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ENTHALPY INCREMENTS OF SILVER FROM 560 TO 900 K

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ABSTRACT

The enthalpy increments of metallic silver have been measured from 560 to 900 K in a diphenyl ether calorimeter. The results can be represented within 0.5% by the equation

$$\{H^{\ominus}(T) - H^{\ominus}(298.15\ \mathrm{K})\}(\mathrm{J\ mol^{-1}}) = 23.2625T + 3.3164\times10^{-3}T^{2} - 7230.5$$

INTRODUCTION

The thermochemical properties of silver seem to have been reasonably well established. The heat capacity values below room temperature were thoroughly assessed by Furukawa et al. [1] in 1968 and their recommenda-

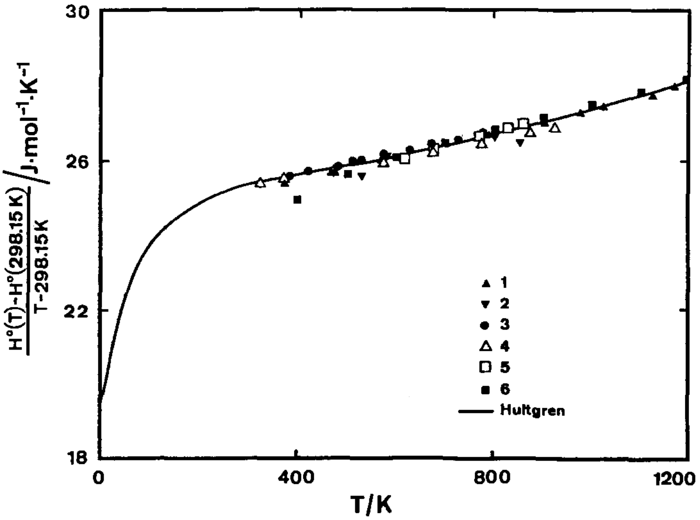

Fig. 1. Reduced enthalpy increment function of silver as recommended by Hultgren et al., also showing some important literature sources supporting the selection: 1, Jaeger et al. [9]; 2, Wittig and Böhm [12]; 3, Bronson et al. [13]; 4, Moser [14]; 5, Weiss et al. [15]; 6, Eastman et al. [16].

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tions for C_p(298.15 K), $S^\ominus$(298.15 K), and $[H^\ominus(298.15\ \mathrm{K}) - H^\ominus(0\ \mathrm{K})]$ have been accepted by the CODATA Key Values Task Group [2]. Recently, Martin [3] re-measured the low-temperature heat capacities of silver, obtaining values which differ only marginally from those selected by Furukawa.

Above room temperature, there is a large number of reported enthalpy increment measurements, the first by Kopp [4] and Bunsen [5] dating from around 1870. The most recent assessment by Hultgren et al. [6] in 1968 covers 14 different data sets for solid Ag, most of which are in reasonably good agreement with the selected values, as is shown in Fig. 1, where the most important ones are plotted along with Hultgren's function. The connection with the low-temperature data, however, is not entirely satisfactory. For this reason we present here the results of enthalpy increment measurements on a very pure sample of silver by drop calorimetry.

EXPERIMENTAL DETAILS

The silver metal was manufactured by Johnson Matthey. The purity of the material was specified to be 99.99 mol%, the total of the metal impurities being 10 ppm.

The enthalpy increments were measured in an isothermal diphenyl ether drop calorimeter as described by Cordfunke et al. [7], which is a modern version of Bunsen's ice calorimeter. Briefly, the spherical sample, which had a weight of 8.84267 g, was heated in a furnace whose temperature was measured to ±0.1 K with a calibrated Pt–(Pt + 10 mass% Rh) thermocouple. After thermal equilibration, the sample was dropped into the calorimeter, where the energy of the sample now melted solid diphenyl ether in equilibrium with its liquid in a closed system. The resulting volume increase of the ether was measured by weighing the displaced mercury. The ratio of heat input to mass of mercury making up the volume increase is a constant for the apparatus, and is obtained by calibration with NIST standard reference material synthetic sapphire (No. 720).

The measurements were corrected to account for the difference in enthalpy between the final calorimeter temperature, 300.06 K, and the standard reference temperature, 298.15 K, using the C_p(298.15 K) value given by Martin [3]. The molar mass of silver was taken as 107.868 g.

RESULTS AND DISCUSSION

The results of the 25 drop experiments, as listed in Table 1, have been fitted to the polynomial

$$\{H^\ominus(T) - H^\ominus(298.15\ K)\}(\mathrm{J\ mol^{-1}}) = 23.2625T + 3.3164 \times 10^{-3}T^2 - 7230.5$$

