

A REDETERMINATION OF THE SPECIFIC HEAT OF WATER

BETWEEN 10°C and 20°C .

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"A consideration of the greatest importance is the argument of hope; I mean that drawn from the errors of past time and of the ways hitherto trodden. . . . For now, when your misfortunes are owing, not to the force of circumstances, but to your own errors, you may hope that by dismissing or correcting these errors, a great change may be made for the better.

It will be of great use, therefore, to set forth what these errors are: for as many impediments as there have been in times past from this cause, so many arguments are there of hope for the time to come. And although they have been touched before, I think fit here also, in plain and simple words to represent them."

NOVUM ORGANUM, XCIV.

A Redetermination of the Specific Heat of Water between
10°C. and 20°C.

Introduction.

The first experiment which showed a quantitative relation between work and heat was described by Count Rumford in 1798. Since this time a large number of determinations of the "Mechanical Equivalent of Heat" have been made. Those made before the time of Joule need not be mentioned here, as in none of them were results of any reliability obtained. The accurate evaluation of the Equivalent dates from the researches of Joule, whose methods of experiment have been used in all the later work on the subject. Joule's first experiments were a result of his discovery of the Law of Electrical Heating and were made by the electrical heating of water; but the large differences between the results given by this method and those obtained by the more direct method of frictional heating, led him to believe that the absolute values of the Electrical Standards were not sufficiently well known. He therefore abandoned the electrical method and obtained his final results by frictional heating.

The heating was produced by rotating a paddle at a constant speed in a calorimeter of water. The calorimeter was prevented from turning by strings passing round it and supporting weights over pulleys. This method was adapted from that used by Hirn.

It provides a direct measurement of the amount of work expended in the calorimeter. The rise of temperature of the water was measured on carefully calibrated mercury thermometers. As the paddles were turned by hand, the rate of rise of temperature was small, but corrections for heat losses were carefully applied, and the results were supposed to be very near the truth.

In 1877-78, immediately after the completion of Joule's work, an experiment on similar lines was made by Professor Rowland. Joule's paddle system was modified so as to ensure more perfect mixing of the water in the calorimeter, and an engine was used for driving. The rapid rise of temperature thus produced made the heat measurements a matter of much less difficulty. The whole apparatus was on a much larger scale than Joule's, and a higher degree of accuracy was aimed at. Hirn's method of measuring the work done was again adopted, but the couple system rendered stable by using a wire suspension for the calorimeter. The mercury thermometers used in the heat measurement were carefully calibrated and corrected to the air scale. Rowland's was the first experiment to shew the existence of a minimum in the Specific Heat of Water at about 30°C .

Since the time of Rowland only two experiments by the water-friction method have been made. One by Miculescu in 1892 gave the Equivalent in terms of the calorie at 11.5°C ; the other by Reynolds and Moorby in 1897 expressed the result in terms of the mean calorie from 0° to 100°C . The same importance can

hardly be attached to Miculescu's results as to those of the other observers mentioned, as no great degree of accuracy seems to have been aimed at in his experiments. The determinations made by Reynolds and Moorby were carried out with the greatest care and on an enormous scale, but their values of the Equivalent are unfortunately not comparable with those obtained in experiments extending over smaller ranges of temperature.

Since the removal of the uncertainties in the absolute values of the Electrical Standards, much accurate work has been done by the method of Electrical Heating. The experiments of Griffiths in 1893, Schuster and Gannon in 1895, Callendar and Barnes in 1902, and Messrs. Bousfield in 1911 may be taken as examples.

Griffiths measured his work in terms of the resistance of the heating coil and the fall of potential in it. Losses of heat from the calorimeter were reduced as far as possible by enclosing it in an evacuated chamber kept at constant temperature. All the errors that were not thus eliminated were carefully determined. The results he obtained were considerably higher than those given by Rowland for the same temperature.

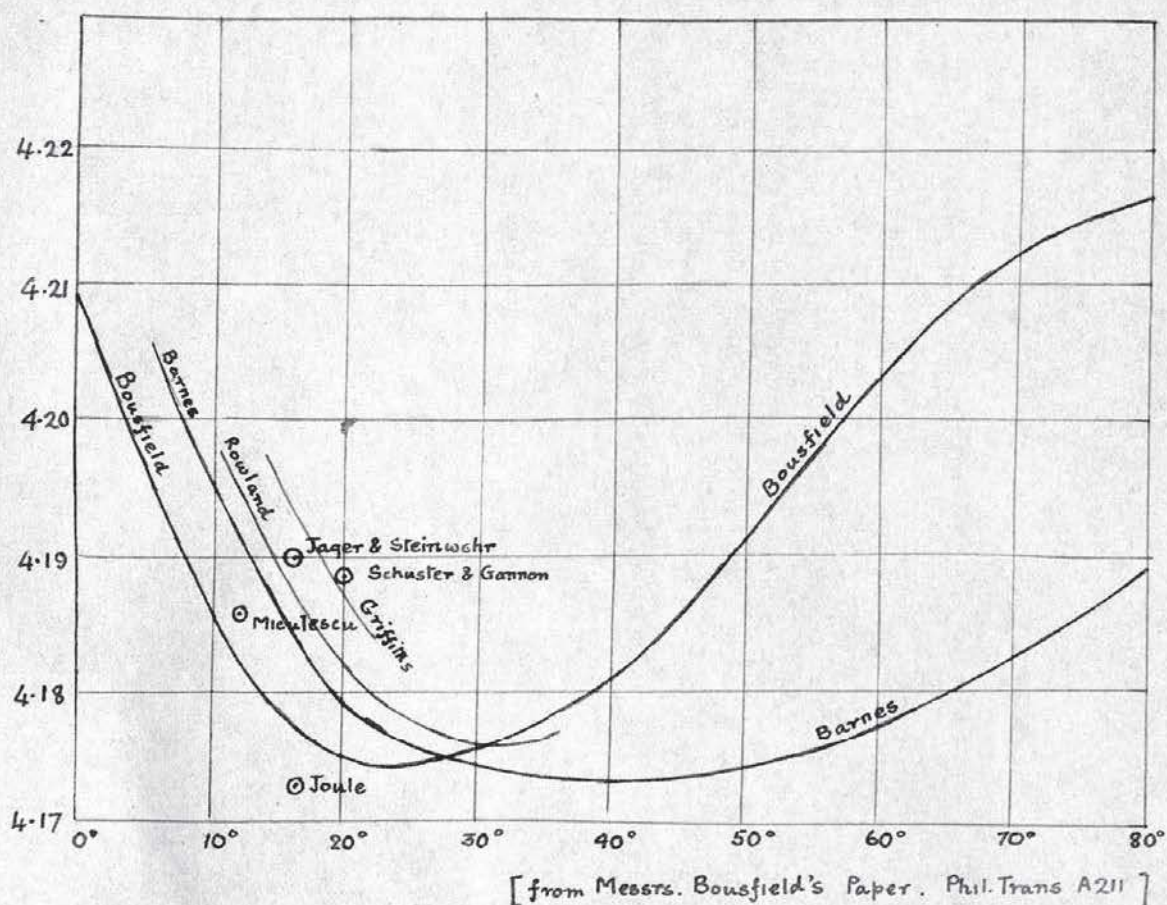
A similar experiment was carried out by Schuster and Gannon, who, however, measured the work done in terms of the E.M.F. applied to the heating coil and the current produced in it. Time measurements were avoided by the use of a silver voltameter in the current measurement. The results obtained

were close to those given by Griffiths.

