National Institute of Standards and Technology (NIST). The sample was a portion of sample 138 that had been prepared at 250 to 300° C in a bomb containing aluminum metal and λ-phosphoric acid. The sample was composed of clear angular grains of about 0.1 mm or smaller size and weighed 35.40 mg.

The second sample was obtained from the U.S. National Museum (USNM) and identified as synthetic #436, berlinite from W. T. Schaller. No details of the synthesis procedure were available. The crystal was water clear. A portion of the crystal was ground to about the grain size used for X-ray mounts and used as a powder for the heat capacity measurements. The sample weighed 33.68 mg.

Heat capacity measurements

Heat-capacity measurements of two samples of berlinite were made between 330 and 1000 K using a Perkin-Elmer DSC-2 differential scanning calorimeter (dsc). Unlike later dsc measurements reported from this laboratory, the results presented here were based upon manual data reduction of information collected on strip charts. Heat capacity measurements were made on two practical temperature scales during the course of this study. The results have been corrected to the practical temperature scale used in most of the studies reported from this laboratory and are listed in Table 1 and shown in Figure 1. See Hemingway et al. (1981) for details of the general experimental procedures.

Heat-capacity values obtained from measurements of the two berlinite samples were in excellent agreement. The values listed in Series 1 - 17 were made using the sample obtained from NIST. The Series 18 - 21 values were obtained using the USNM sample.

Berlinite is isostructural with quartz (as $SiSiO_4$) and exhibits a similar α-β phase change at superambient temperatures. Al and P are of similar ionic size to Si and therefore can crystalize in fourfold coordination with oxygen. The phase change is reflected in the heat capacity measurements as a λ-shaped peak in the heat capacities measured in the temperature interval of 810 to 880 K. The maximum in the observed heat-capacity measurements occurred at 855.1 K based upon an extrapolated onset temperature for quartz of 844 K (McAdie et al., 1972). The uncertainty of this practical temperature scale is of the order of ±2 K.

Values obtained in the Series 17 experiments were not in agreement with the other data on this phase. The measurements of this series were begun within the region of increasing heat capacity and the initial isothermal baseline did not reflect a reproducible equilibrium condition. Therefore, values calculated from this baseline were in error with respect to the magnitude of the heat capacities, with larger errors for the smaller heat-capacity values. These values were not used in calculations of the heat-capacity equations or of the enthalpy of the transition. The data do, however, provide a good check on the position of the heat-capacity peak.

The heat-capacity data for the temperature interval of 330 to 810 K were combined with the heat capacity of 93.18 $J \bullet mol^{-1} \bullet K^{-1}$ for 298.15 K reported by Egan and Wakefield (1960) and fit with an equation of the form suggested by Haas and Fisher (1976). Between 298.15 and 810 K, equation (1) fits the experimental data with an average deviation of ± 0.55 per cent.

$$C_p = 1983.30 - 1.64948T + 7.72\times10^{-4}T^2 - 2.93193\times10^4T^{-0.5} + 2.0607013\times10^7T^{-2} \qquad (1)$$

Heat-capacity data for the temperature interval 880 to 1000 K were fit with equation (2). The data were fit with an average deviation of ± 1.26 per cent.

$$C_p = 124.78 + 1.7677\times10^{-2}T \qquad (2)$$

Values of the thermodynamic properties of berlinite are given at integral temperatures to 1000 K in Table 2.

Enthalpy of the α-β transition

The enthalpy of the α-β phase change in berlinite was calculated from an integration of the differences between the observed heat capacities and equations (1) and (2) in the temperature interval of 810 to 880 K. Equations (1) and (2) were used to and from 855.1 K, respectively. The calculated value was 1694 ± 85 $J \bullet mol^{-1}$.

