XXIV. On the mechanics of luminosity

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XXIV. *On the Mechanics of Luminosity.*
By E. WIEDEMANN*.

[Plate III.]

ALTHOUGH we possess numerous measurements of the positions of lines in the spectrum, and although many attempts have been made to measure the distribution of luminosity and energy in the spectrum, and to express the same by means of formulæ, yet the experiments are few which have for their object to obtain an insight into the mechanics of luminosity. In general, we have contented ourselves with investigating the intensity of radiation without investigating the energy of the vibrating particles which emit the light, upon which it depends.

In what follows we shall attempt to fix the data for investigating the mechanics of luminosity, to verify particular conclusions by means of experiment, and to determine the numerical value of the quantities which occur.

The present research is a continuation of earlier investigations of mine†.

* Wied. *Ann.* xxxvii. p. 177. Translated from a separate impression communicated by the Author.

† E. Wiedemann, Wied. *Ann.* v. p. 506 (1878); vi. p. 298 (1879); ix. p. 157 (1880); x. p. 202 (1880); xviii. p. 508 (1883); xx. p. 756 (1883); xxxiv. pp. 446 and 464 (1888). *Sitzungsber. d. Societas physio-medica Erlangen vom 1 Aug. 1887.* *Bull. Soc. de phys. génèvoise* 6 Oct. 1887. I shall return more at length to numerous obligations to the above-mentioned works—where no special acknowledgment is made—upon a future opportunity. The results of this investigation themselves were communicated to the Physico-Medical Society of Erlangen on Dec. 10, 1888.

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General.—Production of Light.

1. According to the newer views of the constitution of bodies, we assume motions of translation of the molecules with their centre of gravity ; further, rotation and oscillation round the centres of gravity considered as fixed, not only of the material parts of the molecules but also of their æther-envelopes. With *gases* the motions of translation of the centres of gravity produce only feeble emission of light. Sir G. G. Stokes* has sought in this the explanation of the feeble continuous spectrum of sodium seen at the same time as the line-spectrum. I have myself† endeavoured to show that the motions of rotation cannot be the cause of the line- and band-spectra. Consequently we must seek the cause of the production of light in gases in the intermolecular movements which occur within the molecule—either of their material particles or of their æther-envelopes. We shall endeavour to show later on that it can only be the vibrations of the material particles to which the emission of light is due. With *solid* and *liquid bodies* the emission of light may be due to the vibrations of the whole molecule about its position of equilibrium as well as to the intermolecular motions of the constituent atoms of the molecule. Upon the first depends the uniform continuous spectrum of all solid bodies when heated, and upon the last the differences between the light emitted by different bodies.

2. The following theoretical considerations rest upon the conception of *luminosity* introduced by me, and the discrimination of totally different phenomena which have generally been confused.

I designate as *light* the whole complex of rays between the infra-red and the extreme ultra-violet. The motions of the molecules which produce the luminosity I will call, for the sake of brevity, *luminous motions*, in contradistinction to the vibrations of the emitted waves of light.

I shall always designate as *intensity* of the light-vibrations the energy measured in gramme-calories per second which the vibrations of the light-waves emitted by the molecules of the body carry with them ; but as *luminous energy* the energy of those motions of the molecules or their atoms which produce the radiated light. The first energy depends upon the decrease of the second with the time. A chief problem of

* See a Research of A. Schuster, Phil. Trans. Lond. 1879, p. 37.

† Wied. Ann. v. p. 507 (1878).

this research is to show how the luminous energy may be determined from the intensity.

I shall speak of *brightness* when the intensity is measured by photometric methods, that is by a physiological method.

3. I take as the basis of my investigations the kinetic theory of gases. According to this there exists at constant temperature a perfectly definite relationship between the kinetic energy of the motion of translation, corresponding to the temperature, and that of the intermolecular motions, both as a whole as well as for each kind thereof, and consequently also between those of the motion of translation and the luminous motion; otherwise no permanent condition would be possible. This relationship may be regarded as the normal one. If, for any reason, the normal relationship is disturbed in any way, it will in time again become normal.

