FULL RADIATION.

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Part 1.

Historical Introduction.

The study off Full Radiation goes back, roughly to 1791, at which time the "Fluid Theory of Heat" was still believed. The first important investigations seem to have been carried out by Prevost, of Geneva. Of course, there is no mention of such terms as "Full Radiation" in Prevost's work, but his investigations seem to be a starting point from which to build up a history of the subject. Experiments on losses of heat had been done previously by Newton, in 1664 and at the beginning of the 18th century. In 1701, he had made experiments on the rate of cooling of a hot body, finding ~~that~~ it to be proportional to the excess of temperature of the body over the surroundings. This law of Newton's was later found to be erroneous when dealing with great temperature differences. In fact Herschel, basing his calculations on this law, estimated the temperature of the sun many times too great.

In 1791-2, Prevost published his famous "Theory of Exchanges" to explain the effect observed in 1783, by Pictet, commonly called "the Reflection of Cold". This was, that when a lump of ice is placed at the centre of curvature of a concave mirror, and a thermometer is placed symmetrically at the focus of a concave mirror placed symmetrically opposite, this thermometer indicated a fall in temperature.

The following is roughly the main line of Prevost's argument, translated from his paper. He first considered equilibrium as applied to "un fluid tel que le feu". He claimed not to be considering the actual nature of the heat, "whether material or immaterial, contiguous or otherwise the mobility of the "moles de feu", or their means of motion, whether this is vibratory or progressive". All these things he says are not important and tend to make the imagination run wild and to lose sight of the important and true causes. The real constitution of the fluid is based on the theory of 'discrete fluids', already known. Heat is a discrete fluid, elastic on account of its expansive force and affects the movements of the particles caused by the impulse of the fluid. Heat transference is instantaneous, and sensibly rectlinear. Light radiation is a particular kind of fluid. It never stops the path of another beam of light, because beams of light can cross one another without interference, and therefore the particles thereof must be far apart compared with the diameters of the molecules. What is true of light is true of all radiation fluids. Free heat radiation is a very rare kind of fluid, since the particles of it do not mutually interact. It cannot conform to ordinary physical principles, for one says normally that heat itself is coercible and yet one says that contiguous portions, when their temperatures are the same, are mutually restrained. These expressions are not exact. Really the heat from one portion can never stop the heat of another, since two "feu"give each other mutual passage. We must therefore conclude that the two portions give and receive mutually to and from one another in the same way that two masses rebound from one another,after elastic impact.

Exactly what Prevost means by coercible is not clear. It seems that a coercible fluid is one which can,in general language be made to go where one wants. Heat radiation cannot be exactly made to go in the direction one would wish. However, the main thing for our purpose ,is that he realised the presence of a nearby similar "fluid" could not prevent the flow of the "fluid",and he assumed therefore that the apparent equilibrium between two bodies at the same temperature does not mean a state of absolute equilibrium but more a state of statistical equilibrium between the two bodies.

Prevost illustrates his remarks further by this example... "suppose we have two cubes,enclosed in an impermeable enclosure with the two adjacent sides placed together to form a parallelopiped,the six sides of which are solid and without spaces. The outside space is perfectly evacuated ,and into one cube is placed some heat. It makes continuous exchanges and one can confirm,at any instant how much heat is being received by each part,and the state of the heat. While things are so there is no question of anything but equilibrium,'relative equilibrium'. Now suppose into one cube is poured some more heat.The exchanges are not unequal,and one receives,say,eleven particles while it gives back ten..""absolute equilibrium" is where one receives exactly what the other 'laisse ecshapper'

Relative equilibrium is equilibrium between two parts only.." Later he goes on to say "the 'feu'~~at~~ of several portions at the same temperature is in equilibrium.

Prevost's ideas were the first on the subject of "Statistical Equilibrium". Previous to this work ,a radiating body at a higher temperature had been considered as giving heat to the surruondings, but not to be receiving ~~it~~ it from the surroundings ,and when by virtue to the heat lost to the surroundings, the body at the higher temperature reached the same tenperature as that of the surroundings, then heat ceased to flow from the body to the surroundings. Prevost pointed out that the heat possessed by the surroundings could not possibly prevent the body from giving out more heat ,even when the body and the surroundings were at the same temperature, and it was on account of this work by Prevost ,that equilibrium of this kinetic kind was thought of for the first time. Although Prevost does not say so in so many words, it is clear that he considers the radiation from a body,as depending only on the temperature of the body and the nature of the body, and not in any way on the presence of any neighbouring bodies. It is very difficult to make out exactly what is in Prevost's mind at the time of writing. Obviously he considered heat as a fluid consisting of particles,and as temperature as a kind of pressure which caused the fluid to flow from a hot body to a cooler one. This idea of temperature is very interesting for it is still now sometimes said that"Temperature is that which causes heat to flow from a hotter body to a colder one". His paper must have a great impression on the minds of phyicists at the time, for in text-books,"Prevost's Theory of Exchanges" is still quoted.

His view of exchanges does not quite coincide with the present day one,that the emission from a body depends entirely on what takes place within the body,and is not influenced by the surroundings.

After Prevost had published his work, Herschel made a very interesting experiment,which was the first attempt to determine the distribution of energy in a spectrum, although it is doubtful whether Herschel made the experiment with any object in view,or if he did not do it more to see whether the individual components of the sun's rays exhibited heating properties when considered independently as they did when altogether. What he did was to put e thermometer in each of the seven colours of the spectrum, and to observe the temperature to which the thermometer rose. He found that the temperature indicated by the thermometer was different for each of the seven colours,the maximum lying in the red-half of the spectrum. He, noted, also, that the maximum was not definitely fixed,in fact it lay sometimes outside the visible part of the spectrum altogether. It was in this way by placing the thermometer outside the visible part that the invisible radiation, now known as the infra red,was found to exist.

The existence of any invisible radiation was emphatically denied by John Leslie, who asserted that refreagibility must be connected with Visibility, and that the idea of invisible radiation was utterly impossible. His view was that the heating in any spectrum was "direct", and that one part actually "passed on "its heat to the next, perhaps even to the air itself, thus causing a heating effect outside the visible part. He thought that one part was warmed, and then it expanded and passed on its heat to the next part, and when it had given up its heat it contracted again, while the warm part, in its turn, passed on its heat and so on, thus getting a sort of undulatory process. Thus a body radiated heat by the undulations of the air. In spite of the indisputable, discovery, by Ritter of Germany, confirmed by Wollaston, in England that silver muriate is blackened by the invisible rays which extend outside the prismatic spectrum, thus putting beyond all doubt the existence of invisible radiation, Leslie still miantained that his views were correct, in opposition to Herschel, until 1813 when Davy showed that in ordinary air, which had been exhausted to 1/120 of the density of atmospheric air radiation was transmitted three times ~~more~~ as strongly as in the atmospheric air, instead of correspondingly more weakly, as it should do on Leslie's theory.

Although Leslie's views on this subject were wrong, yet his work is of importance and value, because he was the first to give any quantitive information about radiation. He invented two pieces of apparatus named after him, the differential thermometer, and the Leslie-cube, both too well known to need any description.

It was about this time that the fluid thoery of heat was abandoned. In 1803, Rumford made his famous observation on the boring of a cannon-ball and about that time, Davy rubbed two pieces of ice together, and melted them by the process. These two experimenters proved decisively that heat was not a fluid. Unfortunately, no other theory came into being to take the place of the fluid theory and one of the most important questions to be answered at this period was as to the nature of heat. Gradually the similarity between radiant heat and light began to be realised although it was a good many years before the similarity was generally accepted. The following is an extract from Young's Lectures in the year 1807...

"Dr Herschel's experiments have shown us that radiant heat consists of different parts which are differently refrangible and that generally heat is less refrangible than light. This discovery must be allowed to be one of the greatest that have been made since the days of Newton... .. probable that those black, or invisible rays, the violet, blue, green, perhaps the yellow and the red rays of light, and the invisible heat rays constitute seven degrees of the same scale, distinguished from each other into this limited number not by material divisions but by the effects on our senses, and we may conclude that there is some similar relation between the heat and luminous bodies of different kinds..."

Later in the same paper, Young says ."If heat is not a substance it must be a quality and this can only be motion. It was Newton's opinion that heat consists in a minute vibratory motion of the particles of bodies, and that this motion is communicated through an apparent vacuum by the undulations of an elastic medium which is also concerned in the phenomenon of light. If the arguments which have lately been advanced in favour of the undulatory theory of light be deemed valid, there will be still stronger reasons for admitting this doctrine respecting heat, and it will only be necessary to suppose the vibratory undulations principally constituting it to be larger and stronger than those of light, while, at the same time the smaller vibrations of light and even of the blackening rays, derived from still more minute vibrations, may perhaps when sufficiently condensed be concerned in the producing of the effects of heat. These effects, beginning from the blackening rays, which are invisible, are little more perceptible in the violet which still possesses but a faint power of illumination; the green yellow -green affords the most light ; the red gives less light but more heat, while the still larger and less frequent vibrations which have no effect on the senses, may be supposedto give rise to the less refrangible rays, and to constitute the invisible heat."..

Much experimental work was now done on the absorption and transparency of material-in connection with which the names of Melloni, Nobili and Forbes are outstanding. In1831 Nobili and Melloni published their work on the absorption in the sun's spectrum and on the transparency of substances to the invisible radiations, a subject on which Seebeck had already been working . Two years later,Melloni found that different substances had quite different degrees of transparency and on account of this diathermanous property,he explained the different maxima observed by Herschel in his experiment to determine the temperatures of the different colours of the sun's spectrum. At this time then,it was realised that the different maxima in Herschel's experiment were due to the "selective properties" of the thermometer bulb, and also to the fact that the radiator (the sun) was not a full one(in our sense of the word), since in 1814 Fraunhoffer had discovered the spectral lines named after him. No attempt seems to have been made,however, to find a source which gave a complete spectrum, or a receiver which absorbed all the incident radiation although it might be,of course,that in measuring the absorbing properties of the various materials, these experimenters hoped to find a material which was a perfect absorber. Melloni showed experimentally ,that absorption was roughly proportional to the thickness of the material. He also compared the quantities of radiation received from different sources, finding generally that different sources of heat gave rise to different amounts of radiation. He was the first to show that the different reflecting powers depend on the kind of surface, and was independent of the kind of radiation. He also showed that it depended to some extent on the absorbing power of the reflecting ~~surface~~ substance. He verified that heat radiation obeys the same laws of reflection and refraction as light rays, that is, that heat radiation could be bent and reflected according to the laws of light. This similarity was further confirmed by Bartoli,who found that heat radiation could be polarised.

All this experimental work,though no doubt of practical importance, seems to have been marking time while the wave-theory of light was being perfected,and reading the works of the different people written about that time,gives one the impression that they did not wish to commit themselves by expressing a definite opinion. For example this extract from Sir W.Herschel,in 1830,.. "Solar rays possess at least three powers,those of heating, illumination,and effecting chemical constitutions,and these powers, distributed among the differently refrangible rays in such a manner as to show their complete independence of one another"..

The question of the nature of radiant heat now became very important. The undulatory theory of light was almost generally accepted, and on account of the similarity between heat and light ,it seemed to follow that heat radiations should also be a vibratory process. Physicists were divided into two groups; those holding the view that they were similar, and those believing they were not. Ampere belonged to the former and Melloni who had demonstrated their similarity,held the view that they were different.

Melloni's experimental work was continued by Knoblauch. He dealt with ~~it in~~ the subject in exactly the same way as Melloni,but with greater caution in considering sources of error. He worked with better apparatus. His chief works were on " the passage of heat through a diathermanous body", "the emission powers of bodies","the warming of a body by the passage of radiant heat","the creation of heat radiation given out from different surfaces at different temperatures","the creation of different heat sources from light radiation", "different reflecting powers of surfaces"and many more similar subjects. Especially of note among his results is " that the passage of radiation through a diathermanous substance is not dependent on the source" and many other similar results which now seem obvious, were at this time experimentally verified. It was fully realised that different sources of radiation gave rise to quite different spectra. We are, with this realisation slowly approaching the time when the possibility of"Full Radiation" is being realised.

In 1833,Ritchie devised a simple experiment to demonstrate the relationship between emissive and absorptive powers. A Leslie-cube is placed between two bulbs of a differential thermometer and it was shewn that when opposite faces of the cube were,say,blackened and silvered,that no movement in the liquid of the differential thermemoter resulted,if the face of the thermometer opposite to the black face of the cube were silvered,and the one opposite to the silver face blackened.

In 1847,much experimental work was done by Bernard, Fizeau and Foucault on the refraction of heat. All this work was of an experimental nature,and tended to show the similarity between heat radiation and light, although it was not definitely accepted until about 1850.

In 1852, Stokes wrote as follows. .

" Now according to the undulatory theory the nature of light is defined by two things. Its period of vibration and its state of polarisation. To the former corresponds its refrangibility and as far as the eye can judge its colour..."

In the same year Thomson writes...

"...Assumed in this communication that the undulatory thoery of radiant heat and light, according to which the vibrations are performed between certain limits of duration, is true. The chemical rays beyond the violet end of the spectrum consist of undulations of which the full visible vibrations are executed in periods shorter than those of the extreme visible light or than about the eight hundred million-millionths of a second. The periods of vibration of visible light lie between this point and another about double as great, corresponding to the extreme visible red light. The vibrations of the obscure radiant heat beyond the red end are executed in longer periods than this. The longest which has yet been experimentally tested being aboutthe eighty million- millionths of a second"..

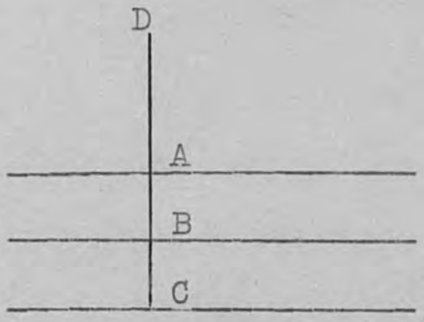
This communication of Thomson's sets beyond all doubt the question of the nature of radiant heat, and the view that heat radiation formed a part of the spectrum of which light was another part, was now generally accepted, as this quotation from Lloyd's"Theory of Light"(1887) shows...

..." It appears then, that sensibility of the eye is confined between much narrower limits than that of the ear. The ratio of the extreme vibrations which effect the eye being only that of 1·58 :1... There is no reason to supposethat the vibrations themselves are confined to these limits..."

A law having an indirect bearing on the subject was given in 1856, by Helmholtz with the enunciation of the law of "Reciprocity", that is that the loss of intensity of a ray of definite colour and polarisation suffered ~~by a ray~~ when it is travelling in one direction through a medium is exactly equal to that suffered by an exactly similar ray travelling in the opposite direction, and pursuing the opposite path."

It was now that the theoretical aspect was extended. The names associated with this are Angstrom, Balfour Stewart and Kirchhoff. In 1855, the first named stated "that a glowing substance must send out all the light which it absorbs at a lower temperature", which statement is the beginning of Prevost's theory carried further some four years later by the other two named. In 1859, Balfour Stewart published a paper entitled" the Absorption of a Plate equals its Radiation, and that for every description of Heat". To explain this, he made the assumption that it is at least possible for a body to emit and absorb the same wavelength and, moreover, that it is possible for a mirror to reflect perfectly all wavelengths. the following is from his paper...

"A more vivid demonstration may be given thus. Let AB",



BC, be two contiguous, equal and similar plates in the interior of a substance of indefinite extent, kept at a uniform temperature. The accumulated radiation from the interior impinges on the upper plate; let us take the portion which falls on the particles A in the direction DA. This ray in passing from A to B will have been partly absorbed by the substance between A and B; but the radiation of the upper plate, being equal to its absorption since the temperature remains the same, the ray will have been just as much recruited by the united radiation of the particles between A and B as it was diminished by their absorption. It will therefore reach B with the same intensity as it had at A. But the <u>quality</u> of the ray at B will also be the same as the quality at A. For if it were different then either a greater or less portion would be absorbed in its passage from B to C than was absorbed of the equally intense ray at A in its passage between A and B. The amount of heat absorbed by the particles between B and C would therefore be different from the amount absorbed by the particles between A and B. But this cannot be, for on hypothesis of an equal and independent radiation of each particle, the radiation of the particles between B and C is equal to that of the particles between A and B and their absorption equals their radiation.

Hence the radiation impinging on B in the directionDB must be equal in quality as well as quantity to that impinging on A and consequently the radiation of the particles between A and B must be equal to the absorption as regards quality as well as quantity. That is this equality between radiation and absorption must hold for every description of heat.

Balfour Stewart and Kirchhoff individually extended Prevost's theory to include the components of the radiation. As we know, Prevost considered the equilibrium of the radiation as a whole and thought nothing about the individual components. The following is an extract from the former's "Elementary Treatise on Heat", containing, incidently, one of the first references to a constant temperature enclosure. ... "We have seen that the stream of radiant heat which strikes a thermometer in our constant temperature enclosure is independent of both the materials and the shape of the walls of the enclosure, so that if the instrument be carried from one part to another there will be no change in the radiation falling upon it. Something more is necessary for we must not only have the quantity of the heat the same throughout, but the quality of the radiation must also be the same"... ..."Now the word ~~qualey~~ quality is here taken to denote any specific pecularity whether of wavelength or polarisation, which causes the ~~the~~ rays to be differently absorbed by any substance,..."

"...Suppose our thermometer is covered with some substance which displays this selective absorption for certain kinds

of heat, and that we carry it about from one part of the enclosure to another. It will not only be necessary that the quantity of radiant heat which beats upon our thermometer shall be the same throughout the enclosure in order that the instrument may preserve its constancy of temperature, but the quality of the radiation must be the same; if it is not we might suppose that in one place the heat is of a kind that is greedily absorbed by the coating of the bulb, and that for another place, it is of the kind that is reflected back from this coating; thus, although the quantity of the heat falling on the bulb in both places might be the same, yet the thermometer would absorb more in the first place than in the second, and its constancy of temperature would not be observed. Therefore it is clearly necessary that the stream of radiant heat which beats against the thermometer as it is carried about the enclosure should be the same at both places as to quantity and quality..."
"...Such a surface (coating of the thermometer) must not only give back as much as it withdraws by absorption, but what it gives back must be of the same quality as it withdraws"...

Kirchhoff's treatment was mathematical. His result was expressed in the form of a well known law, named after him, namely:-

$$e/_a = E$$

where e is the emitting power of a surface, a the absorbing power of the same surface, that is to say, e means the quantity emitted from a given surface or volume of unit area in unit time in certain directions, a means the ratioof the heat absorbed to the total quantity falling on the same surface in the same time and at the same temperature, and E the emitting power of a perfectly "black" surface or volume at the same temperature.

These two investigators were probably the first to realise the significance of radiation in equilibrium inside a constant temperature enclosure and the fact that this radiation does not display the selective properties which the radiation form a material body displays. It might be thought that this realisation might call for a special paper on the subject from one of them, but we have been unable to find any such evidence, and the inference is that although they realised the importance of the constant temperature enclosure, they did not realise that the distribution of energies among the different frequencies was so important.

It was Balfour Stewart who in 1871, suggested that movement inside such an enclosure, the walls of which are maintained at the same temperature throughout, would produce a "Doppler" effect, but he did not work out his suggestion, and it was left to Wien, as we shall see, to make use of the idea.

The work of these two people, Balfour Stewart and Kirchhoff, lead to further studies of relationships between radiation and temperature. Working on the results obtained by Tyndall on the emission of radiation from hot wires, Stefan found that the heat given out was (roughly) proportional to the fourth power of the temperature difference, between the wires and the surroundings. This empirical discovery was made in 1871.

In 1873=,Maxwell deduced thoeretically the existence of "radiation pressure", that is when radiation falls on a surface, it exerts a pressure. This pressure was not experimentally demonstrated until 1900,when it was observed and measured by Nicholls and Hull,and by Lebedew,and in the following year, the tangential pressure measured by Poynting,and others. Attempts had been made long before this to detect the presence of a light pressure. As early as 1753(i.e. before Prevost's time) attempts were made to demonstrate it when the expected pressure would have been attributed to the arresting of the corpuscles of light.

In 1875 a very important piece of work was done by Bartoli who suggested that the equilibrium radiation should be used as the working substance in a Carnot cycle.

The year 1884 was a very important one,for it marked the taking up of the subject by Boltzmann,who applying the methods used by Bartoli(i.e.using radiation as the working substance of a Carnot cycle) deduced theoretically the law observed by Stephan. This law and the experimental determination of the constant have been the subject of much experimental work. The first verifications were carried out in 1897,by Lumner and Pringsheim,and the first determination of the constant in 1898,by Kurlbaum.

Since then, many investigat~~ions~~ors have worked on the law. Their work will be described later.

In 1893, a big step towards the solution of the problem was made by Wien. Working on the suggestion of Balfour Stewart, that movement inside a constant tenperature enclosure would produce a Doppler effect,Wien calculated the effect that a "reversible" expansion of the constant temperature enclosure would produce on the constituents of the radiation within, and found that each individual wavelength would be charged, by reflection at the moving walls. He found also, that after expansion(reversible), the radiation remained full,or black-body radiation,corresponding to a different temperature of the walls of the enclosure. He obtainedthe expression

$$E_\lambda d\lambda = \lambda^{-5}.F(\lambda.T)\ d\lambda$$

where $E_\lambda d\lambda$ is the radiant energy in the small range of frequencies λ to $(\lambda + d\lambda)$, λ being the wavelength,and T is the temperature, measured on the Kelvin work-scale. From this he deduced that if E_λ is to be a maximum, for a particular frequency $\lambda(max)$ and T were the corresponding temperature, then

$$(T.\ \lambda(max))$$ must be a universal constant.

The form of the function F, he was unable to determine from thermodynamical considerations, but in 1896,he published a paper in which he made arbitary assumptions as to the nature of the processes by which radiation was emitted,and obtained a form for the function F. He assumed that λ,the wavelength of the radiation emitted by a molecule moving about within the constant temperature enclosure to be a function of the velocity of the molecule, v, and that E_λ was proportional to the number of molecules whose velocities were between v and $(v + dv)$. Using the classical expression for the distribution of velocities Wien found that

$$E_\lambda = \lambda^{-5}.e^{-b/\lambda T}$$

Rubens and Kurlbaum extended the practical investigations of Lummen and Pringsheim to the infra red regions, and it was shown that although the formula held for wavelengths less than a certain value, that it was not true for greater values than this.

Rayleigh, using statistical methods, and applying the principle of equipartition of energy(that is, if we have a system of particles ,each with one or more degrees of freedom, then the final state of energy equilibriumi is one for which the kinetic energy is equally divided between the degrees of freedom). On these assumptions, Rayleigh deduced a different distribution of energy in the spectrum, namely that

$$E_\lambda d = 8\pi kT\lambda^{-4}.d\lambda$$

If the aether is supposed to have a perfectly continuous structure, then λ can be made to approach to zero, and as $\lambda \rightarrow 0$, E_λ will tend very rapidly to infinity. Thus, as Rayleigh appreciated, the energy will be distributed among the shorter wavslengths, and E_λ will $\rightarrow \infty$ without showing a maximum value as experiment indicated that it should. Thus the energy should be distributed in the shorter wavelengths.

This expression shows no maximum, and Jeans suggested that the formula should only represent the state of affairs in equilibrium. The equilibrium is reached he supposed , only at the infinitely slow rate (that is,it takes an infinite time to be established). This view did not ~~to~~ seem to be experimentally supported, as the experimental agreement with different "black-bodies" was perfect.

Then, in 1900,came Planck,of whom it may almost be said that he gave the final word on full radiation. It might with equal truth be said, that he gave the first word on the subject, so important have proved his assumptions.

Realising that the correct formula must be one which approximated to Wien's for short wavelengths (that is ,small values of(λT)), and to Rayleigh's for long wavelengths, he set out to find a formula which would do this. For some years previously,he had been trying to determine the form of the function F,by some new assumptions as to the nature of the interaction between "oscillators" and the radiation.
He considered the possibility of the oscillator being able to exert an "irreversible" action on the radiation,(much to the consternation of Boltzmann). In the course of his work,he had occasion to use a function,S, given by:-

$$\frac{1}{S} = \frac{d^2\phi}{dE^2}$$

where ϕ is the entropy and E the energy.
He worked out the value of S for Rayleigh's and Wien's formulae,
From Wien,namely $E_\lambda = A\, e^{-B/T}$ where $A = a\lambda^{-5}$
$B = b\lambda^{-1}$
$T =$ absolute temp.
he obtained $S_w = -E.B$

and from Rayleigh's formula,

$$E = C.T. \qquad \text{where } C = 8\pi k.\lambda^{-4}$$

he got $S_r = -E^2/C$

S_w is correct for short wave lengths, i.e. S is proportional to E, and S_r for long wavelengths, i.e. S prop/l to E^2. Planck added the two values for S, thinking that for small energies, the E^2 term would be negligible, and for large energies, E^2 would be more important ~~than~~ in the formula than E, and thus the value tend to S_r.

hence S(Planck) $= S_p = S_w + S_r$

that is

$$\frac{d\phi}{dE^{2}} = - \frac{C}{BCE - E^{2}}$$

which gives

$$E = \frac{B.C}{e^{B/T} - 1} = \frac{b.c.\lambda^{-5}}{e^{b/\lambda T} - 1}$$

where the constants have the values stated previously. Planck now had to find some "physical basis" for the adoption of this formula, which was verfied as experimentally correct. He supposed that the radiating body consisted of a large number of "dipole oscillators", each with its own period of vibration. Kirchoff's law indicates ,that the nature of the body is immaterial to nature of the radiation,and so Planck chose the simplest possible form of oscillator, namely a"simple harmonic one". By adopting the view that the smallest quantity of energy which could take part in the process of emission or absorption was $h\nu$ (where $1/\nu$ is the period of the vibrator), so that energy interchanges took place only in integral multiples of the quantity $h\nu$, Planck worked out the most likely distribution of the vibrators from statistical considerations, and by associating with this state, the condition of maximum entropy (Boltzmann's law), he succeeded in obtaining the formula for the energy distribution of the spectrum of a full radiator.

This idea of quanta was extended by Einstein who considered light as being made up of "bundles of energy" or light quanta. On this basis, he explained certain photo-electric phenomena. The compromise between this "energy bundle" theory, (which seemed to be a reversion to the corpuscular theory) and the "wave-theory" was made by de Broglie who imagined the quanta as being "guided by the waves " in some way. Out of this conception of de Broglie grew the modern "Wave Mechanics".

Part Two

The THEORY OF FULL RADIATION

The notion of full radiation originated,(as the term " black-body radiation" suggests), in the study of surfaces which look black. It was early discovered that surfaces which look black are good emitters and good absorbers - that is to say they emit radiation copiously in the form of electromagnetic waves and the energy falling on them in the form of these waves is completely absorbed and converted into heat. It was experimentally noticed, that however black a surface appeared to the eye, it did not absorb quite completely all the radiation which fell upon it and hence arose the question of how to make a surface which would absorb <u>all</u> the incident radiation. This was ultimately achieved by the device of an enclosure with a small orifice. Radiation falling on this orifice will pass through it into the enclosure, where it will be reflected many times at the walls of the enclosure and at each reflection, it will be partly absorbed and partly reflected, so that any of it which does strike the orifice again will be greatly reduced in intensity,- to the vanishing point if the dimensions of the orifice are small by comparison with the size of the walls. In such a case, therefore, all the electromagnetic radiation which passes the " surface" - shall we say the plane surface bounded by the periphery of the orifice - all this radiation will be completely converted into heat, in other words, completely absorbed.

When the orifice is very small, it is reasonable to suppose that the state of the radiation is the same, within the enclosure, as it would be if the enclosure were completely closed.

Our artificial "black surface", if we may be permitted so to call it, will radiate in virtue of the temperature of the walls of the enclosure. We are extremely interested in this radiation - the radiation from an enclosure every part of the walls of which is maintained at the same temperature. Suppose that the radiation cannot get into or out of the enclosure. Then a state of equilibrium is set up within it, equilibrium between the walls and the radiation.

We can compare this enclosure with a material enclosure containing Some material medium - a gas for example. This medium ~~material~~ ~~enclosure~~ would be exchanging energy copiously with the walls of the enclosure - giving and receiving energy to and from them. We can subject the gas in the enclosure to changes of temperature and volume and if we make the changes so slowly that at any instant the gas may be considered as being in a state of equilibrium, then we say that we have made the changes "reversibly". If we allow no heat to get into or out of the enclosure during such a reversible change, we say that the gas has undergone a reversible adiabatic change. If we maintain the enclosure at the same temperature throughout the change, we say it is isothermal and reversible. In an exactly comparable way, we say that the radiation has undergone a reversible isothermal change if the walls of the enclosure are allowed to expand,

and are maintained at the same temperature; and a reversible adiabatic change if no heat is allowed to pass from the walls to the radiation, or vice versa. We can, moreover, apply the two laws of thermodynamics to the radiation, and in the state of equilibrium we say that the entropy of the radiation is a maximum. The chief difference between the gas enclosure and the one containing radiation, is concerned with the internal energy of the radiation. For a perfect gas, the internal energy remains constant during a reversible isothermal change. That is to say, the total internal energy is independent of the volume of the enclosure. In the case of the radiation, the total internal energy is changed by a reversible isothermal change in volume, but the energy per unit volume remains the same. This amounts to saying that the energy density is independent of the volume of the enclosure, and is dependant on the temperature of the walls of the enclosure only. Thus in applying the laws of thermodynamics to radiation, we write for the total internal energy, U, $U = u.V$

where u is the energy density and V is the volume of the enclosure.

The energy density is defined thus: - The energy in a small volume element surrounding the point in question, divided by the volume of the element,- and u is independent of V.

We shall see that the analogy between the radiation enclosure and the similar one containing a gas can be pushed further The gas exerts a pressure on the walls of the vessel, due to the continual bombardment of the walls by the molecules of the gas. The magnitude of this pressure we shall see is twice as great as that exerted by the radiation on the walls. This latter we shall calculate to be equal to one third of the energy density of the radiation. Recent developments have brought out that the ~~particles of which the~~ radiation is composed of particles, called "Photons" move about in the enclosure carrying with them energy in a very similar way to that in which the molecules of the gas carry energy. In fact, radiation is often refered to as a " Photon Gas", and has properties very similar to those of a gas in a very degenerate state .

Since there is to be complete absorption at our artificial black surface - that is, the surface bounded by the edge of the orifice, - it follows that the medium on both sides of the orifice must be the same, or have the same optical properties. Thus, if we want the surface to be black with respect to water, we must fill the enclosure with water, and so on.

We are mainly concerned with the radiation in vacuo, and generally we shall define Black-body Radiation as - " The Radiation filling a Vacuous Enclosure, the Walls of which, are, at every part, maintained at the same Temperature

Intensity of Radiation.

