XXI. *On the Construction of a new Calorimeter for determining the Radiating Powers of Surfaces in Air; and its Application to the Surfaces of various Mineral Substances.* By W. HOPKINS, *Esq., M.A., F.R.S.*

WHEN my paper on the Conductivity of various Substances was presented to the Society, it was intimated to me on the part of the Council of the Society, that it might be advisable to determine *absolute* instead of *relative* conductivities, the latter being alone attempted in my previous experiments. It has been partly in consequence of this intimation, as well as from the desire to make my investigations the more complete, that I have given my attention to the construction of a calorimeter which might serve for this purpose. The present communication contains a description of this instrument, with the results which it has enabled me to obtain respecting the absolute quantities of heat which emanate from the surfaces of certain substances under given conditions.

1. When a body is placed in atmospheric air (or any gas), the quantity of heat which is lost from its surface in a given time, when its temperature is higher than that of the surrounding medium, will be greater than if it were placed in a vacuum, other conditions remaining unaltered. In the latter case the heat escapes by simple radiation; in the other case a portion of the heat also escapes in consequence of the contact of the air with the surface of the heated body. DULONG and PETIT ascertained by a careful series of experiments, the laws according to which the mercury contained in the bulb of a thermometer cools, or those which govern the quantity of heat which escapes from the surface of the containing bulb, when placed in a vacuum, in air, or in several kinds of gases. These experiments were made with the glass bulb naked, and also when it was silvered, so that the laws of radiation which they established were strictly in reference only to surfaces of glass and those of silver. Certain laws were identical in both these cases, and hence it was concluded, though by a limited induction, that the same laws were applicable to all other surfaces. They did not, however, give the *absolute* quantity of heat which, under given circumstances, and in a given time, emanates from the surfaces of the glass or silver with which they experimented. The instrument which I have constructed gives very easily this absolute amount of heat, as I believe, with very approximate accuracy.

The apparatus devised by DULONG and PETIT is easily described with reference to its essential parts, and independently of the particular artifices which were required to secure its practical working. A hollow globe of thin copper, about a foot in diameter,

was firmly fixed in a vessel containing water in which the globe could be entirely immersed.   An orifice existed in the upper side of the globe, through which a thermometer could be inserted and arranged so that the centre of its spherical bulb might coincide with the centre of the globe, and the orifice be hermetically closed.   In making the experiment, the mercury of the thermometer was heated to any proposed temperature, and then rapidly placed in its position in the globe, where the rate of its cooling was determined by observing at regular intervals of time the temperature indicated by the graduated stem of the thermometer.   The interior surface of the copper globe was blackened to prevent as much as possible all reflexion of heat, and was kept at a constant temperature by means of the water in which the globe was immersed.   The experiments could thus be made at any temperature of the medium immediately surrounding the bulb, and also at any pressure of that medium, by withdrawing a portion of the atmospheric air, if that were the medium; or by withdrawing it entirely, and then filling the globe with any proposed gas at any assigned pressure.   The rate at which the temperature of the mercury decreased gave a measure of the rate of its cooling, and consequently of the quantity of heat which emanated from the surface of the bulb in a given time under given conditions.

This apparatus was admirably adapted for experimenting with those substances of which the bulb of a thermometer might be formed, or with which the surface of the bulb could be uniformly and thinly coated; but was manifestly not applicable to determine the radiating power of the surfaces of mineral and many other substances.   The simpler instrument which I have employed is equally applicable to all such surfaces, while it allows the extent of the radiating surface to be ascertained with greater accuracy than that of the bulb of the thermometer from which the radiation took place in the apparatus just described, and is so far better adapted for finding the absolute quantity of heat which radiates from a given area of a given surface in a unit of time.   It does not, however, afford the means of determining the quantity of heat which radiates from a proposed surface in a vacuum, or when surrounded by different gases at various temperatures and pressures.   To determine the laws of cooling in such cases, it was necessary to have recourse to some more complicated apparatus like that made use of by DULONG and PETIT.

2. The laws of cooling of a body surrounded by air or gas, or when placed in a vacuum, as established by these able experimenters, are embodied in the following formula,—

$$Q = A a^\theta (a^t - 1) + B p^c t^b, \quad \ldots \quad \ldots \quad \ldots \quad (1.)$$

where

Q = quantity of heat which escapes from the radiating surface in a given time;

$a = 1 \cdot 0077$, a numerical quantity which is the same for all radiating surfaces, and surrounding media;

θ = the uniform temperature of the surrounding vacuum or medium, expressed in Centigrade degrees;

$t=$ excess of temperature of the radiating surface above that of the surrounding medium, in Centigrade degrees;

$p=$ the pressure of the surrounding medium, expressed by the height of the mercurial column in metres, which the pressure of the medium supported;

$c=$ a numerical value constant for the same surrounding medium at different temperatures, but different for different media; in the case of atmospheric air it $=·45$;

$b=1·233$, a numerical value which is the same for all radiating surfaces, surrounding media, and temperatures;

A and B are constants depending on the area of the radiating surface, and the time to which Q is referred.

When the radiation took place into a vacuum, the pressure p, and therefore the second term of the above formula vanished, and the quantity of heat which radiated in a given time was expressed by the first term, which exhibits the dependence of Q on θ, the temperature of the surrounding space (or of the physical surface which bounds that space), as well as on t, the excess of temperature of the radiating surface. This term will manifestly vary approximately as the simple power of t when the variations of t and θ are not too large. The second term expresses the quantity of heat carried off from the surface by the contact of a surrounding elastic medium, and expresses the law that this quantity is independent of the nature of the radiating surface, and depends on the surrounding medium only so far as regards the elasticity (p) of that medium, and not directly on its temperature, but only so far as the elastic force is affected by that temperature.

These conclusions, as applicable to all radiating surfaces, were made to rest, as I have already observed, on the somewhat narrow basis of induction from experiments on two kinds of surface only, those of glass and silver. Moreover the complete numerical values of A and B depend upon that of the area of the radiating surface, which, as remarked by MM. DULONG and PETIT, was not easy to determine for the bulbs of their thermometers; nor, in fact, was it their object to determine the numerical value of the quantity of heat denoted by Q, but to ascertain the *laws* according to which the cooling of bodies takes place as depending on simple radiation into a vacuum, or on the contact of a circumambient medium.

It should also be remarked that these experiments can only be regarded as establishing the above formula for those cases in which the surrounding elastic medium is placed under the same conditions as in the apparatus with which the experiments were made. In another instrument these conditions might be different (as they are in that which I am about to describe), and the quantity of heat carried from the heated surface by convection might be different, while that due to radiation in vacuum must be the same. In other words, the relation between A and B might be different for different instruments. In adopting this formula I have assumed this relation to be the same for different instruments. The accordance which will be found between the quantity of heat calculated from the formula and that obtained by experiment, proves that the formula

does give with approximate accuracy the whole quantity of heat which emanates from a given surface under the conditions imposed by the instrument, for any values of t between limits which may be inferred from the experiments themselves. This is sufficient for my principal object—that of determining the *absolute* conductivities of substances of which, in a former memoir, I have given only the *relative* conductivities. It is certain that the whole quantity of emanating heat given by the empirical formula is approximately correct; the relative values of the two terms may possibly not be equally so. All that is proved respecting their relation appears to be, that it is independent of the difference of temperatures denoted by t. I pretend not to enter on the problem of determining the quantities of heat carried off by a surrounding gas by convection and conduction respectively, under any assigned conditions.

Having the formula (1), we have next to determine the numerical values of the coefficients A and B. For this purpose, if effected independently, we should require two determinations of Q, for known values of θ, t, and p. In different series of experiments with radiating surfaces of the same nature (as glass, for example), the values of A are proportional to the areas of the radiating surfaces employed, the time during which the radiation takes place being always the same. These values also vary for surfaces of different kinds according to their radiating powers in a vacuum, of which it affords a relative measure. The values of B are considered the same for all surfaces, but are proportional to the areas of the radiating surfaces. Thus when an apparatus is used for the determination of Q, in which the area of the radiating surface is the same, one determination alone of B is required for any number of surfaces; and for the determination of A one experiment at least is necessary with each kind of surface. DULONG and PETIT determined these coefficients with great care for the surfaces of glass and silver, and the radiating surfaces (the bulbs of their thermometers) which they made use of; and for either of those kinds of surface the values of A and B, in any other sets of experiments with glass or silver, will only vary from the above in the ratio of the areas of the radiating surfaces. In the following comparisons of the results of calculation and observation, I have adopted the values of A and B determined by the French experimenters increased in the proper ratio. Thus, taking A_1 and B_1 to denote their coefficients for glass, we have

$$A = m A_1,$$
$$B = m B_1,$$
$$Q = m . A_1 a^\theta (a^t - 1) + m B_1 p^c t^b, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

and one experiment only with glass is required theoretically for the determination of m. Also the coefficient $m B_1$, when once determined, is determined for all surfaces of equal extent; the coefficient $m A_1$ requires a separate determination for each kind of radiating surface. Practically the process has been to determine the mean value of m from a number of experiments, and then, adopting the corresponding values of the coefficients in (2.), to compare the calculated with the observed values. But before I enter into further details, I will describe the calorimeter which I have made use of.

