AN INVESTIGATION OF SPECIFIC HEATS & LATENT HEATS OF FUSION AT LOW TEMPERATURES

THESIS.

An Investigation of Specific Heats and Latent Heats of Fusion at low Temperatures.

by

L.J. Waldbauer.

(Under the direction of Dr. O. Maass).

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FOREWORD.

The discussion and experimental work given in the following pages are, to a large extent, preliminary to that for the Ph.D. thesis. The latter will deal with "Heat Changes in the Neighborhood of the Critical Temperature". This will involve the determination of the specific heats of compressed gases and liquids in the neighborhood of the critical temperature, to see whether there are energy changes at this point which would correspond to the discontinuities in the usual PV-P curves above the critical temperature. This work, it is hoped, will also lead to theoretical deductions of the specific heats of liquids, as the continual and gradual change from gas to liquid will be followed by specific heat measurements.

Before this work could be undertaken, the equipment for the measurement of small heat changes under the conditions required, had to be built up, and experience obtained in the manipulation of constant temperature baths over the temperature range -200° to 0°C. It was thought that this could best be done by actual specific heat measurements at low temperatures, which are new and of interest in themselves, and at the same time serve to show whether the necessary accuracy required in the subsequent work can be obtained.

The object of the work described in this thesis was the development of a technique by means of which specific heats and latent heats at low temperatures could be accurately measured. The theoretical significance of these measurements is discussed first.

The theoretical values for the specific heats of gases have been worked out and brought into agreement with experimental results by taking into account the construction of the molecules. Theoretical values for the specific heats of liquids have not, as yet, been deduced. In the case of solids, the Dulong-Petit and Kopp laws have been given their theoretical significance by Boltzmann[1)], but, as there are many exceptions to these laws, and as the exceptions become more numerous at low temperatures, many modifications of the classic theory have been suggested, notably by Einstein, Nernst, Lindemann and Debye. Unfortunately there are very few experimental values with which to test these theories.

Although the latent heats of evaporation have been studied so that there is agreement between theoretical and experimental values, studies of the latent heats of fusion have not given similar satisfactory results, due largely to the exceedingly sparse experimental data. Only some twenty or thirty compounds have been studied experimentally, and the accuracy of these results is very dubious. Furthermore, the substances studied have been so diverse in their other physical properties, that this is not to be wondered at.

Specific Heats of Solids.

The following is a brief outline of the present state of the theory of specific heats of solids and latent heats of fusion. Einstein$^{2)}$, by taking into account that the change in the energy of an atom is not a continuous but a discontinuous one, arrived at the equation:

$$\frac{dW}{dT} = 3R\,\frac{e^{\frac{\beta\nu}{T}}\left(\frac{\beta\nu}{T}\right)^2}{\left(e^{\frac{\beta\nu}{T}}-1\right)^2}$$

where $\frac{dW}{dT}$ is the specific heat
R the gas constant per gm.mol
ν the vibration frequency of the oscillator
T the absolute temperature
β a constant for all substances

This expression was found to hold fairly well, but for very low temperatures, it too failed to express the true state of affairs as determined experimentally. It does, however, express the true state of affairs at high temperatures, in that it approaches the required value for the atomic heat according to the law of Dulong and Petit. In order to account for the discrepancies, Nernst and Lindemann$^{3)}$, on the basis of some deductions by Grüneisen, Mie, et. al., worked out the empirical formula:

$$C_v = \frac{3}{2}R\left[\frac{\left(\frac{\beta\nu}{T}\right)^2 e^{\frac{\beta\nu}{T}}}{\left(e^{\frac{\beta\nu}{T}}-1\right)^2} + \frac{\left(\frac{\beta\nu}{2T}\right)^2 e^{\frac{\beta\nu}{2T}}}{\left(e^{\frac{\beta\nu}{2T}}-1\right)^2}\right]$$

Which fits the experimental facts much better than the original equation proposed by Einstein. The first term represents the energy corresponding to the characteristic frequency, ν, while the second represents the energy due to the harmonic vibration which is one octave lower, $\frac{\nu}{2}$ being the vibration frequency. Up to the present there is no reason as to just why the octave should be introduced. The expression fits the experimental values for monatomic solids quite well.

Debye[4)], on a theoretical basis, developed an equation which fits the experimental values even better than the Nernst Lindemann equation. Instead of considering the atoms in a solid as vibrating simply harmonically with a single frequency, he postulated that, due to the nearness of other atoms, and the probability of collisions, the mode of vibration will be complex. As Fourier showed, such complex vibrations may be theoretically treated as being made up of a series of simple harmonic vibrations, and this leads to the necessity of integrating over a whole series or spectrum of vibration frequencies in order to calculate the total energy of a vibrating atom. According to Debye, there is a limiting maximum of the frequency, viz, ν_{max}, beyond which the spectrum does not extend; and the system only possesses three degrees of freedom. Nernst and Lindemann[5)] rearranged Debye's original equation (in regard to the symbols employed) in order to bring it into line with the older expressions, and thus gave it the form:

$$C_v = 3R\left[\frac{4\pi^4}{5}\left(\frac{T}{\beta\nu}\right)^3 - \frac{3\frac{\beta\nu}{T}}{e^{\frac{\beta\nu}{T}}-1} - 12\frac{\beta\nu}{T}\sum_{n=1}^{n=\infty} e^{-n\frac{\beta\nu}{T}}\left\{\frac{1}{n\frac{\beta\nu}{T}} + \frac{3}{n^2\left(\frac{\beta\nu}{T}\right)^2} + \frac{6}{n^3\left(\frac{\beta\nu}{T}\right)^3} + \frac{6}{n^4\left(\frac{\beta\nu}{T}\right)^4}\right\}\right]$$

It was found that the Nernst-Lindemann and Debye equations hold for the atomic heats when the atoms are supposed to be independent of molecules. In the case of compounds, where the smallest particles are polyatomic structures, the formation of crystals is due to intermolecular forces, probably analogous to those forces acting between molecules in the formation of molecular compounds. There are also vibrations of the atoms of these molecular complexes towards one another, As is shown by experimental data, when the temperature is sufficiently high, the energy content of the molecule approaches the value of 3RT, as calculated from ordinary mechanics. Nernst6) considers this made up of the energy content of the atoms, (n-1)3RT, and that of the molecules, 3RT, where "n" is the number of atoms in the molecule. At lower temperatures, the decrease in atomic heat will be expressed by Debye's equation because the molecular vibrations must occur in the same way as the atomic vibrations in a monatomic body. For the vibrations of the atoms within the molecule, the original Einstein equation must hold because the atoms must vibrate about their respective positions of rest;e.g., in a diatomic molecule the atoms must vibrate about the centre of gravity of the molecule. To bring out the meaning of the above conclusions, the case of ice may be taken as an example. Nernst assumed that ice is composed of double molecules, $(H_2O)_2$. At low temperatures, the molecular heat calculated on the basis of $m = 36$, must follow Debye's equation; at higher temperatures according to Einstein's equation, the mutual vibrations of the two water molecules are also brought in, and finally in each water molecule there are the vibrations of the two hydrogen atoms and the oxygen atom. Just how this viewpoint can be reconciled with Bragg's experimental data, which showed that in the solid state molecules lose their identity as such, is not known. Using this method of calculation, Nernst found good agreement with his experimental values. This matter will again be referred to later, when the values obtained by the writer are compared with those of Nernst.

Latent Heat of Fusion.

