

THE SPECIFIC HEAT OF METALS BETWEEN 1200°K AND 2400°K*

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Summary

Specific heat measurements have been made on niobium (from 1471 to 2260°K), molybdenum (from 1288 to 2015°K), tantalum (from 1256 to 2300°K), and tungsten (from 1267 to 2410°K). The experiments were based on a theory first proposed by Corbino in 1911. It is demonstrated that methods based on this theory account for heat losses from the specimen under test to better than 0·5% even at 2400°K. The theory requires a knowledge of the temperature oscillations in thin a.c. heated filaments and this amplitude is here obtained from photoelectric measurements.

The measured specific heat of each one of the four metals was found to rise more than linearly with the absolute temperature, while the specific heat at constant volume was found to increase approximately with the first power of the temperature. This behaviour is briefly discussed.

I. INTRODUCTION

The specific heat of any substance at constant pressure, P , is defined by

$$C_p = (dH/dT)_p, \quad (1)$$

where dH is the increment in the enthalpy or total heat content of the substance, commonly measured in calories per mole, and dT is the corresponding increment in the absolute temperature. The units for C_p are then calories per mole by degree Kelvin.

At high temperatures ($T > 1200^\circ\text{K}$) accurate measurements of the differential quantities entering equation (1) are notoriously difficult to make and it is therefore hardly surprising to find lack of agreement between the specific heat results obtained by different observers and to find this even for the relatively more favourable case of measurements on pure metals; the differences between results being often considerably greater than the sum of the quoted experimental errors. This is illustrated in Figure 1.

Several methods have been employed for these measurements. (i) Conventional drop calorimetry; in this field the most extensive work was done by Jaeger and his collaborators in Holland, whose results, which extend to about 1700°K, have been widely accepted as representing true specific heats to 1% or better (see e.g. Kelley 1949). (ii) Vacuum drop calorimetry, used by Hoch and Johnston (1961) to extend

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the range of method (i) to about 3000°K. (iii) Pulse methods; the earliest variant of this method was due to Worthing (1918), whose procedure was extended and

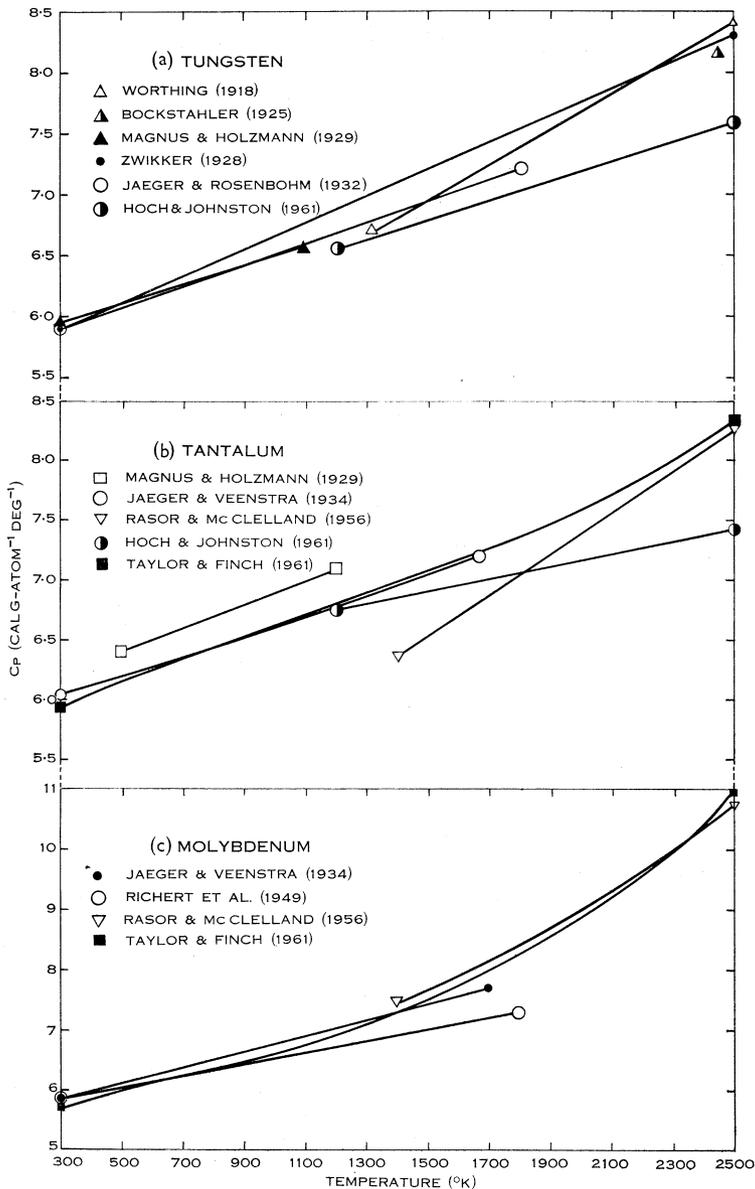


Fig. 1.—Published specific heat results for the metals tungsten, tantalum, and molybdenum.

simplified by Avramescu (1939) and was recently further improved by Wallace, Siddles, and Danielson (1960) and by Taylor and Finch (1961). (iv) A method based

on a theory published by Corbino (1911). So far this method appears to have been used only for tungsten, first by Smith and Bigler (1922), then by Bockstahler (1925), and last by Zwicker (1928).

Corbino's theory was employed for the present work. It requires the measurement of the amplitude of the temperature oscillations in a thin a.c. heated filament. Given conditions which are not very difficult to realize, use of the theory permits the reduction of errors due to heat losses from the specimen to below 0.5%, even at 2400°K. However, the temperature measurements are difficult to make because the theory demands that the amplitude of the temperature oscillation should always be very small relative to the mean temperature of the wire.

Working with tungsten wires, Smith and Bigler, Bockstahler, and Zwicker deduced the amplitudes of the temperature oscillations from the amplitude of the resulting oscillations of the thermionic emission current. These measurements did not yield very consistent results, not least because the dependence of the thermionic emission current on, for example, the microscopic surface structure of the wire and on even monomolecular layers of certain impurities and especially oxygen was not fully realized at that time (Herring and Nichols 1949).

Apart from these more basic difficulties, measurements on pure tungsten were in any case only practicable between about 2000 and 2400°K, and similarly restricted ranges would apply to other hard metals. Outside that range the emission current is either too small or too large to permit of satisfactory measurements.

Here the required data are obtained from measurements of light emission instead of thermionic emission. For measurements within the visible part of the spectrum and the very near infrared optical emissivities are not greatly affected by residual impurities and any surface irregularities likely to be of consequence will be detectable in general by ordinary microscopic investigations (de Vos 1953, 1954). With regard to the practicable range of measurements, it will be seen that measurements can be made from about 1250°K upwards without raising undue experimental difficulties. The upper limit for the measurements is set principally by the effects of the increasing volatilization of the wire material on the transmittance of the glass bulb enclosing the wire.

