SPECIFIC HEAT OF COPPER IN THE INTERVAL 0° TO 50° C

WITH A NOTE ON VACUUM-JACKETED CALORIMETERS

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I. OBJECT AND SCOPE OF THE INVESTIGATION

Apology is hardly necessary for another paper on the specific heat of copper, notwithstanding the large number of determinations which have already been published. One who has need of employing a figure for this quantity and turns to tables of physical constants for it finds a discordance that is somewhat discouraging. For example, in one of these the few results quoted which cover a common temperature interval show discrepancies of 2 per cent and those which are not in the same interval can not be reduced to a basis of comparison because the temperature coefficients there indicated ¹ vary by 60 per cent of the larger or over 100 per cent of the smaller.

There are similar deficiencies in many lines relating to specific heat determinations, but to supply all these will involve an amount of work far outside the possibilities of the Bureau of Standards. However, those constants which enter directly into the primary standardization work of the Bureau must be determined, and in this way the present investigation has come about. Hence, the temperature range of these measurements is quite limited (15° to 50°), although it is obvious that work over a much wider range is needed.

The investigation is a secondary one, related to the fundamental problem of measuring the specific heat of water at various temperatures and the value of the mechanical equivalent of heat; that is, the number of joules in a calorie. A calorimeter employed for this is constructed largely of rolled electrolytic copper, the heat capacity of which forms between 1 and 2 per cent of the heat capacity of the total system as used. Each per cent error in the value used for the specific heat of copper introduces an error of about 1 part in 10 000 in the results obtained with this calorimeter. For reduction of results of the precision now being attained with it redetermination of the specific heat of copper was found to be necessary. Two independent methods were planned, and the apparatus for both was designed and constructed some years ago. Preliminary experiments at that time showed what might be expected, but the actual measurements had to be postponed on

¹ The example is taken from the widely used Landolt-Börnstein *Physikalisch Chemische Tabellen*, edition of 1905, p. 385.

account of more pressing demands on the time of the author. Apparatus for one method has recently been described² and measurements are well under way. The other method³ forms the subject of this paper. It was originally intended that the two be published together, so that comparison of results might be discussed in the communication, but it does not seem advisable to withhold the work now finished, pending completion of that in progress.

Both methods give the specific heat of copper at a certain temperature; that is, the mean value over a small temperature interval. The range of temperatures is from 15° to 50°, this being the range required for the specific heat of water determination mentioned above. Within this range they of course give the temperature coefficient of the specific heat of copper.

This paper is confined to the experimental side of the subject. In the historical sketch only those papers have been reviewed which describe determinations of the specific heat of copper, and in the account of the results of the present determination no discussion has been attempted of their relation to the theories of specific heat. The variation of specific heat with temperature is of the utmost importance in this connection, and there is great temptation to one who is interested in the subject to comment upon the connection between his results and the various formulæ which have been proposed, but this can not be done without a more thorough treatment of the subject than would be proper here.

II. PREVIOUS DETERMINATIONS

1. HISTORICAL SKETCH

The concept of specific heat was formulated in the latter half of the eighteenth century, and the early developments merit a few words, without much regard to whether or not the investigators included copper in their experiments. But the subject soon claimed the attention of many, and the literature of the nineteenth and twentieth centuries is very voluminous. Only the papers containing the results of measurements made on copper are relevant here. Great care has been taken in an endeavor to make

² Harper: *Physical Review* (II), 1, p. 469; 1913.

³ The method is outlined in *Proceedings of Commencement of the University of Pennsylvania*, June 15, 1910.

the list reviewed below complete, but it must be borne in mind that certain classes of papers—e. g., inaugural dissertations and special reports—occasionally escape cataloguers and abstractors and the attention of their contemporaries by cross reference, so that even their existence is unknown to later workers in the same field.

In Table 1 is presented a chronological survey of the subject, and at the close of the chapter is a résumé with an accompanying table and curves which should be ample to meet the requirements of the general reader. The individual reviews presented in the next few pages may be omitted without breaking the continuity of the paper, although they may be seen to have an obvious purpose, both for the needs of the special reader and for reference in clearing up ambiguities in Table 2.

2. REVIEW OF INDIVIDUAL PAPERS

It is hardly possible to assign definite dates to the work of the very early investigators, and not always possible to ascertain what substances they measured. The roll includes Black, Crawford, Deluc, Irvine, Laplace and Lavoisier, and Wilke.

Black, during his lectures as professor of medicine at Glasgow, performed a number of experiments illustrating different capacities for heat for the same mass of different substances. One of his students and devoted followers, Robison,⁴ assigns to these the approximate date 1765–1770, and from his intimate relations with his teacher can not be many years in error. The results of the experiments were not published, and so it is not recorded whether they included copper.

Irvine ⁵ took up the work at Glasgow to which Black was obliged to give less and less attention after 1770. He was the first to publish a clear explanation, disentangling the four entities, specific heat, mass, temperature change, and quantity of heat when more than one was varied at a time.

Crawford ⁶ published in 1777 the results of some experiments on capacity for heat made during the few years immediately pre-

⁴ Black: *Lectures on the Elements of Chemistry*, edited by John Robison; edition of 1807, Philadelphia; p. 81, note 1 by Robison on p. 330.

⁵ Irvine: *Essays, Chiefly on Chemical Subjects*, London; 1805.

⁶ Crawford: *Experiments and Observations on Animal Heat*; London, 1777 and 1788; Philadelphia, 1787.

TABLE 1

Determinations of the Specific Heat of Copper—Chronological Résumé

Year.	Name	Temperature range investigated			Method
		Low	0° to 100° (slightly lower or higher included)	High	
18th cent.	Black.....		See individual reviews		
	Crawford.....				
	Deluc.....				
	Laplace and Lavoisier..				
	Irvine.....				
	Wilke.....				
1817	Dulong and Petit.....		0-100.....	0-300.....	Mixt. & cool.
1831	Potter.....		20-100.....		Mixt.
1834	Hermann.....		10-30.....		Cooling
1835	De la Rive and Marcet..		5-15.....		Cooling
1840	Regnault.....		15-100.....		Mixt.
1843	Regnault.....		5-20.....		Cooling
1856	Bede.....		15-100.....	16-172; 17-247...	Mixt.
1864	Kopp.....		20-50.....		Mixt.
1881	Lorenz.....		-20 to +20; 20-78; 20-131		Mixt.
1884	Tomlinson.....		20-60; 20-100.....		Mixt.
1887	Naccari.....		17-99.....	17-172; 17-253; 17-321	Mixt.
1891	Zakrzewski.....	-100 to 0.....	0-100.....		Ice cal.
1892	Schütz.....	-78 to +15.....	15-100.....		Mixt.
1892	Le Verrier.....			0 to 1000 in stages	Mixt.
1893	Richards and Frazier..			0 to 1000.....	Mixt.
1893	Voigt.....		21-100.....		Mixt.
1895	Waterman.....		23-100.....		Isoth. cal.
1895	Bartoli and Stracciati..		15-100.....		Mixt.
1898	Trowbridge.....	-181 to +11.....	23-100.....		Mixt.
1898	Behn.....	-186 to +18; -79 to +18			Mixt.
1900	Behn.....	Above, continued			Mixt.
1900	Jaeger and Diesselhorst.		At 18°; at 100.....		Cooling
1900	Tilden.....		20-100.....		Steam cal.
1902	Gaede.....		0-100 in small steps		Elect. htg.
1903	Schmitz.....	-182 to +20.....	20-100.....		Mixt.
1904	Glaser.....			To 1000.....	Mixt.
1910	Magnus.....		15-100.....	15-238; 15-338...	Twin cal.
1910	Richards and Jackson..	-190 to +20.....			Mixt.
1910	Schimpff.....	-190 to +17; -79 to +17	17-100.....		Mixt.
1910	Nernst, Koref, Lind'mn.		2-21.....		Mixt.
1911	Koref.....	-190 to -83..... -77 to 0			Mixt.
1911	Nernst and Lindemann..	-250 to -185.....			Elect. htg.
1911	Nernst.....	-250 to -185.....			Elect. htg.
1913	Griffiths and Griffiths..		0-100 in steps.....		Elect. htg.

ceding. These however did not possess his own confidence and were repeated and considerably extended, an edition of 1788 being much more comprehensive than the earlier ones. The subjects of his experiments included foodstuffs, a few of the more common metals, and also their compounds, and some gases inclosed in a bladder. The method employed was that of mixtures. The result of his measurements of the specific heat of copper⁷ was 0.1111.

Deluc gave much attention to the subject of heat and is frequently cited by his contemporaries in connection with measurements of specific heat, but always without definite references. His memoirs published from 1772 to 1810 were widely scattered, and apparently never collected in a single volume. No reports of experiments were found which contained any measurements for copper.

Laplace and Lavoisier⁸ developed the ice calorimeter in 1780 for the purpose of making specific heat measurements and in that year and in 1783 made a great many determinations, the most of which were published in 1793. They record no measurements on copper.

Wilke⁹ is the author of the term "specific heat," the previous usage having been confined to the term "capacity for heat." He made many experiments and prepared reference tables of specific heats. His experiments with copper gave 0.114 as the specific heat.

Dulong and Petit.¹⁰—The first determinations to possess any claim whatever to accuracy were those made by these authors. The copper was heated to the temperature of steam or of boiling mercury, these temperatures being reduced to the gas scale by means of the results of an elaborate comparison of mercury weight thermometers, air and metal expansion thermometers, in a preliminary investigation. The hot metal was plunged into a calorimeter slightly cooler than the room and the temperature rise measured with a mercurial thermometer. The rise was 5° to 6°,

⁷ Figure for the specific heat of copper from p. 288 of the edition of 1788.

⁸ Laplace and Lavoisier: *Memoirs de l'Academie de Science*, 1780, p. 355; *Oeuvres de Lavoisier*, 2, pp. 283, 724; (1862.)

⁹ Wilke: *Transactions of the Swedish Academy*, various years.

¹⁰ Dulong and Petit: *Journal Ecole Polytechnique*, 11, p. 189, 1820; *Annales de Chimie et de Physique* (3), 7, p. 142; 1817.

and the amount of metal employed 1 to 3 kg. The results are given for even hundred-degree intervals and are expressed in terms of specific heat of water equal to unity. (At that time variation with temperature of the specific heat of water was not generally recognized.)

Temperature interval	0° to 100°	0° to 300°
Mean specific heat	0.0949	0.1013

Two years after the publication of the experiments just described a second communication¹¹ was made, describing a series by the method of cooling. The results were deduced from observations of the time taken to cool from 10° to 5° when suspended in an inclosure surrounded by melting ice. Great care seems to have been taken in all details, and sources of possible error received more than a perfunctory consideration. The mean result was

10° to 5° (apparently this range, but not stated clearly)
0.0949

Potter.¹²—The two papers by this author, in conjunction with the criticism of the work by Johnston¹³ form a contribution that can not be said to inspire confidence. By employing the method of mixtures in two ways, hot copper in cold water and cold copper in hot water, he believed that the systematic errors of this method should reverse and the mean be a better approximation to the truth than would a result obtained by the more usual first method alone. The details of making the measurements were evidently very poorly carried out. The first series of experiments gave as mean results

Hot copper (212° F) in cool water (room temperature)	0.0868	} 0.096,
Cool copper (55° F) in hot water (103° F)	0.1014	

having due regard to reversible and possibly irreversible errors.

A second series, including 18 determinations, gave 0.0943 for the hot copper method; the hot water method was not carried out with copper, but a correction to the other results deduced

¹¹ Dulong and Petit; *Annales de Chimie et de Physique* (2), 10, p. 395; 1819.

¹² Potter; *Edinburgh Journal of Science, New Series*, 5, p. 80, 1831; *ibid.*, 6, p. 163; 1832.

¹³ Johnston; *Ibid.*, 5, p. 265; 1831.

from hot water experiments with other metals; the final figure is stated to be 0.096.

Hermann¹⁴ undertook an elaborate investigation for the purpose of ascertaining the fundamental laws of the relations of specific heats of substances, especially compounds. He deemed a re-determination of the values for simple substances to be advisable and employed the method of cooling. The temperature range was 30° C to 10° C. In terms of the mean specific heat of water over this interval as unity, the result for copper was

0.0961 at (20°).

De la Rive and Marcet¹⁵ read a paper to the Geneva society in 1835 giving the results of many determinations of specific heat by the method of cooling. Copper was often the substance experimented upon, but as they originally obtained the heat capacity of their calorimeter by performing similar experiments with copper and assuming a value for its specific heat, 0.095 from the tables of Dulong and Petit, these numerous experiments are but a test of precision, and the final value of 0.095 which they state in their results is not entitled to consideration as an independent determination.

Regnault¹⁶, amongst many hundred determinations of specific heats, includes two series of measurements on copper. The first of these, by the method of mixtures, was performed with extraordinary care because the sample of copper so standardized was to be employed in determining the specific heat of terebenthine (a turpentine oil) for use in a calorimeter where water could not be used, and was therefore a basis of reference for a whole series of measurements. Four experiments with very pure copper, from 98° C to (about) 17°, gave the following results in terms of water as unity (irrespective of temperature, but may be considered to be in terms of the 15° cal within probably one part in 1000):

0.09537; 0.09546; 0.09497; 0.09480; mean 0.09515.

The work of this experimenter upon the effect of hardness on specific heat is important. A specimen of soft copper was used,

¹⁴ Hermann: *Nouveaux Memoires de la Société Impériale des Naturalistes à Moscou*, 8, p. 137; 1834.

¹⁵ De la Rive et Marcet: *Annales de Chimie et de Physique* (2), 75, p. 113, 1840.

¹⁶ Regnault: *Annales de Chimie et de Physique* (2), 73, p. 5; 1840.

then it was hammered cold, and finally was annealed. The results of the specific heat determinations were:

Soft	Hammered	Soft
0.09501 9455	0.0936 933	0.0949 948
0.0948	0.0934	0.0948.

The procedure for the measurements was almost identical, so that the comparative results are worthy of careful consideration. Whatever systematic errors may characterize Regnault's work due to faulty instruments and especially the state of thermometry, his very great care in every detail of experimental work entitles such a comparison to confidence.

The second series of measurements¹⁷ on copper was made in 1843 by the method of cooling in a partial vacuum (1.5 mm of Hg.). The results obtained at that time for a number of metals were extremely discordant and quite irreconcilable with earlier determinations by the method of mixtures. Regnault never had any confidence in this piece of work, nor did he use the results of it, but also he was not able to find a satisfactory explanation of the fault. The mean result for copper was—

$$0.0886 \text{ (20}^\circ \text{ to 5}^\circ \text{?)}$$

Bede¹⁸ employed the method of mixtures. The copper was heated for an hour or more in a tube immersed in an oil bath, the temperature being measured with a mercurial thermometer. The calorimeter thermometer was calibrated for bore and fundamental interval, the scale being arbitrary. The heat capacity of the calorimeter, about 1 per cent of that of its water content, was computed from the weights and specific heats of the parts. The only cooling correction was to start the experiment somewhat below room temperature, ending it a little above. The operations seem to have been arranged with some care and the chief error is most likely in the thermometry. The average results were:

Temperature interval	15°–100°	16°–172°	17°–247°
Mean specific heat	0.09331	0.09483	0.09680

for pure copper. They are expressed in terms of the specific heat of water equal unity at the mean temperature of an experiment,

¹⁷ Regnault; *Annales de Chimie et de Physique*, (3), 9, p. 322; 1843.

¹⁸ Bede: *Academie de Belgique, Memoires Couronnés*, 27; 1856.

which was nearly always within a degree either side of 15° C. Bede considers a linear law of variation to hold for most metals and expresses the results for copper in the form—

$$c_t = 0.0910 + 0.000046t \quad (\text{specific heat at temperature } t).$$

$$c'_0 = 0.0910 + 0.000023t \quad (\text{mean value, } 0^{\circ} \text{ to } t^{\circ}).$$

Kopp¹⁹ made an enormous number of specific heat measurements, chiefly of compounds, to definitely establish the laws of their relationship. He showed beyond doubt that the conclusion of Neumann and Avogadro and others regarding the computation of the specific heat of a compound from the specific heats of its constituent elements was thoroughly sound (the law is frequently referred to as Kopp's law). For the purposes of his investigation high accuracy was sacrificed to multiplicity of experiments, and he is very explicit in explaining that the apparatus and procedure were not arranged for precision.

The method was that of mixtures. The substances were placed in a glass tube, surrounded by an inert liquid so that temperature equilibrium with the surroundings of the tube might be more quickly attained. The tube was heated for 10 minutes in a mercury bath immersed in a hot oil bath, and then transferred to the calorimeter. The only account taken of a cooling correction was to start an experiment below room temperature and end it above, the liquid in the tube was not stirred, and also there is a very large correction in the results due to the heat capacity of the tube and its liquid; nevertheless some control experiments with water indicate that the results attained were rather good. The results for copper were:

Immersed in naphtha	0.0895	} mean 0.0925 (45° to 15°)
	949	
	926	
	930	
Immersed in naphtha	0.0909	} mean 0.0911 (53° to 21°)
	906	
	917	
	902	
	921	

¹⁹ Kopp: *Annalen der Chemie und Pharmacie*, 3 supplement; 1864-5.

