ATOMIC HEATS OF TUNGSTEN AND OF CARBON AT INCANDESCENT TEMPERATURES.

By A. G. Worthing.

Historical Survey.

Of late years great interest has been manifested in the question of atomic heats, particularly at very low temperatures, this interest being especially stimulated because of applications of the quantum theory which have been made in explaining results. Einstein[1] was the first to offer a theory on this basis which could be quantitatively tested. He assumed the energy of a solid to be entirely due to atomic vibrations, having characteristic frequencies, depending on the elastic properties and associated with the reststrahlen of infra-red measurements. The number of such vibrations, or the number of degrees of freedom, was taken as three times the number of atoms in the body. On assigning to these degrees of freedom the mean energies of a linear oscillator in accord with the quantum hypothesis, he obtained for the atomic heat of a substance,

$$(1) \qquad C_v = 3Nk\frac{\dfrac{h^2\nu^2}{k^2T^2}e^{h\nu/kT}}{e^{h\nu/kT}-1} = 3Nk\frac{\dfrac{\theta^2}{T^2}e^{\theta/T}}{e^{\theta/T}-1},$$

in which the various symbols have the meanings usually associated with them in quantum theory (see Table I.). At high temperatures C_v approaches the value $3Nk$ in accord with Dulong and Petit's law. With decreasing temperatures the equation leads to lower values and finally to zero for $T = 0° K$. At low temperatures observed variations were qualitatively accounted for but not quantitatively. Nernst and Lindemann[2] followed with an empirical equation much like Einstein's, which quantitatively fitted the data quite well. Later Debye[3] developed a theory which has been extraordinarily successful in predicting values for atomic heats. His procedure differed from Einstein's particularly in that he assumed a solid to behave as a continuum having all of, and only, the $3N$ lowest vibration frequencies possible in such an elastic

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[1] Ann. d. Phys., 22, p. 180, 1907; Wien, Neuere Probleme der theoretischen Physik, Chap. II.

[2] Zeit. f. Elektroch., 17, p. 817, 1911.

[3] Ann. d. Phys., 39, p. 789, 1912; Wien, Neuere Probleme der Theoretischen Physik, Chap. II.

medium. At about the same time Born and Karman[1] also presented a theory differing from Debye's chiefly in that they assumed a solid to consist of a space lattice of atoms, with a similarly limited number of frequencies which were likewise dependent on the elastic properties of the medium. Both theories predicted a variation of the atomic heat as the third power of the temperature in the neighborhood of absolute zero, but at somewhat higher temperatures the predicted values deviate from each other. In fact the Born and Karman theory, as shown by Born,[2] at the higher temperatures predicts the same results as are expected according to Einstein's theory. The question as to which theory fits the data best in this region is still unsettled.

TABLE I.

Quantities and Symbols.

Symbol.	Quantity.
C_v	Atomic heat under constant volume.
C_p	Atomic heat under constant pressure.
T	Temperature.
N	Number of atoms per gram-atom.
N'	Number of electrons per gram-atom.
ν	Frequency of radiator.
h k	Radiation constants employed in quantum theory.
θ	Characteristic temperature.
V	Potential drop along filament.
I	Current through filament.
R	Resistance of filament.
t	Time elapsing after the sudden change in current through the filament.
m	Mass of filament.
c_p	Specific heat under constant pressure.
$f(T)$ $F(R)$	Rate of radiation of energy by the filament.
P	Pressure.
v	Atomic volume.
α	Linear thermal expansion coefficient.
K	Compressibility.
T_s	Melting-point temperature.

See Table II. for quantities and symbols relating to Corbino's method.

To some extent contesting the application of the quantum theory, there is the agglomeration theory of Richarz's[3] which was put forth somewhat earlier than was Einstein's. In this theory the variations in atomic heat were ascribed to the changes in the number of degrees of

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[1] Phys. Zeit., 13, p. 297, 1912; 14, p. 15, 1913. See also Thirring, Phys. Zeit., 14, p. 867, 1913; 15, pp. 127 and 180, 1914.

[2] Ann. d. Phys., 44, p. 605, 1914.

[3] Marl. Ber., p. 61, 1904; p. 187, 1906; Zeit. f. anorg. Chem., 58, p. 356; 59, p. 146, 1908; Wigand, Jarh. d. Rad. u. Electro., 10, pp. 68–76, 1913.

freedom which came with the associating of two or more atoms into a single oscillating unit. Richarz and others[1] were quite successful in explaining qualitatively, in addition to the main variations of atomic heat at low temperatures, certain other variations for a given substance depending on the allotropic state, the effect of changes in density at a given temperature depending on the treatment of the material, the changes in going from one substance to another having a different atomic volume, etc. Further on this basis Benedicks[2] and Compton[3] have attempted quantitative verifications. Their equations, however, depend on arbitrary constants. In this respect they differ from the equations of Debye and of Born and Karman, which except for the arbitrary constants of the generally accepted Planck equation, are otherwise free from such arbitrary constants.

There should also be mentioned as more recent theories that by Callendar[4] based on his radiation formula, and that by Tolman[5] based on his theory of similitude.

At the higher temperatures, these theories, excepting possibly the one originated by Tolman, predict the value expected according to the older theory of equipartition of energy among the various degrees of freedom. For the atomic heat under the condition of a constant volume change this is $5.95 \frac{\text{calories}}{\text{gram-atom deg.}}$, that is, three times the gas constant of the kinetic theory. All actual measurements of atomic heat are carried out under conditions of constant pressure and it is therefore necessary to make a correction for the change to the condition of constant volume. This involves the determination of elastic constants, determinations which are very difficult under certain conditions as to temperature. After all corrections of such a nature have been made, there are found many substances which at moderately high temperatures, some even at room temperatures, possess greater atomic heats than these theories predict. Suggestions accounting for this increase beyond $5.95 \frac{\text{calories}}{\text{gr. atom deg.}}$ have not been lacking. However, none of them have been put in such a form as to permit of quantitative tests. Exactly what these suggestions are

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[1] (*a*) Richarz, *l. c.*
(*b*) Wigand, Ann. d. Phys., 22, p. 64, 1907.
(*c*) Schlett, Ann. d. Phys., 26, p. 201, 1908.
(*d*) Dewar, Proc. Roy. Soc., 89*A*, p. 158, 1913.
(*e*) Bronsted, Zs. f. Elektrochem., 20, p. 554, 1914; Fort. d. Phys., 70, II, p. 567, 1914.

[2] Ann. d. Phys., 42, p. 133, 1913.

[3] Phys. Rev., 6, p. 377, 1915. See also criticism by Schwers, Phys. Rev., 8, p. 117, 1916.

[4] Phil. Mag., 26, p. 787, 1913; 27, p. 870, 1914.

[5] Phys. Rev., 4, p. 145, 1914.

will be considered later in discussing the results obtained in the present paper.

Inasmuch as the factors which are active in producing these unexpected high values of atomic heat must naturally have some influence in the low temperature range, it would seem natural that the finally accepted theory must be capable of explaining the facts of the entire temperature range. For a more definite test of these theories and suggestions, more data at high temperatures are needed. Much work at moderately high temperatures has been done. However, at the temperatures which may be obtained in incandescent lamps very little work has been done though at such temperatures the theoretical applications would seem to be quite important. Tungsten naturally offers special favorable properties convenient for such tests because of its high melting point and its relatively low rate of vaporization. Carbon likewise because of its high melting point is attractive, but on the whole it is not so favorable because of its much greater rate of vaporization.

In this connection there are to be noted the works of Corbino[1] and of Pirani.[2] Corbino developed a method for measuring specific heat at high temperatures, which is very ingenious and elegant from the theoretical point of view. Application of the method was made to tungsten for the range 1000° K. to 2300° K. However, on the basis of Pirani's previously determined temperature scale for tungsten, very large variations occur in his results. From the constancy obtained at the lower temperatures he concluded that Pirani's scale at the higher temperatures was in error and was led to propose a new temperature scale for tungsten based on an assumed constancy for the atomic heat under constant volume for which he used $7.82 \frac{\text{calories}}{\text{gram-atom deg.}}$, a quantity considerably in excess of the value expected from theory. However, this proposed temperature scale is not consistent with what is believed to be, as a result of more direct measurements, the true temperature scale.

