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High-Speed (Subsecond) Measurement of Heat Capacity, Electrical Resistivity, and Thermal Radiation Properties of Tantalum in the Range 1900 to 3200 K*

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Measurements of heat capacity, electrical resistivity, hemispherical total and normal spectral emittances of tantalum above 1900 K by a pulse heating technique are described. Duration of an individual experiment, in which the specimen is heated from room temperature to near its melting point, is less than one second. Temperature measurements are made with a photoelectric pyrometer. Experimental quantities are recorded with a digital data acquisition system. Time resolution of the entire system is 0.4 ms. Results on the above properties of tantalum in the range 1900 to 3200 K are reported and are compared with those in the literature. Estimated inaccuracy of measured properties in the above temperature range is 2 to 3 percent for heat capacity, 0.5 percent for electrical resistivity, 3 percent for hemispherical total emittance, and 2 percent for normal spectral emittance.

Key words: Electrical resistivity; emittance; heat capacity; high-speed measurements; high temperature; tantalum; thermal radiation properties; thermodynamics.

1. Introduction

Conventional methods of measuring heat capacity, electrical resistivity, and other thermophysical properties at high temperatures employ "drop", steady-state, and quasi steady-state techniques in which the specimen is exposed to high temperatures for long periods of time, ranging from minutes to hours. Extension of these techniques to temperatures above 2000 K creates problems resulting from increased heat transfer, chemical reactions, evaporation, diffusion, loss of mechanical strength, etc. To overcome these limitations, this laboratory has recently developed a high-speed measurement technique in which the specimen is heated and pertinent quantities required for the determination of properties are measured in short times. The duration of an individual experiment, in which the specimen is heated from room temperature to near its melting point, is less than 1 s. A millisecond resolution photoelectric pyrometer is used to measure the specimen temperature. The recordings of experimental quantities are made with a high-speed digital data acquisition system, which has a time resolution of 0.4 ms. The application of this technique to measurements on molybdenum has been published [1].[1] General reviews on high-speed methods for the measurement of thermophysical properties of electrical conductors have been presented recently [2, 17].

In the present study the technique was used to determine the heat capacity and electrical resistivity of tantalum in the temperature range 1900 to 3200 K, and the hemispherical total and normal spectral emittances up to 3000 K.

2. Method

The method employed in this study is based upon rapid resistive heating of the specimen by the passage of high currents and measuring the pertinent quantities with appropriate time resolution. The required quantities are the power imparted to the specimen and the temperature of the specimen, both as functions of time. Imparted power is obtained from measurements of current flowing through the specimen and the potential difference across the "effective" [2] specimen as a function of time.

The relationship for heat capacity is obtained from power balances for the specimen during the pulse heating and the following free cooling periods. The expression for heat capacity, which was derived in an earlier publication [1], is

$$c_p = \frac{ei - \epsilon\sigma A_s(T^4 - T_0^4)}{n(dT/dt)_h} \qquad (1)$$

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] "Effective" refers to the portion of the specimen between the knife-edge voltage probes.

where

c_p = heat capacity in J mol^{-1} K^{-1}

e = potential difference across the effective specimen in V

i = current through the specimen in A

ϵ = hemispherical total emittance

σ = Stephan-Boltzmann constant ($5.6697 \times 10^{-8} W m^{-2} K^{-4}$)

A_s = effective specimen surface area in m^2

T = specimen temperature in K

T_0 = room temperature in K

n = amount of effective specimen in mol

$(dT/dt)_h$ = heating rate in K s^{-1}

The hemispherical total emittance, ϵ, which appears in the radiation loss term of the heat capacity relation, is determined from data collected during the free cooling period. Derived from the power balance relationship during the cooling period and eq (1), the expression for ϵ is

$$\epsilon = \frac{ei}{\sigma A_s (T^4 - T_0^4)(1+M)} \tag{2}$$

where

$$M = -\frac{(dT/dt)_h}{(dT/dt)_c} \tag{3}$$

$(dT/dt)_c$ = cooling rate in K s^{-1}

Equation (2) is used to compute values for ϵ at selected temperatures, which are used to obtain a function for ϵ in terms of temperature. Then, ϵ values from this function are substituted in eq (1) to obtain heat capacity over the entire temperature range.

Data from the heating period is also used to calculate the electrical resistivity with the aid of the equation

$$\rho = \frac{RA_c}{l} \tag{4}$$

where

ρ = electrical resistivity in Ω m

R = resistance of effective specimen in Ω

A_c = specimen cross-sectional area in m^2

l = effective specimen length in m.

The normal spectral emittance, $\epsilon_{n,\lambda}$, is obtained from separate pulse experiments in which radiance from the surface of the specimen is measured. The relation for $\epsilon_{n,\lambda}$ is

$$\epsilon_{n,\lambda} = \frac{L_s}{L_b} \tag{5}$$

where

L_s = radiance from surface of specimen as observed by the pyrometer.

L_b = blackbody radiance from sighting hole in specimen as observed by the pyrometer.

In all the above equations, geometrical quantities are corrected for the presence of the sighting hole, and the quantities related to radiation from the sighting hole are corrected for scattered light and departure from blackbody conditions.

3. Apparatus

A functional diagram of the measurement system used in this study is shown in figure 1. The details of the system were described in an earlier publication [1].

The specimen was a tube approximately 100 mm long with a small rectangular hole fabricated in the wall at the middle of its length to approximate blackbody conditions. The knife-edge probes, which were used for potential measurements, were made of tantalum and were placed 50 mm apart on the middle portion of the specimen. The portion between the probes, defined as "effective" specimen, was free from significant temperature gradients for the duration of an experiment. The specimen and the associated components were contained in a vacuum chamber.

The specimen temperature was measured with a high-speed photoelectric pyrometer [12], which permits 1200 evaluations of the specimen temperature per second. The pyrometer alternately compares the radiance from the blackbody hole in the specimen to that of a reference lamp.

Electrical signals corresponding to voltage, current, and temperature were recorded with a high-speed digital data acquisition system, which consists of a multiplexer, analog-to-digital converter, and a core memory together with various control and interfacing equipment. At the end of each experiment, the data were retrieved and recorded in printed numeric form and on punched paper tape via a teletypewriter. During this retrieval period, data were also sent to a time-sharing computer for immediate processing.

Electrical signals corresponding to voltage, current, and temperature were also monitored simultaneously with oscilloscopes.