A new method was adopted by Callendar and Barnes. A platinum strip resistance passed along a narrow glass tube through which a constant flow of water was maintained. The work was measured in terms of the applied E.M.F. and the current, the latter being determined by measuring the fall of potential through a standard resistance. The calorimeter tube was enclosed in a vacuum jacket and a differential method employed for the elimination of heat losses. Although the Temperature - Specific Heat curve for water obtained by these experiments differs considerably from those given by other observers, it has been generally accepted.

In 1911, however, Messrs. Bousfield described a series of experiments in which the "Thermoid" Effect, discovered by them, was corrected for. Their resistance coils were of mercury enclosed in spiral glass tubes, one end of which was continued vertically and graduated. The height of the mercury in the graduated tube was calibrated against the resistance of the mercury in the coil. Readings of this height thus gave the actual resistance in use during the experiment. All errors due to superheating and to strain in the heating coils were thus avoided. They used as their calorimeter a Dewar Vessel enclosed in a large water bath. The bath was heated at the same rate as the water in the calorimeter. As a result, perhaps, of their special precautions, they obtained a lower value for the Equivalent of the 15^o Calorie than ~~any~~ other observer since Joule. Their Specific Heat curve resembles those of Lüdin and

Bartoli and Stracciati, much more than that of Barnes.



The absolute values given for the calorie are:-

	Joule	4.173×10^7 ergs/cal	at 16.5°C
Mechanical	Rowland	4.187	" " 15°C
Methods.	Miculescu	4.185	" " 15°C
	Reynolds and Moorby.	4.183	" " 15°C
	Griffiths	4.193	" " 15°C
Electrical	Schuster and Gannon.	4.193	" " 15°C
Methods.	Callendar and Barnes.	4.184	" " 15°C
	Bousfield.	4.179	" " 15°C

It will be seen that considerable differences amounting to as much as 0.5% at 15°C . still remain between the results of different experiments. A redetermination of the Equivalent

of the calorie over some convenient range such as 10°C to 20°C cannot be considered superfluous.

Method of Experiment.

If, in an experiment of the type made by Joule and Rowland, a constant rate of working can be maintained, the greatest errors arise in the heat measurements. The necessarily solid construction of the calorimeter makes its water equivalent both large and uncertain, while the slow rate of heating and the metal connections of the paddle shaft make the losses by radiation and conduction a most important source of error. In our experiments a differential method, worked out by Professor Poynting, will be used to eliminate uncertainties of this kind. The method consists essentially in using two different quantities of water in the calorimeter, and adjusting the rate of working so that the rate of rise of temperature is the same in both cases.

Then if J = the mechanical equivalent of the calorie,
 W_1 & W_2 = the quantities of water heated in the two cases.

C = the water equivalent of the calorimeter,

$\frac{d\theta}{dt}$ = the rate of rise of temperature,

$\frac{dE_1}{dt}$ & $\frac{dE_2}{dt}$ = the rates of working in the two cases,

$\frac{dH_1}{dt}$ & $\frac{dH_2}{dt}$ = the rates of loss of heat in the two cases
 by radiation and conduction,

we have

$$J(W_1 + C) \frac{d\theta}{dt} + J \frac{dH_1}{dt} = \frac{dE_1}{dt} \dots \dots \dots (1)$$

$$J(W_2 + C) \frac{d\theta}{dt} + J \frac{dH_2}{dt} = \frac{dE_2}{dt} \dots \dots \dots (2)$$

If the distribution of heat in the calorimeter in the two cases is the same, the rates of loss of heat will be the same. The violent stirring and circulation of the water will cause this condition to be very nearly fulfilled so long as the apparatus is run for some time before readings are taken.

Then from the above

$$J(W_1 - W_2) \frac{d\theta}{dt} = \frac{dE_1}{dt} - \frac{dE_2}{dt} \dots \dots \dots (3)$$

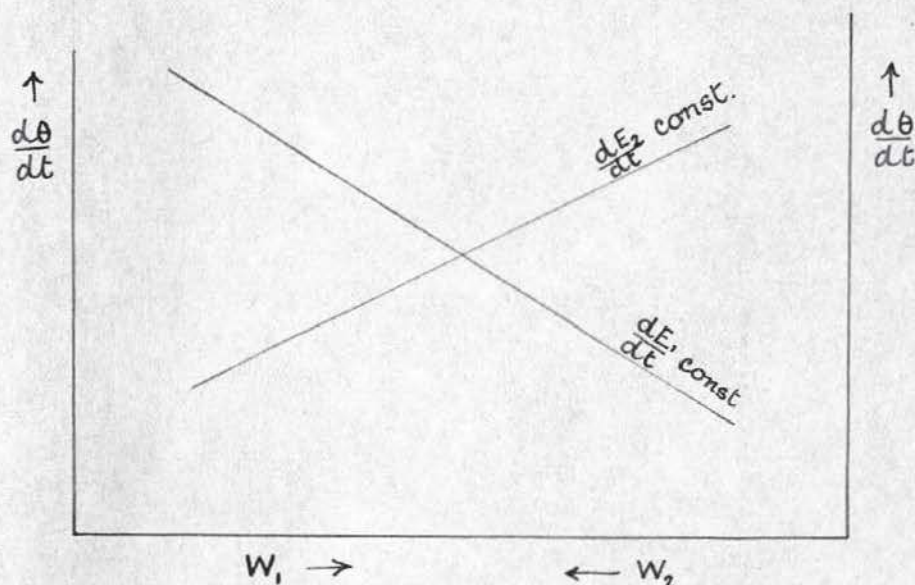
It is impossible to obtain exactly the same rate of rise of temperature in two different experiments. The quantities in equation (3) are therefore obtained by interpolation between the results of a number of experiments. The method used is as follows.

(1) The rate of energy supply is kept constant and a series of experiments made with different quantities of water in the calorimeter.

(2) The series is repeated, but with a different rate of working.

In each series the rate of rise of temperature is then plotted against the quantity of water in the calorimeter. In the second series the quantities of water are plotted backwards so that the point of intersection of the two curves is clear.

The method is shown in the diagram.



As the heat losses in the experiments are not large and are almost constant the two curves will be sensibly straight and their intersection point will be certain. Experiments made with the two quantities of water represented by the intersection point would give the quantities required in equations (1) and (2). The values of W_1 , W_2 and $\frac{d\theta}{dt}$ in equation (3) can therefore be taken from this point on the graph.

In practice it is found impossible to keep the rate of working quite constant through a series of experiments. Actually the couple on the calorimeter is kept constant, and as the speed of the motor is very little altered by changes in the quantity of water in the calorimeter $\frac{d\theta}{dt}$ can be corrected by interpolation for any small variations in $\frac{dE}{dt}$.