Pirani, making use of an oscillograph and noting the rate of change of resistance and of temperature with time, determined specific heats for temperatures ranging from room temperature to 1400° K. His results, while in fair agreement with what might be expected from results at room temperature, are considerably scattered and like Corbino's results, lead to considerably higher atomic heats than would naturally have been expected.

At about the same time that Corbino and Pirani were working on

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[1] Phys. Zeit., 13, p. 375, 1912.

[2] Vehr. Deut. Phys. Gesell., 14, p. 1037, 1912.

their problems, the writer also took up the question of the specific heat of tungsten and of carbon making use of a method which will soon be described. In trying to check up results then obtained by a slight modification of the method first actually used, unexpected variations were found. Since then an enormous amount of time has been spent in trying to reconcile or explain these results and publication of the results has been delayed until the present time.

Method and Apparatus.

Outline of Method.—In general the method has been to operate a filament of the material studied in a vacuum and to note how the filament performed while passing from one steady state to another in consequence of a change in the current passing through it. The fundamental equation, based on the conservation of energy, is the following:

$$VI = f(T) + c_p m \frac{dT}{dt}. \tag{2}$$

The three members of this equation represent respectively the rate of supply of energy to the filament, the rate of radiation of energy from the filament, and the rate of storing of energy in the filament. The latter term may, of course, be positive or negative. Exactly how these quantities were obtained will be shown later. It is sufficient to say here that they were obtained from data on the voltage drop along the filament and the current through it as functions of time. Experimentally the changes in potential and current were brought about by suddenly changing a resistance in series with the filament. Exactly how this was accomplished is described in the next paragraph.

Apparatus.—The apparatus itself is shown diagrammatically in Fig. 1. L_1 represents the lamp containing the filament being studied. In order to eliminate the cooling effects occurring at the ends of the filament, potential lead wires of very fine tungsten wire have been used as is indicated. The switches S_1 and S_2 were electrically operated with the aid of a pendulum device not indicated in the figure. S_1 consists essentially of a block with six mercury cups and a rocking lever at each end of which is carried an electrically insulated cross arm. As the rocker is thrown back and forth the prongs attached to the cross arms and to the ends of the rocker itself are alternately dipped into and pulled out of the adjacent mercury cups. An inspection of the figure will show that essentially the main circuit through the battery B and the adjustable resistance R_2 is divided into two branches, one of which for one of the two positions of the rocker arm contains the lamp L_1 and the other of which contains lamp L_2 a lamp of approximately the same characteristics as L_1 (though this is not essential) and the resistance R_1. For the other position of the rocker arm, one branch contains L_1 and R_1 while the other branch includes L_2 only. As the rocker of S_1 is rocked back and forth, R_1 is shifted from the branch containing L_1 into the branch containing L_2, and vice versa. It will be readily seen that this permits of the passing of the lamp under investigation from one steady state to another without at the same time changing the rates of heating in other parts of the circuit. The switch S_2 is composed of a telegraph sounder with the arm extended and insulated in such a way that when the arm is pulled down, two wires attached to it are thrust into a mercury cup and thereby the circuit connecting the galvanometer G to the potentiometer P is closed. Switch S_3 was manipulated by hand, being thrown one way or another as it was desirable to measure voltage or current, for which purposes the volt box V and the standard resistance I respectively were introduced.

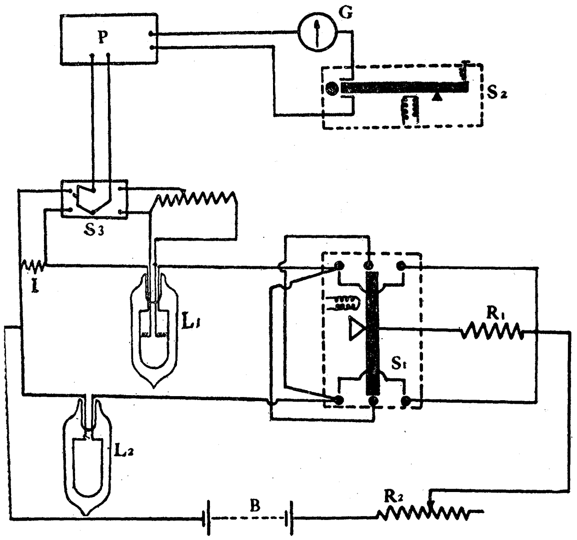

Fig. 1.
Diagram of Apparatus.

The pendulum apparatus, which is not shown in the figure, was operated much as are similar ones which are commonly found in physical laboratories. It differed, however, in that it was constructed so that any desirable period of swing between reasonable limits could be obtained. To the lower part of the pendulum proper two arms each holding a platinum spade terminal were attached. In the movement of the pendulum back and forth these terminals passed through two pairs of small bubbles of mercury which could be adjusted with respect to one another in order to obtain any desired interval of time.

Experimental Procedure.—In order to be able to apply equation (2), it is sufficient to determine experimentally the voltage across the filament and the current through it as functions of the time elapsing following the rocking of the switch S_1. To do this the mercury contacts on the pendulum apparatus were first adjusted for some desired interval; then, with the rocker of S_1 in the initial position and the potentiometer set for some estimated value of the current or voltage, the pendulum, which had previously been drawn back, was allowed to swing. On the passage of the platinum points through the first pair of mercury cups, the rocker S_1 was thrown violently over and caught in this position by means of a lock, not shown. On the passage of the platinum points through the second pair of mercury bubbles, switch S_2 was momentarily operated. In case the estimated setting of the potentiometer was incorrect, a ballistic deflection of the galvanometer followed. Quickly following the noting of this deflection, the pendulum and the rocker of S_1 were brought back to their initial positions and from the direction and magnitude of the galvanometer throw, a new estimated setting of the potentiometer was made. Following at regular intervals, repeated tests were made until the potentiometer setting was such that the galvanometer did not deflect. It was assumed that a potentiometer reading gave correct instantaneous values of the voltage or of the current as the case may have been. This was borne out by tests made with and without a large inductance inserted in the potentiometer branch and by calculations as to the effect of any probable self inductances that might be associated with the standard resistance I, the volt box V and the lamp L. Repetitions of the procedure described for various intervals of time between the rocking of switches S_1 and the operating of S_2 gave, as is evident, the instantaneous values of current and voltage as functions of the time of heating or of cooling of the filament of L_1.

Specimen Data for Filament A-33.—A series of values for instantaneous currents for a particular tungsten filament (*A*-33) are platted in Fig. 2, both for the case when the filament was heating and when cooling during the passage from one to the other of two steady temperatures which were approximately the same in the two cases. In order to eliminate any effects due to changes in the filament or in the battery with time of operation, the points along a curve were obtained in the order 1, 3, 5, 7, 8, 6, 4, 2. Curves showing the variation of the voltage were not actually plotted; instead the instantaneous values of the resistance as a function of time were plotted. Such curves corresponding to those of Fig. 2 are shown in Fig. 3.

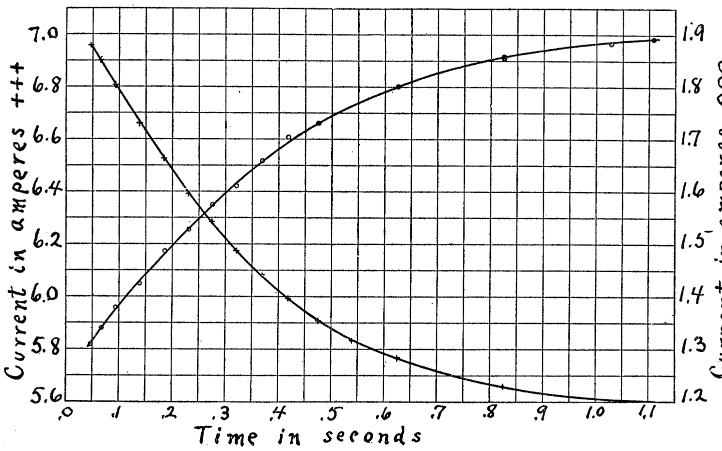

Fig. 2.