Ever since the time og Guldberg, numerous attempts have been made to connect the latent heat of fusion with other physical properties of substances. Guldberg's original formula involved the coefficient of elasticity and the coefficient of cubical expansion, but the expression broke down after working moderately well for several compounds. Pictet derived an equation involving the molecular weight M, the density D, the coefficient of linear expansion a, and the melting point T_m, on the absolute scale.

$$\left(\frac{M}{D}\right)^{1/3} a T_m = k$$

Crompton$^{7)}$ developed several expressions, e.g.,

$$\frac{A\lambda}{Tv} = k \qquad \frac{M\lambda}{T\Sigma v} = 1.38$$

where A = atomic weight
M = molecular weight
T = melting point abs.
v = valence
λ = latent heat of fusion.

He found "k" to vary from 0.58 to 2.56, so that this formula could hardly be considered as exactly expressing the relationship. Later he developed several other formulae, one of them on the basis of the Kinetic Theory, which holds for monomolecular substances such as metals(most metals are monomolecular in the liquid state).

$$\frac{A\lambda}{T} = 2.96$$

Robertson[8)] combined several of the older formulae into:

$$\frac{M\lambda}{T\sqrt[3]{V}} = k$$

where M = molecular or atomic weight
V = molecular or atomic volume

Here there was better agreement, although "k" varied for each class of compounds, being equal to 1.13 for monatomic metals of atomic weight greater than 40; about 2 for inorganic salts; and about 2.2 for organic compounds.

Walden[9)] tried to connect up latent heat of fusion with specific cohesion and Trouton's rule, by postulating that substances at their melting points are in corresponding states. Since his postulate is unwarranted and contrary to actual fact, his formula will not be considered here at all.

Wayling[10)] attempted to formulate a rule analogous to Troutons Rule for liquids.

$$\frac{\text{Latent Heat of Fusion x Molecular Number}}{\text{Melting Point on the absolute scale}} = \text{no. of atoms in the molecule}$$

where the molecular number is the sum of Moseley's atomic numbers. This holds for some inorganic compounds, but breaks down completely for organic compounds, giving absurd results.

H.S. Allen[11)], on the basis of the Quantum Theory deduced an equation:

$$AL = \frac{cN\cdot h\nu}{e^{\frac{h\nu}{RT}}-1}$$

where A = atomic weight
N = Avogadro's Number
c = ratio of the number of oscillators to the number of atoms.
(therefore cN is the number of atoms in 1 gm. mol.)

He postulated that the latent heat of fusion is identified with the energy necessary to counterbalance that of a certain number of oscillators concerned in holding together the crystal structure. This is practically the same expression as that developed by Crompton on the basis of the Kinetic Theory, except that it introduces the idea of the quanta.

Honda[12)] derived an expression for the relation between the latent heat of fusion and the molecular energy. He considered that, in addition to the ordinary vibration of the atoms they also possessed an additional vibration about their centres of gravity, and that while this vibration was exceedingly small at ordinary temperatures, it rose steadily as the temperature rose. The fact that specific heats measured at exceedingly high temperatures is considerably greater than that deduced from the theory(i.e. greater than 3RT) was considered by him as indicating the presence of this additional rotational vibration. As the temperature of the substance approached the melting point, this vibration increased to such an extent that at last, instead of being merely a rotational vibration, it became a continuous rotation, and that at this point it became independent of the translation, the regular spacing in the molecules broke down, and disorder took place. From these postulates, and neglecting the amount of work done in changing the volume from that of the solid to that of the liquid, he obtained the equation:

$$w\lambda = nE_{Tm}$$

where w is the atomic or molecular weight, E_{Tm} the energy corresponding to one degree of freedom, and "n" the degrees of freedom

Using this expression he got fair agreement for the metals, and by varying his "n" he got fair agreement for some inorganic salts, although there are a great many exceptions in this class. It may be pointed out that this is an extension of Crompton's hypothesis, where degrees of freedom other than translatory ones are taken into account.

In summarizing the above information on latent heat of fusion, about the only conclusions at which one can arrive are that the data on which the various formulae are based are very meagre and of questionable accuracy, and also that the complexity of the entire matter has not been fully appreciated. This will be referred to again in a discussion of the latent heat of fusion of methyl alcohol.

Experimental.

In the ordinary method of determining the specific heats of substances, there are always radiation losses which must be corrected for. This is the case with all of the determinations made by Regnault, Longuinine, Andrews, etc. Nernst and his co-workers 13) have developed the copper and the vacuum calorimeter types. The former consists essentially of a hollow copper block provided with a thermo-junction. The substance, contained in a silver or glass bulb, was dropped into the hollow portion, and the change in the temperature of the block noted. In the vacuum type, the substance acted as its own calorimeter, as it was warmed up by means of an electric current of known voltage and amperage, and noting the corresponding temperature change. In this method the platinum heating element was also used as the resistance thermometer. While these methods are very ingenious and of consider able accuracy, it is believed that the method developed in this laboratory possesses a number of advantages, notably directness ease of manipulation, and greater accuracy.

In the ordinary methods of determining latent heats of fusion, the substance is either cooled to a definite temperature and then allowed to warm up in a calorimeter, or it is melted, and at a definite temperature above the melting point allowed to cool down in a calorimeter, and the corresponding change in temperature noted. The radiation losses again enter. In the method outlined here all of these difficulties are obviated.

The calorimeter used in these experiments was of the type known as "adiabatic", and developed, to a large extent, by T.W. Richards of Harvard. As in the usual type of calorimeter, there is an inner vessel containing water, into which the substance whose specific heat or latent heat of fusion is to be measured, is placed. (See Fig.I.) This is surrounded by an air-jacket, which in turn is surrounded by a water-jacket. The air-jacket is provided with a waterproof cover, so that the former can be entirely submerged in the water of the water-jacket. This enables one to maintain or change the temperature within the calorimeter at will. In the present installation the air-jacket is made of copper and is submerged in water contained in a large stoneware crock. The water is thoroughly mixed and stirred by four double bladed