Immersed in water	0.0965	} mean 0.0953 (50° to 21°)
	958	
	953	
	934	

Final mean, 20° to 50°, 0.0930

The sample was the commercial copper wire obtainable at that time. The unit in which the result is expressed is immaterial, as the final cipher is certainly gratuitous.

Lorenz²⁰ determined the specific heat of copper in the course of his work on the measurement of conductivities. The method of mixtures was employed. A rod was heated in a tube immersed in the vapor of boiling ethyl alcohol (78°) or amylalcohol (131°), or was cooled with an ice salt mixture (−20°) and plunged into a calorimeter at about 20°, so that results were obtained corresponding to mean temperatures of about 0°, 50°, 75°. The means of several experiments were

$$0^{\circ}: 0.08988 \qquad 50^{\circ}: 0.09169 \qquad 75^{\circ}: 0.09319$$

The author states the true specific heat at 0° to be slightly different from the mean value −20° to +20°, and gives the figures

$$0^{\circ}: 0.08970 \qquad 100^{\circ}: 0.09421$$

There are no details concerning the temperature scale, the heat unit or the corrections, other than to say that the usual method was followed.

Tomlinson²¹ in an investigation on the influence of stress and strain on the properties of materials, determined the specific heat of some commercial copper wire after thorough annealing. The wire was coiled up inside a small brass holder, and with a thermometer in the center of the coil was heated in an air bath to 60° or 100°, and then plunged into the calorimeter. A series of blanks with the brass holder alone was also made. No details of calorimetric procedure are given, but only a blanket statement, "Every precaution was taken both with regard to the instruments themselves and the mode of using them to avoid error, and the formulæ given may be received with great confidence." Unfor-

²⁰ Lorenz: Wiedemanns Annalen, 13, p. 434; 1881.

²¹ Tomlinson: Proceedings of the Royal Society of London, 37, p. 108; 1884.

unately the results of this work, which have often been quoted, are sadly misleading (temperature coefficient undoubtedly very erroneous, see Fig. 1). These results, expressed in terms of the 0° calorie are:

$$\begin{aligned}\text{Copper of density } 20^{\circ}/4^{\circ} &= 8.851; \\ \text{total heat } 0^{\circ} \text{ to } t^{\circ}, & 0.09008t + 0.0000324t^2; \\ \text{specific heat at } t^{\circ}, & 0.09008 + 0.0000648t.\end{aligned}$$

Naccari²² carried out a very elaborate series of specific heat determinations by the method of mixtures. His thermometry and calorimetry were apparently more careful than were those of any of the preceding investigators and there would seem to be good reason to assign considerable weight to the results. Nevertheless the results with copper show a variation with temperature that can not be reconciled with later determinations (see Fig. 1) pointing to a serious error of some kind not easily ascertainable, which may affect all the experiments. A number of observations were taken in each of several temperature intervals, the mean results being:

$$\begin{aligned}\text{Total heat, } 17^{\circ} \text{ to } 99^{\circ}: & 7.68; & 17^{\circ} \text{ to } 171^{\circ}: & 14.45; \\ & & 17^{\circ} \text{ to } 253^{\circ}: & 22.44; & 17^{\circ} \text{ to } 321^{\circ}: & 29.08.\end{aligned}$$

The least square smoothed curve (for total heat) is given as

$$H_{17}^t = 0.092455 (t - 17) + 10.629 \times 10^{-6} (t - 17)^2$$

and the true specific heat at t° as

$$c_t = 0.092455 + 21.258 \times 10^{-6} (t - 17) \text{ or } 0.09205 (1 + 230.8 \times 10^{-6} t)$$

Zakrzewski²³ measured the specific heats of metals in the ranges -100° to 0° and 0° to $+100^{\circ}$, using a Bunsen ice calorimeter for the purpose. Cooling to -100° was accomplished in a low-temperature thermostat, the refrigeration for which was obtained by the evaporation of a volatile liquid. The results for copper were:

$$\begin{array}{ll}-100^{\circ} \text{ to } 0^{\circ} & 0.08514 \\ +100^{\circ} \text{ to } 0^{\circ} & 0.09217\end{array}$$

²² Naccari: Reale Accademia delle Scienze di Torino, Atti, 23, p. 107; 1887.

²³ Zakrzewski: Krakau Universität Anzeiger, 1891, p. 146 (original paper not accessible for review, which is taken from Fortschritte der Physik, 1891).

Schüz²⁴ measured the specific heats of alloys and amalgams and of the constituent metals. He employed the method of mixtures, using a very small brass calorimeter, about 50 cc, and 30 to 40 grams of copper, so that the temperature change was fairly large. The specimens, little pieces of thick wire placed in a test tube, were cooled in solid carbon dioxide or heated in steam. Temperatures were determined by a thermometer in the midst of the pieces. The low temperature thermometer, an alcohol one, was compared with a specially constructed air thermometer at several points, and in its use stem corrections were taken into consideration. Other details of the measurement seem to have received correspondingly careful attention. The results were

Steam to 15° (about): 0.09307; 9278; 9338; mean 0.0931

Solid carbon dioxide (−78°) to 15°: 0.09041; 9014; mean 0.0903

Le Verrier²⁵ seems to have been the first to measure the specific heat of copper at very high temperatures. The method of mixtures was used and no details are given except that the high temperatures were measured by focussing a Le Chatelier pyrometer on the copper at the instant before plunging it into the calorimeter. The number of observations is not stated.

Temperature interval	Total heat	Mean specific heat
0°– 360°	0.104†	0.104
320°– 380°	Absorbs 2 cal. near 350°	
360°– 580°	37.2+0.125 (t–360)	0.125
560°– 600°	Absorbs 2 cal. near 580°	
580°– 780°	*37.+0.09 (t–580)	0.09
740°– 800°	Absorbs 3.5 cal. near 780°	
780°–1000°	92.+0.118 (t–800)	0.118
	Absorbs 117 cal. about 1020°	

* This figure is obviously a misprint, but all the inconsistencies in the column of total heats can not be so construed.

Richards (J. W.) and Frazier²⁶ made a particular study of copper in a series of measurements of specific heats at high tem-

²⁴ Schüz: Wiedemanns Annalen, 46, p. 177; 1892.

²⁵ Le Verrier: Paris Académie des Sciences, Comptes Rendus, 114, p. 907; 1892.

²⁶ Richards and Frazier: Chemical News, 68, p. 84; 1893.

perature and reached the conclusion that none of the above (Le Verrier's) critical points occur and that the specific heat increases regularly with temperature to 900° according to the formula below. Their work was relative only, a value for the specific heat of platinum taken from other measurements forming the basis of reference. Details of the experiments are not recorded, but they state that it would have been impossible for an absorption of so much heat as 0.5 calorie to have occurred at one of the supposed critical points without detection. Their results were

$$c_t = 0.0939 + 0.00003556t \quad 0^{\circ} \text{ to } 1000^{\circ}$$

Latent heat of fusion (mean of six determinations) = 43.3 cal.

Voigt²⁷ used the method of mixtures. There were no departures from common practice which are worthy of note. By the use of blank experiments and other supplementary experiments bearing upon possible errors, he removed many grounds for suspecting the results, yet it is to be noted that the figure for copper is very low. He claims to have attained an accuracy of 0.2 per cent. The results for copper in terms of 18°7 calories, international hydrogen scale of temperature, were:

21° to 100° , 0.0918; 918; 928; 928; mean, 0.0923.

Waterman²⁸ employed an isothermal calorimeter, running ice water into it immediately after dropping in the hot metal specimen, the rate of supply and the total quantity of ice water being such as to absorb the heat as fast as given up by the metal. The details of all the measurements seem to have received considerable care, and the results indicate a precision that merits a moment's attention to the unit in which they are expressed. This is not explicitly stated, but appears to be the mean heat capacity in the interval 0° to 23° (about) of that mass of water which balances 1 gram of brass (?) in air. Some check on accuracy was obtained by the variation in the quantities of metal and ice water over a range of about two to one. The copper (Lake Superior) was 99.98 per cent pure, and drawn. The mean specific heat from 23° to 100° was found to be

0.09475; 9470; 9467; 9474; average, 0.09471.

²⁷ Voigt: Wiedemanns Annalen 49, p. 709; 1893.

²⁸ Waterman: Physical Review, 4, p. 161; 1896. Philosophical Magazine (5), 40, p. 413; 1895.

Bartoli and Stracciati²⁹ used the method of mixtures, with all details in the usual way. The results given for copper, in terms of 15° calories, were:

Cu with 0.12 % Sn and 0.12 % Au, 0.093392, 15° to 100°

Cu with 0.005 % Sn and traces other metals, 0.093045, 15° to 100°

Trowbridge³⁰ used the method of mixtures. The copper was immersed directly in boiling water and upon removing was rapped sharply against the side of the vessel, the drainage being promoted by rounded ends. Auxiliary experiments gave a correction to be applied for the very small residue of water clinging to the specimen. The calorimetric operations, e. g., thermometry, water equivalent determination, cooling correction, do not appear to have been objects of great care. The exact unit in which results are expressed is immaterial since the observations show large deviations. A process exactly similar was carried out, substituting boiling oxygen for the steam. It was observed that all the oxygen was shaken off the specimen and accordingly no correction was necessary. The temperature of the oxygen was taken as -181°.4. The results were:

23° to 100° 0.09262; 9463; 9399; 9394; 9517; mean 0.0940
-181°.4 to +11° 0.0867; 854; 882; 873; 868; mean 0.0868

Behn³¹ did some very careful work at low temperatures by the method of mixtures. The thermometry was carefully executed with properly standardized instruments, both for the low temperature measurements and the calorimetry. The heat exchanges during transfers of specimens were carefully checked in supplementary experiments, and other details of the measurements were given like attention. The results are expressed in 18° calories, international hydrogen scale of temperature, weighings reduced to vacuo.

Drawn copper containing 0.5 per cent Sb and Ag

-186° to +18°, 0.0796; 0.0795; mean 0.0796

-79° to +18°, 0.0887; 0.0879; 0.0884; mean 0.0883

The small number of observations is not so serious a fault in this

²⁹ Bartoli and Stracciati: Reale Istituto Lombardo di scienze e lettere, Rendiconti (2), 28, p. 5; 1895; (original paper not accessible, review from Fortschritte der Physik, 1895).

³⁰ Trowbridge: Science, new series, 8, p. 6; 1898.

³¹ Behn: Wiedmanns Annalen, 66, p. 237; 1898.

investigation as might appear at first, since the method was carefully tried by large numbers of experiments with substances other than copper, and high precision was found to have been secured.

After publication of the first paper the experiments were continued³² and from the results of both sets the conclusion was drawn that for most metals the variation of specific heat with temperature is expressible by the formula $c = A + Bt + Ct^2$. The later series of experiments are not tabulated in detail. The result³³ for copper was

$$c = 0.0913 + 0.0000676t - 0.00583t^2$$

but the author states that the work with copper was "not satisfactory."

Jaeger and Diesselhorst³⁴ determined specific heats as a necessary factor in their measurements of thermal conductivities. The method employed was in principle a method of cooling, the specific heat being determined from the heat lost by a given mass of copper and the corresponding temperature change. In the earlier developments of this method the heat loss was determined from emission constants of the surface obtained from a similar experiment with a substance of known specific heat, usually water; in this investigation the emission constants were obtained by measuring the amount of energy supplied electrically which was necessary to maintain the calorimeter in equilibrium at a given temperature above that of its environment. The calorimeter consisted only of a portion of the metal itself in the form of a rod or wire. A measured current of the desired intensity was sent through the specimen until equilibrium was established and then suddenly interrupted and the rate of cooling observed at intervals. The process was also inverted, a current being suddenly switched on to the specimen and the rate of warming observed, together with the other necessary quantities.

The method worked quite well for poor conductors, but for the better conductors the various quantities involved proved to be so proportioned that it was not feasible to arrange magnitudes

³² Behn: *Annalen der Physik* (4), 1, p. 257; 1900.

³³ 0.00583 stands for 0.00000583 and similarly throughout this paper.

³⁴ Jaeger and Diesselhorst: *Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt*, 2, p. 362; 1900.

that would permit of accurate determination of all. The authors discarded entirely the values of specific heat they found for silver and copper and in the conductivity paper employed values found by Naccari. The results with copper, very pure (less than 0.05 per cent impurity, mostly Fe, Zn), were:

at 18°	0.381	joules per gram degree
at 100°	0.386	

Tilden³⁵ used a Joly steam calorimeter. The heat unit is that of which 536.5 equal the latent heat of steam at normal pressure. All weighings were reduced to vacuo. The results for pure copper were:

"Room temp." to 100°: 0.09248; 9241; 9205; 9234; mean 0.09232

From sample observations reported in full for other metals, it seems that 20° is a fair figure to take as room temperature.

Some interesting data were obtained concerning the effect of impurities on specific heat. Assuming electrical conductivity to be a criterion of purity, the following results were obtained:

Fairly pure wire (low resistivity), 1.69 microhms per cm cube at 17°.7; 0.09274; 9272; mean 0.09273.

Impure wire (high resistivity), 2.75 microhms per cm cube at 17°.7 (analysis for impurities likely to be present showed no Bi, trace Sb, 0.154 per cent As.); 0.09266; 9267; mean 0.09266.

The difference is not significant.

A sample was then contaminated with known amounts of impurity, and the measurements resulted as follows:

Pure Cu fused in H,	0.09265; 9234; mean 0.0925
Same with 0.002 % P,	0.09368; 9336; mean 0.0935
Same with 0.44 % P,	0.09347; 9320; mean 0.0933
Same with 3.49 % P,	0.09870; 9910; mean 0.0989
Pure Cu fused in air (possibly some oxide),	0.0936; 938; mean 0.0937
Same with 0.49 % Sn,	0.0936; mean 0.0936
Same with 3.29 % Sn,	0.0927; 924; mean 0.0925
Same with 6.64 % Sn,	0.0905; 905; mean 0.0905

³⁵ Tilden: Philosophical Transactions of the Royal Society of London, A194, p. 233; 1900.

Gaede³⁶ made the first point to point determination by a method electrical in all its features. The specimens of metal formed their own calorimeters. These were machined cylindrical, and a deep central core bored out. Into this was thrust a copper core, wound with a properly insulated heater of constantan ribbon and a resistance thermometer of fine copper wire. Thermal contact between the core and the walls of the well was secured by filling the intervening space with mercury, using a thin steel shell when necessary to avoid amalgamation. This calorimeter was suspended in a thermostat and heated through an accurately measured temperature interval of about 15° by an accurately measured quantity of energy supplied electrically. The apparatus and procedure are described in minute detail, and indicate due care in every respect. The statement of results is faulty in omitting to state the basis of the electrical units and the value of the mechanical equivalent used to obtain the final figures which are said to be in terms of 17° calories and are referred to the international hydrogen scale of temperature. The copper was of high degree of purity, density 8.835.

Temperature, $16^{\circ}.7$ $32^{\circ}.7$ $47^{\circ}.0$ $61^{\circ}.9$ $76^{\circ}.4$ $92^{\circ}.3$
 Specific heat, 0.09108 0.09189 0.09244 0.09310 0.09346 0.09403

These results are expressed by a formula which represents them within ± 0.045 per cent (0° to 100°):

$$c = 0.09111 + 0.00005002 (t-17) - 0.001555 (t-17)^2$$

A linear formula is given also, which represents them within ± 0.09 per cent:

$$c = 0.091225 + 0.0000384 (t-17).$$

Schmitz³⁷ used the method of mixtures as ordinarily carried out, and also an inversion of the Black ice calorimeter method. His paper gives evidence of very careful work in every detail. The specimen was cooled in liquid air, the temperature of which was determined by a resistance thermometer calibrated in boiling

³⁶ Gaede: Inaugural Dissertation, Freiburg, 1902. Short paper in *Physikalische Zeitschrift*, 4, p. 105; 1902.

³⁷ Schmitz: Proceedings of the Royal Society of London, 72, p. 177; 1903.

oxygen taken as $-182^{\circ}.5$. The calorimeter thermometer was of the Beckmann type, carefully standardized and properly used. The reductions were made on the basis of specific heat of water being unity at $17^{\circ}.5$ and varying as tabulated in Griffiths Thermal Measurement of Energy, Table VII.

The copper was very pure; source, Johnson-Mathey Co. The mean of 14 experiments in very good agreement was:

Temp. interval,	Mean specific heat,
-190° to $+20^{\circ}$; 0.800 (mercury scale)	$= 0.0798$ (Hyd. scale).

In the next series of experiments the calorimeter was maintained at 0° as closely as could be measured. The cold copper was then introduced, suspended by a thread from a balance arm. After immersion for a sufficient length of time, it was removed from the calorimeter, carefully dried with filter paper at 0° , and weighed to determine the quantity of the ice coating frozen to it. The latent heat of ice was taken as 80.0. In supplementary experiments were investigated the possible sources of error, such as occluded water, the thread, etc. The results obtained were quite consistent, and the mean of the series with copper is:

-190° to 0° (?): 0.0793

To obtain a comparison with the work of other observers he deemed it advisable to determine the specific heat of the same specimen within the temperature interval 0° to 100° . The method of mixtures was employed, with no variations from the usual practice. The mean of a fairly concordant series of 8 measurements was:

20° to 100° 0.0936 Hydrogen scale; probably $17^{\circ}.5$ calories.