II. THEORY

(a) Corbino's Expression and its Application to Tungsten Wires

Corbino considered a long thin wire suspended in vacuum and heated to incandescence by a current due to an e.m.f. (from a source of effectively infinite impedance) having the form $E = E_0 \sin pt$. The temperature of the wire will then oscillate sinusoidally about a steady mean temperature T_a . Heat losses other than by radiation can be ignored in this case. Residual gas conduction is quite negligible provided the gas pressure is less than 1×10^{-6} mmHg (Worthing 1918). Conduction losses through the electrodes and supports of the heated wire are readily kept below 10% of the total heat loss and their effect can be independently corrected to 0.5% or better (Lowenthal 1962).

The radiation losses (total radiant emittance) depend on temperature and total emissivity of the wire material in accordance with a power law of the form sT^n where s and n are commonly constant over wide ranges of temperature. For hard metals values of n lie between about 4.0 and 5.5 (Rutgers 1958, p. 157). If the angular frequency p and the wire diameter d are chosen such that the oscillating component x of the temperature is always small relative to T_a , one can write

$$\begin{aligned} \text{Heat losses (in calories)} &= s(T_a + x)^n \\ &= sT_a^n(1 + nx/T_a + \epsilon). \end{aligned} \quad (2)$$

TABLE 1
VALUES OF TERMS ENTERING EQUATIONS (6), (7), AND (8) FOR
MEASUREMENTS ON A 0.005 CM DIAMETER TUNGSTEN WIRE
HEATED WITH 50 C/S CURRENT

Quantity	Value at 1600°K	Value at 2400°K
P_a (cal/s)	0.273	1.90
$2pc \times 10^3$ (rad/s) · (cal/deg)	70.4	81.1
$Q \times 10^3$ (cal s ⁻¹ deg ⁻¹)	0.933	4.29
$\tan \phi$, eqn. (7)	75.1	18.9
$\sin \phi$	0.9999	0.9985
x_0 , eqn. (6) (degK)	3.88	23.4 ₀
x_0 , eqn. (8) (degK)	3.88	23.4 ₃

Conditions are readily arranged such that $nx_0/T_a < 0.04$, where x_0 is the amplitude. The term ϵ is then less than 0.001 and can be omitted from (2) without affecting heat losses by more than 0.1% (see Table 1). The energy balance for a wire of heat capacity c (in cal/degK) is now

$$c \frac{dT}{dt} + sT_a^n \left(1 + \frac{nx}{T_a} \right) = \frac{E_0^2}{R_T J} \sin^2 pt, \quad (3)$$

where J has the usual meaning. But $dT = dx$ and also, since x is small, R_T , the wire resistance at temperature T , is equal to $R_{T_a} \cdot (1 + \beta x)$, where $\beta = (1/R)(dR/dT)$. Moreover, letting P_a be the mean power (in cal/s) dissipated in the wire, then $P_a = sT_a^n = E_0^2/2JR_{T_a}$. On using these transformations in (3), multiplying out, and retaining terms of the first order in x only, and finally writing $P_a(\beta + n/T_a) = Q$, one is left with

$$c \, dx/dt + xQ = -P_a \cos 2pt. \quad (4)$$

This is a standard type equation with the solution (apart from a transient term not important here)

$$x = x_0 \cos(2pt - \phi), \quad (5)$$

where

$$x_0 = (P_a/2pc) \sin \phi, \quad (6)$$

and

$$\tan \phi = 2pc/Q. \quad (7)$$

The conditions required for ϵ , equation (2), to be small will in general ensure that the phase angle ϕ is close to $\frac{1}{2}\pi$ so that $\sin \phi = 1$, the error being negligible. This is demonstrated in Table 1 for tungsten wires. Similar results could be obtained for wire diameters greater than 0.005 cm if p were appropriately reduced, which could be done with a suitably designed alternator (see e.g. Zwicker 1928).

Setting $\sin \phi = 1$ in equation (6) one gets for the heat capacity c

$$c = P_a/2px_0, \quad (8)$$

and therefore

$$C_p = \frac{A}{m} \cdot \frac{P_a}{2px_0}, \quad (9)$$

where m is the mass of the wire and A the atomic weight of the metal. The error in C_p due to all approximations made to derive equation (9) need not be greater than 0.3%, even at 2400°K, and is readily kept below 0.1% for temperatures below 2000°K. The magnitude of x_0 is here determined from the mean temperature of the wire, T_a , measured with an optical pyrometer, and from the ratio x_0/T_a measured photoelectrically.

(b) *An Expression for x_0/T_a .*

If light from the a.c. heated wire falls upon a photocell with linear characteristics and adequate frequency response, the photocurrent i_p will have a steady component i_a corresponding to T_a and superimposed an oscillating component i_s corresponding to x , so that $i_p = i_a + i_s$, corresponding to $T = T_a + x$. The dependence of i_p on T is given by

$$i_p = gT^{b(T)}, \quad (10)$$

where g is a constant depending largely on the voltage applied across the phototube and on the geometrical arrangement of phototube and wire. The exponent b is a function of temperature because the response characteristics of phototubes depend on the spectral quality of the radiation and so vary with temperature.

On substituting for i_p and T in (10) one obtains

$$\begin{aligned} i_a + i_s &= g(T_a + x)^{b(T)} \\ &= gT_a^{b(T)} \{1 + xb(T)/T_a + \epsilon'\}. \end{aligned} \quad (11)$$

Because $b(T) \approx 2n$ (see Fig. 3), ϵ' is greater than ϵ , equation (2), but is still readily kept small enough to be negligible here.

On separating the steady and oscillating components in equation (11) and neglecting ϵ' , one can write as sufficient approximations

$$i_a = gT_a^{b(T_a)}, \quad (12)$$

$$(i_s)_0 = gx_0 b T_a^{b(T_a)-1}, \quad (13)$$

so that x_0/T_a is given by

$$\frac{x_0}{T_a} = \frac{1}{b(T_a)} \cdot \frac{(i_s)_0}{i_a}, \quad (14)$$

where $b(T_a) = d(\ln i_a)/d(\ln T_a)$. If the value of $(i_s)_0$ is obtained from the a.c. voltage drop ΔV across a suitably chosen load resistor R_L , one has for measurements with an r.m.s. reading instrument

$$(i_s)_0 = 1.414\Delta V/R_L. \quad (15)$$

On substituting from equations (14) and (15) into (9), the specific heat of the wire material is now given by the equation:

$$C_P = \frac{A}{m} \cdot \frac{R_L}{2.828p} \cdot \frac{P_a \cdot i_a \cdot b(T_a)}{T_a \cdot \Delta V} \quad (16)$$

TABLE 2
THE METAL WIRES

	Nb	Mo	Ta I	Ta II	W I	W II
Diameter (cm)	0.0055 ₃	0.0050 ₅	0.0082 ₂	0.0051 ₀	0.0051 ₃	0.0051 ₃
Length (cm)	8.55	12.30	12.80	8.77	14.90	7.30
Mass* (g × 10 ³)	1.76 ₅	2.52 ₀	11.24 ₀	2.97 ₅	5.94 ₀	2.91 ₀
Resistivity at 300°K (ohm-cm × 10 ⁶)	15.5	5.90	13.60	14.05	5.75	5.75
Range of specific heat measurements	1471° -2259°K	1288° -2015°K	1256° -1955°K	1558° -2300°K	1267° -2038°K	1602° -2410°K

* Determined from weighings of known lengths of the wire.

