

bable, therefore, that the remarkable properties of liquid hydrogen predicted by theory will prove to be susceptible of explanation when they are compared with those of liquid air, volume for volume, at corresponding temperatures as defined by van der Waals.

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THE SPECIFIC HEAT OF METALS AT LOW TEMPERATURES.

DR. WOLCOTT GIBBS having requested Professor Rood to make some determinations of the specific heat of a few metals, employing liquid air, the matter was finally handed over to me by Professor Rood, and I herewith give a short account of the method used and the results obtained.

Few experiments on the specific heat of substances at low temperatures have been made. The chief cause of this has been the difficulty experienced heretofore in reducing the temperature of bodies to a definite number of degrees sufficiently below zero, Centigrade. Liquid air affords a means of obtaining a very low temperature, and was procured through the kindness of Mr. Charles E. Tripler, who has devised apparatus for making it in considerable quantities.

In a paper on the liquefaction of gases by Professor Charles Olszewski, in the *Philosophical Magazine*, London, February, 1895, Vol. XXXIX., No. CCXXXVII., pp. 188-212, it is stated, that the boiling point of liquefied air under atmospheric pressure is -191.4°C ., that of liquefied nitrogen -194.4°C ., and that of liquefied oxygen -181.4°C . These temperatures were determined with a hydrogen thermometer, and are generally accepted as correct.

Liquefied air changes in composition when in a state of ebullition, the percentage of nitrogen contained in it diminishing, while that of oxygen increases.

This change occurs because liquid nitrogen is the more volatile of the two liquid gases, and boils away at a higher rate than liquid oxygen; consequently liquid air changes in temperature. If it is allowed to boil for a considerable time it becomes almost pure liquid oxygen and its temperature correspondingly approaches near the boiling point of that liquid gas, or -181.4°C .

Such was the case with the liquefied air procured for the experiments on specific heat; therefore, after standing several hours, the cold liquid employed by me was considered to be liquid oxygen and its temperature -181.4°C .

A series of determinations were made of the specific heat of copper, iron and aluminium between the boiling point of liquid oxygen (-181.4°C .) and about 13 degrees Centigrade.

The method of mixtures was employed and was applied in a manner suggested by Professor Rood.

The experiments were conducted as follows:

A piece of metal of known weight was immersed in liquid oxygen (-181.4°C .); after it had cooled down to the temperature of the liquid, it was lifted out by a silk thread, attached to it, and transferred quickly to a calorimeter containing water of known weight and temperature.

The loss in temperature of the water, due to the insertion of the cold substance, was carefully noted, and the specific heat of the metal computed.

Various precautions were taken to avoid errors in the results, and the usual corrections were applied in the calculations.

Before the determinations of the specific heat of metals between the boiling point of liquid oxygen and normal temperatures (about 13°C .) were begun, a series of experiments were performed on the specific heat of copper between 23°C . and the boiling point of water (100°C .), under condi-

tions as far as possible identical with those anticipated in the experiments with liquid oxygen.

By this means it was ascertained approximately what degree of accuracy could be expected in the results when liquid oxygen was employed.

The manipulation in these preliminary experiments was as follows:

A piece of copper, with a silk thread attached (the identical piece to be used in the low temperature experiments), was immersed in boiling water and allowed to remain submerged for several minutes.

It was then lifted out of the boiling water by the thread, and conveyed as quickly as possible to a calorimeter two-thirds filled with water at 17°C. The rise in the temperature of the water was noted, and the specific heat calculated in the usual way. When the copper was transferred from the vessel containing the boiling water to the calorimeter, it was allowed to strike the edge of the vessel a sharp blow to remove drops of water remaining on the surface of the piece of copper.

It was found, however, that a small amount of hot water, .03 to .04 of a gram, was always carried over to the calorimeter. The quantity was determined experimentally and the proper correction applied in the specific heat calculations.

Five consecutive determinations of the specific heat of copper between 23° C. and the boiling point of water (100° C.), by this method, were as follows:

TABLE 1.

Substance.	Determination Number.	Specific Heat. 23°...100° C.
Copper.	1	.09262
"	2	.09463
"	3	.09399
"	4	.09394
"	5	.09517
Mean		.0940

Average variation of the five determinations from the mean, .0006, or .7 per cent.