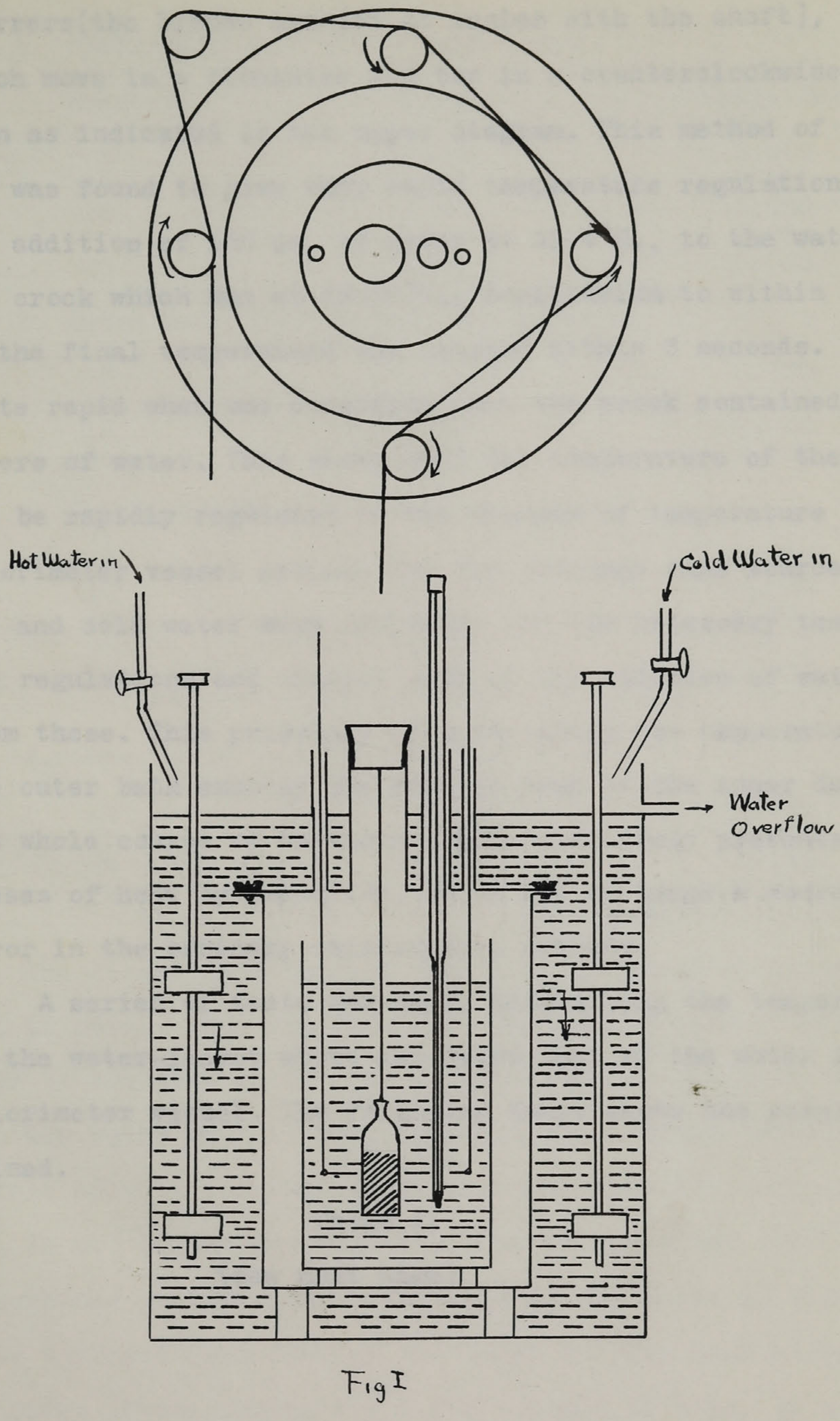

Fig I

stirrers(the blades are set at angles with the shaft), two of which move in a clockwise and two in a counterclockwise direction as indicated in the upper diagram. This method of procedure was found to give very rapid temperature regulation. On the addition of 100 cc. of water at 39.4°C., to the water in the crock which was at 19.95°C., equilibrium to within 0.01° of the final temperature was reached within 3 seconds. This is quite rapid when one considers that the crock contained 12 liters of water. This shows that the temperature of the bath can be rapidly regulated to the changes of temperature in the calorimeter vessel proper. For the ordinary runs sources of hot and cold water were provided, and the necessary temperature regulations and changes made by the addition of water from these. This principle of maintaining the temperature of the outer bath exactly the same as that of the inner during the whole course of the heat change absolutely prevents losses of heat by radiation, which are so large a source of error in the ordinary calorimetric methods.

A series of tests was made, maintaining the temperature of the water-jacket above and below that of the water in the calorimeter vessel. The following table shows the results obtained.

Table I.

(see next page)

Table I.

a. Outer bath 0.5° lower than inner.

Minutes	Change	Total Change
5	0.009	0.009
10	0.009	0.018
15	0.008	0.026
20	0.008	0.034
25	0.008	0.042

Average change 0.00168° per minute

b. Outer bath 0.1° colder than inner.

Minutes	Change	Total Change
5	0.000	0.000
10	0.000	0.000
15	0.000	0.000
20	0.000	0.000

c. Outer bath 0.5° warmer than inner.

Minutes	Change	Total Change
5	0.015	0.015
10	0.013	0.028
15	0.012	0.040
20	0.012	0.052
25	0.012	0.064

Average change 0.00256° per minute

d. Outer bath 0.1° warmer than inner.

Minutes	Change	Total Change
5	0.004	0.004
10	0.004	0.008
15	0.004	0.012
20	0.004	0.016

Average change 0.0008° per minute.

The discrepancy between the rate of change when the outer bath is colder than the inner and when it is warmer than the inner by the same amount may be explained by the fact that when the outer bath is warmer, there is a larger radiating surface than is the case when the conditions are reversed.

In all of the experimental work it was found that the temperature of the outer bath could be regulated so that it never differed from that of the inner by more than a few hundreths of one degree for a few seconds of time. By a careful regulation of the supply of hot and cold water, the temperature of the inner bath can be maintained constant to 0.001° for hours at a time, and this has actually been done in practise.

Considerable difficulty was experienced at first in keeping water out of the air-jacket. Rubber gaskets were used for a time, but after several runs they were found useless. A coating of paraffin wax was then put on each side of the rubber, but it was found necessary to re-coat the rubber after each run, and then one could not always be assured of success. Since the cover and the flange on the air-jacket were both smooth and seemed well machined, it was thought that a film of lubricating grease between the top and the flange would solve the difficulty, provided that the bolts were tightened uniformly. This was done by tightening opposite bolts at the same time, and tightening them uniformly all around. This method was found highly successful.

The stirrer for the water in the calorimeter vessel was a circular copper plate, weighted with a few drops of solder, and provided with holes as shown in Fig.II d. Enough solid portions remained to permit of carrying water from the bottom of the vessel to the top, and yet permit of the free passage of the thermometer and frigitor(see later for definition). The frigitor was suspended in the vessel so that it passed through the largest opening in the stirrer, and the thermometer through one of the smaller ones. The stirring was vertical, and was obtained by passing the cord over a small pulley and thence to an eccentric attached to another pulley which