TABLE 1

Experimental enthalpy increments of silver

T (K)	$H^{\ominus}(T)-H^{\ominus}$(298.15 K)(J mol^{-1})		Deviation (%)
	Exp.	Calc.	
558.4	6806	6793	0.19
576.5	7277	7283	−0.08
577.7	7334	7315	0.26
582.9	7451	7456	−0.07
607.8	8096	8134	−0.46
608.1	8127	8142	−0.18
638.1	8947	8964	−0.19
658.5	9501	9526	−0.26
678.3	10115	10074	0.40
688.7	10362	10363	−0.01
704.1	10783	10793	−0.09
704.3	10813	10798	0.14
718.0	11212	11182	0.27
739.0	11760	11772	−0.10
758.8	12357	12331	0.21
767.6	12577	12580	−0.02
773.8	12768	12756	0.10
798.4	13489	13456	0.24
819.2	14049	14052	−0.02
831.2	14354	14397	−0.30
839.7	14643	14641	0.01
859.8	15223	15222	0.01
880.2	15771	15814	−0.28
880.2	15836	15814	0.14
900.9	16449	16418	0.19

As boundary conditions, $[H^{\ominus}(T)-H^{\ominus}(298.15\text{ K})]=0$ at 298.15 K and $C_p(298.15\text{ K})=25.24$ J mol^{-1} K^{-1} [3] were applied. This equation represents the experimental data to within 0.5%.

Table 2 gives smoothed thermodynamic functions of silver from 0 to 1000 K, based on Martin's low-temperature results and the present data above 298.15 K. The value $S^{\ominus}(20\text{ K})=0.530$ J mol^{-1} K^{-1} has been taken from Furukawa et al. [1].

The data are represented graphically in Fig. 2 in a plot of $[H^{\ominus}(T)-H^{\ominus}(298.15\text{ K})]/(T-298.15)$ versus T, together with the smoothed results of Martin [3], which have been calculated by the present authors from the polynomial coefficients given by Martin. The data from the assessment by Hultgren et al. are also shown. Our data fit excellently the low-temperature data of Martin in the 298.15 K region, but are significantly higher (ca. 1–2%) than Hultgren's recommendations.

A closer examination of the literature sources on which Hultgren's selections for the high-temperature heat capacity of silver are based does not

TABLE 2

Molar thermodynamic properties of silver

T (K)	C_p (J mol^{-1} K^{-1})	$S^{\ominus}$ (J mol^{-1} K^{-1})	FEF [a] (J mol^{-1} K^{-1})	$H^{\ominus}(T)-H^{\ominus}(298.15\ \mathrm{K})$ (J mol^{-1})
0	0.000	0.000	∞	−5734
20	1.650	0.530	286.830	−5726
40	8.355	3.615	144.340	−5629
60	14.200	8.189	98.189	−5400
80	16.258	12.819	76.269	−5076
100	20.120	17.067	64.017	−4695
150	22.896	25.840	49.893	−3608
200	24.112	32.613	44.758	−2429
250	24.802	38.074	42.894	−1205
298.15	25.240	42.480	42.480	0
300	25.252	42.636	42.480	47
400	25.916	49.992	43.479	2605
500	26.579	55.846	45.386	5230
600	27.242	60.750	47.549	7921
700	27.905	65.000	49.745	10678
800	28.569	68.769	51.892	13502
900	29.232	72.172	53.959	16392
1000	30.895	75.287	55.938	19348

[a] FEF $= -[G^{\ominus}(T)-H^{\ominus}(298.15\ \mathrm{K})]/T$

reveal a clear explanation for the difference between the present results and the older data. Some variation may arise from differences in sample purity, but quantitative indications are generally lacking.

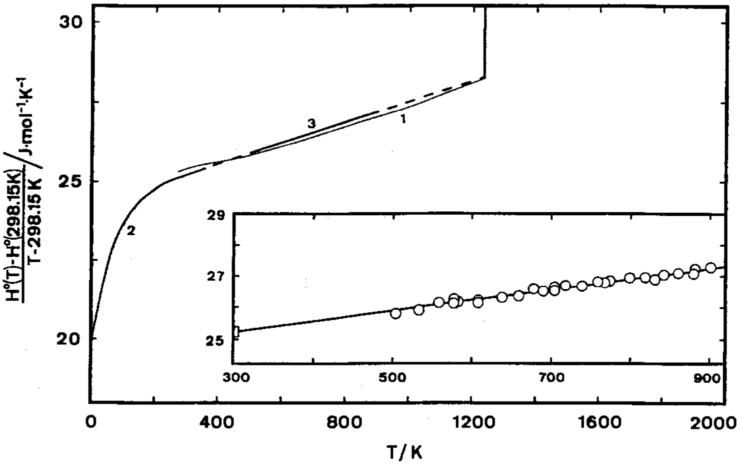

Fig. 2. Experimental enthalpy increment data: 1, Martin [3]; 2, Hultgren et al. [6]; 3, present results. Insert experimental data points of this study.

Takahashi and Akiyama [8], who recently measured the heat capacity of gold, also found a good agreement with previous low-temperature data but a deviation of 1–2% compared with Hultgren's assessment [6]. For both Ag and Au, Hultgren's data are very close to the experimental values of Jaeger and coworkers [9,10]. However, in a recent investigation of the enthalpy increments of Ru and Pd at our institute [11], we found significant deviations from the results of Jaeger and coworkers. The present results show once more that new experimental determination/verification of heat capacity data of transition metals seems desirable in order to establish the thermodynamic properties with the precision presently needed.

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