The error thus introduced is very small; for with the notation used before, if

G = the couple on the calorimeter,

ω = the angular velocity of the paddle,

In all the experiments $G\omega$ should be constant and

$$J(W + c)\{\dot{\theta} + \cancel{\Delta\dot{\theta}}\} + J\dot{H} = G\omega$$

In the actual experiments

$$J(W + c)(\dot{\theta} + \Delta\dot{\theta}) + J\dot{H}' = G(\omega + \Delta\omega)$$

Subtracting

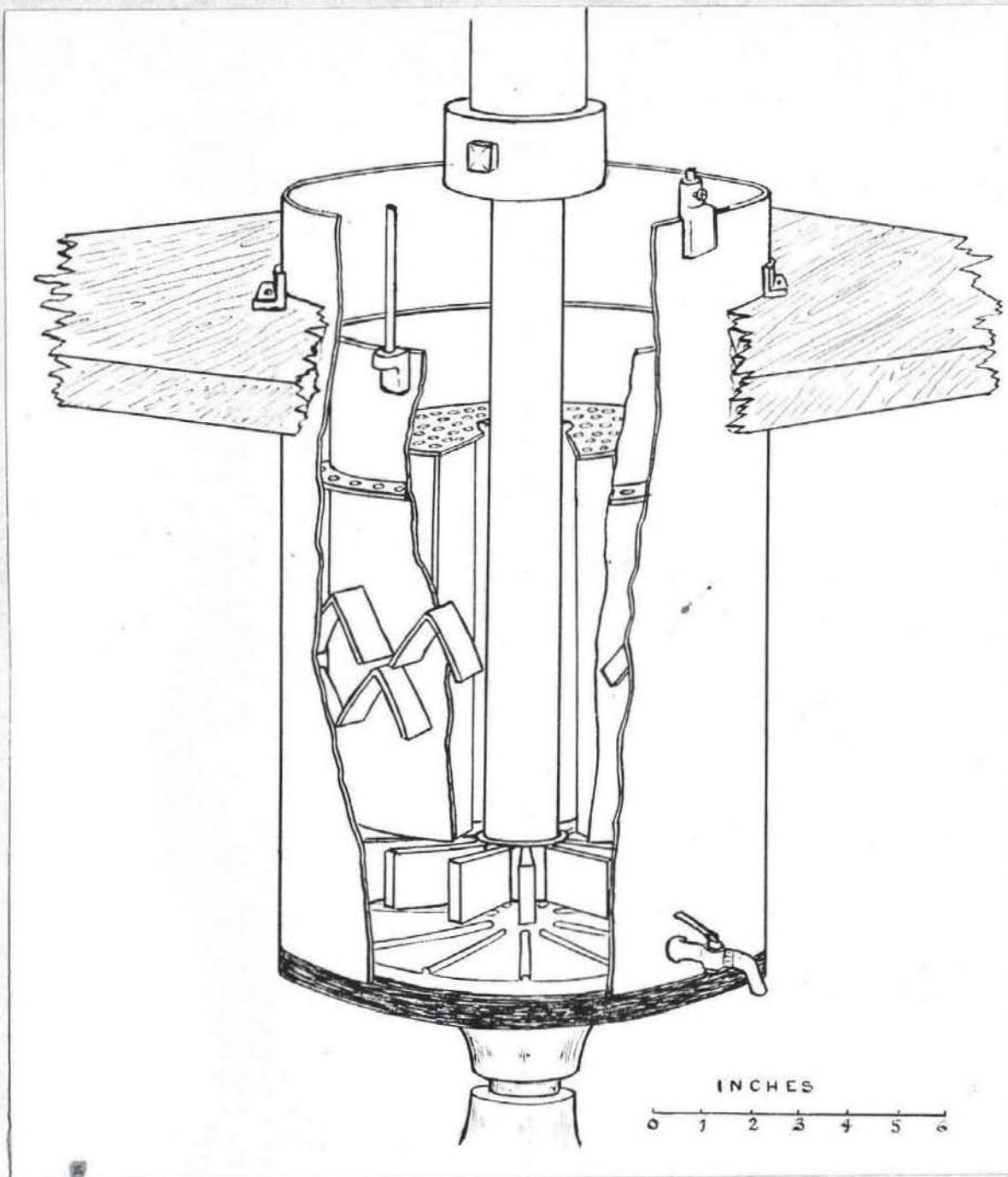
$$J(W + c)\Delta\dot{\theta} = G\Delta\omega - J(\dot{H}' - \dot{H})$$

Now, as the mean temperature of the water is 15 C, \dot{H}' and \dot{H} are very small and nearly equal.

$$\therefore J(W + c)\Delta\dot{\theta} = G\Delta\omega \quad \text{very nearly.}$$

Construction of the Calorimeter.

The construction of the apparatus for the experiment presents considerable difficulty. If the heat losses are to be perfectly eliminated the circulation of the water in the calorimeter must be the same whatever quantity the calorimeter may contain. To achieve this result a calorimeter of somewhat novel construction was designed by Professor Poynting. The construction of the calorimeter is shewn in the diagram.



It consisted of a brass cylinder 10" diameter and 15" high with a thin cast brass base. Under the conditions of the experiment it held 10 - 14 litres of water. Inside the calorimeter was a second cylinder 8" diameter and $9\frac{1}{2}$ " high. One paddle 7" diameter was used, and was placed between the bottom of the inner wall and the bottom of the calorimeter. It had twelve straight vanes $\frac{1}{4}$ " deep and there were twelve corresponding ridges $\frac{1}{2}$ " high on the bottom of the calorimeter. Rows of inverted V-shaped baffles were placed between the two walls

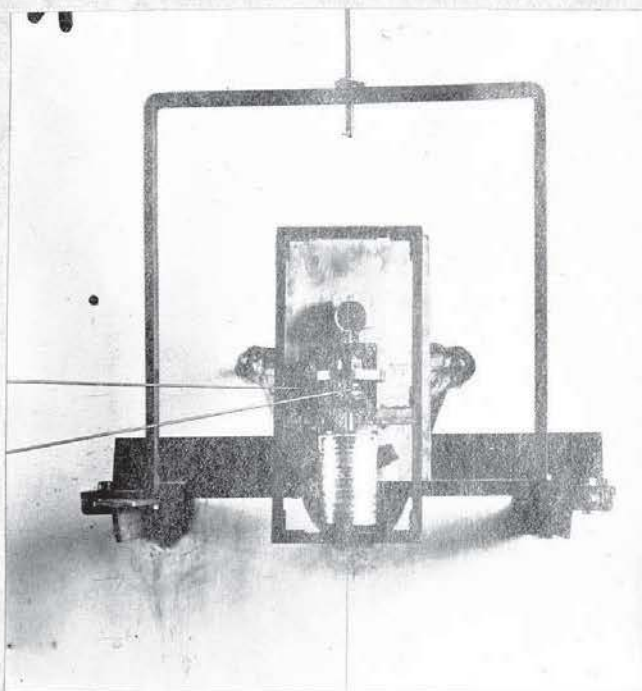
of the calorimeter. There were six vertical vanes inside the inner wall. The paddle shaft passed freely through a hole in the lid, so that no work was done against solid friction. The calorimeter was fixed at the bottom to a sheet of vulcanised fibre, and this was screwed to a casting resting in a double-ring ball bearing. The paddle shaft was coupled direct to a 4 Horse Power 220 Volt motor, running in bearings at about 1000 revs. per minutes. The calorimeter lid was removable and a tap was provided so that the water could be readily changed.

When the paddle turned the water was driven out and up between the walls, and fell back to the paddle inside the inner wall. The vertical vanes there were to prevent the water from being merely driven round inside the inner wall. It was intended to measure the couple on the calorimeter by taking strings from two projecting arms round torsion heads on stretched wires.

Small Apparatus.

Before using this apparatus a number of trials were made with small models holding 200 to 400 c.c. of water. These calorimeters were fixed in a wooden frame, stretched between two steel wires as in the apparatus of Crémieu and Rispaill. At first the paddle was driven by a small 20 Volt motor supported behind the frame and coupled direct to the paddle shaft. The work done was measured as in Rowland's experiment. It was soon found that the driving was very unsatisfactory and that to get the rate of working at all steady a motor with a considerable reserve of power would have to be used. The

arrangement shown in the photograph was then adopted.