3. In the accompanying diagrams A is a cylindrical tin vessel, of which A' represents a vertical section through its axis.   Its top is slightly conical, and has an orifice at its centre to admit the insertion of a thermometer; and its bottom is slightly curved as represented in the section, leaving a space $b\,c\,d\,s\,r$ through which the radiation takes place from the heated surface in the position $r\,s$.   The conical form of the top facilitates the drying of the vessel after it has been immersed in water to obtain a particular
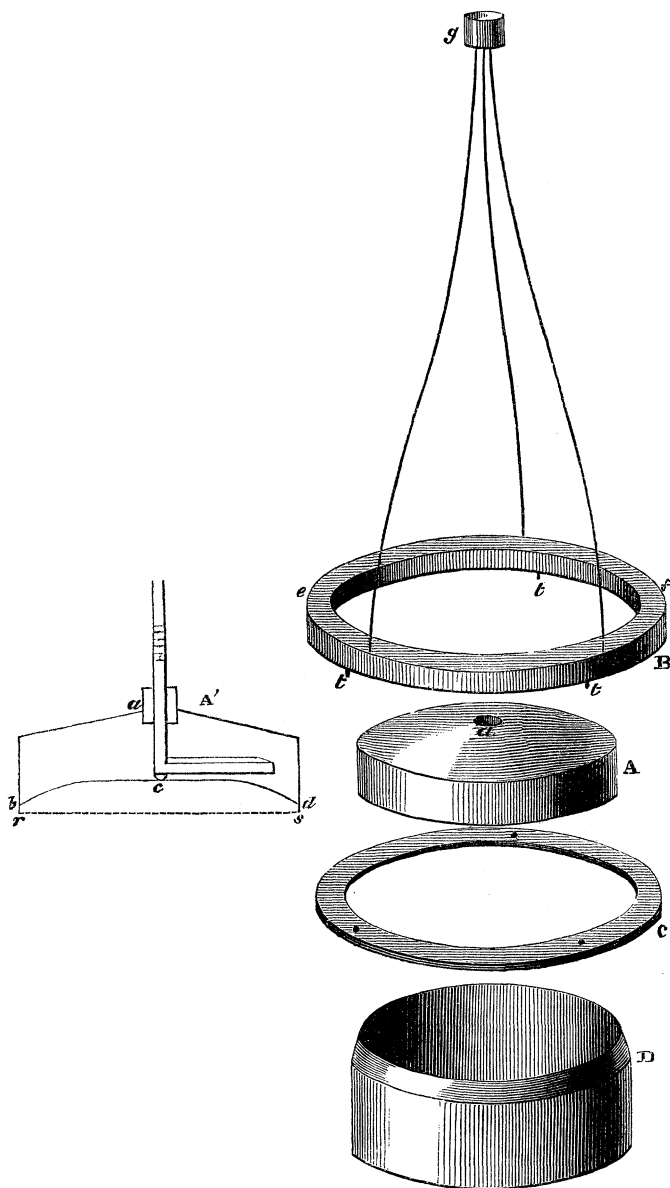

uniform temperature.   The section also represents the thermometer used to ascertain the temperature of the distilled water with which the vessel is filled when the experiments are made with it.   It is of the form of the letter L, the horizontal part being the bulb.   The stem passes through a hole in the cork (a) which fits the central orifice, and

a small piece of cork is fastened on the heel of the instrument at c, on which the thermometer can be freely turned by the finger and thumb applied to the upper extremity of the stem. The horizontal bulb then becomes a most effective *stirrer* during the experiments, by maintaining it in constant rotation about the centre c. The thermometer is extremely delicate, each graduation of about $\frac{1}{10}$th of an inch corresponding to $\frac{1}{10}$th of a degree of FAHRENHEIT. It was easy, therefore, by the aid of a lens, to read to the hundredth part of a degree.

The diagram B represents a wooden rim ef, of which the inner diameter is about half an inch larger than the diameter of the vessel A, so that the vessel can pass freely within it. Three wires are firmly fixed into the upper surface of the rim, and to the block g. When the instrument is put together, the vessel A is placed concentrically within the rim, in which it is firmly supported by three small wooden wedges between itself and the rim, and so that the circumference of the circular bottom of A may be exactly level with the lower surface of the rim ef. Also the thermometer being inserted through a and the orifice corked, the upper part of the stem passes through a central hole in the small wooden block g. The calorimeter thus put together is represented by the diagram E. The upright wires form at once a protection to the thermometer, and a convenient means of handling the instrument without touching the vessel containing the distilled water.
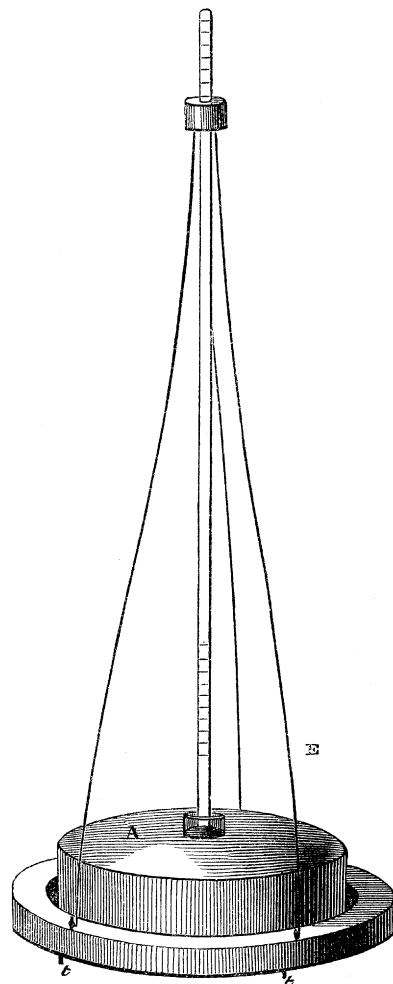
4. In performing an experiment, the substance whose radiating power has to be determined is formed into a thin disc, the diameter of which is such as just to allow it to fit freely into an iron cylindrical vessel represented by D,
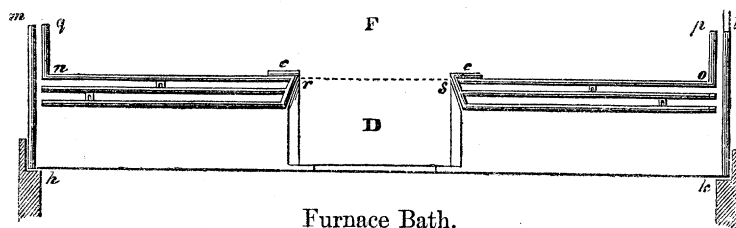
Furnace Bath.

which contains such a quantity of mercury that the disc floating upon it shall have its upper surface exactly on a level with the rim of the cylinder. The required temperature is then given to the disc by heating the mercury on which it rests. This is effected, as represented in the diagram F, by placing the iron cylinder on the thin iron

plate hk which forms the roof of the bath over the furnace, and is covered with a thin stratum of mercury, which is allowed to pass beneath the vessel and in contact with its bottom by means of three slightly projecting points on which the bottom rests. If a lower temperature than would thus be communicated directly to the mercury be required, it is easily regulated by the insertion of one or more iron discs beneath the iron cylinder, or if necessary, discs of paper or other bad conducting substances.

When the radiating surface is heated to the proper temperature, the calorimeter is to be placed above it so as to catch the heat which radiates from it. But if no precautions were taken, it is manifest that a great radiation would take place also from the heated stratum of mercury on hk, and affect the calorimeter placed over the iron cylinder. This is partly prevented by covering the surface hk with cotton or other bad conductor, but effectively by a special contrivance for the purpose. $hklm$ is the section of a square box, open at the top, which fits on to the top of the furnace, of which its sheet-iron bottom forms the roof as above described. $nopq$ is the section of another square open box fitting freely within the former, and with a round hole in the centre just large enough to admit the insertion of the thin rim of the iron cylinder within it, which, however, is prevented passing through it by the increased thickness of the walls of the cylinder immediately below, as represented in the diagram. This inner box is thus entirely supported on the shoulder of the iron cylinder, and so that the internal surface of its bottom is exactly on a level with the rim of the iron cylinder, and therefore also, with that of the radiating surface of the disc placed within it. The bottom of the box is composed of three thin boards separated from each other, to prevent more effectively the transmission of heat through it.

If the calorimeter were now placed over the radiating disc, it would rest with the projecting points t (figs. B and E) on the bottom of the box just described; but as a further precaution against all communication of heat to the calorimeter by conduction, or otherwise than by direct radiation from the radiating surface, a thin wooden rim (diagram C) is placed on the bottom of the box, but unattached to it, so as to surround the central orifice and rim of the cylinder, to the diameter of which its own diameter is exactly equal. The calorimeter is then placed on this rim, on which it rests at the three points marked in the diagram (C). Sections of this rim are represented by c, c in the diagram F, in which also rs represents the section of the radiating surface, over which, during each experiment, the calorimeter is placed as represented in the diagram A′, the distance (br, ds) of the circumference of the base of the calorimeter from the radiating surface being about one-fourth of an inch. On removing the calorimeter after each experiment (which only required a few minutes), the interior box $nopq$, with the rim C, was immediately removed and placed where they might acquire again the temperature of the room before the next experiment.

It might have been supposed that it would be sufficient in the experiments, to place the circumference bd (fig. A′) on the rim C, but in such case the results would have been entirely vitiated by the transmission of heat to the calorimeter by *conduction*, as I found

by tedious experience. In the above arrangement this risk is entirely obviated; for, it will be observed, there is no contact between the rim C and the supporting rim B except at three points; nor, again, is there any contact between the rim B and the vessel A, except at the three points at which they are connected by the wedges inserted between them.

The bottom of the tin vessel A was carefully coated with lamp-black, to prevent, as far as possible, the reflexion of the heat radiating upon it.