III. THE METAL WIRES

Measurements were made on wires drawn from niobium, molybdenum, tantalum, and tungsten. Relevant data about these wires are listed in Table 2. The niobium and tantalum wires were kindly made available by the Fansteel Metallurgical Corporation, Chicago, Illinois, U.S.A., the molybdenum wire by Metallwerk Plansee, Reutte, Austria. Typical metal analyses supplied by the manufacturers are shown in Table 3.

The tungsten wire came from old stock. Spectrographic analysis showed it to be 99.9% pure; the residual impurities were probably tungsten carbides which are stable up to 2700°K (carbides could not be detected because the metal was sparked from graphite electrodes in air). An extra amount of only 0.05% of W₂C and WC is sufficient to explain the differences (+2% at 300°K, +5% at 2400°K) between the resistivities of this wire and of a carefully purified wire measured by Smithells (1952, see p. 71).

The impurities responsible for the higher resistivity of wire Ta II relative to Ta I were most likely interstitial oxygen atoms (Miller 1959). The oxygen content in wire Ta II could then have been somewhat greater than the limit shown in Table 3.

The great sensitivity of the electrical resistivity of metals to even very small concentrations of foreign atoms is well known. However, no such large effects should be expected on high temperature specific heat. This expectation is justified by the

very similar specific heat results for wires Ta I and Ta II. The slight difference between them (about 1%) is smaller than the experimental error in each set of measurements (see Section VI(a)).

Each metal wire was mounted under spring tension about 1.5 cm from the wall of an evacuated and gettered glass envelope, 5 cm in diameter. The estimated pressure after sealing was less than 1×10^{-6} mmHg. The inside surface of the bulb was sand-blasted except for a narrow strip just above the wire.* Tension on the wires was required to avoid sag and to prevent resonance vibrations which occur with a.c. heating. The roughening of the glass served to suppress internal specular

TABLE 3
TYPICAL ANALYSES FOR WIRES
(Supplied by the manufacturers)

Element	Upper Limits (%)		Element	Upper Limits (%)
(a) Niobium and Tantalum (Fansteel)			(b) Molybdenum (Metallwerk Plansee)	
Ta	0.08	99.90	Mo	99.93
Nb	99.7	0.05	Fe	0.01
Fe	0.02	0.01	C	0.01
Ti	0.02	0.01	O ₂	0.005
Zr	0.02	0.01	N ₂	0.001
Ni	0.01	—	H ₂	0.001
W	0.01	0.02	Distill. Residues	0.02
Si	—	0.01		
Mo	—	0.01		
C	0.02	0.015		
O ₂	0.05	0.015		
N ₂	0.05	0.005		

reflection. The length of each wire was such that even at the lowest temperature at which it was used a central part, at least 3 cm in length, remained effectively uninfluenced by end-loss of heat. Each wire was outgassed before the bulb was sealed. After sealing the wire was heated for upwards of 2 hr at the highest temperature at which it was still under tension and at which its resistance-temperature relationship remained reproducible. This temperature became the maximum temperature for the subsequent specific heat measurements.

IV. EQUIPMENT AND ELECTRICAL MEASUREMENTS

(a) Equipment

A schematic diagram of the equipment and the electrical connections is shown in Figure 2. The phototube PT, an R.C.A. multiplier type 7102, and the hot wire

*These bulbs were made for the author in the Development Section of Amalgamated Wireless Valve Co. Pty. Ltd., Rydalmere, N.S.W.. The valuable cooperation received from A.W.V. and especially from Mr. D. Miller during the experiments which led to the final design of the tube is here gratefully acknowledged.

tube, HWT, were surrounded by mild steel envelopes ST and SB respectively, which served for magnetic as well as for optical and mechanical shielding. The internal surface of tubes SP, T, and SB were blackened, and the arrangement was such that no extraneous light could enter. The envelope SB was provided with a 0.3 by 0.5 cm slot and was supported in a manner permitting fine adjustment of the position of this slot relative to the diaphragm D in three directions mutually at right angles.

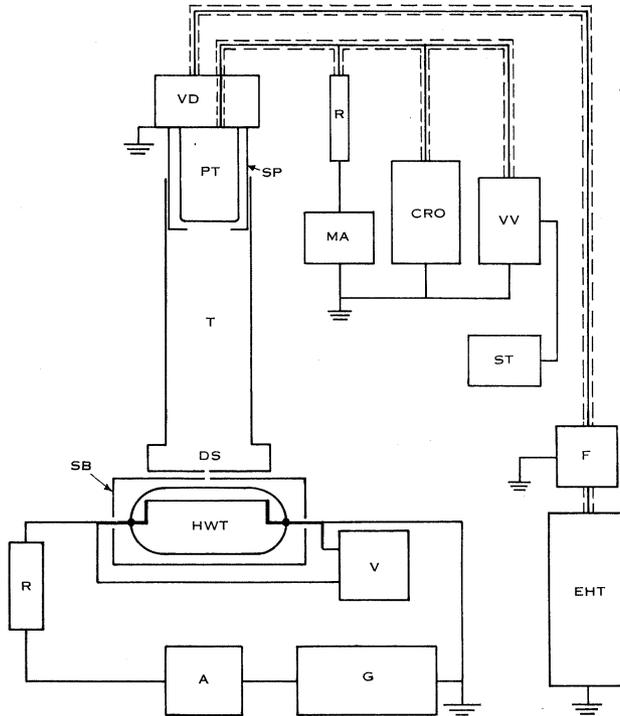


Fig. 2.—Schematic diagram of the equipment and the electrical connections. G, generator; V, voltmeter; A, ammeter; R, rheostat; HWT, hot wire tube; SB, mild steel shield; EHT, high voltage supply for phototube; F, filter to eliminate 100 c/s ripple; VD, voltage divider; PT, phototube; SP, mild steel shield for phototube; T, brass tube, 45 cm long, 5 cm diameter; DS, diaphragm and shutter; R, load resistor; MA, microammeter; CRO, cathode-ray oscilloscope; VV, vacuum tube voltmeter; ST, stabilized supply for meter VV.