Glaser³⁸ employed crude apparatus, violating most of the established principles of calorimetry, and has indicated the extent to which he appreciated the limitations of work of this character by retaining a few superfluous figures. The method was that of mix-

³⁸ Glaser: *Metallurgie*, 1, p. 103; 1904.

tures in a huge calorimeter, capacity 40 liters or more. The high temperatures were measured with a Le Chatelier pyrometer.

			Mean specific heat
95.51 % Cu,	1 expt, 891°.5 to 22°.5		0.112405
	1 expt, 1081° to 24°		0.158455
Pure Cu,	1 expt, 1005° to 29°		0.10884
	1 expt, 1086° to 27°.7		0.152810

Therefore (!) the latent heat of fusion of copper is 41.63 cal.

Magnus³⁹ used a twin calorimeter outfit of very large capacity, about 60 liters. The differential thermometer for this was a 100-junction thermocouple. The water equivalent was determined by immersing copper at 100° in the calorimeter, and also by pouring hot water into it. With the former method the value 0.0933 for the mean specific heat of copper between 15° and 100° was taken, based on the work of Bede and of Naccari.

The results of the two methods were in agreement within the limits of experimental error, and so this may be regarded as an independent determination of the specific heat of copper in terms of a mean 15°–100° calorie. The work was continued at higher temperatures, and the mean results for copper were:

Temperature interval	15°–100°	15°–238°	15°–338°
Mean specific heat	0.0933	0.09510	0.09575

Richards (T. W.) and Jackson⁴⁰ measured specific heats between the temperature of liquid air and 20°. The paper contains a critical review of all previous low temperature determinations. These investigators took especial pains with respect to the apparatus and procedure relating to the low-temperature arrangements, but were somewhat less careful respecting the calorimeter. The description of this indicates possibilities of appreciable errors due to evaporation and to the method of supporting the calorimeter in the jacket. The mean result from ten experiments with copper was:

$$-190^{\circ} \text{ to } +20^{\circ}, \quad 0.0789 \quad (20^{\circ} \text{ calories, int. hyd. scale.})$$

³⁹ Magnus: *Annalen der Physik* (4), **31**, p. 597; 1910.

⁴⁰ Richards and Jackson: *Zeitschrift für Physikalische Chemie*, **70**, p. 414; 1910.

Schimpff⁴¹ employed the method of mixtures, using a very small calorimeter and rather small quantities of the metal specimens. In consequence his experiments were very liable to error. For example, the thermometer, a large Beckmann instrument, was the source of very great uncertainties respecting water equivalent, heat conduction along its stem, and emergent stem correction. The author claims an accuracy of 1 per cent for his results. The copper was 99.91 per cent pure (Fe 0.02 per cent) and was fused before the measurements. The unit is the 17° calorie, international hydrogen scale, and results of the experiments were:

17° to 100°,	0.0926; 924;	mean 0.0925
17° to - 79°,	0.0880; 889; 872;	mean 0.0880
17° to - 190°,	0.0784; 788;	mean 0.0786

These results were expressed by the formula

$$c_t = 0.091996 + 0.0000457090 (t - 17) - 0.006066 (t - 17)^2$$

giving the following values:

Temperature	- 150°	- 100°	- 50°	0°	+ 50°
Specific heat	0.0674	0.0783	0.0862	0.0910	0.0928

Nernst, Koref, and Lindemann⁴² employed for a calorimeter a large hollow cylinder of copper, with a thermoelement embedded in the wall. Heat exchanges with the surroundings were reduced by suspending this cylinder in vacuo. The method of mixtures was used, the heat gained or lost from the specimen being distributed through the calorimeter by metallic conduction, in contradistinction to the more usual stirred calorimeter liquid. Eight experiments with copper are tabulated, the agreement between them being fair. The mean, in terms of a calorie equal to 4.188 joules (international electric units?), is:

$$21^{\circ}.6 \text{ to } 2^{\circ}.4 \quad 0.0915_s$$

Koref⁴³ continued the work with the calorimeter described in the preceding paragraph, obtaining some low temperature meas-

⁴¹ Schimpff: *Zeitschrift für Physikalische Chemie*, **71**, p. 257; 1910.

⁴² Nernst, Koref, and Lindemann: *Königlich Preussischen Akademie der Wissenschaften zu Berlin, Sitzungsberichte*, 1910, p. 165; p. 247.

⁴³ Koref: *Annalen der Physik* (4), **36**, p. 49; 1911.

urements of specific heats by the method of mixtures. The results for copper (commercial, drawn) were:

Temperature interval.	Mean specific heat.
-189°8 to -83°3	0.0720
-189°8 to -82°9	0.0719
-77°0 to 0°	0.0876
-76°2 to 0°	0.0880

Nernst and Lindemann⁴⁴ made a series of point to point determinations at very low temperatures, using a calorimeter developed by Eucken.⁴⁵ A piece of the metal of suitable size was shaped into a hollow cylinder and a loosely fitting core for the same. On the core was wrapped a platinum wire, properly insulated, to serve as a resistance thermometer and also as an electric heater. The core was placed in the cylinder and paraffin poured into the crevices to improve the thermal contact. The whole was suspended in vacuo, and the specific heat over small temperature intervals determined from measurements of energy supplied electrically and of the temperature rise resulting therefrom. The results of the experiments are given in the paper in the form of a series of curves from which the following values for copper have been read:

Temperature,	40°K	60°	80°	100°
Atomic heat,	0.77	1.87	2.96	3.76
Specific heat,	0.0121	0.0294	0.0465	0.0590
(if at. wt. = 63.6)				

Nernst⁴⁶ in a summary paper of the whole specific heat investigation in which he and his associates had been engaged and had published in parts in the *Berliner Berichte*⁴⁷, gives the results of some measurements with copper that do not appear to have been tabulated elsewhere. They were obtained by the method described in the preceding paragraph, the specimen being about 300 g of electrolytic copper. The unit is a calorie equal to 4.188 joules (international electric units?).

⁴⁴ Nernst and Lindemann: *Königlich Preussischen Akademie der Wissenschaften zu Berlin, Sitzungsberichte*, 1910, p. 263; 1911, p. 306, p. 494.

⁴⁵ Eucken: *Physikalische Zeitschrift*, 10, p. 586; 1909.

⁴⁶ Nernst: *Annalen der Physik* (4), 86, p. 395; 1911.

⁴⁷ Loc. cit.; Notes 42, 44.

Temperature,	23°5K	27°7	33°4	87°	87°	88°
Atomic heat,	0.222	0.324	0.538	3.30	3.36	3.38
Specific heat,	0.0035	0.0051	0.00845	0.0518	0.0527	0.0531
(if at. wt. = 63.6)						

Griffiths and Griffiths⁴⁸ used a twin calorimeter, electric heating, point to point method, the specimen measured forming its own calorimeter. Two exactly similar large cylinders of copper were suspended in a jacketing vessel and a measured amount of energy supplied electrically to one, the temperature rise of which relative to the other was measured by sensitive platinum resistance thermometers connected differentially. Every detail of the experiments seems to have received careful attention, and the precision attained was high, the deviations being generally less than one in one thousand. Some variations of method were introduced where possible for the purpose of securing checks on accuracy, which checks were found satisfactory. These experiments for testing the validity of the method were nearly all performed with copper, so that the number of observations secured with this metal was very large, about 35 in the neighborhood of 0° and 3 or 4 each at the other temperatures noted below. The copper, electrolytically deposited, was very pure, 99.95 per cent, the impurities being Pb, Fe, and a trace of SiO₂.

The results are expressed in a calorie equal to 4.184 electric joules and a temperature scale very closely the hydrogen one. The density of the copper was 8.922.

Temperature,	0°	28°42	67°32	97°4
Specific heat,	0.09088	0.09230	0.09387	0.09521
$c = 0.09088 (1 + 0.0005341t - 0.00048t^2)$				

3. RÉSUMÉ

For convenience of reference are collected in Table 2 the final results of the investigations reviewed in this chapter. To make

⁴⁸ Griffiths and Griffiths: Philosophical Transactions of the Royal Society of London, A213, p. 119: 1913.

TABLE 2
The Specific Heat of Copper

Year	Name	Temp.	Result	^{50°} _{49 (DRH)}	Remarks
1817	Dulong and Petit	0-100	0.0949	0.094 ₉	
	do.....	0-300	0.1013		
1819	do.....	5-10	0.0949	0.097	Method of cooling
1831	Potter.....	(50°)	0.096	0.10	Mean of expts. over diff. temp. ranges
1834	Hermann.....	20°	0.0961	0.097 ₄	
1840	Regnault.....	15-100	0.09515	0.094 ₈	Very pure Cu; Hammered Cu 1.5% lower than soft Cu.
1843	do.....	"Room"	0.0886	0.09	Method of cooling. (Results consid- ered worthless by Regnault)
1856	Bede.....	15-100	0.09331	0.093 ₀	{ Pure copper. Results expressed with- in experimental error by the formula c=0.0910+0.000046t
	do.....	16-172	0.09483		
	do.....	17-247	0.09580		
1864	Kopp.....	20-50	0.0930	0.094	Commercial copper wire
1881	Lorenz.....	0°	0.08988		
	do.....	50°	0.09169	0.091 ₇	
	do.....	75°	0.09319		
1884	Tomlinson.....	(50°)	0.09332	0.093	Mean from expts. in diff. temp. ranges, c=0.09008+0.0000648t
1887	Naccari.....	17-99	0.0937	0.093 ₄	
	do.....	17-171	0.0938		
	do.....	17-253	0.0951		
	do.....	17-321	0.0957		
1891	Zakrzewski.....	-100-0	0.08514		Bunsen ice calorimeter
	do.....	0-100	0.09217	0.092 ₂	
1892	Schütz.....	15-100	0.0931	0.092 ₈	Copper wire
	do.....	-78-15	0.0903		
1892	Le Verrier.....	0-360	0.104		
	do.....	360-580	0.125		
	do.....	580-780	0.09		
	do.....	780-1000	0.118		
1893	Richards and Frazier...	0-1000			c=0.0939+0.00003556t
1893	Voigt.....	21-100	0.923	0.91 ₇	
1895	Waterman.....	23-100	0.09471	0.094 ₂	Very pure Cu, drawn
1895	Bartoli and Stracciati...	15-100	0.0932	0.092 ₀	Very pure Cu
1898	Trowbridge.....	23-100	0.0940	0.093 ₆	
	do.....	-181.4-11	0.0868		
1900	Behn.....	-186-18	0.0796		{ Drawn copper, 0.5% Sb & Ag. Final result of these expts. and others, not separately reported, c=0.0913+ 0.0000676t-0.00583t ²
	do.....	-79-18	0.0883		

⁴⁹ This column has been prepared by the author from the figures in the column immediately preceding which are taken directly from the original papers. In copying them, all the figures stated have been retained; in the column containing the results of the computation of the 50° value by the author, only those figures are retained which the precision (or in some cases apparent accuracy) would seem to warrant. The coefficient 0.000044 has been used in reducing results obtained at the various temperatures to the 50° value to permit of comparison; the formula $c=c_0+0.000044t$ being assumed, valid for values of t from 0° to 100°.

TABLE 2—Continued

Year	Name	Temp.	Result	50° (DRH)	Remarks
1900	Jaeger & Diesselhorst....	18°	(0.091 ₀)	0.092	Very pure copper. Method (in principle a method of cooling) not suited to accurate measurements for good conductors. Results considered of no value by Jaeger & Diesselhorst.
	do.....	100°	(0.092 ₂)	0.090	
1900	Tilden.....	15-100	0.09232	0.0920	Pure Cu. Expts. showing phosphor raises and tin lowers sp. ht. of Cu
1902	Gaede.....	1697	0.09108	0.0925	Very pure copper. Electric heating, point to point method Results combined in formulas, $c = 0.09111 + 0.00005002(t-17) - 0.081555(t-17)^2$ within $\pm 0.045\%$ $c = 0.09122_0 + 0.0000384(t-17)$ within $\pm 0.09\%$ Units, 17° calorie, hydrogen scale
	do.....	3297	0.09189	0.0926	
	do.....	4790	0.09244	0.0926	
	do.....	6199	0.09310	0.0926	
	do.....	7694	0.09346	0.0923	
	do.....	9293	0.09403	0.0922	
1903	Schmitz.....	-190-20	0.0798		Very pure copper. 17° calorie, hydrogen scale
	do.....	-190-0	0.0793		
	do.....	20-100	0.0936	0.0932	
1904	Glaser.....	30-1005	0.10884		Pure copper. Procedure such that error of 10% quite probable
1910	Magnus.....	15-100	0.0933	0.093 ₄	20° calories, hydrogen scale
	do.....	15-238	0.09510		
	do.....	15-338	0.09575		
1910	Richards and Jackson...	-190-20	0.0789		Copper 99.91% pure. Results expressed in formula $c = 0.091996 + 0.0000457090(t-17) - 0.0,5066(t-17)^2$ Calorie equal to 4.188 joules
1910	Schimpff.....	-190-17	0.0786		
	do.....	-79-17	0.0880		
1910	do.....	17-100	0.0925	0.092	Commercial drawn copper. Calorie equal to 4.188 joules
	do.....	2-22	0.09155	0.0932	
1911	Nernst, Koref, Lindemann	-190-83	0.0720		Calorie equal to 4.188 joules
1911	Koref.....	-77-0	0.0876		
	do.....	-233°	0.012 ₁		
1911	Nernst and Lindemann..	-213°	0.029 ₄		Electrolytic copper. In terms of a calorie equal to 4.188 joules
	do.....	-193°	0.046 ₆		
	do.....	-173°	0.059 ₀		
	Nernst.....	-24996	0.0035		
1911	do.....	-24594	0.0051		(Assuming ice-point = 273°. 1K) Electrolytic copper. In terms of a calorie equal to 4.188 joules
	do.....	-23997	0.0084		
	do.....	-18691	0.052		
	do.....	-18591	0.053		
	do.....				
1913	Griffiths and Griffiths...	09	0.09088	0.0931	Very pure electrolytic copper. Electric heating, point to point method Results expressed by formula $c = 0.09088(1 + 0.0005341t - 0.0,48t^2)$
	do.....	2894	0.09230	0.0932	
	do.....	6793	0.09387	0.0931	
	do.....	9794	0.09521	0.0931	

The units in terms of which the above results are expressed are not all the same, but the differences need not be taken into account in making comparisons. In every case the difference between the unit employed and the 15° calorie or the 20° calorie (which differ from each other by about one part in a thousand) is less than the probable experimental error.

comparisons between them reference should be had to Fig. 1. In selecting a figure for the most probable value of the specific heat of copper at a given temperature, it is a most difficult task to ascertain the weight to be assigned to these various measurements. The degree of care shown both in the planning of the experiments and the details of manipulation is reflected to a greater or less extent in each of the papers, and in the foregoing pages an effort has been made to indicate this feature, but it must be borne in mind that the evidence is far from being complete. The older determinations, no matter how skillfully carried out, suffered seriously from lack of adequate facilities and very imperfect knowledge of calorimetry and especially of thermometry. For this reason, it is the opinion of the author that two or three recent investigations executed with due care, that are in agreement, may be relied upon to fix the result with almost no consideration given a host of early determinations. Nevertheless it must be admitted that it is gratifying when one finds that the result so chosen is flanked about equally by the older measurements, and is a source of some anxiety if the departures are all to one side.

The results⁵⁰ obtained by Gaede, by Griffiths and Griffiths, and by the present investigation are in substantial agreement (Fig. 1) respecting the rate of increase with temperature of the specific heat of copper. These investigations were all made with the aid of resistance thermometers for the temperature measurements and precise electrical apparatus for the energy measurements. The details of all three were very carefully considered, and great pains taken to avoid error. Although all three determinations were by methods very similar in principle, the radical differences in working out the details were such as to render infinitesimal the probability of systematic error common to all. The coefficient 0.000044 is accordingly adopted by the author with entire disregard of the other determinations which give a coefficient in the range 0° to 100°, namely Lorenz (1881), 0.000045; Tomlinson (1884), 0.000065; Naccari (1887), 0.000021. The coefficient 0.000044 is then used to reduce to a comparable basis (value at 50°) all of the measurements made in the range 0° to 100°.

To deduce the "most probable value" from these is an operation that can not be devoid of individual opinion (whence the quotation

⁵⁰ Gaede, 0.000040 calories per gram degree at 50°; Griffiths and Griffiths, 0.000044; Harper, 0.000048.

Portion of complete diagram below, greatly magnified (ordinates by a factor of ten; abscissae by factor four)

FIG. 1.—The specific heat of copper. Results of measurements made prior to 1914

points). The value selected depends, of course, on the weight assigned to each determination. It is the opinion of the author that 0.0925 is the minimum, 0.0932 the maximum figure to be considered and that in all probability the value lies between 0.0926 and 0.0931, but that closer limits are not defined. If we select the mean of these limits, 0.0928, and the coefficient 0.000044, it is equivalent to collecting the results of all previous measurements of the specific heat of copper between 0° and 100° into the following average figures:

Temperature,	0°	25°	50°	75°	100°
Specific heat,	0.0906	0.0917	0.0928	0.0939	0.0950

Critical analysis of the results obtained outside of the temperature range 0°–100° does not belong to this paper. The low temperature determinations can not be passed by, however, without a comment, often made before, upon the futility of attempting to determine “true specific heat” from mean values over long temperature intervals. As shown in Fig. 1, with the form of the curve well established below the temperature of liquid air by Nernst, and above the temperature of melting ice by Gaede, Griffiths and Griffiths, and the present paper, it is not difficult to supply the intervening portion so as to fit reasonably well the measurements represented by the long lines; but were the entire curve left to determination by such lines, the task would be well nigh hopeless of accurate accomplishment. Above 0°, it has proven correct within reasonable limits to take the mean result of a measurement as the true specific heat at the mean temperature, but this is by no means evident a priori and the assumption might have led into error as serious as it would in the range –200° to 0°. Until the recent point-to-point determinations were made, the common practice of making that assumption had little, if any, justification.