The current through the filament of L_1 as a function of the time of heating (+++) and of the time of cooling (ooo) for a particular tungsten filament (A – 33) on passing from one to the other of two fixed steady states. Values for the time are uncertain by a small constant amount, dependent on the apparatus.

Application of Equation (2).—On the supposition that the resistance and the wattage of the filament are functions of the temperature only,

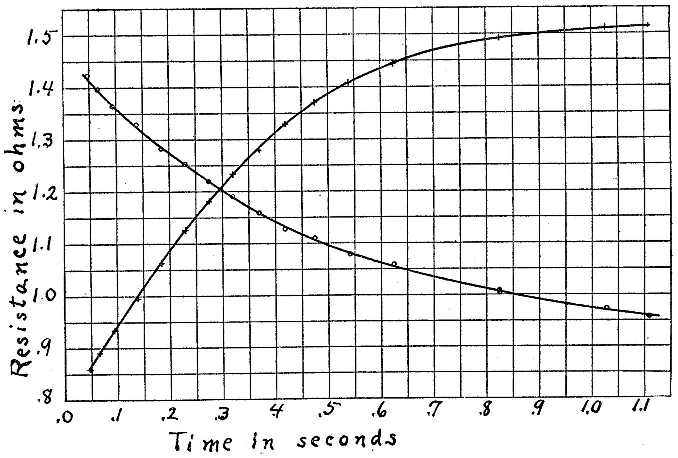

Fig. 3.

The resistance of the filament L_1 as a function of the time of cooling (ooo) for a particular tungsten filament (A – 33) on passing from one to the other of two fixed steady states. Values for the time are uncertain by a small constant amount, dependent on the apparatus.

further data that are necessary are readily obtained. Consider in this connection equation (3) which is term for term identical with equation (2) although written in a somewhat different form.

$$I^2R = F(R) + c_p m \frac{dT}{dR}\frac{dR}{dt}\,. \tag{3}$$

From a plat of the wattage of the filament as a function of its resistance for a succession of steady states, the quantity $F(R)$ may be taken as the wattage corresponding to the resistance R, since for the filament thus operated in a vacuum, the rate of supply of energy to the filament is equal to the rate of radiation of energy from the filament. The quantity dT/dR may likewise be readily obtained from a calibration curve showing for a series of steady states for the filament, the relation between temperature and resistance. Curves giving T[1] and $F(R)$ as functions of R for the filament of (A-33) for which data have already been given, are shown in Fig. 4. The quantity dR/dt may be obtained from the plat of Fig. 3. Finally, after sufficient data of the preceding nature have been obtained, one may obtain the quantity m by breaking the lamp and weighing the filament. There then remains only the quantity c_p as unknown which may be, therefore, determined directly. This quantity multiplied by the atomic weight gives the atomic heat.

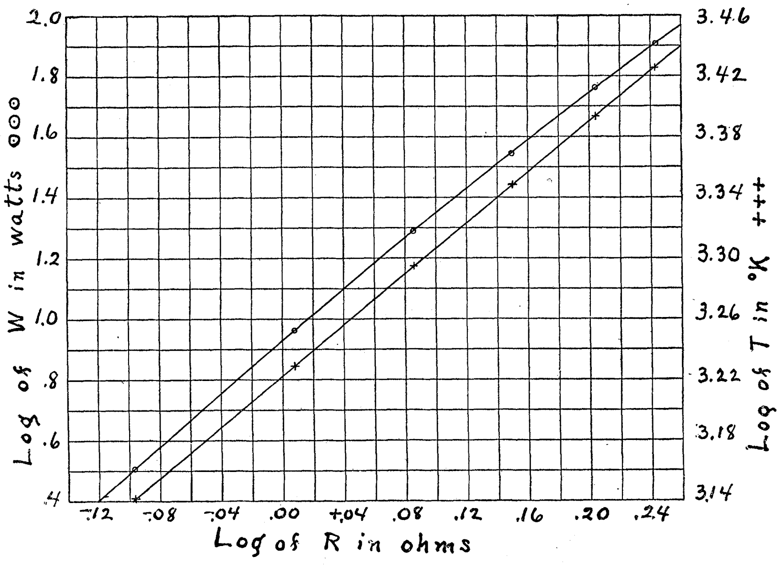

Fig. 4.

The wattage (ooo) and the temperature (+++) as a function of the resistance for a particular tungsten filament (A — 33) when operated at a succession of steady states.

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[1] Worthing, Phys. Rev., 10, p. 377, 1917.

Second Method of Eliminating End Effects.—It should be noted here that in some instances, instead of a lamp with fine potential leads being used as in lamp L_1, two lamps with hairpin-shaped filaments identical as to wire-size and construction excepting that their filaments differed greatly in length were used in a manner to be described presently. In selecting two such lamps from a batch the color match method was employed. For this selection the tip ends of the longer filaments were screened off to such an extent that the portions of the longer filaments visible were about equal in length to the lengths of the shorter filaments. By so doing a pair of lamps was obtained such that by taking differences in voltages, wattages and resistances, one could eliminate the effect of the cooling junctions and lead-in wires and thus obtain results for a uniformly heated filament whose length was equal to the difference in the lengths of the filaments of the pair. When used in place of L_1, these two lamps were connected in series. The method of operation was exactly as has been described excepting that there were required two voltage determinations instead of one as was required otherwise. In the computational work the differences in resistance, etc., were always used in accord with what has already been said.

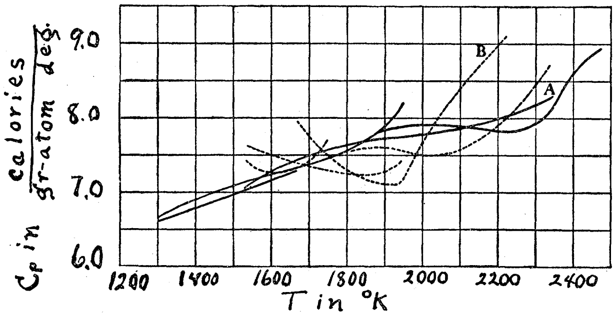

Fig. 5.

Atomic heats at constant pressure as obtained from several series of measurements on a particular tungsten filament (A — 33) when heating (———) and when cooling (- - - -). The curves A and B resulted from data platted in the preceding figures.

Atomic Heat Results Obtained with Filament A-33.—As already stated, in this work determinations have been made both for the filament while heating, that is, passing from a cold state to a hot state, and also while cooling or the reverse process. A series of values for C_p is obtained for each set of data. The results from a series of such sets for the tungsten filament A-33 when operated between various arbitrarily chosen steady states are platted in Fig. 5. It is to be noted that, while for the most part the values by the two methods agree with each other, there are some outstanding differences. In particular the agreement for the various sets using only the results obtained by the heating method are in fairly good agreement.

The writer has in his possession a great many similar sets of curves which show with but very few exceptions, as is shown here, that in the cooling method the final values of a set (that is the low temperature values) are uniformly too high when compared with those obtained by the heating method. The same thing is true though not to quite as great an extent of the initial values, that is, the high temperature end of the series. This difference will be discussed later.

Test Using Corbino's Method.

On account of the differences obtained in the method just described depending on whether the change was one of heating or of cooling, and because of a desire to check the results by a method noticeably different in procedure, tests have also been made using the method devised by Corbino.