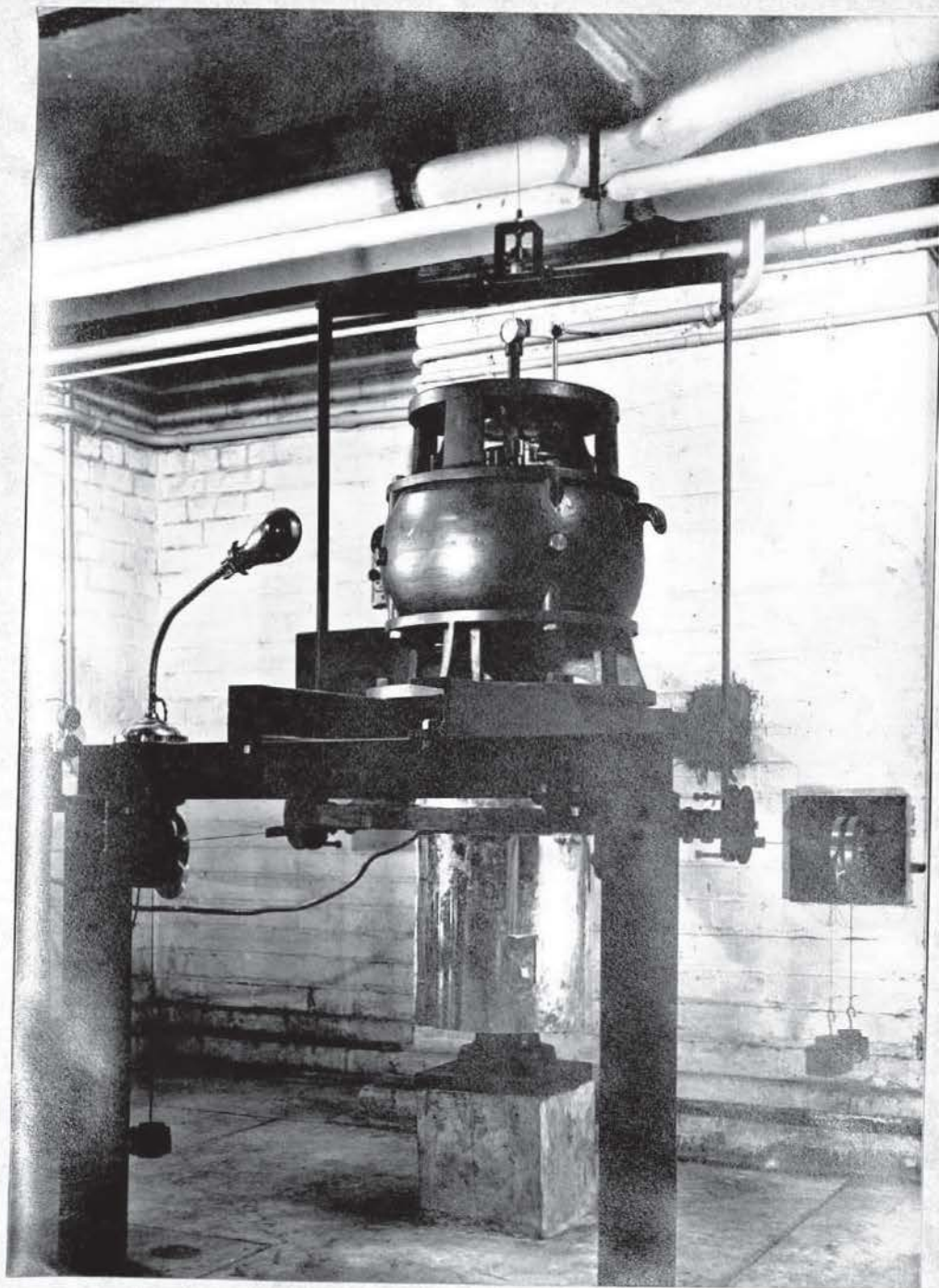


A motor giving about $\frac{1}{4}$ horse power was used. In order to avoid increasing the size of the frame and to obtain a greater range of speed, a belt drive was adopted with a two-speed pulley on the motor. To prevent irregularities due to slipping of the belt a heavy flywheel was mounted on the paddle shaft. With this apparatus the speed of revolution of the paddle could be made as great as 4000 revs./minute. Temperatures were read on a mercury thermometer passed through a tube in the side of the calorimeter. At the higher speeds the rate of rise of temperature was over $1^{\circ}\text{C}/\text{min.}$, but the calorimeter was very unsteady owing to the choking of the water due to sideway oscillations of the calorimeter, and perhaps also to air being sucked down into the paddle. With speeds between 600 and

2,000 revolutions/minute some results were obtained, but the oscillations of the apparatus were still large, and an accuracy of 3% or 4% was the most that could be obtained. These results were sufficiently good, however, to lead us to expect that with certain modifications suggested by the trials, the large calorimeter could be made steady enough to give accurate results.

The Large Apparatus.

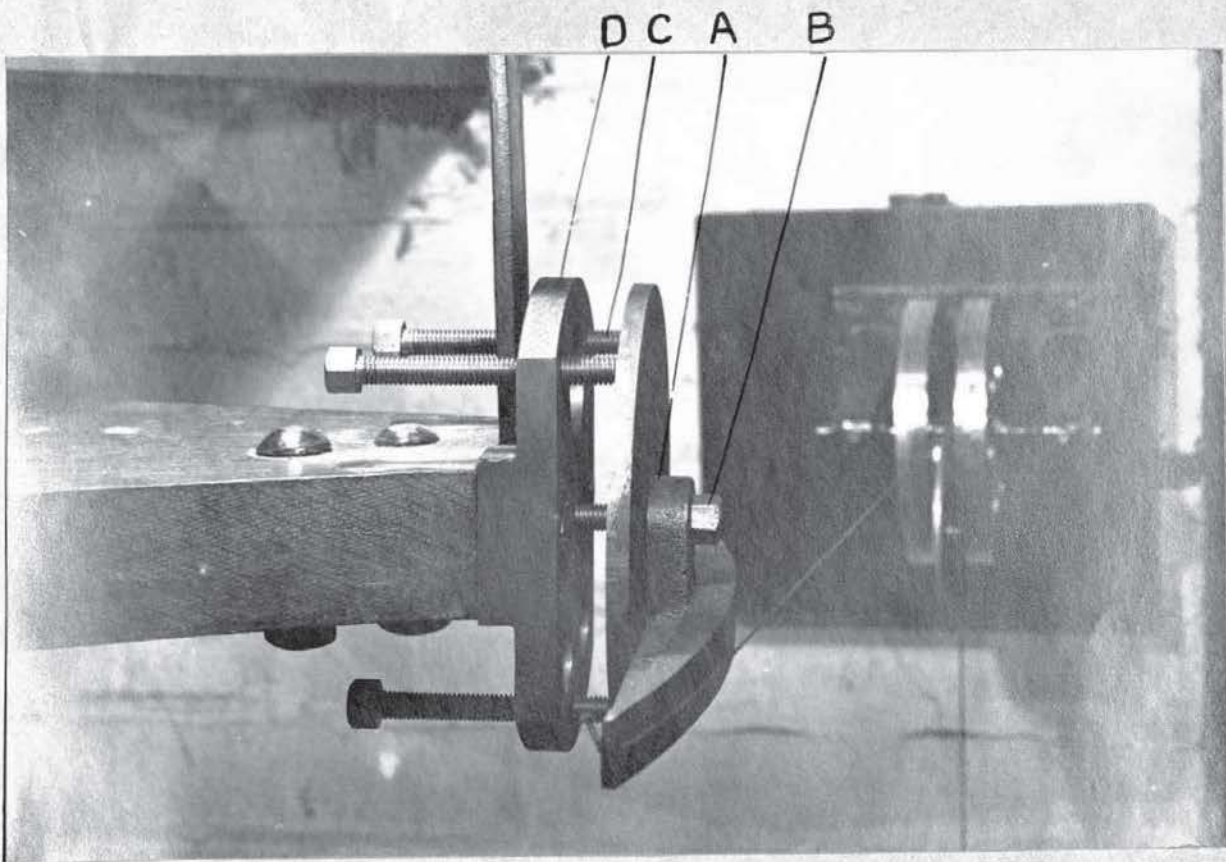
The arrangement in use is shown in the photograph. It had been concluded from the trials that when any considerable fraction of the couple applied to the calorimeter was given by the torsion of a wire, the apparatus was liable to oscillate violently. The original idea of balancing the whole torque by a torsional couple was therefore abandoned and an arrangement similar to that used by Rowland was adopted.