4. Measurements

Measurements were made on four tantalum specimens. The first two specimens were used for experiments in the temperature interval 1900 to 3000 K. To optimize the operation of the pyrometer, this temperature interval was divided into three ranges with three experiments per range. These nine experiments are referred to as a series. The temperature ranges were: low, 1900 to 2250 K; medium, 2100 to 2600 K; and high, 2350 to 3000 K.

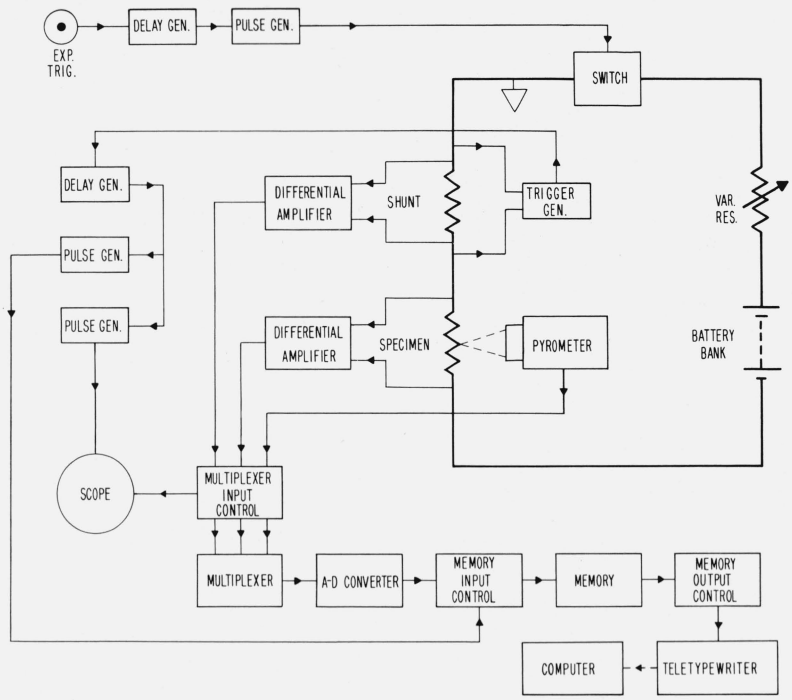

FIGURE 1. *Functional diagram of the complete high-speed measurement system.*

Two complete series of experiments were conducted on the first specimen (Ta–1). During the second series, two additional experiments were conducted, one in the low range and one in the high range, to measure the surface radiance of the specimen. Before the start of the first series of experiments, the specimen (Ta–1) was subjected to approximately 30 heating pulses (in the range 2200 to 3000 K) to anneal the specimen and to determine the optimum heating rate for each temperature range. At the end of the first series of experiments and before the start of the second series, the specimen was pulse heated 15 times to 3000 K. One experiment per temperature range was conducted on the second specimen (Ta–2) without any prior heating pulses.

To obtain heat capacity and electrical resistivity in the temperature range 2950 to 3200 K, two other specimens, (Ta–3) and (Ta–4), were used.

The duration of the current pulses ranged from 280 to 520 ms depending on the temperature. The average heating rate of the specimen was 5700 and 3700 K s^{-1} at 2000 and 3200 K, respectively. At these temperatures, radiative heat losses from the specimen amounted to approximately 3 and 22 percent of the input power, respectively. All of the experiments were conducted with the specimen in a vacuum environment of approximately 10^{-4} torr.

The data on voltage, current, and temperature were used to obtain third degree polynomial functions for each quantity in terms of time, which then provided the input information for the equations of section 2.

During the entire set of experiments, the pyrometer was calibrated five times against a tungsten filament standard lamp, which in turn was calibrated against the NBS Temperature Standard. The digital recording system including the differential amplifiers was calibrated three times during the experiments. The details of the calibration procedures are given in an earlier publication [1].

Prior to the start of the experiments, the optical system of the pyrometer was modified to reduce the effect of light scattered from the area around the sighting hole in the specimen. In the present system this effect is approximately one percent. The blackbody quality of the specimen sighting hole was estimated to be 0.99 using DeVos' [13] method. The temperature data from the pyrometer were corrected for both scattered light and departure from blackbody conditions. The details of the methods employed for these corrections are given in an earlier publication [1].

The nominal dimensions of the tubular tantalum specimens were: length = 4 in (101 mm), outside diameter = 0.25 in (6.3 mm), and wall thickness = 0.02 in (0.5 mm). The outer surface of each specimen was polished to reduce heat loss due to thermal radiation.

Specimen characterization was made on one specimen (Ta–1) by the following methods: photomicrography, chemical analysis, and residual resistivity ratio.

Photomicrographs of the specimen before and after the entire set of experiments are shown in figure 2. It may be seen that considerable grain growth has taken place as the result of pulse heating the specimen to high temperatures.

Chemical analyses were made of the specimen before and after the entire set of experiments. Comparison of results does not indicate any detectable change in impurity content. A list of the nature and composition of impurities in the specimen is given in table 1.

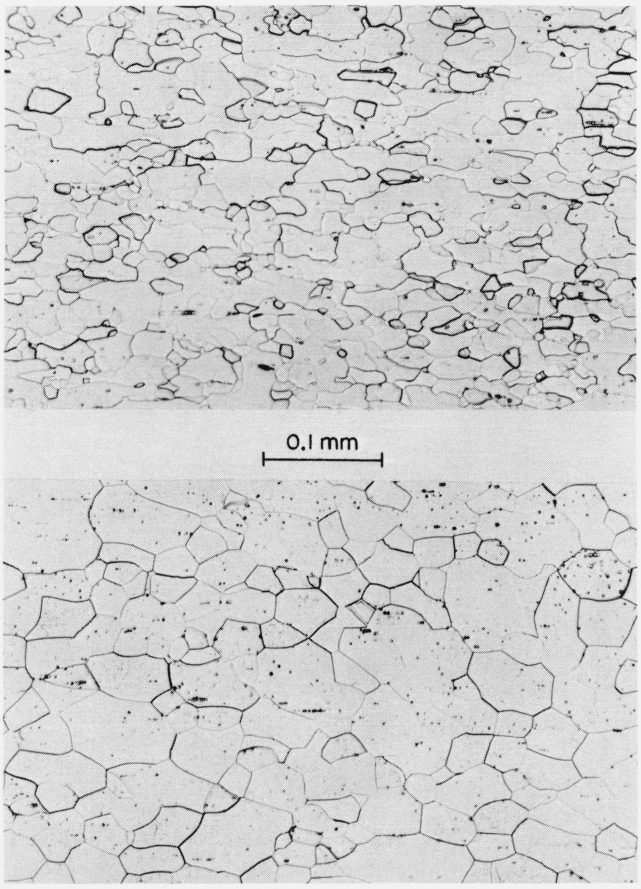

FIGURE 2. *Photomicrographs of the tantalum specimen before (upper photograph) and after (lower photograph) the entire set of experiments.*