5. It has been already stated that the required heat is communicated to the mercury in the iron cylinder by placing it on the heated surface hk (fig. F). If the temperature required was less than 212° FAHR., the bath immediately beneath hk was filled with water, which was kept at the boiling temperature. When the iron cylinder rested immediately on the plate hk, the temperature of the mercury contained in it would rise to nearly 200°, and could be maintained at any lower temperature by placing a sufficient thickness of discs of iron, wood or other substances immediately beneath the cylinder. In this manner the *steadiness* of the temperature could be carefully preserved for any length of time, an essential condition in making the experiments. When the radiating surface was that of glass or iron, the discs of those substances could be rendered extremely thin, so that the temperature of the surface of radiation was very nearly equal to that of the mercury on which they floated, to which it might be considered as approximately equal, or to differ from it by a small correction. The temperature of the mercury immediately beneath the disc was ascertained by a thermometer, the small spherical bulb of which was inserted into it through a small hole in the centre of the disc for that purpose. In the cases of mineral substances (as limestone, sandstone, &c.), the discs could not be made thin enough to prevent a considerable difference of tempera- ture between their upper radiating surfaces and their lower surfaces resting on the mercury. The temperature of the upper surface was then determined by a thermometer made for the purpose with a *spiral bulb* (as represented in the annexed diagram), the coils of the spire lying in one plane perpendicular to the graduated stem. A hollow was worked in the centre of the surface of the disc of sufficient diameter to receive the spiral bulb, and of such a depth that the bulb, when thus inserted, could be easily covered with mercury. The necessary depth did not exceed one-eighth of an inch, so that the temperature indicated by the thermometer, with its bulb placed in the hollow and covered with mercury, was necessarily very approximately that of the surface itself of the disc. Had a thermo- meter with an ordinary bulb been used, the central hollow must have been considerably deeper, and might therefore have been materially different from that of the outer surface, on account of the rapidity with which the temperature varies in a thin disc, in passing from its lower surface in contact with the mercury to the
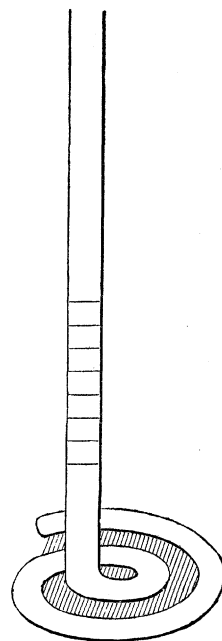
outer one radiating into the atmosphere, when the temperature of the lower surface is much higher than that of the atmosphere*.

6. We may now proceed to describe the manner of conducting each experiment, the radiating surface having attained its required stationary temperature, and the calorimeter being filled with distilled water. A vessel containing water was placed near at hand, the temperature of the water being kept a little lower than that of the surrounding atmosphere of the room. The calorimeter was then immersed in this water, and allowed to remain there till the temperature of the distilled water and the tin vessel (A) containing it became stationary, as indicated by the sensitive L-shaped thermometer already described. It was then taken out of the water, and all the moisture adhering to it externally very carefully removed. The temperature would then remain sensibly stationary, and a little lower than that of the surrounding air. The thermometer was then carefully read, and the calorimeter transferred to its position above described, immediately over the radiating surface. After remaining there a certain observed time (during which the distilled water in it was thoroughly *stirred* as above described), it was removed, and the thermometer again read. The difference of the readings afforded a measure of the quantity of heat which had emanated from the heated surface and been absorbed by the vessel A of the calorimeter through its bottom, the observed result being subject to certain corrections to be hereafter considered.

The time during which the calorimeter was exposed to the influence of the radiating surface was determined with great accuracy. It seldom exceeded five or six minutes, generally not more than three or four. An assistant placed close to his ear a watch which *ticked* very audibly 150 times in a minute. It was easy to indicate to him the exact instant when the calorimeter was placed over the radiating surface, and he then began to count aloud the beats of the watch to a number varying according to the circumstances of each experiment, from 300 to 1000. The instrument was rapidly removed at the instant the counting of the number fixed upon was completed. The error to which the experiments were liable in this estimation of the *time* was very small.

I was also able to make the *readings* of the thermometer very accurately. I have stated that the first reading was made while the mercury was stationary. Such was the case also with the second reading; the rise of the thermometer of the calorimeter during an experiment seldom exceeded three or four degrees, and therefore the temperature of the distilled water and its containing vessel, when just removed from the influence of the radiating surface, differed from that of the surrounding atmosphere only by a small amount. Consequently the thermometer remained sensibly stationary for a longer time than was required to read it with care. I was thus able to obtain the reading with ease within the hundredth part of a degree of FAHRENHEIT.

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* It might seem that a *flat* bulb would have answered the purpose, and been more simple in construction; but it was pointed out to me by Mr. CASELLA that thermometers of this construction are not to be relied upon. They may yield to a small external pressure sufficiently to affect the indication of temperature to the amount of several degrees.

Thus I could observe with great accuracy both the time during which radiation took place, and the increase of temperature acquired in that time by the calorimeter, and these are manifestly the two principal quantities to be determined by observation in the experiments. There are several possible sources of error, however, which require examination.

7. The first obvious consideration is that the water contained in the vessel A of the calorimeter does not, during the experiment, merely receive heat from the heated radiating surface; it will also, at each instant, be gaining or losing heat by the exposure of its external surface to the atmosphere, whenever its temperature differs from the surrounding temperature. I endeavoured to obviate this in the first place by making the vessel A of tin, the external surface of which, exposed to the atmosphere, was *polished*, while that exposed to the radiation from the heated disc, as already stated, was covered with lamp-black. The external surface was therefore a bad radiator of heat from within to the external air, and a bad absorbent of heat from without, and consequently helped to reduce the influence of the external air. Further, it is manifest that no effect could be produced on the experimental results, provided the *mean* temperature indicated by the thermometer of the calorimeter during an experiment were equal to the temperature of the external air. This condition was more or less approximately satisfied in the actual experiments, the results of which have been relied upon; but when not satisfied, it was easy to ascertain and apply the requisite correction when of sufficient amount to be sensible. To ascertain this correction, I made the following experiment. The whole instrument (E) was placed on an iron disc; it rested on its three feet (*t*). The vessel (A) of the calorimeter and the iron disc were immersed in water, of which the temperature was about 5° below that of the surrounding air. When the temperature indicated by the sensitive thermometer of the calorimeter had become perfectly stationary, the instrument and iron disc were taken out of the water, rapidly cleared of the external moisture, and the instrument replaced on the iron disc in the air. The under blackened surface of the vessel A was now exposed only to the surface of the iron disc, which was of the same temperature as the distilled water in A, and could not, therefore, affect its temperature. At the same time the external polished surface of A was exposed to the external air, of which the temperature was about 5° higher than that of the water of the calorimeter. The result, however, was that the thermometer of the calorimeter remained sensibly quite stationary for a considerably longer time than that required for any of the experiments, thus proving that the corrections in my actual experiments due to this cause were of insensible amount.

8. When a thin metal disc was used for the radiating surface, a small orifice was made at its centre, as above stated, just large enough to admit the bulb of a thermometer used to determine the temperature of the mercury beneath the disc. Over the area of this orifice the radiation took place from the surface of mercury, and not from that of the disc. Also, when a thicker disc of a mineral substance was used, the superficial hollow for the coiled bulb of the thermometer was filled with mercury, from the surface of

which, therefore, in the area occupied by it, the radiation took place instead of the radiation from the surface of the disc itself. It will be necessary to examine whether our experimental results were sensibly affected by the difference of radiation in these cases from the mercury and that from an equal extent of the discs made use of. Thus let

r=radius of the radiating disc;

ϱ=radius of the central portion where the radiation takes place from mercury;

T=temperature of the radiating surface;

R=reading of the thermometer of the calorimeter, *i. e.* the temperature of its lower surface, on which the radiating heat falls;

then will

$$c(T-R) \quad \text{and} \quad \varpi(T-R)$$

express the quantities of heat which emanate in air from a superficial unit of the respective surfaces of mercury and glass. The coefficients c and ϖ may be considered approximately as constant for variations of $T-R$ which are not too large, but their ratio (which alone is required for the correction) is easily deduced from the experiments to be given in the sequel, for comparatively large values of $T-R$. Then if Q_1 be the observed quantity of heat which emanates from the disc in a given time,

$$Q_1 = \pi r^2 \varpi(T-R) - \pi \varrho^2(\varpi-c)(T-R)$$
$$= \pi r^2 \varpi(T-R)\left\{1 - \frac{\varrho^2}{r^2}\frac{\varpi-c}{\varpi}\right\},$$

or if Q=the quantity of heat which would emanate from the whole disc without the central orifice,

$$Q_1 = Q\left\{1 - \frac{\varrho^2}{r^2}\left(1 - \frac{c}{\varpi}\right)\right\},$$

$$Q = Q_1\left\{1 + \frac{\varrho^2}{r^2}\left(1 - \frac{c}{\varpi}\right)\right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3.)$$

very nearly. The second term, $\frac{\varrho^2}{r^2}\left(1 - \frac{c}{\varpi}\right)Q_1$, is the correction required. In my experiments this quantity is always small, but in some of them it is sensible.