Enthalpy of formation

The enthalpy of formation of berlinite can be calculated from the study of Juza et al. (1958). Berlinite, aluminum metal, and H_3PO_4 in 1.03 mol H_2O were dissolved in 10 percent HF. The authors report -458.6 $kJ \bullet mol^{-1}$ for the reaction

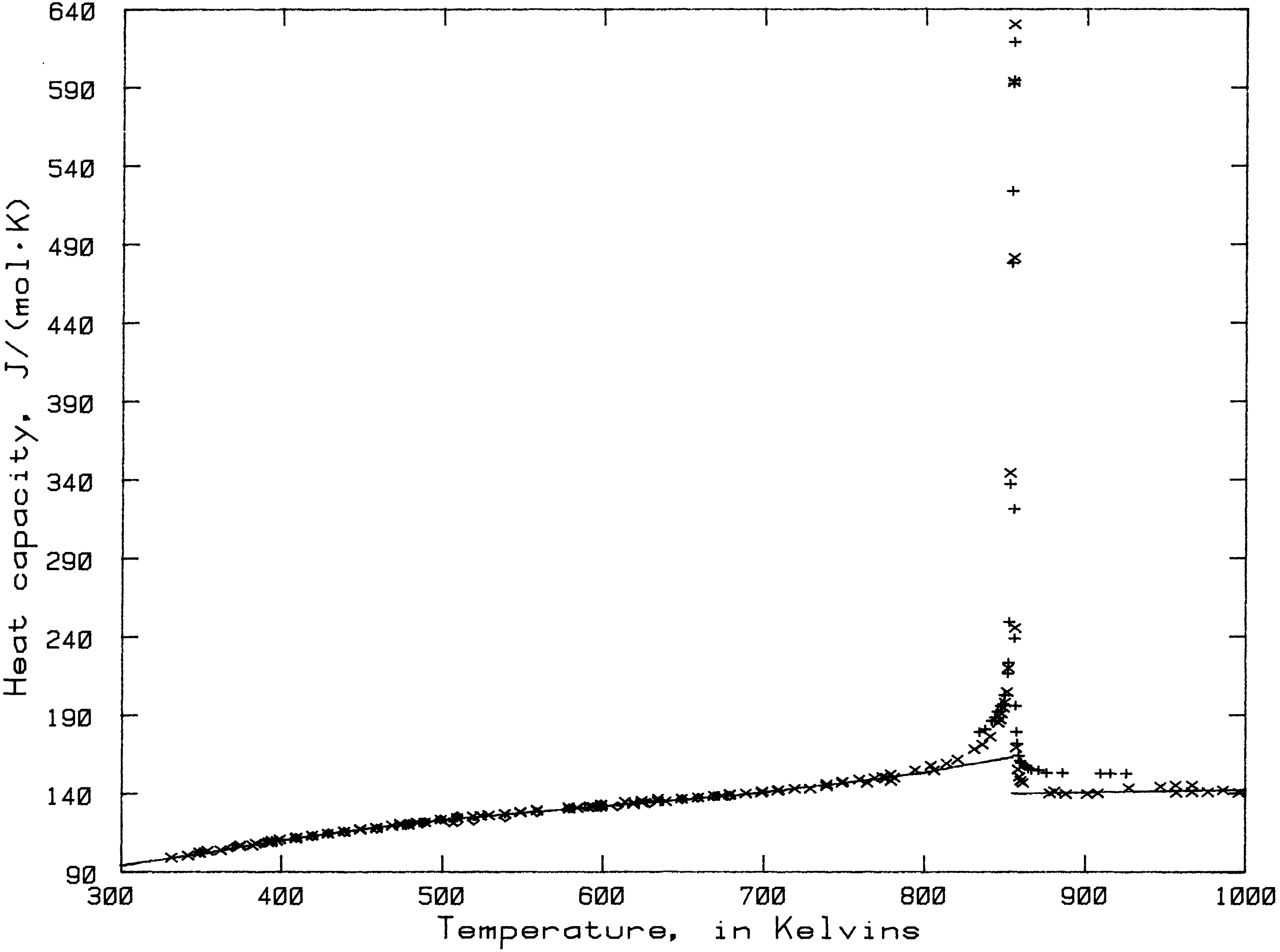
$$Al + H_3PO_4(\text{in } 1.03 \text{ mole } H_2O) = AlPO_4 + 1.5H_2.$$

The enthalpy of formation of H_3PO_4 in 1.0 mole H_2O is -1274.82 $kJ \bullet mol^{-1}$ (Wagman et al, 1982) with white phosphorus as the reference state. The correction to the enthalpy of formation in 1.03 mole H_2O is -0.14 kJ. The enthalpy of formation of berlinite is then -1733.6 ± 3.0 $kJ \bullet mol^{-1}$. For red phosphorus as the reference state, the enthalpy of formation is -1716.0 ± 3.0 $kJ \bullet mol^{-1}$. Values of the enthalpy of formation based upon a red phosphorus reference state are given at integral temperatures to 1000 K in Table 2. Ancillary data are taken from Robie et al. (1979).