TABLE 1. *Impurities in tantalum specimen*

Impurity	Composition ppm (by weight)
Al	< 5
C	60
Ca	< 5
Cr	< 10
Cu	< 5
Fe	70
Mg	< 5
Mo	10
N	20
Nb	500
O	50
W	< 200

710 < Total < 940

The residual resistivity ratio of the specimen (ratio of electrical resistivity at 273 K to that at 4 K) before and after the entire set of experiments was 22 ± 1. The fact that the value of this ratio remained unchanged indicates that the specimen did not undergo any major chemical or physical changes.

The total mass of the specimen was determined before and after each series of experiments. The "effective" mass of the specimen was calculated from the total mass by ratio of the geometric surface area between voltage probes to total surface area. Length measurements at room temperature were made with a micrometer microscope to the nearest 0.03 mm. The thickness of the cylinder wall was calculated from the mass, surface areas, and density.

Density of tantalum at 298 K was obtained by the water displacement method in a pycnometer. The results of three determinations gave a value of 16.65×10^3 kg m^{-3} with an average deviation of 0.03 percent. This compares favorably with the reported value of 16.6×10^3 kg m^{-3} [16].

5. Experimental Results

This section presents the results on the thermophysical properties determined from the measured quantities. All values are based on the 1968 International Practical Temperature Scale [14]. The final results on properties at 100 degree temperature intervals are presented in table 2. In all computations, the geometrical quantities are based on their ambient temperature (298 K) dimensions. The experimental results (individual points) on properties are given in the appendix (tables A–1 to A–5).

TABLE 2. *Heat capacity, electrical resistivity, hemispherical total and normal spectral emittances of tantalum*

Temperature, K	c_p J mol^{-1}K^{-1}	ρ[a] $10^{-8}\Omega$m	ϵ[a]	$\epsilon_{N,\lambda}$
1900	30.66	75.56	[b] 0.288	[b] 0.413
2000	31.19	78.80	[b] .293	.411
2100	31.71	82.00	[b] .298	.409
2200	32.25	85.14	[b] .302	.407
2300	32.83	88.23	.307	.406
2400	33.46	91.26	.312	.404
2500	34.17	94.24	.316	.403
2600	34.97	97.17	.321	.401
2700	35.89	100.04	.326	.400
2800	36.95	102.86	.330	.400
2900	38.16	105.63	.335	.399
3000	39.55	108.34	.340	.398
3100	41.39	111.00		
3200	44.48	113.60		

[a] Based on ambient temperature (298 K) dimensions.
[b] Extrapolated from higher temperature results.

5.1. Normal Spectral Emittance

To calculate the normal spectral emittance, two experiments were performed to measure the surface radiance of the Ta–1 specimen during the second heating series. The measurements were made at the effective wavelength of the pyrometer interference filter (650 nm; bandwidth 10 nm). The normal spectral emittance was calculated using the radiance data from each surface experiment together with the data from a previous or later regular blackbody experiment

according to eq (5). Since the specimen's true temperature could not be measured directly in a surface experiment, the times at which the resistance of the specimen in the two adjacent experiments were equal were taken as the times of equal temperature.

A second degree polynomial function for normal spectral emittance was obtained by least squares approximation of the experimental results. The standard deviation (of an individual point) is 0.3 percent. The function that is valid in the temperature range 2000 to 3000 K is:

$$\epsilon_{n,\lambda} = 0.4892 - 5.644 \times 10^{-5} T + 8.734 \times 10^{-9} T^2 \quad \text{(second series)} \qquad (6)$$

Normal spectral emittance computed using the above equation is given in table 2. The experimental results are presented in figure 3.

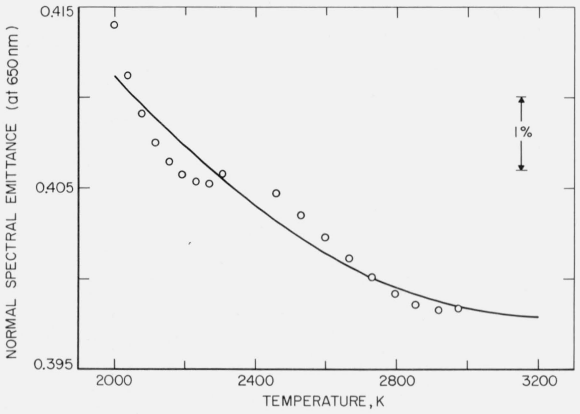

FIGURE 3. *Normal spectral emittance of tantalum at* $\lambda = 650$ *nm.*

5.2. Hemispherical Total Emittance

The hemispherical total emittance of the Ta–1 specimen was computed with the aid of eq (2) using temperature data taken during both heating and initial free cooling periods in an experiment.

A linear function for hemispherical total emittance for each heating series was obtained by least squares approximation of the individual values. The standard deviation of the points from the function for the first and second heating series were 0.7 and 0.5 percent, respectively. The functions that are valid in the temperature range 2300 to 3000 K are:

$$\epsilon = 0.2197 + 4.146 \times 10^{-5} T \quad \text{(first series)} \qquad (7)$$

$$\epsilon = 0.1991 + 4.687 \times 10^{-5} T \quad \text{(second series)} \qquad (8)$$

Hemispherical total emittance computed using eq (8) is given in table 2. The experimental results are presented in figure 4.

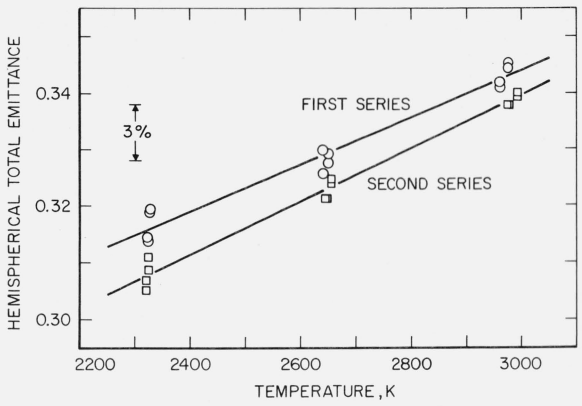

FIGURE 4. *Hemispherical total emittance of tantalum.*

5.3. Heat Capacity

A third degree polynomial function for heat capacity in terms of temperature for each heating series on Ta–1 was obtained by least squares approximation of results from individual experiments. The standard deviation of the points from the function for the first and second heating series were 0.19 and 0.17 percent, respectively. A similar function was also obtained for the combined results of experiments in the first and second series with a standard deviation of 0.18 percent.

