Platinum—A Thermal Expansion Reference Material[1]

R. K. Kirby[2]

Platinum has a face-centered cubic crystal structure and does not have any phase changes between absolute zero and its melting point at 2045 K. High-purity platinum can be readily obtained in rod and sheet form and thus provides an excellent thermal expansion standard. Five investigations that used accurate and precise experimental techniques were used to establish analytical expressions for the coefficients of thermal expansion from 0 to 1800 K.

1. INTRODUCTION

Because platinum is very expensive, the Office of Standard Reference Materials (OSRM) of the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS), never seriously considered purchasing a supply of it for certification as a Standard Reference Material (SRM) for thermal expansion. Platinum, however, has been recommended for use as a reference material for thermal expansion in several "Standard Test Methods" promulgated by the American Society for Testing and Materials (ASTM) and by standards organizations in other countries. ASTM Test Method E228 recommends pure platinum and aluminum as well as SRM 731 (borosilicate glass), SRM 737 (tungsten), SRM 738 (stainless steel), and SRM 739 (vitreous silica) for calibrating dilatometers.

In a recent publication [1] by the CODATA Task Group on the Thermophysical Properties of Solids, values are recommended for the thermal expansion of copper, silicon, tungsten, and Al_2O_3. While these

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materials and the recommended values are very useful for calibration or verification of dilatometers, it is felt that the historical importance of platinum as a reference material for thermal expansion necessitates the same treatment for it.

Previously recommended values for the thermal expansion of platinum were published by Corruccini and Gniewek [2] for the temperature range 0 to 300 K, by Campbell [3] for temperatures from 298 to 1973 K, by Kirby et al. [4] for temperatures from 100 to 1800 K, and by Touloukian et al. [5] for temperatures from 0 to 1900 K. Corruccini and Gniewek used values of enthalpy and heat capacity to extrapolate the smoothed expansion and coefficient data of Nix and MacNair [6] to temperatures below 90 K. Campbell simply reported values derived from an equation obtained by Bockris et al. [7] which was based on the results of Austin [8], Holborn and Day [9], Owen and Yates [10], Esser and Eusterbrock [11], and Edwards et al. [12]. Kirby et al. and Touloukian et al. used graphical techniques to smooth the values of the coefficients of thermal expansion that were obtained from available published data on thermal expansion.

2. DATA SETS

Volume 12 in the TPRC Data Series (Thermal Expansion—Metallic Elements and Alloys) [5] lists 22 sets of data for platinum that were published before 1972. Only those sets of data that were obtained by accurate and precise methods were considered for use in this analysis. These requirements ruled out the sets obtained by push-rod dilatometry and by X-ray diffraction techniques. In addition, the data obtained by Dorsey [13] and by Nix and MacNair [6] using interferometry were not used because of the imprecision of the values. This was also the reason for not using the data obtained by Vertogradskii [14] on wire specimens using an optical comparator. The only set of data that the author is aware of that has been published since 1972 and meets the requirements of accuracy and precision is that of Edsinger et al. [15].

The data sets used in this analysis are as follows.

White [16] used a three-terminal capacitance dilatometer to determine the thermodynamic coefficients of thermal expansion, $\alpha = d \ln L/dT$, of a "thermopure-grade" rod of platinum (obtained from Engelhard Industries) at temperatures ranging from 3 to 283 K. The values used in this analysis were those that were tabulated by White.

Edsinger et al. [15] used a Fizeau interferometer to measure the thermal expansion of a 1-mm-thick sheet of 99.95% pure platinum (obtained from Englehard Industries) from 245 to 840 K. In this analysis selected

values of the expansion were used to calculate the coefficients, $\alpha^* = 1/L_{293}(\Delta L/\Delta T)$, where L_{293} is the specimen length at 293 K.

Austin [8] used a Fizeau interferometer to measure the thermal expansion of a 99.995% chemically pure (CP) platinum rod from 273 to 1173 K. The data given by Austin for the expansion (the average of two runs) were used to calculate the coefficients (α^*). The values for temperatures above 823 K were not used, however, because it appears that the specimen must have been compressed by the weight of the optical flat at the higher temperatures.