9. Again, when discs of glass and metal were used, it was the temperature of the mercury on which they rested that was observed, *i. e.* the temperature of the *lower* surface of the disc. It becomes necessary, therefore, to examine what correction ought to be applied to this observed temperature, in order to obtain that of the upper or radiating surface. Now if t_1 be the temperature of the lower surface of the plate, t_2 that of its upper surface, τ that of surrounding space, or of a surface (like the lower one of the calorimeter) on which the radiation takes place, h the thickness of the plate, k its conducting power, and ϖ the radiating power of its surface in air, we have the approximate formula used in my last memoir (where the symbol p was used instead of ϖ),

$$\frac{k}{\varpi} = \frac{t_2-\tau}{t_1-t_2}h.$$

Hence we obtain

$$t_2 = t_1 \frac{\left(1 + \frac{h\varpi}{k}\frac{\tau}{t_1}\right)}{1 + \frac{h\varpi}{k}};$$

or since, in the present case, h is very small, we have approximately

$$t_2 = t_1 \left\{ 1 - \left(1 - \frac{\tau}{t_1}\right)\frac{h\varpi}{k} \right\},$$

the real temperature of the radiating surface. Hence if Q_1 denote the observed quantity of heat which radiates from the disc, and Q the quantity which would radiate if the temperature of the disc's upper surface were t_1, we have

$$Q_1 = Q \left\{ 1 - \left(1 - \frac{\tau}{t_1}\right)\frac{h\varpi}{k} \right\};$$

and therefore

$$Q = Q_1 \left\{ 1 + \left(1 - \frac{\tau}{t_1}\right)\frac{h\varpi}{k} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.)$$

very nearly. The second term, $Q_1 \left(1 - \frac{\tau}{t_1}\right)\frac{h\varpi}{k}$, is the correction required.

In my former experiments on conductivity, $\frac{k}{c}$ was the quantity determined, c being the radiating power of mercury in air, the upper surface of the substance experimented on having been always covered with mercury, from which, consequently, the radiation took place. The above correction may be put in the form (somewhat more convenient for application) of

$$Q_1 \left(1 - \frac{\tau}{t_1}\right)\frac{hc}{k} \cdot \frac{\varpi}{c}.$$

It is always a very small quantity.

10. Another correction requires to be carefully examined. In order that the calorimeter should receive directly on its blackened lower surface the whole of the heat emanating from the heated radiating surface, it would be necessary that the circumference or rim of its lower surface should coincide with the circumference of the radiating disc. But this condition cannot be accurately satisfied without the risk, as already explained, of deranging the experiments by heat passing to the calorimeter by *conduction*. It was to avoid this the more effectively that the wooden annulus (fig. C) was introduced, and thus a small interval of about the thickness of the wooden annulus existed between the circumference of the hollow bottom of the calorimeter and that of the radiating disc. This interval was equal to 0·21 inch. The heat which radiated on this intervening annulus would not immediately affect the calorimeter, and ought therefore to be added to the quantity which radiated directly on the calorimeter, and was measured by the indications of its thermometer.

The quantity of heat which radiates directly from the heated disc and fell on any

assigned portion of the bottom of the calorimeter (or the corresponding portion of the hemispherical surface of which the radiating surface was a diametral plane) is not easily determinable, on account of the complicated integration to which the investigation leads. It is easy, however, to compare very approximately the amount which thus falls on a very narrow annulus of the hemispherical surface contiguous to the diametral plane formed by the radiating surface, with the whole quantity which radiates from that surface in a given time. Thus let

$\delta q =$ the quantity of heat which radiates in a unit of time from the small element δS of the radiating surface, and falls on the indefinitely small area w of the above-mentioned hemisphere;

I = the intensity of normal radiation;

E$=$ angle of emanation, and therefore I.$\sin$E$=$ the intensity of radiation in a direction making an angle E with the radiating surface;

$\varphi=$ angle of incidence on ω;

$r =$ distance of ω from δS;

$\varrho =$ projection of r on the radiating diametral surface;

$\theta =$ angle which ϱ makes with the diameter of the diametral plane passing through the projection of ω on that plane;

$q' =$ the quantity of heat which radiates on the element ω;

then

$$\delta q' = I \cdot \frac{\omega \cos \varphi}{r^2} \sin E . \delta S ;$$

and if $z_{\prime}$ denote the distance of w from the diametral plane,

$$\sin E = \frac{z_1}{r} ;$$

Also
$$\delta S = \varrho \delta \theta \delta \varrho .$$

The angle φ is that which r makes with the normal to the surface at ω. Instead of expressing its general value, suppose ω to be situated within the diametral annulus above mentioned, and therefore very near to the diametral plane; it may then be considered as lying on the axis of z, assuming the origin of coordinates to be at the extremity of the diameter from which θ is measured. The normal to the point ω may then also be considered as parallel to that diameter, the axis of x, and we shall have

$$\cos \varphi = \frac{x}{r},$$

$$= \frac{\varrho \cos \theta}{r}.$$

Hence

$$\delta q' = I \omega z_1 \frac{\varrho^2}{r^4} \cos \theta \delta \theta \delta \varrho,$$

$$= I \omega z_1 \frac{\varrho^2}{(z_1^2 + \varrho^2)^2} \cos \theta \delta \theta \delta \varrho ;$$

and

$$q' = I \omega z_1 \int \frac{\varrho^2 \delta \varrho}{(z_1^2 + \varrho^2)^2} (\sin \theta + C).$$

The proper limits of θ are $\pm \cos^{-1} \frac{\varrho}{2a}$ ($a =$ radius of the diametral surface), but they would render the next integration unmanageable. Take the integral from $\theta = -\frac{\pi}{2}$ to $\theta = \frac{\pi}{2}$. Then

$$q' = 2 I \omega z_1 \int \frac{\varrho d\varrho}{(z_1^2 + \varrho^2)^2}$$

$$= 2 I \omega z_1 \left\{ C - \frac{\varrho}{2(z_1^2 + \varrho^2)} + \frac{1}{2 z_1} \tan^{-1} \frac{\varrho}{z_1} \right\}$$

$$= I \omega \left\{ \tan^{-1} \frac{\varrho}{z_1} - \frac{\varrho z_1}{z_1^2 + \varrho^2} \right\}$$

since q' vanishes with ϱ.

With the increase of ϱ (z_1 being very small) this expression rapidly approximates to

$$I \omega \frac{\pi}{2};$$

i. e. if z_1 be sufficiently small we shall have approximately

$$q' = \frac{\pi}{2} I . \omega ;$$

or since the ω is an element of our narrow diametral annulus, we have

$$q = \frac{\pi}{2} I . \text{area of the annulus,}$$

q being the quantity of heat which radiates upon the annulus. If the breadth of the annulus be denoted by β, its area will $= 2 \pi a \beta$, and

$$q = \pi^2 I a \beta.$$

Again, let Q be the quantity of heat which radiates in a unit of time from the whole radiating surface. Conceive two right cones with common vertex at δS and common axes perpendicular to the radiating surface, their vertical angles being θ and $\theta + \delta \theta$. The quantity of heat radiating between these two conical surfaces will

$$= \delta S . I \cos \theta . 2 \pi \sin \theta . \delta \theta,$$

and therefore the whole quantity radiating from δS will

$$= \delta S . \pi I \int_0^{\frac{\pi}{2}} \sin 2\theta d\theta,$$

$$= \delta S . \pi I,$$

or

$$\delta Q = \pi I . \delta S,$$

$$\therefore \quad Q = \pi I . \pi a^2$$

$$= \pi^2 I a^2.$$

Hence

$$\frac{q}{Q}=\frac{\beta}{a}$$

$$=\frac{\text{breadth of the annulus}}{\text{rad. of radiating surf.}}.$$

Hence taking Q_1 as before,

$$Q=Q_1\left\{1+\frac{\beta}{a}\right\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.)$$

The expression above obtained for q will only be accurately true when β is indefinitely small, as is easily seen from the limits which have been taken for θ and ϱ in the integration. If β be small but finite, as in our actual case, the above value of q will be approximately true, but somewhat too large.

It may be doubted whether the above investigation is strictly applicable to the whole of the heat which emanates from the heated surface or to that part only which may be conceived to *radiate* through the air to the bottom of the calorimeter, in contradistinction to that which must be borne away by the air from the heated surface by *convection* or *conduction*. As the effect, however, produced on the narrow annulus must be of the same kind, there is probably little error in the correction, by supposing it of the same magnitude.

11. There is another error, which would seem perhaps to be inherent in any experimental determination of the quantity of heat radiating from one surface and falling on another. It arises from the fact of one of these surfaces (as the base of the calorimeter in my experiments, and the internal surface of the surrounding globe in those of Dulong and Petit) not being *perfectly absorbent*, as assumed in the results, which ought, therefore, in the following experiments, to be increased in the proportion which the heat reflected from the blackened surface of the calorimeter bears to the heat absorbed by it. This ratio is probably very small, but I am not aware of any attempt to determine it.

Numerous experiments were made before the calorimeter assumed exactly the form above described; for it was only by a careful observation of the anomalies presented by the earlier experiments that I became fully aware of the importance which attached to different points in the construction of the instrument, and the mode of conducting the experiments. I shall give a few of the later experiments, on which some of my principal results are founded, in full detail, to enable the reader the better to judge of the confidence to which they may be entitled. The following experiments on a glass disc were made for the determination of m (art. 3).

12. Let $T_1 =$ temperature of the radiating surface when the experiment begins;

$T_2 =$ ditto when it ends;

$R_1 =$ reading of the thermometer of the calorimeter at the beginning of the experiment;

$R_2 =$ ditto at the end of it;

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then will $\frac{1}{2}(T_1+T_2)$ be the mean temperature of the radiating surface during the experiment, and R_2-R_1 will = the rise in the temperature of the calorimeter during the observed time of the experiment, expressed in the number of beats of the watch. The time was usually taken longer or shorter, according as the rise of the thermometer of the calorimeter was slower or faster. Five hundred beats corresponded to 3·333 minutes.