Figure 5 shows the deviations of the experimental results from the smooth function for the combined heating series. The figure also shows the deviation of the function for each individual heating series from the heat capacity function for the combined series. Compared to the function for the combined series, the average difference between the functions for the first and second heating series is about 0.1 percent, which is smaller than the measurement resolution. Therefore, it may be concluded that the measured heat capacity shows no significant difference between the two heating series. The function for the combined series that is valid in the temperature range 1900 to 3000 K is:

$$c_p = -6.549 + 4.583 \times 10^{-2} T - 2.013 \times 10^{-5} T^2 + 3.325 \times 10^{-9} T^3 \qquad (9)$$

where T is in K and c_p in J mol^{-1} K^{-1}. Heat capacity up to 3000 K computed using the above equation is given in table 2. In the computations of heat capacity, the atomic weight of tantalum was taken as 180.95 [15].

Without any prior heating pulses, three experiments were conducted on a second tantalum specimen (Ta–2). Figure 6 shows the difference in measured heat capacity between Ta–1 and Ta–2. The base line in figure 6 represents the smooth function for heat capacity of Ta–1 given by eq (9). The maximum deviation between the heat capacity results of the two specimens occurs at the lowest temperature and is less than 1 percent. The tendency for the heat capacity of Ta–2 to approach that of Ta–1 as the temperature increases may be due to annealing effects as the temperature range for the Ta–2 specimen was increased.

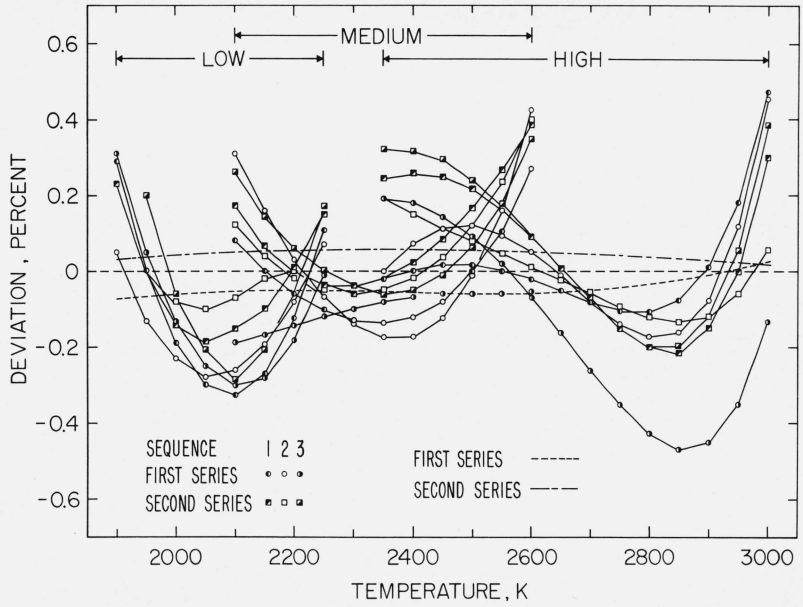

FIGURE 5. *Deviation of heat capacity results for tantalum from eq (9).*

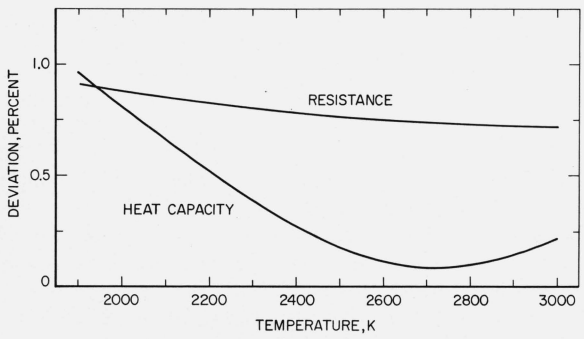

FIGURE 6. *Difference in heat capacity and electrical resistivity between two tantalum specimens.*

Base line represents results for Ta–1 given by eqs (9) and (10).

The preliminary results on heat capacity of tantalum up to 3000 K were reported in an earlier publication [3]. In this study the measurements were extended to 3200 K by performing one experiment each on Ta–3 and Ta–4, and averaging the results. Hemispherical total emittance needed to correct heat capacity above 3000 K was obtained from the extrapolation of the experimental results at lower temperatures. The results of measurements above 3000 K are given in table 2. At 3000 K the heat capacity for this extended temperature range is approximately 0.1 percent lower than the value given by eq (9).

5.4. Electrical Resistivity

The electrical resistivity of the Ta–1 specimen was determined from the same experiments that were used to calculate the heat capacity. A second degree polynomial function for each heating series was obtained by least squares approximation of results from individual experiments. The standard deviation of the points from the function for the first and second heating series are 0.03 and 0.02 percent, respectively.

In contrast to the heat capacity results, the electrical resistivity showed a small but significant difference between the two heating series; the results of the second series being lower than those of the first. The combined data from both heating series were fitted to a second degree polynomial function. Figure 7 shows the deviations of the experimental results from the smooth function for the combined series. The figure also shows the deviation of the function for each individual heating series from the electrical resistivity function for the combined series. The average difference between the functions for the first and second heating series is approximately 0.15 percent. The function for the combined series that is valid for the temperature range 1900 to 3000 K is:

$$\rho = 3.671 + 4.292 \times 10^{-2} T - 2.677 \times 10^{-6} T^2 \quad (10)$$

where T is in K and ρ in $10^{-8} \Omega$ m. Electrical resistivity up to 3000 K computed using the above equation is given in table 2.

The difference between the results on Ta–1 and Ta–2 is presented graphically in figure 6. In contrast to heat capacity, electrical resistivity did not converge as Ta–2 was exposed to high temperatures.

The results of experiments on Ta–3 and Ta–4 were used to compute electrical resistivity above 3000 K. These are included in table 2. At 3000 K electrical resistivity obtained from Ta–3 and Ta–4 was approximately 0.3 percent lower than the value given by eq (10).