In his work Corbino[1] used tungsten in the form of small filaments such as occur in small wattage lamps. Apparently the differential cooling effects due to the lead-in and supporting wires, for the small changes in temperature used by him were not appreciable. However, for this method, the lamps used by the writer (a pair which had previously been used in the method described above) possessed cooling effects such as to require some modification in procedure. Fig. 6 shows the apparatus as used. R' and $R + R'$ represent here the resistances of the two lamps which differed only in the lengths of the filaments used. By locating these lamps as is shown and by choosing other resistances such that the two branches containing these lamps possessed equal resistances, the above-mentioned disturbing factors were theoretically and actually eliminated.

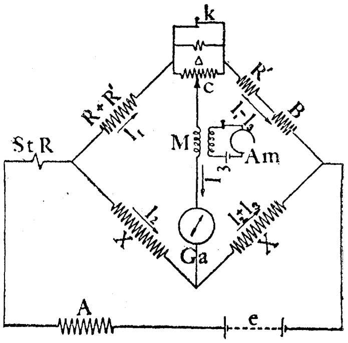

Fig. 6.
Arrangement of apparatus used in connection with Corbino's method.

Corbino showed for his arrangement, and the reasoning holds equally well for the one presented here, that, if the bridge is first balanced with the switch K closed and then again by adjusting C only with the switch

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[1] Phys. Zeit., 13, p. 375, 1912.

K open, there results a discharge through the galvanometer which is of the exponential decay type, *i. e.*,

$$E = E_0 e^{-\gamma t} \tag{4}$$

when the bridge passes from one balanced condition to the other on the closing or the opening of switch K. From measurements of this discharge and of certain other electrical quantities, he further showed how it was possible to compute the time constant $1/\gamma$ of this discharge and finally

TABLE II.

Quantities and Symbols Relating to Corbino's Method which Are Not Given in Table I.

Symbol.	Quantity.
primed (′)	Quantities referring to short filament.
unprimed ( )	Quantities referring to uniformly heated filament.
sub ($_0$)	Initial values.
sub (ϵ)	End values.
E	Potential drop in galvanometer branch.
γ	Inverse of time constant of the discharge through the galvanometer branch.
ΔT	Total change in T.
a	Temperature coefficient of resistance.
r	Resistance of the battery circuit.
Δr	Change in r on opening switch k.
q	Quantity of electricity discharged through galvanometer on closing or opening k.
G	Galvanometer branch resistance.
X	High resistance (see Fig. 6).
M	Mutual inductance (see Fig. 6).
d_1	Deflection of galvanometer on passage of q.
d_2	Deflection of galvanometer per unit change of current in the primary of the mutual inductance.
ϕ'	Correction factor to be applied to d_1 for a prolonged discharge.

the atomic heat itself. Due to the elimination of the cooling effects of the leads, the formulas for computing are slightly different in the present case from what Corbino obtained. However, the methods of arriving at the formula are exactly similar. Only the more important steps and expressions will be given here. For small changes of temperature there results (see Table II for symbols):

$$T_\epsilon - T = \Delta T e^{-\gamma t}. \tag{5}$$

Evidently for small changes

$$\Delta T = \frac{R_\epsilon - R_0}{R_0 a}. \tag{6}$$

In a direct way, as was done by Corbino, it may be shown that

$$\gamma = \frac{1}{c_p m}\left[\left(\frac{dW}{dT}\right)_0 - W_0 a\left(1 - \frac{2R_0}{r} - \frac{4R_0'}{r}\frac{a'}{a}\right)\right], \tag{7}$$

and that for the charge passing through the galvanometer

$$(8)\qquad q = \frac{R_0 a\Delta T}{X + 2G}\, {}_0I_1 \int_0^\infty \left[1 + \frac{\Delta r}{r} - \frac{R_0 + 2R_0'}{r} a\Delta T(1 - e^{-\gamma t}) \right] e^{-\gamma t}dt.$$

By means of a mutual inductance discharge in the galvanometer branch another expression may be obtained for q; viz.,

$$(9)\qquad q = \frac{d_1}{d_2} \frac{M}{X/2 + G} \cdot \phi'.$$

From equations (7), (8), and (9) by eliminating q and γ, an expression for c_p may be obtained in terms of ordinarily measurable quantities.

In Corbino's work the time constants of the discharge were so small compared with the galvanometer period that the factor ϕ' was assumed as unity. In the writer's work it was quite different, the time constant was sometimes greater than the throw period of the galvanometer. The determination of ϕ' for such a case formed the subject of a paper printed elsewhere.[1] Along with the determinations of γ it was there shown how that quantity might be determined independently of equations (8) and (9). In that event c_p is at once directly obtainable from (7).

There is included in Table III. for the sake of illustration the measurements of a particular case, that one in fact for which data on γ are given in Tables III. and IV. of the paper just referred to.

Table III.

Measurements and Computations Relating to the Determination of C_p by Corbino's Method for a Particular Case.

Quantity.	Value.	Quantity.	Value.
I_0	2.3120 amps.	T_0	1492° K.
I_ϵ	2.3290 "	ΔT	5.63°
$R_0 + R_0'$	2.3628 ohms	$\left(\frac{dW}{dT}\right)_0$	0.0230 $\frac{\text{watts}}{\text{deg.}}$
R_0'	1 1109 "	$\gamma c_p m$	0.0200 "
r	19.5 "	γ	0.932 1/sec.
Δr	.1521 "	c_p	0.0345 $\frac{\text{cal.}}{\text{gr. deg.}}$
		C_p	6.35 $\frac{\text{cal.}}{\text{gr.-atom deg.}}$

In case the initial and the end values are interchanged the formulas which apply to infinitesimal changes lead to 6.46 $\frac{\text{cal.}}{\text{gr.-atom deg.}}$ for 1498° K. The average 6.40 $\frac{\text{cal.}}{\text{gr.-atom deg.}}$ has been ascribed to 1495° K.

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[1] Phys. Rev., 6, pp. 165–179, 1915.

The results themselves will be discussed later. The method is very neat generally. The only apparent drawback to the method is the extreme constancy required of the battery and of the circuits and the extreme care that must be taken in making measurements in order that accurate results shall be obtained.

ATOMIC HEAT OF TUNGSTEN AS A FUNCTION OF TEMPERATURE.

Sources of Error.—The discrepancies which have been noted previously in comparing the results of the cooling and the heating methods seem, for the most part, confined to something especially effective in the cooling method. On first thought they might seem suggestive of some source of error such as the conduction of heat due to residual gases, the disturbances due to thermionic currents, the variations in the rate of supply of energy through absorption of radiation present within the bulb, and experimental difficulties. As to each of these possibilities data are at hand permitting the computation of their effects.

Let us consider the thermal conduction due to the residual gas first. The lamps used in this work, as shown by vacuum tests with high frequency discharge apparatus, were of very good quality. This means that the initial vacuum of about one millionth of an atmosphere had been greatly improved. However, let us assume, as limiting unfavorable conditions, a remaining gaseous pressure of 10^{-7} atmosphere due to hydrogen. For further computational purposes let us assume the 0.25 mm. filament mounted axially in a long tubular bulb 10 cm. in diameter, maintained at room temperature, 300° K. At this pressure the mean free path of a molecule of hydrogen in a large vessel is of the order of 180 cm. In our particular problem we may assume that the molecules of gas impact only on the walls of the bulb or on the filament. Assuming further than on the average after an impact on filament or wall a molecule possesses kinetic energy corresponding to their temperatures, we have for the two temperatures 2400° K. and 1200° K., the results shown in Table IV. The $c_p m(dT/dt)$ term of equation (2) was always at least one fourth of the $F(T)$ term under the most unfavorable conditions occurring at low temperatures in the cooling method. It follows that gaseous conduction of heat cannot account for these discrepancies in the specific heat measurements, since nowhere on this account was this $c_p m(dT/dt)$ term, and also therefore C_p, in error by more than 1/3 per cent., a correction which has been neglected.