The term Intensity of Radiation can be used in two senses Firstly, when as we are considering, the radiant energy in our enclosure is isotropic, if u be the energy density, then the quantity of radiant energy per unit volume travelling within the limits of the unit solid angle, will be ; -

$$\frac{u}{4\pi} \, .$$

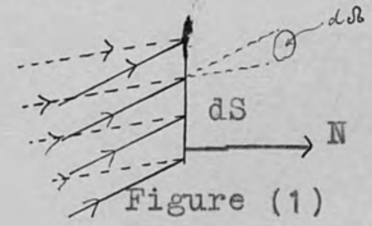


Figure (1)

Assuming, as we must, that the radiation is isotropic, the amount within the limits of the small solid angle dΩ will be : -

(1) $$\frac{u.d\Omega}{4\pi}$$

Now suppose we consider a surface dS in the enclosure,(see fig1) We can easily get an expression for the energy travelling with velocity c through the element dS, in the sense indicated by the arrow N, from one side of dS to the other, and confined, as regards directions, to those parallel to the limits of the solid angle dΩ . We construct on dS as base, a cylinder,abcd, of length c.dt. Evidently the radiation passing through dS, in the time dt, will be the amount within the cylinder, that is, the product of (amount per unit volume)·(volume)

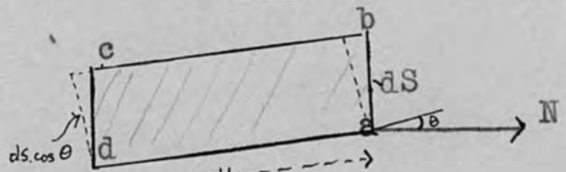


figure (2)

that is

(2) $$\frac{u.d\Omega.}{4\pi} \; c.dt.dS.\cos\theta$$

The amount of radiation passing through a surface dS, in the directions included within $d\Omega$ in the time dt, is proportional to : - $d\Omega$, dt, dS cos e. If we call this factor of proportionality I', we may write for this amount,

(3) $$I'.\cos\theta.\ dS.\ d\Omega\ dt$$

and if we equate this to (2), it follows that I' is

(4) $$I' = \frac{u.c}{4\pi}$$

This I' is one of the two quantities which are called the Intensity of Radiation

The other quantity so called, is obtained from the total quantity passing through dS, in the sense indicated by N, in the time dt, in all directions. This is got by integrating over the appropiate limits, where

$$d\Omega = \sin e.de.\ d\phi$$

where e varies from 0 to $\pi/_2$

ϕ " " 0 to 2π

That is, the total quantity passing through, is

(5) $$I'.dS.dt.\int_0^{\pi/2}\int_0^{2\pi} \cos e.\sin e.de.\ d\phi.$$

If we write this quantity as

(7) $$I.dS.dt.$$

Then, integrating (5) and equating it to (7), it follows that

(8) $$\pi.I' = I$$

but, since I' is $u.c/_{4\pi}$ (see (4).)

(9) then, $$I = \frac{u.c}{4}$$

This quantity I is also used as a measure of the Intensity of Radiation.

If however, we are dealing with quantities which do not refer to the radiation as a whole, but to a particular frequency ν and a small range of frequencies between ν and $\nu + d\nu$ (where $d\nu$ is so small that the difference between ν and $\nu + d\nu$ may be neglected by comparison with ν itself,) then, since in our enclosure we have all frequencies from zero to infinity, we define the intensity for a particular frequency ν so as to make

(10)
$$I' = \int_0^\infty I'_\nu d\nu$$
$$I = \int_0^\infty I_\nu . d\nu$$

where I'_ν and I_ν are the intensities refering to the frequency ν. By analogy with this, we define the <u>density</u> for a frequency ν to be ~~given~~ given by

(11)
$$u = \int_0^\infty u_\nu d\nu = \frac{4\pi . I'}{c}$$

hence $I' = \frac{c}{4\pi} . \int_0^\infty u_\nu . d\nu$

and $I'_\nu = \frac{u_\nu c}{4\pi}$

The energy per unit volume between the limits of wavelength λ and $\lambda + d\lambda$, we define so as to make

(12)
$$u_\nu d\nu = - E_\lambda . d\lambda$$

(where E_λ is the energy density so defined. The minus sign merely indicates that ν increases as λ decreases, and vice versa)

We see, from expressions (11) and (12), that as $d\nu$ and $d\lambda$ approach zero, the energy in the range also tends to zero. This indicates that we cannot have a purely monochromatic wave carrying energy, i.e., we cannot have light which is exactly monochromatic and the transference of radiant energy by a purely plane wave. Fouruer's analysis would indicate the same thing.

Emission and Absorption of Radiation.

(a). Surface Emission and Absorption.

We shall begin with the vacuous enclosure, which has every part of the boundary at the same temperature. We may write for the (electromagnetic or radiant) energy falling on some element, dS, of the boundary, in the time dt, and confined to the limits of direction included within a small solid angle $d\Omega$

(12) $$\frac{u.d\Omega}{4\pi}.c.dt.dS\cos\theta$$

or $$I'.d\Omega.dt.dS\cos\theta$$ (see equations (2) and (3).)

Of this energy, the fraction <u>a</u> is absorbed by dS, while the remainder <u>r</u> is reflected; so that

(13) $$I'.d\Omega.dt.dS.\cos\theta = a.I'd\Omega.dt.dS\cos\theta + r.I'd\Omega.dt.dS\cos\theta$$

We shall term <u>a</u> the <u>absorbing power</u> of the surface
and <u>r</u> its <u>reflecting</u> " .

Now, we have, by hypothesis, a state of equilibrium, and therefore, the amount of energy represented by (12) will be leaving dS, along the directions included within the limits $d\Omega$ in the time dt. Of this, the fraction <u>r</u> has been reflected, and the rest emitted. Therefore : -

(14) $$I'.d\Omega.dt.dS\ \mathrm{cps}\ \theta = \underline{e}.d\Omega.dt.dS\cos\theta + r.I'.d\Omega.dt.dS\cos\theta$$

where <u>e</u> is the <u>emitting power</u> of the surface

On comparing the equations (13) and (14), we see that

(15) $$e = a.I'$$

This result is simply a consequence of the assumption of equilibrium. It was first given by Kirchhoff. Of course, we might have defined the reflecting and absorbing power in terms of the <u>total</u> quantity absorbed, instead, as we have done, of expressing it in terms of the fractions r and a. In this way, we should get

$$A = a.I$$

$$R = r.I$$

(where R and A are the reflecting and absorbing powers expressed in terms of these quantities)

In such a case, Kirchhoff's law becomes

$$e = A.$$

However, it is more convenient to define the quantities in the way we described at first.

When the surface is black ; in other words when it absorbs completely, r is zero, and the equation (13) yields : -

(17) $$I' = a.I'$$

So this definition of absorbing power makes that of a black surface equal to unity .

In the special case of a perfect reflecting surface, a is zero and we find, as we should expect, that r is unity.

We learn, finally, from (15), that for a black surface,

$$e_{(black)} = I'$$

or writing E for the emitting power of a black surface

(18) $$E = I'$$

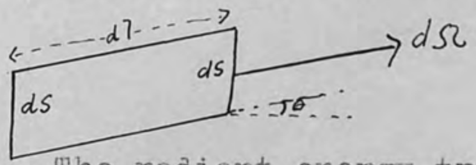
But, we know that for a definate temperature, E is constant and therefore it follows that the ratio

(19) $$\frac{\text{Emitting power of a surface}}{\text{Absorbing power of the surface}} = E$$

where, in (19), E has a constant value, namely the emitting power of a black surface.

(b) Body Emission and Absorption

We shall try to obtain an~~d~~ expression for the 'body' emission and absorption, that is to say, the radiant energy emitted and absorbed by a volume of the medium under consideration, by working on the same lines as in the previous case of surface emission and absorptio.



The radiant energy travelling through the volume shown in the figure, will be proportional : - (per unit time) the energy density; - $d\Omega$; - and the volume.

In fact, we may write for it : -

(20) $$\frac{u.d\Omega.}{4\pi}\ dS\cos\theta.\ dl$$

This will be composed of two parts ; that emitted by the volume, and that scattered. Calling s the coefficient of scattering, and e the emitting power, we may write, as in the previous vase for the surface : - (per unit time)

(21) $$e.d\Omega.dS\cos\theta.dl. + \frac{s.u.}{4\pi}\ d\Omega.dS\cos\theta.dl$$

Equating expressions (20) and (21), we get :-

$$\left(\frac{u}{4\pi}\right)d\Omega.dS.\cos\theta.dl = e.d\Omega.dS.\cos\theta.dl + s\left(\frac{u}{4\pi}\right)d\Omega.dS.\cos\theta.dl.$$

(22) or, writing D for $\left(\frac{u}{4\pi}\right)$, and cancelling out, we get

(23) $$D = e + s.D$$

Similarily, if a is the absorbing power of the medium, the expressiom (20) must be composed of the part which is absorbed, and that which is scattered.

Therefore $$\frac{u.d\Omega}{4\pi}.dS.\cos\theta.dl = (a + s)\frac{.u d\Omega}{4\pi}dS\cos\theta.dl$$

(24) i.e. $$D = a.D + s.D$$

From (23) and (24), we get : -

$$e = a.D$$

(25) i.e $$\frac{e}{a} = D$$

Suppose that s is zero, that is to say, there is no scattering within the medium. Then, from (24), a is unity and the medium is perfectly absorbing. This is the case for a perfectly *black* medium. In this case, then, as in the parallel case for surface emission and absorption, we have, that the ab*sorbing* power of a *black medium* is *unity*.

Substituting the value zero for s in the equation (23) to get the emitting power of a black medium, we get : -

$$E = D$$

where as before, E is the emitting power of a black medium. By substitution for D in (25), we get

(26) $$\frac{e}{a} = E$$

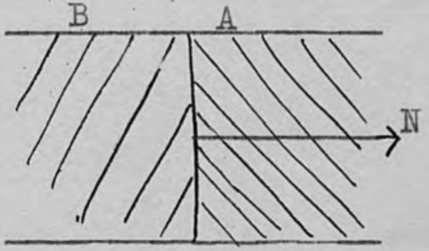
From the expressions (19) and (26), we have then, that

$$\frac{\text{emitting power}}{\text{absorbing power}} = \text{the emitting power of a perfect emitter.}$$

Radiation Pressure.

As we said, when we were comparing our enclosure with a similar one containing a material gas, the radiation exerts a pressure on the walls of the containing vessel (the enclosure) just as the gas exerts a pressure on its surroundings

Let us calculate the magnitude of this pressure. We can do this in two ways : - either by considering the components of the stress tensor in the electromagnetic field, (considering the radiation as ~~an~~ electromagnetic waves), or by considering the change in momentum of the particles on striking the walls, (considering the radiation as a photon gas.)



If t_{xx} is the component of the tension which the medium A exerts on the medium B in the sense of direction indicated by the arrow N, then t_{xx} (measured in Lorentz-Heaviside units for empty space will be : -

$$t_{xx} = (E_x^2 - \tfrac{1}{2}E^2) + (H_x^2 - \tfrac{1}{2}H^2)$$

where E is the electric intensity
" H " " magnetic "

For isotropic radiation, the average of E_x^2 (call it $\overline{E}_x^2$) will be $\frac{1}{3}.(\overline{E^2})$, where $\overline{E}^2$ is the average of the total intensity.
Similarity, $H_x = \cancel{1}.\ \overline{H}_x^2 = \frac{1}{3}.\ \overline{H}^2$
and therefore t_{xx} will be equal to $\left\{\frac{1}{3}\,\overline{E^2} - \frac{1}{2}\,\overline{E^2}\right\} + \left\{\frac{1}{3}\,\overline{H^2} - \frac{1}{2}.\overline{H^2}\right\}$

$$= -\frac{1}{6}\,\overline{E^2} - \frac{1}{6}\,\overline{H^2}$$

$$= -\frac{1}{3}.\left\{\tfrac{1}{2}\,\overline{E^2} + \tfrac{1}{2}\,\overline{H^2}\right\}$$

But, $\left\{ \frac{1}{2} E + \frac{1}{2} H \right\}$ is the energy density of the wave, and therefore $t_{xx} = -\frac{(\text{energy density})}{3} = -\frac{1}{3}.u$

whence the pressure, $p_{xx} = +\frac{u}{3}$

Considering the pressure from the point of view of its being due to the bombardment of the walls of the containing vessel by the corpuscles - just as the walls of the gas enclosure experience a pressure - the kinetic theory og gases shows that the magnitude of this pressure is

$$N.m.u^2$$

where N is the number of particles in the unit volume,

m is the mass of the particle, and u is (shall we say) the x-component of the velocity, c (= u,v,w)

For isotropic radiation, this pressure will be

$$p = \frac{1}{3}.N.m.\overline{c^2}$$

where $\overline{c^2}$ is the average value of c^2 and

$$\overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{1}{3}.\overline{c^2}$$

The expression $N.m.\overline{c^2}$ may be written as $N.\overline{E}$

where, since the particles are moving about with velocities of the order of that of light, we may say that their energy is

$$\overline{E} = m.\overline{c^2}$$

and since N is the number per unit volume, $N.\overline{E}$ will be equal to u the energy density.

Therefore, p will be $\frac{u}{3}$

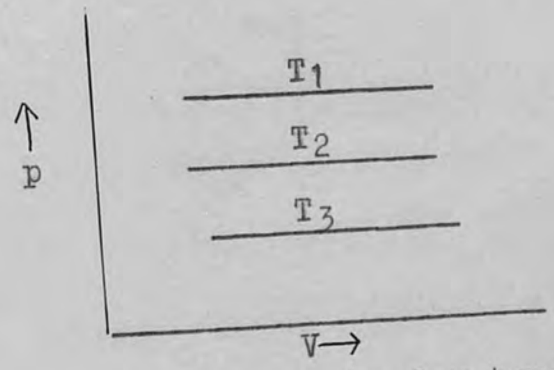
Thermodynamic Considerations.

The Boltzmann Law.

By the aid of the second law of thermodynamics, we can find an expression for the energy per unit volume of the radiation within our enclosure,(every part of the walls of which are maintained at the same temperature.), in terms of the temperature of the walls, T.

We will subject the enclosure to reversible changes of volume and temperature, that is, we will suppose the changes take place so slowly, that at any instant a state of equilibrium may be supposed to be existing

Firstly consider isothermal changes - that is to say changes where the temperature of the walls of the enclosure remains constant throughout the process. We know that the energy per unit volume, u, remains the same, since this depends only on T and we are keeping T constant. We have, moreover, shown that the pressure p of the radiation is equal to one third of u and hence it follows that for isothermal changes, the pressure of the radiation remains constant.



(isothermals for temps T_1, T_2, and T_3

On a p-v diagram therefore, isothermals are represented by straight lines parallel to the volume axis, as the figure shows

For isothermal changes, it is however only the energy per unit volume which remains unaltered, and it follows then, that if the enclosure expand, an amount of heat must pass from the walls to the enclosure, to make up, as it were, the space left empty where the walls have expanded. This amount of heat will be : -

$$u.(V - V')$$

where $(V - V')$ is the change in the volume.

For adiabatic changes, we must have the walls of the enclosure perfectly reflecting, so that the walls cannot absorb from the " radiation gas", or reflect to it, if the temperature of the " gas" is changed by the alteration of the volume.

In an adiabatis change, it follows therefore, that the quantity U remains unchanged, that is, the quantity $(u.V)$ remains the same for this adiabatic and reversible change.

But, if $(u.V)$ remains unchanged, then

$d\,(u.V)$ must be zero (where $d(u.V)$ is the increment in $u.V$)

i.e. $u.dV + V.du = 0$

and since dV is not 0, it follows that du is not zero (as it was for the isothermal case)

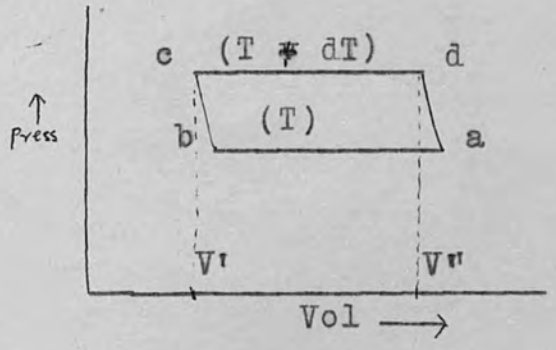
Hence - for adiabatic changes u and therefore T changes.

To sum up:

For reversible isothermal changes u, and T are constant; and U varies

" adiabatic " U is constant; and u and T vary

Following the analogy of a gas or material enclosure, we will subject the radiation in the enclosure to the reversible changes of a Carnot cycle.



Suppose we have the radiation enclosed within a cylinder with a movable piston. If this has the initial volume V' and temperature (T+dT) this state will correspond to the point c on the p-v diagram.

Subjecting the radiation to the reversible Carnot cycle, c d a b, in the usual manner, we can apply Carnot's principle ~~and the second law of thermodynamics~~ to the process.

In the p-v diagram, c→d represents isothermal expansion of the radiation at the temperature (T + dT).

d → a represents adiabatic expansion of the radiation, the temperature falling from (T + dT) to T

a → b represents isothermal compression from the volume V" to the volume V', the temperature being maintained at the value T.

Finally, b → c represents adiabatic compression causing increase in T to (T + dT)

For this reversible cycle, Carnot's theorem ~~and the second law of thermodynamics~~ requires that the ratio

$$\frac{\text{work done}}{\text{Heat supplied}}$$

shall be equal to $\dfrac{dT}{T + (dT)}$

that is, that

(30) $$\frac{\text{area abcd}}{\text{heat supplied}} = \frac{dT}{T}$$

(where we have neglected dT by comparison with T.)

The equation (30) may be written

$$\frac{(V' - V)\,dp}{\text{heat supplied}} = \frac{dT}{T}$$

The heat supplied will consist of two parts,

(1), that required to fill up the space $(V' - V)$ with radiation of energy density u (equals $u.(V' - V)$.)

(2). to do work against the pressure of radiation. ($= \overline{V'-V}.p.$)

Substituting these values, we get

(31) $$\frac{dp.(V'-V)}{u.(V'-V) + p.(V'-V)} = \frac{dT}{T}$$

where, p, the radiation pressure, is equal to $\dfrac{u}{3}$

and therefore, dp equals $\dfrac{du}{3}$

Therefore, (31) becomes,

$$\frac{\frac{1}{3}.\,du}{u + \frac{1}{3}.u} = \frac{dT}{T}$$

and therefore

$$\frac{\frac{du}{3}}{\frac{4u}{3}} = \frac{dT}{T}$$

i.e. $\dfrac{du}{4u} = \dfrac{dT}{T}$

integrating this, we get

$$\log u = 4 \log T \text{ (plus a constant)}$$

or $u = a.T^4$

where a is a constant.

We had an expression for the intensity, namely,

$$I' = \frac{u.c}{4\pi}$$

$$I = \frac{u.c}{4}$$ (see equations (4) and (9).)

and therefore, we may write,

(32) $$\begin{cases} a\,T^4 = u \\ \sigma' T^4 = I' \\ \sigma\, T^4 = I \end{cases}$$

where a σ' and σ are all constants.

The constant σ is called the Stefan-Boltzmann Constant and this fourth power law is called the Stefan-Boltzmann Law.

It follows, moreover, from equations (4),(9), and (32),

(33) that $\sigma = \frac{a.c}{4}$, and $\sigma' = \frac{a.c}{4\pi}$, and $\sigma = \pi\sigma'$.

We have seen that isothermals are represented by lines parallel to the V-axis on a p-v diagram Let us now consider the shape of the ~~isothermals~~ adiabatics. In the same way that the former are distinguished by some numerical quantity, which we call temperature, so the adiabatics are distinguished by another numerical quantity, **entropy**, generally denoted by the letter ϕ. The measure adopted for ϕ is $\left(\frac{\text{heat}}{\text{temperature}}\right)$, and for a change in ϕ of $d\phi$, as $\left(\frac{dQ}{T}\right)$ where dQ is the heat communicated during a reversible adiabatic change at a temperature T.

The second law of thermodynamics requires that $d\phi$ be a perfect differential.

That is to say, if $\phi = (A.dx + B.dy)$

then $\frac{d}{dx}(A)$ (y being kept constant) is equal to

$\frac{d}{dy}(B)$ (x being kept constant)

Applying the first law of thermodynamics to the radiation

$$
\begin{aligned}
dQ &= dU + p.dV \qquad \text{(just as for a material)}\\
&= d(u.V) + p.dV\\
&= u.dV + V.du + p.dV\\
&= V.du + \frac{4u}{3}.dV \qquad \left(\text{since the pressure } p = \frac{u}{3}\right)
\end{aligned}
$$

For an ad-iabatic change, dQ is zero, and therefore, putting $dQ = 0$. we get : -

(34) $$3V.du = -\frac{4}{3}.u.dV$$

But, by Stefan's law, $u = a.T^4$

therefore $du = 4.aT^3$

and by substitution in (34), we get for the adiabatic,

$$3V.dT = -p.dV$$

integrating this, we get

$$T^3.V = \text{constant.}$$

Since $u = 3p$, we could have written (34) in the form

$$3V.3dp + 4.3p.dV = 0$$

and therefore the slope of the adiabatics, $\left(\frac{dp}{dV}\right)$ is

$$-\frac{4}{3}.\frac{p}{V}.$$

Summarizing then for adiabatics, we have

$$T^3.V \text{ is constant}$$

or $$V^4.p^3 \text{ is ''}$$

$$\left(\frac{dp}{dV}\right) \text{ is } -\frac{4}{3}.\frac{p}{V}.$$

Going back to the expression for the first law of thermodynamics,

$$dQ = d(u.V) + p.dV$$

if we substitute for dQ, $(T.d\phi)$ and for p, $\left(\frac{u}{3}\right)$

we get

$$d\phi = \frac{1}{T}(du.V + u.dV) + \frac{1}{3}.\frac{u}{T}.dV$$

$$= \frac{1}{T}.V.du + \frac{4}{3}.\frac{u}{T}.dV$$

and since $d\phi$ is a perfect differential,

$$\frac{d}{dV}\cdot\left(\frac{1}{T}.V\right) = \frac{d.}{dT}\left(\frac{4}{3}.\frac{u}{T}\right)$$

that is,

$$\frac{1}{T} = \frac{4}{3}.\frac{1}{T} - \frac{4}{3}.\frac{u}{T^2}.\frac{dT}{du}$$

i.e.

$$\frac{dT}{du} = \frac{T}{4u}$$

Integrating this expression, we again get the Stefan-Boltzmann law,

$$u = a.T^4$$

this time, without using the artificiality of the Carnot engine.

Let us now try to find an expression for the entropy ϕ associated with the radiation in a volume V at temperature T.

We had $$d\phi = \frac{1}{T}.V.du + \frac{1}{T}.\frac{4u}{3}.dV$$

$$= \frac{V}{T}.\ 4aT^3.dT + \frac{1}{T}.\frac{4}{3}.aT^4.dV$$

(by substituting $u = aT^4$)

that is $$d\phi = 4a.(\frac{V}{T}.T^3).dT + \frac{1}{3}.T^3.dV.\ 4a.$$

and therefore integrating, we get

$$\phi = \frac{4}{3}.aT^3.V \quad \text{(plus a constant)}$$

This constant we choose our scale of measurement to make zero and hence $\phi = \frac{4}{3}.aT^3.V$

if we agree to call the entropy per unit volume, <u>s</u>

then $s = \frac{\phi}{V} = 4.\frac{aT^3}{3}$

i.e.

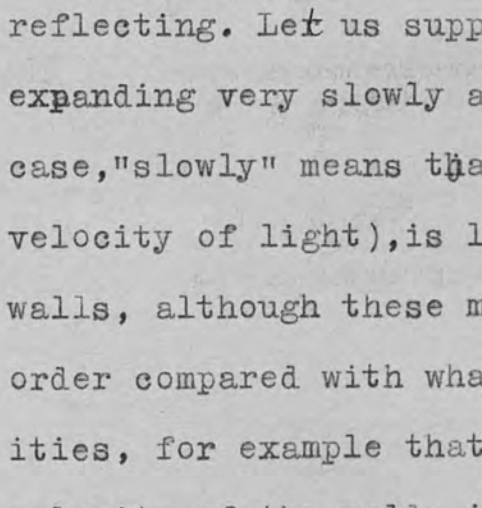
$$\boxed{\begin{aligned} \phi &= \frac{4}{3}.aT^3.V \\ s &= \frac{4}{3}\ aT^3 \end{aligned}}$$

Wien's Law

The chief theoretical problem of full radiation is that of the spectral distribution of energy in it. If we employ u_ν in the sense already described above, that is to say, so that $u_\nu d\nu$ means the energy in the limits of frequency ν and $\nu + d\nu$ per unit volume, then the distribution problem is that ~~of the~~ of the expression of u_ν as a function of ν and T, where T is the temperature measured on the Kelvin scale.

Wien made the first important advance in this direction, by applying the principles of thermodynamics to full radiation and thus discovered something of the nature of the function, without, however, finding its exact form.

Suppose we have full radiation enclosed in a cavity the walls of which are, for the sake of argument, perfectly reflecting. Let us suppose further, that this enclosure is expanding very slowly and adiabatically. In this particular case, "slowly" means that the velocity of the radiation, (the velocity of light), is large compared with the velocity of the walls, although these may be moving with a velocity of a high order compared with what is usually described as high velocities, for example that of an express train, so long as the velocity of the walls is small compared with that of light, then we may consider their motion as reversible in the thermodynamic sense.

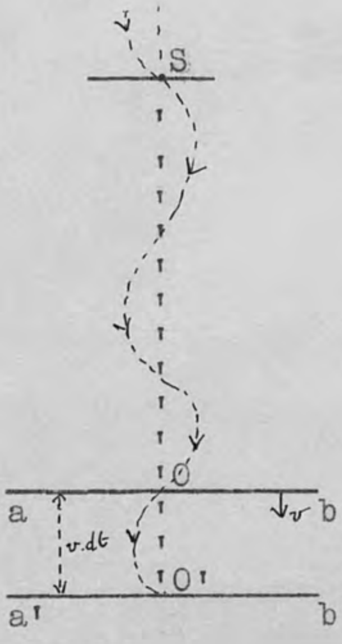


Let a - b be a section of the movin wall and let a'- b' be its position after a short

inteval of time, dt. If ab is moving with the velocity v, then the distance it will have travelled will be (v.dt)
If dS is the area of ab, then the corresponding increase in the volume will be

(35) $$dV = v.dt.dS$$

We have in the first place, to investigate the effect that the movement of the mirror will have on the frequency of the radiation.



Imagine a wave passing through S and travelling towards the point O in ab, with a velocity c. If it take a time dt to travel the distance SO, then the number of waves in SO, is $\nu.dt$ where ν is the frequency of the radiation, i.e. the number of waves passing a point in unit time.

If ab were not moving, these waves would all be reflected back at ab and the number returning to S, per unit time, would be $\nu.dt$ and in the time, dt, ($\nu.dt$). But on account of the motion of ab (say away from S) the waves which would have been reflected back at ab, have to go a further distance equal to twice oo' i.e. 2v.dt.
Thus the number returning to S in the unit time, will be reduced by $\frac{\nu.2v}{c}$

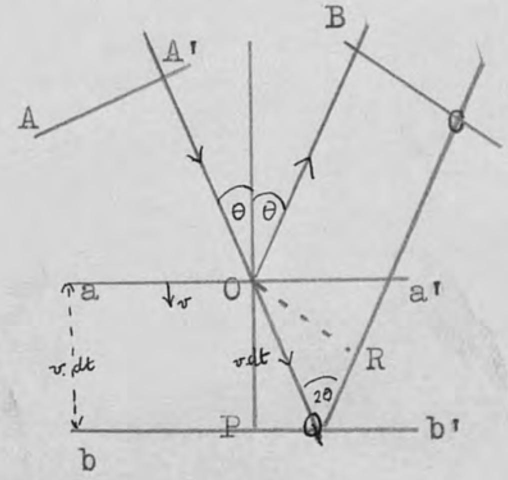
and therefore the number returning, ν', will be given by

$$\nu' = \nu\left(1 - \frac{2v}{c}\right)$$

If ab were approaching S, the number would be increased, and

$$\nu' = \nu\left(1 + \frac{2v}{c}\right)$$

Suppose, now we have radiation incident at an angle θ



the extra distance that the radiation has to travel, on account of the motion of the mirror is obviously, from the figure, $(x+y)$ where AA' is a section of the wave-front before reflection, and BC after reflection. AA' is moving towards the mirror which after a time dt will be in the position ab'.

From the figure, $x.\cos\theta = v.dt$, and it can easily be shown that the angle OQC is 2θ, therefore, $y = x.\cos 2\theta$

and therefore $(x+y) = \dfrac{v.dt}{} + \left(\dfrac{v.dt.\cos 2\theta}{\cos\theta}\right)$

$$= 2v.dt.\cos\theta$$

therefore the number of waves reaching BC in time dt is lessened by $\nu.dt.\dfrac{2v}{c}.\cos\theta$

or $\quad \nu'.dt = \nu\left(1 - \dfrac{2v}{c}.\cos\theta\right)dt$

$$\nu' = \nu\left(1 - \frac{2v}{c}\cos\theta\right)$$

In this we have assumed that the laws of reflection are not altered by the motion of the mirror.

We must now find an expression for the amount of radiant energy falling on the area dS in the time dt, and confined to the limits of direction within the small cone of directions $d\Omega$. where, as usual $d\Omega$ may be written

(36) $\qquad d\Omega = \sin\theta.d\theta.\,d\phi$

where ϕ is the azimouth angle.

For a small range of frequencies, lying between ν and $\nu + \Delta\nu$ the energy will be

(37) $$\frac{u_\nu \Delta\nu}{4\pi} . d\Omega . c . dt . \cos\theta \; dS$$ (see equation (2).)

