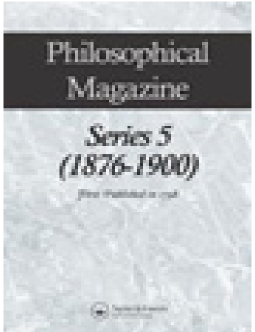

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XXX. On the division of energy in the emission-spectrum of a black body

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and explain the reason for the current belief that the higher regions of the atmosphere and winds which come from them are richer in ozone than the surface air: they also show that there must be enough ozone in the whole atmosphere to have an important bearing on the blue colour of the sky. Hartley drew attention to this matter (Journ. Chem. Soc. xxxix. 1881), but as recent experiments have shown that oxygen in sufficient quantity shows a blue colour by transmitted light, the claims of ozone to a serious share in the blueness of the sky have been rather neglected; but if it is remembered that the blueness of ozone is enormously stronger than that of oxygen under the same conditions, it becomes apparent that the quantity of ozone which has been theoretically shown to have a probable existence in the atmosphere must exercise a considerable influence on the colour of the sky and the colour of distant objects.

From what we have seen we have also to contemplate the possibility of the existence of free ions of oxygen in the outer regions of the atmosphere, but a discussion of the effects of such must be reserved for a future paper.

Melbourne, Aug. 1896.

XXX. *On the Division of Energy in the Emission-Spectrum of a Black Body. By* Willy Wien*.

Although the influence of temperature on the radiation of a black body and the division of this radiation into its component wave-lengths can be deduced from the electromagnetic theory of light by a purely thermodynamic method, the application of the same process to the division of the energy itself has not up to the present been successful.

The cause of this lies in the fact that the dependence of intensity on wave-length must be completely determinable from the properties of the radiation, because the latter only depends on the temperature, and not on the special properties of single bodies.

The radiation of a black body corresponds to the condition of thermal equilibrium, and consequently to the maximum of entropy. If, for example, a process were known by which a change of wave-length could be brought about without any expenditure of work, and without absorption in the sense of an increase of entropy, then the division of energy in the

* Translation furnished by Mr. J. Burke from Wiedemann's *Annalen*, vol. lviii. p. 662 (1896). Communicated by Prof. G. F. FitzGerald, F.R.S.

spectrum of a black body could be completely determined from the law of the maximum of entropy. As I have shown in an earlier paper, the entropy of radiation of a known intensity and colour can be determined, but there is no obvious physical process by which an alteration in colour such as that desired can be observed to be taking place. A determination of the distribution of energy is therefore impossible without hypotheses.

An attempt has been made by E. von Lommel* and W. Michelson† to found a complete law of radiation on certain premises. For this purpose the latter makes the following stipulations :—

(1) Maxwell's Law of the division of velocities among a great number of molecules holds also for solids.

(2) The period of oscillation τ, which is excited by a molecule, is connected with its velocity of propagation v by the equation

$$\tau = \frac{4\rho}{v},$$

where ρ is a constant. (This assumption is based on a definite conception with regard to the excitation of the radiation.)

(3) The intensity of the radiation sent out from a molecule is proportional to the number of molecules having the same time of oscillation, is further an undetermined function of the temperature and a likewise unknown function of the kinetic energy, which by a further hypothesis is restricted to a power of v^2.

The law which Michelson obtains from these assumptions gives for the wave-length λ_m of the maximum of energy

$$\lambda_m = \frac{\text{const.}}{\sqrt{\theta}},$$

where θ denotes the absolute temperature. As for the rest, this law leaves the total emission as a function of the temperature undetermined.

I have now endeavoured to carry out the idea of Michelson, of making use of Maxwell's law of the division of velocities as a basis for the law of radiation, and at the same time to lessen the number of the hypotheses which, on account of our total ignorance of the cause of the radiation, are particularly uncertain, by utilization of the results obtained by Boltzmann and myself by pure thermodynamic treatment.