A steel suspension (15 B.W.G.) is clamped to a girder above and to an iron stirrup reaching round the motor below. The length of the wire is adjusted by a screw. Four angle pieces are fixed to the calorimeter and these rest on an oak beam which is bolted into the bottom of the stirrup. The bottom of the calorimeter rests in the original bearing; but, as this bearing was very

liable to stick, it is now only used as a guide, the whole weight being taken by the suspension wire.

The oak beam is used as a couple arm. On the ends are fixed two cast iron arcs turned accurately to the same diameter ($41\frac{1}{2}$ ins.) The method of fixing is shown in the diagram.



The arc and disc A are held by the screw B against the three stops C. These stops are screwed through the plate D. This arrangement allows the arcs to be rapidly set true, level and at the right distance from the axis. The couple on the calorimeter is measured by strings passing round these arcs and supporting weights over pulleys. The string used is very soft pike line.

At first only one alteration was made inside the calorimeter. In the original form there was a tendency for the water to mount inside the inner wall instead of circulating. This was corrected by fixing a broad brass ring to the bottom of the inner wall so that water could only leave the paddle by the space between the two walls. The calorimeter is surrounded by a bright tin case to screen it from draughts and sudden changes of temperature. The whole apparatus weighs about 120 lbs. with the calorimeter full. It is situated in the basement of the Physics Department. This position is not a good one as the steam pipes of the heating apparatus pass near the ceiling and produce large differences of temperature in the neighbourhood of the apparatus. Moreover, the lift motor is so near that it seriously interferes with any electrical temperature measurements.

This apparatus was completed at the end of November 1911 and was immediately tried. Twelve litres of water were put into the calorimeter and the paddle run at its full speed. The weight over each pulley was about 1300 grams. The rise of temperature was measured by a mercury thermometer. The rate of rise was about 1°C per minute and runs of fifteen minutes were made. The apparatus was surprisingly steady, but the balance point was found to be uncertain within the limits of 20 grams weight over each pulley. It was found that although the pulleys were very free under small loads the limiting friction with the load used was about this amount. The pulleys were thin aluminium discs with steel axles on cone bearings.

A number of trials were made with different forms of pulley bearings, but the friction could not be made sufficiently small for the apparatus to have a definite balance point. There is no need to reduce the pulley friction below this point, for it is easy to shew that the work done against it when the apparatus oscillates is negligible.

For let Mg be the weight over each pulley,

$Y =$ total distance moved through by end of couple arm in one vibration

$T =$ period of vibration,

$\mu =$ coefficient of friction.

$\omega =$ angular velocity of paddle.

$a =$ length of arm

Then Work lost $= \mu MgY$ in time T

Work done by paddle $= 2a\omega MgT$

\therefore Work done on water $= 2a\omega MgT \left(1 - \frac{\mu MgY}{a\omega MgT}\right)$

$= 2a\omega MgT \left(1 - \frac{\mu Y}{a\omega T}\right)$

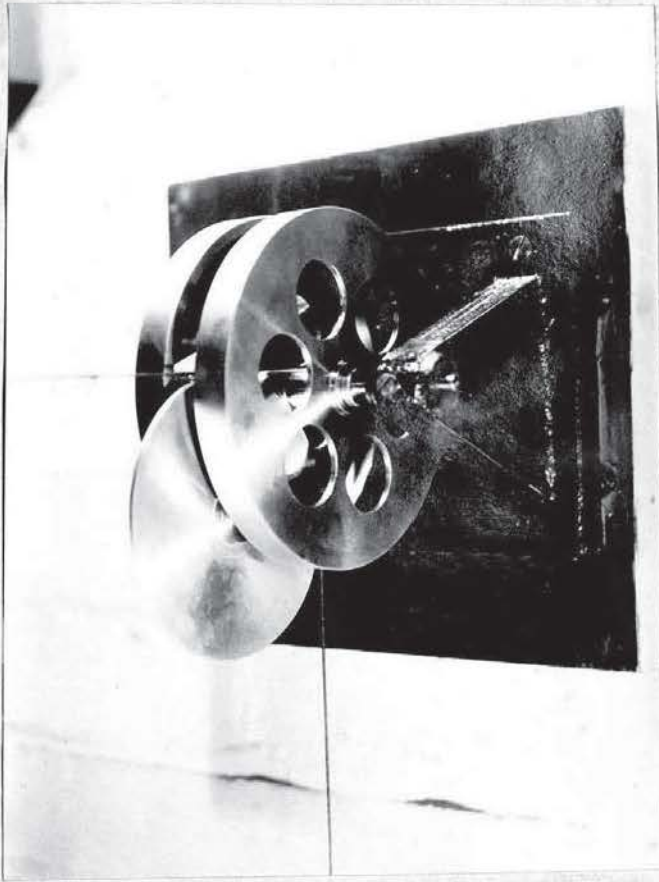
This relation holds for any time t which is an integral multiple of T . As a, ω & T are all large and Y is small, the correction is negligible even if μ is comparatively large; all that is required is a definite balance point.

In spite of this proof, however, ordinary pulleys were found very unsatisfactory, as they refused to settle down to a definite balance point even when there was considerable jarring of the apparatus. In order to avoid the difficulty, the pulleys were removed and two long steel strip springs, clamped at one end, substituted for them. Unfortunately, although the two springs were loaded as as to have very different periods, the apparatus got up considerable oscillations as soon as the paddle was started. In some cases the amplitude of this oscillation was as much as one fifth of the total deflection of the springs. There was also considerable shaking and noise. As any damping arrangement sufficiently heavy to reduce these oscillations to reasonable dimensions would have interfered with the accuracy of the work measurements, it was decided to abandon the springs and to balance the torque by weights hung over pulleys, resting in friction wheels.

The ordinary friction wheels are very inconvenient. They are not adapted for heavy loads or for loads in any direction but vertical. They would have to be tilted to keep the pulleys in place during the experiment, and some arrangement would be necessary to hold the pulleys while the apparatus was standing, and during the sudden changes of couple in starting and stopping.

These disadvantages are avoided in a form of friction wheel suggested by Professor Poynting, and very successfully designed and constructed by Mr. Harrison in the workshop of the department.