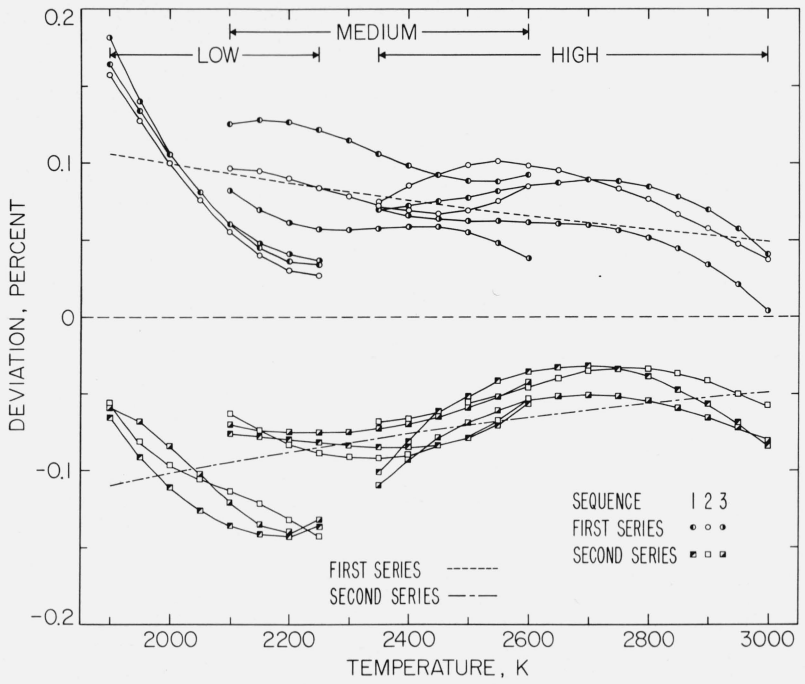

FIGURE 7. *Deviation of electrical resistivity results for tantalum from eq (10).*

In addition, the electrical resistivity of Ta–1 was measured at 293 K under steady-state conditions. The resultant value was $14.0 \times 10^{-8} \Omega$m.

6. Estimate of Errors

Results on imprecision[3] and inaccuracy[4] of measured and computed quantities are given in table 3.

TABLE 3. *Imprecision and inaccuracy of measured and computed quantities*

Quantity	Imprecision (percent)	Inaccuracy (percent)
Temperature	0.02 (0.5 K)	0.2 (4 K) at 2000 K 0.3 (10 K) at 3200 K
Voltage	0.02	0.05
Current	.03	.06
Power	.04	.08
Resistance	.04	.08
Length	.04	.08
Weight	.01	.1
Density	.03	.1
Heat Capacity	.5	2 at 2000 K 3 at 3200 K
Resistivity	.04	0.5
Hem. Total Emittance	.7	3
Norm. Spectral Emittance	.3	2

[3] Imprecision refers to the standard deviation of an individual point as computed from the difference between measured and calculated values.

[4] Inaccuracy refers to the estimated maximum error (random and systematic) approximately equivalent to two standard deviations.

Numbers listed under imprecision were obtained from a least squares analysis of experimental results. Numbers listed under inaccuracy were estimated considering the contribution of various items that introduce random and systematic errors in the pertinent quantities. These items are listed below:

(a) In temperature measurements: pyrometer reproducibility, scattered light correction, light source alinement, radiation standard lamp, blackbody quality, specimen temperature uniformity, magnetic fields.

(b) In electrical measurements: skin effect, inductive effects, thermoelectric effects.

(c) In interpretation of results: specimen evaporation, thermionic emission, time synchronization, measurements of length and weight.

Details regarding the estimates of errors and their combination are given in another publication [1]. Specific items in the error analysis were recomputed whenever the present conditions differed from those in the earlier publication.

7. Discussion

The heat capacity and electrical resistivity results of this work are compared graphically with those in the literature in figures 8 and 9, respectively. Numerical comparisons are given in tables 4 and 5. It may be seen that present results agree favorably with all others at 2000 K and also at higher temperatures, with the exception of heat capacity results of Hoch and Johnston [8]. Estimates of errors in papers cited lead to an estimate of inaccuracies in previously reported heat capacity and electrical resistivity of approxi-

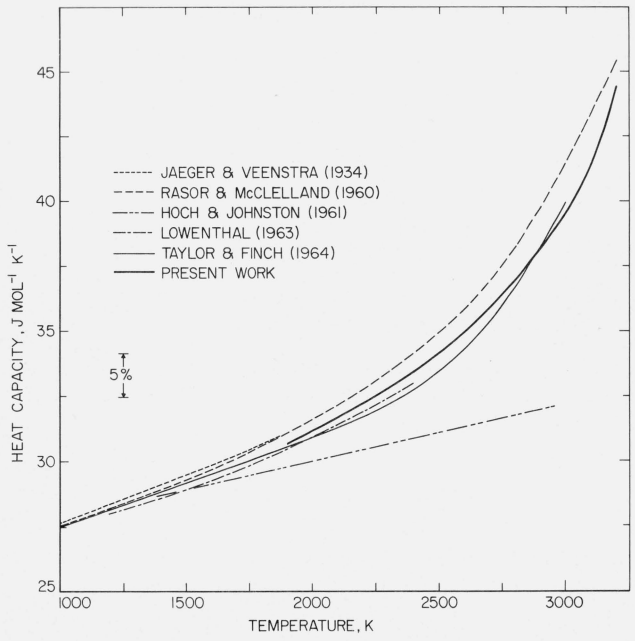

FIGURE 8. *Heat capacity of tantalum reported in the literature.*

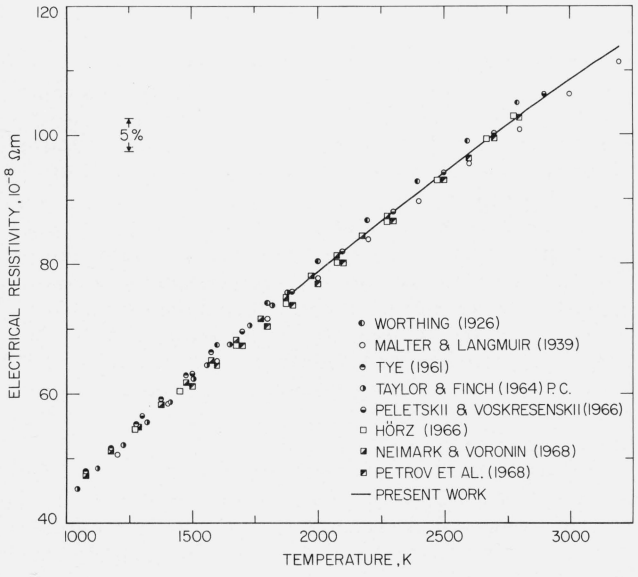

FIGURE 9. *Electrical resistivity of tantalum reported in the literature.*

mately 5 to 10 and 1 to 3 percent, respectively, in the temperature range considered. Measurements of the electrical resistivity of tantalum corresponding to 293 K, as well as values reported in the literature, are given in table 6.