In arriving at corrections for the thermionic currents, certain results obtained by Langmuir[1] are found directly applicable. In particular the

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[1] PHYS. REV., 2, p. 450, 1913.

data contained in Fig. 1 of his paper may be made use of. He used a lamp with two similar U-shaped filaments of 0.069 mm. tungsten wire 10.84 cm. long, distant from each other by 1.2 cm., and differing in potential by 120 volts or 240 volts. In the writer's lamps, only single U-shaped filaments with legs separated usually by more than 2 cm. were used. In the most unfavorable case from the standpoint of this correction, the filament was of 0.25 mm. wire, 32 cm. long, with a maximum potential difference of 27 volts, occurring at the top of the U, where there was a spread of at least 3 cm. For such a voltage difference Langmuir would have obtained as the maximum possible thermionic current density about 0.0016 $\frac{\text{ampere}}{\text{cm}^2}$ of cathode surface. Due to the increased distance in the writer's case, it seems certain in view of the theoretical considerations developed by Langmuir that the maximum current density would be of

TABLE IV.

Data and Computations Relating to the Heat Conduction Due to Hydrogen under a Pressure of 10^{-7} *Atmospheres in a Long Tubular Bulb* 10 *cm. in Diameter with an Axially Mounted Filament* 0.25 *mm. in Diameter when the Bulb is Maintained at* 300° *K. and the Filament at the Temperatures* 1200° *K. and* 2400° *K.*

	1200° K.	2400° K.
Molecular density	$2.7\times10^{12}\,\frac{\text{molecules}}{\text{cm.}^3}$	$2.7\times10^{12}\,\frac{\text{molecules}}{\text{cm.}^3}$
Average molecular path	10 cm.	10 cm.
Probability of a molecule impacting on filament after an impact on the wall	0.0016	0.0016
Square root of mean square velocity	2.0×10^5 cm./sec.	2.0×10^5 cm./sec.
Mean molecular velocity	1.8×10^5 cm./sec.	1.8×10^5 cm./sec.
Average frequency of impacts on filament per unit length of filament	$6.16\times10^{15}\,\frac{1}{\text{sec. cm.}}$	$6.16\times10^{15}\,\frac{1}{\text{sec. cm.}}$
Average amount of energy transferred to bulb following an impact on the filament	$1.85\times10^{-13}\,\frac{\text{ergs}}{\text{molecular impact}}$	$4.3\times10^{-13}\,\frac{\text{ergs}}{\text{molecular impact}}$
Rate of loss of energy per unit filament length by gaseous conduction	$1.14\times10^{-4}\,\frac{\text{watts}}{\text{cm.}}$	$2.65\times10^{-4}\,\frac{\text{watts}}{\text{cm.}}$
Rate of radiation of energy per unit length of filament	$0.135\,\frac{\text{watts}}{\text{cm.}}$	$4.53\,\frac{\text{watts}}{\text{cm.}}$
Ratio of gas conduction loss to radiation loss	0.00085	0.000058

the order of 0.0006 $\frac{\text{ampere}}{\text{cm}^2}$, and the average considerably below this, in fact below 0.00025 $\frac{\text{ampere}}{\text{cm}^2}$. The filament possessed a surface of about 2.5 cm.^{2} The consequent upper limiting value of the thermionic current in this most unfavorable case was not greater therefore than 0.0006 ampere or 0.0001 of the current of 6 amp. which was then used. Since, under this most unfavorable condition, which occurs at high temperatures in the heating method, the $c_p m(dT/dt)$ term of equation (2) which here as used always amounted to at least 1/15 of the $F(T)$ term, the maximum error resulting from neglecting thermionic currents could not account for more than 0.15 per cent. in the final results. An inspection of the data obtained showed that no possibility of a lag in the thermionic discharge, however improbable, could anywhere have accounted for a larger variation. This correction is entirely negligible.

The third possibility of an error due to an appreciable amount of energy being derived by the filament during a change, from reflected radiation within the bulb or from energy radiated by the bulb does not seem, a priori, a probable one. It has been ignored in almost all radiation work. The radiation existing within the bulb is composed of two parts, one representing the radiation arising from the filament which is reflected back and forth within the bulb, the other that radiation arising from the bulb itself. Velocity of light and bulb absorption considerations show at once that there can be no appreciable lag between the first-named portion and the filament temperature; and since this equilibrium state existed also during the temperature and electrical calibrations, there is no possibility of error arising from the reabsorption of this radiation. As to the radiation arising from the bulb itself, there are differences. In the cooling method for instance, the filament was maintained for the larger part of the time at the maximum temperature for which state the bulb temperature is comparatively high. During the cooling process and in particular near the completion of this process, the bulb is noticeably hotter than in the calibration state for the same filament temperatures. At the most, the bulb temperature did not vary more than 50°, say from 300° K. to 350° K. Assuming that the radiation from the bulb was black radiation, it is easy to compute the change in the rate of supply of energy to the filament due to the radiation from the bulb at a given temperature for the two states. For a filament temperature of 1300° K. the lower experimental limit taking recognition of the fact that the absorbing power is proportional to the emissive power, we have these supply rates equal to respectively $\left(\frac{300}{1300}\right)^4$ and $\left(\frac{350}{1300}\right)^4$ or 0.0025 and 0.0052 of the radiation rate, or the change as equal to 0.0027 of the radiation rate. Since, in this most unfavorable condition, the $c_pm(dT/dt)$ term of equation (2) was always at least one fourth of the radiation rate, the error resulting in C_p was never greater than 1 per cent. Usually it was much smaller. This source of error has also been neglected.

It is possible, of course, to ascribe the greater variations of the cooling method directly to the much reduced values of current and voltage which were dealt with in that method and to the greater uncertainties which arise when working appreciably near the limits of instrumental accuracy. However, the data for the cooling method when platted generally appeared to be about as consistent as that obtained with the heating method. Cumulative evidence leads the writer to believe that the difference must be sought elsewhere. Another conceivable experimental difficulty might be considered as having arisen from the necessary inclusion of self-inductances. Computations and experimental tests with large self-inductances intentionally included, however, showed no measurable variation.

A Possible Lag Phenomenon.—It is conceivable that the differences in results from the heating and the cooling methods are real and that in some way the resistance of a filament is not merely a function of the temperature but also to a slight extent a function of the immediately preceding conditions of the filament. In view of the fact that the changes which occur in these methods are quite rapid changes, that the filament expands, that this process takes a finite amount of time, and that the resistance of a filament is a function of the pressure internally as well as externally, one might naturally expect something of a lag as a source of difficulty when the temperature is assumed to be a function of the resistance only. There are no means at present, so far as the writer knows, of computing how large this effect might be expected to be. More refined measurements will be necessary, in fact, before the existence is definitely proved. It is of interest to note here, however, that Stewart[1] has presented theoretical and experimental considerations indicating that a similar lag phenomenon takes place when gases are subjected to changes in internal energy.

Assuming the effects to be real and to represent something of a lag between the resistance and the rate of radiation, it is of interest to consider the effect of such a lag on the results. The discrepancy on this supposition arises when the steady state wattages for a filament are taken according to equation (3) as giving values of $F(R)$ for corresponding resistances. In the cooling method, on account of the relatively

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[1] Phil. Mag., 28, p. 748, 1914.

small values for I and for the quantity IV., the term $F(R)$ is relatively very important in the determination of C_p; on the other hand, in the heating method the term $F(R)$ is relatively unimportant with respect to IV. and consequently also in the determination of C_p. This statement applies particularly when dT/dt is large. As a result on the supposition of a lag we might expect the cooling method to give relatively discordant values and the heating method to give relatively consistent values. A consideration of Fig. 5 shows that such is actually the state as to consistency. However, without the supposition of more than a single lag it is difficult to explain the apparent return of the C_p at the low temperature end of a set in the cooling method, to greater than normal values.