The remaining hypotheses, however, still possess some

* Wied. *Ann.* iii. p. 251 (1877)

† *Journal de Physique* [2] vi. (1887).

uncertainty in their theoretical groundwork, but have the advantage that the deductions from them can be directly compared over a very wide range with the results of experience. Their confirmation or contradiction by experiment will therefore decide the question of the correctness or otherwise of the hypotheses, and thus far be useful as a further development of the molecular theory.

The law that in an exhausted vessel the radiation is the same as that from a black body at the same temperature as the walls of the vessel, holds also if the radiating body be a gas which is shut off from the vacuous space by transparent, and from the exterior by reflecting walls.

But this gas must possess a finite absorptive power for all wave-lengths. There remains, however, no doubt that there are gases, such as carbonic acid and water-vapour, which, by mere elevation of temperature, emit heat rays*. Strongly superheated vapours may be regarded as gases, and by suitable mixing of different substances, it is possible to conceive of a mixture of gases which possesses a finite absorptive power for all wave-lengths. In this case one must not, however, consider that radiation which gases send out under the influence of electrical or chemical processes.

If one radiating body be a gas, then Maxwell's law of the division of velocities will hold if we take as our basis the kinetic theory of gases. The absolute temperature will be proportional to the mean kinetic energy of the gaseous molecule. This assumption has been rendered highly probable by the labours of Clausius † and Boltzmann ‡, and is still further supported by the researches of Helmholtz § on monocyclic systems, according to which researches both the kinetic energy and the absolute temperature have the property of being the integrating denominator of the differential of the added energy.

To avoid the unecessary prolixity which would result from a consideration of the different constituents of a mixture of gases, let us imagine a mixture of such a kind that the homogeneous radiation under consideration is sent out by *one* only of the gases forming the mixture.

The number of molecules whose velocity lies between v and $v+dv$ is proportional to the quantity

$$v^2 e^{-\frac{v^2}{a^2}} dv,$$

* Paschen, Wied. *Ann.* l. p. 409 (1893).
† Pogg. *Ann.* cxlii. p. 433 (1871).
‡ Wien. *Ber.* [2] liii. p. 195 (1866).
§ *Gesammelte Abhandlungen*, iii. p. 119.

where α denotes a constant, which can be deduced from the mean velocity* $\bar{v}$ by means of the equation

$$\bar{v}^2=\tfrac{3}{2}\alpha^2.$$

The absolute temperature is therefore proportional to α^2. But the vibrations sent out by a molecule whose velocity is v are completely unknown in their dependence on the condition of the molecule. A now-a-days generally accepted view is that the electric charges of the molecules can excite electromagnetic waves.

We make the hypothesis, that each molecule sends out vibrations of a wave-length which only depends on the velocity of the molecule moved and whose intensity is a function of this velocity.

It is possible to obtain this deduction by several different special hypotheses with regard to the process of radiation; as, however, such premises at this preliminary stage are completely arbitrary, it appeared to me to be the safest method to make the necessary hypothesis as simple and general as possible.

As the wave-length λ of the radiation sent out by any molecule is a function of v, v is also a function of λ.

The intensity ϕ_λ of the radiation whose wave-length lies between λ and $(\lambda+d\lambda)$ is therefore proportional

(1) To the number of molecules which send out radiations of this period;

(2) To a function of the velocity v, therefore also to a function of λ.

Consequently

$$\phi_\lambda=\mathrm{F}(\lambda)e^{-\frac{f(\lambda)}{\theta}},$$

where F and f denote two unknown functions, and θ denotes the absolute temperature.

Now the change of radiation with temperature is composed, according to the theory given by Boltzmann † and myself ‡, of an increase of total energy in proportion to the fourth power of the absolute temperature and of a change of wave-length of the whole energy comprised between λ and $(\lambda+d\lambda)$ in such a direction that the wave-length belonging to it alters in inverse ratio to the absolute temperature. If we imagine the energy at any temperature plotted as a function of the wave-length, then the curve obtained would remain

* $\bar{v}$ is the square root of mean square of velocity.—Transl.