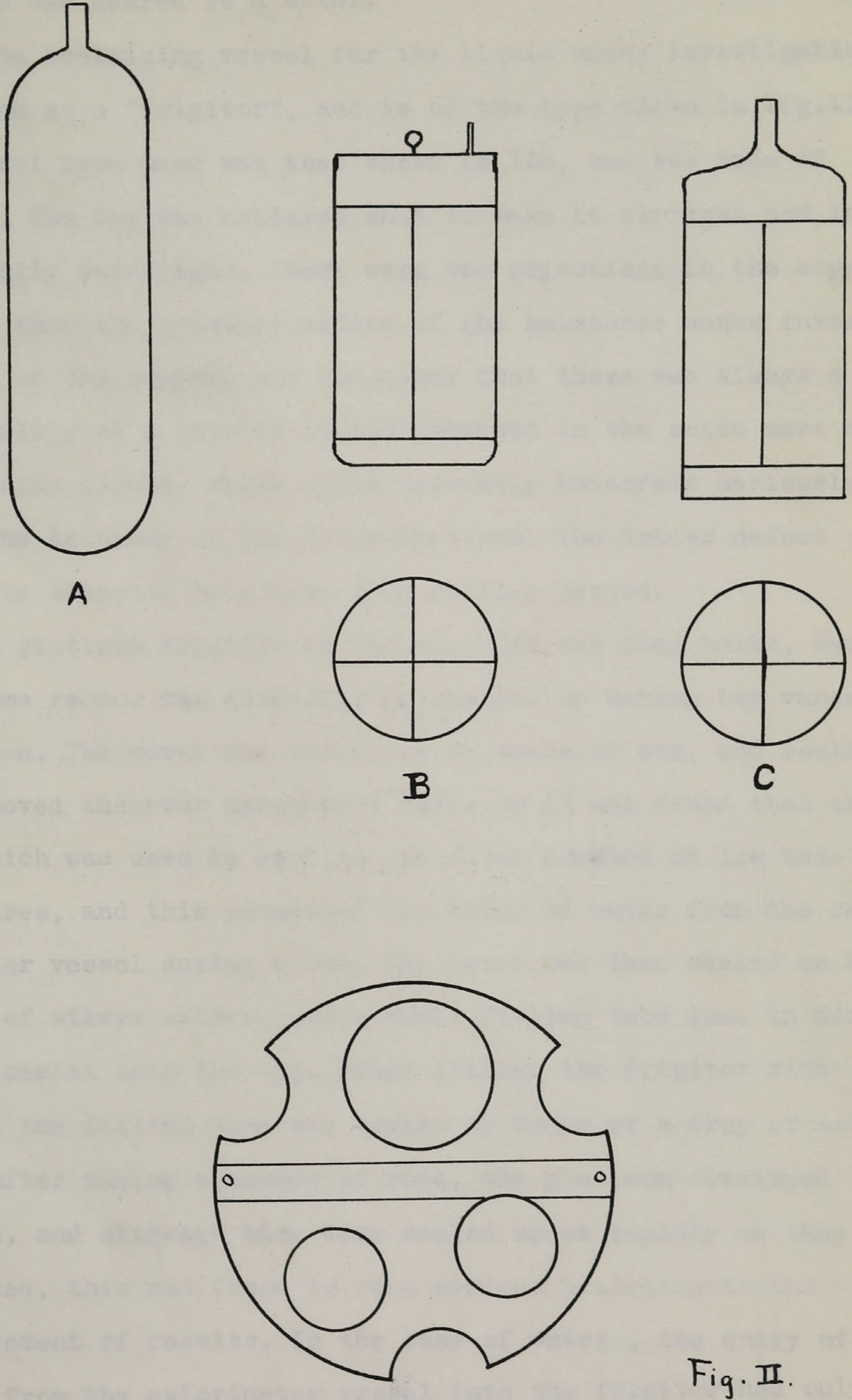

Fig. II.

in turn was geared to a motor.

The containing vessel for the liquid under investigation is known as a "frigitor", and is of the type shown in Fig.II. The first type used was that shown in IIa, and was made of copper. The top was soldered shut to make it airtight and incidentally watertight. There were two objections to the copper, one of them the possible action of the substance under investigation on the copper, and the other that there was always a possibility of a core of liquid imbedded in the solid mass of the frozen liquid, which would naturally interfere seriously with the accuracy of the determinations. The latter defect might be overcome by a very long cooling period.

A platinum frigitor of the type IIb was then built. Here the time factor was considerably reduced by having two vanes as shown. The cover was sealed on by means of wax, and could be removed whenever necessary; later on it was found that the wax which was used to seal on the cover cracked at low temperatures, and this permitted the entry of water from the calorimeter vessel during a run. The cover was then sealed on by means of silver solder, and a small filling tube 1mm. in diameter sealed into the top. After filling the frigitor with liquid the filling tube was sealed by means of a drop of solder. After making a number of runs, the platinum developed cracks, and although they were sealed up as rapidly as they appeared, this was found to be a serious hindrance to the achievement of results. In the case of water , the entry of water from the calorimeter vessel into the frigitor had only a small effect, as distilled water was always used in the calorimeter, and any water that got in could easily be detected by weighing the frigitor before and after each run. In the case of other liquids this would have proved a serious handicap, as the heat of dilution would have introduced a serious error into the determinations. The cracking was probably due to the rapid and drastic temperature changes to which the frigitor was subjected, and was also assisted by the tendency of water to expand on freezing.

A frigitor of 0.5mm thickness sterling silver of the type shown in IIc was then constructed, and this proved highly successful. The greatest difficulty encountered was in sealing up the filling tube. This difficulty arose from the great thermal conductivity of silver. A layer of solder(soft) was placed around the filling tube, and the latter heated by means of one soldering iron, the entire frigitor cooled by means of a mixture of solid carbon dioxide and ether, and additional solder applied by means of a second iron. The purpose of cooling the remainder of the frigitor was to draw the molten solder into the neck of the filling tube, and giving it a chance to harden there. To test the complete closing of the tube, the frigitor was placed in a vacuum dessicator and kept under vacuum for five minutes, and weighed immediately after. If there was no loss in weight, the tube was considered sealed, although the frigitor was weighed before and after each run as a measure of precaution. As a further method of precaution, the filling tube was dipped into a solution of "Zapon" cement (a solution of nitrocellulose in amyl acetate) which dried to a clear transparent waterproof film.

The frigitor was first washed many times with distilled water, and then placed in a glass tube glass sealed to a vacuum pump and phosphorus pentoxide tubes, where it was kept for 12 hours under a vacuum of 0.01mm. of mercury. This insured the complete absence of water. It was then weighed, and filled by means of a wide glass tube drawn out to a fine capillary at the end., weighed again, sealed and again weighed. In the case of alcohol, where the presence of water from the atmosphere would have a deleterious effect upon the results, the filling operation was carried out in a glass case similar to a balance case. About an hour before the frigitor was to be filled, sevreral flat dishes containing phosphorus pentoxide were placed in the case to insure the removal of all moisture from the interior of the case. The filling tube, the frigitor and the measuring cylinder(for measuring the volume of the liquid) were also placed in the case at this time.

In order to cool the frigitor to any desired temperature, it was placed in a copper jacket. At first a copper jacket provided with a side tube was used; provision was also made for the placing of phosphorus pentoxide at the bottom to prevent moisture from condensing on the frigitor, but this type was found to be impracticable as one could not measure the temperatyre by placing a thermometer in the side tube. The next type tried was a steel tube into which the frigitor fitted snugly. It was planned to use mercury as a contact agent be-

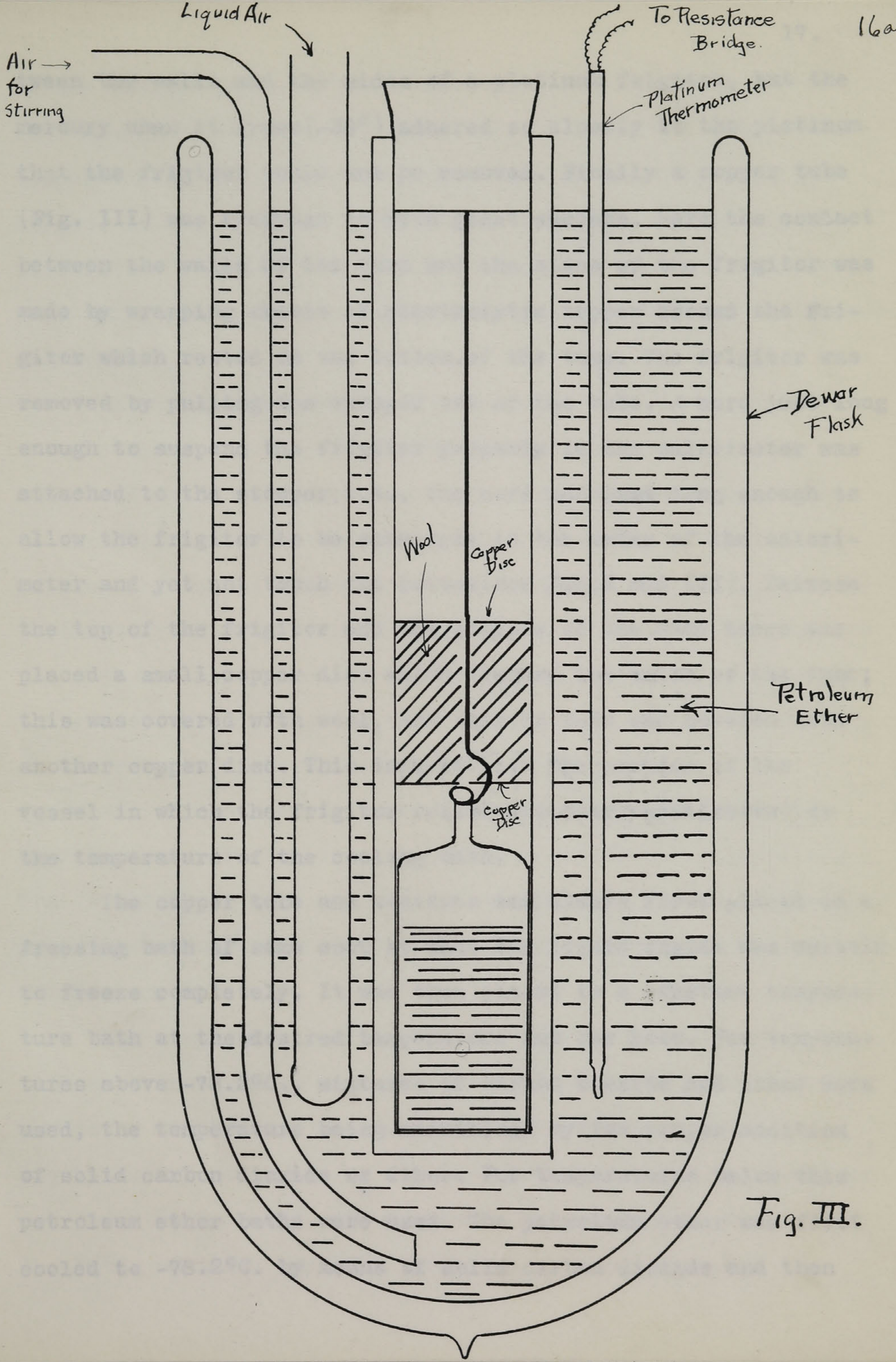
Liquid Air
To Resistance Bridge.
Air for Stirring
Platinum Thermometer
Dewar Flask
Wool
Copper Disc
Copper Disc
Petroleum Ether