It will be observed that in each of the experiments (1), (2), &c. in each series I., II., &c., the temperatures of the radiating surface are approximately equal. These experiments, (1), (2), &c., are in fact repetitions of nearly the same experiment, made with the view of obtaining the mean result of several experiments instead of relying on the result of one. And here I may remark that this was necessary, not merely for the elimination of errors of observation, but also for that of the actual irregularities in the rising of the mercury in the thermometer of the calorimeter. Moreover no high temperature can be maintained perfectly stationary, but is always in a state of oscillation about a mean value. If every experiment could be made *exact*, the numbers registered in the fourth column of the following Table ought to be the same. The irregularities which they present are partly due to the slightly different temperatures (as exhibited in the second and third columns) at which the experiments were made, partly to the causes just mentioned, and partly to the necessary errors of observation. All these irregularities may manifestly be more or less eliminated by taking the mean result derived from a number of similar experiments. For this purpose I have taken the mean (T) of the tabulated values of T_1 and T_2, and the mean (R) of the values of R_1 and R_2, and considered (T)—(R) as the difference between the temperature of the radiating surface and that of the lower blackened surface of the calorimeter to which the heat emanating from the radiating surface was immediately communicated; while the mean of the numbers in the fourth column is taken as the corresponding rise in the temperature of the calorimeter. An inspection of these columns will show how far the result of each individual experiment differs from the mean result, and will afford a measure of the reliance which may be placed on this mode of experimenting.

I. Disc of *Glass*.

Time, or duration of each experiment $=500$ beats.

Height of barometer . . . . . $=30\cdot5$ inches.

$=\quad\cdot77$ metre.

Number of the experiment.	Temperature of the radiating surface.	Readings of the calorimeter.	Difference of the readings $=R_2-R_1$.	Temperature of the air.
(1)	$\left\{T_l=150\overset{\circ}{\cdot}0\right\}$	$\left\{\begin{matrix}R_1=60\overset{\circ}{\cdot}72\\R_2=62\cdot24\end{matrix}\right\}$	$1\overset{\circ}{\cdot}52$	$64\overset{\circ}{}$
(2)	$\left\{\begin{matrix}T_1=151\cdot2\\T_2=159\cdot8\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=61\cdot39\\R_2=63\cdot00\end{matrix}\right\}$	$1\cdot61$	
(3)	$\left\{\begin{matrix}T_1=150\cdot0\\T_2=149\cdot5\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=59\cdot91\\R_2=61\cdot50\end{matrix}\right\}$	$1\cdot59$	
(4)	$\left\{\begin{matrix}T_1=149\cdot2\\T_2=147\cdot0\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=61\cdot25\\R_2=62\cdot77\end{matrix}\right\}$	$1\cdot52$	
(5)	$\left\{\begin{matrix}T_1=147\cdot0\\T_2=147\cdot5\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=61\cdot70\\R_2=63\cdot16\end{matrix}\right\}$	$1\cdot56$	
(6)	$\left\{\begin{matrix}T_1=147\cdot5\\T_2=147\cdot5\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=62\cdot00\\R_2=63\cdot45\end{matrix}\right\}$	$1\cdot45$	64
(7)	$\left\{\begin{matrix}T_1=147\cdot7\\T_2=147\cdot7\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=61\cdot84\\R_2=63\cdot27\end{matrix}\right\}$	$1\cdot43$	
(8)	$\left\{\begin{matrix}T_1=148\cdot6\\T_2=148\cdot8\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=61\cdot95\\R_2=63\cdot46\end{matrix}\right\}$	$1\cdot51$	
(9)	$\left\{\begin{matrix}T_1=149\cdot6\\T_2=149\cdot6\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=62\cdot89\\R_2=64\cdot40\end{matrix}\right\}$	$1\cdot51$	

Hence we obtain the following mean values:—

$$(T)=148^\circ\cdot20 \text{ (F.)},$$

$$(R)=\;\;62^\circ\cdot27;$$

$$\therefore\qquad (T)-(R)=\;\;85^\circ\cdot93.$$

When (R) is expressed in *Centigrade degrees*, its numerical value becomes that of θ in our general formula; and the value of $(T)-(R)$ in the same degrees, is that of t in the formula. Hence for the mean of the above nine experiments,

$$\theta=16^\circ\cdot80,$$

$$t=47^\circ\cdot74.$$

Also, taking the mean of the tabulated values,

$$R_2-R_1=1\cdot52.$$

II. Same Disc of *Glass*.

Time . . . . . $= 300$ beats.

Height of barometer $= 30.25$ inches.

$$= \cdot 76 \text{ metre.}$$

Number of experiment.	Temperature of the radiating surface.	Readings of the calorimeter.	Difference of the readings $= R_2 - R_1$.	Temperature of the air.
(1)	$\begin{cases} T_1 = 246 \cdot 0 \\ T_2 = 244 \cdot 5 \end{cases}$	$\begin{cases} R_1 = 62 \cdot 55 \\ R_2 = 64 \cdot 98 \end{cases}$	$2 \cdot 43$	
(2)	$\begin{cases} T_1 = 246 \cdot 5 \\ T_2 = 245 \cdot 0 \end{cases}$	$\begin{cases} R_1 = 62 \cdot 61 \\ R_2 = 65 \cdot 00 \end{cases}$	$2 \cdot 39$	63
(3)	$\begin{cases} T_1 = 247 \cdot 1 \\ T_2 = 246 \cdot 6 \end{cases}$	$\begin{cases} R_1 = 62 \cdot 65 \\ R_2 = 65 \cdot 23 \end{cases}$	$2 \cdot 58$	64
(4)	$\begin{cases} T_1 = 248 \cdot 4 \\ T_2 = 247 \cdot 4 \end{cases}$	$\begin{cases} R_1 = 62 \cdot 64 \\ R_2 = 65 \cdot 26 \end{cases}$	$2 \cdot 62$	
(5)	$\begin{cases} T_1 = 248 \cdot 8 \\ T_2 = 248 \cdot 5 \end{cases}$	$\begin{cases} R_1 = 62 \cdot 61 \\ R_2 = 65 \cdot 14 \end{cases}$	$2 \cdot 53$	$64 \cdot 5$
(6)	$\begin{cases} T_1 = 249 \cdot 2 \\ T_2 = 248 \cdot 0 \end{cases}$	$\begin{cases} R_1 = 62 \cdot 59 \\ R_2 = 65 \cdot 05 \end{cases}$	$2 \cdot 46$	
(7)	$\begin{cases} T_1 = 249 \cdot 3 \\ T_2 = 249 \cdot 0 \end{cases}$	$\begin{cases} R_1 = 62 \cdot 65 \\ R_2 = 65 \cdot 10 \end{cases}$	$2 \cdot 45$	
(8)	$T_1 = 249 \cdot 5$	$\begin{cases} R_1 = 62 \cdot 50 \\ R_2 = 64 \cdot 97 \end{cases}$	$2 \cdot 47$	64

Hence we obtain

$$(T) = 247^\circ \cdot 6 \text{ (F.)},$$

$$(R) = 63^\circ \cdot 81,$$

$$(T) - (R) = 183^\circ \cdot 79 ;$$

and hence, for the mean of these eight experiments,

$$\theta = 17^\circ \cdot 6 \text{ (C.)},$$

$$t = 102^\circ \cdot 1 ;$$

and the mean value of

$$R_2 - R_1 = 2 \cdot 49.$$

This is for the time of 300 beats; therefore for 500 beats we have, as a mean value,

$$R_2 - R_1 = 4 \cdot 16.$$

III. Same Disc of *Glass*.

Time . . . . . $=300$ beats.

Height of barometer $=30\cdot3$ inches.

$=\ \cdot76$ metre.

Number of experiment.	Temperature of the radiating surface.	Readings of the calorimeter.	Difference of the readings $=R_2-R_1$.	Temperature of the air.
(1)	$\begin{cases} T_1=378\cdot5 \\ T_2=378\cdot5 \end{cases}$	$\begin{cases} R_1=60\cdot81 \\ R_2=66\cdot25 \end{cases}$	$5\cdot44$	$6\overset{\circ}{2}$
(2)	$\begin{cases} T_1=380\cdot0 \\ T_2=380\cdot5 \end{cases}$	$\begin{cases} R_1=61\cdot02 \\ R_2=66\cdot20 \end{cases}$	$5\cdot18$	
(3)	$\begin{cases} T_1=381\cdot5 \\ T_2=380\cdot0 \end{cases}$	$\begin{cases} R_1=58\cdot53 \\ R_2=63\cdot74 \end{cases}$	$5\cdot21$	61
(4)	$\begin{cases} T_1=380\cdot0 \\ T_2=381\cdot3 \end{cases}$	$\begin{cases} R_1=58\cdot90 \\ R_2=64\cdot10 \end{cases}$	$5\cdot20$	
(5)	$\begin{cases} T_1=384\cdot0 \\ T_2=382\cdot5 \end{cases}$	$\begin{cases} R_1=59\cdot13 \\ R_2=64\cdot55 \end{cases}$	$5\cdot42$	62
(6)	$T_1=378\cdot0$	$\begin{cases} R_1=59\cdot36 \\ R_2=64\cdot74 \end{cases}$	$5\cdot38$	
(7)	$\begin{cases} T_1=375\cdot5 \\ T_2=376\cdot0 \end{cases}$	$\begin{cases} R_1=59\cdot63 \\ R_2=65\cdot10 \end{cases}$	$5\cdot47$	