It is here desirable to employ a phototube the spectral response of which should vary as little as possible with the temperature of the radiator. The Cs-O-Ag cathode of the type 7102 meets this requirement relatively better than other cathode materials normally available. On the other hand, Cs-O-Ag cathodes have a much lower quantum efficiency than the more blue-sensitive cathodes; but even so the type 7102 was found to have an adequate sensitivity for the present purpose.

The generator G consisted of shielded transformers selected for minimum distortion in their output. Only 1.5% of the output of 40 V was at higher frequencies than the 50 c/s fundamental. AVO type meters were used for the voltmeter V and the ammeter A, a Cambridge spot galvanometer served as microammeter MA. Instrument VV was an "Advac" type 77 vacuum tube multirange voltmeter which was connected across load resistor R, a 1.015 M Ω high stability carbon resistor.

All meters were carefully balanced and electrically shielded and readings were taken subject to recommended precautions (Smith and Armitage 1960). The equipment was situated in the annex of a temperature-controlled room, where during these measurements, the temperature was always within a degree of 20°C.

(b) Quantities to be Measured

The specific heat (in cal/g-atom.degK) of the material of each wire was calculated from the equation

$$C_p = 1.278 \times 10^{-5} \frac{A}{m} \cdot \frac{P'_a}{T_a} \cdot \frac{i'_a b(T_a)}{\Delta V'} \quad (17)$$

This equation was derived from (16) by making the following substitutions: $R_L = R$ (Fig. 2) = 1.015 $\times 10^6 \Omega$; $p = 100\pi = 314.16$ rad/s; $P_a = JP'_a = 4.1860P'_a$ watts; also $i_a = 0.0997 \times 10^{-6} i'_a$ amperes and $\Delta V = 2.128\Delta V'$ volts, where i'_a and $\Delta V'$ are respectively the microammeter readings expressed in microamperes and the "Advac" meter readings in volts (r.m.s.), each corrected for scale errors of the meter. The factors 0.0997 and 2.128 account in each case for the effects of other circuit components.

(c) Electrical Measurements

The first parameters to be measured for each wire were the mean power dissipation P'_a and the mean wire temperature T_a both as functions of the heating current. The measurement of T_a will be discussed in Section V. The power P'_a was calculated from readings of meters A and V. These were periodically checked against sub-standard dynamometers, the comparison being made with the dynamometers added to the circuit, Figure 2, so that the effect on the AVO meters of the residual harmonic content on the supply from the generator G could be taken into account.

Small corrections to P'_a were also required to compensate for the voltage drop across the supporting structure of the hot wire and also for end-loss of heat (Lowenthal 1962). When fully corrected, P'_a was estimated as accurate to 0.7%.

The power measurements were followed by the photoelectric measurements when i'_a and $\Delta V'$ were determined again as functions of the heating current. At the same time $b(T_a)$ was measured using as many combinations as practicable of photocurrent ratios i_{a2}/i_{a1} corresponding to temperature ratios T_{a2}/T_{a1} with $T_{a2} - T_{a1}$ between 70 and 150 degK; $b(T_a)$ being calculated in each case from the relation $\log(i_{a2}/i_{a1})/\log(T_{a2}/T_{a1})$, where T_a is the average temperature between T_{a1} and T_{a2} . Values of $b(T_a)$ were then plotted against T_a and a smooth graph drawn through the points (Fig. 3); final values of $b(T_a)$ being taken from this graph.

With the pyrometry accurate to 0.5% (see below) and $T_{a2} - T_{a1}$ limited to 150 degK at most, the first plot of b versus T_a was normally subject to substantial scatter. To minimize this scatter, b was recalculated after an appropriate smoothing of the heating current versus wire temperature curve (Fig. 5). The points shown in Figure 3 are a typical set of these recalculated values. The extent of smoothing required to obtain them was at most 0.3% of T_a and so was well within the limits of error of the pyrometric measurements. For light from tungsten wires $b(T_a)$ can be calculated, see Subsection (d).

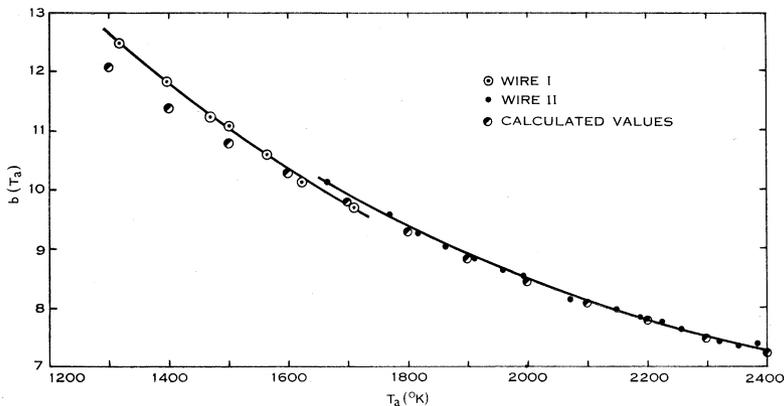


Fig. 3.—Values of $b(T_a)$ as function of T_a for an R.C.A. photomultiplier type 7102 illuminated by light from tungsten wires. The difference between the results for wires W I and W II is due to drift in the spectral sensitivity of the phototube; measurements on wire W I were made several weeks after measurements on wire W II. A drift in $b(T_a)$ was always accompanied by a compensating drift in $i_a/\Delta V$ so that calculated C_p values remained unaffected.

The photoelectric measurements on each wire were made in two overlapping runs, the first one covering the lower and the second one the upper section of the temperature range listed in Table 2; for example, for wire W I the two sections covered the ranges 1267–1679°K and 1624–2038°K respectively. For measurements at the relatively lower temperatures, the aperture of the diaphragm D (Fig. 2) was commonly near 1.5 cm; for the run at the higher temperatures the aperture was near 0.5 cm. During each run the diaphragm setting was kept constant, of course. Each run was repeated three to six times and altogether the number of measurements of i'_a and $\Delta V'$ per wire was never less than 150 and the number of current ratio measurements was never less than 100. Instrument readings were again corrected for scale errors and the readings of the "Advac" meter were also corrected for contributions from phototube noise and for residual circuit noise with these latter corrections reaching 3% at most. With a 50 c/s current heating the metal wire, the light oscillations had a frequency of 100 c/s. Contributions from other than 100 c/s (50 c/s pick-up and harmonics) were measured with a wave analyser as always less than 2% of the 100 c/s signal, and so had no significant effect on the meter readings. The mean of $i'_a/\Delta V'$ values at each temperature as finally used for the calculation of C_p was assessed as accurate to 0.7%.

The constancy of the response of the phototube during each run was checked by frequent remeasurements of an $i_a'/\Delta V'$ ratio at a conveniently selected temperature. In general, no noticeable changes over periods of several hours were observed given normal precautions, including adequate "warming up" periods. Over several days the sensitivity of the tube did sometimes drift by 1–2% upwards or downwards.