Fig. III.

tween the walls and the sides of a platinum frigitor, but the mercury when it froze(-38^{o}) adhered so closely to the platinum that the frigitor could not be removed. Finally a copper tube (Fig. III) was resorted to with great success. Here the contact between the walls of the tube and the sides of the frigitor was made by wrapping sheets of electrolytic copper around the frigitor which rested on the bottom.of the tube. The frigitor was removed by pulling the stopper out of the tube. A cord just long enough to suspend the frigitor properly in the calorimeter was attached to the stopper;i.e., the cord was just long enough to allow the frigitor to be submerged in the water of the calorimeter and yet not touch the bottom(see Fig.I and III). Between the top of the frigitor and the stopper of the tube there was placed a small copper disc which touched the walls of the tube; this was covered with wool, and this in turn was covered with another copper disc. This insured that the portion of the vessel in which the frigitor rested was everywhere(above) at the temperature of the cooling bath.

The copper tube and contents was always first placed in a freezing bath of some sort so that the liquid inside was certain to freeze completely. It was then placed in a constant temperature bath at the desired temperature for one hour. For temperatures above -78.2^{o}C., mixtures of carbon dioxide and ether were used, the temperature being maintained by the proper addition of solid carbon dioxide or ether. For temperatures below this petroleum ether baths were used. The petroleum ether was first cooled to -78.2^{o}C. by means of solid carbon dioxide and then to the desired point by the addition of liquid air to a test-tube suspended in the ether.(See Fig.III). For the liquid air temperatures, the copper tube was immersed directly in liquid oxygen. In all of these baths it was possible to maintain the temperature constant within 0.1° during the time of immersion, this being continually checked by means of a platinum resistance thermometer.

An attempt was made to find some sort of a wax or cement which would not be acted upon by either ether or petroleum ether and which would not crack under the extreme temperatures to which it would be subjected. This would have permitted immersing the entire frigitor jacket in the cooling bath, but unfortunately this difficulty could not be overcome. For this reason a jacket more than double the length of the frigitor had to be used, and immersed almost to its upper edge. This method, as was remarked before, worked very well, however.

All of the temperatures of the cooling baths were measured by means of a calibrated platinum reistance thermometers The calibrations were made at the steam, ice, carbon dioxide and ether, and liquid air points, and the Callendar-Barnes formula applied.

The temperature changes in the calorimeter and water bath were measured by means of two calibrated Beckmann thermometers, which were read to 0.001° by means of a small reading lens. The calibrations for the inner and outer thermometers are given in Table II. The standard thermometer was used in the bath, as there was less danger of breakage there.

Table II.

Inner	Standard	Difference
5.200	5.397	0.197
5.020	5.220	0.200
4.790	4.991	0.201
4.600	4.800	0.200
4.372	4.569	0.197
4.190	4.384	0.194
3.997	4.191	0.194
3.795	3.990	0.195
3.608	3.799	0.191
3.399	3.586	0.187
3.189	3.373	0.184
3.016	3.199	0.183
2.820	3.008	0.188
2.578	2.761	0.183
2.379	2.562	0.183
2.211	2.397	0.186
2.041	2.224	0.183
1.776	1.857	0.181
1.584	1.763	0.179
1.426	1.604	0.178
1.229	1.403	0.174

U.S. Bureau of Standards Thermometer #23851(Standard).

Thermometer Reading	Correction
0.0	0.000
0.5	-0.002
1.0	-0.001
1.5	-0.002
2.0	-0.004
2.5	-0.005
3.0	-0.005
3.5	-0.001
4.0	-0.002
4.5	-0.002
5.0	-0.004

For this thermometer the setting factor was 0.9985 at 15°C

In making an actual run, the copper tube containing the frigitor was placed in a freezing bath for at least an hour which insured the complete solidification of the liquid contained in the frigitor. For the higher temperatures a freezing bath of ice and salt was used, while for the lower ones mixtures of solid carbon dioxide and just enough ether to make a paste were used. The copper tube was then placed in a constant temperature bath which was kept at the desired temperature for at least an hour. Tests were made leaving the tube in the constant temperature bath for various lengths of time, and it was found that an hour was sufficiently long for all practical purposes. Table III. shows the results of this series of tests.

Table III.

Temperature maintained throughout: -78.2°

Time in bath	Heat Capacity of Water per gm.
0.75 hour	129.114
1.25	129.396
1.50	129.276
1.67	129.194

From these values it can be seen that the time of maintaining the temperature constant has very little effect on the results obtained.

During the last fifteen minutes of the cooling, the cold water reservoir was filled with cracked ice, the water in the hot water reservoir heated, the calorimeter vessel filled with a definite weight of distilled water at about 19.6°C. After placing the calorimeter vessel in the air jacket, the flange was greased and the cover bolted on, care being taken to tighten opposite bolts at the same time and tightening all bolts uniformly. The water bath was then filled with water and the temperatures of the inner and outer vessels balanced and kept balanced until the end of the cooling period. When the cooling period was complete, the frigitor was removed from the copper tube and placed in the calorimeter vessel. This transfer required three seconds by actual timing, so that practically no heat was lost; any water vapor that condensed on the outside would, of course, again give up its heat when the frigitor was placed in the calorimeter. Meanwhile the temperature of the outer bath was lowered at the same rate as that of the inner was changing, which prevented radiation losses. When the lowest temperature was reached and maintained at least for five minutes, the final reading of the thermometers was taken and the run finished. This last past required about twenty minutes all told. The frigitor was then removed from the calorimeter, carefully dried and weighed(to guard against leaks) and again put to cooling. The long cooling periods required made it impossible to make more than three runs per full twelve hour day.

Ordinary distilled water was used for filling the frigitor preliminary to making the specific heat measurements on water and ice. In the case of methyl alcohol some highly purified anhydrous methyl alcohol was obtained from the Standard Chemical Co. It gave no test for formaldehyde or acetone and had a sharp freezing point of -97°C.

In order to determine the heat equivalent of the silver frigitor, a sheet of sterling silver was rolled into a cylinder, and the heat capacity determined in exactly the same way as that of the liquids in the frigitor were determined. The two temperatures at which these runs were made were at the liquid oxygen and carbon dioxide and ether points, and the intermediate values calculated from them. The same thing was done in the case of the solder which was used for soldering shut the filling tube.