Taking the means, we obtain

$$(T)=379°\cdot70 \ (F.)$$

$$(R)=\ \ 62°\cdot29,$$

$$(T)-(R)=317°\cdot41\ ;$$

and hence from the mean of these seven experiments we have

$$\theta=\ \ 16°\cdot6 \ (C.),$$

$$t=175°\cdot4,$$

$$R_2-R_1=\ \ \ 5\cdot33 \text{ for } 300 \text{ beats,}$$

and therefore

$$R_2-R_1=\ \ \ 8\cdot88 \text{ for } 500 \text{ beats.}$$

13. Recurring to equation (2.), art. 3, and substituting the numerical values for A_1 and B_1, adopted by DULONG and PETIT, we have

$$Q=m\{2\cdot037a^\theta(a^t-1)+\cdot00919p^{\cdot45}t^{1\cdot233}\}\ ;$$

or putting the last term in a form which may in some cases be rather more convenient for numerical calculation, we shall have

$$Q=m\{2\cdot037a^\theta(a^t-1)+\cdot00793\left(\frac{p}{\cdot72}\right)^{\cdot45}t^{1\cdot233}\}\ .\quad . \quad . \quad . \quad . \quad . \quad (6.)$$

Our first object is the determination of *m*, and for this purpose we must substitute

successively in this equation, the values of θ, t, and p above given as mean values in the series of experiments I., II., and III., and for Q we substitute the corresponding mean values of $R_2 - R_1$, the increase of temperature of the calorimeter due to the radiation upon its lower surface. The quantity of heat represented by Q will thus be measured numerically by the number of FAHRENHEIT degrees by which the temperature of the water in the instrument is augmented. This numerical value may be represented by Q^0. Its proper numerical value will be introduced hereafter.

After tedious numerical calculation, in which I feel satisfied there is no material error, the following values of m were derived from the three series respectively.

$$\text{I. } t = 47°\!\cdot\!7 \text{ (C.)}, \quad m_1 = \frac{1\cdot52}{1\cdot98} = \cdot77;$$

$$\text{II. } t = 101°\!\cdot\!6 \text{ (C.)}, \quad m_2 = \frac{4\cdot16}{5\cdot18} = \cdot80;$$

$$\text{III. } t = 175°\!\cdot\!4 \text{ (C.)}, \quad m_3 = \frac{8\cdot88}{11\cdot33} = \cdot78;$$

$$\text{Mean value of } m = m_0 = \cdot783.$$

I have above stated the various corrections which ought to be applied to the values of $R_2 - R_1$, or of Q in the last formula. They will lead to a corrected value of m_0, which we may now proceed to find. These corrections are as follows:—

(1) *Correction due to the influence of the external air.*—It will be remarked that the difference between this temperature and θ, that of the calorimeter in the preceding experiments, is very small. The correction is inappreciable.

(2) *The correction due to the central orifice in the glass disc* (art. 8).—In the formula of that article

$$\frac{\varrho^2}{r^2} = \cdot006.$$

The ratio $\dfrac{c}{\varpi}$ is found from the experiments which determine the whole radiation in air from the surfaces of mercury and glass to be somewhat different for different temperatures. It may be taken as follows in the mean of each of the preceding series:—

$$\text{In \quad I. } \frac{c}{\varpi} = \cdot6 \text{ nearly,}$$

$$\text{In \quad II. } \frac{c}{\varpi} = \cdot7 \text{ nearly,}$$

$$\text{In III. } \frac{c}{\varpi} = \cdot8 \text{ nearly.}$$

Hence the formula (3.) of art. 8 becomes

$$\text{In \quad I. } Q^0 = Q_1 \; \{1 + \cdot0064(1 - \cdot6)\}$$
$$= 1\cdot52\{1 + \cdot0025\},$$
$$\text{In \quad II. } Q^0 = 4\cdot16\{1 + \cdot0019\},$$
$$\text{In III. } Q^0 = 8\cdot88\{1 + \cdot0013\}.$$

(3) *Correction due to the thickness of the disc.*—This correction must be applied, like the last, to the mean values of Q derived from each of the series of experiments I., II., and III.   Now in

$$\text{I.} \begin{cases} t_1 = 148° \text{ (F.) nearly,} \\ \dfrac{c}{\varpi} = \cdot 6 \text{ (as in (2)).} \end{cases}$$

$$\text{II.} \begin{cases} t_1 = 248° \text{ (F.),} \\ \dfrac{c}{\varpi} = \cdot 7. \end{cases}$$

$$\text{III.} \begin{cases} t_1 = 380° \text{ (F.),} \\ \dfrac{c}{\varpi} = \cdot 8. \end{cases}$$

Also we may take as a mean value of τ for I., II. and III.,

$$\tau = 63° \text{ nearly.}$$

The thickness of the glass plate we have

$$h = \tfrac{1}{16} \text{ inch,}$$
$$= \cdot 005 \text{ foot;}$$

and for glass, I assume

$$\frac{k}{c} = 1 \cdot 0 *;$$

and therefore for our glass plate the values of $\dfrac{hc}{k} \cdot \dfrac{\varpi}{c}$ are

$$\cdot 008 \text{ in experiment I.}$$
$$\cdot 007 \text{ in experiment II.}$$
$$\cdot 006 \text{ in experiment III.}$$

Also the values of $1 - \dfrac{\tau}{t_1}$ $\left(\text{or of } 1 - \dfrac{(R)}{(T)} \text{ in the experiments}\right)$ become

$$\cdot 6 \text{ in I.}$$
$$\cdot 75 \text{ in II.}$$
$$\cdot 83 \text{ in III.}$$

and the formula (4.), art. 9, becomes in

$$\text{I.}\quad Q^0 = 1 \cdot 52 \{1 + \cdot 0048\}.$$
$$\text{II.}\quad Q^0 = 4 \cdot 16 \{1 + \cdot 0052\}.$$
$$\text{III.}\quad Q^0 = 8 \cdot 88 \{1 + \cdot 0050\}.$$

(4) We have finally to take the correction investigated in art. 10.   On account of it we must take

$$Q = Q_1 \left\{ 1 + \frac{\beta}{a} \right\}.$$

* I have not determined the conducting power of glass directly by experiment.   I have assumed it to be the same as for the most compact igneous rock, as given in my former memoir.

Hence, putting $\frac{\beta}{a} = \frac{\cdot 21}{5 \cdot 5} = \cdot 038$, we have

$$\text{I.} \quad Q^0 = 1 \cdot 52 \{1 + \cdot 038\}.$$
$$\text{II.} \quad Q^0 = 4 \cdot 16 \{1 + \cdot 038\}.$$
$$\text{III.} \quad Q^0 = 8 \cdot 88 \{1 + \cdot 038\}.$$

14. Applying all these corrections, we have

$$Q^0 = Q_1^0 \left\{ 1 + \frac{\varrho^2}{r^2} \left(1 - \frac{c}{\varpi} \right) + \left(1 - \frac{\tau}{t_1} \right) \frac{hc}{k} \cdot \frac{\varpi}{c} + \frac{\beta}{a} \right\} \quad \cdots \cdots \quad (7.)$$

$$= Q_1^0 \{1 + E\} \text{ suppose.}$$

Consequently the observed values of Q (or $R_2 - R_1$), the mean results of the series I., II., III. respectively, must be increased in the ratio

$$1 + E_1 : 1 \text{ in series I.,}$$
$$1 + E_2 : 1 \text{ in series II.,}$$
$$1 + E_3 : 1 \text{ in series III.,}$$

when we substitute them in equation (6.) for the purpose of determining m_1, m_2, and m_3; or since an alteration in Q will produce a proportional change in m (as is evident from the equation), we must increase m_1, m_2, and m_3 in the above ratios respectively; *i. e.* for their mean value m_0, we shall have

$$m_0 = \cdot 783 \{1 + \tfrac{1}{3}(E_1 + E_2 + E_3)\}.$$

Now taking the sum of the corrections indicated in the above expression for Q, in each of the three series separately, we have

$$E_1 = \cdot 0453$$
$$E_2 = \cdot 0451$$
$$E_3 = \cdot 0443$$
$$\frac{E_1 + E_2 + E_3}{3} = \cdot 045;$$

and hence we have, finally,

$$m_0 = \cdot 783 \{1 + \cdot 045\}$$
$$= \cdot 818.$$

Finally, substituting this value of m in the formula (6.) of article 13, we have

$$Q^0 = 1 \cdot 666 \, a^\theta (a^t - 1) + \cdot 00648 \left(\frac{p}{\cdot 72} \right)^{\cdot 45} t^{1 \cdot 233} \quad \cdots \cdots \quad (8.)$$

We may now compare the observed quantities of heat radiating from a surface of glass, as ascertained by the above three series of experiments, with the calculated values given by this formula. In doing this, it must be recollected that the formula gives the *whole* quantity of heat which radiates from the given glass surface, whereas the *observed* quantity is that which falls on the calorimeter. The correction E_3 must therefore be omitted, and the above formula becomes

$$Q^0 = 1 \cdot 610 \, a^\theta (a^t - 1) + \cdot 00626 \left(\frac{p}{\cdot 72} \right)^{\cdot 45} \cdot t^{1 \cdot 233}.$$

Series of experiments.	Values of θ (C.).	Values of t (C.).	Calculated values of Q.	Observed values of Q.	Differences.
I.	16·6	47·7	1·56	1·52	0·04
II.	17·6	102·1	4·09	4·16	−0·07
III.	16·6	175·4	8·95	8·88	0·07

The small amount of the differences registered in the last column are sufficient to indicate the very approximate accuracy of the formula for at least a considerable range of temperature, as indicated by the values of t in the third column.