If, for example, we exalt the luminous motion in a molecule in comparison with the motion of translation, the first will be transformed into the latter; if the luminous motion becomes lowered by radiation the loss will be partly replaced from the store of energy of the motion of translation by means of the impacts of the molecules.

Luminescence and Temperature of Luminescence.

4. In special cases, however, the normal relationship between the motion of translation corresponding to the temperature and the luminous motion does not exist.

In a former paper I have ventured to employ the term *luminescence* for all those phenomena of light which are more intense than corresponds to the actual temperature.

In all phenomena in which luminescence is manifested the energy of the luminous motion is higher than that characterized above as corresponding to the relationships determined by the temperature alone. According to the mode of excitation I distinguish Photo-, Electro-, Chemi-, and Tribo-luminescence. In particular, *photo-luminescence*, including fluorescence and a number of cases of phosphorescence, is defined as those phenomena in which the incident light excites vibrations within the molecule of a body which produce directly an emission of light. I do not include in this those cases in which the incident light produces primarily chemical processes, upon which a production of light is secondarily dependent. This occurs for example with a large number of phosphorescent substances, *e. g.* calcium sulphide. These

phenomena apparently belong to photo-luminescence, but really to chemi-luminescence.

The *temperature of luminescence* is defined to be the temperature at which a body, heated without decomposition, would give light of a particular wave-length in each case of exactly the same brightness as it does in consequence of the processes of luminescence.

The production of light in the phenomena of luminescence in gases cannot be explained by assuming that in consequence of the different velocities of the individual molecules, as assumed by the kinetic theory of gases, the individual molecules possess a very high temperature, and therefore become luminous. For at the temperature of ignition, defined by the great velocity of the motion of translation, most substances would be decomposed. Certainly all organic substances, fluorescent or phosphorescent, in the gaseous condition. The like holds good for solid bodies and for liquids, only that here the limits within which the velocities of the molecules are included are much narrower than with gases.

The Temperature of Luminescence and the Second Law of the Thermodynamic Theory.

5. In a number of phenomena we have to take account of the temperature of luminescence.

In all mathematical developments which are based upon the second law of the thermodynamic theory expressions such as $\frac{dQ}{T}$ occur, involving quantities Q of heat communi-

cated to or withdrawn from the body, divided by the absolute temperature T at which this takes place.

If luminescence occurs in consequence of this addition of energy, then the temperature corresponding to certain intermolecular motions, to be defined later on (39), upon which the luminescence depends, *i. e.* the temperature of luminescence, is much higher than the temperature of the luminescent body as measured by the thermometer*.

We must therefore divide the changes of energy which

* The assumption upon which deductions from the second law rest, viz. that heat cannot be conveyed from a body of lower temperature to one of higher temperature without the expenditure of work, must therefore be otherwise conceived in accordance with the above considerations upon the temperature of luminescence, since when phenomena of luminescence occur such a transference may very well take place, as I shall show more fully further on.

occur into two parts—the first, which corresponds to the prevalent mean temperature as defined by the motion of translation of the molecules; and the second, which is determined by the intermolecular motion. Consequently the expression $\int dQ/T$ must be divided into two parts corresponding to these two processes. If the luminescent light is not homogeneous, but if it consists of separate bright lines, or if it yields a continuous spectrum, then for each ray of light of definite wave-length emitted the temperature of luminescence and the corresponding quantity of energy must be determined. Each member of $\int dQ/T$ takes then the form $\Sigma_{\alpha} dQ_{\alpha}/T_{\alpha}$ where T_{α} represents the temperatures defined by the motions of translation or by the internal motions, and dQ_{α} represents the corresponding quantities of heat. We must further remark that in the integral all the members whose temperature of luminescence is very high become very small, whilst according to the usual mode of treatment they have a considerable value.

