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HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF ZINC METAARSENATE IN THE RANGE 298.15–673 K

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The isobaric heat capacity of $Zn(AsO_3)_2$ *is measured by a calorimetric method in the range 298.15–673 K. From the data obtained the temperature dependences of the functions* $C_p^o(T)$, $S^o(T)$, $H^o(T) - H^o(298.15)$, *and* $\Phi^{**}(T)$ *are calculated.*

In metallurgical processes arsenic is trapped and removed from a technological cycle in the form of almost insoluble arsenates of transition metals. In the process of their utilization, it is often ignored that many of the arsenates of transition metals exhibit valuable physical properties in common with semiconductors, ferroelectrics, etc. A physicochemical modeling of technological processes with the participation of arsenic compounds and a directed synthesis of arsenates are impossible without knowledge of their thermodynamic properties. Moreover, the collected new thermodynamic constants can be used as the initial files of information for a data base of physicochemical constants.

The aim of the present work is to study the heat capacity of a typical representative of arsenates of transition metals, i.e., zinc metaarsenate $Zn(AsO_3)_2$. Zinc metaarsenate is synthesized by solid-phase interaction of ZnO and As_2O_5 in the range 450–500°C for more than 400 h. The initial zinc oxide was the analytical-grade ZnO, whereas As_2O_5 was obtained by oxidizing As_2O_3 with hydrogen peroxide followed by dehydration and calcination. The purity of the arsenic oxide (*V*) obtained was confirmed by x-ray phase analysis [1]. The formation of the equilibrium composition of $Zn(AsO_3)_2$ was also controlled by the *x*-ray analysis method. We used the homology technique [2] to identify the powder of $Zn(AsO_3)_2$ in orthorhombic symmetry with the following lattice constants: $a = 0.8625$ nm, $b = 0.9035$ nm, $c = 1.2494$ nm, $V = 0.933$ nm^3, $Z = 8$; $\rho_{\text{pycnomet}} = 4.21 \pm 0.2$ g/cm^3; $\rho_{\text{x-ray}} = 4.43$ g/cm^3.

We investigated the isobaric heat capacity in the range from 298.15 to 673 K using a commercial IT-S-400 calorimeter designed for determining the temperature dependence of the specific heat of solids and loose and fibrous materials. Measurements over the entire temperature range with the processing of experimental data did not last more than 2.5 h. The processing of experimental data included the determination of the thermal conductivity of a heat flow meter K_T, the lag time of the latter in the experiments with the compound studied τ_T, sec, and its lag time in the experiments with an empty ampoule τ_T^0, sec. The specific heat of arsenate was determined by the formula

$$C_p = \frac{K_T}{m_0} (\tau_T - \tau_T^0) , \tag{1}$$

where m_0 is the mass of the arsenate, g. The mean value of the time lag at each temperature on the heat flow meter was determined as the arithmetic mean of five parallel experiments. The lag in the time of heating a sample to the required temperature was determined with a stopwatch. The certified limiting acceptable error of the device is ± 10.0%. We estimated the errors of parallel experiments in the following manner. At each temperature we determined the standard deviation $\bar{\delta}$ for the averaged values of specific heats and calculated the random component error $\overset{o}{\Delta}$, %, for the averaged values of mole heat capacities by the formula

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TABLE 1. Experimental Values of the Heat Capacity of Zinc Metaarsenate ($C_p^0 \pm \overset{\circ}{\Delta}$, J/(mole·K)).

T, K	$\bar{\tau}_T^0$	$\bar{\tau}_T$	$C_p^0 \pm \overset{\circ}{\Delta}$ (exp)	C_p^0 (cal)
298.15	13.37	15.01	227 ± 18	226 ± 13
323	14.30	16.96	231 ± 14	232 ± 13
348	14.0	16.70	237 ± 20	236 ± 13
373	13.57	16.30	239 ± 19	239 ± 14
398	13.13	15.86	242 ± 14	242 ± 14
423	12.87	15.63	245 ± 21	244 ± 14
448	12.47	15.22	247 ± 12	247 ± 14
473	12.03	14.80	248 ± 16	248 ± 14
498	11.73	14.51	250 ± 14	250 ± 14
523	11.57	14.34	252 ± 16	251 ± 14
548	11.49	14.17	253 ± 8	253 ± 14
573	11.23	13.97	254 ± 11	254 ± 14
598	10.90	13.65	255 ± 13	255 ± 15
623	10.73	13.44	256 ± 11	256 ± 15
648	10.60	13.31	256 ± 4	257 ± 15
673	10.53	13.20	257 ± 10	257 ± 15