Holborn and Day [9] used an optical comparator to measure the thermal expansion of a CP platinum rod (obtained from Heraeus) from 273 to 1273 K. All of the observed values of expansion except the one at 1273 K were used to calculate the coefficients (α^*).

Hahn and Kirby [17] used a Fizeau interferometer at temperatures from 293 to 1100 K and an optical comparator at temperatures from 1000 to 1900 K to measure the thermal expansion of three specimens of platinum rod. These specimens had purities of at least 99.99% and were obtained from J. Bishop and Co., Sigmund Cohn, and Heraeus. Observed values of expansion were used to calculate the coefficients (α^*).

3. ANALYSIS

Polynomials of the form

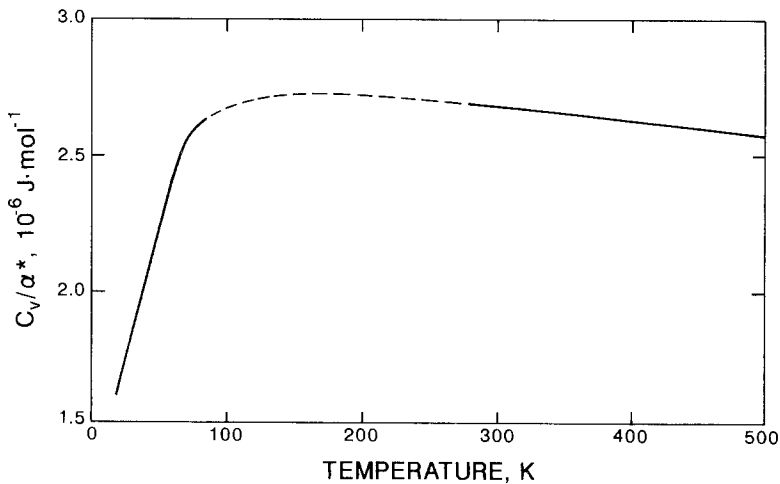$$\alpha^* = A_0 + A_1 T + A_2 T^2 + A_3 T^3 + A_4 T^4 + A_5 T^5 + A_6 T^6 + A_7 T^7$$

Fig. 1. Empirical fit to the ratio of the Debye heat capacity ($\Theta_D = 265$ K) to the coefficient of thermal expansion (α^*).

were fitted to the "observed" (calculated from the measured values of expansion) values of the coefficients of thermal expansion (α^*). Except for the temperature range from 3 to 22 K, all of the coefficients were fitted using third-order polynomials. The temperature range of each fit was selected by trial and error to minimize the differences between the fit and the "observed" values. An empirical fit to values for C_v/α^* from 20 to 85 K and from 274 to 500 K (Fig. 1) was used to guide the fits between 85 K and room temperature due to the lack of "observed" values within that temperature range. The values of C_v were calculated by use of the Debye function, in which the value of Θ_D was set equal to 265 K.

This analysis resulted in the following values for A_i for eight temperature ranges.

Range 0 to 22 K:

$$A_1 = +1.90 \times 10^{-3}$$
$$A_3 = +4.800 \times 10^{-5}$$
$$A_5 = +4.701 \times 10^{-8} \tag{1}$$
$$A_7 = -4.97 \times 10^{-11}$$

Range 22 to 50 K:

$$A_0 = +0.374$$
$$A_1 = -7.731 \times 10^{-2}$$
$$A_2 = +5.064 \times 10^{-3} \tag{2}$$
$$A_3 = -4.333 \times 10^{-5}$$

Range 50 to 100 K:

$$A_0 = -4.558$$
$$A_1 = +0.25322$$
$$A_2 = -2.0807 \times 10^{-3} \tag{3}$$
$$A_3 = +6.758 \times 10^{-6}$$

Range 100 to 200 K:

$$A_0 = +0.693$$
$$A_1 = +9.360 \times 10^{-2}$$
$$A_2 = -3.9219 \times 10^{-4} \tag{4}$$
$$A_3 = +5.867 \times 10^{-7}$$

Range 200 to 285 K:

$$A_0 = +4.378$$
$$A_1 = +3.650 \times 10^{-2}$$
$$A_2 = -1.0286 \times 10^{-4}$$
$$A_3 = +1.067 \times 10^{-7}$$