III. METHOD EMPLOYED

The method was simple in principle, although somewhat complex in the details pertaining to the measurements. The important considerations that enter into the determination of each factor are discussed briefly in this section, detailed description both of apparatus and manipulation being reserved for separate sections.

The specimen of copper was a long wire, suspended in vacuo, and connected as part of an electric circuit. A measured quantity of heat could thus be imparted electrically and the temperature rise found by using the specimen itself as a resistance thermometer. The test specimen was thus its own calorimeter, no other substance being included in the "water equivalent" with the single exception of a few grams of mica necessary for electrical insulation.

The chief difficulty encountered was to arrange a large enough amount of copper in a form suitable for the electrical measurements. The wire was compactly coiled into a number of flat spirals, and these, superposed with mica plates between, built up a cylinder (Fig. 3) which included a considerable mass of copper and at the same time possessed electrical resistance large enough to make the necessary electrical measurements with the requisite accuracy. Potential leads tapped in at a distance from the ends of the wire served to define a portion the mass of which was the mass of copper involved in the determination. The resistance of this portion was that which was comprehended in the thermometric factor, and the energy supplied to it was the product of the current in the coil by the potential drop between these leads, integrated over the time the heating circuit was closed.

In equational form, the method may be stated:

$$MSK (R_2 - R_1) = \int_{t_1}^{t_2} e i dt - H. \quad (1)$$

M = mass in grams between potential leads.

S = specific heat (in joules per gram per degree).

K = factor reducing resistance change to temperature change.

R = resistance in ohms (at times t_1 , t_2).

e = drop of potential in volts.

i = current in amperes in specimen between instants t_1 and t_2 .

dt = increment of time in seconds.

H = "heat losses"; taking account of the cooling correction, heat conduction in the lead wires, energy necessarily supplied while measuring R_1 , R_2 , etc.

The surface of unit length of a wire being rather large with respect to the volume, the difficulty of determining H with extreme precision may be readily appreciated, and the feasibility of the method rests largely on the degree of success attained in making H small, so that a reasonable percentage error in its determination

shall be insignificant in the final result. By suspending the wire in vacuo, the cooling correction was reduced to less than half of what it would otherwise have been. The electrical method of heating the specimen in situ by a current traversing it, distributed the heat uniformly, so there was scarcely any lag in the attainment of equilibrium conditions and the measurement of the final temperature could be commenced very shortly after switching off the heating current, thus avoiding any long interval of time in the cooling correction period.

The electrical lead wires conducted an appreciable quantity of heat to or from the specimen and this subject is discussed in the section entitled "Cooling correction." The coil was supported in the vacuum chamber by silk cords, securing excellent thermal and electrical insulation so that any heat loss by conduction along the supports was entirely negligible.

A determination may be outlined as follows:

A small current was switched on to the specimen, heating it very slowly, and was measured by reading the drop of potential across the terminals of a resistance standard in the circuit. These readings alternated with a series taken on the potential leads from the specimen and the slowly rising temperature of the latter, measured by its resistance, was thus defined by a number of readings, constituting the ordinary preperiod of a calorimetric run. With the throw of a switch which exchanged the small current for a large one, the middle period began, and the specimen was heated through the desired range. This was usually 3° to 5° , and the current employed was such as to require seven or eight minutes, giving ample time to secure sufficient potentiometer readings of current and voltage to determine the average power with precision. The time factor of the energy measurement was given by automatic record on a chronograph of the instants when the heavy current was switched on and off. The final temperature of the specimen was determined in exactly the same manner as the initial one.

The precision of measurement of each factor may now be considered. The determination of the energy supplied to the specimen was not a problem offering great difficulty. The ordinary five decade potentiometer reads to one part in fifty thousand on the midsetting, so that moderate care in the selection of a steady storage battery, rheostats of small temperature coefficient and

good contacts, etc., resulted in securing a precision of at least one part in five thousand and probably much better in the measurement of power. The time, say 400 seconds, could be measured to about 0.02 second with the instruments at hand.

The determination of a temperature change of three degrees within one part in five thousand, calls for resistance measurements dependable to one part in five hundred thousand. To this end every feature of precise electrical measurements had to be considered carefully. Properly designed and carefully calibrated auxiliary apparatus was of course essential, and in addition, leakage from unknown sources, thermoelectric disturbances, fluctuations of battery and all similar possibilities of error received care in detection and avoidance. Although for just such reasons as those enumerated, the potentiometer method of reading a resistance thermometer may be as a rule inferior to the Wheatstone bridge method, the author chose the former because of conditions which seemed extremely unfavorable to the bridge method. The leads possessed resistance of the order of that of the coil to be measured, precluding the possibility of precise work with a simple bridge connection. The Thomson double bridge and similar devices eliminating lead resistance require more than one step in adjusting a balance, and appeared unsuited to the measurement of a resistance changing quite so rapidly as in this work.

The mass of the specimen between the potential leads was determined to one part in five thousand or better by direct weighing. The total length of the wire was about 50 meters and the uncertainty of location of the exact junctions of the potential leads was probably within a millimeter each. A slight amount of solder was included in the weighing, but not sufficient to be taken into account.

IV. APPARATUS

1. THE CALORIMETER AND ACCESSORIES

The parts pertaining to the calorimeter are shown in Fig. 2. The specimen (S) forming the calorimeter proper is in the center of the photograph, suspended by silk cords from a circular brass plate which hangs on a clamp stand. This plate is the lid of the vacuum chamber (V) beneath it, and when in use it rested on the

heavy brass reenforcing ring which is just visible at the top of this chamber. The contact surfaces were ground and a lip surrounded the joint so a seal of wax could be poured in if necessary. This was, however, not used, the ground joint proving water-tight. The vacuum around the specimen was secured by exhausting this vessel through the tube (P), the inverted U copper tube (G) at the right being connected to a McLeod gauge.

The outer walls of the evacuated space (i. e., the walls of this chamber) were maintained at uniform temperature by immersion in a well-stirred water bath contained in the large vessel (B) at the right of the figure. An electric heating coil (H), at the extreme left of the figure, was suspended in this water bath and served the double purpose of heating the bath to any desired temperature, and of keeping it there. It would dissipate up to 2 kilowatts safely, heating the bath 2 degrees per minute. When used to maintain a constant temperature it was supplied with current through a relay controlled by a thermostat, shown in the photograph partially hidden by the vacuum chamber. The bulb (T_b) is a long spiral tube of thin glass, and is under the protecting wire screen. The stem (T) with the mercury make and break for the relay circuit can be seen clearly. Immersion in the bath was total except for the mercury in the capillary, and the control of the temperature was all that could be desired.

The relative positions of the parts when assembled may be understood from the picture without description. The course of the circulating water in the large vessel was as follows: Down the offset tube, impelled by the motor-driven propeller stirrer, through a port into the main vessel, passing under the vacuum chamber and striking the thermostat bulb there, rising on all sides of this chamber and flowing back across the top, where it was sucked through an upper port into the offset tube again. The top water surface was several centimeters above the top of the vacuum chamber, so that the tubes inclosing the electrical lead wires (L) from the specimen were immersed for a considerable length, in order that the lead wires might acquire the temperature of the bath as closely as possible no matter how different from room temperature this might be. The thermal contact between these

FIG. 2.—The calorimeter. *Detail of parts*

FIG. 3.—Specimen of copper wire in the form used for the specific heat determinations

leads and the bath was fair, considering the necessity of very high electrical insulation and of an absolutely air-tight construction. The leads were bare copper, kept from touching one another by surrounding each by a tube of thin glass, with the space between completely filled with Khotinsky cement, and the glass tubes were embedded in Khotinsky cement in the metal tubes soldered through the brass plate. The construction is shown in both Figures 2 and 3.

Details of the form of the specimen may be seen in Fig. 3. About 50 meters of copper wire 2.5 mm in diameter were coiled into a number of spirals of the form shown in the corner of the figure, each double spiral containing about 3 meters. After winding, the two layers were separated electrically by inserting a very thin plate of mica. Such a unit is noninductive, has a resistance of the order of one one-hundredth of an ohm, and contains about 150 grams of copper. Sixteen of these units were superposed with mica insulation between, forming a cylinder about 10 cm high and 10 cm diameter. Alternate layers were faced in opposite ways and the ends of the wire, previously squared off neatly and tinned, were butt soldered. Uniformity of resistance was thereby easily secured, with no hot spots due to high resistance junctions.

The potential leads were soldered to the centers of the end units, so that the extreme end layers performed no other function than that of current leads, since only the portion of the wire between the potential leads entered into any measurement, as already explained. This design tended to reduce possible error due to thermal conduction along the leads, rather large and therefore requiring precautions in this respect. Over 150 cm of wire separated the specimen from external heat sources or sinks, making the temperature gradient small.

The leads attached to the specimen were five in number, two current leads of copper, approximately 2.5 mm in diameter, two potential leads of enamel-covered copper about 0.3 mm diameter, and one very fine constantan wire, soldered to the copper specimen at a convenient point, making a thermojunction which would indicate the temperature of the specimen relative to the temperature of the other junction of the couple. The latter was

usually dipped in mercury in a thin-walled glass tube immersed in the water bath surrounding the calorimeter, the temperature of this bath being measured with a mercurial thermometer.

The mica insulation forming part of the heat capacity of the calorimeter included 18.5 grams in all, the amount being determined by weighing the mica stock from which the 31 insulating plates were made, and weighing all clippings.

2. ELECTRICAL APPARATUS

A large amount of electrical apparatus was required, a general view of all being shown in Fig. 4. A schematic diagram of the principal circuits forms Fig. 5, in which for the sake of simplicity all detail of the two potentiometer circuits is omitted, also the chronograph circuit and those for the control of the water-bath temperature.

The potentiometer used for the resistance measurements pertaining to the determination of the temperature of the specimen was of the Diesselhorst⁵¹ type constructed by Otto Wolff. This is a low resistance instrument with five dial decades, and as special features avoids errors due to thermal emf generated in the dial contacts and possesses constant galvanometer sensibility, permitting accurate interpolation for a sixth figure. The galvanometer was a Leeds and Northrup instrument of fairly high sensibility and the resistance of the circuit was adjusted so that one microvolt produced a scale deflection of 2 mm. One-tenth microvolt could thus be read without difficulty. In Fig. 4 this potentiometer and accessories are shown in the foreground, on the table at the right of the observer's chair. The galvanometer is just behind the chronograph cabinet.

To the left of the observer's chair, on the wall bench, is the potentiometer system employed for the power measurements. This was a Leeds and Northrup type K slide-wire potentiometer and the galvanometer was a type P instrument of the same maker. This was mounted on the brick wall. Near this potentiometer, between it and the watch, the operating switch (S) of Fig. 5 may be dimly seen, and close at hand were the switches for the control of the chronograph.

⁵¹ *Zeitschrift für Instrumentenkunde*, 26, pp. 173 and 297, 1906; and 28, pp. 1 and 38, 1908.

Gauges Vacuum Pump

Calorimeter
L. & N. Potentiometer
Dresselhorst Potentiometer

Miscellaneous Electrical Apparatus
Chronograph

FIG. 4.—General view of entire apparatus

The chronograph was of the ticker tape form made by R. Fuess, the tape feeding from the reel at a uniform rate, approximately one cm per second. Seconds were marked by a needle operated from a Riefler clock, the secondary time standard of the Bureau. The reliability of the measurements was about 0.02 second. This chronograph was mounted in a cabinet as a portable unit and appears at the extreme right of Fig. 4.

The resistance standards, rheostats, ammeters, etc., were on the wall bench, mostly hidden in Fig. 4 by the chronograph cabinet. The rheostat (*L*) of Fig. 5 was a bank of carbon lamps and (*r*), (*C*) were Gebr. Ruhstrat rheostats of suitable ranges. All the con-

FIG. 5—Diagram of electric circuits

tacts were very good, and in spite of the very exacting requirements, they proved quite satisfactory. The 0.1 ohm resistance standards (*Q*), (*q*), were of manganin of very small temperature coefficient, and were immersed in oil. During the time of an experiment (*q*) was probably constant to better than one part in a million. The absolute value of (*Q*) enters into the measurements, and was determined to within 1 part in 50 000 by comparison with the resistance standards of the Bureau. The standard cell used to adjust the potentiometer current (for the power measurement) was evaluated in terms of the emf standard, and the coils of both potentiometers were carefully calibrated.

3. THE VACUUM PUMP AND ACCESSORIES

The vessel surrounding the calorimeter was exhausted with a May-Nelson rotary pump, a vacuum of the order of 0.2 mm of mercury being the average. The performance of the pump was most unsatisfactory, but no other was available at the time, and the results secured were sufficient for the purpose, as is more fully discussed in the appendix. The residual pressures were measured with a small McLeod gauge, amply sensitive for the purpose. The assembled vacuum apparatus is shown in Fig. 4, mounted as a portable unit on a table at the left. The pump, with its motor and control, and the radiator can for its water-cooling system, were all mounted beneath the table; the McLeod gauge, mercury manometers, stopcocks, etc., being on top.

V. MANIPULATION AND MEASUREMENTS

1. TEMPERATURE CHANGES

(a) CALIBRATION OF THERMOMETER

The exact calibration of the thermometer was postponed to the end of the investigation because the method used necessitated changes in the form of the specimen which would have prevented further heat capacity determinations. An approximate calibration, which need not be described, was made earlier and gave the data necessary for operation of the calorimeter while making those determinations.

Final calibration was accomplished by comparison with two standard platinum resistance thermometers, at 10°, 20°, 30°, 40°, and 50°, in a stirred bath of an oil of good electrical insulating properties. Uniformity of temperature throughout the comparator being essential to the success of this method, it was deemed necessary to remove the mica plates which separated the layers of the copper specimen, so that the oil might be circulated freely, with no pockets of unstirred liquid at uncertain temperature. To prevent contact of adjacent layers of the copper spiral after removing the mica, these were pried a safe distance apart and hard-rubber wedges inserted at appropriate points. When ready for the comparator, the specimen was altered from the appearance shown in Fig. 3 by being elongated to about three times the height shown there.

The comparator was a tall cylindrical vessel of about 10 liters capacity provided with a propeller stirrer in an offset tube and with an electric heating coil. It was protected from drafts and other causes tending to change the rate of cooling, and temperature regulation was obtained by changing the current in the heater. When a very slow, uniform rate of rise or fall of temperature was secured, readings of the standard thermometers and the copper one were taken alternately every 20 or 30 seconds until 10 readings were obtained, 6 of the standards and 4 of the unknown. The sequence of readings was based upon the principle 1, 2, 3, 3, 2, 1, so that the means pertaining to each thermometer were cotemporary and therefore a basis for comparison, provided only that the change of temperature of the bath had not deviated sensibly from a linear relation to the time intervals of reading. In this respect the comparisons at 10° were not satisfactory, as the work was done in a room at 25° and the temperature of the comparator rose so rapidly that it was impossible to time the readings with anything like the necessary precision to have 0.001 significance. For the sake of completeness the measurements made at 10° are tabulated with the rest, but little weight was assigned to them in drawing conclusions.

The standard thermometers employed were of the calorimetric type developed by Messrs. Dickinson and Mueller, of this Bureau, and described elsewhere.⁵² Using them, a temperature difference of 10° could be determined with an accuracy of about one part in ten thousand. The agreement between their simultaneous indications in the comparator bath was quite satisfactory, within a few thousandths of a degree, indicating that no serious lack of uniformity of temperature of the bath existed.

The method of measuring the resistances of the thermometers and the apparatus employed both merit more full description than can be incorporated in this paper. Neither has been described as yet, but it is hoped that both will be the subject of communications from the Bureau in the near future. The Wheatstone bridge was sufficiently sensitive and accurate to have measured the resistances of the standard thermometers to 0.00002 ohm corresponding to 0.0002, but because of the limitations imposed by other considerations it was useless to record more precisely

⁵² Dickinson and Mueller; *This Bulletin*, 9, p. 483; 1913.

than to the nearest 0.001. The same bridge, with its sensibility increased by increasing the strength of the measuring current, was used to measure the resistance of the copper thermometer to 0.000 002 ohm, corresponding to 0.002. The reliability of these measurements was attested by the results obtained, as will be more fully explained below. The quantity measured was the "branch point resistance" of the copper thermometer plus certain connecting resistances of the Wheatstone bridge. These were constant throughout any one day, and do not affect the differences 10° to 20° to 30°, etc., since they affect each point to exactly the same extent. Through oversight of the fact that differences in these connectors (η , ϵ , of Fig. 6) would interfere with the comparison of different days' results, no pains were taken to keep them the same from day to day, and in making Table 3 it has therefore been necessary to arbitrarily bring the results into agreement at one point (30°), so that the differences at other points would serve as the measure of the variations which occur.