The design is shewn in the photograph.



The two wheels are made from gun metal castings. The inside of the rim is turned very true and accurately to size. The pulley is a light aluminium disc mounted on a steel axle. This axle rolls inside the rims of the wheels and is prevented from running skew by a radius turned on it working against the edge of each rim. The wheels are mounted quite free on a steel axle resting in cone bearings. The cone is not a good form of bearing for heavy loads, but as friction at this bearing is of no importance the cones have been retained for convenience in setting.

The advantages of this design are very great.

(1) There are only two wheels to make and balance.

(2) Very heavy loads can be used.

(3) Loads can be applied at any angle without altering the position of the bracket.

(4) The pulley can never get out of its bearings.

Its disadvantages are:-

(1) The weight of the pulley enters into the couple.

(2) The position of the pulley in the wheels varies slightly with the amount of the load.

Both of the above are easily allowed for: (1) disappearing entirely in differential experiments.

Owing to a delay of five weeks in obtaining the castings, the friction wheels were not finished until the end of February. As soon as they were in position the apparatus was again tested. It was found that there were large variations in the torque, partly periodic, partly casual. After a number of trials it was decided that these were due to three causes.


(1) Air was carried down into the paddle and disturbed the water circulation.

(2) The paddle shaft was too thin and whipped slightly.

(3) The coupling between the two shafts had got out of truth.

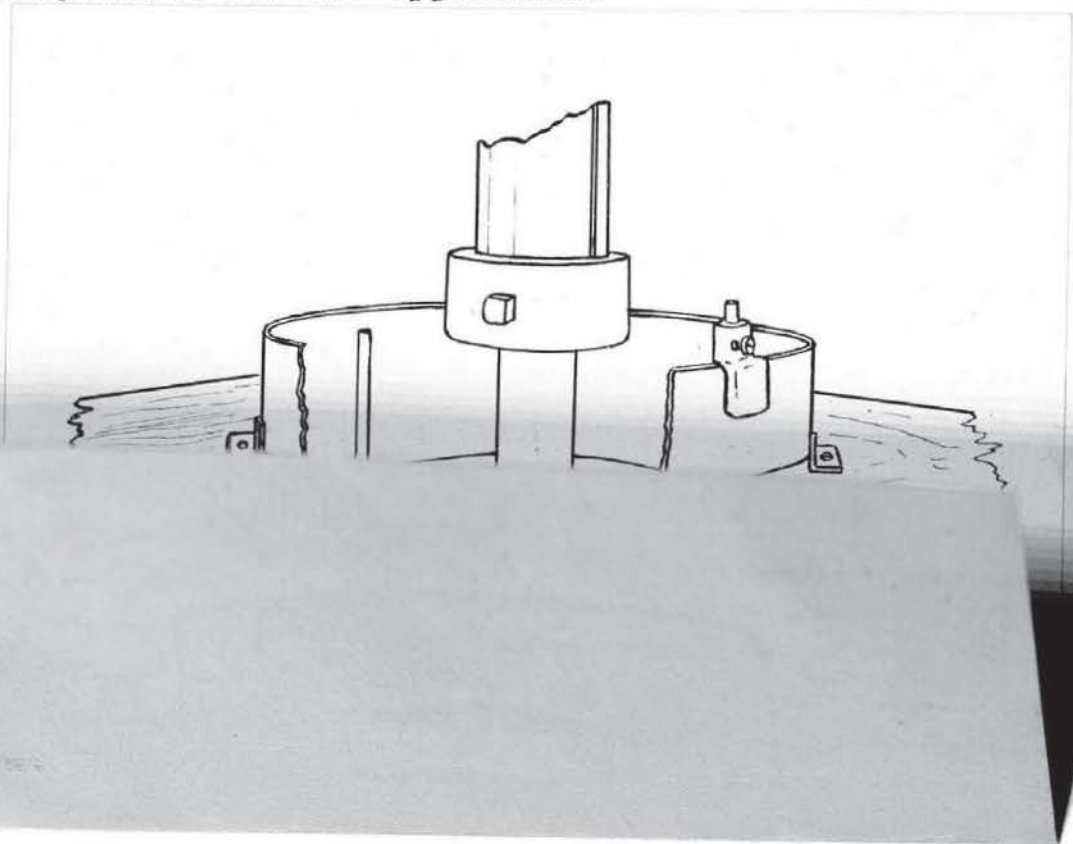
A new paddle shaft of Delta metal $1\frac{5}{16}$ " diameter was made and a new coupling fitted To keep the air away from the

paddle a disc $6\frac{1}{2}$ " diameter was fitted on the top of the vertical vanes. A hole was left in it for the shaft; and a ring, fitting freely on the shaft, rested on the disc and acted as a stuffing-box. The falling water banked up on the disc and found its way down through the space round it. A vortex in the middle of the calorimeter was thus avoided, but air still found its way down to the paddle, and the unsteadiness continued. The only advance was the reduction of shaking in the apparatus, due to the perfect truth of the new shaft.

The next step taken was to replace the V baffles by rings of perforated sheet copper spun to a  shaped section so as to fit tightly between the two walls of the calorimeter. A much less turbulent circulation was thus produced and the air bubbles in the water were thoroughly broken up. The resistance to the flow was greater and a much more rapid rise of temperature was produced, but the irregularity due to the air was not removed except when the calorimeter was full. With smaller quantities of water in the calorimeter much air was still trapped by the water falling over the inner wall. To avoid this a third wall was placed inside the inner wall of the calorimeter so that the falling water completely filled the space between. This was not successful.