15. I now proceed to detail three other series of experiments similar to the above, with a *disc of Chalk* made as dry as possible.

IV. Disc of *Dry Chalk*.

Duration of each experiment $= 1000$ beats.

Height of the barometer . . $= 30\cdot33$ inches.

$\qquad\qquad\qquad\qquad = \quad\cdot77$ metre.

Number of experiment.	Temperature of the radiating surface.	Readings of the calorimeter.	Difference of the readings $= R_2 - R_1$.	Temperature of the air.
(1)	$T = 135\cdot2$	$\left\{ \begin{array}{l} R_1 = 57\cdot92 \\ R_2 = 60\cdot57 \end{array} \right\}$	2·65	60·5
(2)	$T = 135\cdot6$	$\left\{ \begin{array}{l} R_1 = 58\cdot95 \\ R_2 = 61\cdot60 \end{array} \right\}$	2·65	
(3)	$T = 135\cdot6$	$\left\{ \begin{array}{l} R_1 = 59\cdot52 \\ R_2 = 62\cdot17 \end{array} \right\}$	2·65	61
(4)	$T = 135\cdot5$	$\left\{ \begin{array}{l} R_1 = 59\cdot28 \\ R_2 = 61\cdot99 \end{array} \right\}$	2·71	61
(5)	$T = 136\cdot4$	$\left\{ \begin{array}{l} R_1 = 59\cdot25 \\ R_2 = 61\cdot76 \end{array} \right\}$	2·51	61·5

Hence, adopting the same notation as above for the mean values, we have

$$(T) = 135°\cdot66 \text{ (F.)},$$
$$(R) = \ 60°\cdot30 \text{ (F.)} = 15°\cdot7 \quad (C.) = \theta,$$
$$(T) - (R) = \ 75°\cdot36 \qquad = 41°\cdot66 \ (C.) = t.$$

Also, taking the mean of the " Differences,"

$$R_2 - R_1 = 2\cdot66 \text{ for } 1000 \text{ beats},$$
$$= 1\cdot33 \text{ for } \ 500 \text{ beats}.$$

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V. Same Disc of *Chalk*.

Duration of each experiment $=500$ beats.

Height of the barometer . $=30\cdot22$ inches.

$=$ $\cdot767$ metre.

Number of experiment.	Temperature of the radiating surface.	Readings of the calorimeter.	Difference of the readings $=R_2-R_1$.	Temperature of the air.
(1)	$T=213\cdot0$	$\begin{cases} R_1=58\cdot85 \\ R_2=61\cdot76 \end{cases}$	$2\cdot91$	
(2)	$T=212\cdot7$	$\begin{cases} R_1=58\cdot44 \\ R_2=61\cdot36 \end{cases}$	$2\cdot92$	60
(3)	$T=213\cdot5$	$\begin{cases} R_1=58\cdot50 \\ R_2=61\cdot34 \end{cases}$	$2\cdot84$	
(4)	$\begin{cases} T=214\cdot4 \\ T=215\cdot5 \end{cases}$	$\begin{cases} R_1=58\cdot14 \\ R_2=61\cdot22 \end{cases}$	$3\cdot08$	$60\cdot5$
(5)	$T=216\cdot2$	$\begin{cases} R_1=58\cdot43 \\ R_2=61\cdot39 \end{cases}$	$2\cdot96$	$61\cdot5$

Hence we have

$$(T)=214^\circ\cdot2 \text{ (F.)},$$
$$(R)=\ 59^\circ\cdot94=15^\circ\cdot55 \text{ (C.)}=\theta,$$
$$(T)-(R)=154^\circ\cdot26=85^\circ\cdot7 \quad \text{(C.)}=t.$$

Also, taking the mean value of the " Differences,"
$$R_2-R_1=2\cdot94.$$

VI. Same Disc of *Chalk*.

Duration of each experiment . $=400$ beats.

Height of the barometer   .   . $=30\cdot22$ inches.

$=$ $\cdot767$ metre.

Number of experiment.	Temperature of the radiating surface.	Reading of the calorimeter.	Difference of the readings $=R_2-R_1$.	Temperature of the air.
(1)	$T=295\cdot5$	$\begin{cases} R_1=58\cdot41 \\ R_2=62\cdot68 \end{cases}$	$4\cdot27$	
(2)	$T=290\cdot0$	$\begin{cases} R_1=58\cdot19 \\ R_2=62\cdot25 \end{cases}$	$4\cdot06$	$60\cdot5$
(3)	$T=289\cdot5$	$\begin{cases} R_1=58\cdot21 \\ R_2=62\cdot25 \end{cases}$	$4\cdot04$	$60\cdot5$
(4)	$T=288\cdot5$	$\begin{cases} R_1=58\cdot30 \\ R_2=62\cdot28 \end{cases}$	$3\cdot98$	
(5)	$T=289\cdot0$	$\begin{cases} R_1=58\cdot53 \\ R_2=62\cdot60 \end{cases}$	$4\cdot07$	$61\cdot5$

Hence we have
$$(\text{T}) = 290°\!\cdot\!5 =$$
$$(\text{R}) = 60°\!\cdot\!35 \ (\text{F.}) = 15°\!\cdot\!75 \ (\text{C.}) = \theta,$$
$$(\text{T}) - (\text{R}) = 230°\!\cdot\!15 \ (\text{F.}) = 127°\!\cdot\!85 \ (\text{C.}) = t;$$

and for the mean value
$$R_2 - R_1 = 4\!\cdot\!08 \text{ for 400 beats,}$$
$$= 5\!\cdot\!10 \text{ for 500 beats.}$$

16. We may now apply these results to obtain the expression for the quantity of heat emanating from our chalk disc. Since its area is the same as that of the glass disc, the second term of the expression (2) of article 3 will be the same for all substances, and therefore the same as that already determined for glass. Thus we have

$$Q = A a^\theta (a^t - 1) + \cdot00648 \left(\frac{p}{\cdot72}\right)^{\cdot45} t^{1\cdot233}. \quad \ldots \quad \ldots \quad (9.)$$

Q here represents the whole quantity of heat which would radiate under the conditions of the experiment, from a disc of chalk of the given area; but the observed values of this quantity, as represented by $R_2 - R_1$ in the previous experiments, is the measure of the heat only which falls on the calorimeter, and consequently requires the two following corrections:—

(1) The temperature of the surface of the disc was obtained from that of the mercury occupying a shallow central hollow of which the diameter was 1·5 inch, that of the whole disc being 5·5 inches. Throughout this small central circle the radiation took place from mercury instead of chalk, and consequently a correction must be made similar to the correction investigated in article 8. Here we have

$$\frac{\rho^2}{r^2} = \cdot074;$$

and in the series of experiments

IV. $\frac{c}{\varpi} = \cdot58$ nearly.

V. $\frac{c}{\varpi} = \cdot62.$

VI. $\frac{c}{\varpi} = \cdot70.$

Hence, so far as depends on this correction,
$$Q^0 = (R_2 - R_1)\left\{1 + \frac{\rho^2}{r^2}\left(1 - \frac{c}{\varpi}\right)\right\}$$
$$= 1\!\cdot\!33\{1 + \cdot031\} \text{ in series IV.}$$
$$= 2\!\cdot\!94\{1 + \cdot028\} \text{ in series V.}$$
$$= 5\!\cdot\!10\{1 + \cdot022\} \text{ in series VI.}$$

(2) All the heat which emanates from the surface of the disc does not fall on the bottom of the calorimeter, as explained in article 10. Consequently a correction also
<center>3 H 2</center>

is required, such as is investigated in that article. Its amount is the same in all the experiments. Hence, on account of this correction, we have

$$Q^0 = (R_2 - R_1)\left\{1 + \frac{\beta}{a}\right\} \text{ (art. 10),}$$

$$= 1\cdot33\{1 + \cdot038\} \text{ in series IV.}$$

$$= 2\cdot94\{1 + \cdot038\} \text{ in series V.}$$

$$= 5\cdot10\{1 + \cdot038\} \text{ in series VI.}$$

Taking the sum of these two corrections in each series respectively,

$$Q^0 = 1\cdot33(1\cdot069) = 1\cdot42 \text{ in series IV.}$$

$$Q^0 = 2\cdot94(1\cdot066) = 3\cdot13 \text{ in series V.}$$

$$Q^0 = 5\cdot10(1\cdot060) = 5\cdot41 \text{ in series VI.}$$

These are the corrected values which are to be substituted for Q in the formula (9.). After the requisite numerical calculation, we thus obtain the following three values of A:

$$A = 1\cdot781 \text{ from series IV.}$$

$$A = 1\cdot420 \text{ from series V.}$$

$$A = 1\cdot444 \text{ from series VI.}$$

Mean value $= 1\cdot548$.