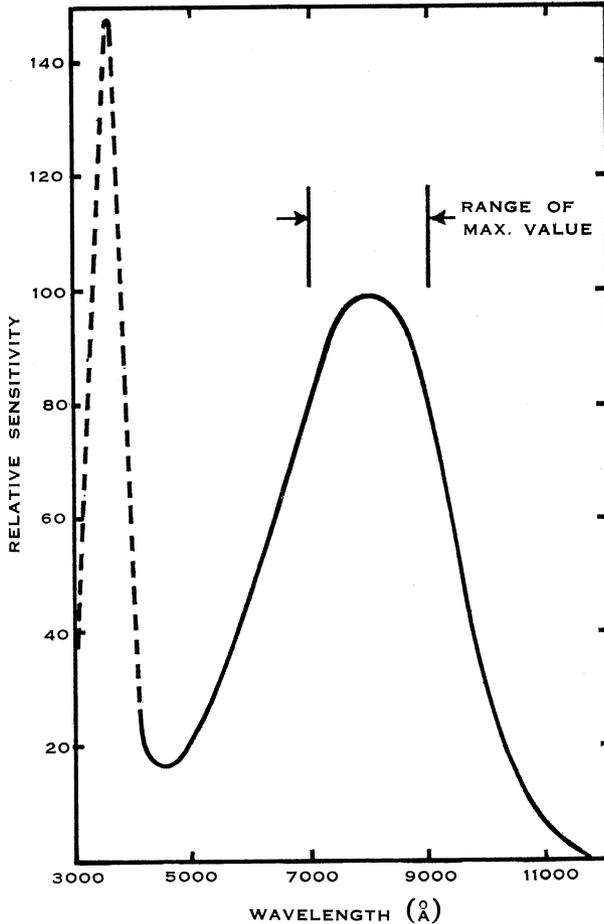


Fig. 4.—Relative spectral sensitivity of a typical type 7102 R.C.A. photomultiplier (from R.C.A. catalogue).

Such drifts caused changes in both $i_a/\Delta V$ and also in b for a given geometry and temperature (see Fig. 3), but the product $i_a \cdot b(T_a)/\Delta V$ (equation (16)) remained constant.

(d) *The Calculation of $b(T_a)$ for Tungsten Wires*

For tungsten wires data is available to calculate the relation between b and T_a . Other hard metal wires can be expected to have similar b versus T_a relationships

because hard metal wires have broadly similar light emission characteristics (Rutgers 1958). For tungsten wires one has

$$\ln\left(\frac{i_{a2}}{i_{a1}}\right) = \frac{(I'_{\text{P}})_{T_{a2}}}{(I'_{\text{P}})_{T_{a1}}} = \frac{\int_0^{\infty} [(I_{\lambda T_{a2}})_{\text{W}} \cdot S_{\lambda} \cdot t_{\lambda}] d\lambda}{\int_0^{\infty} [(I_{\lambda T_{a1}})_{\text{W}} \cdot S_{\lambda} \cdot t_{\lambda}] d\lambda}. \quad (18)$$

The term $(I'_{\text{P}})_{T_{\text{a}}}$ stands for the radiant energy absorbed at the photocathode when the mean temperature of the radiating tungsten wire is T_{a} . The factors under the integral sign are firstly $(I_{\lambda T_{\text{a}}})_{\text{W}}$, the radiant emittance from tungsten wires as function of wavelength and temperature (see e.g. de Vos 1953, 1954). The remaining factors are the spectral sensitivity of the receiver, S_{λ} , and the transmittance of the light path, t_{λ} . In the visible and near infrared region the transmittance of glass and air is effectively independent of the wavelength (see e.g. Forsythe 1954, p. 512). Accordingly, t_{λ} will cancel from (18) certainly for photocathodes which show little or no response at wavelengths below 4000 Å. Using the relative spectral response of the average R.C.A. multiplier phototube, No. 7102, (Fig. 4), and de Vos's values for $(T_{\lambda T})_{\text{W}}$, $\ln(i_{a2}/i_{a1})$ was computed from equation (18) by numerical integration. Values of $b(T_{\text{a}})$ could then be calculated. They have been added to Figure 3. The agreement between the calculated and measured values of $b(T_{\text{a}})$ is quite satisfactory; the increasing differences below about 1600°K are very likely due to the infrared sensitivity of the phototube used for these measurements decreasing a little more quickly than that of the average tube (Fig. 4).

V. TEMPERATURE MEASUREMENTS

(a) Pyrometry

The temperatures of the metal wires were measured with a Leeds and Northrup optical pyrometer which had been calibrated just prior to these measurements at the Australian National Standards Laboratory, Sydney, to an accuracy of 0.4%. The calibration was made on the International Practical Temperature Scale of 1948 (see e.g. Stimson 1961). Readings were taken in accordance with a procedure described by Jones (1961).

The pyrometer readings obtained with the two tungsten wires are shown in Figure 5; each point on the curve represents the average of four to eight independent measurements. Similar sets were obtained for the other metals. The smoothed pyrometer readings were estimated as accurate to 0.5%.

(b) Corrections

(i) *The Effect of Light Transmission.*—The pyrometer readings were corrected for the loss in light intensity (8%) at the thin glass envelope surrounding the hot wire. The light reaching the phototube had to pass two glass envelopes; the transmittance t_{PT} being then 0.85 (Harrison 1960, p. 45). The phototube therefore

“saw” the wire at a lower temperature X_{PT} (say) than its true temperature where the relation between X_{PT} and T is given by the equation

$$1/X_{PT} - 1/T = (\lambda_{PT}/c_2) \ln t_{PT}. \tag{19}$$

Here $c_2 = 1.438$ cm deg and λ_{PT} is the effective wavelength at which the R.C.A. type 7102 operates.

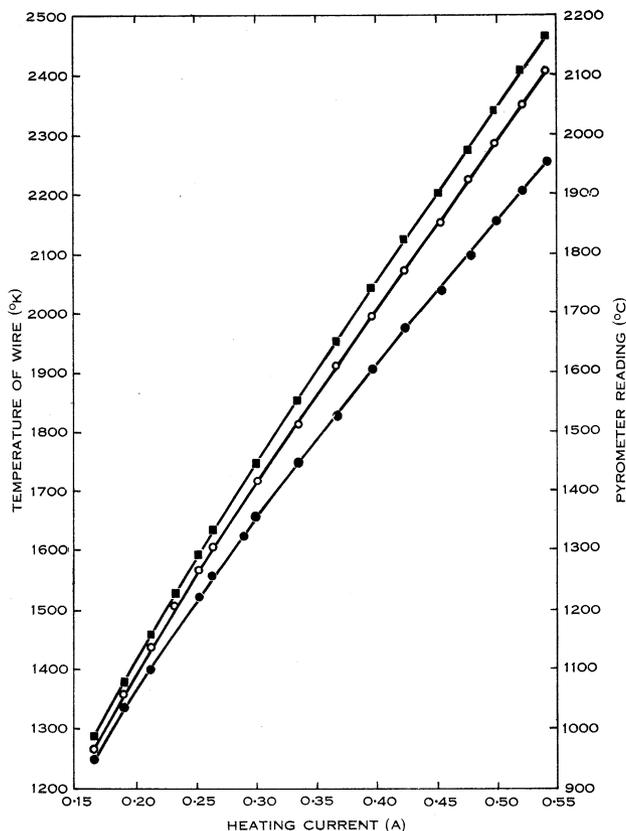


Fig. 5.—Temperature versus heating current curves for the tungsten wires W I and W II.