$$\overset{\circ}{\Delta} = \frac{\bar{\delta} t_p}{\bar{C}} \cdot 100\,, \tag{2}$$

where t_p is the Student coefficient. The systematic component error Δ_{com} and errors in the measurement of temperature were not included in calculation, since in our case they were negligibly small as compared with $\overset{\circ}{\Delta}$. According to the theory of errors, if $\overset{\circ}{\Delta} \gg [\Delta_{\text{com}} + \Delta_{\text{scale of dev}}]$, then the accuracy of measurements will be determined by the random error [3]. Table 1 presents the results of calorimetric investigations (for convenience $\overset{\circ}{\Delta}$ is expressed in joules).

On the basis of the experimental data, it is established that the temperature dependence of C_p^0 for $Zn(AsO_3)_2$ in the range from 298.15 to 673 K is described by the equation

$$C_p^0 = (256 \pm 15) + (11.7 \pm 0.7)\cdot 10^{-3}\,T - (29.50 \pm 0.17)\cdot 10^5\,T^{-2}\,,\ \ \text{J/(mole·K)}\,. \tag{3}$$

To determine the errors of the coefficients in Eq. (3), we used the mean random error component, equal to 5.7%, for the entire temperature range under consideration.

In view of the fact that the specifications of the device do not provide for determining the standard entropy directly from experimental data, we estimated it by means of reliable computational methods. The system of Kumok's thermochemical increments on entropy [4] appeared to be the most precise for a given case. The value of $S^0(298.15)$ calculated for $Zn(AsO_3)_2$ according to Kumok is equal to 177 ± 4 J/(mole·K). The error of $S^0(298.15)$ for arsenate was determined from the errors of the entropy increments of ions entering into its composition.

The temperature dependences of the thermodynamic functions were calculated using the following relations:

$$H^0(T) - H^0(298.15) = \int_{298.15}^{T} C_p dT\,, \tag{4}$$

TABLE 2. Thermodynamic Functions of Zinc Metaarsenate

T, K	$S^0(T)$	$H^0(T) - H^0(298.15)$	$\Phi^{**}(T)$
298.15	177 ± 4	–	177 ± 4
300	179 ± 14	500 ± 30	177 ± 14
325	202 ± 16	6800 ± 400	181 ± 14
350	222 ± 18	13100 ± 750	185 ± 15
375	241 ± 19	19400 ± 1100	189 ± 15
400	259 ± 21	25700± 1450	195 ± 16
425	275 ± 22	32000 ± 1800	200 ± 16
450	290 ± 23	38200 ± 2200	205 ± 16
475	304 ± 24	44500 ± 2550	210 ± 17
500	318 ± 25	50800 ± 2900	216 ± 17
525	331 ± 26	57000 ± 3250	222 ± 18
550	343 ± 27	63300 ± 3600	228 ± 18
575	354 ± 28	69500 ± 3950	233 ± 19
600	365 ± 29	75800 ± 4300	239 ± 19
625	376 ± 30	81500 ± 4650	246 ± 20
650	386 ± 31	88200 ± 5050	250 ± 20
675	395 ± 32	94400 ± 5400	255 ± 20

$$S^0(T) - S^0(298.15) + \int_T^{298.15} \frac{C_p}{T} dT, \tag{5}$$

$$\Phi^{**}(T) = S^0(T) - \frac{H^0(T) - H^0(298.15)}{T}. \tag{6}$$

The values of these functions are given in Table 2.

The errors of the temperature dependence of enthalpy are estimated with the mean random error component of the heat capacity (5.7%), whereas the errors of the temperature dependence of $S^0(T)$ and Φ^{**} are calculated by summing the mean error of the experimental determination of the heat capacity (5.7%) and the accuracy of the calculation of the entropy (2.3%). The results of the calculations are approximated within the limits of the calculation accuracy.

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