The results for hemispherical total and normal spectral emittances of this work and those in the literature are presented in figures 10 and 11, respectively. Because of the strong dependence of emittance on surface conditions, considerable deviations exist in the results of various investigators.

Heat capacity results at high temperatures are considerably higher than the Dulong and Petit value of $3R$. Some of this departure is due to $c_p - c_v$ and the electronic terms. However, they do not account for the entire departure. Heat capacity above the Debye temperature may be expressed by

$$c_p = A - \frac{B}{T^2} + CT + \Delta c \qquad (11)$$

where the constant term is $3R$ (24.943 J mol^{-1} K^{-1}), the term in T^{-2} is the first term in the expansion of the Debye function, the term in T represents $c_p - c_v$ and electronic contributions, and the quantity Δc represents excess in measured heat capacity at high temperatures, which is not accounted for by the first three terms. The coefficients $B(4.88 \times 10^4)$ and $C(2.59$

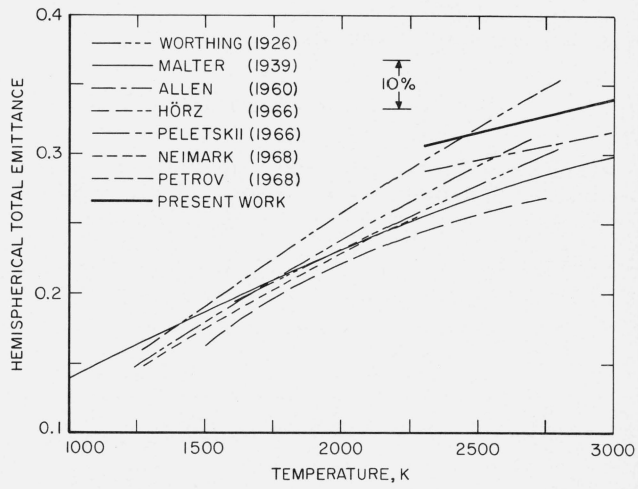

FIGURE 10. *Hemispherical total emittance of tantalum reported in the literature.*

TABLE 4. *Tantalum heat capacity difference (previous literature values minus present work values) in percent*

Investigator	Ref.	Year	Method	Temperature, K						
				2000	2200	2400	2600	2800	3000	3200
Jaeger and Veenstra.....	7	1934	drop	[a] +1.2						
Rasor and McClelland.....	5	1960	pulse	+1.3	+1.4	+1.9	+2.4	+3.4	+5.0	+2.0
Hoch and Johnston.....	8	1961	drop	−3.8	−5.6	−7.6	−10.4	−14.0		
Lowenthal.....	4	1963	modul.	−0.8	−1.0	−1.3				
Taylor and Finch.....	6	1964	pulse	−0.9	−1.6	−2.2	−1.9	−0.8	+0.9	

[a] Extrapolated from 1873 K.

TABLE 5. *Tantalum electrical resistivity difference (previous literature values minus present work values) in percent*

Investigator	Ref.	Year	Temperature, K						
			2000	2200	2400	2600	2800	3000	3200
Worthing	18	1926	+2.3	+2.1	+2.1	+2.2	+2.4		
Malter and Langmuir	19	1939	−1.2	−1.3	−1.5	−1.6	−1.8	−1.9	−2.0
Peletskii and Voskresenskii	21	1966	+0.2	−0.1	−0.1	+0.1	+0.4		
Hörz	20	1966	−1.0	−0.8	−0.4	+0.1	+0.9		
Neimark and Voronin	22	1968	+0.4	+0.2					
Petrov et al	23	1968	−2.1	−1.8	−1.4	−0.8	−0.1		

TABLE 6. *Electrical resistivity of tantalum at 293 K (literature)*

Investigator	Ref.	Year	Resistivity $10^{-8}\Omega$m
Worthing	18	1926	14.2
Malter and Langmuir	19	1939	13.5
White and Woods	25	1959	[a] 13.1
Tye	26	1961	14.5
Hörz	20	1966	13.4
Peletskii and Voskresenskii	21	1968	13.7
Neimark and Voronin	22	1938	15.0
Present work			14.0

[a] Ideal resistivity.

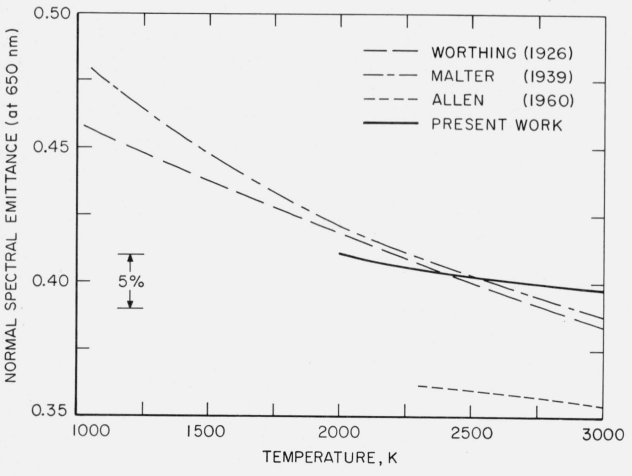

FIGURE 11. *Normal spectral emittance of tantalum at $\lambda' = 650$ nm reported in the literature.*

$\times 10^{-3}$) were obtained from data on heat capacity at low and moderate temperatures (at 250 and 1000 K) given by Hultgren et al. [11].

Using eq (11) and the heat capacity results of this work, the quantity Δc was computed for temperatures above 1900 K. The results are tabulated in table 7. The estimated uncertainty in the computed Δc may be as high as 1 J mol^{-1}K^{-1}. This was obtained from the combined uncertainties in the coefficients in eq (11) and the measured heat capacities.