Equation (37) is the expression for the energy reaching the surface ab (dS). But, dS is moving, and therefore the frequency ν is changed by reflection, and consequently the radiation which previously was in the range $\Delta\nu$ will enter some other range while radiation from another range will enter this range $\Delta\nu$. Suppose that this latter is u'_ν. Then

$$u'_\nu = u_\nu + \left(\frac{du_\nu}{d\nu}\right)(\nu' - \nu) + \frac{1}{2}\left(\frac{d^2 u_\nu}{d\nu^2}\right)(\nu' - \nu)^2 + \dots$$

by Taylor's theorem)

That is, neglecting higher powers,

$$u'_\nu - u_\nu = \left(\frac{du_\nu}{d\nu}\right)(\nu' - \nu)$$

In this, since $(\nu' - \nu)$ is the change in frequency of the wave, $(\nu' - \nu)$ means $\left(2\frac{v}{c}\cos\theta\right).\nu$

This enters the range $\Delta\nu$, and so the expression corresponding to (37) for the energy entering the range between ν and $(\nu + \Delta\nu)$ in the direction $d\Omega$. becomes

(37') $$\frac{u'_\nu \Delta\nu}{4\pi} . d\Omega . c . dt . \cos\theta \; dS$$

$$\text{or} \left[u_\nu + \left(\frac{du_\nu}{d\nu}\right)(\nu' - \nu)\right] . \frac{\Delta\nu}{4\pi} . d\Omega . c . dt . \cos\theta \; dS$$

therefore the excess of energy entering the range $\Delta\nu$ over that leaving is : -

$$\left(\frac{du_\nu}{d\nu}\right)(\nu' - \nu) . \frac{d\Omega}{4\pi} \; c . dt . \cos\theta dS . \Delta\nu$$

which is equal to

$$\frac{\Delta\nu}{4\pi}\left(\frac{du_\nu}{d\nu}\right) 2\frac{v}{c} \cos\theta . d\Omega . dt . \cos\theta \; dS . c . \nu$$

$$= \frac{\Delta\nu}{4\pi}\left(\frac{du_\nu}{d\nu}\right)2dV.\cos^2\theta.\sin\theta.d\theta.d\phi.\nu$$

(by substituting for $d\Omega$ and for dV from (36) and (35)

When we sum for all the possible values of θ and ϕ

we get : - $$\int_0^{\frac{\pi}{2}}\int_0^{2\pi}\frac{\Delta\nu}{2\pi}\left(\frac{du_\nu}{d\nu}\right)dV.\cos^2\theta.\sin\theta.d\theta.d\phi.\nu$$

$$= \frac{1}{2\pi}.\left(\frac{du_\nu}{d\nu}\right)\Delta\nu.\nu.\int_0^{\pi/2}\int_0^{2\pi}\cos^2\theta.\sin\theta.d\theta.d\phi.dV$$

(39) $$= \frac{1}{3}.\frac{du_\nu}{d\nu}\Delta\nu.\nu.dV$$

We may now obtain another expression for this increment, (39), by applying the first law of thermodynamics. It is simplest to proceed by regarding

(40) $$-\frac{1}{3}.\left(\frac{du_\nu}{d\nu}\right)\Delta\nu.dV.\nu$$

as the decrement in the range $\Delta\nu$ associated with the change in volume dV. We must equate this to the work done in the reversible adiabatic process

Now in the reversible adiabatic process : -

(41) $$0 = d(u.V) + p.dV$$

is the equation which deals with the change in the total energy. Its corresponding equation in which we are more particually interested is, of course that dealing with the energy for a particular range of frequencies $\Delta\nu$, and for the frequency ν

(40') the equation becomes $0 = \Delta\nu.d(u_\nu V) + \frac{\Delta\nu(u_\nu d\nu)}{3}$

and the energy decrement with which we are especially concerned is $-\Delta\nu.d(u_\nu V)$ (which is the work done in the expansion

(42) or, $-\Delta\nu.(V.du_\nu + u_\nu dV)$

equating (40) and (42), we get

$$+ \frac{1}{3}\cdot\left(\frac{du_\nu}{d\nu}\right)\nu . dV = V.du_\nu + u_\nu dV$$

(43) $$\text{or } - V.du_\nu = \left[u_\nu - \frac{\nu}{3}\left(\frac{du_\nu}{d\nu}\right)\right] dV.$$

It should be pointed out here that the du_ν used here really means $\left(\frac{du_\nu}{dT}\right)dT$ [Partial differentiation of u_ν with respect to T] since we are investigating over a small range of frequencies so that we may think of $\left(\frac{du_\nu}{d\nu}\right)d\nu$ as zero, and since u_ν is independant of the volume, $\left(\frac{du_\nu}{dV}\right)dV$ is also zero

(44) From (43) therefore, $$- V\left(\frac{du_\nu}{dT}\right)dT = \left(u_\nu - \frac{\nu}{3}.\frac{du_\nu}{d\nu}.\right).d\nu$$

Now, dV is the change in V for a reversible change (adiabatic) in volume, and we may, with the aid of (41), replace it by an expression containing the corresponding expression for dT, the corresponding temperature increment. We have, namely, that -

$$\begin{aligned} 0 &= u.dV + V.du + p.dV \\ &= v.du + (u+p)dV \\ &= 4V.aT^3.dT + \frac{4}{3}.aT^4.dV \quad (\text{ using } u = aT^4) \\ &= V.dT + \frac{1}{3}.T.dV \end{aligned}$$

So that $dV = - 3\frac{V.dT}{T}$

On substituting this expression for dV in (44), we get :-

$$- V\left(\frac{du_\nu}{dT}\right). dT = - \left(u_\nu - \frac{1}{3}.\nu\frac{du_\nu}{d\nu}\right). 3\frac{V.}{T}dT$$

or finally,

(45) $$3u_\nu = T.\left(\frac{du_\nu}{dT}\right)_\nu + \nu\left(\frac{du_\nu}{d\nu}\right)_T$$

The term " $3u_\nu$" in the expression (45), suggests how we should proceed. We introduce a function f, defined by

$$f = \frac{u}{\nu^3}$$

so that, $u_\nu = \nu^3 . f.$

(where f is a so far unknown function of T and ν)

Substituting this expression in the equation for u_ν

we get $$3\nu^3 . f = 3\nu^3 . f + \nu^4 . \left(\frac{df}{d\nu}\right) + \nu^3 . T\left(\frac{df}{dT}\right)$$

(46) and therefore, $\nu\left(\frac{df}{d\nu}\right) + T\left(\frac{df}{dT}\right) = 0$

In this equation it may be pointed out that

$\left(\frac{df}{d\nu}\right)$

means the differentiation carried out under the condidions that T is not altered. We may, if we wish, mark this specially by writing $\left(\frac{df}{d\nu}\right)_T$

Similarily, $\left(\frac{df}{dT}\right)$ means here the differentiation when ν is constant, and may be written, $\left(\frac{df}{dT}\right)_\nu$

We can make progress by writing the differential equation (46)

(47) in the form $T + \nu\left(\frac{df}{d\nu}\right) . \left(\frac{dT}{df}\right)_\nu = 0$

Now df is $\left(\frac{df}{dT}\right)_\nu . dT + \left(\frac{df}{d\nu}\right)_T d\nu$

and if we consider for a moment, a change when f does not alter, i.e., for which $df = 0$,

$$0 = \left(\frac{df}{dT}\right)_\nu dT + \left(\frac{df}{d\nu}\right)_T d\nu$$

$$= \left(\frac{df}{dT}\right)_\nu + \left(\frac{df}{d\nu}\right) . \left(\frac{d\nu}{dT}\right)_f$$ (by dividing by dT and remembering f is constant)

or, $\left(\frac{df}{dT}\right)_\nu = -\left(\frac{df}{d\nu}\right)_T . \left(\frac{d\nu}{dT}\right)_f$

substituting this in equation (47), we have

$$T - \nu\left(\frac{df}{d\nu}\right)_T \cdot \left(\frac{d\nu}{df}\right)_T \cdot \left(\frac{dT}{d\nu}\right)_f = 0$$

or $T = \nu\left(\frac{dT}{d\nu}\right)_f$

since $\left(\frac{df}{d\nu}\right)_T \cdot \left(\frac{d\nu}{df}\right)_T = 1$

So long as f is constant, therefore,

$$\frac{d\nu}{dT} = \frac{\nu}{T}$$

or $\frac{d\nu}{\nu} = \frac{dT}{T}$

This means that (by integrating) log ν/T and hence ν/T remains constant, so long as the function f remains constant.

We may, in other words, say that the function f is a function of the single variable $\left(\frac{\nu}{T}\right)$ or $\left(\frac{T}{\nu}\right)$

and if we write (T/ν) as x,

(49) then $u = \nu^3.f(x)$

This is one form of the expression for Wien's law.

If we express the energy in terms of the wavelength, λ instead of in terms of ν, we shall get another expression for Wien's law.

If c is the velocity of light, $c = \nu . \lambda$

$$\lambda = \frac{c}{\nu}$$

$$d\lambda = - \frac{c . d\nu}{\nu^2}$$

and since $E\, d\lambda = -u_\nu d\nu$

substituting for u_ν from (49), we get

(50) $$E\, d\lambda = \frac{c^2}{\lambda^5} . F(\lambda T)$$

where F is an unknown function of (λ, T)

If we differentiate the expressions for u and E and equate the result to zero, to find what condition must hold for a maximum or minimum value of the energy, we get, differentiating (50)

$$\frac{dE}{d\lambda} = -5\lambda^{-6}.F(\lambda.T) + \lambda^{-5}.T.F'(\lambda.T)$$

Putting $\frac{dE}{d\lambda}$ equal to zero for a stationary value,

$$0 = \lambda.T.\ F'(\lambda.T) - 5F(\lambda.T)$$

whence it follows that for the value of the wavelength for which the energy has a stationary value, say λ_m

51) $(\lambda_m.T)$ is a universal constant.

Substituting this in the equation (50), we get for this stationary value for E_λ

$$E_\lambda = \frac{c^2}{\lambda_m^5}.F(\lambda_m.T)$$

which may be written,

$$= \frac{c^2}{(\lambda_m.T)^5}.\ F(\lambda_m T).\ T^5$$

and since $(\lambda_m.T)$ is constant,

52) E_λ is proportional to T^5

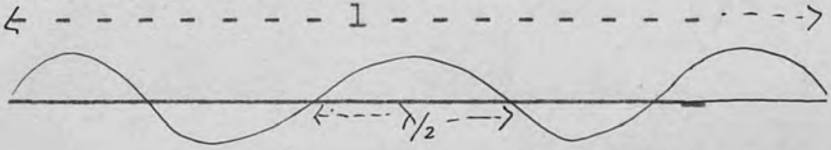
The expressions (51) and (52) are respectively known as Wien's Displacement Law, and the Fifth power law

The formula of Wien at which we arrived, namely

$$u_\nu = \nu^3 .f(x), \quad \text{where } x = T/\nu$$

and f is a so far unknown function of x, is the limit to which thermodynamical arguments will take us towards the solution of the problem of full radiation. To make further progress, we may regard the radiation in the enclosure as a super-position of plane harmonic waves, travelling in all directions and of all wavelengths. Fourier's theorem would, in fact, express the state of affairs in the enclosure in much the same way.

The method may be illustrated by applying it to the case of a stretched string or cord.



Each of its simple modes of vibration may be regarded as the superposition of harmonic waves travelling in opposite senses, so that the nodes are produced at distances $\frac{1}{2}\lambda$ apart. In the fundamental mode of vibration there is a node at each end and no nodes inbetween,(see figure (2).)

figure(2)

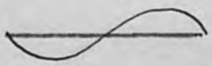


figure (3)

figure (4)

In the next mode of vibration,there is a node just half way inbetween the two end nodes(figure 3); in the next, two equally spaced nodes inbetween the end ones (fig4) and so on.

If l is the length of the cord and n is the number of intervals,(that is to say there are (n+1) nodes altogether) if v is the velocity of the wave, and ν its frequency, then

$$v = \nu.\lambda$$

and $\frac{1}{2}\lambda.n = 1$

(53) or $\nu = \frac{v}{21.n}$

It follows that the different modes of vibration, if we include frequencies up to ν and no further, are, in number

$$\frac{21.\nu}{v}$$

In any <u>one</u> of these modes of vibration, the motions of the different parts of the cord are <u>not</u> independant. Then the number of <u>independant</u> modes of vibration of frequencies between zero and ν is $\frac{21.\nu}{v}$

and finally, the number associated with the range between ν and $(\nu + d\nu)$, is $\frac{21.d\nu}{v}$

or if we consider a<u>l</u>l the fibrations of the cord, twice this,

(53) i.e. $\frac{41.d\nu}{v}$ (Since we have considered vibrations only in plane of paper)

Now the statistical mechanical theory, (and in particular the mechanical theory of gases), establishes that the state of statistical equilibrium is associated with an <u>average</u> <u>kinetic</u> energy of $(\frac{kT}{2})$ per degree of freedom.

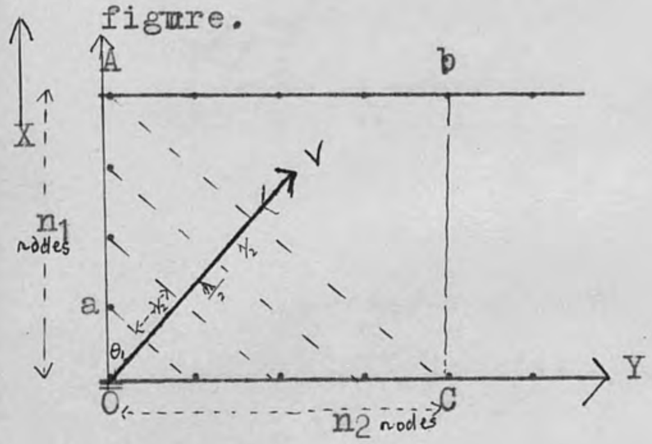
Now simple harmonic vibrations, to which category these simple modes of vibration belong have the average kinetic energy equal to the average potential energy, and therefore the <u>average</u> <u>energy</u> of a vibration is <u>kT</u>, (where K is Boltzmann's constant) If we multiply the expression (53) by kT, we get for the energy

(54) $$\frac{41.kT.d\nu}{v}$$

Our problem for radiation is slightly more complex, because we have to consider the states of motion of a medium extended in space in three dimensions, whereas our cord has only one dimension.

Let us consider a cubical region of our enclosure, the sides of which we will, for simplicity, take to be unity.

Our cubical region will be filled with waves (stationary waves) the nodal planes of which are shown by the diagonal lines in the figure.



Suppose that OV and VO are the directions of propagation of the progressive waves, giving rise to the stationary waves. (The arrow OV is not necessarily confined to the plane of the paper.

If there are n_1 intevals in the edge OA (in the X-axis)
n_2 " " " " OB Y-"
n_3 " " " " OC Z-"

and if cos O_1 ,cps O_2, and cos O_3 are the direction cosines of the line OV, then $Oa = \frac{1}{n_1}$

and $\cos\theta_1 . Oa = \frac{1}{2}\lambda$

therefore $\lambda . n_1 = 2\cos\theta$

and similarily $\lambda . n_2 = 2\cos\theta_2$

$\lambda . n_3 = 2\cos\theta_3$

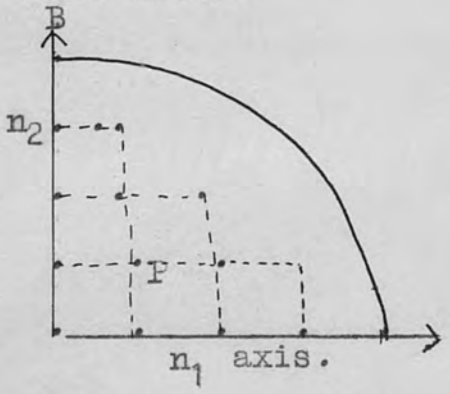
and since cos θ cos θ and cos θ are direction cosines of the line OV, the sum of their squares is unity, and therefore

$$\lambda^2 . (n_1^2 + n_2^2 + n_3^2) = 4,$$

(55) since $\lambda = \frac{c}{\nu}$, then $\left(n_1^2+n_2^2+n_3^2\right) = \frac{4\nu^2}{c^2}$

By giving n_1 n_2 and n_3 different positive integral values we obtain the different modes of vibration for a medium, (i.e. in this case, the ether.)

If we represent n_1 n_2 and n_3 by distances measured along rectangular axes of coordinates, then the points representing the various modes of vibration will be at the corners of the unit cubes.



for example, P would represent the point for which n_1 was one and n_2 also 1 Each other corner of a unit cube will represent a mode of vibration.

Consider the totality of vibrations, the frequencies of which lie between 0 and ν. Clearly the number of them will be the number of unit cubes in the octant of the sphere of radius $\left(n_1^2+n_2^2+n_3^2\right)^{1/2} = \left(\frac{2\nu}{c}\right)$ (using (55)

The volume will therefore be $\frac{1}{8}\cdot\frac{4\pi}{3}\cdot\left(\frac{2\nu}{c}\right)^3$

$$= \frac{4\pi}{3}\cdot\frac{\nu^3}{c^3}$$

and the number in the range of frequencies between ν and $(\nu+d\nu)$ will therefore be

(56) $$\frac{4\pi\cdot\nu^2\cdot d\nu}{c^3}$$

If we remember, (just as in the case of the cord) that we are dealing with transverse vibrations, the motions of which may be resolved into parts at right angles to one another, and which are independant of each other, we have for the number of vibrations

(57) $$\frac{8\pi.\nu^2.d\nu}{c^3}$$

If we call the average energy for each degree of freedom <u>kT</u> as in the parallel case for the cord, then the expression for the energy becomes

(58) $$\frac{8\pi.\nu.^2 d\nu.kT}{c^3} = u_\nu d\nu = \frac{8\pi\nu^2 kT}{c^3}.d\nu$$

which is known as <u>Rayleigh's</u> formula.

Expressing it in terms of E_λ and λ, we get

$$\frac{8\pi.kT.d\lambda}{\lambda^4} = E_\lambda d\lambda$$

Let us investigate how these formulae agree with Wien's law. This law requires that u_ν shall be expressible in terms of a function f, such that

$$u_\nu = \nu^3.f(x)$$

$$E_\lambda = \lambda^{-5}.F(X)$$

where x is $\left(\nu/_T\right)$ and X is $\left(\lambda.T\right)$ (see equations (49) and (50) and, moreover, the displacement law requires that

$\lambda_m.T$ = constant (that is, shall have the same values for all temperatures.)

Rayleigh's formula may be put

(58) $$u_\nu = \frac{8\pi.\nu^2 kT}{c^3} = \frac{8\pi.k.}{c^3}.\nu^3\left(.\frac{T}{\nu}\right)$$

comparing the two formulae then

$$u = \nu^3.\frac{8\pi k.}{c^3}.\left(\frac{T}{\nu}\right) \qquad \text{(Rayleigh)}$$

$$u = \nu^3.\ f\left(\frac{T}{\nu}\right) \qquad \text{(Wien's law)}$$

we see that the formula of Rayleigh is in agreement with the expression for Wien's Law.

Similarily, comparing

(58') $$E_\lambda = \frac{8\pi kT}{\lambda^4} = \frac{8\pi k\,(\lambda . T)}{\lambda^5} \qquad \text{(Rayleigh)}$$

and $$E_\lambda = \frac{1}{\lambda^5} F(\lambda . T) \qquad \text{(Wien)}$$

We see, a gain, that a function can be found such that the two expressions are in agreement.

But we shall see that, although Rayleigh's formula can be made to fit Wien's law, in spite of this formal agreement, it does not agree with experiemntal observations.

The displacement law requires that the maximum values for E_λ at different temperatures, shall be such that the wavelength where the maximum occurs shall obey the law

$(\lambda_m . T) =$ constant for all temperatures.

Let us find the maximum or minimum given by (58')

Differentiating the expression (58') with respect to λ and equating $\frac{dE_\lambda}{d\lambda}$ to zero, we get

(59) $$0 = \frac{dE_\lambda}{d\lambda} = -\,(\text{constant}) . \left(\frac{T}{\lambda^5}\right)$$

which gives an infinite value for λ for a maximum or minimum.

If we differentiate a second time, we get, (apart from constants

(60) $$\frac{d^2E}{d\lambda^2} = \frac{T}{\lambda^6}$$

and as we are measuring T on the Kelvin work scale, the expression (60) must always be greater than 0 for all values of λ. It follows therefore, that as λ tends to ∞ E_λ tends not to a maximum (as experiment indicates it should but to a minimum. Figure (8) shows a rough form of the curve. Moreover, we have seen that the total energy E is equal to the integral of $E_\lambda d\lambda$ over all possible values of λ

that is $E = \int_0^\infty E_\lambda \, d\lambda$

$$= (\text{constant}) . \int_0^\infty \frac{1}{\lambda^4} . d\lambda$$

E is therefore equal to $(\text{constant}) . -\left[\frac{1}{\lambda^3}\right]_0^\infty = +\infty$

But it is inconceivable that E should be infinite and so the expression for the energy cannot be correct.

A different formula was given by Wien for the energy distribution. As we indicated earlier, he made certain assumptions about the velocities of the molecules and arrived at the formula

(61) $$E_\lambda = \frac{a_1}{\lambda^5} . e^{-\frac{a_2}{\lambda T}}$$

where a_1 and a_2 are constants

(62) From (61) $$u_\nu = \frac{a_1 . \nu^5 . c}{c^5 . \nu^2 . e^{-\frac{a_2 \nu}{cT}}} = \frac{a_1 . \nu^3}{c^4 . e^{a_2 \nu / cT}}$$

From (61) and (62) it can be seen that the expressions satisify Wien's law, as they are expressible in the forms

$$\nu^3 . f\left(\frac{T}{\nu}\right) \text{ and } \lambda^{-5} . F(\lambda . T)$$

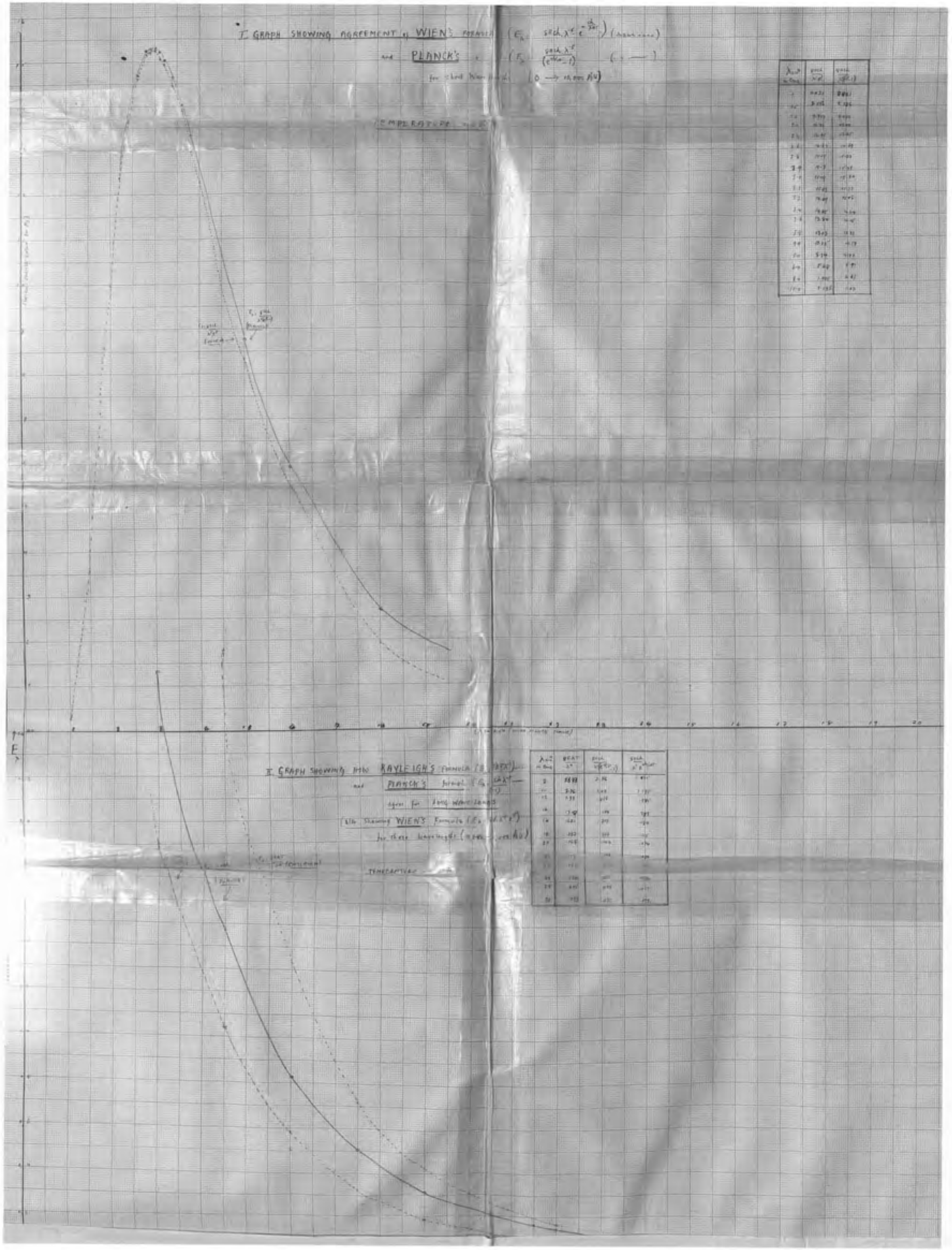
Differentiating (61), we get

$$\frac{dE}{d\lambda} = \frac{-5 a_1 . e^{-\frac{a_2}{\lambda T}}}{\lambda^6} - \frac{a_1 a_2 . e^{-\frac{a_2}{\lambda T}}}{\lambda^5 . T . \lambda^2}$$

and for a stationary value, $\frac{dE}{d\lambda} = 0$

therefore $5 = \frac{a_2}{\lambda . T}$ or $\lambda T = \frac{a_2}{5}$

Thus Wien's formula shows a stationary value, which, incidently is not very different from the one calculated from the acceptedly correct formula. It was found experimentally that the agreement


I GRAPH SHOWING AGREEMENT of WIEN'S FORMULA
and PLANCK'S
for short wavelengths
TEMPERATURE
II GRAPH SHOWING HOW RAYLEIGH'S FORMULA
and PLANCK'S formula
agree for long wavelengths
(also showing WIEN'S formula
for these wavelengths)
TEMPERATURE
E
1
2
3
4
5
6
7
8
9
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20

Calculation for WIEN-PLANCK [illegible]

A	B	C	D	E	F	G	H.	I	J	K	L	M	N	4P	O	Q
[illegible]	[illegible]	[illegible]	(C−B)	[illegible]	(G−E)	[illegible]	[illegible]	5+(B)	(H−I)	(J−G)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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TEMPERATURE [illegible]

c = 2.998 × 10¹⁰ cm/sec

k = [illegible]

π = [illegible]

h = [illegible]

log c = [illegible]

log k = [illegible]

log π = [illegible]

log h = [illegible]

∴ log (8πch) = [illegible]

$\log \frac{ch}{kT}$ = [illegible]

log 8πkT = [illegible]

A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U
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5.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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8.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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12.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
14.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
16.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
18.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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22.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
24.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
26.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
28.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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of Wien's formula , while being good for short wavelengths, was not good for longer wavelengths, whereas Rayleigh's formula was in agreement for long wavelengths, with experimental observations, but that it did not agree for the short wavelenghts, as the rough figure shows

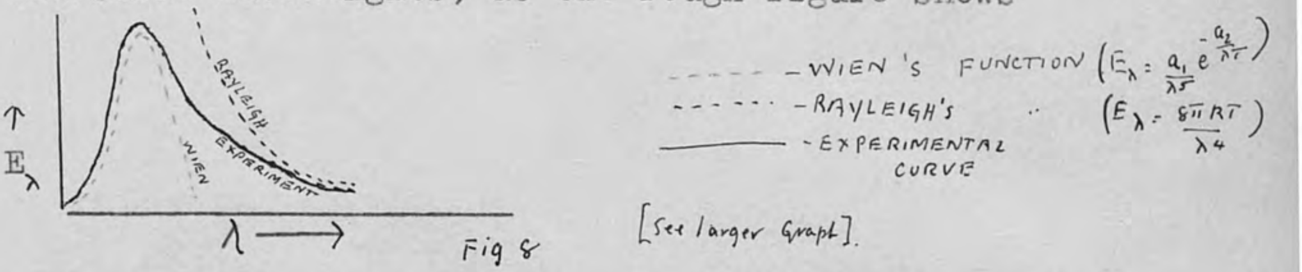

Fig 8

[See larger Graph].

It seems then that the correct formula must approach Rayleigh's as λ becomes large, and approach Wien's as λ becomes smaller.

If we write Wien's formula as

$$\frac{a_1}{\lambda^5 . e^p} \qquad \text{where } p = a_2/\lambda.T$$

We see, that if we put instead of ~~is~~ this,

$$\frac{a_1}{\lambda^5 . (e^p - 1)}$$

we shall be very near what we want, for as λ becomes small, e^p becomes very big, and we may write for $(e^p - 1)$, e^p without appresiable error for these small values of λ Consequently, equation (63) becomes

$$\frac{a_1}{\lambda^5 . e^p} \qquad \text{which is Wien's formula.}$$

On the other hand, as λ becomes big, e^p becomes small, and we may expand e^p, as $(1 + p + \frac{p^2}{2} + \frac{p^3}{3} \ldots)$ and neglecting powers higher than the first, $(e^p - 1) \simeq p$ and substituting in (63),

$\frac{a_1}{\lambda^5 . p}$ which is, substituting for p,

$$\frac{a_1 . \lambda T}{\lambda^5 . a_2} = \frac{a_1}{a_2} . \frac{T}{\lambda^4}$$

which is Rayleigh's formula.

It seems that the expression (63) will meet the case for the extreme values for λ, of $\lambda \rightarrow 0$ and $\lambda \rightarrow \infty$.

Without enquiring into the agreement of the intermediate values of the function, let us see what value we must give to the average energy, $\overline{E}$, associated with a single vibration.

We know(from equation (57).) that the number of vibrations between frequencies ν and $(\nu+d\nu.)$ per unit volume, is

(57) $$\frac{8\pi . \nu^2 . d\nu}{c^3}$$

and if $\overline{E}$ is the average energy, then the product of

(64) the expressiom (57) and $\overline{E}$ must be $u_\nu d\nu$.

Since we are assuming $E_\lambda d\lambda = \frac{a_1 d\lambda}{\lambda^5 . (e^p - 1)}$ Where $p = \frac{a_2}{\lambda T}$

(65) then $u\, d\nu$ will be $\frac{a_1 c . d\nu}{\nu^2 . \frac{c^5}{\lambda^5}(e^p - 1)} = \frac{a_1 \nu^3 d\nu}{c^4 (e^p - 1)}$ $= \frac{a_2 \nu}{cT}$

Substituting this in the expression (64)

$$\frac{c . 8\pi . \nu^2 \overline{E} . d\nu}{c^4} = \frac{a_1 \nu^3 d\nu}{c^4 (e^p - 1)}$$

(66) i.e $$\overline{E} = \frac{a_1 \nu}{8\pi c . (e^p - 1)}$$

Now, for large values of λ (i.e. small values of ν), we know that this must approach Rayleigh's formula, i.e. $\overline{E} \xrightarrow{ac} kT$

As λ becomes big, $(e^p - 1) \longrightarrow p$, where p is $\frac{a_2 c}{c \lambda . T} = \frac{a_2 . \nu}{cT}$

and therefore as $\lambda \longrightarrow \infty$, we have

(66') $$\overline{E} = \frac{a_1 . \nu}{8\pi c.(\ p)} = \frac{a_1}{a_2}\,\frac{T}{8\pi}$$

and this must approach the classical (Rayleigh's) value, kT

therefore $$\frac{a_1}{a_2}.\frac{T}{8\pi} = kT$$

(66") or $$\frac{a_1}{a_2} = 8\pi k$$

Consider now the expression for $\overline{E}$. We had

$$\overline{E} = \frac{a_1\nu}{8\pi c}\,\frac{1}{(e^p - 1)}$$

Thue $\overline{E}$ is expressed as a function of $e^{-\frac{a_2.\nu}{cT}} = e^{-\frac{a_2}{c}.\frac{\nu}{T}}$
(since p is $\frac{a_2\nu}{cT}$)

We have had similar sorts of expressions for the energy , for example, in the Maxwellian distribution, we have that the energy is a function of $\left[e^{-\frac{energy}{kT}}\right]$

Let us put our expression for the energy in a similar sort of way. We had it as a function $\left[e^{-\frac{a_2\nu}{cT}}\right]$

This index, $-\frac{a_2 . \nu}{cT}$

may be put as $$-\left(\frac{a_2 . k}{c}\right).\frac{\nu}{kT}$$

where the part $\frac{a_2k}{c}$ is constant. Representing this by the letter "h", we have the energy as a function of $e^{-\frac{h\nu}{kT}}$

where h is given by

(67) $$h = \frac{a_2 . k}{c}$$

Let us investigate more of its value. Substituting for $\overline{E}$, the average energy
We had (page 62.)

(66) $$\overline{E} = \frac{a_1 . \nu}{8\pi c\,(e^p - 1)}$$

and from (66") $\left(\frac{a_1}{a_2}\right) = 8\pi k$

therefore, using (67)

$$a_2 = \frac{h.c}{k}$$

and $a_1 = 8\pi ch$

$$\therefore \bar{E} = \frac{h.8\pi c}{8\pi c} \cdot \frac{\nu}{e^p - 1} = \frac{h\nu}{(e^p - 1)}$$

where $p = h\nu/kT$

It now remains to justify theoretically, the assumption that we may write

$$E_\lambda \, d\lambda = \frac{a_1 \, d\lambda}{\lambda^5 . (e^p - 1)}$$

or

$$u_\nu d\nu = \frac{a_1 \nu^3}{c^4 (e^p - 1)}$$

or in other words

$$\bar{E} \text{ as } \frac{a_1 . \nu}{8\pi c(e^p - 1)} \qquad \text{where } p = \frac{a_2 \nu}{cT}$$

$$= \frac{h . \nu}{e^p - 1} \qquad p = \frac{h\nu}{kT}$$

and where $a_1 = 8\pi ch$

$$a_2 = \frac{ch}{k}$$

The two expressions for the number of vibrations or vibrating systems between ν and $(\nu - d\nu)$, (see (56) and (57).) are not open to any question and consequently the expression kT for the average energy is suspect. This amounts to saying that the principle of equipartition of energy is faulty. This equipartition of energy principle is, however a necessary consequence of the classical dynamics, and the removal of this equipartition of energy principle would cause the shattering of classical mechanics. Hence, the only way to to make further progress, as Planck appreciated at the close of the last century, was to modify them. The exponential in equation (66), $e^{-\frac{h\nu}{kT}}$, and other formulae above, suggests how we should proceed. In Maxwell's distribution formula in the kinetic theory of gases, we have the exponential : -

$$e^{-\frac{\text{energy of a molecule}}{kT}}$$

and we are lead to contemplate only such energy transferences of amounts equal to $\underline{n}.h\nu$ at a time (where $\underline{n}$ is an integer).

