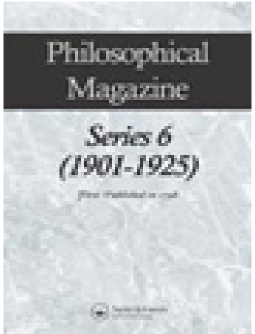

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XCVI. Thermodynamics of radiation

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length. That is, they contract in a particular azimuth only, retaining in the azimuth normal to this the diameter of the unstretched wire. The cross section of a wire behaving in this way appears to be roughly elliptical, so the contraction is approximately uniform across the wire. The minor axis of such a cross section is, in the case of tin, often only 0·4 of the major. The ring-shaped markings appear on the flatter surfaces of the wires, which are shown in the photographs; they are similar on each flattened side and run together at a sharp angle at the edges of the flattened wire. The plane in which the flattening takes place must be determined by chance asymmetrical irregularities, for with tin two or more such different planes sometimes occur on the same wire, separated by small lengths in which the wire retains its original circular form, and shows no regular markings.

Thus on extending wires of the soft pure metals mercury, tin, and lead (and also sodium and potassium, as shown by Baker), we are able to get surface markings of great regularity, accompanied by a contraction of the wire in one particular direction only. The markings present the appearance of a series of equal layers which have been sheared over one another, as would be the case with a half cylinder composed of semicircular plates if the plates were all tilted over to make an acute angle with the axis of the cylinder. They are probably due to large uniform crystals, of a size comparable with the diameter of the wire, arranged in layers, which behave somewhat in the way suggested. It is noticeable that the metals which give the phenomenon are all very soft, a condition to which large crystals are known to be favourable. The purer lead which shows the markings is softer than ordinary commercial lead. The phenomenon has evidently nothing to do with the processes to which the wire is subjected during manufacture, as the specimens of lead and tin have to be thoroughly annealed if they are to show it well.

XCVI. *Thermodynamics of Radiation.* *By* H. L. Callendar, *M.A., LL.D., F.R.S., Professor of Physics at the Imperial College, S.W.**

IN the number of this Journal for October 1913, p. 787, I gave a brief sketch of a theory of radiation and specific heat, which appeared to be worth recording on account of its simplicity and its good agreement with experiment. The formula given for the distribution of energy in full radiation

* Communicated by the Author.

was deduced, in the first instance, from a quasi-molecular theory of radiation, and free use was made of the close analogy between full radiation and an ideal vapour, as being the method most likely to appeal to experimentalists familiar with the application of the gas analogy to other branches of physics. The same result might have been deduced in a variety of other ways, since it is to a great extent independent of the particular analogy employed. It now seems desirable to give an alternative method, which has the advantage of being more direct and of throwing more light on the essential points of difference between the proposed theory and that commonly accepted.

In order to explain the notation and to indicate the assumptions which are taken as the basis of the present method, it will be well to give a brief summary of the fundamental facts, which are generally accepted, and are to be found in many textbooks, such as Poynting's 'Heat,' cap. xx. p. 333.

The Energy Stream Q.—A study of the laws of emission and absorption of radiation in relation to the equilibrium of temperature, has led to the conclusion that the condition existing inside a vacuous enclosure at a uniform temperature T may be represented by an isotropic energy-stream Q per second per sq. cm., which is the same in every direction and in all parts of the enclosure, and is a function solely of the temperature. A similar proposition must be true for each separate frequency into which the radiation may be analysed. We may define q as the energy-stream of a particular frequency ν per unit range of frequency, such that $qd\nu$ represents the energy-stream included between the limits of frequency ν and $\nu+d\nu$ in full radiation. The partial stream q is a function only of the temperature T in addition to the frequency considered. Its rate of variation with temperature $(dq/d\mathrm{T})_\nu$ at constant frequency is equally definite.

The Energy Density U.—If we suppose the radiation to be continually travelling in all directions with the velocity of light c, the energy-density of the stream Q, or the quantity existing in the medium at any moment per c. c., will be $4\mathrm{Q}/c$, for the full stream Q. Similarly the energy-density u per unit range of frequency will be $4q/c$, for the partial stream q.