TABLE 7. *Excess heat capacity Δc in equation (11) and estimated vacancy contribution to heat capacity of tantalum*

T K	Δc J mol^{-1}K^{-1}	c_{vac} J mol^{-1}K^{-1}
2000	1.08	0.003
2200	1.62	.01
2400	2.31	.04
2600	3.30	.10
2800	4.76	.21
3000	6.84	.41
3200	9.70	.73

Although the mechanisms of vacancy generation become important at high temperatures, it was not possible to attribute the high values entirely to vacancies. To demonstrate this, a crude estimate of the contribution of vacancies to heat capacity was made using the following equation [1]:

$$c_{vac} = \frac{N_A A E_f^2}{kT^2} e^{-E_f/kT} \tag{12}$$

where

N_A = Avogadro's number

k = Boltzmann constant

E_f = vacancy formation energy

A = constant which is obtained from vacancy concentration at the melting point.

If one assumes that vacancy formation energy is approximately proportional to the melting point and considers the value of 3.3 eV reported by Schultz [9] for tungsten, one obtains 2.9 ± 0.5 eV for the vacancy formation energy for tantalum. There are no accurate measurements on tantalum related to vacancy concentrations. Results of quenching experiments on various refractory elements [9, 10] have indicated that vacancy concentrations are probably in the range 0.01 to 0.1 percent at their melting points. Estimates corresponding to a vacancy concentration of 0.1 percent at the melting point and a vacancy formation energy of 2.9 eV are given in table 7. The results indicate that vacancy contribution is small, less than 0.7 J mol^{-1}K^{-1} (upper limit) at 3200 K, and does not account for high heat capacity values. A

possible contribution of higher order terms in the electronic heat capacity may partially account for high values of heat capacity at high temperatures.

If the entire deviation of measured heat capacity from the sum of $3R$ and the linear term at high temperatures is represented by an expression similar to eq (12), one could obtain after rearrangement

$$\ln (T^2 \Delta c) = \ln I - \frac{S}{T}. \tag{13}$$

This equation indicates that a plot of the left side versus $1/T$ should yield a straight line with slope equal to $-S$. From the data on tantalum in the range 1900 to 3200 K, a straight line with a standard deviation of 0.8 percent was obtained. However, the parameters obtained through this fit do not seem to have any physical significance. As a crude analogy to vacancy concentration, the computations yielded a value of 1.4 eV for energy and 4.2 percent for concentration at the melting point. Both of these values seem to be unrealistic for tantalum.

In order to give a simple expression for the heat capacity of tantalum over a wide temperature range, an empirical term in T^5 for the quantity Δc in eq (11) was substituted. The coefficient of this term was obtained from the results of the present work in conjunction with the values given by Hultgren et al. [11] at temperatures below 1000 K. Then, eq (11) for the range 300 to 3100 K becomes

$$c_p = 24.943 - \frac{4.88 \times 10^4}{T^2} + 2.59 \times 10^{-3} T + 2.85 \times 10^{-17} T^5 \tag{14}$$

where T is in K and c_p in J mol^{-1} K^{-1}. Average deviation of the individual points from the function over the temperature range considered is 0.4 percent. Equation (14) is presented graphically in figure 12.

The T^{-2} term in eq (14) corresponds to a Debye θ of approximately 200 K for tantalum. This value is somewhat lower than the generally accepted value of 247 K [28]. Such a deviation may be expected since in the above analysis only data above 250 K were considered while determinations reported in the literature were based on more elaborate treatment of lower temperature data.

It was interesting to note that the difference in heat capacity between Ta–1 and Ta–2 was reduced from approximately 1 percent at 1900 K to 0.2 percent at 3000 K. The convergence of the results as Ta–2 was exposed to high temperatures indicates the difference in the initial states of the two specimens; Ta–1 was preheated while Ta–2 was used as received from the manufacturer prior to the start of the measurements.

There was a small, but significant difference in electrical resistivity between the two heating series of Ta–1. The second series results, which were lower than those of the first by approximately 0.15 percent, indicate that the specimen had undergone additional annealing during its exposure to high temperatures.

Unlike most metallic elements, the electrical resistivity of tantalum, in the range of present measurements, showed a negative departure from linearity in the curve of electrical resistivity against temperature. A small Fermi energy is believed to be responsible for some of this negative departure [27].

The experimental results reported in this paper have further substantiated the feasibility of accurate measurement of heat capacity and electrical resistivity of electrical conductors above approximately 2000 K by a pulse method of millisecond resolution. The results also indicated that under proper surface and environmental conditions the technique allows the measurement of hemispherical total and normal spectral emittances.

The authors extend their appreciation to M. S. Morse for his contribution in connection with electronic instrumentation, which is a vital part of the entire measurement system.

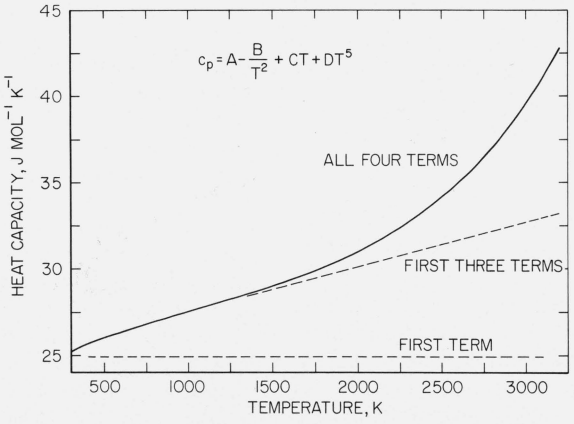

FIGURE 12. *Heat capacity of tantalum according to eq (14).*

8. Appendix

TABLE A–1. *Experimental results on heat capacity and electrical resistivity of tantalum–1* [a]