Before making this vital step, Planck considered very carefully the expression for the number of vibrations : -

$$\frac{8\pi.\nu^2.d\nu}{c^3}$$

and being satisfied that it was correct, tried to find an assumption which would justify writing the average energy $\overline{E}$ as

$$\frac{h\nu}{e^p - 1} \qquad \text{(where } p = \frac{h\nu}{kT}\text{)}$$

To do this, he supposed that the walls of the enclosure were made up of oscillators, each of which could vibrate with its own particular frequency, ν, and the energy of which was an integral multiple of $h\nu$.

In this way, he succeeded in arriving at the formula for $\overline{E}$, given above, namely

$$E = \frac{h\nu}{e^p - 1}$$

Planck's Formula for the Distribution of Energy in the Spectrum of a Black-Body.

We shall not arrive at the formula for the distribution of energy, in exactly the same way as that in which Planck arrived at it.

We shall suppose that we have a definite number of systems, (say N ,) and that N is made up of numbers of systems of different energy values, say we have,

N_1 with the energy E_1
N_2 " " " E_2
etc:

and in general
N_s with the energy E_s

We shall then consider the the various ways in which the distributions of these numbers can be made, so that the total number N remains the same, and so that the total energy remains constant. The total energy, E , must be equal to the sum of $N_s . E_s$, and N will be the sum of N_s. That is

$$N = \sum N_1 + N_2 + N_3 + \ldots\ldots + N_s + \ldots$$

and $$E = \sum N_1E_1 + N_2E_2 + N_3E_3 + \ldots N_sE_s$$

so that $$\frac{E}{N} = \sum \frac{N_s . E_s}{N} = \sum f_s . E_s$$

where f_s has been written for $\frac{N_s}{N}$

$\frac{E}{N}$ is the average energy, $= \overline{E}$

and since $f_1 = \frac{N_1}{N}$; $f_2 = \frac{N_2}{N}$; etc;

~~whence~~ it follows that

(70) $$f_1 + f_2 + f_3 + \cdots + f_s + \cdots = \sum_{0}^{\infty} f_s = \frac{N_1}{N} + \frac{N_2}{N} + \frac{N_3}{N} + \cdots = 1$$

(70') since $\sum N_s = N$

Let us consider the various ways in which the energy of these systems may be distributed among them, and which distribution is most likely to occur. Then having found the distribution which is most probable, we must assume that this distribution is ultimately established. It will be the distribution corresponding to statistical equilibrium, namely the state with which we agreed to associate <u>maximim</u> <u>entropy</u>.

Let us compare the distribution with the placing of balls in receptacles. If we have a definite number of balls - say six ~~-~~ and two boxes, A and B and let us fix on a particular distribution, say we would have four in A, and 2 in B. Then the number of ways in which this distribution can be made, is

$$\frac{6\,!}{4\,!\;2\,!}$$

different ways.

We are going to assume that the receptacles are exactly alike, and that the a priori probabilities associated with them are the same. We are also assuming that the presence of a ball already in a box does not prevent another ball from coming into the same box. We could have other distributions, such as 6 in A and 0 in B, which could be done in only one way.

or, we might have had 5 in A and 1 in B (6 ways)
4 in A and 2 in B $\left(\frac{6.5}{2} \text{ " }\right)$
and so on.

Therefore the total number of different ways in which we can make the distribution, is

(72) $$1 + \frac{6}{1!} + \frac{6.5}{2!} + \frac{6.5.4}{3!} + \ . \ . \ . \ + 1 = 2^6$$

different ways. Therefore, if we distribute the balls at random the chances of a 4 in A and 2 in B, distribution, is as the ratio of (the ways of distributing 4 in A and 2 in B) to (the total number of ways). That is the ratio is (the expression (71).) to (the expression (72).)

(73) That is $$\frac{6!}{4!\ 2!} \div 2^6$$

In the general case of N balls and n boxes, the chance of a particular distribution is

(74) $$\frac{N\,!}{N_1!\ N_2!\ldots N_n\ !} \times (n^{-N})$$

In this we have agreed to let "certainty" be represented by unity. If we agree to let certainty be n^N then the probability (used in this sense, generally called " the thermodynamic probability"), P, becomes

(75) $$P = \frac{N!}{N_1!\ N_2!\ldots N_n!}$$

It follows, then that

$\log P = \log N! - (\log N_1! + \log N_2!\ .\ .\ .\ + \log N_n!)$

By Stirling's theorem, that $\log N! = N.\mathrm{Log}\, N$, when N is very big, it follows that

$$\log P = N \log N - \sum_0^\infty N_s \log N_s$$
$$= N \log N - \sum_0^\infty N_s \log(N.f_s)$$

$$\text{i.e } \log P = N \log N - \sum_{0}^{\infty} N f_s \log f_s - \sum_{0}^{\infty} N.f_s \log N$$

$$= N \log N - \sum_{0}^{\infty} N.f_s \log f_s - N \log N \sum_{0}^{\infty} f_s$$

5) $$= -N.\sum_{0}^{\infty} f_s \log f_s \quad \text{(using (70).)}$$

6) If we wri~~/~~te $\log P = \Psi$

6') then $\Psi = -N \sum f_s \log f_s$

It follows that the most probable distribution is that for which P (and hence Ψ) is a maximum

Differentiating (76) and equating $d\Psi$ to zerp

(77) $d\Psi = 0 = -N.\sum (\log f_s + 1).df_s$

This differentiation must be carried out under the conditions of constant energy and constant N, that is

$\sum df_s = 0$ and $d\bar{E} = 0 = \sum E_s.df_s$

Therefore we must have the three following equations holding

(78) $\sum \log f_s df_s = 0$

(79) $\sum E_s.df_s = 0$

(80) $\sum df_s = 0$

In order that these three hold simultaneously, we must have

(81) $\log f_s - \beta E_s - \alpha = 0$

and consequently, on integrating

(82) $f_s = B.e^{-\beta E_s}$

where α, β, and B are all constants

This value of f_s in (82) corresponds to a maximum of Ψ.

Substituting for f_s in (76') and writing Ψ_m for the max. of Ψ

(83) $\Psi_m = -N \sum B e^{-\beta E_s} (\log B - \beta E_s) = -N \log B + \beta E$

since $\sum f_s = 1 = \sum B e^{-\beta E_s}$

thus we have $\boxed{\Psi_m \text{ is } -N \log B + \beta E}$

Suppose, now, that we change E by a small amount dE, and that $d\Psi_m$ is the resulting change in Ψ_m. Differentiating (83), to find dU_m, we get : -

$$d\Psi_m = -N\frac{dB}{B} + \beta\, dE + E.d\beta$$

(since B and β will no longer remain constant if E changes.) We are assuming that N suffers no change, i.e. that $\sum f_s$ remains the same. Therefore,

$$d\sum f_s = 0 = dB \sum e^{-\beta E_s} - B \sum E_s.e^{-E_s\beta}.d\beta$$

$$\text{i.e.} \quad 0 = \frac{dB}{B} - \frac{E}{N}.d\beta$$

substituting this for $\frac{dB}{B}$ in the expression for $d\Psi_m$, we get

(84) $$d\Psi_m = -\frac{E}{N}.d\beta N + \beta\, dE + E.d\beta \qquad = \beta\, dE$$

We must now find something out about the constants, β and B If we associate with the state of maximum entropy, the state of greatest probability, then let us put : -

$$g.\Psi_m = \phi$$

where g is some constant and ϕ is the corresponding entropy. Differentiating this, and substituting for $d\Psi_m$, we get : -

$$d\phi = g\beta.dE$$

and therefore $\beta g = \frac{d\phi}{dE}$

which, by the definition of entropy, is a measure of the reciprocal of temperature

therefore, $g\beta. = \frac{1}{T}$

or $\beta = \frac{1}{gT}$

This g is identically the same as k, Boltzmann's constant, and the law that the entropy is proportional to the logarithm of the probability is known as Boltzmann's law.

We can further demonstrate that this constant is an equivalent of the reciprocal of temperature, by considering the statistical equilibrium of two assemblages A and B, the total energy of which, E, remains constant, while their individual energies vary, subject to this condition,

(86) $$E = E_a + E_b$$

where E_a is the energy of the assemblage A and E_b that of B.

If P_a and P_b are the probabilities that A and B are in certain states, then the combined probability that they are so at the same instant is

$$p = P_a \cdot P_b$$

(86') and hence $\Psi = \Psi_a + \Psi_b$

Differentiating (86) and (86')

(87) $$d\Psi = d\Psi_a + d\Psi_b$$

and $dE = dE_a + dE_b$

But the condition for equilibrium (statistical) of the two systems is that

$$d\Psi = 0$$

$$dE = 0$$

and therefore, substituting in (87)

(87') $$d\Psi_a + d\Psi_b = 0$$

$$dE_a + dE_b = 0$$

and, by (84)

$$d\Psi_a = dE_a \cdot \beta_a$$

$$d\Psi_b = dE_b \cdot \beta_b$$

and therefore, substituting,

$dE_a.\beta_a - dE_a\beta_b = 0$

(88) whence $\beta_a = \beta_b$

This is then the condition that two assemblages be in statistical equilibrium with one another.

If $\beta = \frac{1}{kT}$

then this condition for statistical equilibrium is that

$$T_a = T_b$$

That is to say if the temperatures of the two assemblages are the same, then there will be a state of statistical eqiulibrium between them.

Suppose, now that the two systems have not reached equilibrium, then, by the second law of thermodynamics, ø must increase, or dø must be greater than zero. That is to say, dΨ must be greater than zero, and therefore

$dE_a.\beta_a - dE_a.\beta_b$ must be greater than 0

Suppose that dE_a is positive,

then, $\beta_a > \beta_b$ or $\frac{1}{\beta_a} < \frac{1}{\beta_b}$

i.e, energy will flow to the system with the greater 'β' or to the system with the lesser $\frac{1}{\beta}$, i.e. energy will flow to the system with the lesser temperature, T.

We have thus found an expression for β. To find a value for the other constant, B, of equation (83), we consider the expression that we had for f_s, namely

$$f_s = B.e^{-\beta E_s}$$

If we sum f_s for all values of s from 0 to ∞,, we get

$$\sum f_s = 1 = B.\sum e^{-\beta E_s}$$

(89) and therefore $B = \dfrac{1}{\sum e^{-\beta E_s}}$

To evaluate the denominator of this expression, we have to make use of Planck's quantum condition, that the energy exchanges can only take place in integral multiples of the quantity, $h\nu$. That is to say, for E_0, we substitute $\underline{0}.h\nu$; E_1 as $\underline{1}.h\nu$; etc:, in general E_s as $\underline{s}.h\nu$ and therefore

$$\sum_{s=0}^{\infty} e^{-\beta E_s} = (1 + e^{-\beta h\nu} + e^{-2\beta h\nu} + \ldots)$$

$$= \frac{1}{1 - e^{-\beta h\nu}}$$

writing β as $\frac{1}{kT}$ and substituting in (89), we get : -

(89') $$B = 1 - e^{-\frac{h\nu}{kT}}$$

The average energy, $\bar{E}$, is equal to $\sum f_s E_s$ and is therefore equal to $\sum B, sh\nu . e^{-s.p}$ where $p = \frac{h\nu}{kT}$

$$= B.h\nu.e^{-p}.(1 + 2e^{-p} + 3e^{-2p} \ldots)$$

$$= B.h\nu.e^{-p}.(1 + e^{-p})^{-2}$$

therefore, substituting for B, we get

(90) $$\bar{E} = \frac{h\nu.e^{-p}}{1 - e^{-p}} = \frac{h\nu}{e^{p} - 1}$$

(90') that is $$\bar{E} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

Substituting this value for $\bar{E}$ in the radiation formula, we get

(91) $$u_\nu d\nu = \frac{8\pi\nu^2.d\nu}{c^3} . \frac{h\nu}{e^{h\nu/kT} - 1}$$

(92) $$E_\lambda d\lambda = \frac{8\pi.ch.}{\lambda^5} \frac{d\lambda}{e^{\frac{ch}{\lambda kT}} - 1}$$

Thus we see that the " required condition" to obtain a formula which agrees with the experimental observations is that the energy is an integral multiple of $h\nu$ where h is Planck's constant and ν is the frequency of the radiation.

We can, from Planck's law of energy distribution, obtain a value for σ, the coefficient of total radiation, or, if we assume the experimentally observed value for σ and also the experimental value for the constant of Wien's displacement law, we can calculate the value for h and k, (Planck's and Boltzmann's constants).

We defined u, the energy density, as the integral

$$u = \int_0^\infty u_\nu \, d\nu$$

and, from Planck's law,

$$u_\nu d\nu = \frac{8\pi h \nu^3 . d\nu}{c^3 \left(e^{\frac{h\nu}{kT}} - 1\right)}$$

and therefore, by the Stefan-Boltzmann law, $u = aT^4$

$$aT^4 = \frac{8\pi h}{c^3} \int_0^\infty \frac{\nu^3 . d\nu}{e^{\frac{h\nu}{kT}} - 1}$$

$$= \frac{8\pi k^4 T^4}{h^3 c^3} \int_0^\infty \frac{x^3 . dx}{e^x - 1} \qquad \text{where } x = \frac{h\nu}{kT}$$

hence, we have

$$a = \frac{8\pi k^4}{h^3 . c^3} \int_0^\infty \left[x^3 . dx . (e^{-x} - e^{-2x} \; .... e^{-nx} \; ..)\right]$$

$$= \frac{48\pi . k^4 \pi^4}{h^3 \; c^3 . 90}$$

since $\int_0^\infty x^3 \; e^{-nx} . dx = \frac{6}{n^4}$ and $\sum_1^\infty \frac{1}{n^4} = \frac{\pi}{90}$

therefore $\sigma = \frac{a.c}{4} = \frac{2}{15} . \frac{\pi^5.k^4}{c^2.h^3}$

giving h the value $(6.547).10^{-27}$ erg.sec^{-1}

and k " " $(1.3708).10^{-16}$ erg.deg^{-1}

" c " " $(2.994).10^{10}$ cm sec^{-1}

we calculate σ as $(5.713).10^{-5}$ erg.cm^{-2}.deg^{-4}.sec^{-1}

Wien's constant, b, is according to the displacement law equal to $\lambda_m.T$, and we can get λ_m from equating $\frac{dE_\lambda}{d\lambda}$ to zero.

From Plaćnck's law, therefore, differentiating, we get

$$e^{-x} = 5(1 - e^{-x})$$ where, as before $x = \frac{h\nu}{kT} = \frac{ch}{\lambda kT}$

and therefore

$$x = 4.9651.$$

or $b = \frac{ch}{k.\ 4.9651.} = .2863$ (using the value 1.4317 for $\frac{ch}{k}$.)

The experimental values of these constants are given here : -

	Calculated value	Experimental value
σ	$(= \frac{2\pi^5.k^4}{15\ c^2h^3} = 5.713 . 10^{-5}$	$5.735 . 10^{-5}$
b	$(= \frac{ch}{k.\ 4.9651} = .2863$	.2940

Einstein's Deduction of Planck's Law

When Planck first deduced the law for the distribution of energy in the spectrum of a black-body, he had to introduce the idea of an "oscillator" as the " go-between" of the radiation and the matter within the uniform temperature enclosure. He was forced to introduce this idea of a " dipole oscillator", because the mechanism of emission and absorption of energy by atoms was not known at the time. It was not until about 1912 or 1913, that Bohr published his theories about spectral radiation. He associated in atoms, different levels of energy with the electron orbits, and he supposed that when an electron was transferred from one orbit to another, that an amount of energy equal to $h\nu$ was radiated, where ν is the frequency of the radiation emitted. That is to say, in the transference from an orbit of energy E_n to one of energy E_m, radiation of frequency ν_{nm} is emitted, such that

(93) $$E_n - E_m = h.\nu_{nm}$$

Einstein supposed that a number of these Planck vibrators were placed in a constant temperature enclosure, and investigated the nature of the energy exchanges due to the emission and absorption of energy by them, in a way implied by equation (93).

Let N_n be the number having the energy E_n
" N_m " " " " " " E_m
& " u_{nm} " " density of the radiation of frequency ν_{nm}.

Then, if the radiation of thid frequency fall on an atom in the state E_m, it may be absorbed by it, and raised to the level E_n. If b_{mn} is the probability that the radiation be absorbed, then the amount of the radiation absorbed will be equal to the product

(94) $$N_m.u_{nm}.b_{mn} \quad \text{(per unit time.)}$$

The amount of radiation emitted will be divided into two parts. Firstly, that emitted spontaneously by the N_n atoms (equal to N_n multiplied by the probability factor that the atoms will emit, i.e. $N_n.a_{nm}$) and secondly, that emitted under the influence of the radiation already present, (equals $N_n.b_{nm}.u_{nm}$. where b_{nm} is the probability factor of emission and is not, as far as we know, yet, equal to b_{mn}.)

Since we have assumed a state of equilibrium to exist within the constant temperature enclosure, we must therefore equate the amounts of radiation emitted and absorbed.

$$\text{i.e. } N_m.u_{nm}.b_{mn}. = N_n(a_{mn} + u_{nm}.b_{nm})$$

$$\text{or} \quad N_n,a_{mn} = N_m.u_{nm}.b_{mn} - N_n.u_{nm}.b_{nm}.)$$

$$\text{that is} \quad u_{nm} = \frac{N_n.a_{mn}}{N_m,b_{mn}. - N_n.b_{nm}}$$

(95) $$= \frac{a_{mn}}{b_{mn}.\dfrac{N_m}{N_n} - b_{nm}}$$

If we assume the canonical law of distribution to hold, then, $N_m = A.e^{-E_m/kT}$ N_n $A.e^{-E_n/kT}$

and therefore, $$\frac{N_m}{N_n} = e^{+\frac{(E_n - E_m)}{kT}}$$

and therefore, using (93),

$$N_m/N_n = e^{+h\nu_{nm}/kT}$$

Substituting this in (95), we get : -

$$\underline{u_{nm}} = \frac{a_{nm}/b_{nm}}{\frac{b_{mn}}{b_{nm}}\cdot e^{h\nu_{nm}/kT} - 1}$$

Since we have been considering only radiation of a particular frequency, ν_{nm}, it follows that the equation (96) is the expression for the variation of the energy density u_{nm} with temperature. If therefore, we make $T \to \infty$ we know that u_{nm} must also approach ∞, and for this, the denominator of (96) must approach zero.

Since $e^{h\nu_{nm}/kT} - 1 \to 0$, (because $e^{h\nu_{nm}/kT} \to 1$ as $T \to \infty$)

then b_{mn} must be equal to b_{nm}, and we may write u_{nm} as

$$u_\nu = \frac{a_{nm}/b_{nm}}{e^p - 1}$$

where as usual, p stands for $\frac{h\nu}{kT}$

But for small values of ν, the equation (97) must approach the classical formula, and, therefore, making $\nu \to 0$

$$\frac{a_{nm}}{b_{nm}} \cdot \frac{1}{p} = 8\pi\nu^2 \frac{kT}{c^3}$$

and therefore, $\frac{a_{nm}}{b_{nm}} = \frac{8\pi h\nu^3}{c^3}$

and on substituting this in (97) we get Planck's formula.

$$u_\nu = \frac{8\pi h\nu^3}{c^3(e^p - 1)}$$

These considerations by Einstein, which are chiefly of historical importance, lead to an interesting paper by Strum[x], wherein he considers the possibility of generalising Planck's law, by widening the considerations of Einstein, and he deduces a possible variation in the value of σ, the Stefan-Boltzmann radiation constant.

Strum considered that the probability of emission, which we have called b_{nm} in the previous pages, should, instead of merely being proportional to the density u_{nm} , should be some function of the density, F(u), where F is given by

(98) $$F(u) = A + Bu + Cu^2 \text{ (neglecting higher powers)}$$

and the probability of absorption should be : -

(98') $$f(u) = a + bu + cu^2 \ldots$$

basing his calculations on these assuptions, he deduces that the density of radiation of a particular frequency ν, shall be,

(99) $$u_\nu = \frac{\alpha\nu^3}{(e^p-1)} - \beta\frac{\nu^6/T^3}{(e^p-1)^2} \qquad \text{where } p = \frac{h\nu}{kT}$$

and where α and β are constants.

Strum integrates this expression for u_ν to get u

(99') $$u = \int_0^\infty u_\nu \, d\nu = aT^4 = \sigma . T^4 . \frac{4}{\underline{c}}$$

(where we have written $\underline{c}$ for the velocity of light to distinguish it fron the 'c' of equation (98').)

From (99) and (99'), he gets for σ

$$\frac{8\pi^5 . k^4}{15 c^2 . h^3} + \left(\frac{6.47568 . k^7}{h^7}\beta\right) T^4$$

The value for β he maintains can be calculated from (99)

---

ref. x. Strum. Zeits. f. Phys. 51. 267. 1928.

He obtained from the Physikalsch Technischen Reichsantalt an average value of σ, as $\sigma = 5.77 \times 10^{-5}$ erg.sec^{-1}deg^{-4} cm^{-2}. He maintained that the calculated value for σ is

$$\sigma = (5.715. \pm 0.009) \times 10^{-5}.$$

The difference between these two, he maintains is of the order of the second term of the expression for σ (where the first term gives the usual Planck formula value.)

He asserts, that on these assumptions, that the energy E_λ will be given by

$$E_\lambda = \frac{c_1}{\lambda^5 (e^{c_2/\lambda T} - 1)} + \frac{c_3}{T^3 . \lambda^8 . (e^{c_2/\lambda T} - 1)^2}$$

where the value of this third constant c_3 can be calculated from the difference between the experimental and theoretical values of σ. Calling this difference $d\sigma$ ($= .06 \times 10^{-5}$) then c_3 must be

$$\frac{\beta c^8}{8\pi} = \frac{1}{2\pi\, 6.47568} . (hc/k)^7 . d\sigma$$

$$= 1.82 \times 10^{-7}$$

The criticism of this conclusion is that, in the first place no indication is given of the way in which the theoretical value for σ was obtained; of the possible errors in the values of the constants from which it was obtained. Secondly, that the more recent values of σ show a variation of much less than the earlier values, - a variation of about $.05 \times 10^{-5}$ and the mean value of the measurements (as calculated by Hoare, see later.) gives the mean experimental value of σ as $\sigma = 5.735 \times 10^{-5}$ which differs from the value calculated from values of h, k, and c, giver earlier ($= 5.713 \times 10^{-5}$) by $.022 \times 10^{-5}$ as compared with the value for $d\sigma$ of 0.06, given by Strum.

About the same time as this paper of Strum's was published, another one was given on the same subject by Majumdar and Kothari(x), which criticised both Einstein's deduction and also Bose's(x'), the former on the grounds that the ratio $a_{nm} : b_{nm}$ cannot be directly calculated, and the latter because of assumptions which the writers class as " arbitary"; for example, that he uses the mathematical probability instead of the thermodynamical one, and also that the Bose formula does not reduce to the classical one as it should.

The writers claim to obtain ~~the~~ Planck's formula without assumptions of this kind, but although interesting, their paper is not worth considering in further detail, for our present purpose.

Ref. (x) Zeits. f. Phys. 60. 251. 1928
(x') " " " 27. 384. 1924.

We have arrived at Planck's formula by adopting the undulatory theory of the nature of radiation and applying the methods of Statistical Mechanics combined with the hypothesis borrowed from the early form of the quantum theory that the energy of a simple harmonic system is an integral multiple of $h\nu$. In recent times, however, there has been a tendency to revert in some degree to views about the nature of light or electromagnetic radiation resembling those of Newton. This has resulted from the study of photoelectric phenomena more especially. The well known experimental fact that the maximum velocity of ejection of photoelectrons is independent of the intensity of the exciting radiation, is entirely incompatible with the naïve undulatory theory. Bragg's early experiments on X-rays convinced him that they were a corpuscular phenomena. On the other hand, a naïve corpuscular theory of radiation is just as unsatisfactory as an undulatory one, since it is inadequate to deal with the phenomena of interference. It appeared, in fact at one time, that an undulatory theory was necessary to explain many optical phenomena, and some sort of corpuscular theory for photoelectric phenomena. More than a quarter of a century ago, Einstein suggested that light consisted of small bundles of energy, each equal to $h\nu$ that is, it consisted of small particles, now called photons with each of which a definite frequency and energy proportional to it was associated. Indeed, Newton found it necessary to endow his " rays " with a periodic phenomenon, the fits of east reflection and transmission. Louis de Broglie introduced in 1924 a sort of hybrid theory in which he imagined light to

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Oct. 8th 1934.

W.A.Baron, Esq:,
Clerk in the Academic Dept:,
University of London,
South Kensington
S.W.7.

Dear Sir,

I herewith forward you a Copy of my Dissertation, bound in accordance with your specification, in order that the Degree of M. Sc: may be conferred on me by the Senate at their next meeting.

Yours faithfully,

Mary Barton

be made up of Einsteinian bundles(photons) which he imagined to be guided by waves. Out of this theory has emerged the present day Wave Mechanics which associates with the ultimate particles; photons,electrons etc: trains of waves, or groups of waves. These waves are not, it would seem, themselves physical entities. The square of the amplitude, for example does not measure the/energy or energy flow,(except when deal-with things on a macroscopic scale), but the probability of the presence of photons. Interference fringes receive now a slightly modified explanation. The bright fringes are formed at places where the probability (measured by the square of the amplitude) for the arrival of photons is large; dark fringes where it is small or zero. The rules for determining these positions happen to be identical with those for determining or calculating places of reinforcement or destructive interference of waves.

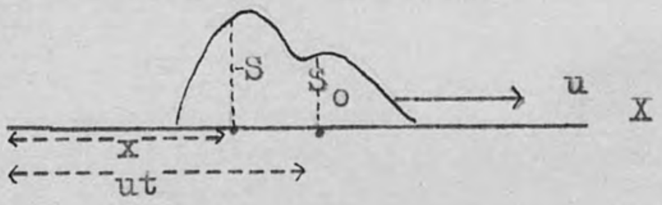
The further development is largely due to Schroedinger, who widened dynamics by extending the analogy which Hamilton had discovered between classical dynamics and geometrical optics, so that dynamics became analogous to optics.

Before giving an acciunt of de Broglie's work, let us obtain an expression for the Phase Velocity of a Wave, and obtain one for the Group Velocity of a superposition of waves.

Consider again the case of a stretched cord, fixed at both ends. Suppose this is given a sudden jerk at one end, causing a displacement there. This displacement will travel along the cord without change of shape or change of velocity, (to a first approximation.), and we may write for the displacement,

$$S = f(ut - x)$$

where u is the velocity with which the displacement travels, and x is the distance travelled, (see figure.).



For a simple harmonic disturbance, S will be given by : -

$$S = A \cos w(t - {}^{x}/_{u})$$

where, if T is the period, $w = {}^{2\pi}/_{T}$

At any given instant, the value of S for different values of x will be given by

$$\begin{aligned} S &= A.\cos\,(\,u.t.w. - {}^{w.x}/_{u}\,) \\ &= A.\cos\,(\text{constant} - {}^{w.x}/_{u}\,) \end{aligned}$$

If λ is the wave-length of the disturbance then

$$S = A.\cos 2\pi.\left(\frac{t}{T} - \frac{x}{\lambda}\right)$$

Differentiating this expression, we get ; -

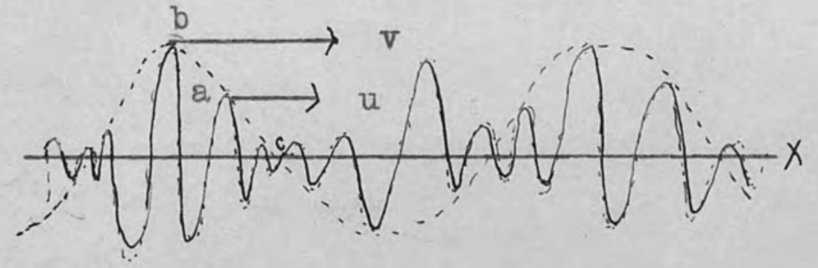
$$-\frac{d^2S}{dt^2} = \frac{4\pi^2 S}{T^2} \; ; \qquad -\frac{d^2S}{dx^2} = \frac{4\pi^2.S}{\lambda^2}$$

therefore $$\frac{d^2S}{dx^2} = \frac{T^2}{\lambda^2}\frac{d^2S}{dt^2} = \frac{1}{u^2}\cdot\frac{d^2S}{dt^2}$$

or the more general expression for a plane wave travelling in any direction is $$\nabla^2 S = \frac{1}{u^2}\frac{d^2S}{dt^2}$$

where u is the phase velocity.

Suppose now we consider the superposition of two harmonic waves. Then the outline of the wave resulting from a superposition ~~of these waves~~ will travel with a different velocity from the phase velocity of the individual components of the group. This velocity we call the group velocity.



The group velocity with which the point b in the figure is moving forward we will, for simplicity suppose, results from the superposition of two plane waves, the amplitudes of which are equal to A and the periods and wavelengths of which differ by a small amount, only. If T and T' are the periods, then $(T - T')$, $(= dT)$ we suppose very small by comparison with T itself, and similarily $d\lambda\ (= (\lambda - \lambda'))$ very small compared with λ.

The displacement will be given by the sum of the individual components, namely,

(100) $$S = A\cos 2\pi\left(\frac{t}{T} - \frac{x}{\lambda}\right) + A\cos 2\pi\left(\frac{t}{T'} - \frac{x}{\lambda'}\right)$$

$$= 2A \cos 2\pi \left\{ \tfrac{1}{2}\left(\frac{1}{T} - \frac{1}{T'}\right)t - \tfrac{1}{2}\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right)x \right\} . \cos \pi \left\{ \left(\frac{1}{T} + \frac{1}{T'}\right)t - \left(\frac{1}{\lambda} + \frac{1}{\lambda'}\right)x \right\}$$

(101) $$= \left\{ 2A . \cos \pi \left\{ d\left(\frac{1}{T}\right)t - d\left(\frac{1}{\lambda}\right)x \right\} \right\} . \cos 2\pi \left(\frac{t}{T} - \frac{x}{\lambda}\right)$$

where we have written

$$\frac{1}{T} + \frac{1}{T'} = \frac{2}{T}$$

and $$\frac{1}{T} - \frac{1}{T'} = d\left(\frac{1}{T}\right) \quad \text{etc:}$$

The expression (101) may be written thus : -

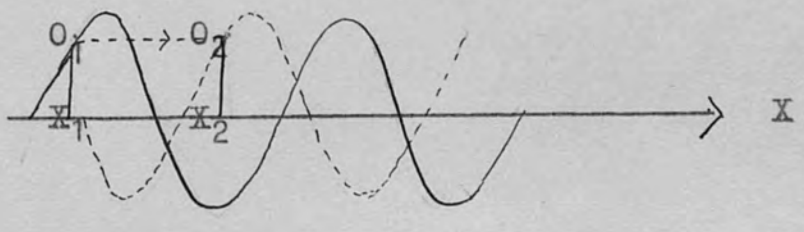
$$\underline{2a} . \cos 2\pi \left(\frac{t}{T} - \frac{x}{\lambda}\right)$$

which is an expression for a wave of phase $\left(\frac{t}{T} - \frac{x}{\lambda}\right)$

and amplitude $\underline{2a}$, where

(101a) $$2a = 2A \cos \pi \left\{ d\left(\frac{1}{T}\right)t - \left(\frac{1}{\lambda}\right)x \right\}$$

The expression (101a) will itself have the form of a wave and its outline will represent, at any instant, the amplitude of the resultant of the superposition of the two waves. If the outline ——— represent the position of the group at an instant t_1 and ---- represent it at a later instant t_2 and suppose that X_1 and X_2 are the positions of a point at these times,



then O_1X_1 and O_2X_2 will be given by substituting the appropiate values for t and X in (101), and since $O_1X_1 = O_2X_2$

$$t_1 d\left(\frac{1}{T}\right) - x_1 d\left(\frac{1}{\lambda}\right) = t_2 d\left(\frac{1}{T}\right) - x_2 d\left(\frac{1}{\lambda}\right)$$

and therefore the velocity with which the wave moves forward, v, will be

$$\frac{x_2 - x_1}{t_2 - t_1} = \frac{d\left(\frac{1}{T}\right)}{d\left(\frac{1}{\lambda}\right)}$$

This then is the group velocity

A specially interesting case of a group is one which, over a limited region, and during a limited time, is identical, or nearly so, with a plane harmonic wave of constant amplitude.