Greatest variation of any one determination from the mean, .00138, or 1.5 per cent.

The weight of water used in each determination was 70.00 grams, and the water equivalent of the calorimeter and thermometer, 5.87 grams.

The weight of copper employed in each determination was 63.493 grams.

The temperature of the boiling water was determined from the atmospheric pressure, the barometric height being measured at intervals during the experiments.

The mean value obtained for the specific heat of copper, .0940, is in agreement with the value generally accepted for that metal for the same range of temperature, the best values ranging from .0933 to .0949.

Also the percentage error of each determination as compared with the mean value, .0940, is small, being less than 1 per cent.

These facts seemed to warrant proceeding with a series of determinations of the specific heat of copper and other metals at low temperatures by the same method, employing liquid oxygen.

Five determinations of the specific heat of copper between the boiling point of liquid oxygen, under atmospheric pressure (−181.4°C.), and 11 C. were as follows:

TABLE 2.

Substance.	Determination Number.	Specific Heat (−181.4°... 11°C.)
Copper.	1	.0867
"	4	.0854
"	7	.0882
"	10	.0873
"	13	.0868
Mean		.0868

Average variation of the five determinations from the mean, .0007, or .8 per cent.

Greatest variation of any one determination from the mean, .0014, or 1.6 per cent.

Weight of water used in each determination, 70.01 grams.

Weight of copper used in each determination, 63.493 grams.

By these experiments the specific heat of copper between -181.4° and 11° C. was found to be .0868.

As previously stated, the specific heat of copper between 23° and 100° C. was found to be .0940.

The two sets of determinations were made by the same method, the accuracy of manipulation in each being about equal, and the same piece of copper was used for both ranges of temperature.

A comparison of the two values shows the specific heat of copper between -181.4° and 11° C. to be 7.6 per cent. less than that found in determinations between 23° and 100° C.

The specific heat of iron between -181.4° and 13° C. and that of aluminium between -181.4° and 15° C. were also found.

Five determinations of the specific heat of iron between -181.4° and 13° C. were as follows :

TABLE 3.

Substance.	Determination Number.	Specific Heat. (-181.4° ... 13° C.).
Iron.	3	.0890
"	5	.0883
"	8	.0949
"	11	.0912
"	14	.0939
Mean		.0914

Average variation of the five determinations from the mean .0025, or 2.4 per cent.

Greatest variation of any one determination from the mean, .0035, or 3.8 per cent.

Weight of water employed in each determination, 70.01 grams.

Weight of iron, 51.93 grams.

Five determinations of the specific heat of aluminium between -181.4° and 15° C. were as follows :

TABLE 4.

Substance.	Determination Number.	Specific Heat. (-181.4° ... 15° C.).
Aluminium.	2	.1814
"	6	.1827
"	9	.1851
"	12	.1815
"	15	.1861
Mean		.1833

Average variation of the five determinations from the mean, .0018, or 1 per cent.

Greatest variation of any one determination from the mean, .0028, or 1.5 per cent.

Weight of water employed in each determination, 70.01 grams.

Weight of aluminium, 19.86 grams.

All of these experiments on specific heat, employing liquid oxygen, were performed consecutively, without interruption.

The determinations were made alternately, and with one exception in the order : copper, iron, aluminium.

The 'determination number' in the foregoing tables of the specific heats of the metals between 181.4° and about 13° C. shows the order followed.

By this arrangement any change in the temperature of the cold liquid used (liquid oxygen), during the time occupied in performing the experiments, would have been indicated in the results obtained. No such indication is apparent.

The assumption made that the liquid employed had already been transformed by ebullition from liquid air to liquid oxygen was, therefore, virtually substantiated.

Liquid oxygen placed in a vessel surrounded by air at ordinary temperatures boils away rapidly ; consequently in the foregoing experiments it was contained in a cylindrical copper receptacle, set inside of another about twice the diameter of the first, which also contained liquid oxygen. With this arrangement the oxygen in the inner receptacle can be made to cease boiling.

This simple method of rendering liquid

gases free from ebullition has been employed by Mr. Charles E. Tripler, and was adopted in the present investigation with a slight modification; the liquid oxygen in the inner receptacle being kept always at a higher level than that in the outer, allowed feeble ebullition in the inner vessel and assured the liquid therein being at its boiling point.