6. That such phenomena of luminescence actually occur may be directly shown in numerous cases, as in gases which are made luminous by electric discharges without any corresponding elevation of temperature; further, in cases of *chemi-luminescence*, and indeed in processes where one would not have expected it. The experiments of W. von Siemens* have shown that gases heated far above 1000°C . emit no light; and yet an alcohol flame is luminous. It produces preeminently ultraviolet rays; in the combination of the constituents of the alcohol with the oxygen internal motions arise, for which the corresponding temperature of luminescence is situated far above the temperature of the flame. The case is similar with burning carbon disulphide, and sulphur, and in many other cases; so also with the luminosity of phosphorus at low temperatures, the emission of light by arsenious acid upon crystallization attended with rearrangement of its molecules, &c.

7. In these phenomena of luminescence the occurrence of internal motions of other temperature than that shown by the thermometer may be perceived immediately by the eye. Hence the necessity of dividing the quantities of heat into two parts is at once apparent. But analogous processes occur in many other cases, as in most chemical changes, although they may not be directly perceptible, *e. g.* when the lumines-

* Wied. *Ann.* xviii. p. 311 (1883).

cence is restricted to rays of greater or smaller wave-length than those which the eye can perceive.

Besides these oscillatory internal motions, of other temperature than the mean, which produce this luminescence, yet others may occur, rotatory and others, which are not of a nature to produce light-waves in the surrounding æther, as may be the case in the conduction of electricity through electrolytes. But of this I make here only a preliminary mention.

Luminescence and Kirchhoff's Law.

8. The production of light may therefore occur in consequence of a rise in temperature, as well as in consequence of a rise in luminescence. But these two modes must always be considered separately if we wish to obtain an insight into the mechanics of luminosity.

For luminosity resulting from a rise of temperature Kirchhoff's Law as to the relationship of emission and absorption holds good. Upon this rests the well-known reversal of the lines of the spectrum. The light produced by luminescence does not obey the same law, as is shown for example by the behaviour of fluorescent substances, which emit light of a refrangibility different from that of the incident light. In trying whether Kirchhoff's Law holds good or not, we are often able to distinguish the two phenomena. (See further on under 30.)

To discover the reasons why in glowing bodies Kirchhoff's Law of the ratio between emission and absorption holds good, and why this is not generally the case with luminescent bodies, let us consider the following circumstances:—

As we have said, there takes place in a gas a constant exchange between intermolecular energy and that due to motions of translation in consequence of the impact of molecules (the luminous energy forming a part of the intermolecular energy), so that a mean condition ensues. If any molecule suffers an increase of intermolecular energy, *e. g.* in consequence of the absorption of incident light, this is given up again in the next impact or so, and if it has a deficiency in intermolecular energy this is made good. The emission-coefficient depends upon the ease with which part of this intermolecular energy produced by the impacts, corresponding to the luminous energy, is given up again in the form of *light-vibrations*, that is upon the friction between the vibrating molecules of the body and the surrounding æther. The absorption depends upon the same quantity, and thus also upon the structure of the molecule. But since,

on the one hand, the coefficient of emission is greater the greater the friction, and on the other hand the coefficient of absorption equally increases with this; the coefficients of absorption and emission must run together; and so for all bodies in which this reciprocity exists Kirchhoff's Law must hold good.

The applicability of Kirchhoff's Law to the phenomena of luminosity thus assumes a uniform transmutability of luminous energy with that of translation, and *vice versa*, for only in this case can the ratio between absorbed and emitted energy be a function of the wave-length. But if the conditions are such that intermolecular energies produced by the absorption of incident light &c., are not converted back into motions of translation after a few impacts, then the store of luminous energy will gradually increase, and a new emission will be added to that dependent on the temperature—that is to say, luminescence is produced. That Kirchhoff's Law no longer holds good here, and cannot hold good, is clear, since the structure of the molecule is such that the uniform transformation of luminous energy into that of motion of translation, and of that of translation into luminous energy no longer takes place. Indeed, it would seem as if Kirchhoff's Law only held good for an ideal case, viz. only if no increase of the luminous motions could be produced in the luminous body by absorption. Hence Kirchhoff's Law can only hold good for that part of the luminous motion which does not consist in luminescence. Moreover, Kirchhoff's Law has not been quantitatively proved for luminous gases; but we have contented ourselves with verifying certain qualitative-quantitative consequences of it.

Dependence of Luminescence on the Mode of Excitation.