Gibbs energy of formation

The Gibbs energy of formation of berlinite may be calculated from the enthalpy of formation and heat-capacity equations given above, and the entropy of berlinite at 298.15 K as given by Egan and Wakefield (1960) of 90.79 ± 0.42 $J \bullet mol^{-1} \bullet K^{-1}$. At 298.15 K, the Gibbs energy is -1605.47 ± 3.0 $kJ \bullet mol^{-1}$. Values of the Gibbs energy of formation are given at integral temperatures to 1000 K in Table 2.

Figure 1. Experimental heat capacities for berlinite. Data obtained in the Series 17 experiments are shown with the + symbol and were not used in the calculations. The solid curves were derived from equations (1) and (2). The diamond symbol represents data obtained from the USNM sample. The x symbol represents data obtained from the NIST sample.



Berlinite, Figure 1

88, 88, 88, 88, 88

References

Egan, E. P. and Wakefield, Z. T. (1960) Low temperature heat capacity and entropy of berlinite. Jour. Phys. Chem., 64, 1953-1955.

Haas, J. L., Jr. and Fisher, J. R. (1976) Simultaneous evaluation and correlation of thermodynamic data. Amer. Jour. Sci., 276, 525-545.

Hemingway, B. S., Krupka, K. M., and Robie, R. A. (1981) Heat capacities of the alkali feldspars between 350 and 1000 K from differential scanning calorimetry, the thermodynamic functions of the alkali feldspars from 298.15 to 1400 K, and the reaction quartz + jadeite = analbite. Amer. Mineral., 66, 1202-1215.

Juza, R., Wainoff, G., and Uphoff, W. (1958) Bildungsenthalpie von Aluminiumphosphat. Z. anorg. Chem., 296, 157-163.

McAdie, H. G., Garn, P. D., and Menis, O. (1972) Selection of differential thermal analysis temperature standards through a cooperative study [SRM 758, 759, 760]. U. S. Nat. Bur. Stds. Spec. Publ. 260-40.

Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1979) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (15^5 Pascals) pressure and at higher temperatures. U. S. Geol. Surv. Bull. 1452.

Tomson, M. B. and Vignona, L. (1984) Phosphorus in the environment. in Phosphate Minerals. eds. Nriagu, J. O. and Moore, P. B., Springer-Verlag, New York, 386-399.

Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., and Nuttall, R. L. (1982) The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C_1 and C_2 organic substances in SI units. Jour. Phys. Chem. Ref. Data, 11, Supl. 2.

Table 1. Experimental heat capacities for berlinite.

Temp. K	Heat capacity J•mol^{-1}•K^{-1}	Temp. K	Heat capacity J•mol^{-1}K^{-1}	Temp. K	Heat capacity J•mol^{-1}•K^{-1}
Series	1	Series	7	Series	16
332.5	98.92	861.8	146.6	957.4	140.0
342.5	100.4	881.8	141.1	967.2	140.5
362.6	103.8	901.8	139.2	977.0	140.5
382.6	106.8			986.8	141.9
392.6	108.7	Series	8	996.5	140.3
397.6	109.7				
		349.8	102.0	Series	17
Series	2	354.7	103.1		
		374.7	106.8	834.5	178.7
374.6	106.2	394.7	109.6	838.5	180.7
384.6	107.9	409.6	111.6	842.5	186.0
394.6	108.9			844.5	188.1
409.6	111.3	Series	9	846.4	191.7
429.6	114.3			848.4	195.7
449.6	116.8	399.5	110.4	850.3	202.2
469.6	119.4	409.5	111.4	852.3	216.3
		419.5	112.9	852.8	222.9
Series	3	439.5	115.6	853.3	249.0
		459.5	117.6	853.8	337.0
439.6	115.4	479.5	119.6	854.3	477.8
449.6	117.1	484.5	120.5	854.6	523.5
459.6	118.1			854.8	591.7
474.6	119.7	Series	10	855.1	618.4
489.7	121.3			855.2	594.2
509.7	124.4	474.5	120.6	856.2	320.9
529.7	126.1	484.5	121.4	856.7	238.7
		499.5	123.1	857.2	195.7
Series	4	519.5	124.9	857.7	178.7
		539.5	126.9	858.2	171.1
524.7	125.6	549.5	128.1	859.2	163.7
529.7	126.1	559.5	129.2	860.2	160.4
539.7	126.8			861.1	159.0
559.7	129.1	Series	11	863.1	157.4
579.8	130.3			865.1	155.8
599.8	132.5	549.5	127.8	867.0	155.1
619.8	134.1	559.5	128.9	871.9	154.3
		579.5	131.0	876.8	152.7
Series	5	599.5	132.8	886.6	152.8
		614.5	134.4	910.2	152.5
584.6	130.5	624.5	135.1	916.1	152.4
594.6	131.5	634.5	136.4	925.9	152.2
599.6	131.2				