The Doppler Effect.—The simplest case to consider is that of a perfectly reflecting sphere expanding symmetrically with uniform velocity, small compared with that of light, and filled with a homogeneous and isotropic mixture of different frequencies. As the sphere expands, the wave-length of every component in the mixture will increase in direct proportion to the radius of the sphere, whatever the angle of incidence. Each component may be regarded as retaining its identity while its frequency varies, and any arbitrary distribution of components will be permanent as regards the ratio of the energies of the different components*.

Law of Adiabatic Expansion.—The simplest assumption to make with regard to the variation of energy is that, when a given quantity of radiation is adiabatically compressed or expanded in a perfect reflector, the whole energy of each component which retains its identity varies directly as its frequency. This assumption is in agreement with electromagnetic theory, and is equivalent to various other assumptions which have been made for the deduction of the pressure. The energy stream $q d\nu$ of the component included between limits ν and $\nu + d\nu$ of frequency in an expanding sphere of radius r, is transformed into a stream $q' d\nu'$ when the radius has increased to r', and is included in an interval $d\nu'/\nu'$ which is equal to $d\nu/\nu$, where $\nu'/\nu = r/r'$ in virtue of the Doppler effect. The whole energy of the component $q d\nu$ at any stage is the product of the volume $4\pi r^3/3$ and the energy-density $4q d\nu/c$. By the above assumption the whole energy varies as $1/r$, so that $r^4 q d\nu$ is constant. The energy-stream $q d\nu$ of each component varies directly as the fourth power of its frequency ν, or inversely as the fourth power of the radius r.

The Radiation Pressure.—The pressure $p d\nu$ due to the stream $q d\nu$ is directly deducible by equating the work done $p d\nu \times 4\pi r^2 dr$ in a small expansion dr to the loss of energy of the stream. The expression for the whole energy of the stream may be written $(r^4 q d\nu) 16\pi/3rc$. Since $r^4 q d\nu$ is constant, the loss of energy in a small expansion dr is $(r^4 q d\nu) 16 dr/3r^2 c$. Equating this to the work we obtain $p = 4q/3c$, which is true for each component separately; and similarly $P = 4Q/3c$ for the whole radiation. It will be observed that the pressure and the work result essentially from change of frequency caused by the Doppler effect.

The Temperature of Full Radiation.—It is shown in many textbooks (*e. g.* Poynting, p. 337) that "full radiation remains full radiation in any adiabatic change." It follows by a direct application of Carnot's cycle to full radiation, that the temperature T, as defined by Carnot's principle, varies directly as the frequency of each component, or inversely as the radius of the expanding sphere. The energy-density and the pressure vary as the fourth power of the temperature for the radiation as a whole (the Stefan-Boltzmann

* Larmor, Brit. Assoc. Rep. 1900, p. 657.

law), and also for each component considered separately. The product λT, or the ratio ν/T, remains constant for each component, which is Wien's displacement law. Both laws are summed up in Wien's general expression for the distribution in full radiation, which gives for q as already defined,

$$q = C\nu^3 F(\nu/T) = CT^3 f(\nu/T), \quad . \quad . \quad . \quad . \quad (1)$$

where F and f are undetermined functions expressing the distribution in full radiation.

Extensions of the Theory.

So far we have been considering only those theoretical relations which result from the Doppler effect on components of variable frequency which retain their identity in adiabatic expansion. These relations have been verified indirectly, and are universally admitted. The extensions which I have pro posed result from a consideration of *isothermal emission* at constant frequency. In experimental work it is impossible to isolate and trace the components of variable frequency (ν/T constant), or to perform an adiabatic expansion. We have to deal with rays of constant frequency, separated and measured under the condition of steady flow at constant temperature.

The main points which I have endeavoured to establish are the following:—

(1) Since, so far as we know, each frequency is propagated without change in free space, the heat taken from the source by the emission of a steady stream of a particular frequency should, by the first law of thermodynamics, be equal to the heat evolved on condensation of the same stream in the receiver. Although it is not possible to trace all the steps of an irreversible process, such as radiation from a higher to a lower temperature, the change of total heat must be the same as that calculated by a reversible path. The first requisite, therefore, is to find the latent heat of isothermal emission of a particular frequency.