9. Luminescent light is in a high degree dependent in colour and intensity upon the mode of production, so that in investigating it it is necessary to consider both of these qualities. In photo-luminescence, and so in fluorescence and phosphorescence, the colour of the emitted light is dependent upon that of the incident light. In electro-luminescence, discharges of various strengths call forth different assemblages of rays. The borders of the stratifications in discharge-tubes, as is well known, are of different colours towards the positive and negative poles. This occurs with hydrogen or air alone, but, as I have observed, more distinctly if the discharge-tube contains hydrogen and sodium vapour. Further, the glow-light and the positive light are, *cæteris paribus*, differently coloured.

The sulphur compounds of the metals of the alkaline earths, glowing in consequence of chemi-luminescence, yield light of different colours according to difference of temperature.

The order of intensity of emission of light may be completely reversed by change in the mode of excitation. Thus if, in electro-luminescence, a body A shines as bright as, or brighter than, another body B, this will not necessarily be the case upon ignition or with chemi-luminescence. Mercury and sodium give us examples of this. The first, introduced in the gaseous state into the flame, gives scarcely any light, whilst in a Geissler's tube it gives an intensely bright light; sodium, on the other hand, is very bright in both cases.

10. In many cases luminescence and ignition occur together. If we wish to arrive at conclusions in such cases we must endeavour to separate the two phenomena. The following are probably processes in which both phenomena occur together:—

In flame the production of light depends partly upon chemi-luminescence and partly upon phenomena of ignition, so soon at least as solid particles are separated.

If electric discharges pass between metal electrodes the metal is disintegrated and volatilized, and the vapour is heated to incandescence, at the same time it may be brought to luminescence by the electric current.

If we pass through a tube filled with hydrogen discharges of such a strength that the line-spectrum just appears, the hydrogen is far from being heated to the temperature of incandescence. If, on the other hand, we employ very strong discharges, we have, in addition to the original luminosity, a very great rise in temperature, which produces incandescence. We can expect to obtain an absorption corresponding to Kirchhoff's law only for the rays emitted by the process of incandescence, but not for the others.

The phenomena of long and short lines observed when an image of a horizontal flame is thrown upon the vertical slit of a spectroscope depend, no doubt, in part at least, upon the different processes of luminescence and incandescence. Several factors are simultaneously concerned in their production. Thus, for example, the short lines appear in the inner portions, and the long lines both in the inner and outer portions of the flame. But in the inner portions, according to the usual arrangement of the experiment, both the temperature and the quantity of incandescent material are greater than in the external portion. Experiments are in progress to separate these different conditions; this is especially important in order to decide which lines in the spectrum are produced by luminescence and which by incandescence; and how these

are arranged, as well as on account of their application to the (iron) lines of the solar spectrum.

Differences in the Mode of Evolution of Light, and of Emission of Light. Continuous and Discontinuous Excitation. Store of Luminous Energy.

11. In all investigations on luminosity two chief classes of phenomena are sharply to be distinguished: first, those where it is *always the same* particles which emit the light; and, secondly, those where *continually new* molecules take up the luminous motions.

The first is the case in the usual phenomena of luminosity, fluorescence, electro-luminescence, &c. ; the second case occurs when the luminosity is produced by chemical changes, *e. g.* combustion, oxidation of phosphorus, of lophine, crystallization of arsenious acid, and, as I shall show further on, also in the luminous phenomena of phosphorescent calcium-sulphide compounds.

In the present treatise only the phenomena of the first class will be treated at length.

12. In considering the mechanics of luminosity, we must observe that there are two factors to be considered together.

First, a definite amount of energy must be communicated to the molecules, which gives rise to the production of the luminous motions; and, secondly, in consequence of the radiation of light a continuous diminution of this energy is brought about. The final condition of the body, as far as the phenomena of light are concerned, depends on the relation between these two quantities. A stationary condition ensues when the supply of energy is equal to the loss of energy.

(a) The *addition of energy producing light* may either be continuous, or it may be repeated after longer or shorter intervals.