Even if this group possessed, at a given instant, the form

$$\Psi = A \cos 2\pi \left(\frac{t}{T} - \frac{x}{\lambda}\right)$$

exactly over a wide but limited spectral region, it would obviously not retain such a form; but would in the course of time, spread out and behave physically as a superposition of plane harmonic waves of slightly varying amplitude, frequency and wavelength and travelling in slightly different directions which we might regard as contained within the limits of the solid angle $d\Omega$. In fact, we should, in order to make it satisify the partial differential equation

$$\Psi = \frac{1}{u^2}\left(\frac{\partial^2 \Psi}{\partial t^2}\right)$$

be obliged to represent it as such a superposition by Fourier's theorem.

This group will travel almost like a rigid configuration with the velocity v, where

$$v = \frac{d\left(\frac{1}{T}\right)}{d\left(\frac{1}{\lambda}\right)}$$

while the individual harmonic waves of which it is constituted will travel with the phase velocities approximately equal to

$$u = \frac{\lambda}{T}$$

in directions making small angles with the axis of Z.

Mathematical investigation of such a group by means of Fourier's theorem, (see, L. de Broglie's " Wave Mechanics") shows that

(101c) $$\Delta\left(\frac{1}{\lambda}\right) . \Delta z$$

is of the order of unity, where $\Delta\left(\frac{1}{\lambda}\right)$ represents the extreme variation of the reciprocal of the wavelength, and Δz represents the linear range of the group along the z-axis.

The wave-mechanical significance of the group is that the particle (electron or what not) travels with the velocity $\underline{v}$ and therefore always remains within the group, the probability of its being in any given small volume being proportional to the square of the amplitude of the approximately harmonic wave.

If we multiply (101c) by $\underline{h}$, we get

$$\Delta p . \Delta z \sim h$$

an equation which expresses the indeterminancy pointed out by Heisenberg.

The year 1922 was that in which de Broglie first published any suggestion that Full Radiation might be treated as a sort of gas, made up of light quanta or photons. Photoelectric phenomena, and associated things, had convinced him that light must be of a corpuscular nature, and he tentatively introduced the idea of a "quantum gas", neglecting altogether at first, the wave side of light. His success in his first paper was such that he developed his theory further, introducing the hypothesis that the particles of the quantum gas were moving about in such a way that their motions were governed by waves in some way.

Some years earlier, Davisson had noticed that when dealing with streams of electrons, he had obtained effects which he thought to be due to some fault in his experimental method. Working in association with Germer, he set out to re-obtain the effects and he succeeded in demonstrating the diffraction of electrons, showing that "waves" could be associated with streams of moving "particles", and gave indirect evidence that de Broglie's idea, that light was of a "particle" nature, was correct.

In his first paper, based on the assumption that radiation was a particle phemomena, de Broglie supposed that the photons were all moving about in the uniform temperature enclosure, each with a velocity c (the velocity of light in empty space). He supposed that all the photons were identical with each other in every way, except as regards the period and energy associated with each one. He adopted the relativistic formula, that the energy, E, of each photon, was $E = m.c^2$
where m is the supposed " mass" of the photon.

The energy, E, he wrote as $E = h.\nu$ (where $\nu = \left(\frac{1}{T}\right)$; T being the period.)

In his first paper, he neglected all the photons, the energy of which was a higher integral multiple of $(h\nu.)$ than unity.

The <u>momentum</u> of the photon, on this basis, is : -

$$p = \frac{h\nu}{c} = \frac{E}{c}$$

Using these assumptions, and the canonical law of distribution, de Broglie managed to obtain an expression similar to Wien's expression for the distribution of energy in the spectrum. (See equation (61).)

He sums up his paper in the following words. . .

..." By means of the quantum theory of light, coupled with the laws of statistical mechanics, we can re-obtain all the results of the thermodynamics of radiation, and even of the Wien-Planck law of distribution. These results however, expressly assume that the formulae of relativity dynamics are used for light..."

In a subsequent paper, two years later, which de Broglie called " A Tentative Theory of Light", he revised this earlier paper, and pushed his ideas still further. He obtained Planck's formula for the energy distribution in the spectrum of a black-body radiator, on this important assumption -
" that each atom of velocity Bc, may be considered as linked with a group of waves, whose <u>phase</u> velocity $u = c/B$, whose frequency ν is $\frac{m_0 c^2}{h(1-B^2)^{1/2}}$ and whose group velocity, $v = Bc$ (He supposes that the photons have not all the same velocity c, but some fraction, B, of c, where B varies for the individual photon.) .."

Turning back to equation (56). let us reconsider the expression for the number of vibrations in our enclosure, which we thought of as being filled with stationary waves.

The difference between the earlier proceedure and the present one being that we can no longer endow the waves with a constant velocity, c, except in the limiting case of B → 1. The earlier part of the calculation will be identical with that of finding the number of waves in a unit cube of our enclosure, the frequencies of which lie between ν and zero). This number we found to be

$$\frac{4\pi.\nu^3}{3\ c^3} \qquad \text{(see equ/n (56).)}$$

In the present instance, however, we can no longer write c for the velocity of the wave, but we must write u, the phase velocity of the wave,(and $u = B.c$, where B varies.)

Proceeding as in the earlier instance, we differentiate the expression for the number of vibrations in the unit cube, whose frequencies range form ν to zero, in order to get the number in the small range from $(\nu + d\nu)$ to ν.

This will be given by

102) $$n_\nu d\nu = \frac{d}{d\nu}\left(\frac{4}{3}.\pi.\frac{\nu^3}{u^3}\right)$$

This time we must introduce a term $\left(\frac{du}{d\nu}\right)$, which wes zero in the previous case,

Differentiating the right hand side of 102)

$$n_\nu d\nu = \frac{4\pi\,\nu^2 d\nu}{u^3} - \frac{\nu^3}{u^4}.4\pi.\left(\frac{du}{d\nu}\right).d\nu$$

103) $$= \frac{4\pi\nu^2}{u^3}.d\nu\left[1 - \frac{\nu}{u}\left(\frac{du}{d\nu}\right)\right]$$

It now remains to find an expression for $\left(\frac{du}{d\nu}\right)$

We can do this by considering the relativistic equation for the energy

$$h\nu = \frac{m_o.c^2}{(1 - B^2)^{\frac{1}{2}}} = m_o.c^2.(1 - \frac{c^2}{u^2})^{-\frac{1}{2}}$$

Differentiating this : -

$$h.d\nu = m_o.c^2.-\tfrac{1}{2}\left(1 - \frac{c^2}{u^2}\right)^{-3/2}.2\frac{c^2}{u^3}.\,du$$

(104) $$= \frac{m_o.c^2.}{(1 - \frac{c^2}{u^2})^{\frac{1}{2}}} . \frac{-c^2}{u^3(1 - \frac{c^2}{u^2})}.du$$

and since $h\nu = \dfrac{m_o.c^2}{(1 - \frac{c^2}{u^2})^{\frac{1}{2}}}$

It follows from (104) that : -

$$\nu.\left(\frac{du}{d\nu}\right) = \frac{u}{c^2}.(c^2 - u^2) = u(1 - \frac{u^2}{c^2})$$

therefore $\left[1 - \dfrac{\nu}{u}\left(\dfrac{du}{d\nu}\right)\right] = \dfrac{u^2}{c^2}$

and substituting in (103), we get

(105) $$n_\nu d\nu = \frac{4\pi.\nu^2 d\nu}{u^3} . \frac{u^2}{c^2} = \frac{4\pi\nu^2 d\nu}{u.c^2} = \frac{4\pi\nu^2 B.d\nu}{c^3}$$

The energy of each photon is

$$E = h\nu = m_o c^2\gamma \quad \text{where } \gamma = (1 - B^2)^{-\frac{1}{2}}$$

so that if the kinetic energy of a photon is W,

6) then $m_o c^2 \cancel{\gamma} + W = E$

7) so that $E = m_o c^2.(1 + a)$

8) where $a = \dfrac{W}{m_o c^2}$

now $h\nu = m_o c^2 (1 - B^2)^{-\frac{1}{2}}$

whence $B = \dfrac{\sqrt{a(2 + a)}}{1 + a}$ 9)

10) and $$\nu = \frac{m_0 c^2 (1 + a)}{h}$$

11) $$d\nu = \frac{dW}{h}$$

and substituting from (109),(110) and (111) in (105)

$$n_\nu d\nu = \frac{4\pi}{c^3} \cdot \frac{m_0^2 c^4 (1 + a)^2}{h^2} \cdot \frac{\sqrt{a(2+a)} \cdot dW}{(1 + a)\, h}$$

112) $$= \frac{4\pi}{h^3} \cdot m_0 c (1+a)^2 \cdot \sqrt{a(2+a)} \cdot dW$$

De Broglie, now in the paper quoted, says . . .

" Every phase wave can carry with it, one, two, or more atoms, so that according to the canonical law of distribution, the number of these atoms whose energy is $h\nu$, will be proportional to $$\frac{4\pi}{h^3} \cdot m_0^2 \cdot c(1+a) \cdot \sqrt{a(2+a)}\, dW.dx.dy.dz. \sum_1^\infty e^{-\frac{nh\nu}{kT}}$$

By summing this series (i.e. $\sum e^{-nh\nu/kT}$)

de Broglie finds that the radiant energy density is proportional

113) to $$\frac{8\pi}{h^3 . c^3} \cdot W^3 \sum_1^\infty e^{-nh\nu/kT} = \frac{8\pi h}{c^3} \cdot \frac{\nu^3 \, . d\nu}{\left(e^{h\nu/kT} - 1\right)}$$

and the factor of proportionality he has already shown to be 1

Thus on the basis of these further assumptions, he managed to arrive at a formula similar to Planck's, for the energy distribution in the spectrum of a black-body.

Louis de Broglie's efforts to represent Full Radiation as a Photon Gas, mark the initiation of Wave Mechanics. He was forced, as we have seen, to make use of certain relativistic formulae, in particular, the well known relationship between mass and energy. The assumption of the relationship

$$v.u = c^2$$

of which he also made use, has a relativistic basis. He came to the conclusion that light, an undulatory phenomenon, was constituted of particles, or something very like particles and he suspected that electrons, a characteristically " particle" phenomenon might be associated with waves, and with each electron, as with each photon, a periodic phenomenon of frequency ν could be associated, so that the energy of an electron would, like that of a photon, be $\underline{h\nu}$. If this particle phenomenon be represented in the case of an electron at rest, by

$$\Psi = A \cos 2\pi \nu t$$

it will become

(116) $$\Psi = A \cos 2\pi \nu\left(\gamma(t' - \frac{vx'}{c})\right)$$

when refered to axes X',Y',Z', travelling relatively to the electron with the velocity (-v), or if the electron is moving relatively to the axes with a velocity v

The formula (116) may be written

$$\Psi = A \cos 2\pi \nu' \left(t' - \frac{x'}{u}\right)$$

where $\nu' = \gamma . \nu$

and $u = \frac{c^2}{v}$

the velocity v, it is easy to show, happens to be the group velocity of the waves, whose period is in the neighbourhood of

$$T = 1/\nu$$

We have shown that the group velocity is equal to

(117) $$v = \frac{d\left(\frac{1}{T}\right)}{d\left(\frac{1}{\lambda}\right)} = \frac{d\left(\frac{h}{T}\right)}{d\left(\frac{h}{\lambda}\right)}$$

but, since $h\nu$ or $\left(\frac{h}{T}\right)$ is the energy E and $\left(\frac{h}{\lambda}\right)$ is the momentum p

It would seem that we can write the equation (117) as

118) $$v = \frac{dE}{dp}$$

We can justify this substitution from the corpuscular point of view in the following way.

The energy of a moving particle is $E = m_o c^2 \gamma$

and the momentum, p is $m_o(\gamma v)$

therefore, $$\frac{dE}{dp} = \frac{m_o . c^2 . d\gamma}{m_o . d(\gamma v)}$$

119) $$= c^2 . \frac{d\gamma}{v . d\gamma + \gamma . dv}$$

where γ means $\left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}}$

and thus, $$d\gamma = \tfrac{1}{2}\left(1 - \frac{v^2}{c^2}\right)^{-3/2} . -2\left(\frac{v}{c^2}\right) dv$$

$$= -\gamma^3 . \frac{v . dv}{c^2}$$

and therefore substituting for $d\gamma$ in (119)

$$\frac{dE}{dp} = \frac{v.\gamma^3.dv}{v^2.\frac{\gamma^3.dv}{c^2} - \gamma.dv} = \frac{v.\gamma^2}{\gamma^2\left(\frac{v^2}{c^2} - 1\right)}$$

$$= v$$

We can show that Hamilton's principal function, **S**, in dynamics, is ~~equivalent~~ analogous to the phase in a wave, in wave propogation. **S** is given by

$$\mathbf{S} = \int (2T - E)dt.$$

In the case of a photon, moving in the X direction only, and for which we shall suppose the potential energy is constant

(120) $$\mathbf{S} = (px - Et)$$

where x is the positional coordinate.

For the phase of a wave, we had : -

(121) $$\phi = 2\pi\left(\frac{t}{T} - \frac{x}{\lambda}\right)$$

If we put ϕ equal to, say μH

then, from (121)

22) $$\mu H = 2\pi\left(\frac{t}{T} - \frac{x}{\lambda}\right)$$

23) and by (120) $\mu H = -\mu E.t + \mu p.x$

therefore , comparing (122) and (123)

$$\mu p = -2\pi/\lambda$$

$$\mu E = -2\pi/T$$

If we now put $-\frac{2\pi}{\mu} = h$

we get $p = h/\lambda$

$E = h/T$

and **S** will be $h\left(\frac{t}{T} - \frac{x}{\lambda}\right)$ compare with (121)

At

and for the phase velocity, u, we shall have

$$u = \frac{E}{p}$$

Considering again the expression for a plane wave

$$\psi = A \cos 2\pi \left(\frac{t}{T} - \frac{x}{\lambda} \right)$$

We may write this as

4) $$\psi = A \cos \frac{2\pi}{h} \left(\frac{h}{T}.t - \frac{h}{\lambda}.x \right)$$

Following de Broglie's idea that we may associate with a particle, a wave, we may write (124) in the form

(125) $$\psi = A \cos \frac{2\pi}{h} (Et - px)$$

where E is the energy of the particle, and p its momentum, and $E = h\nu$ and $p = h/\lambda$

The equation (125) is now the equation of the wave associated with the moving particle of energy E and momentum p. Differentiating the equation (125) twice, we get

$$\frac{d^2\psi}{dx^2} = -4\pi . \frac{p^2}{h^2}.\psi = -4\pi \frac{E^2}{u^2 h^2}$$

and $$\frac{d^2\psi}{dt^2} = -4\pi . \frac{E^2}{h^2}.\psi$$

26) therefore $$\frac{d^2\psi}{dx^2} = \frac{p^2}{E^2}.\frac{d^2\psi}{dt^2} = \frac{1}{u^2} \frac{d^2\psi}{dt^2}$$

where $\frac{p^2}{E^2} = \frac{1}{u^2}$

To solve this equation, let us apply Bernoulli's method.

Suppose $\psi = U.W.$

where U is a function of x only, and W is a funcion of t only

Substituting in (126), then, we get

$$W.\frac{d^2U}{dx^2} = \frac{1}{u^2}.U.\frac{d^2W}{dt^2}$$

and therefore $\frac{1}{W.u^2}.\frac{d^2W}{dt^2} = \frac{1}{U}.\frac{d^2U}{dx^2}$

The left-hand-side of this equation is expressed in terms of t only, and the right-hand-side in terms of x only.

In order that they may be equal therefore, both sides must be equal to a constant, say n

Then, $\frac{1}{W.u^2}.\frac{d^2W}{dt^2} = n$ or $\frac{d^2W}{dt^2} = n.u^2.W$

and a solution is

$$W = C.e^{\sqrt{n}.ut}$$ Where C is some constant

i.e. $\sqrt{n}.u = 2\pi i.\nu$

or $n = -\frac{4\pi^2.\nu^2}{u^2}$

but since n is also equal to $\frac{1}{U}.\frac{d^2U}{dx^2}$

it follows that $\frac{d^2U}{dx^2} + \frac{4\pi^2.\nu^2}{u^2} = 0$

Putting $\left(\frac{\nu}{u}\right)^2 = \frac{2m}{h^2}.(E-V)$

where E is the energy of the particle, V its potential enengy, and m its mass, we get therefore

(127) $$\frac{d^2U}{dx^2} + \frac{8\pi^2.m.(E-V).U}{h^2} = 0$$

The equation (127), when generalised for three spacial co-ordinates,(x,y,andz,), becomes

$$\nabla^2U + \frac{8\pi^2.m.(E-V)}{h^2}.U = 0$$

and is sometimes called the Amplitude Equation, since U is the amplitude in

$$\Psi = U.W$$

In order that U may be one-valued and vanish at ∞, it is necessary that E should have particular values, (Eigenwert) These are the energy levels of the older Quantum Theory.

The development of Wave Mechanics is largely due to the work of E. Schroedinger, who extended the anology between classical dynamics and geometrical optics, discovered in 1828, by Hamilton. So that Schroedinger's dynamics may be described as analogous to optics (not merely geometrical optics). These analogies appear most clearly by comparing the principles of Fermat and Maupertuis. The former determines the path of a ray of light, or a photon, from a point A to another, B, by

$$\delta\int_A^B \frac{dz}{u} = 0$$

or

$$\delta\int_A^B \frac{dz}{\lambda} = 0$$

where dz is an element of the optical path and u is the phase velocity. In the variation, δ, the frequency, i.e. $\left(\frac{1}{T}\right)$ is constant.

Maupertuis' principle, (the principle of least action), for a single particle, has the form,

$$\delta\int_A^B p.dz = 0$$

and comparison with Fermat's principle brings out the analogy between p and $\frac{1}{\lambda}$.

Both principles fail under exactly analogous circumstance
That of Fermat's fails when λ is very great by comparison with the dimensions of the lenses, apertures, etc: while Maupertuis' principle fails when E and p are very small and the essence of Wave Mechanics lies in the principle of amending classical dynamics in the same way as we amplify the optical theory when the laws of geometrical optics fail.

We will now apply Schroedinger's equation, (equation (128),) to a Planck oscillator. This, we shall suppose, is vibrating in one dimension only, and for this simple harmonic oscillator, the potential energy, V will be a function of the displacement only, and will be equal to $2\pi.\nu_0^2.m.q^2$ where q is the displacement and ν_0 is the proper mechanical frequency. Equation (128) becomes therefore,

(129) $$\frac{d^2U}{dq^2} + \frac{8\pi^2m}{h^2}.(E - 2\pi.m.\nu_0^2.q^2).U = 0$$

Writing,

(130) $$\frac{8\pi^2.m.E}{h^2} \text{ as } a \text{ ; and } \frac{8\pi^2.m}{h^2}.2\pi.\nu_0^2.m \text{ as } b$$

in equation (129), we get

$$\frac{d^2U}{dq^2} + (a - bq^2).U = 0$$

(131) $$\text{or } \frac{d^2U}{dx^2} + (A - x^2).U = 0$$

(132) where, from (130), $A = \frac{a}{b^{1/2}} = \frac{2E}{h\nu}$

and where $x = q\sqrt[4]{b}$

The solutions of the equation (131) are of the type known as Hermite's orthogonal functions. The first of these function is $\exp(\frac{-x^2}{2})$, or $e^{-\frac{x^2}{2}}$

Differentiating this, we get

$$\frac{dU}{dx} = -x.\exp(-\frac{x^2}{2}) \; ; \quad \text{and} \quad \frac{d^2U}{dx^2} = (x^2 - 1).\exp(-\frac{x^2}{2})$$

and therefore substituting in (131), A turns out to have the value

$$\underline{1}$$

The next of these functions of Hermite

$$2x.\exp(-\frac{x^2}{2})$$

gives $\frac{dU}{dx} = (-2x).\exp(-\frac{x^2}{2}) + 2.\exp(-\frac{x^2}{2})$

and $\frac{d^2U}{dx^2} = (2x^3 - 6x).\exp(-\frac{x^2}{2})$

and therefore $A = \underline{3}$

The next function, $(4x^2 - 2).\exp(-\frac{x^2}{2})$

gives $A = \underline{5}$

and so on.

In general, A will be $(2n + 1)$ (where n is any positive integer)

and from (132), therefore,

$$E = (2n + 1).\frac{h}{2}$$

(133) $$= (n + \tfrac{1}{2}).h)$$

These are the " Eigenwerte) to which reference has already been made.

We will now substitute this value for the "E_s" which we used in dereving Planck's formula for the distribution of energy in the spectrum of a black-body.

We had,(see equations (89),etc:)

$$\sum_0^\infty f_s = 1 = B.\sum_0^\infty e^{-\beta E_s}$$

where now, instead of giving 's' integral values, we must put $(n+\frac{1}{2})$ for s and give n integral values.

Hence we get,

$$\sum f_s = 1 = B.\sum e^{-\beta(n+\frac{1}{2}).h\nu}$$

$$= B.e^{-\frac{1}{2}p}.\sum e^{-np} \qquad \left(\text{where } p = \beta h\nu = \frac{h\nu}{kT}\right)$$

$$= B.e^{-\frac{1}{2}p}.(1 + e^{-p} + e^{-2p} + \ldots)$$

$$= \frac{B.e^{-\frac{1}{2}p}}{1 - e^{-p}}$$

therefore, $B = \dfrac{e^p - 1}{e^{-\frac{1}{2}p}}$

For the average energy $\overline{E} = \sum E_s.f_s = \sum(n+\frac{1}{2}).h\nu.f_s$

$$= \sum n.h\nu.f_s + \tfrac{1}{2}h\nu\sum f_s$$

$$= e^{-\frac{1}{2}p}.h\nu.B\sum n.e^{-np} + \tfrac{1}{2}h\nu \quad (\text{since } \textstyle\sum f_s = 1)$$

$$= e^{-\frac{1}{2}p}.h\nu.B.\frac{e^{-p}}{1 - e^{-p}} + \tfrac{1}{2}h\nu$$

$$= \frac{h\nu}{e^p - 1} + \tfrac{1}{2}h\nu \quad (\text{ substituting for } B\ )$$

and therefore for E_ν we get

$$E_\nu d\nu = \frac{8\pi\nu^2.d\nu}{c^3}.\left\{\frac{h\nu}{e^p - 1} + \frac{h\nu}{2}\right\}$$

This formula is only different from Planck's original one in the term :—

$\frac{h\nu}{2}$

which is added on.

This will, however, not affect the distribution of the energy in the spectrum of a black-body, since we shall not be able to detect its presence, for it will affect the radiator and receiver alike. Moreover, if we consider " differences of energylevels", between two levels, this " $\frac{1}{2}h\nu$ " term will again not be detectable, as it will disappear when differences are taken.

The presence of this $\frac{1}{2}h\nu$ term in the expression for the energy, indicates that at the absolute zero of temperature the energy of the oscillator is not itself zero. That is to say, when $T = 0^{\circ}$ absolute, the energy will be $\frac{1}{2}h\nu$ since the first term $\frac{h\nu}{e^{p}-1}$ will have vanished.

Matrix Mechanics.

We shall now consider the problem from a totally different point of view, namely that of Heisenberg's Uncertainty Principle, using for the purposes of calculation, certain quantities, called matrices and we shall find that we arrive at the same series of proper values (Eigenwerte) for the energy.

Heisenberg's principle affirms that it is impossible to measure, simultaneously and with precision, the position and the momentum of an elementary particle, such as an electron or photon The more accurately is the momentum measured, the more uncertain do we become of its exact position at that particular instant, and vica versa. If we make the measurement of p, the momentum, and if dp is the uncertainty in the value of p, that is, the value of p lies between p and (p + dp) and similarily, if dq is the uncertainty in the positional co-ordinate q, then Heisenberg's principle requires that the product

(dp).(dq) shall be of thr order of h (Planck's constant)

Heisenberg regarded p and q not as mere numbers, but as matrices. A matrix is a set of numbers, usually arranged in the following way.

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} & a_{14} & \cdots \\ a_{21} & a_{22} & a_{23} & a_{24} & \cdots \\ a_{31} & a_{32} & a_{33} & a_{34} & \cdots \\ \cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \end{pmatrix}$$

and the rules for multiplication, addition etc: are set out below

The term a_{nm} of a matrix, means the term occuring in the n^{th} row and the m^{th} column.

If a and b are matrices,

$$a = b \quad \text{means} \quad a_{nm} = b_{nm}$$

Addition. $a + b = c$ " $a_{nm} + b_{nm} = c_{nm}$

Multiplication. $a.b = c$ means

$$\sum_k a_{nk}.b_{km} = c_{nm}$$

The following ardinary algebraical laws hold : -

$$a + b = b + a \; ; \qquad (a + b) + c = a + (b + c)$$

$$(a + b).c = ac + bc \; ; \qquad (a.b).c = a.(b.c)$$

But in general a.b is *not* equal to b.a.

A matrix in which all the terms are zero except those for which $n = m$ is called a *diagonal* matrix

$$\begin{array}{cccccc} \underline{a}_{11} & 0 & 0 & 0 & 0 & \dots \\ 0 & \underline{a}_{22} & 0 & 0 & 0 & \dots \\ 0 & 0 & \underline{a}_{33} & 0 & 0 & \dots \\ 0 & 0 & 0 & \underline{a}_{44} & 0 & \dots \\ 0 & 0 & 0 & 0 & \underline{a}_{55} & \dots \end{array}$$

and a very special case of a diagonal matrix is that for which

$$a_{11} = a_{22} = a_{33} = \dots a_{nn} = 1$$

This is called a *UNIT* matrix, and has the special property that $a.1 = 1.a = a.$

A *differential* function of a matrix

is $\dot{a} = \dot{a}_{nm}$

and $\frac{d}{dt}.(a.b) = \dot{a}.b + a.\dot{b}$

and is not equal to $\dot{a}.b + \dot{b}.a$

Suppose that q is a matrix,

$$\begin{pmatrix} q_{11} & q_{12} & q_{13} & q_{14} & \cdots \\ q_{21} & q_{22} & q_{23} & q_{24} & \cdots \\ q_{31} & q_{32} & q_{33} & q_{34} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix}$$

We are particularily interested in the form of matrix

(134) $$q_{nm} = a_{nm} \exp(2\pi i \nu_{nm}.t)$$

where a_{nm} is a complex ampiltude, (on Bohr's theory representing the transition probability from an energy level 'n' to a level 'm'.)

It follows that

$$\nu_{nm} = -\nu_{mn}$$

and hence $$\nu_{nn} = 0$$

Differentiating (134), we get

35) $$\frac{dq_{nm}}{dt} = \dot{q}_{nm} = 2\pi i.\nu_{nm}.q_{nm}$$

36) and $$\frac{d^2q_{nm}}{dt^2} = -4\pi^2.\nu_{nm}^2.q_{nm}$$

The energy E of an oscillator, is also a matrix, a typical constituent of which is, let us suppose,

$$E_{nm} = A_{nm}.\exp\left(\frac{2\pi i}{h}.\nu_{nm}.t\right)$$

E is a constant for these systems which we are considering, that is, E_{nm} does not vary with the time, t, and thus the factor in the expression for E_{nm}

$$\exp\left(\frac{2\pi i}{h}.\nu_{nm}.t\right)$$

must be zero.

It follows therefore that ν_{nm} must be zero, and as we have seen, this is so when $n = m$

E is therefore the diagonal matrix

$$\begin{pmatrix} \underline{D} & 0 & 0 & 0 & \cdots \\ 0 & \underline{D} & 0 & 0 & \cdots \\ 0 & 0 & \underline{D} & 0 & \cdots \\ 0 & 0 & 0 & \underline{D} & \cdots \end{pmatrix}$$

Heisenberg founded his mechanics on an assumption equivalent to

137)
$$\begin{aligned} p_{nk}.q_{km} - q_{nk}.p_{km} &= \frac{h}{2\pi i} && \text{if } m = n \\ &= 0 && \text{"}\ m \neq n \end{aligned}$$

and we shall make use of this condition for the Planck oscillator . The equation of motion for such an oscillator is

138)
$$m.\ddot{q} - \mu q = 0$$

where $\mu = 4\pi^2.m.\nu_o^2$ and ν_o is the freqeuncy in the ordinary mechanical sense.