It will be observed that the first of these values of A is considerably larger than the two others. It is that which corresponds to the smallest value of the difference of temperature denoted by t, or $R_2 - R_1$, and small values of this quantity are unfavourable for the accurate determination of A, since, in such case, a small error in the experimental result will lead to a considerable error in the value of A. The above mean value, $1\cdot548$, is probably too large, and I should rather adopt $1\cdot5$ as a more probable value, thus giving greater weight to the two last determinations than to the first. The formula (9.) then becomes

$$Q = 1\cdot500\, a^\theta (a^t - 1) + \cdot00648 \left(\frac{p}{\cdot72}\right)^{\cdot45} t^{1\cdot233}. \quad \ldots \ldots \quad (10.)$$

Comparing the values of Q obtained from this formula, with the values of $R_2 - R_1$ as corrected above, we have the following results:—

Comparison of the Observed and Calculated Values of Q for *Dry Chalk*.

Series of experiments.	Values of θ (C.).	Values of t (C.).	Calculated values of Q.	Corrected observed values of Q.	Differences.
IV.	15·7	41·66	1·29	1·42	·13
V.	15·55	85·70	3·19	3·13	·06
VI.	15·75	127·85	5·46	5·41	·05

17. Three similar series of experiments were made with a disc of *New Red Sandstone*. It will be sufficient, I conceive, to give the results without details, which are exactly

similar to those given in the preceding series.   Calling these series VII., VIII., IX., the values obtained for A are

$$A=1\cdot526 \text{ from VII.}$$
$$A=1\cdot508 \text{ from VIII.}$$
$$A=1\cdot341 \text{ from IX.}$$

Mean value of A=1·459, and the general formula becomes

$$Q^0=1\cdot459a^\theta(a^t-1)+\cdot00648\left(\frac{p}{\cdot72}\right)^{\cdot45}t^{1\cdot233}. \quad . \quad . \quad . \quad . \quad . \quad (11.)$$

Comparison of Observed and Calculated Values of Q for dry *New Red Sandstone*.

Series of experiments.	Values of θ (C.).	Values of t (C.).	Calculated values of Q.	Corrected observed values of Q.	Differences.
VII.	16·22	45·86	1·44	1·47	0·03
VIII.	15·18	87·83	3·24	3·29	0·05
IX.	16·95	141·57	6·24	6·15	−0·09

18. From two series of experiments (X. and XI.) on a disc of *Sandstone* used for building purposes, I obtained the following values of A:—

$$A=1\cdot620 \text{ from series X.}$$
$$A=1\cdot475 \text{ from series XI.}$$

In X. the temperature t was $= 93^\circ\cdot7$ (C.),
In XI. the temperature t was $=151^\circ\cdot14$ (C.).

The mean value of A=1·547, and our general formula becomes

$$Q^0=1\cdot547a^\theta(a^t-1)+\cdot00648\left(\frac{p}{\cdot72}\right)^{\cdot45}t^{1\cdot233}. \quad . \quad . \quad . \quad . \quad . \quad (12.)$$

19. Two other series of experiments (XII. and XIII.) were made in a similar manner, with a disc of limestone, the surface of which was highly *polished*.

$$A=1\cdot660 \text{ from series XII.}$$
$$A=1\cdot513 \text{ from series XIII.}$$

Mean value of A=1·586, the value of t being

$$97^\circ\cdot65 \text{ (C.) in XII.}$$
$$155^\circ\cdot1 \text{ (C.) in XIII.}$$

The general formula becomes

$$Q^0=1\cdot586a^\theta(a^t-1)+\cdot00648\left(\frac{p}{\cdot72}\right)^{\cdot45}t^{1\cdot233}. \quad . \quad . \quad . \quad . \quad . \quad (13.)$$

20. Two similar series (XIV. and XV.) were made with the same disc, the radiation taking place from its *unpolished* surface.   The following values were obtained:—

$$A=2\cdot060 \quad . \quad . \quad . \quad . \quad t= 63\cdot5 \text{ (C.)}.$$
$$A=2\cdot161 \quad . \quad . \quad . \quad . \quad t=125\cdot7 \text{ (C.)}.$$

Mean value of $A = 2 \cdot 110$; and therefore

$$Q^0 = 2 \cdot 110 a^0 (a^t - 1) + \cdot 00648 \left(\frac{p}{\cdot 72}\right)^{\cdot 45} t^{1 \cdot 233}. \quad \ldots \quad (14.)$$

21. It only remains to determine the capacity for heat of the calorimeter, and so to modify the numerical values of the coefficients in the preceding formulæ as to obtain numerical values of Q in which unity shall represent the quantity of heat required to raise a given weight of distilled water *one degree Centigrade*. I shall assume this given weight to be 1000 grains.

In the first place it was necessary to determine the weight of the distilled water used in the experiments, and that of the tin vessel containing it. For this purpose the vessel was filled with water while the bulb of its thermometer was still inserted in it. The thermometer was then removed, and the vessel and contained water was found to weigh

<div align="center">8524 grs.</div>

When empty and dry, the vessel itself weighed

<div align="center">3170·5 grs.,</div>

and consequently the weight of water was

<div align="center">5353·5 grs.</div>

The tin plate of which the vessel was formed consisted of thin sheet iron coated with tin, the weight of which was $\frac{1}{10}$th of that of the iron. Also the capacity for heat of sheet iron may be taken $= \cdot 11$, and that of tin $= \cdot 06$, the capacity of water being unity. Let w_1 and w_2 be the weights of iron and tin respectively in the tin plate, and c its capacity for heat. Then if $W =$ the weight of the vessel,

$$w_1 + w_2 = W,$$

$$w_2 = \frac{w_1}{10};$$

also

$$w_1 = \frac{10}{11} W, \text{ and } w_2 = \frac{1}{11} W,$$

and the weight of water equivalent to w_1 of iron and w_2 of tin,

$$= w_1 (\cdot 11) + w_2 (\cdot 06)$$
$$= W(\cdot 1 + \cdot 0055)$$
$$= 319 \text{ grs.}$$

Another small correction is required for the bulb of the thermometer and the small portion of the glass tube inserted within the vessel of the calorimeter, and the mercury contained in the thermometer. The volumes of the glass and mercury were carefully estimated, and thence their weights ascertained. It was then easy to estimate approximately their capacity for heat, which was found to be equal to that of about 17 grains of water. This, being added to the correction of the last paragraph, gives 336 grains as the equivalent quantity of water to be added to the 5353·5 grains contained in the

calorimeter. Hence the heat communicated to the calorimeter in each experiment may be considered to have been employed in raising by the observed amount in the observed time the temperature of 5689·5 grains of distilled water. Taking 1000 grains as the unit of weight, this weight will be represented by the number 5·6895.

Again, the time corresponding to 500 beats of the watch employed (the time to which all the experimental results were reduced) was $=3\cdot3333$ minutes. Now the above quantity of water was raised Q^0 in that time, or $\dfrac{Q^0}{3\cdot3333}$ in one minute, which we may take as the unit of time. Consequently the heat would have raised a unit of water (1000 grs.) $\dfrac{Q^0}{3\cdot3333}\cdot5\cdot6895$ degrees in one minute; or if Q^1 denote the numerical value of the heat communicated to the calorimeter with the thermal unit above mentioned, we have

$$Q^1=Q^0\cdot\frac{5\cdot6895}{3\cdot3333}$$
$$=1\cdot706\,Q^0.$$

Also the area of the radiating surfaces was 23·758 square inches, and therefore if Q denote the quantity of heat emanating from a *square foot*,

$$Q=Q^1\cdot\frac{144}{23\cdot758},$$
$$Q^1=6\cdot060;$$

or finally,

$$Q=10\cdot338\,Q^0.$$

Hence in each of the preceding expressions for Q^0, we must multiply the numerical factor of each term by 10·338, and we shall obtain the numerical value of the quantity of heat which would emanate in *one minute* from a *square foot* of the proposed surface for any assigned value of the temperature denoted by θ (Cent.), and the difference of temperatures denoted by t (Cent.), the *unit of heat* being that heat which would raise the temperature of 1000 grains of distilled water 1° (Cent.). Our formulæ thus become for

Glass.

$$Q=9\cdot566\,a^{\theta}(a^t-1)+\cdot03720\left(\frac{p}{\cdot72}\right)^{\cdot45}t^{1\cdot233}.$$

Dry Chalk.

$$Q=8\cdot613\,a^{\theta}(a^t-1)+\cdot03720\left(\frac{p}{\cdot72}\right)^{\cdot45}t^{1\cdot233}.$$

Dry New Red Sandstone.

$$Q=8\cdot377\,a^{\theta}(a^t-1)+\cdot03720\left(\frac{p}{\cdot72}\right)^{\cdot45}t^{1\cdot233}.$$

Sandstone (building stone).

$$Q = 8 \cdot 882 \, a^\theta(a^t - 1) + \cdot 03720 \left(\frac{p}{\cdot 72}\right)^{\cdot 45} t^{1 \cdot 233}.$$

Polished Limestone.

$$Q = 9 \cdot 106 \, a^\theta(a^t - 1) + \cdot 03720 \left(\frac{p}{\cdot 72}\right)^{\cdot 45} t^{1 \cdot 233}.$$

Unpolished Limestone (same block).

$$Q = 12 \cdot 808 \, a^\theta(a^t - 1) + \cdot 03720 \left(\frac{p}{\cdot 72}\right)^{\cdot 45} t^{1 \cdot 233}.$$

The approximate equality of the different values of Q for these substances under similar conditions, is what would have scarcely been anticipated. The value of Q, however, for the surface of silver, as shown by DULONG and PETIT, is very much smaller than the preceding values. Such appears also to be the case with mercury and polished steel. But in this last case the surface of the steel and its radiating power are affected by high temperatures, at which also an amount of vaporization takes place from the surface of mercury, which affects the indications of the instrument.