A *continuous* addition occurs when a body is brought to photo-luminescence by means of incident light. The interruptions observed in the phosphoroscope are of course not to be taken into account, since in comparison with the vibration-period of light they are infinitely long. To the same category probably belong electro- and kathode-luminescence; since in the anode light the changes in the dielectric polarization of the molecules produce vibrations, whilst the kathode-rays are probably connected with the ultra-violet rays*.

A *discontinuous* excitation occurs in many other cases, as in glowing gases. In the contact of two molecules a part of the energy of translation is converted into luminous energy,

* Wied. *Ann.* xx. p. 781 (1883).

a part of which is lost by external radiation on the free path between two impacts.

The two cases require separate consideration, for the mode of excitation is essentially different. In incandescence it is the reciprocal relationships between the impinging molecules, whether of the same, or of different kinds, which produce the motions causing light; while in photo- and electro-luminescence these are due to an external motion affecting the particles.

(b) *The loss in luminous energy* may also have various causes. A loss of energy ensues in consequence of the issuing light-vibrations; further, in luminescent bodies in consequence of the impact of two molecules a part of the energy of the luminous motions may be converted into energy of translation and thus produce a rise of temperature. Further, within each molecule only those atoms associated in a particular way, the chromogenic, which we will here call *lucigenic*, may perform luminous vibrations together. These motions may in part be transferred to the neighbouring non-lucigenic atoms, and may thus suffer diminution. According to the structure of the molecules, only a particular kind of vibrations will be checked in any high degree, whilst others will remain undisturbed—a process to which numerous analogies are well known in acoustics.

We have appropriate examples amongst the phenomena of light in the observations on solutions of fluorescein and eosin in gelatine, which I have previously communicated*, where the gelatine is mixed with solutions of the substances and allowed to dry. In the fluorescent light yielded by these substances, observed while illuminated, the spectrum appears almost continuous from red to green. On the other hand, the phosphorescent light observed some time after the illumination has ceased, shows a very dark band in the orange. The phosphorescent light was examined in the phosphoroscope described by me, the arrangement being such that the phosphorescent light was examined from the same side as that on which the incident light fell†. The absorption of the light excited before the observation was diminished as much as possible. We must conclude from these observations that in these bodies the loss of luminous energy for the complex of rays in the orange is determined, not only by radiation, but also by an absorption within the molecule itself.

13. We will now consider the intensity-relationships of the light emitted by a body, and will investigate the two cases :

* *Sitzungsber. d. physikal-med. Soc. Erlangen*, July 1887.

† *Wied. Ann.* xxxiv. p. 453 (1888).

first, that the body is continuously excited ; and, secondly, that at any time the exciting cause is removed, and then the body, left to itself, gradually radiates its store of luminous energy.

A. If the body is continuously excited we may use the equation

$$di = \{\phi - bi\} dt. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The change of intensity di which occurs in the element of time dt is equal to the change of intensity ϕdt produced by the external cause, diminished by the change of intensity $bi dt$ in consequence of radiation, where we assume that the decrease in intensity is proportional to the intensity existing at the moment*.

b is, as follows from the equation, the reciprocal value of the time in which the unit of intensity is radiated if the radiating body is maintained at unit brightness. The decrease in brightness may be produced both by radiation and by internal absorption.

The function ϕ is essentially different according to the mode of excitation.

For phenomena of photo-luminescence we may assume that $\phi = \Delta J$, *i. e.* that ϕ is proportional to the intensity J of the incident light. Δ is the reciprocal value of the time necessary for unit intensity to be excited by incident intensity 1. We may also say that Δ expresses how large a fraction of the incident intensity is converted into excited intensity in unit time. Then

$$di = (\Delta J - bi)dt.$$

Hence, if C is a constant,

$$i = \frac{1}{b} (\Delta J - Ce^{-bt})$$

If $i=0$, for $t=0$, then $C=\Delta J$, and

$$i = \frac{\Delta J}{b} (1 - e^{-bt}). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we make some other assumption for the relationship between the decrease in intensity di and the intensity i , equa-

* This equation holds good in the first instance for the communicated and radiated intensities ; but if we assume that the radiated intensity is proportional to the luminous energy existing at the moment, it may further be applied without alteration to the intensities of the luminous motions.

tion (1) and consequently equation (2) will take a different form; but since with increasing intensity the quantity radiated must also increase, we shall have an equation analogous to (2). The further conclusions will therefore not be essentially affected.