For q in equation (138), we must put the matrix whose typical constituent is q_{nm} , and therefore substituting from equ/ns (134),(135), & (136), we get

$$-4\pi^2.\nu_{nm}^2.m.q_{nm} - 4\pi^2.\nu_o^2.m.q_{nm} = 0$$

and therefore,

$$\nu_{nm}^2 - \nu_o^2 = 0$$

Thus ν_{nm} can only have the values $+\nu_o$ and $-\nu_o$

Shall we put $\nu_{nm} = \nu_o$ and $\nu_{mn} = -\nu_o$,

The energy equation for a simple harmonic vibrator is

$$\tfrac{1}{2}.m.\dot{q}^2 + \tfrac{1}{2}\mu.q^2 = E$$

In this system of mechanics, this amounts to

$$\tfrac{1}{2}m.2\pi i.\nu_{nk}.q_{nk}.\ 2\pi i.\nu_{km}.q_{km} + 2\pi^2 m\nu_0^{\,2}.q_{nk}.q_{km} = E_{nm}$$

We can simplify this by writing $m = m$, and since ν_{nm} can only have the values specified above, it follows that k can only have two values, the simplest of which will be $(n-1)$ and $(n+1)$, we get ; -

$$+\left[2\pi^2.m.\nu_0^2.(q_{n,n-1}\ q_{n-1,m}) + 2\pi^2.m.\nu_0^2(q_{n,n+1}\ q_{n+1,n})\right]$$

$$+\left[2\pi^2.m.\nu_0^{\,2}.(q_{n,n-1}\ q_{n-1,n} + q_{n,n+1}\ q_{n+1,n})\right]$$

$$= E_{nn}$$

that is $4\pi^2.m.\nu_0^{\,2}\left[\ q_{n,n-1}\ q_{n-1,n} + q_{n,n+1}\ q_{n+1,n}\right] = E_{nn}$

(139) i.e. $(q_{n,n-1}\ q_{n-1,n}) + (q_{n,n+1}\ q_{n+1,n}) = E_{nn} \Big/ {+4\pi^2 m\nu_0^2}$

Turning back to equation (137),

(137) $p_{nk}.q_{km} - q_{nk}.p_{km} = \dfrac{h}{2\pi i}$ or 0

and substituting in this

$$p_{nk} = m.\frac{dq_{nk}}{dt} = m.\dot{q}_{nk} = 2\pi i.m.\nu_{nk}.q_{nk}$$

we get
$$2\pi i.m.\left(\nu_{nk}.q_{nk}.q_{km} - \nu_{km}.q_{nk}.q_{km}\right) = \frac{h}{2\pi i} \quad \text{or } 0$$

giving k the two values $(n-1)$ and $(n+1)$

$$2\pi i.m\left[\left(\nu_{n,n-1}q_{n,n-1}\ q_{n-1,m}\right) - \left(\nu_{n,n+1}q_{n,n+1}\ q_{n+1,m}\right)\right]$$

$$- 2\pi i.m\left[\left(\nu_{n-1,m}\ q_{n,n-1}\ q_{n-1,m}\right) - \left(\nu_{n+1,m}q_{n,n+1}\ q_{n+1,m}\right)\right] = \frac{h}{2\pi i}$$

or 0

Substituting in this, m = n and remembering $\nu_{nk} = -\nu_{kn}$ etc:

we get, putting in the value ν_0

$$2\nu_0^2\left\{(q_{n,n-1}q_{n-1,n}) - (q_{n,n+1}q_{n+1,n})\right\} = \frac{h\nu_0}{2\pi i . 2\pi i . m}$$

that is to say,

$$(q_{n,n-1}q_{n-1,n}) - (q_{n,n+1}q_{n+1,n}) = \frac{-h\nu_0}{8\pi^2 . \nu_0^2 . m}$$

and putting in the other values for n, (n-1),(n-2), etc: we get the series : -

$$(q_{n,n-1}q_{n-1,n}) - (q_{n,n+1}q_{n+1,n}) = \frac{-h\nu_0}{8\pi^2 . \nu_0^2 . m}$$

$$(q_{n-1,n-2}q_{n-2,n-1}) - (q_{n-1,n}q_{n,n-1}) = \frac{-h\nu_0}{8\pi^2 . \nu_0^2 . m}$$

$$(q_{n-2,n-3}q_{n-3,n-2}) - (q_{n-2,n-1}q_{n-1,n-2}) = \frac{-h\nu_0}{8\pi^2 . \nu_0^2 . m}$$

- -

$$(q_{0,-1}q_{-1,0}) - (q_{0,1}q_{1,0}) = \frac{-h\nu_0}{8\pi^2 . \nu_0^2 . m}$$

and adding these up, we get : -

$$-(q_{n,n+1}q_{n+1,n}) + (q_{0,-1}q_{-1,0}) = \frac{-(n+1).h\nu_0}{8\pi^2 . \nu_0^2 . m}$$

Calling the smallest one zero, for simplicity, we get, if we substitute these values in equation (137), with appropiate values for 'n',

$$\frac{nh\nu_0}{8\pi^2 . \nu_0^2 . m} + \frac{(n+1).h\nu_0}{8\pi^2 . \nu_0^2 . m} = \frac{2.E_{nn}}{8\pi^2 . \nu_0^2 . m}$$

that is

$$(n+\tfrac{1}{2}).h\nu_0 = E_{nn}$$

Which is the same result as we obtained by the aid of Wave Mechanics.

We have already discussed the effect that this extra " $\tfrac{1}{2}.h\nu$ " will have on the distribution formula,(see page 101.)

This agreement is no mere coincidence. It can be shown that the basic equation

$$p_{nk}.q_{km} - q_{nk}.p_{km} = \frac{h}{2\pi i}$$

can be deduced from Wave Mechanics.

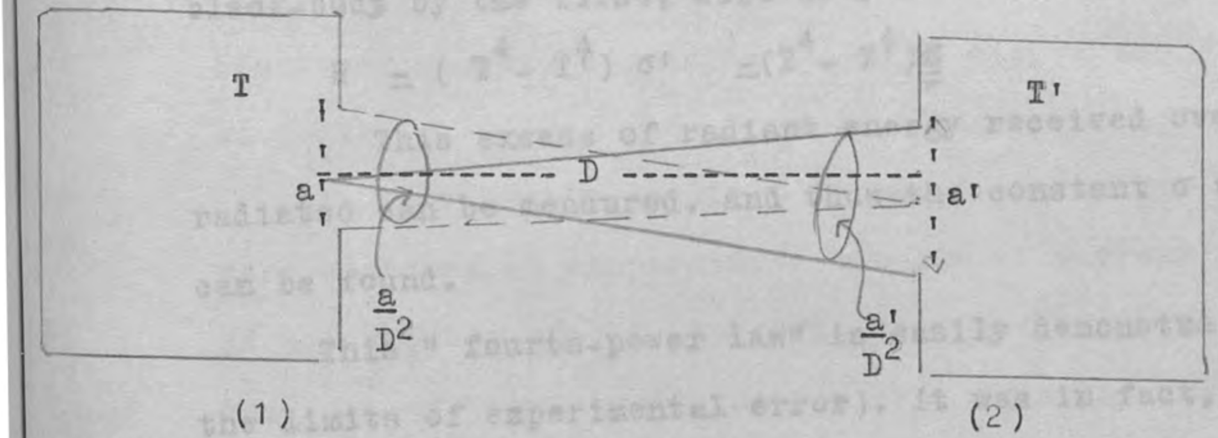
Part 3.

EXPERIMENTAL METHODS OF DETERMINING THE RADIATION CONSTANTS.

We have already obtained the following expression for the relationship between the absolute temperature of the radiation and the energy density,(or the intensity of radiation.

$$u = a.T^4$$
$$I' = \sigma'.T^4$$
$$I = \sigma.T^4 \qquad \text{(see equation (32).)}$$

Suppose that we have two enclosures at temperatures T and T', having very small orifices of area a and a', at a distance D apart.



The amount of radiation coming from (1), in the directions within the small solid angle $\frac{a'}{D^2}$, through the orifice a in the unit time, will be

$$I'.a.\frac{a'}{D^2}$$

which, using the above equations, will be

$$\sigma'.\frac{a.a'}{D^2}.T^4$$

Similarity, the amount of radiation coming from the enclosure (2), in the directions within the small solid angle $\frac{a}{D^2}$ though the orifice a', will be $\sigma'.\frac{a.a'}{D^2}.T'^4$

If the enclosure (1) is at a higher temperature than the enclosure (2), then the excess of radiation received by (2) over that lost to (1), will be

$$\sigma'.\frac{a.a'}{D^2}\,T^4 - \sigma'.\frac{a.a'}{D^2}\,T'^4 = \sigma'.\frac{a.a'}{D^2}.(T^4 - T'^4)$$

If we make a, a' and D all equal to unity, we see that R, the excess of radiant energy leaving an enclosure at a temperature T, through an orifice of unit area, towards a similar orifice of an enclosure at a temperature T', placed unit distance away, over the energy received from the second black-body by the first, will be : -

$$R = (T^4 - T'^4)\,\sigma' = (T^4 - T'^4)\frac{\sigma}{\pi}$$

This excess of radiant energy received over that radiated can be measured, and thus the constant σ or σ' can be found.

This " fourth-power law" is easily demonstrated, (within the limits of experimental error). It was in fact, as we know, first discovered experimentally. But - the precise determination of the value of the constant σ is not at all easy, as a study of the range of the values obtained by the various investigators would indicate. The measurement of this constant has been undertaken by about a score of investigators, and the range of the values given for σ varies from

$\sigma = 5.30\ (\text{ergs.cms}^{-2}.\text{sec}^{-1}.\text{degrees}^{-4}) \times 10^{-5}$ to

$\sigma = 6.51$ " " " " " "

The former value was obtained by Bauer and Moulin in 1909, and the latter by Fery, and Drecq, in 1911.

The difference between these two extreme values - about 20% - seems to point to many sources of error to be overcome in the determination.

The earliest methods were, naturally, very rough, and corrections now thought to be necessary were neglected. For example, no correction was made for the absorption of the radiation by the water-vapour or by carbon di-oxide, and the degree of perfection of the black-body was not at all good. In the early determinations of Lebnebach and Christiansen, " black-bodies" were used which were made of such things as blackened plates, blackened balls of copper and glass, and so forth.

In many of the earliest forms of apparatus, the radiators were operated at temperatures too low to warrant the neglect of the effects of the shutters, etc: and to justify disregarding the loss of heat by conduction away from the receiver. On the other hand, however, too high a temperature of the radiator necessitates that the receiver shall not be " sluggish" in its response to the radiation, and although attempts were were made to overcome this, the experiments using a radiator at high temperatures were not a success as they were accompanied by too slow a response, and the receiver could not be properly calibrated.

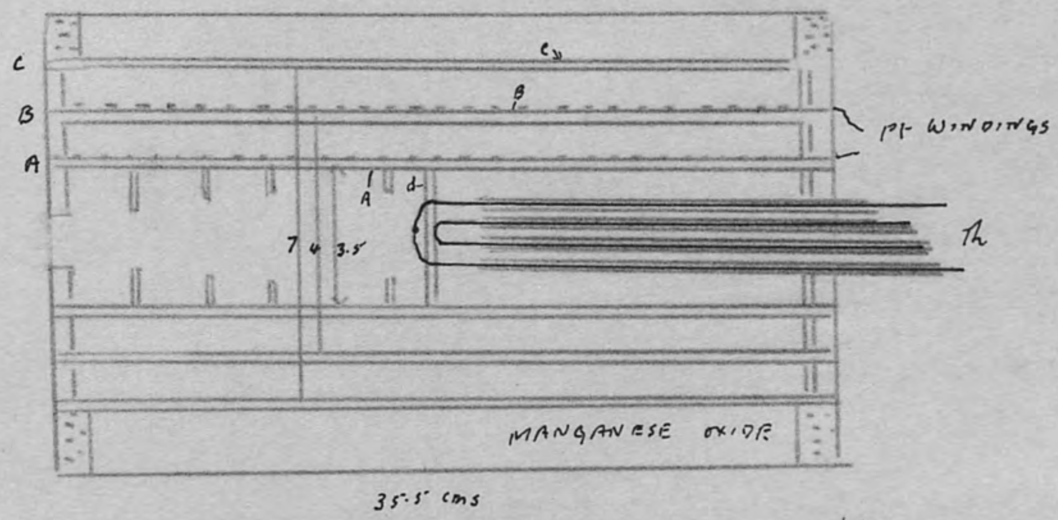
Radiation from a material body, in the ordinary way, has a more or less determinate spectrum which is characteristic of the material. The spectrum of radiation from an orifice, on the other hand, is determined solely by the temperature of the walls of the enclosure, and it is entirely independent of the nature of the material of the walls. It is therefore the same for every material enclosure. The present-day black-body used in practise is a development of the early, simple experiments of St.John, Draper, and Christiansen. Draper found that the interior of a rifle barrel became luminescent when heated to certain temperatures. Christiansen observed that the scratches and holes on the surface of a heated metal box were brighter than the plane surface, while St.John observed that the selective emission of certain oxides disappeared when these were heated in an enclosure.

From these and similar observations, grew the "Black-Body" which is used in more modern times, in practice, for the determination of the constants σ, etc:, which characterise full radiation. Actually it was an invention of Wien and Lummer in about 1895, with improvments added later by Coblentz.

A diagram of the black body of Wien and Lummer is shown in figure (1A). It consists essentially of a porcelain tube, with a diaphram at one end. The tube is electrically heated, being wound with platinum ribbon through which an electric current passes. Coblentz modified the instrument by having two more porcelain tubes outside this one. The inner tube,(A), consists of Marquardt porcelain, uniformly wound with platinum ribbon, which is uniformly thick, but varies in width from 10mm at the ends, to 20 mm at the centre. Thus, when an electric current passes through the windings, there will be more heat developed

ELECTRICALLY HEATED "BLACK BODY" [WIEN-LUMMER]

FIGURE I.

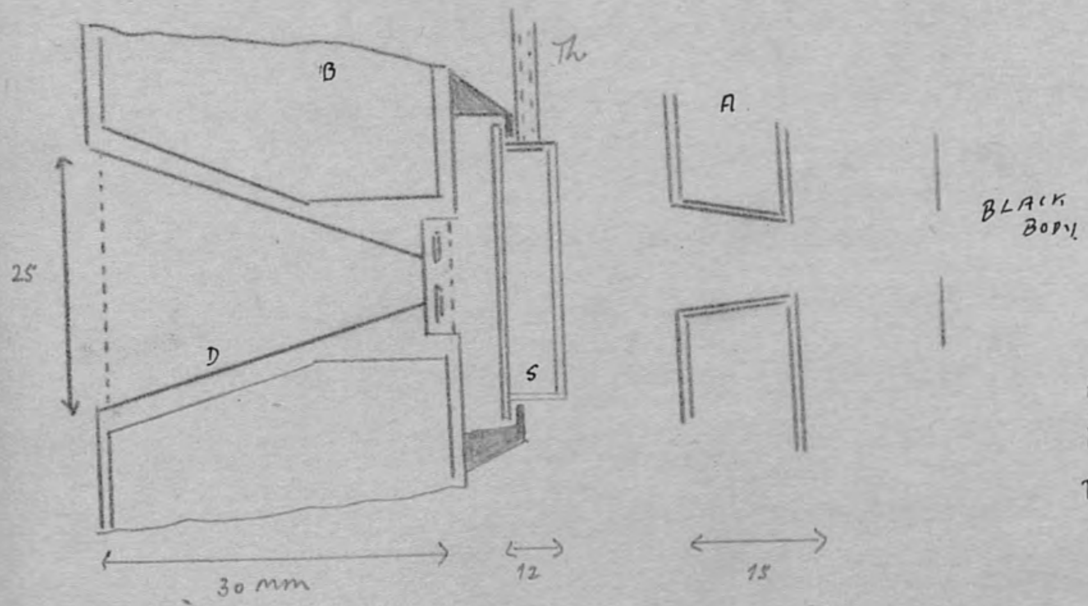


(A).

A = inner porcelain tube.

Th = Thermoelement for measuring temperature of black body.

WATER-COOLED SHUTTER - (COBLENTZ)



A : water cooled shield.

B = tank.

Th : thermometer.

S = Shutter.

(B)

in the narrow part of the windings, on account of the greater resistance, than in the centre, and this will compensate thus, the greater loss of heat at the edges. The tube outside (A), (B in the figure,) is wound with uniformly wide platinum ribbon, but the windings are nearer together at the ends than in the centre. By regulating the currents through these windings, the enclosure can be maintained at a uniform temperature throughout, as was experimentally demonstrated by Waidner and Burgess.

Black-body radiators of this type, develop a "sag" at high temperatures, and to overcome this, Coblentz introduced a small wedge of porcelain to support the inner tube, when operating the radiator at temperatures over 1200 degrees centigrade.

Further improvments were made by painting the inside walls and front sides of the diaphram with a composition of chromium and cobalt oxides. This becomes conducting at temperatures over 1200°C, so that the thermocouple had to enclosed in an insulating porcelain tube, and the part immediately in front of the diaphram painted with the paint, to prevent 'direct radiation'.

The question of deficiency in "blackness" in the receiver was discussed thoroughly by Wien and Lummer, who gave a method for computing the correction for the opening in the receiver, on the assumption that it is spherical and diffusely reflecting. The amount of energy that can escape through the orifice, is practically determined by the size of the orifice in comparison with the size of the enclosure. Coblentz, in his determination, makes use of this.

The experimental determination of the constant, consists essentially in, either measuring the heat transferred from one black body to another, both being at known temperatures, or, in measuring the difference in the heat transferred when the receiver is exposed to first one black-body and then another both at known temperatures. The radiator at the lower temperature can be, and in fact, generally is, used as a shutter, which stops the radiation from the hot black-body reaching the former. If the temperature of the shutter is lower than that of the receiver, the latter radiates to the former, and consequently it is important to have the receiver face of the shutter, a large,(say water-cooled) diaphram, which can be maintained at constant temperature in spite of its receiving radiation from the receiver. At the back of this water-cooled face, is placed the shutter, and behind that, the radiator. Thus arranged, the surrounding conditions facing the receiver are not changed when the shutter is open or shut. The figure (1.8) shows the shutter used by Coblentz in his determination of σ .

The water-cooled shield consists of a tank A, 25cms in diameter and 1.5cm thick, and a tank B which faced the receiver. The water-cooled shutter,S, consisted of a thin metal box, of dimensions 3.5 by 3.5 by 0.8 cms. A mercury thermometer was placed at th to measure the temperature of the shutter, which was the temperature of the water circulating in the shutter. The side facing the radiometer was blackened with a sperm candle and the conical opening in the shutter formed a black-body, the temperature of which remained constant throughout the experiment as the temperature of the water could easily be kept constant.

The openings in B were defined by a series of holes in a brass disc, with accurately cut knife edges.. The size of B could easily be changed by substituting another disc at B.

The first serious attempt at measuring the radiation constant, was made by Kurlbaum, in 1898. Since that time, about a score of other experimenters have been made ' serious' attempts. The following table shows a chronological list of the measurements, but, in describing them, we shall divide them into three groups, : -

(i). Bolometric methods (using blackened strips as receivers)
(ii) Thermometric " (" 'black'receivers.)
(iii) Substitution " .

Throughout the following description, we shall merely give the " significant figures" for σ, without writing the power of ten which shpuld multiply it, and writing the "units" every time.

For example; $\sigma \doteq 5.735.$

means,

$$\sigma \doteq 5.735 . 10^{-5} \text{ ergs. cm}^{-2}\text{.degrees}^{-4}\text{.sec}^{-1}$$

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te	Observer	Method	experimental value for σ	corrected value
98	Kurlbaum	Bolometer	5.32	(2%.correction ,Coblentz, atmospheric abs.) 5.45
09	Fery	Fery pyrometer	6.30	
10	Bauer and Moulin	Thermoelectric receiver	6.0	(12% corr, experimenters 5.3 Further, for atmos.abs. 5.7
09	Todd	Thermal conductivity	5.48	
10	Valintiner	Bolometer	5.36	(2.5%, reflection at bolom. surface 5.68 later, to 5.75
11	Fery and Drecq	Thermoscope	6.51	
12	""	Fery pyrometer	6.2 5.57	(.82% corr,by observers for absorption(This too small)) (2% by Bauer, 5.68.)
12	Shakespere	Ratio of emissions	5.67	
12	Puccianti	Bolometer	5.96	
12	"	Thermoscope	6.0 -6.3	
16	Westphall	Ratio of emissions	5.54	
			5.57	(at higher temperatures)
			5.7	
16	Gerlach	Bolometer	5.85	(corrections by subsidiary experiments.)
20	"	Modified Angstrom pyrheliometer	5.80	
13	Keene	Thermoscope	5.89	
15	Coblentz	Mod: Angstrom pyrhel:	5.722 (5.70 - 5.75)	(1.2% for relection losses) 5.73
19	Kahanowicz	" " "	5.61	
19	"	" " "	5.61	
23	Kussmann	" " "	5.764	
24	Hoffmann	Ration of emissions	5.795	
	Hoare	Radio balance	5.735	

Hoare Radio balance	5.735
Mendenhall Ratio of emissions	5.79

(i) BOLOMETER METHODS.

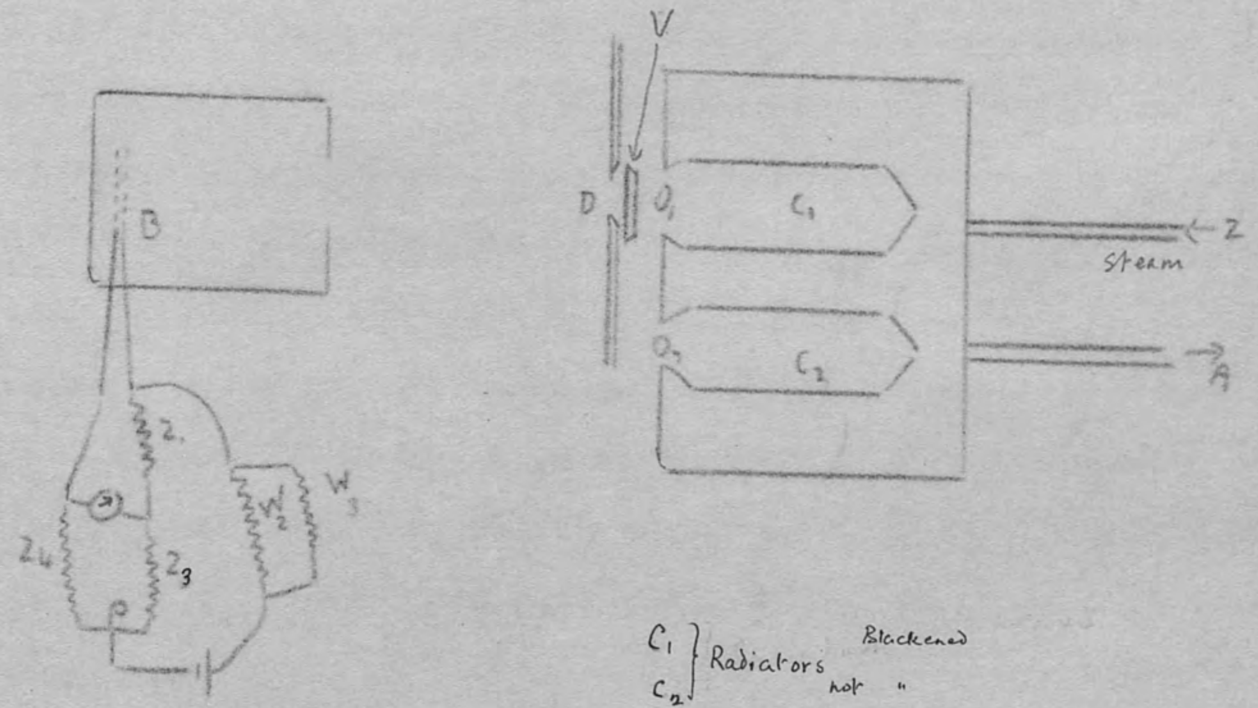
The principle of the method is roughly the following. Three branches of a Wheatstone bridge are composed of thick manganin strips or wires, which do not change in resistance in consequence of heating by an electric current which passes through them, or as the current heating them is altered. The fourth branch of the bridge is made of thin strips of platinum, the resistance of which is readily affected by changes in the bridge currents. The bridge is carefully balanced, and then this fourth branch is exposed to radiation the energy of which it is required to measure. The change in the resistance of this bolometer strip is noted, or simply the galvanometer deflection is noted. The bolometer strip is then shielded from the radiation and the bridge current altered until the galvanometer shows the same deflection as when the strip was exposed to the radiation. By measurement of the current in this strip, the energy of the radiation can be computed. The difficulty of this method is that the bolometer strip is not a perfect absorber, and corrections have to be made for this. These estimations are not at all easy to make accurately, - in fact, in the earliest determinations, they were what might be described as " rough guesses".

Kurlbaum's measurement

Figure (1) shows the arrangement of his apparatus. C_1 and C_2 are two cylinders with openings at O_1 and O_2. C_1 is blackened, and C_2 is left unblackened.

KURLBAUM'S ARRANGEMENT.

FIGURE 2.



C_1 } Radiators Blackened
C_2 } not "

O_1 } Orifices.
O_2 }

D : diaphram with circular hole

B. bolometer strip (s).

V : Shutter.

They are placed in a boiler in which the water boils under atmospheric pressure. Z and A are the inlets and outlets for the steam to the boiler. Between the receiver and the source are rows of blackened diaphrams, to prevent the radiation reflected from the walls of the radiator from reaching the receiver (the bolometer strip.) D is a diaphram with a circular hole in it, with sharp edges and the radius of which is accurately known, D is placed exactly in front of the source, O, and the bolometer strip placed in line with these two. The diaphram O can be closed with a shutter V which prevents the radiation from reaching the strip. In his early experiments, Kurlbaum took no precautions to ensure that the temperature of the shutter was the same as that of the bolometer strip, although he later remedied this.

By measuring the energy in the radiation (- by measuring the current in the bolometer strip required to produce the same deflection -) Kurlbaum obtained a value for the radiation constant.

Sources of error in his measurement,

Kurlbaum himself admitted that the bolometer strip was not a perfect absorber, and to overcome this difficulty, he blackened the strip with such substances as lamp-black and platinum black, and with a deposit of the latter over the former. He admits of two further sources of error. Firstly that the bolometer's temperature may be different when it is electrically heated from when it is heated by the radiation. That is to say, the latter method of heating will affect the nearest surface first and then the whole strip by conduction away from this surface, whereas, by the electrical heating, the whole strip will be warmed more or less uniformly, and thus, the electrical input may not be the same as the radiation energy received, which causes the same change in the resistance of the strip. Kurlbaum realised that " the better the ~~blac~~ blackening deposit, the worst the conduction capabilities of the blackened surface, " and he allowed a difference of about 1% for a temperature difference between the actual surface, and the outer surface of the blackening.

Kürlbaum made, at first, no correction for the lack of blackness in the receiver and for absorption of the radiation by the atmosphere. He arranged two bolometer strips, one behind the other, as the figure shows, and in his earliest determination merely blackened them with surface blackening. In a later experiment, however, he made a further determination of the constant in which he allowed for loss by reflection of about 2.5% from the surface of the bolometer strip. Later investigations by Coblent_z, who, using the blackest obtainable deposits, found ~~a~~ that the reflecting power is about 2% for wavelengths up to about 2μ. A microscopic examination of the surfaces showed that there were patches of bright platimum on even the blackest obtainable surface.

The final average value of all his radiators and receivers was given by Kurlbaum as $\sigma = 5.32$. This was corrected later to $\sigma = 5.45$.

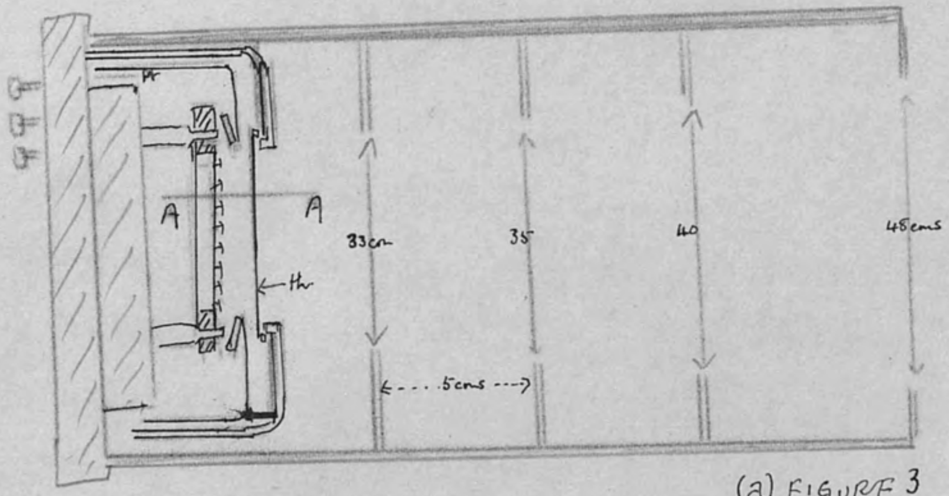
Valintiner's Determination.

Kurlbaum's method was carried further by Valintiner some years later, (in 1909) He used essentially the same apparatus as Kurlbaum, but worked to much higher temperatures, and used much larger bolometer strips. He took his observations up to temperatures of 1400°C. The essential difference, therefore, in the methods is that of the heating of the full radiator. In the high temperature determinations, he used the electrically-heated black body, previously described. The value that he gave for σ was $\sigma = 5.36$

On further considerations, he added corrections for reflection from the bolometer, of 2.5%, making $\sigma = 5.68$. Allowing a further correction for atmospheric absorption, the final value was given as $\sigma =$ from 5.68 to 5.75.

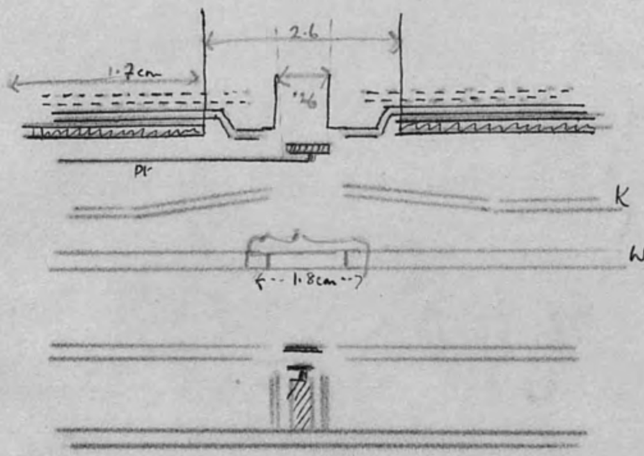
The third name associated with this method of determining σ, is that of GERLACH. Although his method is not, strictly speaking a bolometric one in exactly the same way that the previously described ones were, we shall include it in this group because, firstly, it is of a very similar nature, consisting in the balancing of the change in resistance of a strip against the change in resistance of a similar strip, caused by a temperature change in it; and secondly, because a description of Gerlach's work must necessarily be placed adjacent to that of Kurlbaum and Valintiner, on account of the numerous communications that were published by them, as to sources of error in each others' work.

GERLACH's RECEIVER (Modified Angstom Pyrheliometer)



(a) FIGURE 3

Section through AA



D = stops

th = Receiver.

Gerlach used, instead of a bolometer strip, a form of Ångstrom Pyrhrliometer. In the original form of this apparatus the receivers are two thin strips of manganin, to each of which is attached one junction of the thermoelement, which is joined through a galvanometer. One of these strips is exposed to the radiation while the other is heated with an electric current. Equality of temperature in the strips is indicated by no current in the galvanometer.

Gerlach's instrument consisted of only one manganin strip, at the back of which is placed a thermopile consisting of forty-five thermoelements, (joined through a galvanometer). The pile is heated by the radiation from the strip. Gerlach used so many elements in order to eliminate the effect of inequality of the receiver. The receiver is blackened electrolytically with platinum black and the manganin strip is heated electrically to such a temperature that the effect on the pile is the same as when it is heated with radiation from the black-body. By knowing the resistance of the strip and the electric current, the electrical energy can be calculated and hence the radiant energy computed.

Gerlach had great difficulty in knowing exactly when he had compensated the receiver with the electrical heating. He found that covering the sides of the receiver with knife edged slits had no effect on the final value, but that covering the ends of the manganin wires to shield them from the radiation caused an increase in the value of σ from 5.85 to 6.14, when the ends were covered 15mm, or more.

He attributed this to the conduction of heat from the receiver to the heavy copper electrodes. In practice, he exposed the whole of the length of the strip to the radiation, claiming that the heat conducted from the ends of the strip will be the same when it is electrically heated as when it is heated by the radiation.

His work aroused considerable discussion among the other experimenters and it was very vigorously attacked by Valintiner and Kurlbaum. The outcome of these attacks was that Gerlach went to a great deal of trouble to determine independantly the various correction factors, such as the effects of absorption of the water vapour in the air, and the carbon di-oxide, and the reflecting power of the various blackening materials, etc: and to eliminate the sources of error pointed out to him. Finally, he operated his apparatus in a bolometric way, similar to the method used by Kurlbaum, and he showed that he obtained the same value for σ as when he used the apparatus in the other way.

The initial value given for σ was 5.85, which was subsequently corrected, after many experiments, to 5.80.

<u>Coblentz's</u> determination of the constant

The most important investigation of this type, up to this time (1915) was made by Coblentz, after a careful study of the work of the three previous investigators. He tried to eliminate the bad points in their apparatus, and to embody the good ones, and so to eliminate the sources of error.

Firstly, as we indicated in describing it, Coblentz improved the black-body radiator of Wien and Lummer to make it as'black' as possible. Secondly, he greatly improved the shutter and thirdly, he tried to employ a perfectly black receiver.