The method, which is that used by E. F. Mueller, of this Bureau, for precision work with the potential lead or "branch point" type of thermometer, required two readings of the thermometer, with commutation by a mercury cup switch, and is most easily described by the equations and Fig. 6.

Commutator in position 1; battery switch also; variable arm adjusted to balance, R_1 ; (ratio arms assumed to be absolutely equal).

$$R_1 + \eta + a = T_1 + b + \epsilon.$$

Commutator reversed to 2; battery switch on 2; variable arm adjusted to balance, now reading R_2 .

$$R_2 + \eta + b = T_2 + a + \epsilon.$$

Add the two equations,⁵³ and a , b , the lead resistances are eliminated.

$$\frac{T_1 + T_2}{2} = \frac{R_1 + R_2}{2} + \eta - \epsilon.$$

FIG. 6.—Wheatstone bridge connections for double Siemens type resistance thermometer, completely eliminating lead resistance by commutation

⁵³ Mr. Mueller's method also includes the elimination of $\eta + \epsilon$ by substituting a short circuiting link for T , and reading the "zero balance" of the bridge $0 = \frac{Z_1 + Z_2}{2} + \eta + \epsilon$; or $\eta + \epsilon = -\frac{Z_1 + Z_2}{2}$

The value of T being desired at a given minute, the balance R_1 was obtained about 10 seconds before this, and R_2 about 10 seconds after the minute. The assumptions made are accordingly (1) that the change of T with time was a linear one; (2) that the total change in the resistance $a-b$ during 20 seconds was negligible in comparison with R .

The effect of η , ϵ , the connecting resistances between the Wheatstone bridge and the commutator, has been sufficiently discussed in an earlier paragraph (p. 296).

Two series of calibration data were obtained by the method just described, and then a crucial test for accuracy was applied by employing a method quite independent, namely, using a potentiometer for the measurement of resistance of the copper coil. The instrument was the Wolff-Diesselhorst potentiometer described in an earlier section (p. 292), and more complete details concerning the method will be found in the next section (p. 300). The method consisted in measuring the ratio of the drop of potential across the terminals of the copper coil to the drop across the terminals of a 0.1 ohm manganin resistance standard when the two were connected in series. The temperature coefficient of the manganin standard was small, about four parts in a million per degree temperature change, so that it was reliable to about one part in a million as a reference standard by which to measure changes in the resistance of the copper. The absolute value of the standard was not accurately known, so that in this case also an arbitrary constant correction is applied to every reading tabulated in Table 3, so as to bring the 30° value to identity with the other 30° values.

The results of the intercomparisons are collected in Table 3. The data comprised therein are as follows: The unit group consisted of 10 readings, 6 on the standards and 4 on the copper coil, at small equal intervals of time. From three to five such groups constituted a determination at a temperature near 10°; then the comparator was heated to 20° and an equal number of readings secured, and so on at 30°, 40°, and 50°.

TABLE 3

Resistance, in Ohms, of the Copper Coil at the Temperatures Shown

Method	10°000	Dif.	20°000	Dif.	30°000	Dif.	40°000	Dif.	50°000
Wheatstone bridge.....			0. 221666	8776	0. 230442	8770	0. 239212		
Do.....	0. 21286	880 _x	. 221666	8776	. 230442	8773	. 239215	8775	0. 247990
Potentiometer.....	. 21287 ₉	8790	. 221662	8780	. 230442	8771	. 239213	8777	. 247990
Mean.....			. 221665	8777	. 230442	8771	. 239213	8777	. 247990

There is no very good reason for assuming that the resistance of copper after increasing with temperature at a certain rate between 20° and 30° continues at diminished rate between 30° and 40° only to resume the larger value again between 40° and 50°; and there is reason to admit probability of an error as great as 0.002 in the mean results at any one temperature. The result of the measurement is accordingly taken to be the linear relation

$$R = 0.204119 + 0.008774 t \quad (2)$$

valid between 15° and 50°. The deviations between the formula and the observed results of Table 3 form Table 4. The work done at 10° is almost wholly disregarded for reasons stated above (p. 295).

TABLE 4

Deviations of the Linear Formula (2) from Values of Table 3

	20° 0.221667 ohm	30° 0.230441	40° 0.239215	50° 0.247989
Wheatstone Bridge I.....	+0.000001	— 1	+ 3	
Do. II.....	+ 1	— 1	± 0	— 1
Potentiometer.....	+ 5	— 1	+ 2	— 1
Mean.....	+ 2	— 1	+ 2	— 1

The only part of the result which has significance is the increase in resistance per degree, since the R_0 is arbitrary to the extent of perhaps 0.000020 ohm as already fully explained. Throughout the paper this increase is taken to be 0.008774 ohms per degree; reciprocal 1139.7 equal 1 ohm. This is a temperature coefficient of increase of resistance equal to 0.004298 at 0°, or 0.003958 at 20°, and indicates a very pure grade of copper.⁵⁴

⁵⁴ Dellinger: The Temperature Coefficient of Resistance of Copper, this Bulletin, 7, p. 83, p. 85; 1911.

Temperature Scale.—The unit of temperature in which these measurements are expressed is very closely the degree of the International Hydrogen Scale, as closely so as the reproducibility of this scale admits. The scale actually employed is somewhat more accurately reproducible than is the International Hydrogen Scale and is defined by the following relations:

The "platinum scale" (pt), of the standards employed, by definition,

$$pt = \frac{R_t - R_o}{R_{100} - R_o} 100$$

was very closely the scale which is related to the thermodynamic scale (T) by the value $\delta = 1.49$, substituted in the equation

$$T - pt = \delta \left(\frac{T}{100} - 1 \right) \frac{T}{100}$$

as applied to the observed values of R obtained in ice, steam and sulphur vapor (S. B. P. = 444.5° thermodynamic). It was therefore the scale defined by the purest platinum of Heraeus or of Johnson and Mathey, and is accurately reproducible by using platinum for which the thermometric constants δ and α have the values 1.49 and 0.391 to 0.392, respectively.

The scale employed (t) was that related to the "platinum scale" of the standards by the equation

$$t - pt = 1.48 \left(\frac{t}{100} - 1 \right) \frac{t}{100}$$

and is therefore as reproducible as the (pt) scale discussed above. The reason for choosing 1.48 rather than 1.50 or any other number which might be arbitrarily selected, is that when the scale so defined by 1.48 was compared⁵⁵ within the interval 0° to 100° to the International Hydrogen Scale, through the medium of the primary mercurial standards by which this scale is distributed⁵⁶ from the Bureau International des Poids et Mesures no differences could be detected which were greater than the uncertainties of the mercurial thermometers.

⁵⁵ The method followed in the comparison was that described in this Bulletin, 3, p. 650; 1907.

⁵⁶ A complete discussion of this subject is given in this Bulletin, 3, p. 663; 1907.

(b) CALORIMETRIC THERMOMETRY

In each experiment for the determination of specific heat, the specimen was heated through a temperature range of the order of 5 degrees, about 0.0044 ohms. That this interval might be measured to an accuracy of about one part in five thousand required that the resistance measurements be made to within 1 microhm. The potentiometer method was employed, the electric circuits being shown in Fig. 5 (p. 293), the switch (S) in position (m).

Current from a three-cell Exide storage battery (b) was regulated to about 0.3 ampere by the rheostat (r). The potential drop across the terminals of the 0.1 ohm standard (q) was therefore about 30 000 microvolts, and across the specimen about 70 000 microvolts. Measurements to 0.1 microvolt therefore corresponded to resistance determinations well within 1 microhm, provided only that the standard remained constant. The power converted to heat by 0.3 ampere in the specimen was about 0.02 watt, which raised the temperature 0°0013 per minute. The heating of the standard can not be readily computed, but as the power was less and the heat capacity many times greater on account of the oil immersion, it is evident that no significant change of temperature occurred within an hour due to the measuring current passing through it. The relation between change of resistance of this manganin standard and change of temperature was about four parts per million for each degree change of temperature (at 25° C).

The resistance of the specimen formed only a small fraction of the total resistance in the circuit, so that a considerable change in its value did not greatly affect the current strength. The drop of potential across the terminals of the 0.1 ohm standard was therefore nearly constant, while that across the specimen was almost directly proportional to the resistance of the latter. The temperature march of the calorimeter was thus given by the "potential" readings on the potentiometer, while the current readings varied only by a very small amount, due to the discharge characteristics of the battery, etc. Accordingly, it seemed desirable to multiply the number of the former at the expense of the latter, and the procedure adopted was as follows:

The potentiometer was read at intervals of 30 seconds, first two potential readings, then with the switch (p) thrown to the other side, one current reading, then two more potential readings, and so on until four pairs of these were obtained with three current readings between, the process consuming five minutes. The potential readings were timed within a second or two; a degree of care which was entirely unnecessary for the nearly constant current readings. Both series of readings were plotted against time and the smooth curves drawn which seemed best to represent the points. While usually linear, these occasionally possessed a slight curvature. The ratio of simultaneous values taken from these curves defined the resistance of the specimen for the instant chosen in terms of the resistance of the standard.

From observations taken in the manner described, data were secured which fixed from a considerable number of individual readings the value to be assigned to the temperature of the specimen at such times as the value was required, both before switching on the heating current and after switching it off. The details of computing the temperature rise of the calorimeter from the data so secured are given in Chapter VI (p. 308).

2. ENERGY SUPPLIED ELECTRICALLY

The determination of the energy supplied to heat the specimen involved the measurement of the average power and the time. The power was measured as the product of potential difference and current, obtaining the latter, however, by a measurement of a potential difference and a resistance of known value.⁵⁷

The circuit is shown diagrammatically in Fig. 5, the switch (S) being in position (h) when the heating current was passing through the specimen. During such interval the measuring current of the circuit (b-r-a-q) was diverted to a "spill" (C) of the same resistance as the specimen, so that the battery (b) was held to constant

⁵⁷ The joule used in this paper is therefore defined by the relation $\frac{e^2}{R}$, where e is in international volts and R is in international ohms. The difference between it and the international joule defined by the relation ei , where i is in international amperes, is certainly less than any amount significant in the results. The international volt is determined by the relation emf of Weston cell at 20° C equals 1.0183 volts; the international ohm is the resistance offered to an unvarying current by a column of pure mercury at 0° C of length 106.300 cm and uniform cross section such that the mass is 14.4521 grams.

discharge rates. Vice versa, during the greater part of the time, when the measuring current traversed the specimen, the heating current traversed the spill so that battery (B) was held constant.

(a) CURRENT STRENGTH

The current strength was maintained nearly constant, the arrangement toward this end being to use a rheostat L of resistance many times that of the specimen, and a battery (B) of sufficiently high potential to secure the desired current intensity of about 6 amperes. (B) was about 120 volts, (L) about 20 ohms, and the specimen about 0.2 ohm. A variation of 1 per cent of the resistance of the latter, such as would result from heating it through about 3°, therefore changed the current strength by only one part in 10 000.

The potentiometer was balanced on the drop of potential across the resistance standard (Q) three times during the interval of heating the specimen, once near the beginning, the middle, and the end of the period. The precision of these readings was one part in 60 000 and the time corresponding to a balance was indicated by a signal to a second observer, who read a watch and then recorded the values. Just prior to a series of readings the potentiometer current was adjusted, with the aid of an unsaturated Weston cell, to within 3 parts in 100 000 of its proper value, and at the end of the series this adjustment was checked. The temperature of the resistance standard (Q) was measured with a mercurial thermometer located at the center of the standard and in the oil bath in which the standard was immersed.

(b) POTENTIAL DIFFERENCE

This measurement was accomplished by throwing the switch (P) so as to connect the potential leads from the specimen directly to the potentiometer. Owing to the rapid change of resistance of the specimen while heating, the potential drop across it changed so rapidly as to preclude the possibility of accurate measurement by balancing the slide wire setting at a given moment and reading the value. The inverse method was employed, the instrument being set to a given value, and the corresponding time called off. For example, the potentiometer was set to the value 1.47200, and

when the potential had attained very nearly this value the potentiometer key was held closed for a few seconds, and just as the galvanometer deflection become zero, a signal was given to the other observer; then the potentiometer was set to 1.47300 and the process repeated, and so on. The sensitivity of the galvanometer and precision of setting the slide wire would have permitted obtaining the last figure indicated (fifth decimal place) within two units, but the accuracy of timing was such as to correspond to an error of from three to five such units. It is fairly certain that the figure next the last was obtained correctly (as to precision)—i. e., the measurements were precise to about 1 part in 15 000. Moreover, the errors were accidental rather than systematic,⁵⁸ so that the mean of the series was probably even more reliable. A series was usually composed of 12 readings, 4 groups of 3 each, the three current determinations described in the preceding section (p. 303) being interspersed between the four groups. The increase of the potential difference so measured was found to occur in a strictly linear relation to time, within the limits of accuracy of measurement.

The average power during the interval of heating was accordingly the product of the values of current and potential at the mid-instant, but these values were determined by interpolation from series of 3 and 12 independent settings, respectively, and not from single readings at that instant.

(c) TIME

The time factor of the energy measurements was given by an automatic chronograph record of the instant when switch (S) was closed in position (h) and again when it was returned to position (m). The time actually recorded in the latter instance was not the opening of the heating circuit, but the closing of the other circuit a fraction of a second later. This fraction was

⁵⁸ A systematic error of about 2 parts in 15 000 is introduced by neglecting the lag of the galvanometer. This correction was of the same magnitude and in the same direction for all the experiments, and therefore it was most convenient to neglect it entirely in the computations pertaining to individual experiments and apply only to the final result of the investigation. It is less than one unit in the last figure of this result (p. 315) and is mentioned only to show that the subject received consideration.

The effect of galvanometer lag upon the readings of electrical thermometers is treated in a paper by Harper: this Bulletin, 8, p. 694; 1912.

inappreciable owing to the shape of the switch blade which is shown in Fig. 7.

By reference to Figs. 5 and 7 it may be seen that two blades of (S) carried the calorimeter currents, and that the third was reserved entirely for the chronograph. All three were of the same shape, and bound together by a common handle, so that the contacts were made simultaneously. The operation of the mercury tube shown in Fig. 7 may not be clear without explanation. In the position shown, the only break in the circuit is at (f, y), so that closing this operates the chronograph stylus. Until the circuit is opened at some point, the stylus would remain pressed

FIG. 7—Details of switch and diagram of chronograph circuits

down against the tape and be useless for further record and also wear unnecessarily. The desired opening of the circuit is effected by the motion of the mercury in the glass tube. Throwing the switch tilts the tube, the mercury flows to the opposite end and the connection (x, f) is broken. The motion of the mercury was damped by glycerine, and the dimensions of the tube and quantity of mercury were such that the break (x, f) and connection of (x, g) occurred after the contact (f, y), never before, the time elapsing being perhaps 0.4 second. It should be noticed that breaking the circuit at (x, f) leaves everything in readiness to record the contact (g, y) when the switch (S) is thrown back to its original position.

3. COOLING CORRECTION

The energy supplied electrically to heat the specimen was not quite all available for this purpose because a certain amount was lost to the surroundings during the progress of the experiment. As actually carried out, this "loss" was usually negative, the calorimeter being cooler than its surroundings during most of the time, but the term "cooling correction" is the customary one and applies equally to cooling or warming. The heat exchange between the specimen and its envelope was computed on the basis of Newton's law of cooling. The cooling constant was determined separately for each individual experiment, inasmuch as its value was a function of the degree of exhaustion of the vacuum chamber, and of the mean temperature of the experiment. The residual pressure varied only slightly during the course of a day's series of experiments, rising a little as if due to a very small leak, and the values found for the cooling constant formed a progression that was very satisfactory.

The data which determined the cooling constant and convergence temperature were used directly in computing the cooling correction, although for the sake of comparison of experiments, the actual value of the constant was usually computed also. These data were the time rates of change of temperature of the calorimeter in the periods just before switching on the heating current and just after switching it off. The rates of change being dependent not only on the exchange of heat between the calorimeter and surroundings, but also on the heat introduced by the small current employed to make the resistance measurements, corrections for the latter were applied in order to secure the basis for the cooling correction computation.

The transfer of heat between the calorimeter and envelope was partly by conduction of the rarefied air, partly by radiation and partly by metallic conduction along the electrical lead wires. Insofar as the latter was proportional to the difference of temperature between the calorimeter and the water bath, it was correctly taken into account by the computations which were based on Newton's law of cooling. This condition would have been realized exactly if the leads in passing through the water bath had acquired its temperature, independent of all outside circumstances. To test

the deviation from such condition the following experiment was carried out.

The water bath was heated to about 50° and maintained at constant temperature by the thermostat system, the room being at about 20° . The calorimeter was heated to the same temperature within a few thousandths of a degree, as measured by the differential thermocouple. The temperature of the calorimeter was then measured every fifteen minutes for an hour or more, and was found to drop regularly to a very slight extent. Had the jacketing been perfect, no such drop would have occurred, since the calorimeter and envelope were at the same temperature and any heat transferred to the room by the lead wires would have been supplied entirely by the water bath and without any effect on the calorimeter. The fall of temperature in an hour was appreciable, but so small that any correction applied for this effect in an interval of seven minutes and with less than 30° temperature difference between calorimeter and room would be less than the limit of accuracy of the measurement of the temperature rise of the specimen, so no correction was applied.