(2) It has always been tacitly assumed that the energy-density of each frequency in an isothermal enclosure is directly proportional to the heat measured on absorption, which is equivalent to assuming the latent heat of emission per unit volume proportional to the energy-stream q. I have maintained on the contrary, in the paper already quoted, that the latent heat of emission per unit volume for each frequency should be that given by Carnot's principle, namely $T(dp/dT)_\nu$,

which is proportional to $T(dq/dT)_v$, but is not proportional to q. It may be objected, with apparent reason, that Carnot's principle cannot be applied to each particular frequency in isothermal emission under equilibrium conditions on account of the change of frequency caused by the Doppler effect at the moving piston or expanding wall of the enclosure. It is therefore necessary to show that the expression $T(dp/dT)_v$ for the latent heat given by Carnot's principle, is not in conflict with the Doppler effect in adiabatic expansion, but follows directly from it.

Latent Heat l of Isothermal Emission of a Particular Frequency.—Taking the perfectly reflecting sphere already considered, and supposed full of radiation in equilibrium at a temperature T, let the radius of the sphere expand by a small increment dr, so that the enclosed radiation falls to a lower temperature $T-dT$, where $-dT=Tdr/r$ as already explained. The stream of energy q per unit range of a particular frequency ν at the original temperature T will be reduced at the lower temperature $T-dT$ to the value $q-(dq/dT)_\nu dT$, where $(dq/dT)_\nu$ is the rate of change of q with temperature for a *constant* frequency, which has a perfectly definite value for each frequency in full radiation. If now the perfectly reflecting surface is replaced by an emitting surface at the original temperature T, equilibrium will be restored by the absorption of the existing stream $q-(dq/dT)_\nu dT$ and the emission of a stream q at constant volume. The volume, which remains constant during this process, may be taken as $4\pi r^3/3$. The final energy-density is $4q/c$. The *net* energy emitted will therefore be $16\pi r^3(dq/dT)_\nu dT/3c$, which reduces to $16\pi r^2 T(dq/dT)_\nu dr/3c$, by substituting for dT its value given above. The latent heat of emission l *per unit increase of volume* is obtained by dividing this by the increase of volume, namely, $4\pi r^2 dr$, which gives $l=4T(dq/dT)_\nu/3c$, or $T(dp/dT)_\nu$, since $p=4q/3c$.

The above method may appear at first sight to be unnecessarily circuitous, but it is really the most direct for deducing the required result from the *admitted* properties of the energy-stream and the Doppler effect in adiabatic expansion. The same procedure is applied in the reverse direction in elementary thermodynamics in deducing the fall of temperature dT for a small adiabatic expansion dv in the case of a perfect gas, by equating the heat, sdT, required to raise the temperature at constant volume, to the work done pdv, or the heat absorbed $RTdv/v$, in the same expansion performed under isothermal conditions.

Admitting the existence of the Doppler effect in isothermal emission under equilibrium conditions at the slowly expanding wall of the enclosure, it is easy to see why the latent heat of a particular frequency per unit volume should be different from the density of the energy-stream of the same frequency together with the external work. The higher frequencies are being continually degraded into lower during the motion, so that the actual net amount of a high frequency emitted may be greatly in excess of the quantity $4p$ per unit volume which would be required if there were no degradation of frequency. On the other hand, for a low frequency, the amount required to maintain the energy-stream at its equilibrium value is greatly reduced by the return of energy degraded from the higher frequencies. The two effects balance in the case of full radiation at the mean point where $T(dp/dT)_\nu = 4p$.

The nature of the effect considered may also be illustrated by a consideration of the relation between the partial differential coefficients. If $(dp/dT)_x$ represents the rate of change of p with T in adiabatic expansion when λT or ν/T is constant, we have the general relations, representing Wien's displacement law (1),

$$T(dp/dT)_x = 3p = \nu(dp/d\nu)_x = T(dp/dT)_\nu + \nu(dp/d\nu)_T. \quad . \quad (2)$$

Similar relations hold for q and u, which are simply proportional to p. The latent heat $T(dp/dT)_\nu$ is not equal to $4p$, but to $3p - \nu(dp/d\nu)_T$. The coefficient $(dp/d\nu)_T$ is obviously positive on the low frequency side of the curve representing p plotted against ν at constant temperature, where the latent heat is less than $3p$. It vanishes at the maximum of the pressure curve, where $T(dp/dT)_\nu = 3p$, but it may attain large negative values for high frequencies.