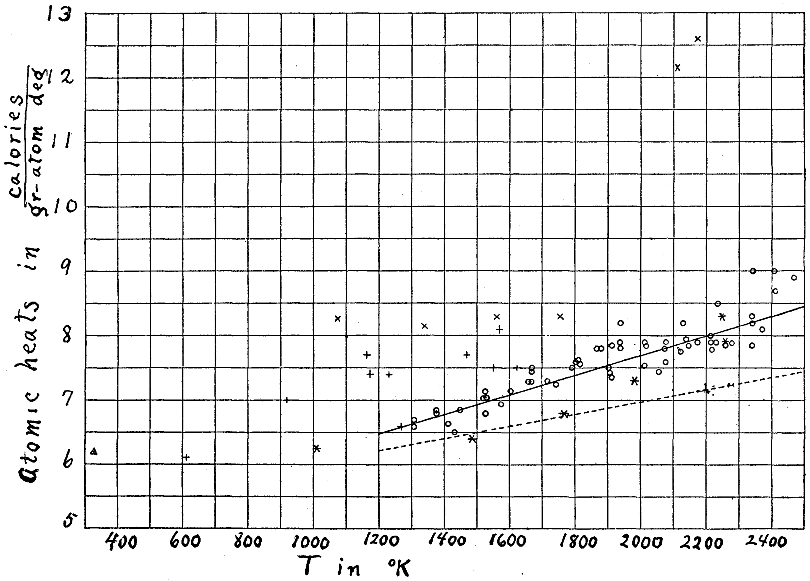

Fig. 7.

Atomic heats of tungsten as a function of temperature.

Atomic heats at constant pressure.
××× Corbino (Pirani's Temperature Scale).
+++ Pirani.
△ Average of several at 50° C.
⊙⊙⊙ Worthing, by heating method.
* * * Worthing, by Corbino's method.
——— Worthing, weighted value for C_p.
– – – – Worthing, weighted value for C_v.

Atomic Heat under Constant Pressure.—Because of the great variations in connection with the cooling methods in contrast to those occurring in the heating methods, the results by the former method have not been included finally in arriving at atomic heats. In Fig. 7 there are shown results by the heating method on two filaments with potential lead wires and on three filaments which represent the differences obtained on each of three sets of two lamps which possessed filaments and construction that were identical except for the lengths of the filament used. There are no very noticeable differences in the results from these various sets. There are also shown the results obtained from one of the pairs of lamps when Corbino's method was used. These results lie somewhat below those obtained by the other method. The writer has no explanation to offer for this. For comparison purposes there have been included the results obtained by Corbino as well as those obtained by Pirani. The great variations in the values for C_p obtained by Corbino are to be ascribed in part at least to the fact that the temperature scale used by him was incorrect. Because of variations in the manufacture and treatment of tungsten filaments, no satisfactory correction to the present scale seems possible. In view of the great care which was used in the determination of a temperature scale for the writer's work and of the comparatively good agreement which was found using the two methods noted, the writer believes that the results obtained indicate the true values to within a fairly small degree of uncertainty, perhaps something of the order of 5 per cent. As a whole the author's data do not justify any relation more complex than the linear one represented, although it is evident that such a relation could not be continued to noticeably lower temperatures.

Table V.

Test of Grüneisen's conclusion as to variations in α/C_p.

T.	α.	C_p.	α/C_p.
330° K...	$4.44\times10^{-6}\,\frac{1}{\text{deg.}}$	$*6.20\,\frac{\text{cal.}}{\text{gr.-atom deg.}}$	$7.16\times10^{-7}\,\frac{\text{gr.-atom}}{\text{cal.}}$
1200......	5.06	6.50	7.78
1500......	5.50	6.95	7.91
1800......	6.06	7.40	8.19
2100......	6.74	7.85	8.58
2400......	7.54	8.30	9.08

It is of interest to compare these results with certain conclusions obtained by Grüneisen.[1] From experimental data on eight metals for temperatures ranging from about − 150° C. to about 850° C., he arrived at the empirical law that α/C_p is a constant depending only on the

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* Average value of several determinations at room temperatures as recorded in Landolt and Bernstein.

[1] Ann. d. Phys., 26, p. 211, 1908.

substance. The results by the writer[1] on the thermal expansion of tungsten are based on the same temperature scale[2] as the data recorded here and may be used in this connection. That these results deviate from Grüneisen's conclusions may be seen from an inspection of Table V. No approximate agreement can be obtained through any reasonable shift or change in the curve of Fig. 7 giving C_p as a function of T.

Atomic Heat under Constant Volume.—In order that these results might be tested for their agreement or lack of agreement with theories, it is necessary to correct these values of atomic heat to what would be obtained if determined under the condition of constant volume. Thermodynamically there is the formula which holds for all cases,

$$C_p - C_v = - T\frac{\partial p}{\partial v}\left(\frac{\partial v}{\partial T}\right)^2. \tag{10}$$

(See Table I. for meaning of symbols.) This may be changed at once to

$$C_p - C_v = 9\frac{\alpha^2 v}{K}T. \tag{11}$$

So far as the writer knows, there is not in existence at present the data necessary for the application of these formulas as they stand to tungsten at the temperatures used in this work. However there is the approximation formula according to Nernst and Lindemann,[3] which is based in part upon the applicability of the equipartition theory of atomic heat to substances at high temperatures, the assumed constancy of $3\alpha v/KC_v$[4] and of $T_s K/v$[5] for which ranges of 1 : 3 and 1 : 5 respectively have been found experimentally. Equation (11) under these conditions reduces to

$$C_p - C_v = C_p{}^2\frac{T}{T_S}A_0, \tag{12}$$

where A_0 supposedly represents a universal constant equal to 0.0214 $\frac{\text{gram-atoms deg.}}{\text{calorie}}$. The application of this equation to the weighted curve for C_p gives approximately the curve for C_v which is noted in Fig. 6 by the dashed line. In justification of this application, it should be stated that the corrections obtained at room temperature and particularly at 915° K. are of the same order of magnitude as those which the writer has obtained by using the rigid thermodynamic formula together with measurements of the thermal expansion,[6] Young's modulus, and the

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[1] PHYS. REV., 10, p. 638, 1917.

[2] Worthing, PHYS. REV., 10, p. 377, 1917.

[3] Zeit. f. Elektrochem., 17, p. 817, 1911.

[4] Mie, Ann. d. Phys., 11, p. 687, 1903; Grüneisen, Ann. d. Phys., 26, p. 393, 1908.

[5] Grüneisen, Ann. d. Phys., 39, pp. 300–301, 1912; Blom, Ann. d. Phys., 42, p. 1397, 1913.

[6] Worthing, PHYS. REV., 10, p. 638, 1917.

rigidity at these temperatures. The values for Young's modulus, and rigidity while considered only fairly accurate are values which the writer has obtained on a specimen of wire for which the thermal expansion coefficient had been carefully measured previously. They show relatively about the same variation with temperature as have been found by Dodge[1] and by Schriever at the University of Iowa in some of their preliminary works which they have kindly communicated to the author. The writer's results, their application in determining $C_p - C_v$ and the difference in agreement between the results depending on whether (11) or (12) is used in computing $C_p - C_v$ are shown in Table VI.

Table VI.