● Pyrometer readings (right-hand scale); ■ true temperature of wire (left-hand scale); ○ temperature of wire as seen by phototube (left-hand scale).

The effective wavelength is defined as the value of λ at which the ratio of the spectral radiation intensities for two radiator temperatures T_1 and T_2 is equal to the ratio of the respective brightness integrals as seen by the receiver (see e.g. Jones 1961). Expressing the spectral radiation intensities in accordance with Wien's law (the result is 0.003% low at 1300°K and 0.3% low at 2500°K) and using the

brightness integrals for tungsten light falling upon the photocathode (equation (18)), the equation for $(\lambda_{PT})_W(T)$ takes the form

$$(\lambda_{PT})_W(T) = \frac{c_2(1/T_1 - 1/T_2)}{\ln [(I_P)_{T_2}/(I_P)_{T_1}]_W}, \quad (20)$$

where T is the average temperature between T_1 and T_2 . Values of $(\lambda_{PT})_W(T)$ obtained from (20) are 9007, 8600, and 8311 Å at 1350, 1850, and 2350°K respectively.

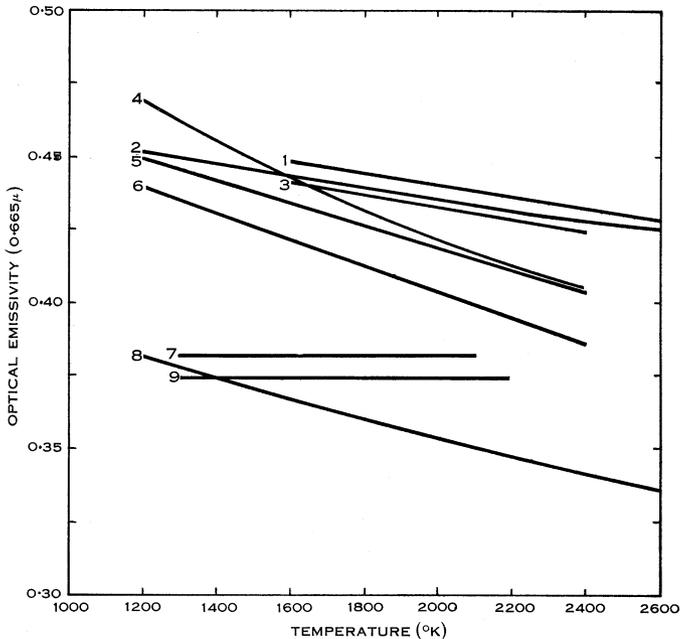


Fig. 6.—Optical emissivities at $\lambda = 0.665 \times 10^{-4}$ cm for tungsten, tantalum, molybdenum, and niobium. Tungsten—1: de Vos (1953); 2: Worthing (1917); 3: Larrabee (1959). Tantalum—4: Malter and Langmuir (1939); 5: Worthing (1926); 6: Wahlin (see Forsythe 1954). Molybdenum—7: Whitney (1935); 8: Worthing (1926). Niobium—9: Whitney (1935).

The left-hand side of equation (19) is not very sensitive to changes in λ_{PT} . For example, on using $(\lambda_{PT})_W = 8500$ Å (0.85×10^{-4} cm) independent of temperature instead of the values quoted above, the change in the difference $X_{PT} - T$ is only 1.2 degK at 1300°K and -1.3 degK at 2400°K. Radiation from the three other metals yield closely similar values of λ_{PT} to that for tungsten radiation. The difference is relatively greatest for niobium light but even then on setting $(\lambda_{PT})_{Nb} = (\lambda_{PT})_W = 0.85 \times 10^{-4}$ cm, again independent of temperature, the error introduced into (5) was calculated as 3 degK at most. It was then decided to use $\lambda_{PT} = 0.85 \times 10^{-4}$ cm equally for all four metals. Errors introduced by this simplification are evidently much smaller than errors in the pyrometry and it seemed justified therefore to ignore them.

(ii) *Emissivity Corrections*.—Published emissivities for the four metals here used are reproduced in Figure 6. The good agreement between Worthing's and

Larrabee's results for tungsten is noteworthy if only because Larrabee's tungsten was certainly very much purer than that used by Worthing. (The small effect of impurities on optical emissivity was also noted by Malter and Langmuir (1939)). Worthing's results were used up to 1600°K and then those of Larrabee. Had de Vos' results been used instead, the temperature range 1600–2400°K would have been shortened by just under 0.4%.

For tantalum the linear average of the three published values was used. If any one of the published sets had been chosen instead, the change in the length of the temperature range 1200–2300°K would have been 0.7% at most. For molybdenum, Worthing's values were used; for niobium only Whitney's values were available. Whitney obtained $e_\lambda(T)$ constant for both molybdenum and niobium. It seems more probable, though, that $e_\lambda(T)$ falls with rising temperatures. If this is so, the use of Whitney's values for niobium could well have shortened the temperature range for this metal, thus leading to higher specific heats than the true values.

It is estimated that the overall probable error in T_a due to the uncertain knowledge of optical emissivities was about 0.5% for tungsten but probably over 1% for niobium. The errors for molybdenum and tantalum would lie between these two extremes.

VI. RESULTS

(a) C_p versus T curves

Using data obtained from tungsten wire W I for specimen examples, one has $A = 184.0$, $m = 5.95 \times 10^{-3}$ g (see Table 2) so that equation (17) now becomes

$$C_p = \frac{0.3952 P'_a \cdot i'_a b(T_a)}{T'_a \Delta V'} \quad (21)$$

The C_p values calculated from (21) are entered as full squares in Figure 7(d). The remaining squares in this figure were obtained from measurements on tungsten wire W II. Results from wires W I and W II are seen to effectively overlap.

Results for niobium, molybdenum, and tantalum, obtained in a similar manner as those for tungsten, are entered in Figures 7 (a)–(c). For each metal results of earlier work are shown for comparison. For convenience the present results have been tabulated (Table 4). The entries for tantalum are those obtained with wire Ta I; results above 1960°K were extrapolated parallel to those for wire Ta II. This was done because the results for Ta I were considered to be more accurate.