The same weight of water to a gram was used in the calorimeter throughout the experiments of both the specific heat at low temperatures and those between 23° and $100^{\circ}\text{C}.$, and also in determining the water equivalent of the calorimeter and thermometer.

It was found necessary to filter the liquid oxygen in which the metals were immersed, in order to free it from the solid matter that was present in the liquid. Unless this precautionary measure had been adopted, some of the frozen masses of carbondioxide, water and other compounds that are in unfiltered liquid oxygen would have adhered to the metals (as was found by experiment), and would have affected the accuracy of the determinations.

The metallic objects of which the specific heat was determined were cylindrical in form and all about equal in volume. The measurements of each were as follows:

Copper—Length, 5.5 cms.; diameter, 1.2 cms.; weight, 63.493 grams.

Iron—Length, 5.5 cms.; diameter, 1.2 cms.; weight, 51.93 grams.

Aluminium—Length, 5.6 cms.; diameter, 1.2 cms.; weight, 19.86 grams.

These pieces were specially constructed on a lathe, and were made with rounded instead of flat ends, so that the liquid oxygen and boiling water would be less apt to adhere to them when they were lifted from these liquids. A small button was turned on the end of each of the metal pieces in construction, and to this a silk thread was attached for transferring them from the hot

or cold liquids to the water in the calorimeter in the two series of experiments. It was considered unadvisable to bore holes in the metal pieces through which to fasten the threads, because drops of the liquids would have been caught in such recesses.

In all of the above experiments with liquid oxygen, before the metals were transferred from the liquid oxygen to the water in the calorimeter, the water was heated a few degrees above the room temperature. The amount that it was thus previously raised was approximately equal to half the number of degrees that the water would fall in temperature when the cold metal was placed in it.

A value for this fall of temperature was determined by a preliminary experiment.

By this means changes in temperature of the water and calorimeter, due to radiation and conduction of heat, and caused by a difference in temperature existing between them and surrounding bodies, were approximately compensated for.

The method of eliminating errors arising from causes similar to those just under consideration was originated by Rumford.

In calculating the values of the specific heats in the above experiments it was assumed that the temperature of the metals in transference from the liquid oxygen to the water in the calorimeter did not change to an appreciable amount. This assumption was apparently substantiated by the following experiments:

The metals were lifted out of the liquid oxygen, and again immersed after a period of two seconds. It was noted that no boiling whatever could be observed as they were replaced in the liquid. In ten observations made with a watch provided with stop attachment, in which the time that the metals were held out of the liquid air varied from $1\frac{3}{5}$ sec. to $2\frac{1}{5}$ sec., no boiling was perceived when they were replaced in the liquid.

With an extension of the time that the metals were held out of the liquid to three seconds, a slight effect of boiling was apparent when they were replaced.

In the determinations of specific heats for low temperatures it required only one second or less to transfer the metals from the liquid oxygen to the water in the calorimeter. It, therefore, seems probable that little heat was absorbed by the substances during the time required for their transference from the liquid oxygen to the calorimeter. In the experiments with liquid oxygen transference of the metallic objects from the cold liquid to the water in the calorimeter was accomplished with less difficulty than the transference of the same objects from boiling water to the water in the calorimeter, as performed in the preliminary experiments on the specific heat of copper between 23° and 100° C.

Little or no liquid oxygen was carried over to the calorimeter on the metal pieces, it having boiled off before they were placed in the water; therefore a correction similar to that applied in the experiments with boiling water was not necessary.

The value of the specific heat of iron between —181.4° and 13°, C., as determined by the foregoing experiments, is .0914.

The lowest value for the range, 15°...100° C., according to recorded results, appears to be about .113 (.1130, 0°...100° C., Tomlinson).

The value for the specific heat of iron between —181.4° and 13° is, therefore, approximately 19 per cent. less than the lowest value for the range, 15°...100° C.

The specific heat of aluminium for the low temperature range was found to be .1833.

The lowest value for the range 15°...100° C. seems to be about .212 (15°...97° C., Regnault).

The value for the specific heat of this metal between —181.4° and 15° C. is 13.6

per cent. less than the lowest value for the range 15°...100° (97°) C.