Strictly speaking a separate equation of the form of (1) is required for rays of each wave-length. For the value of b may be very different for the rays of different wave-length emitted, as the experiments described above with eosin and fluorescein show; and, again, the value of A is very different for exciting light of different colours, as we learn from numerous experiments with fluorescent substances.

The intensity i_f of the *fluorescent light*, i. e. the intensity of the light observed upon continuous illumination, is determined by the value of i for $t=\infty$. It is so great that the loss is equal to the gain; hence $di/dt=0$. Hence it follows that

$$i_f = \frac{AJ}{b} \cdot \cdot \cdot \cdot \cdot \cdot (3)$$

From this expression we see that the brightness of the fluorescent light depends upon two quantities—first, on the fraction of the incident energy converted into light-vibrations; and, secondly, on the loss of energy determined by b . The first quantity is dependent upon absorption &c.; but the second upon the strength of the emission and the loss of energy either in the impact of two molecules or in consequence of mutual attractions of the constituent atoms of a molecule.

The great increase in intensity of the fluorescent light, which occurs when solutions of fluorescent substances are thickened by addition of glycerine, gelatine, &c., may be referred to the decrease in that portion of b which corresponds to the loss of energy by mutual impacts, since, in consequence of the greater friction and consequent less mobility, the molecules of the same kind impinge much less frequently.

In other cases we may find in solutions of the same substance in different media hardly any difference in the intensity of the absorption, but a displacement of the absorption-bands, as with saffranine and magdala-red, and at the same time a complete disappearance of fluorescence. The explanation in my opinion is to be sought in the formation of hydrates &c., and a consequent alteration of absorption-relationship within each molecule in a way as

yet unmeasurable. F. Stenger has published another explanation*.

B. Let us now turn to the second case. Let the luminous energy be brought by any cause to a constant height, and then at a time $t=0$ let the radiating body be left to itself, after the exciting cause has been removed. We will further assume that the loss of energy takes place by radiation and not by absorption. Further, the luminous energy contained in a particle shall not receive any further increase during the radiation, in consequence of processes going on within the molecule itself, or by the impact of two molecules.

If, then, i is the intensity measured in any units, *i. e.* the energy emitted in the unit time at the time t , and b the constant introduced above, then during the time dt the radiating body suffers a loss of luminous energy

$$di = -bidt.$$

If we integrate this expression from 0 to ∞ we obtain the total store of energy of the vibrating particles, for in an infinitely long time all the energy will be radiated; hence the total luminous energy present is

$$L = \int_0^\infty i dt = \int_0^\infty i_0 e^{-bt} dt = \frac{i_0}{b}.$$

If, then, we know the intensity i_0 at the time 0, and the constant b , we can find the total luminous energy contained in the luminous body under the above assumptions. *The store of luminous energy is equal to i_0 , the initial intensity, divided by b , the constant of loss of energy.*

Total and True Coefficient of Emission.

14. We may express the energy emitted by the unit weight of a body in the unit time contained in the rays lying within an infinitely small breadth of the spectrum between wave-length λ and $\lambda + d\lambda$ by $s_\lambda d\lambda$; s_λ would then denote the energy contained in the region between λ and $\lambda + 1$ if at all points within the same the energy is yielded as at the point λ ; we may appropriately call s_λ the true coefficient of emission at the point λ , referring, of course, to the unit weight. The radiating layer is supposed to be so thin that the absorption of the emitted rays within it may be neglected. The energy is to be measured in calorimetric units. If the region of the spectrum that we are considering extends from λ_1 to λ_2 , the

* Wied. *Ann.* xxxiii. p. 577 (1888).

