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ON THE INTERACTION OF RADIATION WITH MATTER AND ON FLUORESCENT EXCITING POWER

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Abstract

The interaction of radiation and matter is discussed on the basis of Einstein's theory. The distribution of energy in an enclosure containing quantized particles is indeterminate unless there is thermal or other non-radiative interaction between the particles; the latter process is therefore essential to the production of the black-body distribution. Fluorescence cannot lower the entropy of the system.

Exciting power for fluorescence.—No sharp distinction can be drawn between thermal emission and fluorescence. If ψ_{yx} is the fluorescence of frequency ν_y excited by radiation of frequency ν_x and if α_x, α_y, u_x, u_y are the corresponding absorption coefficients and black-body densities, respectively, then on certain assumptions $\psi_{yx}=k\alpha_x\alpha_y u_y/\nu_x$, k being independent of ν_x and ν_y. Much more general assumptions lead to: $\psi_{yx}/\psi_{xy}=\nu_y u_y/\nu_x u_x$. These equations ought to apply to gas fluorescence, and it is quite possible that the latter may hold generally for liquids and solids and the former in those cases where the shape of the fluorescence band does not vary with the exciting frequency. The equations agree with the few data in existence.

Introduction

The relation between fluorescence and thermal radiation was discussed a decade ago by several authors[1] and an equation connecting them was obtained by the present author and found to be confirmed by experiment. In the present paper the same problem is attacked from the standpoint of the present-day theory of radiation, and similar but slightly modified results are obtained.

In Part I some general theorems are deduced concerning the equilibrium between radiation and atoms which, while not bearing directly upon present-day observations, yet possess a certain theoretical interest. In Part II the excitation of fluorescence is considered. Throughout the paper Einstein's theory[2] of emission and absorption will be employed as a basis.

I. Equilibrium Between Radiation and Atoms

Suppose we have, in an enclosure, N similar atoms whose state is characterized by a single quantum number capable of assuming different values. The results deduced below will hold also, mutatis mutandis, for a mixture of atoms or molecules of any sort, but it will be sufficient

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[1] E. Pringsheim, Phys. Zeits. **14**, 129 (1913); E. H. Kennard, Phys. Rev. **11**, 29 (1918)

[2] A. Einstein, Phys. Zeits. **18**, 123 (1917).

to give the proofs for the simple case just specified. Suppose further that collisions are either rare or at least without effect upon the quantum number. Let the quantum levels be numbered 1, 2, 3, $\cdots$, ω, in the order of increasing energy and let there be N_1 atoms in level 1, N_2 in level 2, etc. Then

$$\sum_{i=1}^{\omega} N_i = N. \tag{1}$$

Now, in general, if radiation is present in the enclosure it will progressively alter the distribution of the atoms among the quantum levels. The condition that the radiation should leave the atomic distribution unaffected is:

$$N_i \sum_{k=1}^{\omega} k(A_{ik}+B_{ik}\rho_{ik}) = \sum_{k=1}^{\omega} k(A_{ki}+B_{ki}\rho_{ik})N_k, \quad (i=1,\ 2,\ \cdots,\ \omega) \tag{2}$$

Here A_{ij} is Einstein's probability per unit time that an atom in the i-level will jump spontaneously to the j-level, and $B_{ij}\rho_{ij}$ is the similar probability that it will make the same jump under the influence of radiation density ρ_{ij} of the frequency ν_{ij} corresponding to this jump; $A_{ij}=0$ if $j \geqq i$ and $B_{ii}=0$. The equation simply states that the losses from any level must equal the gains.

On the other hand, by emission and absorption the atoms will in general alter the distribution of radiation. The condition that this should not occur is that for each frequency corresponding to a quantum jump emission must equal absorption, or

$$(A_{ij}+B_{ij}\rho_{ij})N_i = B_{ji}\rho_{ji}N_j \tag{3}$$

for all values of i and all values of $j<i$.

The total energy of radiation and of atomic excitation will be, provided the mean radiation density is uniform throughout the volume V of the enclosure,

$$U = V \sum_{i=1}^{\omega} \sum_{j=1}^{j=i-1} \rho_{ij} + \sum_{i=1}^{\omega} N_i \epsilon_i \tag{4}$$

where ϵ_i is the excitation energy of the i-level.

From these equations we can obtain at once a number of interesting theorems.

1. *A distribution of radiation that shall leave a given atomic distribution undisturbed can be chosen in many ways, in fact with* $(\omega-1)$ $(\omega-2)/2$ *degrees of freedom.* For to find such a distribution we need only determine the $\omega(\omega-1)/2$ ρ_{ij}'s so as to satisfy equations (2) for given values of the N's and only $(\omega-1)$ of these equations are independent, since

if we add all of them we obtain an identity corresponding to the physical fact that the sum of all losses must equal the sum of all gains.