In making the calculations of the heat changes, the temperatures were corrected to bring the readings to those of the standard thermometer, and then the standard thermometer corrections were apllied. The total heat change in the calorimeter vessel, water, and thermometer was then calculated. From this was subtracted the heat taken up by the silver frigitor, and this gave the heat taken up by the liquid in the frigitor. On dividing this value by the weight of the liquid used, the heat capacity per gram of the liquid was obtained. However, since all of the runs were not made from the same initial temperature in the calorimeter vessel, a correction had to be applied, in order to bring all of the results to the same standard temperature. The standard temperature chosen was 16.5 $^{\circ}$C., and by taking the specific heat over the range as being constant, the difference between the final temperature and 16.5° was multiplied by the specific heat, and this value was added or subtracted from the heat capacity of the liquid, and all of the runs were thus put on a comparable basis. A detailed calculation is given on the next page.

SAMPLE CALCULATIONS.

Temperatures	Initial	4.730	Final	1.232
Correct'n. from Calibration		0.200		0.175
Reading referred to Standard		4.930		1.408
Correct'n. for Standard		-.004		-.002
Corrected Temperatures		4.926		1.406
		1.406		
Temperature Change in Cal.		3.520		

log. 3.520	0.54654
log. 0.9985	$\bar{1}$.99935
log real temp. chge.	0.54589
log. cal. factor#	2.91726
	3.46315

This refers to the heat equivalent of the calorimeter vessel and water in it per degree. This was a constant for all runs.)

Antilog 3.46315	2905.00	calories
Thermometer lost	7.04	"
Total Heat lost by cal.	2912.04	"

log specific heat of silver(0.0521)	$\bar{2}$.71684
log weight silver (36.2762)	1.55962
	0.27646

Heat equivalent of the silver in frigitor per degree 1.89 cal.

Heat equivalent of solder per gm. 0.0363

log. 0.0363	$\bar{2}$.55991
log. wt. solder used	$\bar{1}$.99149
	$\bar{2}$.55140

Heat equivalent of silver used	1.8900	cal.
" " " solder used	0.0356	"
" " " frigitor	1.9256	"

log. heat equiv. per degree	0.28457
" temp. range (199.106)	2.29908
	2.58365

frigitor gained	383.40	calories
total lost	2912.04	"
water gained	2528.64	"

log. 2528.64	3.40289
log.wt. water used(16.0237)	1.20449
	2.19840

Antilog.2.19840	157.907	cal. gained per degree
Correction to 16.5^0	.094	"
	158.001	" heat capacity per gram.

The results obtained in this way have been tabulated as follows:

Table IV.

Temperature	Heat Capacity per Gram
-3.18	97.5
28.6	109.37
41.8	115.18
58.2	122.06
78.2	129.86
110.0	141.25
138.7	149.46
182.7	158.16

Each value in the above table is the mean of two or three determinations which, in every case, checked within 0.20 calories. These value are graphically represented in Fig. IV. Any point on this curve represents the amount of heat required to heat up one gram of water(ice) from that particular temperature to 16.5°C.

It is very simple, of course, to obtainethe average specific heat of ice over any desired temperature range by subtracting the extreme ordinates from one another and dividing by the temperature difference, but, on account of the variation in the curvature, this value for the specific heat is not the true one for the mean temperature. It is possible to obtain an equation which approximately represents the heat capacity H as a function of the temperature T, and $\left(\frac{dH}{dT}\right)_T$ will give the true specific heat at the temperature T. Since, however, the equation: $H = f(T)$, could only be obtained approximately for the whole range, it was decided to employ a graphic method for obtaining $\frac{dH}{dT}$. The curve as represented by Fig. IV.

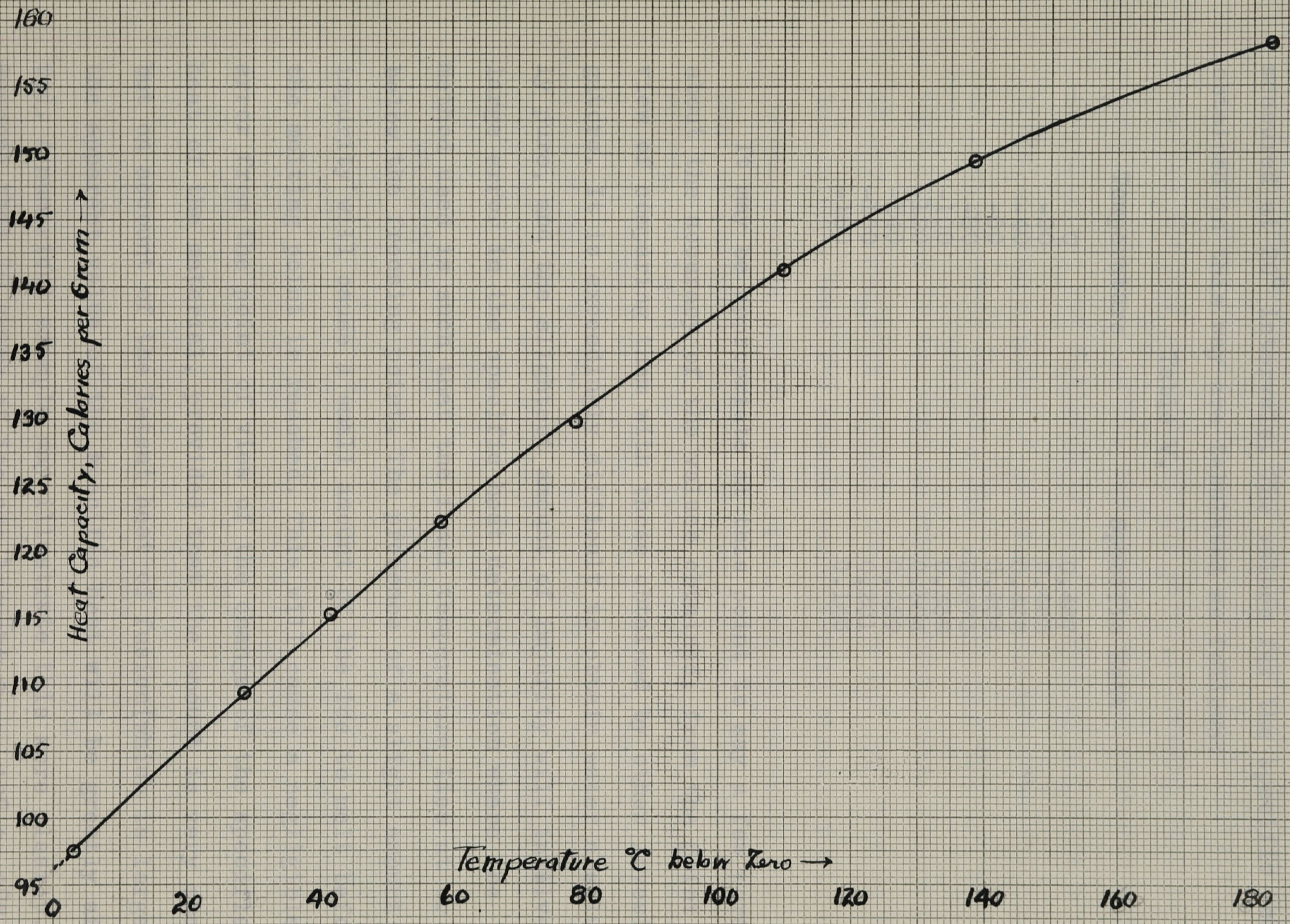
Heat Capacity, Calories per Gram →
160
155
150
145
140
135
130
125
120
115
110
105
100
95
0
20
40
60
80
100
120
140
160
180
Temperature °C below Zero →

Fig. IV.

was plotted on a large scale, and the gradient of the tangent measured at 20° intervals. The values for the specific heats obtained in this way are tabulated as follows:

Table V.