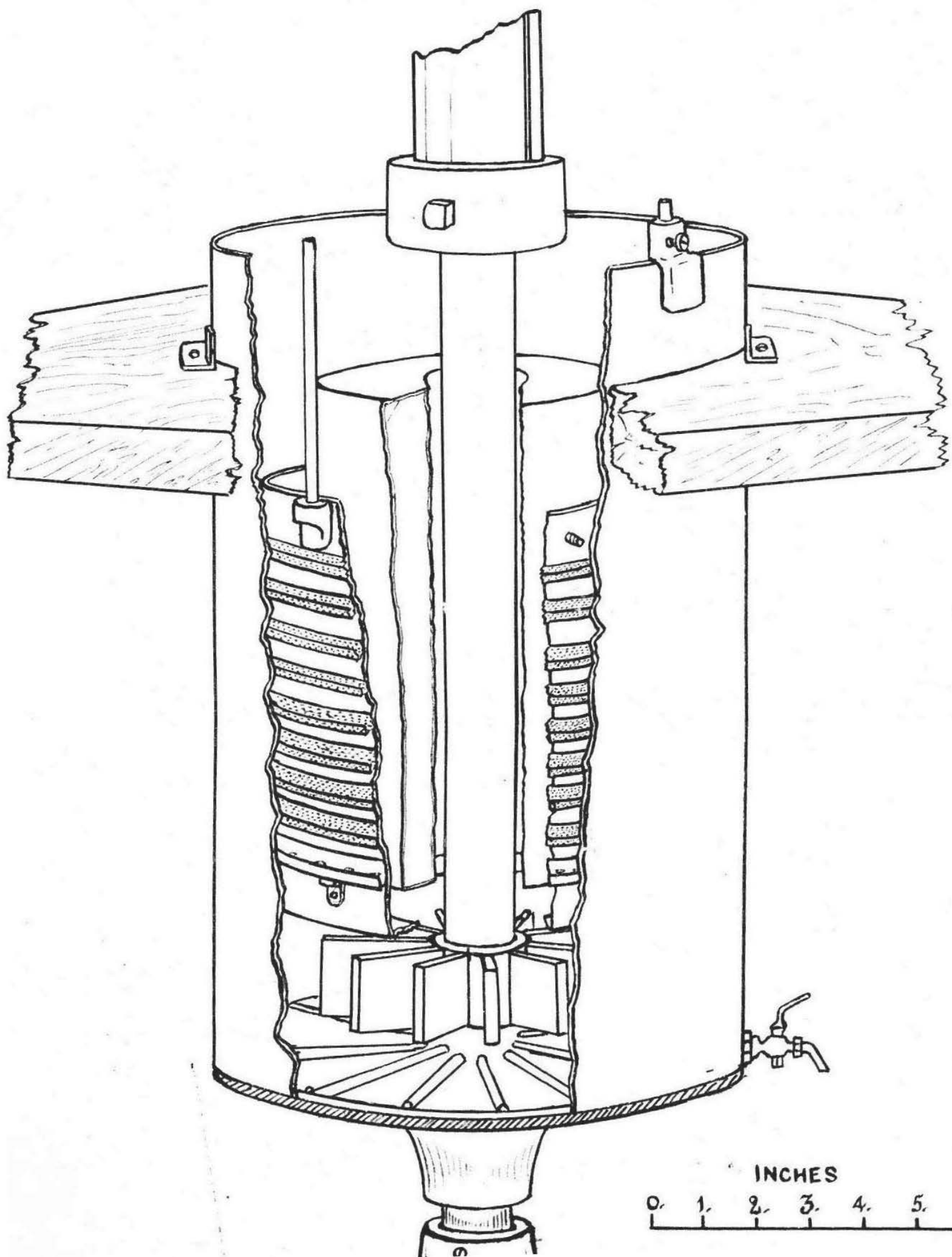
- (i) Some air was still carried down by the falling water.
- (ii) Each rate of working required a special third wall.
- (iii) There was some risk of the water in the calorimeter not circulating.

The irregularities of working were always much less marked when the calorimeter was full, and Professor Poynting suggested that when using smaller quantities of water, a hollow metal cylinder should be fixed inside the calorimeter so as to raise the surface level. The diagram shews the arrangement of this cylinder in the apparatus.



It is held vertical by three set screws at the top of the inner wall, so that the paddle shaft runs quite freely in the central tube. A floating ring on the top of this tube, fitting loosely round the shaft, prevents air from being sucked down into the paddle.

With this apparatus in use no air is trapped by the circulating water, so long as the water level is above the top of the hollow cylinder. When this condition is



realised the couple on the calorimeter is very steady, only varying by about 5 parts in 1200 in a ten minutes' run. The time taken by the water to make a complete circuit of the calorimeter is about two seconds. This should be rapid enough to justify the use of the differential method. The surface of the water is quite steady and there is no splashing, so that the calorimeter can be filled to within an inch of the top. This allows a maximum of 13 litres of water in the calorimeter with the cylinder in position. When larger quantities of water are used, the hollow cylinder is replaced by a similar one of almost equal water equivalent, but with holes in the top and bottom, which allow the water to pass freely through. With this cylinder in the calorimeter quantities of water between 13 and 16 litres can be used. The two pieces of apparatus thus allow a range of 11 to 16 litres for differential measurements. As this apparatus was not in working order until May 13th. only rough measurements have so far been made.

MEASUREMENTS.

1. Work Measurement. The couple to be used in the series of experiments is put on and the current through the motor increased until the calorimeter is brought back as nearly as possible to the balance point, the final adjustment being made

by altering the small weights on one of the pans. The speed of revolution of the motor is obtained by timing a thousand revolutions before and after the experiment. As the ^{motor} ~~water~~ is run from accumulators of large capacity the speed of revolution of the paddle is very constant, measurements before and after an experiment generally agreeing as nearly as can be measured, and never differing by more than one-quarter per cent. The length of the couple arm is measured by taking two strings round the arcs and setting them parallel. The distance between them gives the length of the arm. This length is about 105 cms. and has been measured for the rough experiments to about 1 in 500.

The weights over the pulley have been adjusted to the nearest 5 grams, and an attempt has been made to estimate the centre point of the oscillation during each experiment. It is hoped that the couple weights are correct to 1 part in 400. To be certain of a greater accuracy than 1 in 300 or 400 in this measurement some means of recording the oscillations of the apparatus will be necessary. A chronograph taking paper 8 inches wide is now being made for this purpose. The balance position and time, temperature and revolution records will be made on the same sheet as the oscillation. If the deflections of the apparatus are calibrated in terms of the couple producing them, and lengths measured along the time scale, the difference between the

areas described on either side of the centre line will give the correction required for any variations in the rate of working. This, of course, will only hold good if it can be shewn that the areas described on opposite sides of the centre line by oscillations of the apparatus about the balance point will cancel out.

The proof which follows is due to Professor Poynting.

P. T. O.

Let the paddles exert a torque G_p on the calorimeter.

Then the energy passing into the calorimeter is

$$G_p d\phi \text{ for angle of turn } d\phi$$

Let the string torque be G_s and let A be the angular momentum of the calorimeter.

$$\text{Then } G_p - G_s = \frac{dA}{dt}$$

Now $\frac{dA}{dt}$ is periodic and A is nearly constant, so that, integrating over a sufficient length of time,

$$\bar{G}_p = \bar{G}_s$$

$$\text{Work done by paddles} = \int_0^\phi G_p d\phi = \int_0^\phi G_p \omega dt$$

ω is not quite constant, but if we take its average
 work done = $\omega \int_0^\phi G_p dt = \omega \int_0^\phi G_s dt$ the error
 introduced is only $\int_0^\phi dG \cdot d\omega \cdot dt$

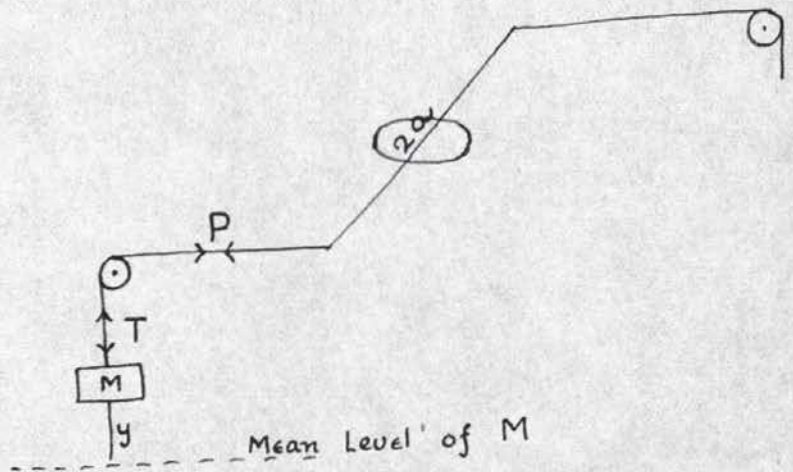
To find G_s

Let the height of the weight above its mean level be y

$$\text{Then } T - Mg = M\ddot{y}$$

or

$$T = M(g + \ddot{y})$$



$$\left. \begin{aligned} P &= T + F \text{ where } \dot{y} \text{ is } + \\ P &= T - F \text{ where } \dot{y} \text{ is } - \end{aligned} \right\} \text{ where } F = \mu Mg$$

Then

$$G_s = 2a \{ M(g + \ddot{y}) \pm \mu Mg \}$$

Work done by paddles

$$\omega \int_0^t G_s dt = 2a\omega M \int_0^t (g + \ddot{y} \pm \mu g) dt$$

But $\int_0^t \ddot{y} dt = 0$ in a long run

also $\pm \int_0^t \mu g dt = 0$ " " " " .