Data Used and the Results Obtained in the Application of (11) *and* (12) *at Two Different Temperatures.*

Quantity.	Values at Temperatures	
	300° K.	915° K.
Rigidity	$1.48\cdot10^{12}\ \frac{\text{dynes}}{\text{cm.}^2}$	$1.39\cdot10^{12}\ \frac{\text{dynes}}{\text{cm.}^2}$
Young's modulus	$3.77\cdot10^{12}$ "	$3.69\cdot10^{12}$ "
Bulk modulus, $1/k$	$2.77\cdot10^{12}$ "	$3.55\cdot10^{12}$ "
Linear exp. coef., α	$4.44\cdot10^{-6}$ 1/deg.	$4.75\cdot10^{-6}$ 1/deg.
Atomic volume, v	$9.7\ \frac{\text{cm.}^3}{\text{gram-atom}}$	$9.8\ \frac{\text{cm.}^3}{\text{gram-atom}}$
$C_p - C_v$ according to equation (11)	$0.034\ \frac{\text{calories}}{\text{gr.-atom deg.}}$	$0.156\ \frac{\text{calories}}{\text{gr.-atom deg.}}$
Melting point,[2] T	3675° K.	3675° K.
C_p (assumed)	$6.0\ \frac{\text{calories}}{\text{gr.-atom deg.}}$	$6.0\ \frac{\text{calories}}{\text{gr.-atom deg.}}$
$C_p - C_v$ according to equation (12)	0.063 "	0.192 "

Discussion of Explanations Suggested for Atomic Heats in Excess of $3Nk$.—It is to be noted that, while the results obtained more nearly check the limiting value $3Nk$, or $5.95\ \frac{\text{calories}}{\text{gram-atom deg.}}$, which is quantitatively predicted for high temperatures by most theories, than do the results of Corbino or of Pirani, they still noticeably exceed that limiting value. There seems to be no way of explaining this discrepancy by any reasonable supposition of error of method, of calibration, or of lack of uncertainty in the correction for $C_p - C_v$. Regarding this last-mentioned uncertainty it may be stated that according to Table VI. the discrepancy would be apparently increased in case the exact correction could be made.

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[1] Phys. Rev., 11, p. 311, 1918.

[2] Worthing, Phys. Rev., 10, p. 377, 1917.

As has already been stated work done on other substances has demonstrated that $3Nk$ is not the actual limiting value for C_v. Among many investigations there may be cited in particular as more recent ones that by Protz[1] on Na and K, that by Koenigsberger[2] on Pt and Ag, that by Schubel[3] on Fe, Ni, Co, Cr, Bi and Sn, that by Griffith and Griffith[4] on Fe and Na and that by Lewis Eastman and Rodebush[5] on Mg, K, Na and Ca.

Einstein[6] in developing his theory of atomic heat represented by Equation (1) recognized the existence of values in excess of $3Nk$. From his viewpoint it was natural to account for this by assuming that to the electrons contained in a body there should also be ascribed energy according to Planck's quantum hypothesis. Quantitative tests of this view may be carried out since, as Drude showed in his theory of optical dispersion, there are ultra-violet frequencies which are to be ascribed to electronic vibrations just as the infra-red frequencies have been ascribed to atomic vibrations. Since the frequencies for the former are very great compared with the latter, in fact according to Haber[7] varying inversely as the square root of the ratio of the vibrating masses, it is to be expected that the electrons will not contribute noticeably to atomic heats until high temperatures are attained, and then generally in accord with the diagram of Fig. 8. Such a representation at first glance would seem to be qualitatively in agreement with the results of the writer. In view of Einstein's theory having been shown not to be in accord with data at low temperatures, and in view of the good agreement using Debye's theory, the writer has attempted a quantitative test using Debye's equation. It is with the understanding, however, that theoretically such a procedure is probably not justified because from Debye's[8] viewpoint the body is a continuum, and strictly only the first $3(N + N')$ —where N' represents the number of electrons per gram atom—frequencies should be considered, resulting in a magnified *a-a* curve (Fig. 8). From the viewpoint of Born and Karman[9] this procedure might possibly be justified. In this test it matters little which of the two theories is selected, hence the selection of Debye's because of completeness of published results. Assuming Lindemann's[10] formula for infra-red frequency

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[1] Ann. d. Phys., 31, p. 127, 1910.

[2] Verh. d. Deut. Phys. Gesell., 14, pp. 275 and 540, 1912.

[3] Zeit. f. anorg. Chem., 87, p. 81, 1914; Fort. d. Phys., 70, II, p. 561, 1914.

[4] Proc. Roy. Soc., *A*, 90, p. 557, 1914; Phil. Trans., 214, p. 319, 1914.

[5] Proc. Nat. Acad. Sci., 5, p. 25, 1918.

[6] Ann. d. Phys., 22, p. 180, 1907.

[7] Verh. d. Deut. Phys. Gesell., 13, p. 1117, 1911.

[8] Ann. d. Phys., 39, p. 789, 1912.

[9] Phys. Zeit., 14, p. 15, 1913.

[10] Phys. Zeit., 11, p. 609, 1910.

as used by Blom[1] one arrives at 5.8×10^{12} vib./sec. as the characteristic infra-red frequency and 277° K. as the value of θ the characteristic temperature, for tungsten. This gives a curve of the type shown by *a-a* in Fig. 8, which is consistent with the value of $1.75 \dfrac{\text{cal.}}{\text{gr.-atom deg.}}$ obtained by Dewar[2] at 50° K., though one which yields a value somewhat lower than has been obtained for room temperature.

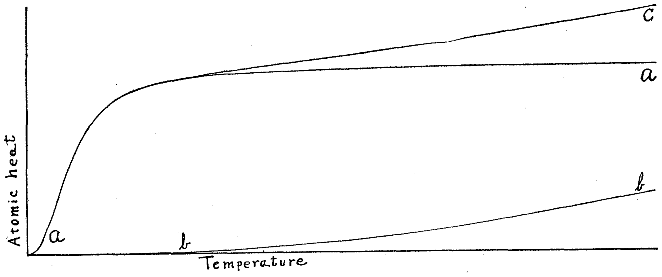

Fig. 8.

Diagram showing according to Einstein's view the separate contributions of atomic (*a* — *a*) and of electronic (*b* — *b*) vibrations toward the atomic heat as a whole (*a* — *c*) as functions of temperature.

The ultra-violet frequency obtained by Haber's[3] method gives a characteristic electronic frequency 3.4×10^{15} vib./sec. and a characteristic temperature of about 160,000° K. The supposition of 6 such valence electrons each contributing separately to the atomic heat, will at a temperature of 2400° K. add only about $0.01 \dfrac{\text{cal.}}{\text{gr.-atom deg.}}$ a value considerably smaller than will account for observed deviations. Nor will the ascribing of energy thus to all of the electrons, usually considered as included within the atom, a doubtful procedure, help essentially. The use of Lindemann's[4] formula for computing the ultra-violet frequency directly does not yield noticeably different results. Further assumptions or perhaps better theoretical considerations may lead to a better agreement.

In 1908 Planck[5] called attention to the fact that the energy of radiation filling intermolecular spaces should theoretically be taken into account in determining atomic heats. He showed that in a perfect gas under 0.001 mm. pressure at 2050° K., this energy amounts to about 25 per

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[1] Ann. d. Phys., 42, p. 1397, 1913.

[2] Proc. Roy. Soc. Lond., 89*A*, p. 158, 1913.

[3] Verh. d. Deut. Phys. Gesell., 13, p. 117, 1911.

[4] Verh. d. Deut. Phys. Gesell., 13, p. 482, 1911.

[5] Ann. d. Phys., 26, p. 1, 1908.

cent. of the kinetic energy of the atoms. Evidently the importance of this factor decreases with an increase in density, and it may be considered entirely negligible in connection with solids even at the much higher temperatures attainable. Taking a cue from this suggestion, it has been further suggested that the difference between observed values and $3Nk$ might be ascribed to the energy of radiation, and that thus these differences at high temperatures would be proportional to the radiation intensities. Assuming the results reported here for tungsten, no confirmation of this view will be found. Further, this view seems untenable since with continued increases in temperature it would lead to values in excess of $3(N + N')k$.

Richarz[1] advanced the idea that the conduction electrons, while free, represented additional degrees of freedom, and that internal energy should be ascribed to them. This view, in conjunction with the earlier theory of Lorentz as to the continuous existence of free electrons in conductors, was capable of explaining the observed excesses of C_v over $3Nk$. However, according to J. J. Thomson's electrical doublet theory of conduction, this explanation does not necessarily serve. Moreover, the discovery of K. Onnes[2] of the superconducting state seems to have verified Thomson's[3] theory. It should be further noted that Richter[4] concluded from observations of electrical conductivity and specific heat of lead-bismuth and tin-bismuth alloys at 100° C. that the conducting electrons played only a very subordinate part in atomic heat phenomena. K. Onnes and Holst[5] reached the same conclusion from measurements on the specific heat of mercury above and below 4.19° K., the temperature at which it becomes super-conducting. The viewpoint that conduction electrons during their intervals of freedom add noticeably to the number of degrees of freedom of a body does not seem to have much experimental backing.