Table 1. Continued.

Temp. K	Heat capacity J•mol^{-1}•K^{-1}	Temp. K	Heat capacity J•mol^{-1}K^{-1}	Temp. K	Heat capacity J•mol^{-1}•K^{-1}
Series	5	Series	12	Series	18
619.6	133.1	624.5	134.1	350.1	102.0
639.6	134.7	634.5	134.9	370.0	105.4
659.6	137.4	649.5	136.6	390.0	108.1
679.6	139.2	669.5	138.0	409.9	111.1
		689.4	139.8	419.9	112.6
Series	6	699.4	140.4	429.9	114.2
		709.4	141.9		
674.6	138.0			Series	19
679.6	139.1	Series	13		
699.7	141.0			419.9	112.6
719.7	142.8	699.2	140.8	439.9	114.9
739.7	144.5	709.2	141.4	459.8	117.0
764.7	146.6	729.2	142.9	479.8	119.9
779.7	147.8	749.2	146.6	489.8	121.3
		769.2	149.4	499.7	122.8
Series	7	774.2	150.1	509.7	125.0
776.7	149.9	Series	14	Series	20
781.7	150.0				
806.7	154.7	739.6	145.6	504.9	121.3
821.7	161.2	749.6	147.3	509.9	121.2
831.7	167.8	759.6	148.6	519.9	122.1
836.7	170.8	779.6	151.9	539.8	124.3
841.7	176.0	794.6	154.7	559.8	127.4
846.8	184.7	804.6	157.5	579.8	130.2
847.8	186.9	814.6	158.8	589.8	131.4
848.8	190.5			599.7	132.6
849.8	194.6	Series	15		
850.8	197.8			Series	21
851.8	204.3	878.8	139.9		
852.8	219.6	888.6	139.4	594.8	130.8
853.8	344.1	908.3	139.8	599.7	130.8
854.8	593.2	927.9	143.1	609.7	131.5
855.2	629.9	947.5	143.8	629.7	133.3
855.8	480.9	957.1	144.7	649.7	135.8
856.8	245.4	967.1	145.0	659.6	136.7
857.8	168.7			669.6	137.7
858.8	155.1			679.6	138.3
859.8	150.5				
860.8	147.9				

Note: Series 1 - 17 NIST sample, no. 138; Series 18 - 21 USNM sample, no. 436.

Table 2. Thermodynamic properties for berlinite.

Temp.	Heat capacity	Entropy	Enthalpy function (a)	Gibbs energy function (b)	Enthalpy of formation	Gibbs energy of formation
K	$J \bullet mol^{-1} \bullet K^{-1}$				$kJ \bullet mol^{-1}$	
298.15	93.96 ±0.20	90.79 ±0.42	0.000	90.790	-1716.00 ±3.00	-1605.47 ±3.00
400	109.9	120.52	25.862	94.658	-1716.52	-1567.60
500	122.8	146.52	44.045	102.48	-1715.98	-1530.43
600	131.8	169.74	57.950	111.79	-1714.81	-1493.41
700	140.8	190.71	69.125	121.59	-1713.20	-1439.04
800	153.4	210.28	78.822	131.46	-1796.41	-1442.31
900	140.7	229.96	88.618	141.35	-1791.51	-1398.34
1000	142.5	244.88	93.916	150.96	-1800.10	-1353.99

a. $(H^{\circ}_{T} - H^{\circ}_{298})/T$

b. $-(G^{\circ}_{T} - H^{\circ}_{298})/T$

Note: Dashed line indicates transition in berlinite.