Temperature	Specific Heat
0	0.487
-20	0.463
-40	0.435
-60	0.404
-80	0.373
-100	0.339
-120	0.304
-140	0.259
-160	0.201
-180	0.146

It may be appropriate at this point to say a few words about the accuracy of the values obtained, from the point of view of comparing them with those obtained by other investigators. It is exceedingly difficult to obtain water absolutely pure, and the slightest amount of impurity will involve a large error in the specific heat determination where the method used is such that the final temperature lies at or below the freezing point. The presence of a slight amount of impurity will cause a small amount of the ice to melt before the melting point is reached. This will cause a negligible error from the point of view of the change of the specific heat of the material, provided that the amount is very small, but on account of the latent heat of fusion(which is large), the apparent value of the specific heat will be greatly affected. A numerical example may illustrate this more clearly. Suppose that 10 grams of ice are brought from -10° to 0°C., and that, in consequence of the presence of a slight amount of dissolved matter, 0.1 gram melts. Then the heat required to cause this temperature change will be 47.5 calories. Correcting for the presence of the water, assuming that it begins to appear at -5°C., the amount of heat required will be 48 calories; but 0.1 gram of ice on melting requires 8 calories, giving a value of 56 calories as the measured quantity of heat required to raise the temperature from -10° to 0°C., thus leading to too high an experimental value. This source of error disappears entirely in the method employed in this laboratory. Here the method consisted in warming up to a temperature above the melting point, and consequently the latent heat of fusion of <u>all</u> of the ice entered into each determination, and since it was a constant quantity, was eliminated.

The reason for laying stress on this source of error will be apparent when the writer's values are compared with those of Nernst and others at the higher temperatures.

Table VI.

Temperature	Calc. (Nernst)	Observed		
		Nernst	This Lab.	Dickinson & Osborne 14)
0	0.622	------	0.487	0.5057
-10	0.532	0.533	-----	0.4871
-20	0.475	0.478	0.463	0.4684
-30	0.440	0.451	-----	0.4498
-40	-----	-----	0.435	0.4312
-50	0.404	0.410	-----	
-60	0.000	-----	0.404	
-70	0.378	0.374	-----	
-80	0.349	0.367	0.373	
-100	-----	-----	0.339	
-110	0.302	0.309	-----	
-120	-----	-----	0.304	

-140	0.260	0.277	0.259
-160	-----	-----	0.201
-170	0.217	0.214	-----
-180	0.201	0.199	0.146

The comparison is brought out best of all by the graphs shown in Fig. V. Curve I represents the values obtained by Nernst, curve II those obtained in this laboratory, while the red points indicate the values obtained by Dickinson and Osborne. It will be seen that Nernst's higher temperature values are probably due to errors in his experimental method. Dickinson and Osborne who lay great stress on the purification, have obtained values within 2% of the values obtained in this research, but these investigators only covered the temperature range to -40°C.

The value for the specific heat of ice is of practical importance, and the values now quoted in the handbooks of various sorts vary from 0.58 to 0.52 at 0°C. From the results obtained, it seems probably that the true value is 0.49, which, by the by, is in close agreement with that obtained by Dickinson and Osborne.

From a theoretical point of view, it will be seen that if the present values are correct, the close agreement of the calculated and observed values of Nernst is due to chance, and the hypotheses upon which the calculations were based must be wrong. The first assumption made was that ice is composed of double molecules, $(H_2O)_2$; this, apart from any specific heat considerations, is not in agreement with the usual views15), which are, that, if any molecular complexity at all can be

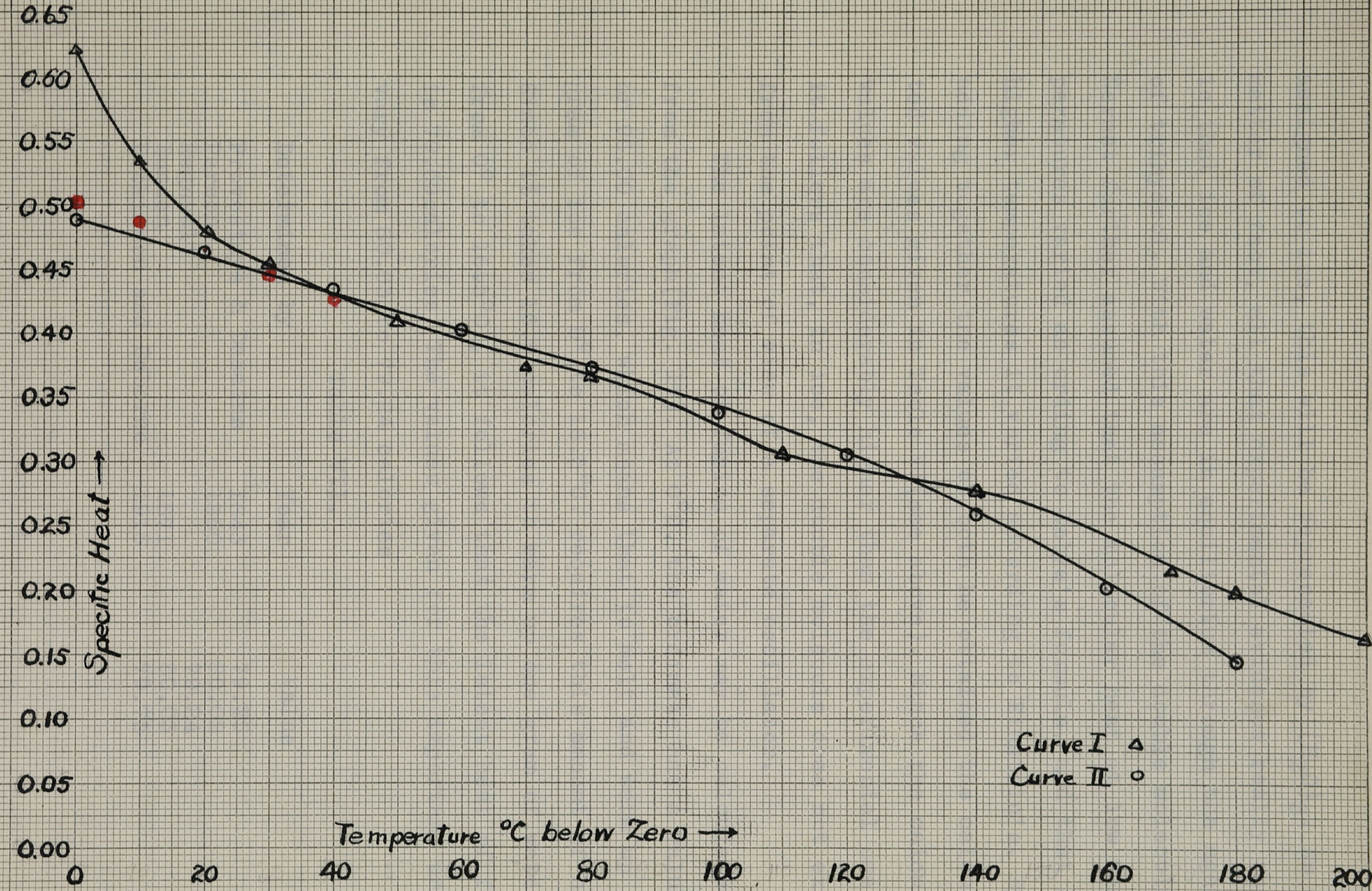
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Specific Heat →
0
20
40
60
80
100
120
140
160
180
200
Temperature °C below Zero →
Curve I ∆
Curve II ○

Figure V.

assigned to ice, this will be represented by $(H_2O)_3$. As a matter of fact, all that experimental evidence really shows is that ice and water are in equilibrium through the agency of trihydrol. With this assumption of the double molecule, Nernst further assumed that the molecular heat at low temperatures varied according to Debye's formula, and that at higher temperatures it varied according to Einstein's. By adding together the values of both he obtained the calculated values given in Table VI(see above). Since the calculated values are considerably higher than the experimental ones, it follows that, in ice, the double molecule does not exist from the point of view of a separate oscillator.