In other words the computations have been carried out on the assumption of heat transfer along the lead wires strictly proportional to the difference of temperature between the calorimeter and its water bath, and therefore additive to the transfers by means of the rarefied gas, and resulting only in giving to the value of the constant in the equations derived from Newton's law a greater magnitude than it would have had if the lead wires had not been present.

4. MASS

The details pertaining to a mass determination are so familiar that they need no description here. The principles involved in securing the proper portion of the wire for the weighing, and the magnitude of the possible errors have both been discussed in Chapter III on "Method," (p. 289). Two weighings were made, one by substitution, using a counterpoise, and the other a double weighing in right and left hand pans successively. The independence of these two methods was a safe check upon the correct reading of the weights. The mass of the specimen was 2254.7 grams.

5. PROGRAM FOR AN EXPERIMENT

The measurement of each quantity having been considered in detail, it remains to sketch briefly how the various steps were interrelated. The main operations prior to a day's series of determinations were the cooling of the specimen to the lowest temperature at which the atmospheric humidity would permit of making the electrical measurements, the exhaustion of the vacuum chamber to a limit set by the pump, and the closing of the circuits to bring the batteries (B, b) (Fig. 5) to a steady discharge condition. A series of from five to nine determinations was then carried out, heating the specimen 3° to 5° in each, stopping when 50° was reached, a limit set at the beginning of the investigation (see p. 260), and in accordance with which the apparatus had been so made that it did not permit of higher temperature without remodeling.

For each experiment the program followed was this: The temperature of the water bath was raised about 3° above that of the calorimeter and the thermostat set to maintain it at this temperature. Then determinations of the temperature of the calorimeter were commenced, following the manner described in the section on measurement of temperature changes (V-I, b, p. 300). These continued during five minutes, and then three or four minutes were devoted to reading the temperature of the room, the temperature of the water bath, the pressure in the vacuum chamber, the temperatures of the resistance standards, and to adjusting the two potentiometer currents to their correct values by the aid of their respective standard cells. A second series of determinations of the temperature of the calorimeter occupied the next five minutes, and in conjunction with the earlier series furnished the data necessary for obtaining both the temperature and its rate of change at the instant of switching on the heating current.

Within the 30 seconds following the close of the readings just described, the switch (W, w) (Fig. 5) was thrown from position (w) to (W), switch (P) was thrown to connect the specimen to the Leeds and Northrup potentiometer which was set to an appropriate value, obtained from the close of the preceding experiment, or by the use of the ammeter (A) and the approximate resistance

of the specimen. Then the chronograph was started, and after the sounder in the circuit beating seconds from the master clock missed a beat, indicating the fifty-ninth second of a minute, the operator threw switch (S) as soon as the next beat occurred. Turning to the potentiometer, the time of balance on the reading previously set was called for an assistant to note, the potentiometer was quickly set to a new value and the power measurement carried out as described in the section on "Energy Supplied Electrically" (V; 2-a, b, p. 302).

Toward the end of the sixth or other chosen minute, the potentiometer readings were discontinued, and following the missing clock beat, the switch (S) was thrown to position (m). (W) was returned to position (w) and readings begun on the Diesselhorst potentiometer to measure the temperature of the specimen and the rate of change thereof. This process consumed two intervals of about five minutes each, with three or four minutes separating the two. Following it, the temperature of the water bath was raised for the succeeding experiment and the entire program repeated.

VI. REDUCTION OF OBSERVATIONS

1. THEORY OF THE COMPUTATION

From the observed data the following working data were computed:

- (1) The values of the following quantities at the instant t_1 when the heating current was switched on:
 - R_1 , the resistance, in ohms, of the specimen.
 - r_1 , the rate, in ohms per second, at which this resistance was increasing.
 - i_1 , the intensity, in amperes, of current used in measuring R_1 .
- (2) The values of similar quantities R_2 , r_2 , i_2 at the instant t_2 when the heating current was switched off.
- (3) The value of W , the quantity of energy supplied electrically between instants t_1 and t_2 .
$$W = \int_{t_1}^{t_2} e i d t$$

The unknown heat capacity, M , may be expressed most conveniently in terms of the joule as a heat unit and the arbitrary resistance scale of temperature, that is in joules per ohm. This can easily be converted later into joules per degree or calories per degree.

The exchange of heat between the calorimeter and its envelope may be expressed with sufficient accuracy ⁵⁹ by Newton's law of cooling.

$$-\frac{du}{dt} = \alpha(u - U_e) \quad (3)$$

u = temperature of calorimeter

U_e = temperature of envelope.

Employing the arbitrary resistance scale of this paper,

$$-dR = \alpha(R - R_e)dt \quad (4)$$

gives the change of temperature, while the quantity of heat, if the heat capacity be M , is

$$-MdR = \alpha'(R - R_e)dt$$

designating by α' the quantity of heat gained or lost per second ($dt=1$) for unit difference of temperature (one ohm) between calorimeter ⁶⁰ and envelope.

The energy supplied electrically by current i in an increment of time dt is $eidt$. In the absence of other sources and sinks, that supplied electrically to material of heat capacity M , less that lost to the envelope, raises the temperature of this matter, and the temperature change may be written $r dt$ if r be defined as the rise of temperature per second, $r = \frac{dR}{dt}$. In algebraic terms, then,

$$\left. \begin{aligned} eidt - \alpha'(R - R_e)dt &= Mrdt \\ ei - \alpha'(R - R_e) &= Mr. \end{aligned} \right\} (5)$$

⁵⁹ The total heat interchange, namely the sum of the transfers in both directions, the difference of which transfers forms the actual cooling correction applied, included only about 2 per cent of the total heat involved in an experiment. An error of 5 per cent in its determination would therefore affect the final result by about one part in a thousand.

⁶⁰ The difference between the average temperature of the specimen as measured by its resistance and the surface temperature, which is the one concerned in the radiation losses, etc., is here neglected. For the magnitude of the possible error introduced cf. footnote 59.

This equation expresses the condition at every instant of the experiment. Selecting particular instants, which correspond to the known values,

$$e_1 i_1 - \alpha' (R_1 - R_e) = Mr_1 \quad (6)$$

$$e_2 i_2 - \alpha' (R_2 - R_e) = Mr_2 \quad (7)$$

$$\int_{t_1}^{t_2} e i dt - \alpha' \int_{t_1}^{t_2} (R - R_e) dt = M \int_{t_1}^{t_2} r dt. \quad (8)^{61}$$

The equations (6) and (7) determine the values of α' and R_e for substitution in (8), which then expresses the result of the experiment in terms of the quantities measured.

Since by definition, $r \equiv \frac{dR}{dt}$.

$$\int_{t_1}^{t_2} r dt \equiv \int_{t_1}^{t_2} \frac{dR}{dt} dt = R_2 - R_1$$

So that (8) may be written in the form

$$W - \alpha' \int_{t_1}^{t_2} (R - R_e) dt = M(R_2 - R_1) \quad (9)$$

In evaluating the integral, it is to be borne in mind that it is small with respect to the other two terms. Since the heating current was constant to within a few parts in ten thousand, R may be taken as a linear function of time without introducing any error of appreciable magnitude, the heat being supplied in its final distribution without lag.

Substituting a value $R_1 + p(t - t_1)$ for R , where p is defined by $R_2 = R_1 + p(t_2 - t_1)$ and abbreviating $(t_2 - t_1)$ to T , the elimination of α' and R_e results in a reduced form of equation (9) as

$$M = \frac{W - T \left(\frac{R_1 i_1^2 + R_2 i_2^2}{2} \right)}{R_2 - R_1 - T \left(\frac{r_1 + r_2}{2} \right)} \quad (10)$$

From some points of view it is more convenient to express all the small terms as corrections to the observed increase of resistance,

⁶¹ In equation (8) are neglected second order terms due to the fact that α' and M vary slightly with temperature and therefore with time between instants t_1 and t_2 , and can not be removed from the integrations without such approximation.

a practice very common in calorimetric computations. So written

$$M = \frac{W}{(R_2 - R_1) + T \left(\frac{R_1 i_1^2 + R_2 i_2^2}{2M} - \frac{r_1 + r_2}{2} \right)} \quad (11)$$

where a very inexact approximation to the value of M is sufficient to compute the terms $\frac{R i^2}{M}$ with sufficient accuracy.

A comparison of the quantities involved in equation (11) with those enumerated in the opening paragraph of this chapter (p. 308) shows that M is here expressed in terms of quantities all of which are given by the measurements.

2. DETAILS OF COMPUTATION—EXAMPLE

The application of equation (11) to the observed data may be explained with the aid of the sample laboratory record forming Fig. 8. Many of the details have necessarily been described previously and need not be repeated, but are indicated by appropriate references.

W—Energy Supplied Electrically.—The data pertaining to this measurement are collected in the blocks forming the left central portion of the record sheet. Full details regarding the potentiometer readings and the method of determining the mean values have been given. (Chapter V, section 2, p. 301.) To these mean values, 1.5076 and .66079, are applied potentiometer corrections the values of which depend on the setting and on the standard cell used to adjust the potentiometer current. The results are the potential differences across the specimen and the resistance standard. A correction for the departure of this standard resistance from exactly 0.1 ohm is then made and the current in amperes found. The product of the emf and current is labeled "Power," and this multiplied by "Time" is "Energy." The latter⁶² is the W of equation (11) and is expressed in joules.

A valuable check is furnished by taking the values of emf and current corresponding to the exact beginning and end of the

⁶² Although $E_{AV} \times I_{AV} \times T$ is not mathematically identical with $\int_0^T E I dt$ when both E and I vary (linearly), nevertheless the difference is only of the order of a few parts in ten million when the variation in I is as small as here.

Department of Commerce
BUREAU OF STANDARDS
Washington

Observers DRH WSJ
Computed by DRH

Date July 28, 1918
Expt. No. 3

CALORIMETER RECORD

		(r ₁)	(r ₂)	TIME	DIF.	RESISTANCE	NOTES
t _R	2-21-00	dR	0.000116	0.000138			Potentiom. 6162
t ₁	2-22-14	dt	720	940			Calib. of 4-26-13
dt	74	$\frac{dt}{d\tau}$	0.0 ⁶ 161	0.0 ⁶ 164			Std. Res. 7354
r ₁	0.0 ⁶ 159	Cor.	2	9			Temp. 33 ⁹ 3 (2-13)
r ₁ dt	+ 12	r	+0.0 ⁶ 159	-0.0 ⁶ 173			
R ₁	0.225969	a	0.0 ⁴ 80 ₀			0.1 ohm Specimen	
R ₁ cor.	0.225981+0.00017	R ₀				(l) (e)	Ratio $\frac{e_{cor}}{l_{cor}}$
Potentiometer No. 9143		Cell No. 2682 (1.0187 ₃ volts)		2-07-00 30		312736 706261	
Volt Box No.		Std. Res. No. Wolff 1408		08-00 30		287 299	0.225844
Temp.		Temp. 31 ⁹ 8		09-00 30		734 324	853
2-23-01	1.4970 ₀			10-00 30		730 338	862
-13	98	2-24-16	66081	11-00 30		361 372	871
-26	99						
25-06	1.505	26-06	66079				
-19	06						
-32	07	27-41	66076				
26-52	1.512						
27-07	13			2-17-00 30		706517	
28-20	1.518			18-00 30		312707 541	0.225941
-38	19			19-00 30		704 551	950
-52	20			20-00 30		577 588	960
29-08	1.5210 ₀	Mean (2-25-44)	66079	21-00 30		760 614	969
Mean (2-25-44)	1.5076 ₄	Pot. Cor.	00	22-00		629	
Pot. Cor.	0	Res. Std.	— 13				
Volts	1.5076	Amperes	6.606 ₆				
Resist. 0.22613 (R ₁ =0.22615)		Power	9.960 ₂				
0.23030 (R ₂ =0.23031)							
on	2-22-14.45	Time 420.11	Energy 4184. ₃				
off	29-14.56			2-30-00 30		719350	
t _R	2-32-00	Calorimeter No.	6907	31-00 30		336	
2	2-29-14	(Copper spiral)		32-00 30		312600 292	0.230106
dt	166			33-00 30		599 276	097
r ₂	0.0 ⁶ 173	Pressure in mm of Hg.	{0.12 at start 0.13 at end	34-00 30		245 226	087
r ₂ dt	+ 28			35-00 30		597 191	077
R ₂	0.230107	COOLING CORRECTION		36-00 30		595 174	067
R ₂ Cor.	0.230135+0.00017	R ₁ l ₁ ² =0.0221 { R ₁ l ₁ ² +R ₂ l ₂ ² =0.0722 ₃ R ₂ l ₂ ² =0.0225 } 2		37-00 30		139 120	
R ₁ Cor.	0.225981+0.00017						
diff	0.004154	r ₁ =+0.0 ⁶ 159 } $\frac{r_1+r_2}{2}=+0.0707$					
Res. Std.	+ 3	r ₂ =-0.0 ⁶ 173 }		2-45-00 30		312571 718848	
Cool. Cor.	+ 12	(T=420) +0.0729		46-00 30		814 800	0.229968
dR	0.004169	420×0.0729=+0.000012		47-00 30		569 764	959
K	1139. ₇			48-00 30		565 748	950
dθ	4 ⁹ 751	ROOM TEMP.	JACKET	49-00 30		716 699	941
Equiv.	880.6	THERM. 5900	THERM. 8290 _c				
Mn. Temp.	0.22823=27 ⁹ 48	Time Temp.	Time Temp.				
880.6-15.9 (for mica)		2-05 30 ⁹ 3	2-05 27 ⁹ 28				
=864.7 joules/deg. (2254.7g)			2-13 27 ⁹ 30				
=0.3835 joules/gram-degree			2-38 27 ⁹ 38				
		2-45 30.6	2-50 27 ⁹ 42				

FIG. 8.—Laboratory record of an experiment

heating period (t_1 , t_2) and using these to compute the resistances for comparison with the resistances R_1 , R_2 found by the more precise measurements. In the example the values found from the "middle period" measurements are 0.22613 at 2-22-14 and 0.23030 at 2-29-14, which are to be compared to 0.22615 and 0.23031 respectively.

T-Time (Duration of the Heating Period).—The chronograph record showed that the current was switched on at 2-22-14.45, (t_1) and off at 2-29-14.56, (t_2), an elapsed time of 420.11 seconds. The mean time of these two, 2-25-44 is that employed for the mean potentiometer readings in the above.

R-Resistance of the Specimen.—Data pertaining to these measurements are tabulated in the long columns to the right of the record sheet. The readings were taken as described in Chapter V, section 1 (b) (p. 300), and after correcting from the calibration certificate of the potentiometer, they were plotted against time as explained in the same section (p. 301) and served to give the resistances at desired even minutes. These appear in the last column, and are expressed in terms of the resistance of the manganin standard (L & N 7354 at 33°.3) and not reduced to international ohms.

In the preperiod the series of values extends to 2-21, so that this value of R , 0.225969, must be employed to determine the value at the desired instant, t_1 , namely 2-22-14, which is 74 seconds later. The computation is given in full in the extreme upper left hand corner of the sheet, and the R_1 *cor* is 0.225981, expressed in units which are reduced to international ohms by adding +0.000176. (The standard resistance was about 0.075 per cent larger than its nominal value, and 0.075 per cent of 0.226 is 0.000170.)

In the afterperiod, inspection of the values corresponding to the times 2-32 to 2-36, leads to a choice of 0.230107 at 2-32-00 rather than 0.230106 given by the single reading at that time. From this the value of R_2 *cor*, corresponding to t_2 , 2-29-14, is obtained, the computations being shown in the lower left corner of Fig. 8. The difference, R_2 *cor* - R_1 *cor*, is 0.004154, expressed in the working unit. The resistance of the 0.1 ohm standard was 0.100075 international ohms, 7.5 parts in 10 000 larger than

the nominal value, which being 3 parts in 4100, gives the correction +3 that is entered just beneath the 0.004154.

r—Rate of Resistance Change.—The computation of the rates r_1 and r_2 is to be found at the top of the sheet (Fig. 8). Between 2-09 and 2-21, the resistance increased 0.000116 ohms and dividing this change by the interval in seconds, gives an average rate r , which is almost exactly the actual rate at the mean time 2-15. At 2-22-14 the rate (r_1) is not greatly different, although slightly so. The correction to obtain it was computed thus: $r = -\alpha (R - R_e)$, so that unless $(R - R_e)$ remain constant, r will vary. R_e , the measure of the temperature of the envelope, may or may not remain constant, but R will certainly change (slightly) by virtue of the cooling or warming of the calorimeter. To find the effect of a change in $(R - R_e)$ on r , differentiate; $dr = -\alpha d(R - R_e)$. In the example, R increased 0.000058 ohms in the six minutes between 2-15 and 2-21, and so if R_e had remained constant, $d(R - R_e)$ would have been +0.000058. The value of α was 0.000080, giving⁶³ for dr -0.000046, an appreciable correction to the value of r , 0.00161. However, in this case the temperature of the envelope was rising rapidly, the experiment being carried on at a temperature below that of the room, and when this is taken into account, assuming the change to be nearly linear, the correction evaluates to -0.00002, instead of -0.00005 as above. The corrected r , 0.00159, may be taken for 2-22 as well as 2-21, and is therefore r_1 . It was used for the determination of R_1 *cor* from the observed value of R obtained 74 seconds before, and also in computing the cooling correction.