The values for the specific heat for the ranges, 0°...100° C. and 15°...97° C. given, were taken from *Physikalisch-chemische Tabellen*, by Landolt and Börnstein, 1894 Ed.

The variation in the values, as given by different authors, of the specific heat of certain metals for the range 15°...100° C. is no doubt partly due to the employment of metals of different degrees of purity. For this reason the specific heat of the pieces of iron and aluminium used in the experiments with liquid oxygen have been determined between 23° and 100° C. in the manner that the specific heat of the copper for the same range was found.

The determinations were as follows :

TABLE 5.

Substance.	Determination Number.	Specific Heat. (23°...100° C.)
Iron.	16	.1175
"	17	.1151
"	18	.1185
"	19	.1164
"	20	.1136
Mean		.1162

The weight of water and other quantities were the same in these experiments as those with copper (23°...100° C.).

The determinations of the specific heat of aluminium between 23°...100° C. were as follows :

TABLE 6.

Substance.	Determination Number.	Specific Heat. (23°...100° C.)
Aluminium.	21	.2190
"	22	.2165
"	23	.2225
"	24	.2128
"	25	.2158
Mean		.2173

The accuracy of manipulation in these two sets of determinations was about equal to that of the experiments on copper for the same range of temperature.

If the results of the determinations just given and those for copper for the same range, 23°...100° C., are employed, a comparison can be made between the specific heat of pieces of certain metals (copper, iron, and aluminum) determined between —181.4° C. and 13° C. and the specific heat of the same pieces of metal determined between 23° and 100° C., by the same method.

The following table has been arranged to show this comparison :

TABLE 7.

Metal.	Specific Heat. —181.4°...13° C., (employing liquid oxygen).	Specific Heat. 23°...100° C., (employing boil- ing water).	Actual difference between two values.	Percentage differ- ence between two values.
Copper.	.0868	.0940	.0072	7.6 %
Iron.	.0914	.1162	.0248	21.3 %
Aluminium.	.1833	.2173	.0340	15.7 %

It is shown by this table that the specific heat of copper, iron and aluminium between —181.4° C. and about 13° C. were found to be, respectively, .0868, .0914 and .1833, or 7.6, 21.3 and 15.7 per cent. less than the specific heat of these metals determined between 23° and 100° C.

An error of several degrees in the low temperature value (—181.4° C.) would affect the accuracy of these results only to a small amount. If, for example, the specific heat of iron for the low range of temperature is assumed to be the same as between 23° and 100° C. it would mean that an error of over 40 degrees had been made, which is obviously impossible. If there are errors in the results given above, the present indications are that they are less than one per cent.

The value of the water equivalent of the calorimeter and thermometer finally used in the calculations in all the specific heat experiments was obtained from the mean of

ten determinations. The mean value was 5.87 grams.

The calorimeter was made of copper, cylindrical in form ; height, 9.75 cms.; diameter, 4.0 cms.; and weight, 35.498 grams.

The thermometer was one made by Henry J. Green, No. 8407, graduated to $\frac{1}{10}$ of a degree Centigrade, and could be read to $\frac{1}{100}$ of a degree.

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COLUMBIA UNIVERSITY, June 16, 1898.

THE FLICKER PHOTOMETER.

PROFESSOR ROOD's interesting article in SCIENCE of June 3d prompts me to add a few words corroborating his statement as to the ease with which the flicker photometer is handled by observers unaccustomed to its use. If the lights to be compared differ at all in color, it is probably more easy to use, for the unskilled observer, than ordinary photometers, as the following experience, among others, shows. While I was experimenting, in 1895, with the revolving disk instrument to which Professor Rood refers, two chemists, in the course of an investigation, found it necessary to compare photometrically the illuminating powers of several different specimens of refined petroleum. I placed at their disposal a Lummer-Brodhun and a Bunsen Photometer, and showed them, as a matter of interest, the newly-devised flicker instrument. The standard lamp differed slightly in color from the flames given by the oils under investigation, so that the two observers found it somewhat difficult to obtain concordant results with either of the two ordinary photometers. They, therefore, reverted to the flicker instrument, using it to check all their results, finding its use, under the conditions, more agreeable and certain than either of the others.

With the Lummer-Brodhun or the Bunsen instrument they experienced all that unpleasant sensation of uncertainty which