† Wied. *Ann.* xxii. p. 291 (1884).

‡ Wien, *Ber. d. Berlin. Akad.* 9th Feb., 1893.

unaltered at a different temperature, if the scale of the drawing were so changed that the ordinates were decreased in the relation of $1/\theta^4$ and the abscissæ increased as θ. The latter is with our value of ϕ_λ only possible if λ and θ occur in exponents only as the product $\lambda\theta$.

If c denote a constant, then

$$\frac{f(\lambda)}{\theta}=\frac{c}{\lambda\theta}.$$

The increase of total energy determines the value of $F(\lambda)$. Indeed the relation must hold

$$\int_0^\infty F(\lambda)e^{-\frac{c}{\theta\lambda}}d\lambda=\text{const. }\theta^4.$$

$F(\lambda)$ can be found by the method of undetermined coefficients. We imagine $F(\lambda)$ expanded into a series and make $\lambda=c/y\theta$, then

$$F(\lambda)=F\left(\frac{c}{y\theta}\right)=a_0+a_{+1}\frac{\theta y}{c}+a_{+2}\frac{\theta^2y^2}{c^2}+\ldots a_n\frac{\theta^n y^n}{c^n}\ldots$$

$$+a_{-1}\frac{c}{\theta y}+a_{-2}\frac{c^2}{\theta^2y^2}+\ldots a_{-n}\frac{\theta^{-n}y^{-n}}{c^{-n}}.$$

Integration of this gives

$$\int_0^\infty F(\lambda)e^{-\frac{c}{\theta\lambda}}d\lambda=\frac{c}{\theta}\int_0^\infty F\left(\frac{c}{y\theta}\right)e^{-y}\frac{dy}{y^2}=\Sigma_n a_n\frac{\theta^{n-1}}{c^{n-1}}\int_0^\infty e^{-y}y^{n-2}dy.$$

Therefore
$$\text{const. }\theta^4=\Sigma_n a_n\frac{\theta^{n-1}}{c^{n-1}}\Gamma(n-1).$$

All the coefficients are therefore nothing except one of them, the coefficient of $\theta^{n-1}=\theta^4$;

therefore
$$n=5.$$

Consequently
$$F(\lambda)=\frac{\text{const.}}{\lambda^5}.$$

Accordingly the equation for ϕ_λ is

$$\phi_\lambda=\frac{C}{\lambda^5}e^{-\frac{c}{\lambda\theta}}.$$

From this follows :—

$$\frac{d\phi}{d\lambda}=-\frac{Ce^{-\frac{c}{\lambda\theta}}}{\lambda^6}\left(5-\frac{c}{\lambda\theta}\right),$$

$$\frac{d^2\phi}{d\lambda^2}=\frac{Ce^{-\frac{c}{\lambda\theta}}}{\lambda^7}\left(30-\frac{12c}{\lambda\theta}+\frac{c^2}{\lambda^2\theta^2}\right);$$

for

$$\lambda = \frac{c}{5\theta}, \quad \frac{d\phi}{d\lambda} = 0,$$

$$\frac{d^2\phi}{d\lambda^2} = -\frac{5Ce^{-5}}{\lambda^7};$$

$\frac{d^2\phi}{d\lambda^2}$ is negative, therefore the value corresponds to a maximum. Let this value be called λ_m. The corresponding value of ϕ is

$$\phi_m = \frac{C}{\lambda_m^5} e^{-5}.$$

As both ϕ and $d\phi/d\lambda$ vanish for $\lambda = \infty$, the curve is an asymptote to the λ-axis.