Similarly, from the resistances at 2-32 and 2-46, and the corresponding change in the temperature of the envelope, the rate r_2 comes out (-)0.00173. This is used to obtain R_2 *cor* from the observed data beginning nearly three minutes later than t_2 , and likewise occurs in the cooling correction. It is for this latter that it is necessary to determine the rates as accurately as here indicated.

Cooling Correction.—This subject has been fully discussed in an earlier section bearing this title (Chapter V, section 3, p. 305). The computation consisted in substituting the proper values in the expression contained in equation (11). All these values occur

⁶³ Notation .06 is explained in footnote 33, p. 274.

on the record sheet except M . This was computed approximately and found to be very closely 10^8 , when the unit is joules per ohm (880 joules per degree and 1140 degrees to the ohm). Both i_1 and i_2 were 0.313 amp. The computation is shown in detail in Fig. 8, the result being +0.000012 ohms to be added to the value 0.004157 found for $R_2 - R_1$ (*cor*).

Reduced to degrees by the results of Table 3, the denominator in equation (11) becomes $4^\circ.751$, and the result of the experiment is 880.6 joules per degree at a mean temperature of $27^\circ.48$. This heat capacity is for 2254.7 grams of copper and 18.5 grams of mica. The specific heat of mica was taken as 0.206 calories per gram·degree,⁶⁴ equal to 0.86 joules per gram·degree, so that the heat capacity of 18.5 grams was taken to be 15.9 joules per degree, and this quantity subtracted from 880.6. The last step in the computation was to divide by the mass of copper and the final figure for this particular experiment was 0.3835 joules per gram·degree at $27^\circ.48$.

VII. RESULTS

1. EXPERIMENTS IN 1910

The apparatus was assembled in 1910, when the specimen was built into the form used. Preliminary experiments were made, nine determinations in all, for the purpose of trying the method. While these offered fair evidence that the work was worthy of continuation the results attained were of no other value, and need not be dwelt upon further.

2. EXPERIMENTS IN 1913

In May, June, and July, 1913, 27 determinations were made at various temperatures between 14° and 50° , grouped in five separate series, each of which was begun at the lowest temperature which the prevailing humidity would allow and carried as far as time would permit. The results of these determinations are collected in Table 5 and shown graphically in Fig. 9.

The mean result (Equation 12) is discussed in the next section. Using it to compute the specific heat at the various temperatures listed in the second column, and comparing the results of the

⁶⁴Landolt, Börnstein, Roth: *Physikalisch-Chemische Tabellen*, 1910 edition, p. 759.

computation to those actually observed (fourth column), the differences found are entered under the caption "Deviation."

TABLE 5
Results of Experiments

Date	Mean Temp.	Joules degree	Joules gram-degree	Deviation from equation (12)
1913	°			
May 30.....	26.18	881.5	0.3839	+0.0002
	31.26	883.3	.3847	0
	36.38	887.2	.3864	+ 7
	41.68	888.6	.3871	+ 4
June 4.....	27.17	882.2	.3842	+0.0004
	31.93	883.3	.3847	- 1
	37.61	884.7	.3853	- 6
June 10.....	14.32	876.3	.3816	+0.0003
	18.29	876.1	.3815	- 6
	22.05	878.2	.3824	- 4
	25.25	879.5	.3830	- 5
	28.46	881.1	.3837	- 4
	31.69	885.5	.3857	+ 10
	35.00	884.1	.3850	- 4
	38.34	885.4	.3856	- 4
June 27.....	26.20	881.8	.3840	+0.0003
	29.81	884.1	.3851	+ 7
	33.18	884.4	.3852	+ 2
	36.32	885.5	.3857	0
	39.46	(Accident)		
	42.72	887.6	.3866	- 3
	46.10	888.7	.3871	- 5
July 28.....	22.61	878.5	.3826	-0.0003
	27.48	880.6	.3835	- 4
	32.31	883.5	.3848	- 1
	37.28	886.5	.3861	+ 2
	42.38	887.8	.3867	- 1
	46.77	890.8	.3880	+ 3

Mean result, 0.3834 ± 0.00020 ($t=25$)

(12)

Average deviation of observed values from this mean, 0.00036, or very closely one part in one thousand.

3. THE SPECIFIC HEAT AT 25° AND THE TEMPERATURE COEFFICIENT

It is evident from Fig. 9 that within the limited interval of 15° to 50° the relation of the specific heat of copper to temperature may be represented by a straight line as well as, if not better than, by any other curve. Employing the relation $c = c_{25} + \beta(t - 25)$ and assigning equal weight to all the observations in Table 5, a least square solution gives $c_{25} = 0.3834$ and $\beta = 0.00020$.

This line is the one shown on Fig. 9, and the deviations of the observations from it may be taken from the figure or from the last column of Table 5. As regards precision, inferred from the agreement of the experiments, it would seem that an error in the result greater than one part in five hundred was most improbable, and no systematic error so great as this, affecting all the results, is suspected, although the latent possibilities of all calorimetric work for containing systematic errors are keenly appreciated by the author.

FIG. 9.—The specific heat of copper; results of measurements described in this paper

It seems safe to conclude that the third decimal figure is given correctly by the formula, and that the temperature coefficient is correct within 10 per cent, in stating the result of these measurements to be

$$c = 0.383_4 + 0.00020(t - 25) \frac{\text{joules}}{\text{gram} \cdot \text{degree}}$$

and if 4.182 joules equal one 20° calorie,

$$c = 0.0917 + 0.000048(t - 25) \frac{\text{cal}_{20}}{\text{gram} \cdot \text{degree}}$$

The units have been defined elsewhere: the joule in footnote 57, page 301; the degree on page 299; the gram is mass (i. e., correction for buoyancy applied to weighings).

4. PURITY OF COPPER

Chemical analysis by J. A. Scherrer of the Bureau, using a representative sample of the wire, showed a purity of 99.87 per cent. High degree of purity was also indicated by the electrical

properties, the temperature coefficient of increase of resistance, 0.00396 at 20°, indicating 100.5 per cent conductivity of "pure" copper by the old much-used "Matthiessen standard."

The density was 8.86. The wire having been once annealed in the process of manufacture, was of course hardened slightly in the process of shaping into spirals and was not again annealed.

VIII. SUMMARY

1. A critical review of all previous determinations of the specific heat of copper is given in extenso. For the general reader the essentials of this are condensed into two tables and a short explanatory note. The determinations in the temperature range 0–100° are interpreted to indicate that the specific heat of copper (hard-drawn probably excepted) at 50° is between 0.0926 and 0.0931.

2. The general principles of the method employed in this determination are discussed, together with a consideration of the precision necessary in measuring the various quantities, and a full description of the apparatus and the details of making each measurement follow. Fifty meters of copper wire 2.5 mm in diameter served the fourfold function of being at the same time the test specimen, the calorimeter itself, the heater, and the thermometer. Suspended in vacuo and heated with a measured quantity of energy supplied electrically, the resulting temperature rise was measured by the change in resistance.

3. Sources of possible error are carefully considered in the separate discussions pertaining to the measurement of each factor. The precision and the magnitude of the several correction terms are fully indicated by detailed explanation accompanying a sample laboratory record of an experiment.

4. The copper was annealed wire, 99.87 per cent pure, according to chemical analysis, high degree of purity being likewise indicated by the electrical properties.

5. The results of 27 determinations at temperatures between 15° and 50° possess an average deviation of one part in a thousand from

0.383₄ + 0.00020(*t* – 25) international joules per gram degree
equivalent to

0.0917 + 0.000048(*t* – 25) calories₂₀ per gram degree

if 4.182 joules equal one 20° calorie.

6. Appended to the paper is a discussion of the use of the vacuum jacket as a means of reducing the cooling correction in calorimetry, the relative magnitudes of the heat transfer due to conduction by air in various stages of rarefaction, and to radiation from some of the more commonly used surfaces being compared. The note is intended to indicate the degree of exhaustion profitable to attain for a given set of fixed radiation conditions when thermal insulation by means of a vacuum jacket is planned.

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WASHINGTON, May 30, 1914.

APPENDIX

NOTE ON VACUUM JACKETED CALORIMETERS

With Especial Reference to the Degree of Thermal Insulation Secured by the Use of a Vacuum Jacket

INTRODUCTION

At the beginning of this investigation it was assumed that the improvement in thermal insulation secured by the use of the vacuum jacket would justify the very considerable disadvantages both in design of calorimeter and manipulation which were introduced thereby. That this was somewhat doubtful developed as soon as some of the heat-transfer measurements were made, as may be seen from the following pages.

However, the difficulties attendant upon exhausting the air space were not without compensation by reason of a material increase in the confidence to be placed in the accuracy of the cooling correction of the calorimeter for causes quite apart from reduction of the magnitude of the correction. In ordinary calorimetric procedure the cooling corrections are computed from data which are obtained while the calorimeter temperature is changing very slowly, i. e., "drifting" slowly at very nearly constant rate toward the jacket temperature, and are applied for the period in which the calorimeter temperature is changing very rapidly. It is a bold assumption that the convection currents existing in the quasi equilibrium state effect the same result in transfer of heat as do the convection currents existing in the very disturbed state,⁶⁵ which assumption is justified only if the conclusions to which it leads are substantiated by experimental test. This seems to be the case, at least within fair limits, with an air gap of approximately 1 cm separating calorimeter and jacket, but with the very wide gap of 5 cm or more with which this calorimeter was constructed there is much greater reason for doubt. Since neither radiation nor conduction is subject to the same uncertainty, the entire absence of convection by reason of exhaustion to a small fraction of an atmosphere affords a much greater degree of confidence in the accuracy of the cooling correction.

⁶⁵ Dickinson, Combustion Calorimetry: this Bulletin 11, p. 199, 1914.

GENERAL CONSIDERATIONS

The efficacy of a vacuum jacket in securing thermal insulation merits some discussion in view of a more or less common tendency to overrate it, or at least to carry evacuation far beyond the necessary or useful stage, frequently at the sacrifice of very considerable time and trouble in arranging apparatus to do so. No degree of exhaustion can reduce heat transfers below the limit set by radiation, and furthermore, when conduction and convection have been reduced to less than the radiation it is obvious that the advantage of continued pumping diminishes rapidly.

The magnitude of the radiation in any given case is therefore the first quantity to claim consideration. Since this paper is concerned only with the heat transfer due to small differences of temperature at ordinary room temperatures, the calculations may be limited to such conditions. From the Stefan Boltzman law

$$\frac{dQ}{dt} = \sigma(T_1^4 - T_2^4)$$

$\frac{dQ}{dt}$ = quantity of heat radiated per second.

T_1 = absolute temperature of radiator.

T_2 = absolute temperature of absorber.

the quantity of heat lost per second by unit area of a black surface at 301° K completely inclosed in a black chamber at 300° K (27° C, the temperature of a warm room) is

$$\begin{aligned} \frac{dQ}{dt} &= 5.7 \times 10^{-12} (301^4 - 300^4) \\ &= 0.00063 \text{ watts (per cm}^2 \text{ per degree C)} \end{aligned}$$

This quantity is compared in Table 6 to others which have a bearing upon the subject. This table does not contain data pertaining to wires and very small pipes, which subject is further discussed below, but contains all the data pertaining to conditions resembling those occurring in calorimetry, which the author could assemble from the literature. Excluding MacFarlane's results, the convection-conduction ranges from about 0.00020 to 0.00070 watts (per cm^2 per degree) with every indication that the smaller of these two figures is about what one may expect to be true for a piece of apparatus built so as to confine the air circulation in about the same manner as does a calorimeter, which jacketing arrangement is rather common for both scientific and industrial apparatus. Since 0.00020 watts per cm^2 per degree is about 30 per cent of the figure computed above for black radiation, another

way of stating this conclusion is that the convection-conduction heat loss is about equal to the radiation from a surface 30 per cent black.

TABLE 6

Heat Transfers Found by Experiments under Conditions Stated (In Still Air at Atmospheric Pressure When Not Otherwise Stated). Watts per cm² per Degree C Difference of Temperature from Surroundings at About 300° K

No.	Name	Conditions	Watts
1		Radiation; black radiator to black surroundings.	0.00063
2	MacFarlane ⁶⁶	Copper ball diam. 4 cm, to large jacket black- ened inside; moist air; } Polished ball, total conv., conduc., and rad.. temperature differ- } Blackened ball, total conv., conduc., and rad. ences 15° to 65° give about same figure	0.00085 0.00118
3	Langmuir ⁶⁷	Convection-conduction; vertical plane surface; temperature difference about 25°	0.00044
4	Wamsler ⁶⁸	Convection-conduction; outer surface cylin- } Pipe 9 cm diameter..... drical pipe, horizontal in large room; tem- } perature difference about 50° } Pipe 6 cm diameter.....	0.00053 0.00070
5	Dickinson ⁶⁹	Convection, conduction, and radiation; ordinary cylindrical calorimeter can, 4 liter content, in jacket such that air gap is 1 cm; bright nickel surface; temperature difference about 5°	0.00030
6	Lees ⁷⁰	Convection, conduction, and radiation; nicked bar, 2 cm in diam., suspended horizontally (?) in jacket 55 cm in diameter	0.00041
7	Harper ⁷¹	Copper spiral and jacket described in fore- } Convection-conduction... going paper, i. e., large similar cylinders, } 5-cm air gap all around; temperature dif- } Radiation	0.00018 0.00012
8	Harper ⁷²	Polished copper cylinder, 10 cm diam., 10 cm } Convection-conduction... high, in similar jacket of 20 cm dimensions } (same as No. 7) } Radiation	0.00022 0.00006
9	Soddy and Berry ⁷³	Conduction in rarefied nitrogen or oxygen for each 0.01 mm (of Hg) residual pressure, so long as mean free path of molecules is not materially less than distance between the two walls	0.00008

It becomes evident at once that in such a case as where the effective emissivity of two walls taken together is 30 per cent, no amount of pumping out the conducting gas between them can reduce the heat transfer to less than 50 per cent of its magnitude before pumping. If it be worth while to evacuate at all, for the sake of gaining this degree of thermal insulation, it must be evident that the difference between a rather poor vacuum and the very highest would be hardly appreciable so far as total heat transmitting power is concerned.

⁶⁶ MacFarlane: Proceedings Royal Society of London, 20, p. 90; 1871-2.

⁶⁷ Langmuir: Transactions American Electrochemical Society, 23, p. 299; 1913.

⁶⁸ Wamsler: Zeitschrift des Vereines Deutscher Ingenieure, 55, p. 628; 1911.

⁶⁹ Dickinson, Harper, and Osborne: This Bulletin, 10, p. 242; 1913. Surface of calorimeter 1700 cm².

⁷⁰ Lees: Philosophical Magazine (5), 28, p. 438; 1889.

⁷¹ The surface of the copper spiral, while approximately that of a cylinder 10 by 10, was by no means definitely measurable as in No. 8. The agreement of the results (0.00018 and 0.00022) is satisfactory, considering all conditions. The difference in the radiation is discussed on p. 324.

⁷² Experiments described more fully on p. 327.

⁷³ Soddy and Berry: Proceedings of the Royal Society of London, A83, p. 254; 1910.

Now let us consider an emissivity that is very small, say 2 per cent black, which is perhaps the correct value for a well silvered Dewar flask. The conduction-convection is reduced to an equality with the radiation⁷⁴ (at 300° K) only when evacuation has reached the stage where the former has but one-fifteenth of its value at atmospheric pressure. It is quite worth while then to continue to the one-thirtieth stage and probably to the one-sixtieth before the radiation is so great a percentage of the total transfer (80 per cent in this instance) that the further improvement in insulation might cease to repay the trouble necessary to secure it. One-sixtieth of 0.00020 is 0.00033, and from datum 9 of Table 6 the requisite vacuum is 0.0003 mm of Hg.

The two examples, 30 per cent emissivity and 2 per cent, are quite sufficient to indicate the general procedure in deciding upon a useful degree of evacuation, and the next important consideration is the probable magnitude of emissivity which will characterize various pieces of apparatus. Before passing to this topic, however, there is a supplement to Table 6 which requires a moment's attention.

WIRES

Until very recently the figures obtained experimentally for the heat loss from small wires remained uncorrelated and it is only within the last year or two that any general conclusions of value have been put forth.⁷⁵ It has, however, always been evident that the heat loss per unit area increased as the diameter of specimens was decreased, so that there was no possibility of inferring directly the correct figure for an extended surface from the loss from a small wire, yet this error has been made frequently. Taking the actual surface of the wire as the basis of the per cm² computation, Table 7 presents a few representative figures to show that the conduction-convection is very much greater than any figure quoted in Table 6. The depressed ciphers are added so as to carry the same number of figures in the two tables.

EMMISSIVITIES

Turning now to the question of emissivities, only a few remarks can be made in this paper, as the subject is too comprehensive for a satisfactory digest within reasonable space.

First of all it must be borne in mind that at 300° K the wave length of maximum emission is about 10μ and the total emission

⁷⁴ Attention is directed to the fact that a Dewar flask is frequently used at temperatures where the radiation is but a small fraction of the radiation at 300° K and in such case the conclusions of this paragraph must be modified accordingly.