There should also be mentioned the theories of Reinganum[6], of Rasch[7] and of Skaupy[8] concerning the merit of which the writer is unable to say much owing to not having access to the published works.

Thirring[9] in his application of Born and Karman theory discusses the possibility of applying it to lattices of atomic residues and electrons,

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[1] Zeit. f. anorg. Chem., 58, p. 356; 59, p. 146, 1908; Beibl., 33, p. 152, 1909.

[2] Proc. Kon. Akad. Amsterdam, 14, p. 113, 1911.

[3] Proc. Phys. Soc. Lond., 27, p. 527, 1915.

[4] Ann. d. Physik., 39, p. 1590, 1912; 42, p. 779, 1913.

[5] Proc. Kon. Akad. Amsterdam, 17, p. 760, 1914.

[6] Sitz. Heid. Akad., 10, p. 22, 1911; Fort. d. Phys., 67, II, p. 36, 1911.

[7] Mitteil. Kgl. Materialsprufungamt, 30, p. 320, 1912.

[8] Verh. d. Deut. Phys. Gesell., 17, p. 269, 1915; Sci. Abs., A, 18, p. 660, 1915.

[9] Phys. Zeit., 15, pp. 132 and 133, 1914.

and showed some interesting possibilities. This method might be capable of predicting atomic heats at high temperatures satisfactorily.

Another possible method explaining an excess in the number of degrees of freedom over what has been expected is that of ascribing degrees of freedom to rotational movements of the atoms in their space lattices. Of course, such a concept carries with it a supposition of atoms capable of orientation, a natural one in accord with present theories of atomic structure. Whether or not such a procedure is equivalent to the one indicated by Thirring, the author is not quite clear. It is worthy of notice that this view is consistent with the recent results by Hull[1] pointing toward relatively stationary electrons in space lattices.

Regardless of the particular method of picturing the existence of the excess in the number of degrees of freedom, the existence of an excess seems fairly well proved, if we are to accept the method of the degrees of freedom as the necessary method of explaining the upper limiting values of atomic heat. The results of this paper together with those already noted by Corbino and Pirani confirm this in the case of tungsten. That tungsten is not peculiar in this property is shown by results on other substances as has already been mentioned.

For the determining of the type of an atomic heat curve at high temperatures which the accepted theory must fit, there are but few satisfactory data. Manifestly it is of prime importance to know whether the variation above $3Nk$ is in accord with a magnified curve of the *a-a* type, Fig. 8, or with a curve of the *a-c* type. The discussion of existing data on *Pt* and *Ag* led Koenigsberger[2] to results in accord with the *a-c* type. It is significant that the results of the present work on tungsten taken together with the values obtained by others in the neighborhood of room temperatures leads to a variation of the same type. The excellent data by Protz,[3] Schübel,[4] and Griffith and Griffith[5] already referred to unfortunately do not extend over satisfactory ranges or are rendered inapplicable without further data because of the changes occurring in magnetic properties of the substances investigated. More exact measurements over large ranges of temperature would seem quite essential. It is worth pointing out that tungsten is especially favorable as a material for such an investigation in that it attains the $3Nk$ value at ordinary temperatures and may be experimented on in the solid state over a very great range beyond.

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[1] Phys. Rev., 9, p. 84, 1917.

[2] Verh. d. Deut. Phys. Gesell., 14, pp. 275 and 540, 1912.

[3] Ann. d. Phys., 31, p. 127, 1910.

[4] Zeit. anorg. Chem., 87, p. 81, 1914.

[5] Proc. Roy. Soc., *A*, 90, p. 557, 1914; Phil. Trans. Roy. Soc., 214, p. 319, 1914.

ATOMIC HEAT OF CARBON.

For this study an untreated carbon filament was made use of. The data were obtained in the earlier part of the work and due to the lack of certain refinements in the method, they are not as accurate as those obtained in connection with tungsten. The methods used both as to heating and cooling, are those which have been described in connection with results for tungsten.

Results have been obtained by Hyde[1] and by Hyde, Cady and Forsythe[2] which would indicate that untreated carbon is nearly gray in its radiation and that the regular Stefan-Boltzmann fourth power law may be used to determine temperatures for such a filament when the temperature for some one standard condition is known. One direct conclusion from their work is that the color temperature is also quite closely the true temperature. For the particular lamp which the writer used it was found that the fourth power law held when applied to two certain color temperatures. These color temperatures were obtained by color-matching the

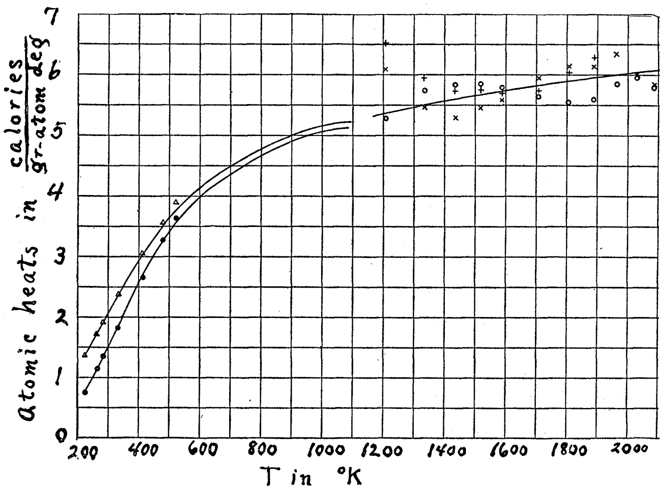

Fig. 9.

Atomic heats of carbon under constant pressure.
△ Graphite according to Weber.
○ Diamond according to Weber.
+
● } Untreated carbon according to Worthing.
×

The continuations of the graphite and the diamond curves represent the results of Magnus's reconsideration of Weber's data at the higher temperatures.

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[1] Astrophys. Jour., 36, p. 89, 1912.

[2] PHYS. REV., 10, p. 395, 1917.

lamp with a subsidiary standard which had previously been color-matched with a black body. In computing the results for carbon these color-matching temperatures and the fourth power law have been made use of. The results themselves are shown in Fig. 9. It is interesting in this connection to compare these results with those which have been obtained by Weber[1] for diamond and for graphite at low temperatures and with his determinations at high temperatures as discussed by Magnus,[2] a result of considering a changed temperature scale and more refined measurements on the specific heat of platinum in terms of which Weber expressed his results at high temperatures. The agreement is quite satisfying. It is to be noted that the maximum value in this connection does not noticeably exceed the expected theoretical limit. Undoubtedly corrections for the difference between the atomic heats under conditions of constant pressure and constant volume would lead to results which are perfectly in accord with expectations.

Summary.

The atomic heat of tungsten under constant pressure C_p has been measured by two methods for the region 1200° K. to 2500° K. The atomic heat for carbon has been measured by one method for the region 1200° K. to 2100° K. The results on tungsten when corrected to give atomic heats under constant volume lead to values considerably greater than $5.95 \frac{\text{calories}}{\text{gr.-atom deg.}}$ the value ordinarily expected in accordance with many theories. The carbon values agree well with this expected limit.

Indications of an apparent lag between resistance and temperature or some other functions, have been found which the writer is unable to explain.

Nela Research Laboratory,
National Lamp Works of General Electric Company,
Nela Park, Cleveland, Ohio,
May, 1918.

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[1] Pogg. Ann., 154, pp. 367 and 553, 1875; Phil. Mag., 49, pp. 161 and 276, 1875.

[2] Ann. d. Phys., 48, p. 983, 1915.