2. *Among these distributions of radiation that leave a given atomic distribution unaffected there is just one and,—it is the only one,—which is itself unaffected by the emission and absorption of radiation by the atoms.*

For if the radiation is thereby unaffected, there must occur as many jumps per second in one direction as in the other between any given pair of levels, in order to secure equality of emission and absorption for the corresponding frequency; and such an equality of jumps will necessarily also have no tendency to change the distribution of atoms. To find such a distribution of radiation we have only to solve equations (3) for the ρ_{ij}'s, which are just equal in number to the equations. Such a state might be described as one of "mutual equilibrium" between the radiation and the atoms.

On the other hand, if we start with a prescribed distribution of radiation and seek the equilibrium distribution of atoms, the possibilities are more limited:

3. *Given a distribution of radiation, the atoms can always be distributed so that they will be undisturbed by the radiation; but mutual equilibrium with the given radiation is usually impossible.* In other words, if we illuminate the atoms, we shall cause them to distribute themselves in a certain definite manner among their various energy levels, but when thus distributed they will usually subject the incident radiation to continuous transformation (fluorescence). For we can solve the $(\omega-1)$ independent equations (2) and (1) simultaneously to determine the ω N_i's in terms of the given ρ_{ij}s but eqs. (3) will then usually fail to be satisfied.

4. *The equilibrium distribution of a given total amount of energy U among the energies of excitation of the atoms in the enclosure and the corresponding quantum frequencies of the radiation is indeterminate in the absence of collision effects (provided $\omega>2$), possessing $(\omega-2)$ degrees of lability.* For Equations (2) are deducible by adding up suitable combinations out of Equations (3), and Eqs. (1), (3) and (4) give us only $\omega(\omega-1)/2+2$ equations to determine the $\omega+\omega(\omega-1)/2$ unknown N_i's and ρ_{ij}'s. Under these conditions the actual final distribution of energy will be determined by initial conditions.

This theorem is particularly interesting because it shows clearly that:

5. *Thermal agitation plays an essential part in producing and in determining the special distribution of black-body radiation.* We obtain Planck's radiation law only if we assume that thermal agitation sets

up the Boltzmann distribution among the atoms[3]; then $N_i = \text{const.} \times w_i e^{-\epsilon_i/kT}$, where w_i is the statistical weight of the i-level, and, if we assume also that[2] $\epsilon_i - \epsilon_j = h\nu_{ij}$ and

$$w_i B_{ij} = w_j B_{ji}, \tag{5}$$

we have from (3) for the black-body spectral density referred to frequency

$$u_{ij} = \rho_{ij} = \frac{A_{ij}}{B_{ij}} \frac{1}{e^{h\nu_{ij}/kT} - 1}, \tag{6}$$

The theorem here stated merely repeats with a modern proof a conclusion reached long ago on classical grounds[4]

An old question to which a peculiarly keen point can be given in terms of current theory is that concerning the relation between violations of Stokes' Law and the Second Law of Thermodynamics. Suppose, for instance, that in our case $\omega = 3$. Then we can easily make ρ_{13} negligibly small and yet have many atoms raised to the third level by absorption of ρ_{12} and ρ_{23}; and there seems to be no reason in principle why we should not have $\nu_{12} = \nu_{23}$. Under these conditions we should have incident radiation causing fluorescence of higher frequency (ν_{13}) than its own with an entire absence of fluorescence of lower frequency. At first glance one might expect that such a fluorescent process would increase the availability of the radiant energy.

The explanation lies in the fact that the entropy of radiation depends not only upon its frequency but also upon its density; and the laws of emission and absorption are such that the following theorem holds:

7. *The interaction between radiation and atoms or molecules cannot lower the entropy of the radiation without causing at least a compensating increase in the Boltzmannian entropy of the atoms or molecules.* As usual we shall give the proof only for the simple case described at the beginning of this paper. The entropy per unit volume of monochromatic radiation of density ρ_{ij} is ρ_{ij}/T where T is the temperature of the corresponding black body, i. e. by (6)

$$\frac{1}{T} = \frac{k}{h\nu_{ij}} \log\left(1 + \frac{A_{ij}}{B_{ij}\,\rho_{ij}}\right) \tag{7}$$

This equation applies separately to beams moving in different directions,

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[3] In consequence of the theorems here stated, the view of A. E. Eddington (Phil. Mag. **50**, 803 1925), according to which the black-body law might well be regarded as a primary law and the Boltzmann law should then be deduced from it, although of course logically sound, seems rather unnatural.