⁷⁵ Langmuir, loc. cit.

in the visible spectrum is an inappreciable fraction of the whole. For the reflection coefficients in the infra red it is quite usual to employ the figures given by Hagen and Rubens, as quoted in the Landolt-Börnstein tables of physical constants and from these copied into others. While these figures are no doubt excellent, they may lead to very erroneous conclusions by failure to recognize the tremendous changes in emissivity which sometimes occur for a small change in condition of surface.

TABLE 7

Conduction-convection from Wires in Still Air at Atmospheric Pressure. Watts per cm^2 per Degree Difference of Temperature from Room at 300°K

Name	Remarks	Diameter cm	Watts per cm^2 per degree
Bottomley ⁷⁶	Various sizes between limits given.....	0.08 0.04	0.0021 ₀ 0.010 ₀₀
Schleiermacher ⁷⁷ ..	Wire horizontal in glass tube 2.4 cm diameter.....	0.040	0.0033 ₀
Kennelly ⁷⁸	Temperature difference of about 50° . (No great difference between figures for 15° and 70°). {	0.069 0.021 0.011	0.0041 ₀ 0.0072 ₀ 0.014 ₀
Langmuir ⁷⁹	Horizontal in room at 300°K . Same figures within 10 per cent for temperature differences 10° to 200° . {	0.051 0.025 0.0126 0.0059	0.007 ₀₀ 0.011 ₀₀ 0.017 ₀₀ 0.027 ₀₀
Knudsen ⁸⁰	Wallaston wires.....	0.00042	0.046 ₀₀ "2000 times black ra- diation."

For illustration, consider copper, the metal most important for this paper. In such tables the reflecting power is given as over 97 per cent between 3μ and 14μ and probably averages 98 per cent in the range with which we are concerned, or the emissivity is 2 per cent. But this refers to pure copper quite free of oxide, the surface having been renewed immediately before measuring. With very slight oxidation, the least one would find on an ordinary copper surface in air, the emissivity appears to be several times greater. A copper cylinder of dimensions about the same as the overall dimensions of the spiral described in this paper radiated

⁷⁶ Bottomley: Proceedings of the Royal Society of London, 37, p. 177; 1884.

⁷⁷ Schleiermacher: Wiedemann's Annalen, 34, p. 623; 1883. Results not given in absolute measure. Assumptions made by author in deducing them may therefore possibly lead to erroneous figures.

⁷⁸ Kennelly, Wright, and Van Bylevelt: Transactions American Institute of Electrical Engineers, 28, p. 363; 1909. Figures copied from Langmuir, Ibid. 31, p. 1234; 1912.

⁷⁹ Langmuir: Physical Review, 34, p. 401; 1912.

⁸⁰ Knudsen: Annalen der Physik (4), 34, p. 593; 1911.

to nickeled surroundings 10 per cent of the black body figure quoted, yet it was bright and not oxidized apparently. The spiral itself lost heat by radiation at a rate about 20 per cent that of a black body. Its surface also was bright and not apparently oxidized, but it must not be overlooked that the recesses at the meeting points of the layers approximate the condition for black radiation and probably increase materially the average radiation from that due to the polished copper surface not so recessed.

Wamsler⁸¹ found the emissivity of polished copper 50° above room temperature to be 18 per cent, increasing as it oxidized with heat, the increase being very rapid above 250° C. Langmuir⁸² found an emissivity of 39 per cent for "calorized" copper and 77 per cent for oxidized copper, both at 325° K.

Iron surfaces seem to show the same latitude of variation. From the table of Hagen and Rubens, 8 per cent is a fair average figure to take for the spectral interval in question. Wamsler found highly polished (wrought) iron to have an emissivity of 30 per cent, while matt oxidized surface was about the same as a black body. Langmuir found 17 per cent for bright cast iron, 50 per cent for the same oxidized.

Platinum and silver, on the other hand, seem to give more reasonably concordant results, agreeing at least in the order of magnitude. Platinum, for example, might be taken as 8 per cent from the table of Hagen and Rubens; Bottomley, reviewing Schleiermacher⁸³ quotes figures which give 10 per cent (100° C to 300° C); Bottomley⁸⁴ himself gets 13 per cent; Soddy and Berry⁸⁵ find 10 per cent (60° C to 15° C), and Knudsen⁸⁶ finds 12 per cent (100° C to 0° C).

Since the usual tables of reflection coefficients in the far infra red show few if any figures less than 90 per cent, this is sufficient cause for a rather current impression that almost any metal surface, polished to a fair degree, is a very good reflector, or low emissive power radiator, of the long heat waves. That this is by no means true is sufficiently well indicated above; indeed for a metal like copper which appears to change in emissivity so greatly for different degrees of oxidation of the surface, it would seem almost impossible to predict the radiation, and that direct experimental measurements with the surface in question would be the only means of determining it.

⁸¹ Wamsler: *Zeitschrift des Vereines Deutscher Ingenieure*, 55, p. 599; 1911.

⁸² Langmuir: *Transactions American Electrochemical Society*, 23, p. 299; 1913.

⁸³ Schleiermacher: *Wiedemanns Annalen*, 26, p. 287; 1885.

⁸⁴ Bottomley: *Philosophical Transactions of the Royal Society of London*, A178, p. 429; 1887.

⁸⁵ Soddy and Berry, *loc cit*.

⁸⁶ Knudsen: *Annalen der Physik* (4), 34, p. 593; 1911.

CONDUCTION IN RAREFIED AIR

1. HIGH VACUA. (LOW RESIDUAL PRESSURE)

When thermal insulation by employing a vacuum jacket is sought and consideration of the radiation has led to an estimate of the degree to which it is profitable to reduce the conduction, the question next in order is what degree of evacuation corresponds to a given conducting power. The answer has been anticipated by including datum 9 in Table 6, but a somewhat more full discussion is in order.

The theory of thermal conduction in highly rarefied gas has been admirably treated by Smoluchowski⁸⁷ and Knudsen⁸⁸ and can not be dwelt upon here. Soddy and Berry⁸⁹ have stated the results of their very careful measurements in a form which is very convenient of application. Their conclusions may be stated as follows: A body surrounded by a chamber which is distant from it by no more than the mean free path of the molecules of gas filling the intervening space, loses heat, in addition to the radiation, according to the law

$$\frac{dQ}{dt} = ks\theta p$$

If $\frac{dQ}{dt}$, the rate of loss of heat from the body, be in cal per sec.;

s , the area of the surface of the body, be in cm^2 ;

θ , the difference in the temperatures of the body and the surrounding chamber, be in $^{\circ}\text{C}$;

p , the pressure of the gas, be in units of 0.01 mm of Hg,

then k , the coefficient or conductivity of the gas, is a numerical constant for a considerable range of variation of the other factors entering into the relation. It is about the same for oxygen and nitrogen, numerically 2×10^{-5} , and accordingly this figure may be used for air. The law was tested for a sufficient number of pressures to establish it satisfactorily with respect to this factor, for temperature differences up to about 50° , and for a considerable number of gases, each of which was found to give a definite value for k .

A restatement of the equation in words is that each square centimeter loses 2×10^{-5} cal per sec, which is 8×10^{-5} watts, for

⁸⁷ Smoluchowski: Wiedemanns Annalen, 64, p. 101; 1893, or Philosophical Magazine (5), 46, p. 192; 1898. Kaiserlichen Akademie der Wissenschaften zu Wien, Berichte der Mathematisch-Naturwissenschaftlichen Klasse, 107, IIa, p. 324; 1898. Ibid., 108, IIa, p. 5; 1899. Philosophical Magazine (6), 21, p. 11; 1911. Annalen der Physik (4), 38, p. 983; 1911.

⁸⁸ Knudsen: Annalen der Physik (4), 24, p. 593; 1911. Ibid., 35, p. 389; 1911. Ibid., 36, p. 871; 1911.

⁸⁹ Soddy and Berry: Proceedings of the Royal Society of London, A83, p. 254; 1910. Ibid., A84, p. 376; 1911.

each degree (C) excess of temperature above that of the surrounding envelope if the intervening air be at a pressure of 0.01 mm of Hg, provided the distance separating the body and the envelope be not over 8 mm, the mean free path corresponding to 0.01 mm pressure. From this figure, 0.00008 watt per cm^2 per degree, the heat transfer by gas conduction at any other pressure lower (except for air gaps narrower than 8 mm) can be readily computed. For instance at one-eighth this pressure, or 0.0012 mm of Hg, the conduction would be the round number 0.00001 watt per cm^2 per degree, for any width of air gap up to about 7 cm.

LOW VACUA. (RESIDUAL PRESSURE "LARGE")

Since the terms high and low vacua are relative only, it will be necessary to adopt some arbitrary division and this is here taken to be the pressure at which the mean free path of the gas molecule is equal to the distance between the walls confining it. In high vacua (small residual pressure) the heat transmission is proportional to the pressure, but very soon after passing the division indicated, the increase in conduction becomes less and less for a given increase in pressure, and soon the conduction becomes constant, independent of the pressure. This condition continues to hold as the pressure is increased, probably well on beyond atmospheric pressure, but the total heat transfer is augmented by convection which becomes appreciable at a pressure which apparently varies greatly with different conditions. No doubt the shape of the surfaces plays a very important part in determining the convection, but it is unsafe to advance detailed theories. A few typical experiments are reviewed below, mainly as illustrations of the latitude in the results which have been obtained. Since almost nothing has been done yielding results in absolute measure, it is quite impossible to prepare a table of comparisons, similar to Tables 6 and 7, upon a satisfactory basis. The best which can be done is to employ some arbitrary way, as for instance by placing the heat loss due to the gas (total loss less the radiation) as unity at atmospheric pressure and comparing the fractional values of this loss at various other pressures. This is done in Table 8 by tabulating the pressures corresponding to a given fractional value of the conduction-convection loss.

A more detailed review of these experiments brings out a great many very interesting points, but as it is hopeless to reach any general conclusions of value, there would appear to be no pressing need for presenting such review here. Those interested in them are referred to the original sources which are almost all in periodicals commonly found in the better scientific libraries. The sub-

ject is one which needs further experiments carried out so that the results may be expressible in absolute measure, before generalizations can be expected.

TABLE 8

Pressure at Which Convection-conduction in Air was Found to be a Given Fraction of its Magnitude at one Atmosphere. Radiation has in Each Case been Subtracted From Total Heat Transfer

Name	Conditions	Relative conduction-convection			
		1.00	.75	.50	.25
Dulong and Petit ⁹⁰ ..	Mercury thermometer in large spherical globe.	mm of Hg 760	mm of Hg 360	mm of Hg 180	mm of Hg 45
Kundt and Warburg. ⁹¹	Mercury thermometer in 6-cm spherical globe.	760		150	Below 0.5
	Mercury thermometer in tall narrow cylinder.	760		Below 0.5	
Crookes ⁹²	Mercury thermometer in 1½-inch spherical globe.	760	1	0.1	0.01
Brush ⁹³	Mercury thermometer in large pear-shaped globe.	760	270	90	0.08
	Mercury thermometer in tall cylinder.	760	0.15	0.05	0.015
Harper	Copper cylinder, 10 cm diameter, 10 cm high in 20 by 20 jacket.	760		Above 63	0.07
Bottomley ⁹⁴	0.4 mm wire in 25-mm tube	760	5	1.5	0.4
Soddy and Berry ⁹⁵ ..	Thin narrow strip in 1-cm tube..	760	4	.15	0.05
Eucken ⁹⁶	Fine wire in 1-mm tube.....	760		Below 4	

The experiments by the author have not been published elsewhere and require description sufficient to permit of a proper criticism. They were performed as preliminaries to the calorimetric measurements described in the foregoing paper, and were never intended to be separated as a properly planned investigation of the heat transmission in rarefied air; consequently there are omissions of measurements at pressures which are very desirable, and the care and time spent upon the measurements was by no means what it might have been, and the precision is not high. Nevertheless the results are certainly good to the order of magnitude (say 20 to 50 per cent, and probably very much better than this) and being in absolute measure and made with an air space of definite shape and dimensions, they may be of interest for comparison with the results of subsequent investiga-

⁹⁰ Dulong and Petit: *Annales de Chimie et de Physique*, 7, pp. 225, 337; 1817. *Journal Ecole Polytechnique*, 11, p. 234; 1819.

⁹¹ Kundt and Warburg: *Poggendorfs Annalen*, 156, p. 177; 1875.

⁹² Crookes: *Proceedings of the Royal Society of London*, 31, p. 239; 1880.

⁹³ Brush: *Philosophical Magazine* (5), 45, p. 31; 1898.

⁹⁴ Bottomley: *Philosophical Transactions of the Royal Society of London*, A178, p. 429; 1887.

⁹⁵ Soddy and Berry: *Loc. cit.*

⁹⁶ Eucken: *Physikalische Zeitschrift*, 12, p. 1101; 1911.

tions better planned to shed light on the apparent anomalies of Table 8.

Two or more measurements were made at each of the pressures indicated in Table 9, and several series of pressures were used on different days, the agreement of the entire set being satisfactory for the purpose in view.

TABLE 9

Convection-conduction in Rarefied Air Between a Cylinder 10 cm by 10 cm and a Similar Inclosure 20 cm by 20 cm. Temperature Differences About 5°, and Mean Temperature 300° K. Watts per cm² per Degree C

Pressure in mm of Hg	760	2.30	0.77	0.24	0.12	0.083	0.046	0.024	0.016	0.014	0.003 ₂
Total watts per cm ² per degree.....	0.0 ₃ 34	0.0 ₃ 18	0.0 ₃ 18	0.0 ₃ 17 ₅	0.0 ₃ 17	0.0 ₃ 16	0.0 ₃ 15	0.0 ₃ 14	0.0 ₃ 14	0.0 ₃ 14	0.0 ₃ 12
Conduction - convection.....	0.0 ₃ 24	0.0 ₃ 08	0.0 ₃ 08	0.0 ₃ 07 ₅	0.0 ₃ 07	0.0 ₃ 06	0.0 ₃ 05	0.0 ₃ 04	0.0 ₃ 04	0.0 ₃ 04	0.0 ₃ 02

Later Series, Same Apparatus with Radiant Emissivity Diminished

Pressure in mm of Hg	760	63	0.014	0.009	0.0031	0.0017
Total watts per cm ² per degree.....	0.0 ₃ 28	0.0 ₃ 15	0.0 ₃ 12	0.0 ₃ 09	0.0 ₃ 08	0.0 ₃ 08
Conduction-convection.....	0.0 ₃ 22	0.0 ₃ 09	0.0 ₃ 06	0.0 ₃ 03	0.0 ₃ 02	0.0 ₃ 02

A large hollow cylindrical shell of copper was suspended in the jacket of the calorimeter described in the foregoing paper. The copper cylinder was 10 cm in diameter and 10 cm high, approximately the dimensions of the copper spiral used in the specific heat measurement described in the foregoing paper, but presenting a more definitely defined surface. It was closed at both ends, and the cylindrical wall was thick, with a constantan ribbon heating coil and sensitive platinum resistance thermometer imbedded in the copper mass but insulated from it by mica.

This cylinder was brought to a temperature about 5° above or below that of the jacket, and then the rate of cooling or warming was determined during a period of about 10 minutes, employing the resistance thermometer. From this rate, the heat capacity (1200 joules per degree), the surface (470 cm²), and the temperature difference, the total dissipation (per unit area, etc.) was calculated in absolute measure. From this total dissipation was subtracted the radiation, computed in the following manner:

The jacket being about 20 cm in diameter and 20 cm high, the air space between the copper cylinder and jacket was about 5 cm

all around, a distance which is the mean free path of a molecule of air at a pressure of about 0.002 mm of Hg. Accordingly, the figures given by Soddy and Berry⁹⁷ are applicable to the measurements made at 0.0032 mm and 0.0017 mm (Table 9), and upon computing the conduction at these pressures and deducting, the figures obtained for radiation are 0.00010 and 0.00006 watts per cm² per degree, respectively, for the two parts of Table 9. It should be noted that a very large error in the figures given by Soddy and Berry would have very little effect upon the result, provided only that the order of magnitude is correct, i. e., the conduction quite small as compared to the radiation. The process is therefore not the circle which it might appear to be at first sight. It was made necessary by reason of failure to secure a vacuum higher than indicated in the table at the times when heat transfer measurements were obtainable. The actual limit of the pump, a double-cylinder Geryk oil pump of the Fleuss type, was apparently in the neighborhood of 0.001 mm of Hg.

Pressures were measured with a McLeod gauge sensitive to about 0.0001 mm. This was connected to one pipe leading into the vacuum chamber and the pump to another, so that the apparatus was in series in the order pump, vacuum chamber, gauge, and therefore the vacuum attained was certainly as high as the gauge measurements indicated. The connecting tube was 6 mm internal diameter and not excessively long, and no great differences of temperature occurred here, so that it is not likely that the vacuum was appreciably higher than the measurements indicate. A large drying tube of phosphorus pentoxide was connected to the vacuum chamber by 15 cm of brass tubing 8 mm in diameter.

RÉSUMÉ

This chapter makes no pretense of being a thorough review of the whole subject of heat transfer in gases. It is but a note gathered from the literature and from the author's experience, attempting to set forth a little more clearly than seems to have been done elsewhere the relative magnitudes of the radiation and the convection-conduction in air at atmospheric pressure and at various stages of evacuation, for such conditions as are likely to be found in calorimetry and work with similar apparatus whether scientific or industrial.

⁹⁷ Soddy and Berry, loc cit.