energy emitted is

$$S_{\lambda} = \int_{\lambda_1}^{\lambda_2} s_{\lambda} d\lambda.$$

The quantity S_{λ} we will designate as the *total coefficient of emission* of the unit weight between the wave-lengths λ_1 and λ_2 . It is the energy emitted in the unit time by the unit weight of the body in question corresponding to all rays between the wave-lengths λ_1 and λ_2 . The two quantities S_{λ} and s_{λ} are exactly analogous to the total quantity of heat necessary to heat a body from t_1° to t_2° and the true specific heat. The two quantities S_{λ} and s_{λ} in the form given above have not been experimentally determined as yet. We have above all not referred the emission to a definite quantity of the radiating body, but only to the unit of surface of the particular body. The molecular coefficients of emission are obtained by multiplying s_{λ} and S_{λ} by the molecular weight of the body under investigation.

15. In this investigation of spectra two problems may occur. We determine

(1) The *total coefficient of emission* $S_{\lambda_1\lambda_2}$ between the wave-lengths λ_1 and λ_2 of a body which is maintained in a constant condition (*e.g.* of a platinum wire of constant temperature). Then the total coefficient of emission can be determined for the whole spectrum from $\lambda=0$ to $\lambda=\infty$, or for particular parts of it, which may ultimately consist of one or more so-called spectral lines or bands stretching continuously between every two wave-lengths. Then S assumes the value

$$S_0^{\infty} = \int_0^{\infty} s_{\lambda} d\lambda \text{ and } S = \int_{\lambda_1}^{\lambda_2} s_{\lambda} d\lambda + \int_{\lambda_3}^{\lambda_4} s_{\lambda} d\lambda + \dots$$

It is to be observed that the value of the first integral cannot be directly determined, since we do not know what the radiation is either for very small wave-lengths or for very great wave-lengths, but our experiments are limited to a very small portion of the possible rays. Further, we must observe that in our experiments as soon as s_{λ} relates to rays which are also given off by surrounding bodies, we determine not the coefficient itself but $s_{\lambda} - a_{\lambda}$, where a_{λ} denotes the coefficient of emission of the bodies serving for the measurement of the wave-length λ , also in calorimetric measure.

(2) We determine the *true coefficient of emission* s_{λ} for a *single* wave-length if belonging to a definite point of the spectrum. Here we must observe that line-like portions of the spectrum are not directly comparable with continuous

spectra, but account must be taken of dispersion (see further on).

16. For the experimental determination of the two coefficients of emission in the visible spectrum measured in calorimetric measure, we must determine for a definite body, best a perfectly black one, the radiation in calorimetric measure, and compare (by the method to be explained immediately) with its brightness that of the body to be investigated, by making the brightness of the two bodies exactly the same, since with equal brightness the energies of the rays perceived by the eye in the same regions of the spectrum are equal. We thus fix the ratio of the energies received by the apparatus; these are themselves proportional to the coefficients of emission of the two sources of light, and are further dependent upon the distance of the luminous body, the thickness of the radiating layer, &c. (see further on). Further, the dispersion must be taken account of.

[To be continued.]

XXV. *Note on the Thermoelectric Position of Platinoid.* By J. T. BOTTOMLEY, M.A., F.R.S., F.C.S., and A. TANAKADATÉ, *Rigakusi* *.

IN carrying out a series of experiments on radiation of heat by solid bodies, an investigation to which one of the present writers has for some time past devoted considerable attention, it became necessary, for a purpose which need not here be detailed, to select a thermoelectric pair of metals, of which one metal was essentially platinum, as it had to pass through glass. Various pairs were considered, and some trials were made; and it was finally determined to make use of platinum and platinoid. The latter metal is an alloy whose electrical and mechanical properties were investigated some years ago by one of the present writers†; and since that time it has assumed considerable importance in the construction of electrical instruments and resistance-coils. Partly on this account, and partly from present requirements, it became both interesting and necessary to determine the thermoelectric constants for a specimen of this alloy.

Platinoid is in composition very similar to German silver. In the manufacture of the alloy, however, phosphide of tungsten is employed; and although an exceedingly minute

* Reprinted at the request of the Authors, having been read before the Royal Society, June 20, 1889.

† J. T. Bottomley, Roy. Soc. Proc. 1885.