The Entropy, and Intrinsic Energy.—If the latent heat is represented by $T(dp/dT)_\nu$ per unit range and volume, the entropy should be simply $(dp/dT)_\nu$. The *internal latent heat* per unit volume, $T(dp/dT)_\nu - p$, or the intrinsic energy denoted by E/v in the previous paper, is the energy carried by the stream of a particular frequency, and given up on condensation in addition to the work p. It follows from Wien's displacement law (1) that the ratio, E/pv, of the intrinsic energy to the pressure, *must* be some function of (ν/T), depending on the distribution. It was assumed in the previous paper that E/pv for full radiation was of the form $b\nu/T$ (where b is a constant required by the arbitrary nature of the units) on the ground that the intrinsic energy of a given quantity varies as the frequency. This assumption fixes the distribution in full radiation, and leads to the simplest relations between the various quantities, in addition to giving very good agreement with experiment. The intrinsic energy of a volume v such that $pv=RT$, is simply $Rb\nu$, and the corresponding expression for the entropy is $R(1+b\nu/T)$.

If the latent heat equation, $T(dp/dT)_\nu = E/v + p$, is integrated at constant frequency on the assumption $E/pv = b\nu/T$, we obtain immediately the expressions previously given (*loc. cit.*) for the partial pressure, intrinsic energy, and latent heat, per unit range of ν, namely,

$$\text{Partial Pressure,} \quad p d\nu = C\nu^2 T e^{-b\nu/T} d\nu, \quad . \quad . \quad . \quad (4)$$

$$\text{Intrinsic Energy,} \quad (E/v) d\nu = Cb\nu^3 e^{-b\nu/T} d\nu, \quad . \quad . \quad (5)$$

$$\text{Latent Heat,} \quad l d\nu = C\nu^2 T(1 + b\nu/T) e^{-b\nu/T} d\nu, \quad (6)$$

The partial pressure p is proportional to the energy-stream q in an isothermal enclosure, and is identical in form with the expression originally proposed by Lord Rayleigh (Phil. Mag. xlix. p. 539, 1900) to represent the energy-stream. His method was founded on the doctrine of the equipartition of energy, and gave no explanation of the exponential term. This factor arises in the present investigation directly from Carnot's principle, and is explained by the continual degradation of the higher frequencies owing to the Doppler effect in isothermal emission, which appears to afford a possible way out of the difficulty raised by Jeans in discussing the problem from the point of view of equipartition.

Comparison with Experiment.

The quantity measured in experimental work is either the rate of loss of heat of a more or less perfect adiator, or else the rate of reception of heat by a receiver absorbing a known fraction of the radiation from a source of the "black body" type. In either case the quantity measured is proportional to the latent heat of emission as already defined, and not to the energy-stream existing in the state of equilibrium, except in the case of full radiation for which $T(dQ/dT)=4Q$. The full stream, $Q=\sigma T^4$, emitted per second per sq. cm. from a small aperture in a black body at a uniform temperature T, is equal to $c/4$ of the full energy density U, or to $3c/4$ of the full pressure P, and is the same as $T(dQ/dT)/4$. But the quantity measured for each separate frequency per unit range is *not* $q=cu/4=3cp/4$, as generally assumed, but $T(dq/dT)_\nu/4$, which is proportional to the latent heat of emission $T(dp/dT)_\nu$ per unit volume. The value of the full pressure P, obtained by integrating the partial pressure $pd\nu$ from 0 to infinity at constant T, is

$$P = 2CT^4/b^3 = 4Q/3c = 4\sigma T^4/3c. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

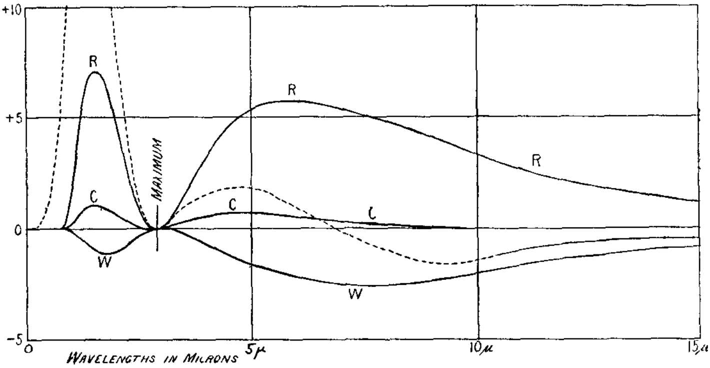
Whence the value of the constant C is $2\sigma b^3/3c$. Substituting this value of the constant C in the equation for the latent heat $ld\nu$ per unit volume, we obtain the equation for the latent heat of emission per second, per sq. cm., in terms of the radiation constant σ,