Further, $d^2\phi/d\lambda^2 = 0$ for the roots of the equation

$$30\lambda^2\theta^2 - 12c\lambda\theta + c^2 = 0;$$

therefore for

$$\lambda = \lambda_m\left(1 \pm \sqrt{\frac{1}{6}}\right).$$

For these two points the curve has points of inflexion. If we put $\lambda = \lambda_m(1+\epsilon)$, then

$$\phi_\lambda = \frac{Ce^{-\frac{c}{\lambda_m(1+\epsilon)\theta}}}{\lambda_m^5(1+\epsilon)^5} = \frac{Ce^{-\frac{5}{1+\epsilon}}}{\lambda_m^5(1+\epsilon)^5};$$

therefore

$$\log\frac{\phi}{\phi_m} = -5\left(\log(1+\epsilon) - \frac{\epsilon}{1+\epsilon}\right) = -5(\tfrac{1}{2}\epsilon^2 - \tfrac{2}{3}\epsilon^3 + \tfrac{3}{4}\epsilon^4 \ldots).$$

If we put $-\epsilon$ for ϵ, then

$$\log\frac{\phi}{\phi_m} = -5(\tfrac{1}{2}\epsilon^2 + \tfrac{2}{3}\epsilon^3 + \tfrac{3}{4}\epsilon^4 \ldots).$$

In this case the absolute total of the series is greater and therefore ϕ/ϕ_m less than when ϵ is positive. So far as $\epsilon < 1$, the ordinates at an equal distance from the maximum are less on the side of small wave-lengths.

In an earlier work* I showed that the energy curves of black bodies at different temperatures cannot cut one another.

From this it may be deduced that the curve must fall away slower toward the side of the long waves than the curve

$$\frac{\text{const.}}{\lambda^5}.$$

But this is in reality the case with our curve: $d\phi_\lambda/d\lambda$ is in absolute magnitude always less than $5C/\lambda^6$, and only reaches

* Wied. *Ann.* lii. p. 159 (1894).

the maximum value for $\theta=\infty$. For infinitely increasing temperature ϕ_λ would equal C/λ^5, and the maximum of energy would approach infinitely near to the wave-length zero.

While I had deduced the formula for ϕ_λ from the theoretical considerations just brought forward, Prof. Paschen found independently that the formula

$$\phi_\lambda = \frac{C}{\lambda^\alpha} e^{-\frac{c}{\lambda\theta}},$$

where α is a constant, was the one which reproduced best the results of his observations, and was kind enough to communicate this to me and to allow me to publish his formula here. Prof. Paschen intends to determine the value of the constant α from a complete calculation and comparison of his experiments. If α is not equal to 5, the total emission would not follow Stefan's law.

Charlottenburgh, June 1896.

XXXI. *On Lagrange's Determinantal Equation.* *By* Thomas Muir, *LL.D.**

1. VARIOUS proofs† have been given of the reality of the roots of the equation

$$\begin{vmatrix} a-x & b & c & \dots \\ b & d-x & e & \dots \\ c & e & f-x & \dots \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix} = 0,$$

and more than one extension‡ of the theorem has been made. Apparently, however, no departure from axi-symmetry of the determinant has ever been contemplated until quite recently. This new and important step is due to Professor Tait, who in a paper read before the Royal Society of Edinburgh in May is led to the conclusion that the cubic equation

$$\begin{vmatrix} \frac{A}{p}-x & \frac{c}{p} & \frac{b}{p} \\ \frac{c}{q} & \frac{B}{q}-x & \frac{a}{q} \\ \frac{b}{r} & \frac{a}{r} & \frac{C}{r}-x \end{vmatrix} = 0$$

* Communicated by the Author.

† For three of them see Salmon's 'Modern Higher Algebra,' 4th edit. pp. 28, 48-56.

‡ See Sylvester, *Crelle's Journal*, lxxxviii. pp. 6-9. Routh, 'Dynamics of a System of Rigid Bodies,' part ii. 4th edit. pp. 36-38, 41. Muir, 'Messenger of Math.' xiv. pp. 141-143.