(5)

Range 285 to 480 K:

$$A_0 = +9.284$$
$$A_1 = -7.865 \times 10^{-3}$$
$$A_2 = +3.123 \times 10^{-5}$$
$$A_3 = -2.933 \times 10^{-8}$$

(6)

Range 480 to 1250 K:

$$A_0 = +7.897$$
$$A_1 = +4.236 \times 10^{-3}$$
$$A_2 = -2.889 \times 10^{-6}$$
$$A_3 = +1.589 \times 10^{-9}$$

(7)

Range 1250 to 1800 K:

$$A_0 = -5.838$$
$$A_1 = +3.3900 \times 10^{-2}$$
$$A_2 = -2.3297 \times 10^{-5}$$
$$A_3 = +5.9630 \times 10^{-9}$$

(8)

The deviations of the "observed" values from the fitted equations are indicated in Fig. 2. The values for the linear thermal expansion, $\Delta L/L_{293}$, were obtained by intergrating the fitted equations for the coefficients. The recommended values for the coefficients and the expansion are given in Table I. The thermodynamic coefficient, $\alpha = d \ln L/dT$, can be obtained by multiplying α^* by

$$1/(1 + \Delta L/L_{293})$$

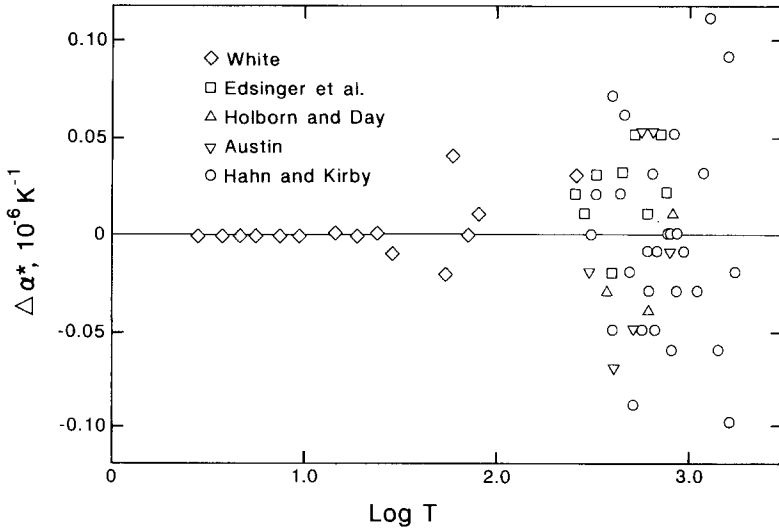Values for the volume coefficient, β, can be obtained as $\beta = 3\alpha$.

Fig. 2. Deviations of coefficients of thermal expansion (observed − calculated).

Table I. Recommended Values of α^* and $\Delta L/L_{293}$ for Platinum

T (K)	α^* $(10^{-6}\,\mathrm{K}^{-1})$	$\Delta L/L_{293}$ (10^{-6})	T (K)	α^* $(10^{-6}\,\mathrm{K}^{-1})$	$\Delta L/L_{293}$ (10^{-6})
10	0.071	−1927	200	8.42	−811
12	0.116	−1926	250	8.74	−382
14	0.178	−1926	293.15		0
16	0.263	−1926	300	8.94	61
18	0.373	−1925	350	9.10	512
20	0.509	−1924	400	9.26	971
25	0.93	−1921	500	9.49	1910
30	1.44	−1915	600	9.74	2871
35	2.01	−1906	700	9.99	3858
40	2.61	−1895	800	10.25	4870
50	3.75	−1863	900	10.53	5909
60	4.60	−1821	1000	10.83	6976
70	5.29	−1771	1100	11.18	8076
80	5.84	−1715	1200	11.57	9213
90	6.31	−1655	1300	11.96	10390
100	6.72	−1589	1400	12.32	11604
120	7.29	−1449	1500	12.72	12856
140	7.72	−1299	1600	13.19	14151
160	8.03	−1141	1700	13.76	15497
180	8.26	−978	1800	14.48	16908

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