(b) An Estimate of Errors

The relatively largest part of the error in C_p is due to effects of the uncertain knowledge of optical emissivities on T_a and $T_{a2} - T_{a1}$. For example, the temperature of molybdenum has here been calculated from Worthing's emissivities. Had Whitney's values (see Fig. 6) been used instead, the result would have been the same at 1300°K but 17.7 degK higher at 2100°K; these 17.7 degK are just under 0.9% of 2100°K; but they are 2.2% of the 800 degK range. Specific heats calculated from data employing Whitney's emissivities would therefore be over 3% higher at 2100°K

than the values listed in Table 5. Errors resulting from the uncertain knowledge of

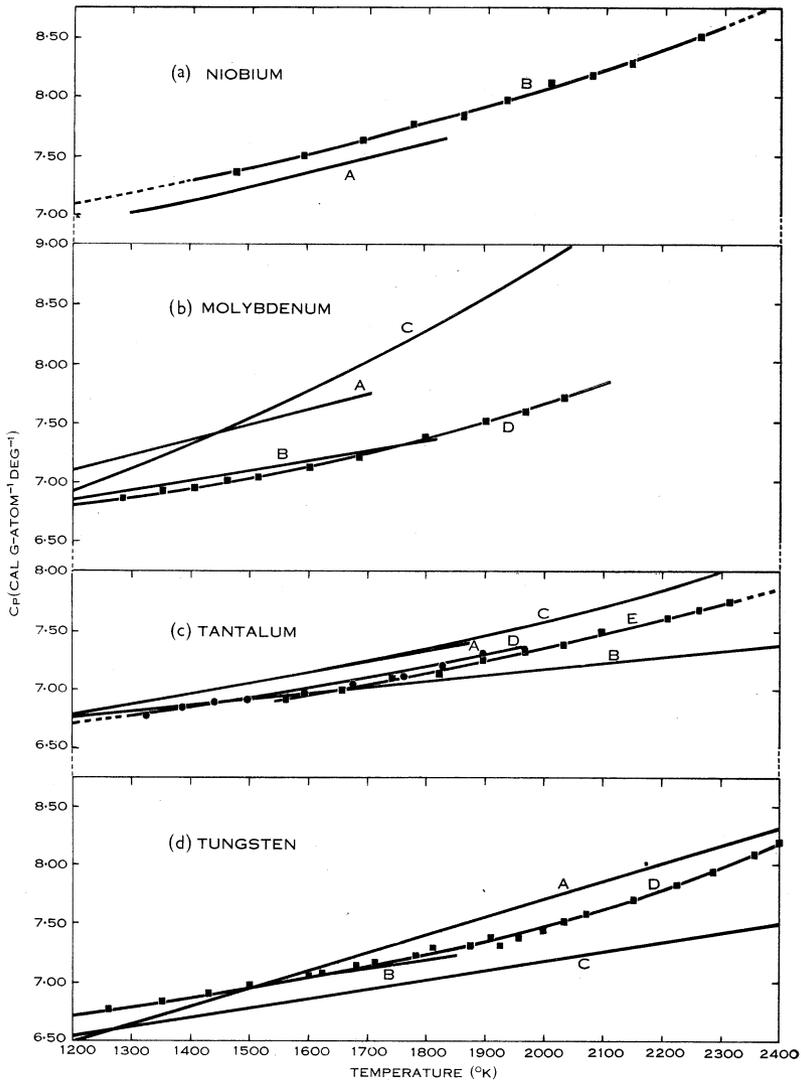


Fig. 7.—Results of the specific heat measurements; niobium: curve B; molybdenum: curve D; tantalum: Ta I, curve D; Ta II curve E; tungsten: curve D. The results shown for comparison are: Niobium—A, Jaeger and Veenstra (1934). Molybdenum—A, Jaeger and Veenstra (1934); B, Richert, Beckett, and Johnston 1949; C, Taylor and Finch (1961). Tantalum—A, Jaeger and Veenstra (1934); B, Hoch and Johnston (1961); C, Taylor and Finch (1961). Tungsten—A, Worthing (1918). B, Jaeger and Rosenbohm (1932); C, Hoch and Johnston (1961).

the emissivity of molybdenum were then estimated as 0.5% near 1300°K rising to 1.5% near 2100°K.

For tantalum the position is somewhat more favourable. Uncertainties introduced by errors in T_a and $T_{a2}-T_{a1}$ were estimated as rising from 0.5% near 1300°K to 1.5% at 2300°K; for tungsten they were probably little more than 1% even

TABLE 4
SPECIFIC HEATS, C_p , OF NIOBIUM, MOLYBDENUM, TANTALUM, AND TUNGSTEN
(cal g-atom⁻¹ degK⁻¹)

T(°K)	Nb	Mo	Ta	W	T(°K)	Nb	Mo	Ta	W
300	6.03*	5.90*	6.03*	5.91*	1800	7.80	7.49	7.18	7.24
1200	(7.08)†	6.83	6.69	6.72	1900	7.95	7.64	7.28	7.35
1300	(7.18)	6.92	6.76	6.80	2000	8.10	7.81	7.39	7.47
1400	7.29	7.01	6.83	6.88	2100	8.25	8.00	7.51	7.62
1500	7.40	7.11	6.91	6.96	2200	8.43		7.63	7.79
1600	7.53	7.22	6.99	7.05	2300	8.61		7.76	7.96
1700	7.66	7.35	7.08	7.14	2400	(8.82)		7.89	8.16

* From measurements of Jaeger and co-workers.

† Figures in brackets signify extrapolations by more than 100 degK.

at 2400°K. Measurements on niobium, on the other hand, were subject to the relatively greatest uncertainties because its optical emissivity is less well established

TABLE 5
VALUES OF C_E/T^* AND OF dC_V/dT † FOR NIOBIUM,
MOLYBDENUM, TANTALUM, AND TUNGSTEN
(cal g-atom⁻¹ degK⁻²)

Metal	$10^4 C_E/T$	$10^4 dC_V/dT$		
		1300°	1800°	2300°
Mo	5.1	4.0	6.0	—
W	3.6	4.0	4.5	6.0
Nb	20.5	5.5	8.0‡	11.0‡
Ta	13.0	4.0	5.0	7.0

* Measured at liquid helium temperatures; results quoted by P. H. Keesom and N. Pearlman (1956).

† C_V was calculated from equation (23) using the C_p values in Table 7 and published values of α_L and $(V/k_T)_{300}$.

‡ This steep rise in dC_V/dT could be due to errors in the temperature measurements (see text).

than that of the other three metals. If the true emissivity of niobium should fall with rising temperatures, similarly to Worthing's values for molybdenum, the specific heat could at 2250°K be well over 3% lower than the value here reported. The error in the specific heat of niobium due to the uncertain knowledge of the optical emissivity of this metal is then estimated as 1% at 1500°K rising to 3% at 2250°K.