With regard to the radiator. He heated uniformly the interior over a range of 8 - 10 cms, although he used only a length of 2.5 cms. The total area of the enclosure was 37.6 sq.cms, and that of the opening was 3.1 sq.cns. He assumed that the reflecting power of the interior of the painted receiver was 7% and the loss of energy of the receiver by diffuse reflection at the orifice was .63%. Using a painted Marquardt porcelain radiator, the coefficient of total radiation, σ, was decreased by about 1%, and this demonstrates the importance of the question of " blackness" in the radiator.

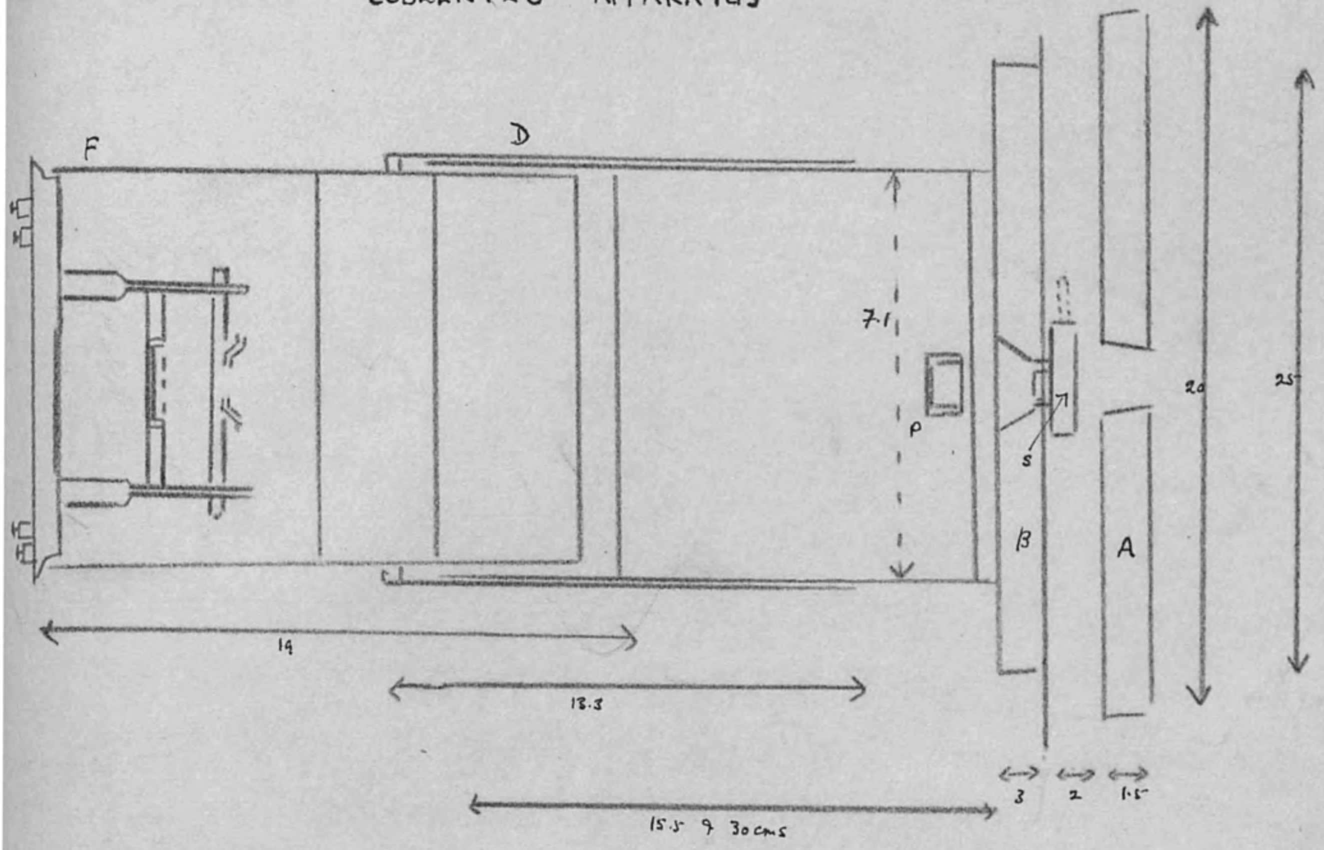
The employment of the water-cooled shutter was a new feature, not previously employed, the former investigators having given little attention to this question. This feature we have already described.

For the receiver, it was decided to use a form of modified Ångstrom pyrheliometer, embodying further improvments not tried out before. To provide better insulation and to reduce the heat capacity of the manganin strip, the thermopile was placed a short distance to the back of the receiver as shown in the figures (3&4) in a way similar to that used by Gerlach. The difference between their methods lay in the fact that in Coblentz's apparatus, the potential terminals were mounted actually on the receiver R and at a sufficient distance from its ends to avoid the difficulty encountered by Gerlach of the conduction of heat to the electrodes. The potential wires were from .003 - .025 in diameter and accurately defined the central part of the receiver which was used for the measurement. By exposing the whole of the receiver to the radiation in this way, the conduction losses from its ends do not enter into the question. The actual effects of the terminals were determined by using a third terminal P' and found to be negligible, viz about .3%. This method of finding the potential difference between the two terminals attached to the receiver seems more certain than finding the potential difference between two heavy electrodes, as used by Gerlach,

Coblentz at first used the receiver in conjunction with a hemispherical mirror, placed in front of the receiver, but after some discussion as to whether this caused further sources of error when the receiver is electrically heated, and on deciding that it would, he dropped this feature of the apparatus. Subsequently this mirror was used to determine the diffuse reflection from lamp-blackened surfaces and platimum black ~~surfaces~~ deposits, and finally for determining the losses by reflection of some of the receivers actually employed in the determinations. As a result of these experiments, he was able to correct for the energy losses from the receiver-surface on account of its lack of blackness, to such a degree of accuracy, that had he actually used a 'black-body' he would have obtained the same value for σ.

To test further the accuracy of the various corrections that had been made for eliminating the losses by reflection, a series of observations were made on one receiver. In this case the slits

COBLENTZ'S APPARATUS



A }
B } water cooled diaphrams

S : Shutter.

F : Radiometer (Receiver).

D : telescoped tubes (for drying).

FIGURE 4.

in front of the receiver and all other conditions remained unchanged. The only variation was the smoking of the platinum receiver with a sperm candle after making the first set of observations. The reflecting power of the platinum receiver, blackened with platinum black was taken as 1.7%, and with lamp-black, as 1.2%. The respective determinations, after corrections for the losses of energy by reflection were 5.814 and 5.822, differing by 1%.

Figure (4) shows as assembled form of the apparatus. A and B are water-cooled diaphrams, S the shutter, F the radiometer, and D the telescoped tubes containing phosphorus pentoxide for drying the tubes. The absorption by the intervening air was estimated at .1%, which was confirmed by Gerlach.

The thermopile was connected to a well-shielded galvanometer which served as a null instrument for indicating the rise in temperature, for the electrical and radiant heating.

The method of taking observations consisted in exposing the receiver to the radiation, noting the deflection of the galvanometer and then heating the strip to give the same deflection. The electric power in the strip, was measured with a potentiometer, which was also used for measuring the temperature of the radiator. Coblentz experienced no difficulty in determining when the electric and radiant heating were compensated.

The exact amount of electrical energy necessary to produce the same deflection of the galvanometer as the radiation was obtained by the ratio of the deflections. He followed the previous investigators in reducing the data. The area of the receiver exposed to the radiation, A_2 and the areas of the diaphrams of the water-cooled shutter~~s~~ must be known accurately. If this latter is A_1, and D is the distance between these two surfaces, then equating the electrical energy to the radiant energy, we get : -

$$E.I = \sigma.(T^4 - T'^4).\frac{A\ .A}{D^2}$$

where T and T' are the temperatures of the radiator and receiver respectively.

If the distance D is small compared with the diameters of the orifices, a correction term must be applied to the equation, namely : - $\frac{A_1\ A_2}{D^2}\left(1 - \frac{1}{6}\,\frac{a^2 + a'^2 + b^2 + b'^2}{D^2}\right)$

where a, b, a', b' are the ~~areas~~ sides of the rectangular openings in the diaphrams.

This latter correction can be reduced to

$$\frac{A_1\ A_2}{D^2}.\left(1 - \frac{1}{4}.\ \frac{a^2 + b^2}{D^4}\right)$$

Coblentz found that this second correction term was sufficiently accurate, as it amounted to less than .2%.

He operated his receiver at temperatures of 800 - 1000°. He used 10 different receivers, applying to them a correction of 1.2% for losses by reflection. He gave σ as 5.722.

In this value there is no correction for the atmospheric absorption. Allowing for this, the value for σ is increased to

$$\sigma = 5.73.$$

The method of determination is unsymmetrical in that, when exposed to the heating, the heating is produced in the lamp-black surface, while the electric current generates heat within the receiver. Coblentz made a separate determination to find the effect of this and he found that it was negligable.

For any one receiver, the results agreed to within 1% while for the different receivers, the agreement was about .5 - 2%. The result seemed independent of the length and width of the receiver, and of the slits used.

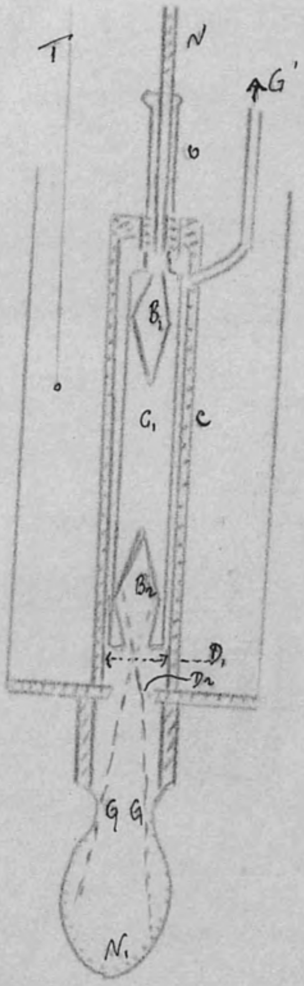
Kahanowicz's apparatus was essentially a form of modified Angstrom pyrheliometer.

The receiver was placed in the middle of a spherical mirror with an opening at one side to admit the radiation. The corrections for reflection are thus eliminated. The shutter is placed close up to the receiver. If its temperature were different from that of the water-cooled shutter, errors would occur, and so the shutter is placed in between the diaphram and the radiator, to avoid changes in the surroundings facing the radiator when the shutter is closed, or raised.

The temperatures ranged from 260 - 530 C. The distance from the radiator to the receiver was 55 cms. A series of 25 measurements gave σ as 5.61 and 11 of them gave 5.7. Later determinations with higher temperatures gave 5.61. He made no correction for the absorption of the intervening air, which is not negligible for these temperatures. It appears necessary to make a correction of 1.7 - 2% for this source of error, and a total correction of 1.7 - 2%, which will bring σ to the value (5.69 - 5.72.)

Puccianti employed the opposite method from the usual one in his determination of the constant. The weak point in his work is the comparatively large losses, due to convection and conduction

PUCCIANTI'S FIRST (BOLOMETER) APPARATUS.



B_1, B_2 } Black bodies in form of frustums of cones.

N_1 = Receiver (Blackened glass-bulb).

G = diameter of "

D_1, D_2 } Diaphrams

C_1 = evacuated vessel

C = water bath.

T = Thermometer.

FIGURE. 5

The bolometer was constructed in the form of a black-body which is kept at room temperatures, and the other black-body, instead of being at a higher temperature is at a lower one,- that of snow, liquid carbon dioxide or liquid air. He measured the power necessary to maintain the former black-body at a constant temperature, to compensate it for losses to the second black-body. He had two bolometer branches exactly alike, and one was exposed to the radiation, whole the other was protected form it. Each of the black-bodies consisted of a copper vessel, made in the form of a frustum of a cone, united at the bottom, as shown, (B_1 and B_2 in the figure). The length of B_1 and B_2 was 12 cms and the maximum internal diameters were 4 cms. The internal surface was blackened with smoke and the external polished, and on it were wound thin, insulated wires. One of these wires was used as the bolometer branch, while the other, made of manganin, formed the heating resistance. The other two branches of the bridge were formed of resistance coils. The two sensitive branches of the bridge were placed in the evacuated vessel C_1 which was kept in a tank of water. The receiver was a blackened glass bulb, N_1, immersed in liquid air, and the bolometer was allowed to radiate to this. The constant K of the instrument, (which depends on the dimensions of the apertures etc:) was determined from the diameters D_1 and D_2 (see fig.) A correction for the energy interchange between these two, is necessary.

Puccianti assumed that the shutter and the bolometer were at the temperature of the water bath. The resistance of the manganin heating coil surrounding the black-body B_2 was its resistance at the temperature of the water bath,T. In the course of the test, Puccianti measured the compensating voltage,E, when the branch B_2 was exposed to the ~~radiation~~ receiver N_1 at the temperature T_0. He gave his final value for σ as

$$\sigma = 5.96.$$

The fault of the apparatus lies in the fact that it should have been constructed so that both branches could have been used as radiators. From the figure, it seems that the radiation from one branch falls on the other branch. Another uncertainty is the temperature of the bath, and also the method of operation of the shutter.It was suggested that Puccianti should test whether a balance was maintained when a heating current was passed through both branches, without either branch being allowed to radiate to the receiver and that a heating coil should be put inside the radiator temporarily, to determine the energy input, as compared with the energy required to sustain the balance.

The device is unsymmetrical in that the heating coil is not put on the proper place to operate most efficiently.

The sources of error indicated should give σ too big a value. Indeed, it is 4% higher than Coblentz's value.

A recent determination (in 1922) of this type was made by KUSSMANN. His apparatus is shown in the figure.6 on following page. D is a water-cooled diaphram through which the radiation passes to the receiver R, the temperature of which can be determined by the radiomicrometer, M. He used four black-bodies, as radiators,(S.K.1,2,3,4, in the figure.) The smallest one was made of copper and could be used up to temperatures of 500°C, while the other three were of the usual Lummer-Kurlbaum type, heated in the usual way by passing a current through platinum windings. Between the radiator and the diaphram was a water-cooled trough, T maintained at room temperature, the mouth of which could be closed with a lid K. When this lid is closed, Kussmann says, " it is equivalent to a small black-body at room temperature, and thus if the receiver is also at room temperature, radiation from the lid will not affect the receiver. The temperatures of the radiators could be measured with a thermoelement, th, and their temperatures could be kept constant over a long period of time. Round the lid were placed a row of " sheet protecters", not shown in the diagram, to protect it from the radiation, from the surroundings. The distance between the radiator and the diaphram was 34 cms.

The receiver was made of manganin or constantin, and placed in a vulcanite support of dimentions,(10.6 x 5.8 x .5) The actual receivers were blackened in various ways. This table shows the kinds of receivers employed.

Receiver	Kind of Metal	Length	Breadth	Thickness	Method of blacking
1	constantin	4.0250 cm	2,9428 cm	6 u	" Berussung "
2	"	40027 "	2.9602 ""	" u	" Crovaruss "
3	manganin	2.7559 "	3.0690 "	5 "	"
4	constantin	4X0369 "	2.8867 "	" "	"
5	"	2.9804 "	2.9158 "	7 "	"
6	"	{4.0315 1.9114 "	{1.5444 " } "	7 "	"
7	manganin	4.0355 "	3.0038 "	10 "	"

The strips had very small temperature coefficients, and their edges were accurately defined and cut to suitable shapes, being made exactly parallel to one another.

Kussmann heated the strips by allowing radiation to fall on them from the black-body and concentrated the radiation emitted from the strips onto the radiometer, by means of the lens, L. When steady conditions were established, he noted the deflection of the radiometer, and then closed the shutter K. He heated the receiving strip in the same way as his predecessors had done and so obtained a comparison between the electrical heating, and that by the radiation. The rest of his determination is very similar to that of Coblentz and he made similar corrections for lack of blackness etc:. The final value he gave for σ was $\sigma = 5.79$.

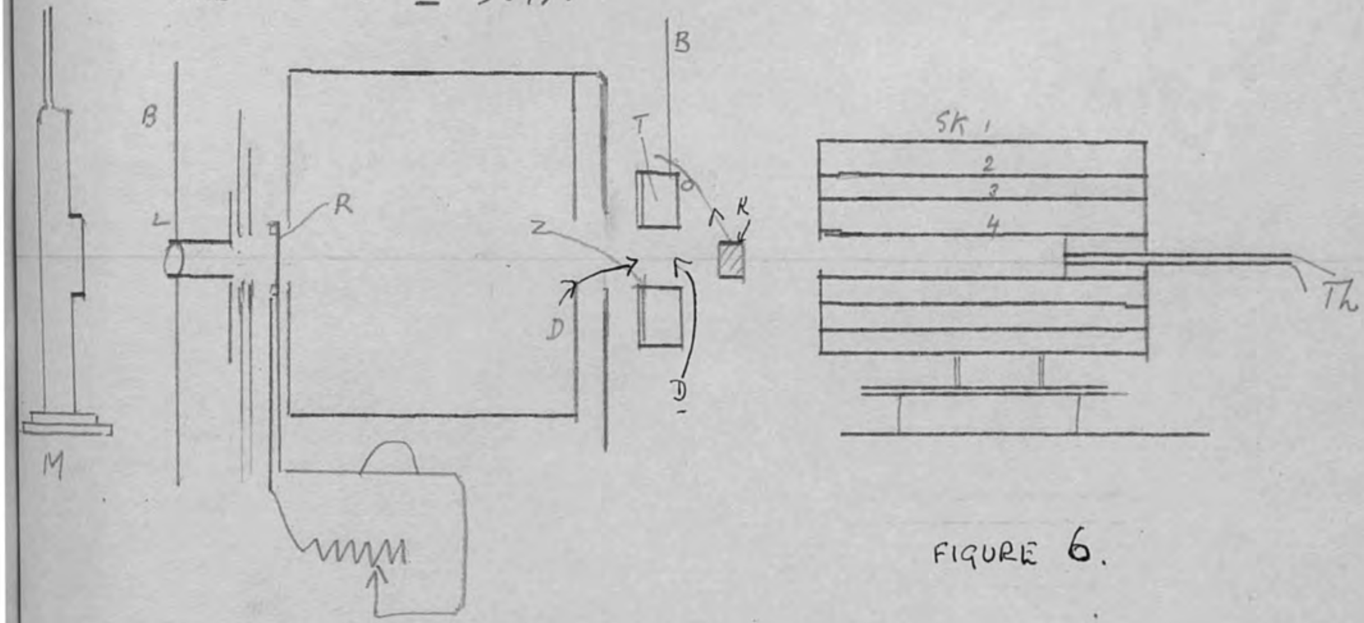


FIGURE 6.

M = radiometer.
D = diaphram. (water cooled).
R = receiver.
Sk 1, 2, 3 = Black bodies (porcelain).
Sk 4 . " body (copper).
K = lid

Th = Thermoelement.
L = lens.
Z = Accurately cut edge of diaphram.
B = Screens.

(ii) THERMOMETRIC METHODS, USING ' BLACK ' RECEIVERS.

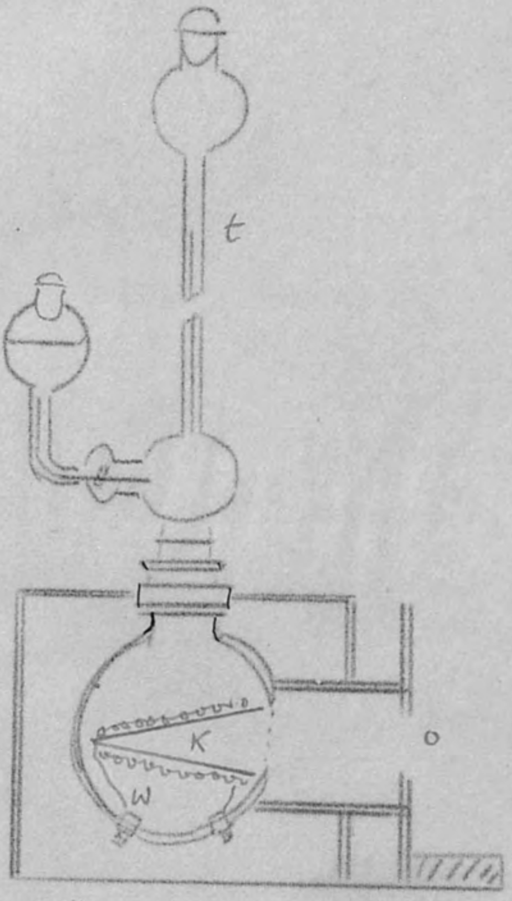
<u>Fery</u> evolved a method to eliminate the question of reflection at the surface of the receiver. His receiving thermojunction was formed from a long conical-shaped metal receiver, blackened on the inside. Outside was wound an insulated heating coil, of known resistance, to calibrate the receiver. This was done, by noting the temperature,(or galvanometer deflections) with energy input into the heating coil. The receiver is then exposed to the radiation, at temperatures varying from 500 - 1200°C and the galvanometer deflections noted. His method was, however, not accurate, and he obtained a large value for σ, namely

$$\sigma = 6.30$$

The work was carried on by <u>FERY</u> and <u>DRECQ</u>. Their apparatus is shown in figure (7). They used two receivers of brass cones of apertures of 30°, placed within a sphere of brass surmounted by a glass tube of capillary bore, which would indicate a temperature change as small as .005°. Surrounding the outside was a coil of wire, through which an electric current passes, and the energy input which caused the same rise in temperature as that indicated when the receiver was exposed to the radiation, noted. The mean value for σ was $\sigma = 6.51$.

The individual determinations are consistent with one another but not with the results obtained by the previous investigators. This seems to indicate that there is a systematic error running throughout the determinations. Various suggestions have been made to account for this, one being the unsymmetrical operation of the receiver. It is calibrated with the heating coil in associa-

FERY & DRECQ's APPARATUS



t = thermometer.
K = Receiver (Conical shaped,
blackened inside)

O = opening
W = windings.

FIGURE 7.

tion with the thermometer and this can be warmed by conduction as well as by radiation of energy. On the other hand, the incoming radiation must be transformed by absorption in the cone and reached the alcohol in the thermometer principally by conduction. It was also suggested that the heating coil should be placed within the receiver, and constructed so that very little or none of the radiation entering the cone or the energy radiated from the heating coil can escape through the opening in the receiver. This could have been done by putting the heating coil inside, and using a double cone as Puccianti did.

Later they made further determinations, using the radiation from an electric furnace, and allowing it to fall on a platimum strip. The radiation measurements were made by " sighting" on the front and rear surfaces with a Fery pyrometer at an angle of incidence of 30°.

The mean value obtained for σ was $\sigma = 6.2$ Measurements on the posterior surface gave σ as 5.57 which is said to correspond to the anterior surface if this is plane. Correcting this value by 2% gives $\sigma = 5.68$, but the experimenters themselves only allowed .82 - .84% for losses by reflection, which seems very low considering the values obtained later by Coblentz. Attention was called to the point by Bauer, who estimated that their value must lie between 5.1 & 5.8. The value given by Fery and Drecq themselves was

$$\sigma = 6.2$$

which, when corrected by 2% for reflection, gives

$$\sigma = 5.68.$$

Bauer and Moulin used a similar method to that of Fery and Drecq but to overcome the difficulty of calibration, they sighted their receiver on a platinum strip, heated to different temperatures by electric currents. To determine the radiation falling on the receiver, it was necessary to eliminate the errors caused by the conduction and convection losses from the strip, and so they heated it in vacuo. Having calibrated the instrument they sighted on a black body, heated to different temperatures and noted the galvanimeter deflections. Firstly, they got

$$\sigma = 6.0$$

but for reasons previously indicated, they corrected this to

$$\sigma = 5.3$$

This correction of 12% seems to be rather large. They made no correction for atmospheric absorption, which would increase their value to

$$\sigma = 5.6 - 5.7.$$

Puccianti continued his studies of the radiation constant and gave the following method for the determination of σ wherby the temperature changes are measured by a toluene thermometer bulb, made in the form of a hollow cone that is allowed to radiate to a black-body receiver at the temper-ature of liquid air. The heat to compensate the loss of energy by the thermometer ~~reflection~~ was measured by the application of an electric current. The apparatus is not differential, and so the bath must be kept at exactly the same temperature. The response to the radiation was sluggish The criticisms that were earlier applied to the Fery and Drecq experiment may be applied here also. In this case, however, the compensating heating is applied by heating a coil which is in contact with liquid air on the wall opposite to that on which the incoming radiation impinges. In this the receiver is unsymmetrical and more symmetrical heat interchanges could have been obtained by having the coil within the receiver, if care is taken that none of the heat escapes through the opening. The way that the apparatus is used provides ample opportunity for loss of energy, so that in the compensating, the tendancy would be to give too high a value for σ

Puccianti himself considered that the precision of the instrument was as high as that of the bolometer. His values range form 6.00 - 6.3, and the average σ is

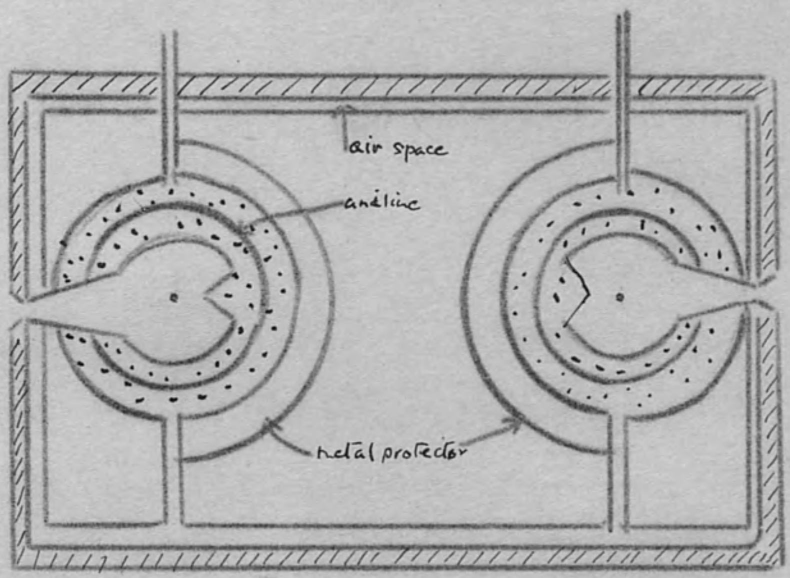
$$\sigma = 6.15.$$

All the values obtained by this method seem to be higher than those obtained by the bolometer method, all being in the region of 6.0 whereas the bolometer way gave about 5.7. and therefore, in 1913, <u>KEENE</u> undertook a measurement of this kind, with an improved form of apparatus.

His source of radiation was an electric furnace which could be used up to temperatures of 1000°. For receiver, he used a hollow spherical, double-walled thermometer bulb, provided with a small aperture to admit the radiation, (see figure (8).) The thermometer was filled with aniline. Variations in the room temperature were eliminated by using two thermometers differentially. The radiant energy is admitted to one of them, and the difference in the levels indicates the energy input

KEENE'S APPARATUS

FIGURE 8.



In this apparatus, the calibration was done by having the heating coil within the thermometer bulb. The bore of the capillary tube was such that a rise of 1mm division, indicated a temperature difference of $.0005^{\circ}$C.

Keene found that he had to make a correction for the energy interchange between the two radiating coaxial circular openings, for which he found the approximate formula which is ordinarily used for corrections, was not accurate enough.

Sources of error in Keene's measurement. As the radiator and receiver are fairly close together, and the time for attaining equilibrium rather long, there is a possibility of diffusion of hot gases into the receiver, when the shutter is raised to admit the radiation. It was suggested that a determination should have been made with the opening closed to prevent the possible escape of hot gases while calibrating the device, and to see if in this case, it would have required less power in the heating device,

The value obtained for σ was

$$5.89$$

which agrees fairly well with that obtained by Gerlach, bolometrically, of 5.80.

(iii) INDIRECT and SUBSTITUTION METHODS.

We come. now to the third group of methods for determining the radiation constant, by experiments wherein, instead of directly attempting to measure the heat radiated from one black-body to another, the heat is compared with emissivities under different conditions and the emission for a black-body estimated.

The earliest experimenter in this group was SHAKESPERE in 1912. His value for σ was obtained on the principle that a body loses heat, when suspended in the air, by three methods, namely conduction, convection and radiation. If the losses observed in two instances, the only difference being that of the emissivities of the two surfaces, then, as the losses by conduction and convection are to remain the same, the ratio of the losses will be as the ratio of the emissivities.If therefore, these two surfaces be exposed in turn, at the temperature of boiling water, to the face of a radiomicrometer, at room temperature, we shall get the emissivities of the two surfaces.

Shakespere had a plate of metal with a silvered surface heated electrically to a temperature of 100°C and close to it another plate, blackened with soot, kept cool with water. Between the two plates was air at atmospheric pressure. The energy input required to keep the plate at 100°, was measured with a radiometer. He then compared the emissivity of the soot-blackened layer with that of a black-body at 100° and was thus able to calculate a value for σ, which he gave as

$$\sigma = 5.67.$$

In Todd's experiments on the thermal conductivity of gases, he was able, as a subsidiary experiment, able to make a determination of the radiation constant. He enclosed a thin layer of air between two horizontal plates, maintained at different temperatures. The colder plate receives heat by radiation, and by conduction through the air from the hotter plate. which is placed above it. The plates are cut off in communication from the surrounding air and convection currents were eliminated by having the two plates close together. He determined the energy lost, with different distances between the plates, x, noting the different quantities of heat, Q, passing from the upper to the lower plate. The values of x and Q were graphed and the horizontal asymptote to the rectangular hyperbola drawn, to give the value R of the radiation. The energy input was determined, and by comparing the emissivity of the plate with that of a black-body at the same temperature, the value for σ could be found.

The sources of error in this determination are chiefly in the bad conductivity of the layer of soot.

Todd gave as his value of σ,

$$\sigma = 5.48.$$

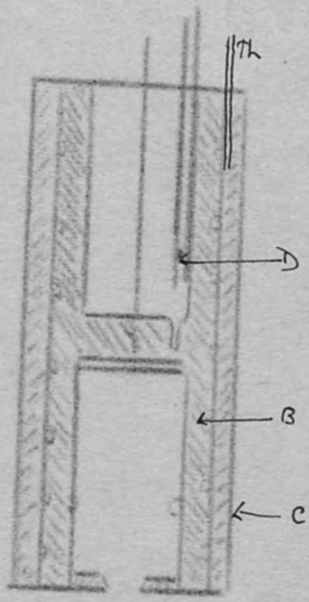
Observations of Westphall.

Westphall compared the emissivity of a black-body with that of a cylindrical copper block, when the latter was firstly polished and secondly, blackened on the surface. The figure(9) shews the arrangement of the apparatus. The black body is contained within the cylinder and the cylinder could be electrically heated. To reduce energy losses, the whole was

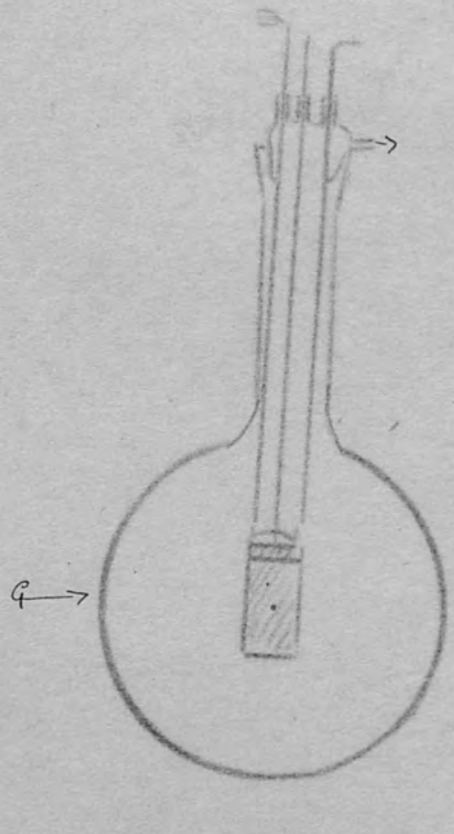
WESTPHALL'S APPARATUS

FIGURE 9.