Range	Series	First series						Second series					
	Run	1		2		3		1		2		3	
	T	c_p	ρ	c_p	ρ	c_p	ρ	c_p	ρ	c_p	ρ	c_p	ρ
Low	1900	30.75	75.68	30.67	75.68	30.75	75.70	30.73	75.51	30.73	75.52	30.83	75.51
	1950	30.92	77.29	30.88	77.29	30.94	77.30	30.92	77.12	30.92	77.13	30.98	77.14
	2000	31.12	78.89	31.11	78.89	31.14	78.89	31.14	78.72	31.16	78.73	31.16	78.74
	2050	31.35	80.48	31.36	80.47	31.36	80.47	31.39	80.31	31.41	80.33	31.38	80.33
	2100	31.60	82.05	31.62	82.05	31.61	82.05	31.65	81.89	31.68	81.91	31.63	81.90
	2150	31.88	83.62	31.91	83.61	31.88	83.62	31.94	83.46	31.96	83.48	31.91	83.46
	2200	32.20	85.17	32.22	85.17	32.18	85.18	32.25	85.02	32.24	85.03	32.22	85.02
	2250	32.56	86.72	32.55	86.72	32.52	86.72	32.57	86.57	32.51	86.57	32.58	86.58
Med.	2100	31.73	82.10	31.80	82.08	31.65	82.07	31.76	81.94	31.74	81.95	31.79	81.94
	2150	31.97	83.69	32.02	83.66	31.92	83.64	31.99	83.51	31.98	83.52	32.02	83.52
	2200	32.22	85.25	32.25	85.22	32.20	85.19	32.24	85.07	32.24	85.07	32.26	85.08
	2250	32.49	86.80	32.50	86.77	32.49	86.74	32.51	86.62	32.51	86.62	32.52	86.63
	2300	32.77	88.33	32.77	88.30	32.78	88.28	32.80	88.16	32.80	88.15	32.80	88.16
	2350	33.08	89.85	33.07	89.82	33.10	89.80	33.12	89.68	33.11	89.67	33.10	89.69
	2400	33.41	91.35	33.39	91.33	33.42	91.32	33.46	91.19	33.44	91.18	33.43	91.20
	2450	33.76	92.85	33.75	92.82	33.77	92.81	33.82	92.68	33.80	92.68	33.79	92.70
	2500	34.15	94.33	34.15	94.31	34.13	94.30	34.21	94.17	34.20	94.17	34.18	94.19
	2550	34.58	95.80	34.60	95.79	34.52	95.76	34.63	95.65	34.63	95.65	34.60	95.66
	2600	35.05	97.26	35.11	97.25	34.92	97.23	35.09	97.12	35.10	97.12	35.08	97.13
High	2350	33.12	89.82	33.12	89.82	33.19	89.82	33.21	89.66	33.19	89.69	33.23	89.65
	2400	33.45	91.33	33.47	91.34	33.51	91.32	33.53	91.19	33.50	91.20	33.55	91.18
	2450	33.80	92.83	33.83	92.85	33.84	92.82	33.87	92.70	33.83	92.70	33.89	92.69
	2500	34.16	94.32	34.20	94.34	34.18	94.30	34.23	94.19	34.18	94.19	34.24	94.18
	2550	34.54	95.79	34.58	95.81	34.55	95.77	34.60	95.67	34.56	95.66	34.60	95.66
	2600	34.95	97.25	34.98	97.27	34.93	97.23	34.99	97.14	34.96	97.13	34.99	97.12
	2650	35.38	98.70	35.40	98.71	35.34	98.67	35.40	98.58	35.39	98.57	35.40	98.56
	2700	35.85	100.13	35.85	100.13	35.78	100.10	35.85	100.01	35.85	100.01	35.85	99.99
	2750	36.35	101.55	36.34	101.54	36.26	101.52	36.33	101.42	36.35	101.43	36.33	101.41
	2800	36.89	102.95	36.87	102.94	36.77	102.92	36.86	102.82	36.89	102.83	36.86	102.81
	2850	37.49	104.33	37.46	104.32	37.34	104.30	37.44	104.20	37.47	104.21	37.44	104.19
	2900	38.15	105.70	38.11	105.69	37.97	105.67	38.08	105.57	38.10	105.58	38.09	105.56
	2950	38.88	107.05	38.86	107.04	38.68	107.02	38.81	106.92	38.79	106.94	38.83	106.91
	3000	39.72	108.39	39.72	108.38	39.48	108.35	39.65	108.25	39.55	108.28	39.69	108.25

[a] Temperature in K.
Heat capacity in J mol^{-1} K^{-1}.
Electrical resistivity in $10^{-8}\Omega m$.

TABLE A–2. *Experimental results on heat capacity and electrical resistivity of tantalum–2*

Range	T K	c_p J mol^{-1}K^{-1}	ρ $10^{-8}\Omega$m
Low	1900	31.02	76.29
	1950	31.20	77.90
	2000	31.40	79.50
	2050	31.64	81.09
	2100	31.90	82.66
	2150	32.20	84.22
	2200	32.52	85.78
Med.	2100	31.88	82.72
	2150	32.11	84.29
	2200	32.36	85.85
	2250	32.62	87.40
	2300	32.90	88.94
	2350	33.21	90.47
	2400	33.54	91.98
	2450	33.90	93.48
	2500	34.30	94.98
	2550	34.74	96.46
High	2350	33.21	90.43
	2400	33.54	91.96
	2450	33.88	93.47
	2500	34.23	94.97
	2550	34.61	96.45
	2600	35.00	97.92
	2650	35.42	99.37
	2700	35.88	100.81
	2750	36.37	102.23
	2800	36.90	103.63
	2850	37.49	105.02
	2900	38.15	106.39
	2950	38.89	107.75
	3000	39.73	109.08

TABLE A–3. *Experimental results on heat capacity and electrical resistivity of tantalum–3 and tantalum–4*

Temperature	Tantalum–3		Tantalum–4	
K	c_p J mol^{-1}K^{-1}	ρ $10^{-8}\Omega$m	c_p J mol^{-1}K^{-1}	ρ $10^{-8}\Omega$m
2950	38.88	106.82	38.67	106.64
3000	39.42	108.14	39.48	107.96
3050	40.15	109.45	40.42	109.28
3100	41.12	110.75	41.50	110.58
3150	42.43	112.04	42.77	111.87
3200	44.22	113.32	44.31	113.15

TABLE A–4. *Experimental results on normal spectral emittance of tantalum at* $\lambda = 650$ nm

T K	$\epsilon_{N,\lambda}$
1999	0.414
2038	.411
2076	.409
2115	.408
2154	.406
2192	.406
2231	.405
2269	.405
2307	.406
2458	.405
2528	.404
2597	.402
2664	.401
2730	.400
2794	.399
2857	.399
2917	.398
2975	.398

TABLE A–5. *Experimental results on hemispherical total emittance of tantalum*

T K	ϵ
First Series	
2324	0.315
2324	.314
2328	.319
2328	.319
2640	.326
2640	.330
2650	.329
2650	.328
2961	.342
2961	.341
2975	.345
2975	.344
Second Series	
2319	0.307
2319	.305
2325	.311
2325	.309
2646	.321
2646	.321
2655	.325
2655	.324
2980	.338
2980	.338
2994	.340
2994	.340

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