In addition to the errors due to the uncertain knowledge of the temperature of the wire there are those given earlier in the text; power: 0.7%; pyrometry: 0.5%; $i_a/\Delta V$: 0.7%. The uncertainty in the results for i_{a2}/i_{a1} were estimated as 0.4%, the error in m , the mass of the wire, as 0.3%, and effects due to variations in the supply frequency and due to uncertainties in the measurement of the circuit parameters referred to when discussing equation (17) were estimated as 0.7%. Adding these figures in quadrature leads to a total of about 1.4%.

Finally, there are the systematic errors arising from the approximations in the treatment of heat losses (equations (2), (8), (11), and (13)) and from the approximations in the calculation of the effects of light transmission on the temperatures "seen" by the phototube. Each of these errors was estimated as 0.3% at most. Systematic errors due to contributions from harmonics of the 100 c/s signal (see Section IV(c)) were estimated as less than 0.1%.

The estimated overall errors are then: niobium: 2.5% at 1500°K rising to possibly over 4% at 2250°K, the C_p values here given being then more likely too large than too small—molybdenum: 2% to 1700°K and 3% at 2100°K; tantalum: 2% to 2000°K and 2.5% at 2300°K; tungsten: 1.7% to 2000°K and 2.0% at 2400°K.

(c) Comparisons with Earlier Work

Referring back to Figure 7 it is evident that agreement with the most recently obtained results (Hoch and Johnston 1961; Taylor and Finch 1961) is far from satisfactory, especially above 1700°K. Up to 1700°K the drop calorimetry results of the Dutch workers are available for comparison. Here it is only for molybdenum that the Dutch results differ appreciably from the present results. The gradients of the C_p versus T curves obtained by Jaeger and his co-workers are, however, in every case nearly identical with the gradients obtained here. The significance of dC_p/dT in the evaluation of specific heat results will be considered in the following section.

VII. DISCUSSION

The measured specific heat C_p of a metal can be written

$$C_p = C_v + \frac{\alpha^2 V}{k_T} \cdot T, \quad (22)$$

where C_v is the specific heat at constant volume, α is the cubical expansion coefficient of the metal, V is the atomic volume, and k_T is the isothermal compressibility.

A full discussion of C_v may be found in standard texts or review articles (see e.g. Blackman 1955). Here it is sufficient to note that for metals C_v is not commonly constant at high temperatures as predicted by lattice theory* but increases linearly with T on account of the electronic contributions to the lattice heat (see also Mott and Jones 1936, p. 131). Above the Debye temperature the thermal expansion

* Anharmonic contributions to C_v are here ignored. For transition metals they are probably in most cases much smaller than electronic contributions (see e.g. Mott and Jones 1936, p. 12).

coefficient of metals also increases approximately with the first power of T (Nix and MacNair 1941; and for the metals here measured Edwards, Speiser, and Johnston 1951; and Smithells 1952). The compressibility has not yet been measured successfully at high temperatures and it is necessary, therefore, to employ approximations to calculate $C_p - C_v$ from equation (22). An approximation most recently used by Myers (1960) is based on the assumption that the ratio V/k_T is independent of temperature (see also Eucken and Dannohl 1934). Equation (22) can then be written

$$C_p = C_v + A\alpha^2 T, \quad (23)$$

where $A = V/k_T$. According to (23) dC_p/dT will increase with T^2 whenever α increases with T ; dC_v/dT being assumed constant.

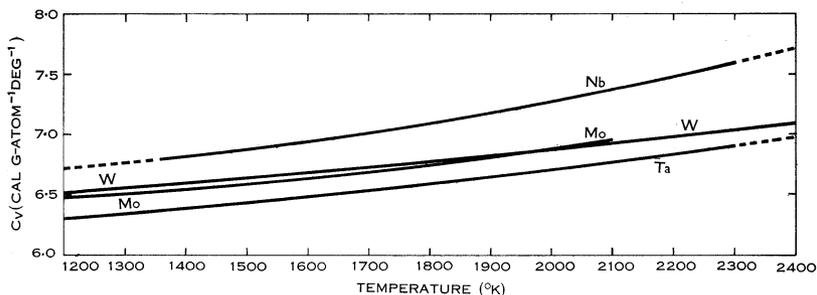


Fig. 8.—Summary of results for C_v .

The thermal expansion coefficients of the metals here measured are less than $1 \times 10^{-5} \text{ degK}^{-1}$, even at 2000°K . For these small values of α the difference $C_p - C_v$ is still only a few percent of C_p even at 1500°K . For example, for tungsten $(C_p - C_v)/C_p$ is 0.01 at 300°K , is still less than 0.05 at 1500°K , and it is not until 2200°K that $(C_p - C_v)/C_p$ exceeds 0.10 . Figure 7 shows that the four C_p versus T curves are effectively linear up to about 1600°K ; it is only as T rises further that the non-linear character of these curves becomes increasingly apparent.

It should still be mentioned that in all cases where measurements on a metal extend to temperatures exceeding about $0.8T_m$, T_m being the absolute melting temperature, C_p may be further increased as a consequence of the creation of vacancies in the crystal lattice (see e.g. Feder and Novick 1958). This effect is not important here since the temperature $0.8T_m$ is above the upper limit of each one of the present series of measurements.

One can calculate C_v for all four metals from equation (23) using the results in Table 5 for C_p and calculating α from published values for the linear thermal expansion coefficient α_L (Edwards, Speiser, and Johnston 1951; Smithells 1952) since for these isotropic metals $\alpha = 3\alpha_L$. The term V/k_T is assumed to remain unchanged at its 300°K value which is known (Forsythe 1954). The results are plotted in Figure 8. For tantalum and tungsten dC_v/dT is nearly constant; for niobium and to a lesser extent for molybdenum there is a significant rise but the C_p values for niobium could well have been overestimated here (see Section V(b)). One would be justified, therefore, to assign at least some of the rise in dC_v/dT for

niobium to the result of errors in C_p ; dC_V/dT is then nearly constant for all four metals. The slight increase with temperature could be a true rise but it may also be merely a consequence of errors in the measurements of C_p and in the calculation of C_V .

In Table 5 the gradients of these C_V curves are compared with values of C_E/T as measured at liquid helium temperatures, C_E being the electronic specific heat on the assumption of a degenerate electron gas (Mott and Jones 1936). Allowing for the uncertainties in dC_V/dT as just discussed, the agreement between this term and C_E/T is satisfactory for molybdenum and tungsten. For niobium and tantalum, this is not so; but then for the latter two metals the results for C_E/T obtained at very low temperatures may not apply at higher temperatures (Wilson 1954, p. 150).

Clusius and his co-workers (Clusius and Losa 1955; Clusius, Franzosini, and Piesbergen 1960) measured C_E/T for niobium and tantalum between 15 and 300°K, using a procedure claimed to be especially applicable for this range. Their results (in cal g-atom⁻¹ degK⁻²) were Ta: 7.65×10^{-4} and Nb: 5.3×10^{-4} , which is in much better agreement with the corresponding results for dC_V/dT than the C_E/T values shown in Table 5.

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