$$2T(dq/dT)_\nu d\nu = \sigma b^3 \nu^2 T(1 + b\nu/T)e^{-b\nu/T}d\nu, \quad . \quad . \quad (8)$$

which represents the curve of distribution of energy, as experimentally observed, plotted against the frequency as abscissa. The corresponding curve with the wave-length λ as abscissa is obtained by substituting $\nu = c/\lambda$, and $d\nu = -cd\lambda/\lambda^2$. The curve plotted in terms of wave-length has a maximum at the point where $\lambda T = (\sqrt{2} - 1)bc/2 = \cdot 2071bc$. The mean of various experimental determinations puts the maximum of the wave-length curve at $\lambda T = \cdot 290$, when the wave-length is measured in cms. Whence the value of the constant $bc = 1 \cdot 400$. The curve obtained with this value of the constant bc gives very good agreement with experiment, both for the distribution curve at constant temperature, and for the variation with temperature of the energy of a particular frequency, both of which are included in the same formula (8) by putting either T or ν constant,

It is at once evident that a formula of the type shown in (8) must be capable of representing the distribution curve with considerable accuracy, since it reduces to the same type as Wien's when λT is small or $b\nu/T$ large, and to the same type as Rayleigh's when λT is large or $b\nu/T$ small. It would be tedious and unnecessary to analyse all the observations (though this has been done) since it is generally admitted that Planck's formula fairly represents the experimental data. It may be of interest, however, to give curves showing the differences between the formulæ, if only to illustrate the limitations of experimental verification. The formulæ compared are those of Wien, Planck, Rayleigh, Walker and Callendar. The value of the distribution constant b is calculated for each formula from the position of the maximum by taking the same value of $\lambda_m T$, namely, $\cdot 290$, for all. If the same absolute value of the Stefan constant σ were also taken for all, the absolute value of the maximum would be different for each formula. But since only relative values are obtainable experimentally in the distribution curve, the maximum for each formula has been reduced to 100, and the differences from Planck's formula (represented by the base line), expressed as a percentage of the maximum, are plotted in the curves. The differences are plotted on a wave-length base for a temperature T = 1000° Abs., for which the maximum occurs at the point $\lambda = 2{\cdot}9\,\mu$ where all the formulæ are made to agree. It is well known that the formulæ of Wien and Rayleigh (R) differ appreciably from experiment, but it is remarkable how closely the sum of the two, represented by curve (C), agrees with Planck's expression $q_\lambda d\lambda = k\lambda^{-5}(e^{bc/\lambda T}-1)^{-1}$. The maximum difference of 1 per cent, which occurs on the short wave-length side of the maximum, would be difficult to verify in the distribution curve owing to its steepness on this side, and might be compensated by a very slight shift of the maximum. There are, however, several observations which indicate that Planck's formula gives results a little too low for short wave-lengths.

Fig. 1.



Differences of Distribution Formulæ from Planck's Formula at 1000° Abs. on wave-length base, expressed in per cent. of maximum. R, Rayleigh; C, Callendar; W, Wien; dotted, Walker.

On the short wave-length side, an interesting contrast is presented by the ingenious empirical formula recently proposed by G. W. Walker (Proc. R. S. A lxxxix. p. 393, 1914) on dynamical grounds, as representing the harmonic analysis of an arbitrary series of disturbances with strictly aperiodic damping. Walker's formula is a modification of that of Kövesligethy, 1890, and is of the type,