The latent heat of fusion of water may be calculated from the graph(Fig. IV). At 0°C. the ordinate has a value of 96.00 calories, which means that to melt and warm up one gram of ice from 0° to 16.5°C. requires this amount of heat. Since it takes 16.5 calories to warm up one gram of water from 0° to 16.5°C., it follows that the latent heat of fusion is 79.50calories. The values given for this important unti vary from 80.03 to 79.24 calories

Table VII.

Determined by	Year	Value
Provostaye & Desains	1843	79.25
Person	1850	80.02
Regnault		79.24
Bunsen	1871	80.03
Dickinson and Osborne	1915	79.75

The experimental method, as developed, lends itself admirably to the determination of latent heats of fusion of substances having very low melting points, and whose latent heats of fusion have not been measured. Methyl alcohol, melting at -97°C. was examined. The following determinations of the heat capacity were made up to 16.5°C., and calculated in the same manner as those of water.

Table VIII.

	Temperature	Heat Capacity per Gram
1.	-78.2	52.52
2.	-90.0	58.88
3.	-104.0	87.66
4.	-182.7	120.82

The determinations for #3 were made 7° below the freezing point of the alcohol, insuring that it was perfectly solidified. Before placing it in the constant temperature bath, the alcohol was kept in liquid air for an hour. The above values are plotted in graphic form in Fig. VI., and it will be seen that the latent heat of fusion can be deduced directly from the curve. The value was found to be 22.00 calories, which is probably accurate to within 1% of the true value. The average specific heat of the solid alcohol from -182.7° to -97°C., is 0.448 as compared to 0.250, the average specific heat of ice over the same temperature range. No generalization can be made or hypothesis profitably suggested until a large number of compounds, preferably organic ones with low melting points, have had their specific heats in the solid condition investigated at low temperatures. This work will be of considerable importance, in view of recent

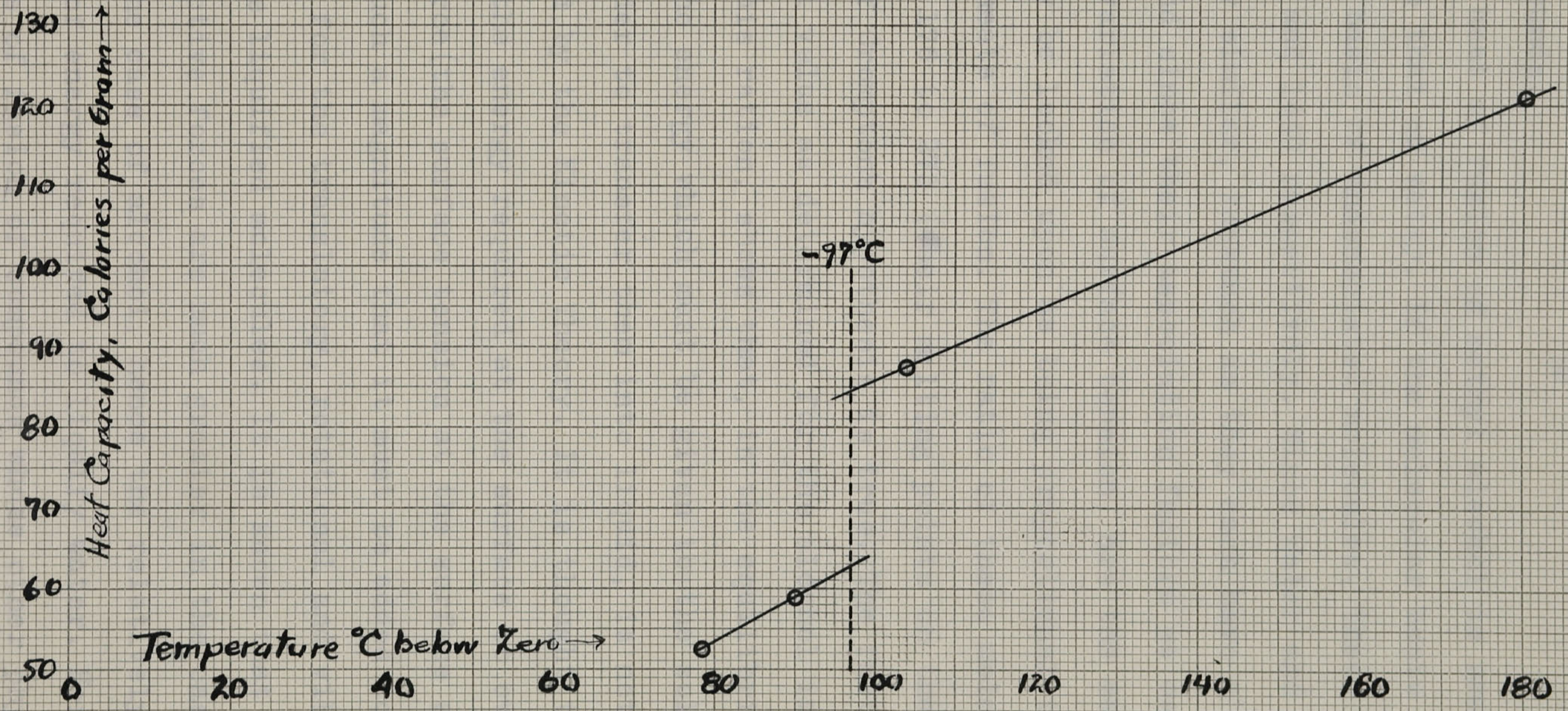
130
120
110
100
90
80
70
60
50
Heat Capacity, Calories per Gram →
0
20
40
60
80
100
120
140
160
180
Temperature °C below Zero →
-97°C

Fig. VI.

developments in the X'ray analysis of the crystal structure of organic compounds.

The latent heat of fusion of methyl alcohol is small when compared to that of water. If the molecular heats are compared on the basis of unassociated molecules, these are found to be 704 and 1440 respectively. Since water and methyl alcohol are very similar, inasmuch as they each have a hydroxyl group, and since their association factors as calculated from the variation of surface tension, are the same, these values may be looked upon as being proportional to the true molecular heats of fusion. The ratio of these molecular heats should be 176 to 273 (their melting points on the absolute scale) if Crompton's hypothesis is true. The fact that the experimental value as determined for the alcohol is much too small for this ration, shows that, in the equilibrium liquid-solid, the energy which must be given to the solid molecules in order to transfer them into liquid, is not solely that demanded by the Kinetic Theory. It is thought that, added to this, the energy required at the surface to overcome the field of force (the surface tension at the surface solid-liquid) is of such a magnitude that it must be added to the energy required for the translatory, rotational and vibratory movements of the liquified molecules. It is known that the molecular attractive forces are much greater in the case of water than in the case of alcohol, hence the relatively greater amount of energy required to liquify water. Here again, the heats of fusion of compounds whose other physical properties are well known should be determined, in order to test the truth of this hypothesis.

An apparatus by means of which heat measurements can be accurately determined, has been described in detail. A method for determining the specific heats of substances at low temperatures has been devised. The latent heats of fusion of substances, particularly those with very low melting points, can be determined by the same method. Methyl alcohol and water have been examined, and in the case of water, the values compared with those obtained by other investigators. The theoretical significance of specific heats has been discussed, and the probable source of error of previous determinations by Nernst, has been pointed out. The relation between the latent heat of fusion and molecular forces of attraction has been indicated.

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