[A]



[B].



A = windings

B = copper block.

C = " tube

D = Thermoelement.

Th = " (as used by Hoffmann).

G = Glass vessel (internally blackened).

suspended in a glass vessel which could be exhausted. The cylinder was first highly polished to give a low emmisivity, E_1 and then blackened to give high emissivity E_2, the end surfaces remaining undhanged. The losses by conduction and convection are therefore the same throughout the experiment and the difference of energy input was therefore the loss by emission.

If the temperature, T, of the glass flask is kept constant throughout the experiment, and the blackened cylinder heated electrically to T', then the energy input required to maintain the copper at constant temperature, T', is

$$W_1 = O.\sigma.E_1 \, (T'^4 - T^4) + f(T,T')$$

where O is the area of the surface of the cylinder, and f(T,T') is unknown, being the loss by conduction and convection. W is the energy input

Similarily, when the cylinder is polished,

$$W_2 = O.\sigma.E_1 \, (T'^4 - T^4) + f(T,T')$$

and therefore $\sigma = \dfrac{W_1 - W_2}{O(E_1 - E_2).(T'^4 - T^4)}$

The value given by Westphall for σ, over a range of temperature $350^\circ - 425^\circ$, was $\sigma = 5.54$

Later he extended his work to higher temperatures and gave

$$\sigma = 5.57.$$

After still further determinations, he got

$$\sigma = 5.7$$

Gerlach criticised the work on the grounds that the layer of soot had not the same temperature as the metal surface on which it was deposited, which would give too low a value for the radiation constant. All three attempts by this " indirect" method have given values which are very much lower than those by the thermometric methods, and a more recent attempt by this method of Westphall, was made in 1923, by <u>Hoffmann</u>. The arrangement of his apparatus was essentially the same as that of Westphall (see figure for Westphall's apparatus)

Hoffmann used a massive copper block, cylindrical in shape and with a spiral grove running round it, in which he wound the heating coil. This was electrically insulated from the copperblock itself, and it's resistance was of the order of 11 ohms.Over the cylindrical block was placed an accurately fitting copper tube, fixed at the corner by a metal screw. A fine longtitudinal hole bored into this tube, admitted the thermoelements into the tube. These were made of manganin-constantin, and arranged in this way, were very near to the surface of the mantel tube. The whole radiating body was hung inside a glass flask, the walls of which were blackened inside with a special preparation of lamp-black. Care was taken to hang it in the centre of the flask, so that it could always be replaced in the same position, and so that the same external conditions would hold for when the outside was polished as for when it was blackened. The flask was evacuated to what was found by trial, to be the optimum pressure,- .1mm of mercury.

Hoffmann took special precautions to eliminate the error which might arise from the difference in the temperature between the metal and the radiating surface. He pointed out that a difference of 1° would affect the result by as much as 1% and on making measurements on these temperature differences, he found that they might be as much as .4%. He put the flask in ice, and the energy measurements were carried out exactly similarily to Westphall's measurements, by estimating the the energy imput into the heating wire, and measuring the temperature with the thermoelements. The following is a list of his results for the various temperatures of the radiator.

temp.°C	σ	temp.°C	σ	temp.°C	σ
90.0	5.78	140.95	5.72	166.5	5.79
93.4	5.75	150.0	5.80	181.5	5.80
100.4	5.74	150.85	5.78	191.7	5.78
106.8	5.74	154.6	5.72	200.5	5.74
119.0	5.78	164.25	5.79	206.2	5.74
132.9	5.75	170.1	5.75	216.6	5.78
115.4	5.78	174.7	5.80	217.5	5.78
137.65	5.76	185.7	5.80	195.7	5.78

He made the following <u>corrections</u>.

Firstly, since there is a layer of soot of about 60µ, this will radiate sideways. This, he estimates will affect the result by + .2%

Secondly, for the temperature difference between the metal and surface, he allowed .02%, and between the outside of the glass flask and the inside, .05%.

A further correction of .4% was allowed for the inside of the flask not being a perfect absorber.

Altogether, he allowed a correction of +.05%, giving σ the value 5.764.

The <u>accuracy</u> of his determination, he says is .9% - for he maintains that the maximum error in each of the energy determinations is .2%; the temperature is at the most in error by .2%, affecting the result by .2%; the errors in the wattmeters is also not more than .2%; hence, he calculates the maximum error at .9%. He writes his final value as

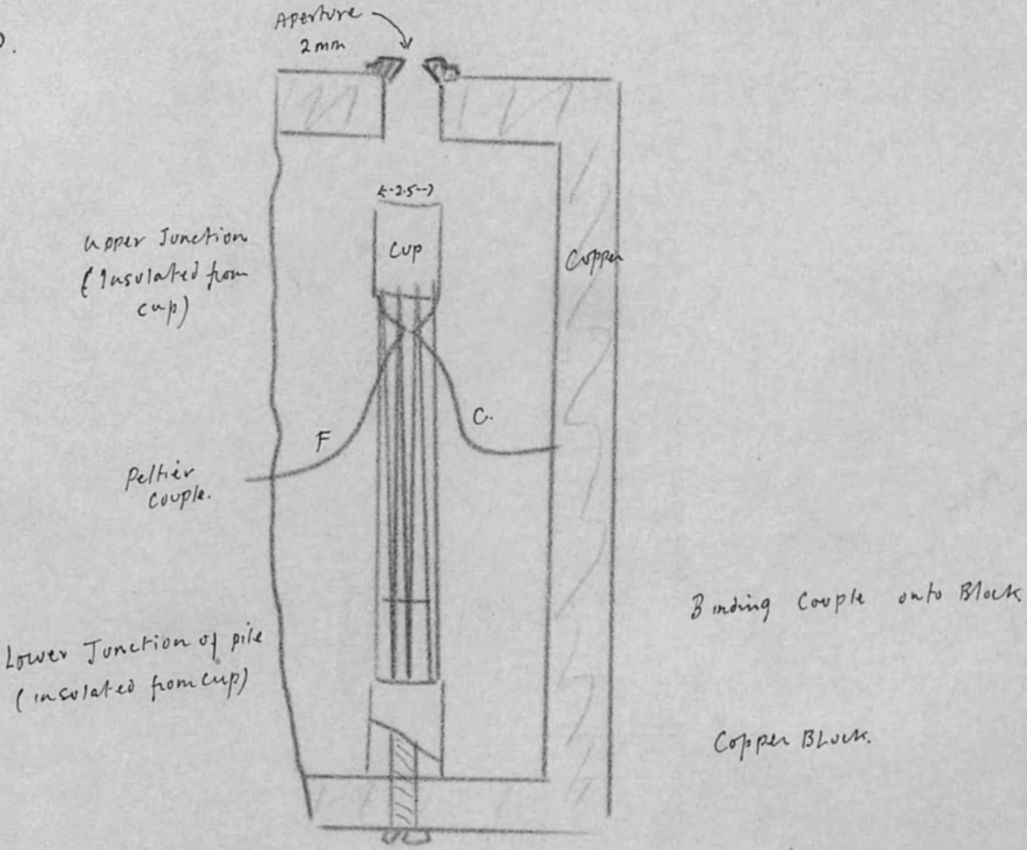
$$\sigma = (5.76_4 \pm .052.)$$

Two very recent determinations have been made by <u>HOARE</u>[7] using a CALLENDAR RADIO BALANCE. In this apparatus, the heating effect caused by the passing of an electric current through the junction of two dissimilar metals, and the corresponding cooling effect and the other junction, is balanced by the heating effect of the radiation which is allowed to fall on the cooled junction, and to heat it to the same temperature as the other junction. Equality in the temperature of the two junctions is indicated by no current in a galvanometer which is connected to the two junctions, in such a way that the Peltier current cannot pass through it.

The arrangement of a radio balance in shown in figure (10). Radiation passes through the circular aperture and is caught in the cup, which is about 1cm in length and 3mm in diameter. The Peltier couple, of iron and constantin, is soldered to the bottom of the cup, which is mounted on a tubular pile consisting of twelve elements. These are insulated from electrical contact with the cup, by very thin paper and shellac as it is required to make good thermal contact without making electrical contact. The lower junction of the pile is screwed into a thick copper of a hollow cylinder of 3 x 3 sq.cms internal diameter.

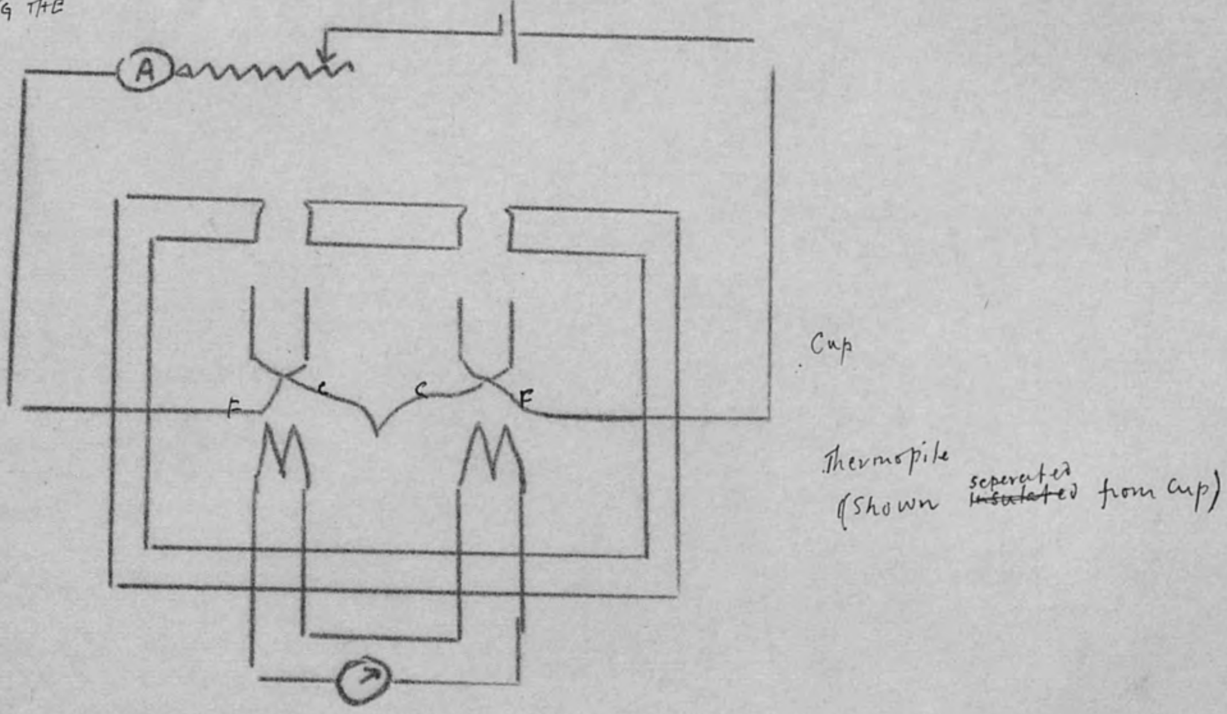
CALLENDAR'S RADIO BALANCE

FIGURE 10.



(A)

DIAGRAM SHOWING THE ELECTRICAL CONNECTIONS



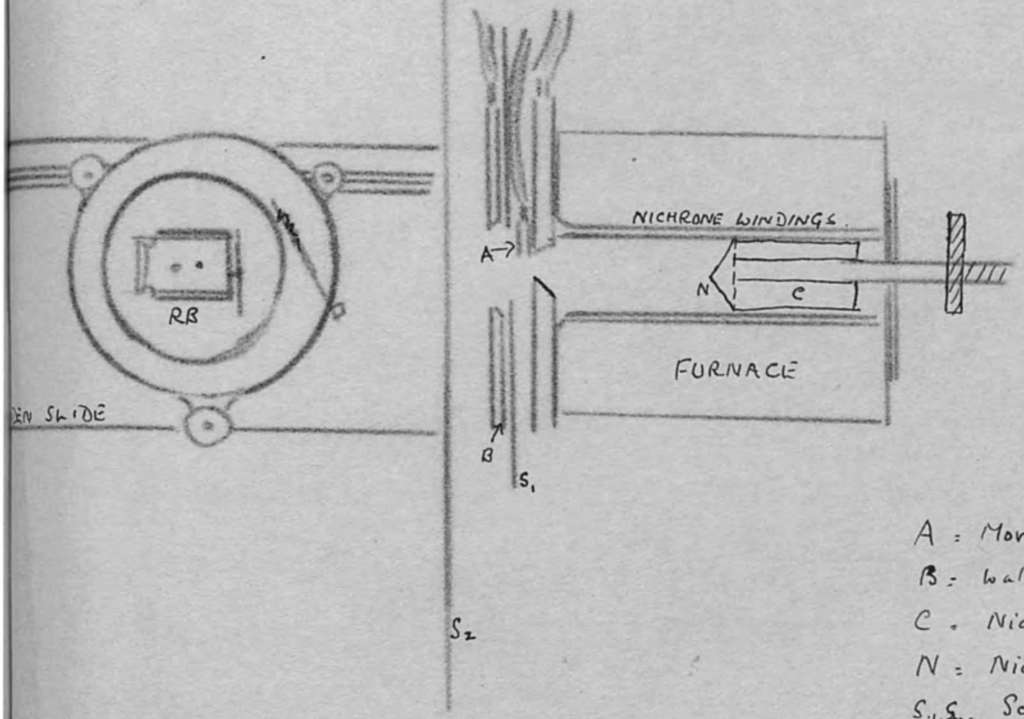
(B)

The current through this Peltier couple is adjusted until the galvanometer, in series with the thermopiles, shows no deflection; then the cups are interchanged. This eliminated the Joule effect of the current. In practice, there is always a slight current in interchanging the cups but this can be allowed for by shielding both cups from radiation and noting the deflection on interchanging a known current through the cups. It was found in experiments to determine the " blackness" of the cups as receivers, that the cups, when in the highly polished state in which they came from the spinner, gave an absorbing power of about 94%, as compared with about 30% for a similar metal disc. This latter, when blackened, can be made to absorb up to 96%, and assuming therefore that blackening the inside of the cups would increase the absorbing power of the cups correspondingly, it seems that they may be regarded as practically "black".

To calibrate the balance, it is necessry to find the value of the Peltier coefficient under conditions similar to those under which the measurement is made. Hoare made, very carefully, two resistance coils, equal to nine ohms and accurate to one part in a thousand. These were fitted into the cups, a little oil being introduced to better the thermal contact. He placed the top of the coil at least 2 mm below the top of the cup, and they were arranged so that the heating current passed through one coil at a time, but through both leads, so that the compensating effect due to the leads was eliminated. The heating effect of the Peltier coefficient for both cups was balanced against the heating effect of the coils and Hoare found the relation for the variation in the tem-

FIGURE 11.

HOARE'S ARRANGEMENT.



A : Movable water cooled Shutter

B : Water cooled diaphran.

C . Nickel ~~cylinder~~ block.

N : Nickel cylinder.

S.$_1$.S$_2$. Screens

RB. - Radio balance.

erature of the surroundings, for temperatures up to 25°C

$$P_t = P_{20} + 0.066,(t - 20^\circ)$$

where $t^\circ C$ is the temperature of the surroundings, and P the coefficient

In his first determination, Hoare used electrical means of heating as his source of radiation,(see figure 11)

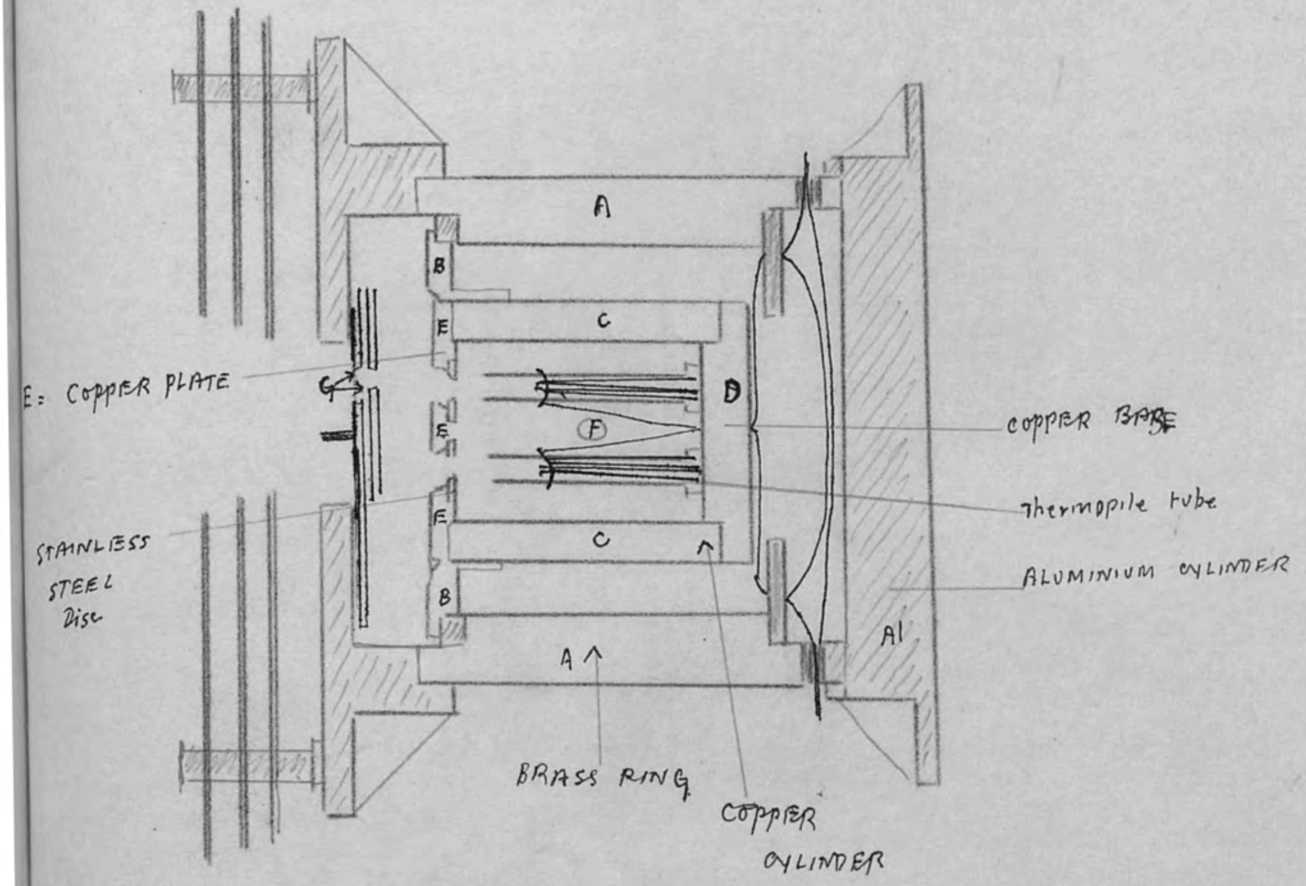
The measurements of the diameters of the apertures were to .0001cm, and he took the mean of 52 readings.

In his subsequent determination, he arranged his receiver a little differently, having the copper block enclosed in a large aluminium box. He used a steam heater for this determination, but the novel part of the apparatus being the receiver we will describe this in detail.

The figure (12) shows the arrangement of the receiver. Al. is an aluminium cylinder of 7.2cm diameter and 5.2cm long. The ends of it are cut in steps, so that by means of vulcanite rings screwed into the aluminium, the brass cylindrical ring, A, 3.5cm in diameter is kept in position in the aluminium. C is a copper cylinder, .5cm thick and closed with another copper ring D, to which the thermopile mountings are brought, and which supports the copper receiving cups. At the other end of this cylinder is another plate of copper,E, with conical holes,blackened on the inside. Behind these two holes are screwed discs of stainless steel with bevelled apertures of about 2mm diameters arranged exactly in front of the cups. The edges of these are accurately cut, and foil put over them to give a final 'sharpness' F is a brass tube let into the apparatus to take a thermometer

HOARES RECEIVER (RADIOBALANCE)

FIGURE 12.



G = SHUTTER

F = THERMOMETER

Al = Aluminium cylinder.

A : Cylindrical brass ring.

C : copper cylinder.

D : .. ring.

E : .. plate

F : thermometer tube.

It is very important that the temperature of the cups is taken right in the middle of the apparatus.

The two holes in front of the cups admit the radiation to the cups, and the radiation can be screened from either cup by a ~~do~~ double shutter, G. The separation of the shutter and the cups is exaggerated in the figure. This double shutter is made of two pieces of brass, separated from one another by a piece of fibre. The radiation passes through the conical holes in the shutter, to either cup. The three screens in front of the apparatus shield it from stray radiation, and also give 'direction' to the radiation coming in. The thermopiles were made of copper-constantin to prevent rust. The receiver was built to have a very large space between the cups themselves and also betweem them and the brass cylinder. It was found that arranged in this way, the temperatures of the surroundings were maintained at very constant temperatures.

After a series of measurements, Hoare gave

$$\sigma = 5.735.$$

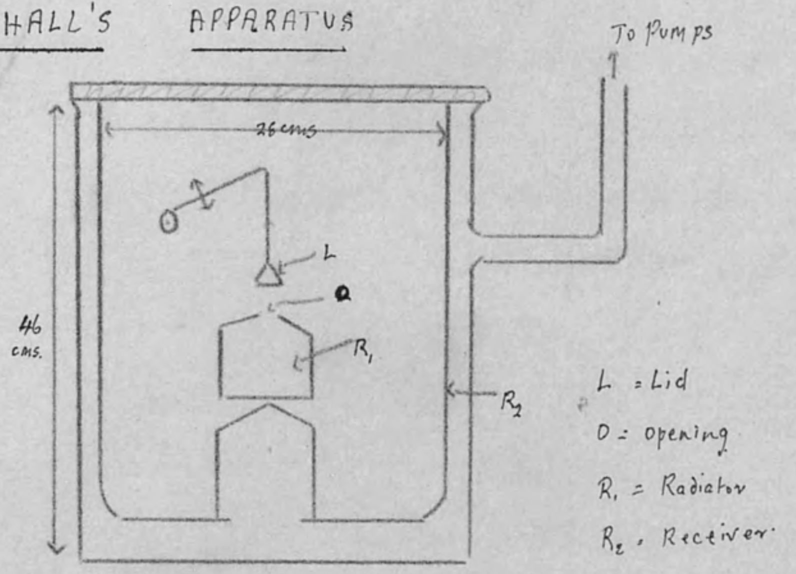
Mendenhall attempted to measure σ, by comparing the emissivity from an enclosure with an orifice, when this is closed with when it is open, that is to say, comparing the emission from the enclosure when this is emitting as a black-body with when the enclosure is losing heat only by emission from the walls (the conduction and convection effects remaining the same in both cases.)

The author himself thinks that this method is capable of great experimental accuracy.

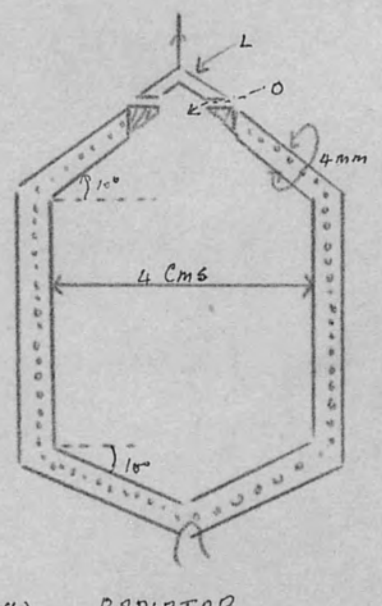
MENDENHALL'S APPARATUS

FIGURE 13.

for Comparing the emissions from the Radiator R_1 with the lid closed, and with the lid open



GENERAL ARRANGEMENT. Figure 13 (a)



(b) RADIATOR
(R_1 IN FIG. ABOVE).

In the figure (13) the experimental arrangement can be seen.
The radiator is made of copper, in three parts. The inner wall is .1mm thick and blackened on the inside. At the top is a circular aperture with a gold rim. The outer surface is entirely covered with wire, the two ends of which are at the closed end of the radiator. They are coated with shellac to insulate them from the outer vessel. The part of the radiator round the aperture is made from solid gold. The inside edges are carefully bevelled while the outside ones are ground and polished to almost optical flatness.

Nickel wire was used as the resistance thermometer, because of its large temperature coefficient, and because it made a reliable resistance thermometer. The outer surface of the radiator was made of polished gold, to reduce the external heat losses.
The lid was, first of all, made of copper and gold plated, but, later it was made of solid gold, because the emissivity of solid gold could be reproduced with greater accuracy, and it made better contact with the rim of the radiator. The edge of the lid was ground and polished to give good contact. The inner surface was blackened with lamp-black and shellac. The receiver could be evacuated to 10^{-6} mm of mercury. The lid was suspended with a silk thread and could be raised or lowered by external application of a lever.
The receiver and bath were both brass vessels, blackened internally with lamp-black and shellac. The temperature of the bath could be kept constant, with ice, or by means of a thermostat.
The equation for σ is

$$\sigma = \left[(i_0^2 - i_s^2)R + \sigma_g A_L (T_L^4 - T_1^4) \mp H_c - \sigma_g A_2 (T_2^4 - T_1^4)\right] \div a(T_2^4 - T_1^4)$$

where i_0 = equilibrium current with the lid open
" i_s = " " " " " shut
" R = resistance of the radiator coils at the temperature T_2 °C, in ohms
" H_c = conduction loss by thermocouple when used to operate lid.
" T_1 = Temperature of receiver
" T_2 = " radiator
" T_3 = " lid
" σ_g = emissivity of gold
" a = area of aperture,
" A = " " exposed surface of lid

The low emissivity of the external gold surface has two advantages, (a) that the radiation through the aperture is relatively large - from one third to one half of the total loss which takes place when the aperture is closed, (b), that the term depending on σ_g is only small so that it need not be known to a high degree of accuracy.

Measurements of the resistance coils were made with a Wheatstone's bridge, (10 : 1).

Current measurements were made with a Taisley potentiometer, measuring the voltage drop over a 10 ohm coil inserted in series with the radiator.

To determine σ_g. It was at first intended to measure σ_g from the area of the closed radiator and the energy input required to maintain equilibrium. This method is subject to unavoidable errors, due to the crevices where the two parts of the outer join, and to the variable contact between the outer shell and the coil. Also the effect of plating the gold on copper causes some variation. Therefore a solid gold lid was used, 5mm in diameter, and 1.5mm thick. It was made in two parts, with silk enamel nickel coil stuck in between the two parts with shellac. All the cracks were carefully sealed. With this arrangement, a very constant value for σ_g was got, namely

$\sigma_g = 1.496$; and 2.372×10^{-13} watts.cm^{-2}.deg^{-4}. It was found that the concordance between these two values was sufficient.

A different emissivity was obtained by using a receiver and lid which was platinum plated, in which case the emissivity of the lid was found fron the total area of the lid, and the total emissivity of the closed radiator.

The aperture had to be measured accurately. Its value ranged from.7 to 1.5mm in diameter. The edges were extremely sharp, being formed by the intersection of conical and external flat surfaces, this latter being ground and polished.

The degree of accuracy of the measurement was

temperature	to within .03°C
resistance	greater than 1 part in 5000
current	" " 1 part in 10,000.

It was found that any one radiator would give very consistant results.

The following are the chief sources of error in the measurement Firstly, of course that the radiator is not a perfectly black-body If E is the emissive power, R the reflecting power of a black-body aperture, then, $E = 1 - R$

and $R = R_s \int e' . ds + R_s \int e'' . ds + \ldots$

where R_s is the intrinsic reflecting power of the inner surface, e' is the percentage of the radiation striking an element which, reflected more than once, according to Lambeth's law, escapes the aperture, e'' is the percentage after two reflections, etc:
Since R can be made quite small, the higher powers are practically negligible. In practice, the integration is replaced by summation, which is done graphically. Mendenhall allowed R = .0011 and therefore E = .9989.

Correction also had to be made for the fact that the receiver was not a perfectly black-body. For this, he put A = .999.

Thirdly there is the temperature drop between the coil and the radiating surface, through the silk insulation of the coil and the blackening of the walls, to be corrected.

After allowing for all these corrections, the value given for the constant was

$$\sigma = 5.79$$

A SUMMARY OF THE VALUES OBTAINED FOR THE CONSTANT σ was published recently by Hoare[x] in a paper in which he expresses his views on the relative merits of the various values obtained experimentally for the radiation constant, (the Stefan-Boltzmann constant,) σ.

He says that the various investigators have made attempts to improve the constancy for the value, by application of corrections, (as we have seen in the foregoing account.) Hoare maintains that these proceedings are " dangerous", for not only, he says, are the published details usually insufficient for such a correction to be applied with certainty, but also, .." there will be , quite unconsciously, a bias in favour of a correction which will bring the results of the other investigators in substantial agreement with one's own "..

He then proceeds to give " weights" to the values obtained by the previous workers, and he allots equal weights under the following headings

(1).Design of Radiator
(2). " " Receiver
(3).Efficiency of receiving apparatus,(i.e. whether good or poor absorber, abd method of applying correction).
(4).Method of operation of water-cooled shutters
(5). " " " " receiver,(symmetrical or unsymmetrical)
(6).Accuracy of susbidiary measurements,(e.g.lengths, areas, electrical measurements,etc:.)
(7). Range of conditions taken
(8). Number of results and the individual variation.

Without details of the actual calculation, he gives the following table for the results and the " weights" as he has calculated them. The maximum " weight"for any determination is 4

ref.x. Phil.Mag. 14.445. 1932.

	σ	WEIGHT.
Kurlbaum	5.45	½
Fery	6.30	½
Bauer & Moulin	5.3	½
" " "	5.7	1
Todd	5.43	½
Valintiner	5.58	1
Fery & Drecq	6.51	0
" " "	6.20	½
Shakespere	5.67	2
Puccianti	5.96	1
"	6.15	1
Gerlach	5.85 5.80	2
Westphall "	5.54 5.57	2
Keene	5.89	1
Coblentz	5.722	3
Kahrowicz "	5.61 5.61	2
Hoffmann	5.764	2
Kussmann	5.795	2
Mendenhall	5.79	1
Hoare	5.735 5.735	3½

Weighted mean = 5.742 ± 0.27

Birge[x] puts the most probable value as

$$\sigma = 5.735 \pm .011$$

Hoare calculates the value for Planck's constant, h from the value for σ = (5.742 ± .019), and the generally accepted values for the constants, "k" and "c", and obtains

$$h = (6.536 \pm .011) \times 10^{-27}$$

The following table shows the values calculated by Birge : -

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ref. Birge, rev.mod. phys. 1. 1. 1929.

Method of calculating.	value of h .	
Rydberg's constant	6.547	± .011
Ionisation potentials	6.560	± .015
X-rays	6.550	± .009
Planck's radiation constant c_2	6.548	± .015
Photoelectric	6.543	± .010

It is interesting to notice that the limiting values of σ, given by Birge, by calculation from other constants,, namely

$$\sigma = 5.746 \quad \text{to} \quad \sigma = 5.724$$

are completely contained within the limits of the values given by Hoare, from experimental values,

$$\sigma = 5.761 \quad \text{to} \quad \sigma = 5.723$$

If Birges limits of error are correct, then this would seem to indicate that the correct value lies between

$$\sigma = 5.746 \quad \text{and} \quad \sigma = 5.724.$$