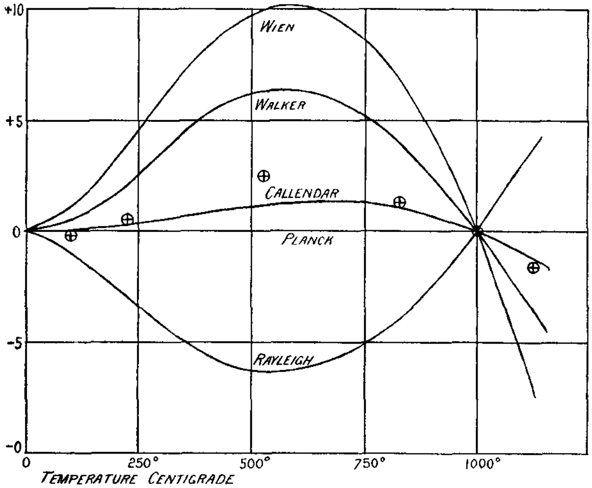
$$E_\lambda = kT^5[\lambda T/(\lambda^2T^2+a^2)]^4, \quad \ldots \quad (9)$$

which evidently satisfies the conditions laid down by Wien, but does not otherwise conform to the present theory. The curve as shown by Walker is very similar in general appearance to the distribution curves of Lummer and Pringsheim, especially on the side of long wave-lengths, where the comparison is fairly easy. But if the *differences* are plotted as in figure (1) (dotted curve), they amount, on the short wave-length side, to something of the order of 20 per cent. of the maximum ordinate, which considerably exceeds the possible limits of error of the verification of Wien's or Planck's formulæ in this region. According to Walker's formula the thermal intensity of the ultra-violet light of wave-length $\cdot 29\mu$ in the radiation from a black body at 727° C. (a dull red heat) should be ·154 per cent. of the maximum ordinate, and might be detected with a sensitive thermopile. As a matter of experiment no radiation of this wave-length from such a source can be detected by the most delicate photographic methods, and it is much more likely to be of the order of 10^{-15} of the maximum, as given by Wien's formula. The exponential rate of diminution of the curve on the short wave-length side is one of the most certain results of experiment, and it is one of the strongest points of the present theory that the exponential term in the formula follows so directly from the application of Carnot's principle.

Another method of comparing the formulæ with experiment is to observe the variation with temperature of the intensity of a particular wave-length. Among the best known applications of this method are the experiments of Rubens on the *Reststrahlen* of quartz, fluorite, and rocksalt. His experiments showed clearly that the distribution formula must reduce to the Rayleigh type $k\lambda^{-4}T$ for large values of λT, but indicated appreciable deviations from Planck's formula in the case of the quartz Reststrahlen. The *difference* between his results and Planck's formula is shown by the crosses representing the observations in fig. 2. Planck's formula itself is represented by the base-line as in the previous figure.

Here again, as Rubens points out, comparison of the relative values alone is experimentally possible. The values given by the various formulæ for radiation of wave-length $8\cdot 85\,\mu$, corresponding to the quartz *Reststrahlen*, with the source at 1000° C. and the receiver at 0° C., are accordingly reduced to a common value, so that all the curves agree at 0° C. and 1000° C., and the differences from Planck's formula at intermediate points are plotted in terms of the radiation at 1000° C. The observations are seen to agree distinctly better with the thermodynamical formula (8) than with Planck's. The observations on the *Reststrahlen* of fluorite and rocksalt show a similar result, but are not so decisive, because the formulæ approximate so closely to the Rayleigh type for long wave-lengths, and the observations are less concordant on account of the feebleness of the radiation to be measured, which is about 200 times less for rocksalt than for quartz at 1000° C.

Fig. 2.



Difference of Rubens' Observations on Quartz Reststrahlen from Planck's formula, compared with other formulæ.

The agreement of the proposed formula (8) with direct experiments on radiation is seen to be satisfactory. As indicated in the previous paper, the agreement with atomic theory as regards (1) the number of atoms $N = 6{\cdot}12 \times 10^{23}$ in a gramme atom, and (2) the atomic unit of energy per unit frequency $Rb/N = 6{\cdot}34 \times 10^{-27}$, is equally satisfactory, according to the estimates of these quantities obtained from other sources. The variation of specific heat at low temperatures can also be represented by the thermodynamical formula with fewer arbitrary hypotheses than by Planck's. These, however, are questions involving many speculative elements, and are of little weight compared with the thermodynamical argument on which the formula is founded. The Doppler effect must occur in the isothermal emission of an energy-stream, and has not been considered in this connexion. That it should lead directly to Carnot's expression $T(dp/dT)_v$ for the latent heat per unit volume, is too striking a confirmation of the principles of the classical thermodynamics to be disregarded. According to my view, it affords an additional relation, which suffices, in conjunction with Wien's law, to fix the distribution in full radiation.