If the oscillations take equal times on the two directions,
work done by paddle is

$$2a\omega Mgt.$$

Now consider energy passed on from the calorimeter by the strings. It is

$$\begin{aligned} 2 \int P dy &= 2 \int M(g + \ddot{y}) dy + 2 \int F dy \\ &= 2 \int M(g + \ddot{y}) dy + 2 \int F \dot{y} dt \\ Mgy &= 0 \text{ in a long run,} \end{aligned}$$

and $\int_0^y M \ddot{y} dy = \int_0^t M \ddot{y} \dot{y} dt = \left[M \frac{\dot{y}^2}{2} \right]_0^t = 0$ in a long run.

$$2 \int F \dot{y} dt = 2FY \text{ where } Y \text{ is the arithmetical}$$

sum of the rises and falls, for F changes sign with \dot{y}

Hence, energy lift in calorimeter is

$$\begin{aligned} 2a\omega Mgt - 2FY &= 2a\omega Mgt - 2\mu MgY. \\ &= 2a\omega Mgt \left(1 - \frac{\mu Y}{a\omega t} \right) \end{aligned}$$

$a\omega t$ is the distance run by the end of the arm if it went round with the calorimeter, and is very great compared with μY

\therefore Energy remaining in calorimeter

$$= 2a\omega Mgt \text{ very nearly,}$$

the effect of oscillations of the apparatus cancelling out.

2. Temperature Measurement. As the tap water which has been used in the rough experiments is at about 14°C . all the measurements have been made between 20°C . and 30°C . The time taken to heat the water from 14°C . to 20°C . has been allowed in order to get a steady condition before taking readings. A mercury thermometer with graduations of 0.2°C . has been used in the temperature measurements. The error on a 10°C . run cannot therefore be as much as 1%.

An attempt has been made to construct a quick reading platinum resistance thermometer for more accurate work. The coil is wound on a brass tube coated with shellaced paper and insulated by dipping in molten shellac. It has not, however, proved satisfactory as the insulation is by no means perfect. The lag of an ordinary platinum thermometer is much too great for our purpose.

A rough estimate of the radiation and conduction losses has been obtained by means of a cooling curve. This gave a mean rate of cooling of about 0.025°C . per minute from 30°C . to 20°C . This rate of cooling would make the results about 2% too high. Under the conditions of the experiment the rate of cooling is certainly greater than this, for, when the paddle is not working the colder water outside is prevented from circulating by the baffles, thus considerably diminishing the heat loss.

A further error is introduced by evaporation of the water during the experiments. If the latent heat

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be taken as 580 cal./gram (its value at 25°c.) the evaporation of 1 gram of water during an experiment would cause a loss of 580 calories. This is equivalent to an error of nearly $\frac{1}{2}\%$ for each gram of water evaporated.

In order to obtain some idea of the amount of evaporation a few experiments have been made with the lid of the calorimeter waxed on, the only opening left being the hole for the paddle shaft. The mean result of these experiments is 2.5 % lower than that of the others.

3. Time Measurement. All time measurements have been made by means of a stop watch reading to one-fifth second, rated by a standard clock.

4. Measurement of Water. The water is measured into the calorimeter by means of graduated flasks. As the errors in the heat measurements are so great, further accuracy is not necessary.

The following results have been obtained by assuming a value for the water equivalent of the calorimeter of 2100 grams. In this value no allowance has been made for the vulcanised fibre at the bottom of the calorimeter. The results have not been corrected for heat losses.

No. of expt.	Mass of water heated in grams.	Wt. on each end of cple arm in grams.	Time for 1000 revs of paddle in seconds.	Rate of rise of temp. in deg. per sec.	J in abs. units.
1	13000	1163	82.4	.0135	4.48
2	14000	1280	75.2	.0153	4.47
3	16000	1290	75.0	.0138	4.47
4	16000	1281	75.0	.0136	4.49
5	14000	1288	75.0	.0156	4.43
6	16000	1489	69.8	.0174	4.38
7	14000	1491	69.7	.0199	4.38
8	14500	1495	69.7	.0191	4.40
9	13000	1322	75.2	.0170	4.44
10	12000	1324	75.2	.0183	4.42
11	11000	1307	75.4	.0195	4.41
12	11000	1185	79.8	.0166	4.42
13	11000	1154	79.9	.0125	4.47
14	11000	1295	75.8	.0190	4.42
15	11000	1234	78.0	.0175	4.41
16	11000	1319	75.1	.0193	4.50
17	12000	1151	80.4	.0146	4.50
18	12000	1220	78.0	.0162	4.44
19	12000	1237	77.6	.0166	4.40
20	12000	1296	75.6	.0177	4.44
21	13000	1292	75.8	.0164	4.45
22	13000	1232	77.4	.0153	4.44
23	13000	1167	80.2	.0141	<u>4.44</u>
				Mean.	<u>4.443</u>

This result is 6.4% higher than that given by Barnes for the equivalent at 25°C. We have already seen that at least two per cent of this is accounted for by cooling during the experiment. The correction for loss of energy by shaking would further reduce the results. In some of the experiments this might have been appreciable.

With the present construction of the calorimeter the difference in quantity of water available for differential measurements is only 2 to 4 kilos while the water equivalent heated in the experiments is from 13 to 18 kilos. The experimental errors in the differential results will therefore be greatly magnified, but the mean value should be about 4.2. With the results we have at present it would be useless to employ the graphical method described in the earlier part of the paper. The values below have therefore been obtained by eliminating between the results of different experiments with rates of rise of temperature of the same order.

Number of the experiments taken.	J in ergs per gram calorie.
1 & 4	4.64 x 10 ⁷
3 & 23	4.66 "
8 & 14	4.24 "
12 & 21	4.69 "
6 & 15	4.25 "

The large differences between these numbers is accounted for by the smallness of the quantities dealt with in the differential calculation, and the haste with which the measurements have been made; but it is difficult to explain why they should all be so much above the accepted values. It seems probable that the heat losses with different quantities of water in the calorimeter are not the same. This may be due to differences in the form of the circulation and in the quantities of water evaporating in the two cases.

The results given below were obtained in experiments with the lid of the calorimeter waxed on, in order to reduce the evaporation as far as possible.

The 2% cooling correction has not been subtracted.

No. of expt.	Mass of water heated in grms	Wt. on each end of cple arm in grms	Time for 1000 revs of paddle in secs.	Rate of rise of temp. in deg. per sec.	J in abs. units.
1	13000	1185	79.2	.0145	4.42
2	15000	1513	70.6	.0187	4.34
3	16000	1326	76.2	.0143	4.25
4	16000	1519	70.8	.0177	4.33
5	14000	1510	70.8	.0198	4.34
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These results were really obtained too hastily for any definite conclusion to be drawn from them, but it seems probable that the first results given should be reduced by 2 or 3 per cent to correct for losses by evaporation. With the 2% cooling correction this makes a total reduction of 4 or 5%, leaving the results still $1\frac{1}{2}$ - $2\frac{1}{2}$ % too high. Further experiments are now being made to discover the source of the remaining difference.