[4] Cf. concluding section of Planck's Wärmestrahlung, 2d edition.

each having its own temperature; but for our present purpose we can assume the radiation to be uniformly distributed in direction, since, if it is not, then the process of absorption and re-emission will tend to make it so and will thereby tend to raise the entropy. We can then write, for the gain or loss of radiant entropy due to the emission or absorption, respectively, of a quantum $h\nu_{ij}$, $h\nu_{ij}/T$, and the total net gain of radiant entropy S will be

$$\begin{aligned}\frac{dS}{dt} &= k\sum_{i=1}^{\omega}\sum_{j=1}^{j=i-1}[(A_{ij}+B_{ij}\rho_{ij})N_i-B_{ji}\rho_{ji}N_j]\log\left(1+\frac{A_{ij}}{\rho_{ij}B_{ij}}\right)\\ &= k\sum_{i=1}^{\omega}\sum_{j=1}^{j=i-1}\{(A_{ij}+B_{ij}\rho_{ij})N_i-B_{ij}\rho_{ij}N_{ij}\}\{\log[A_{ij}+B_{ij}\rho_{ij})N_i]\\ &\qquad\qquad -\log[B_{ij}\rho_{ij}N_j]\}\\ &\quad + k\sum_{i=1}^{\omega}\left\{\sum_{j=i+1}^{\omega}[(A_{ji}+B_{ji}\rho_{ij})N_j-B_{ij}\rho_{ij}N_i]\right.\\ &\qquad\qquad \left.-\sum_{j=1}^{j=i-1}[(A_{ij}+B_{ij}\rho_{ij})N_i-B_{ji}\rho_{ij}N_j]\right\}\log N_i\end{aligned}$$

Here in the right-hand member each term in the first double sum is necessarily positive or zero; and the coefficient of log N_i in the second sum is simply the net rate or gain of atoms in the i level. Hence

$$\frac{dS}{dt}\geqq k\sum_{i=1}^{\omega}\frac{dN_i}{dt}\log N_i=-\frac{d}{d\,t}\sum_{i=1}^{\omega}k(N_i-N_i\log N_i). \tag{8}$$

The last sum in this equation is, except for an additive constant, the entropy of the atoms in the extended sense given to the term by Boltzmann.[5] The theorem stated follows at once; continuous decrease in radiant entropy is impossible without continuous change either in the atomic distribution itself or in some other part of the system which acts so as to preserve the atomic distribution.

II. The Excitation of Fluorescence

We shall now turn to the question of the laws governing the excitation of fluorescence. We may note first that the modern theory of radiation seems to make impossible any sharp distinction between luminescence and thermal emission. For emission of any sort depends essentially upon the presence of atoms or molecules in an excited state and is independent of the nature of the agent producing these. In an isothermal enclosure, for instance, either the radiation alone or thermal agitation alone is competent to maintain the existing distribution among

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[5] Cf. Planck, Wärmestrahlung. 4ed. Eq. (173).

the energy levels; hence any division of the emission into thermal emission caused by thermal agitation and fluorescence excited by the thermal radiation must be, to say the least, highly artificial. It seems best to say that in this case the distinction between thermal emission and luminescence has entirely disappeared.[6]

At the other extreme stands the case of *weak excitation*. The criterion for this is that the density shall be *relatively little* disturbed by the exciting beam in any quantum state that is associated (as initial or final state) with two or more constituent frequencies of the exciting light, and, furthermore, that if any quantum state is associated with only one such constituent, then the term B_ρ for that state and that frequency in the exciting beam shall be small as compared with A; the second of these requirements is amply met if the energy density ρ is small relative to the density u in black-body radiation which has its maximum at the frequency in question, for at this maximum $e^{h\nu/kT} = 60$ and $Bu/A = 1/59$. Under these conditions the excited emission or increment of emission will enjoy the properties that are most distinctive of classical fluorescence, for it will be proportional in intensity to the exciting radiation and it will obey the law of superposition, since two different wavelengths incident together will produce the sum of their separate effects.

In intermediate cases both proportionality and superposition may fail (e. g. in some of Wood's experiments on gases).

In the *case of weak excitation*, as just defined, the modern theory leads, on certain further assumptions, to two important results concerning the exciting power.

Let us consider, first, a collection of atoms or molecules whose state is characterized by two quantum numbers, m and n. Let m be practically unaffected by thermal agitation; then normally it has nearly always a certain value, m_1, and after being changed by excitation it is restored only by the process of emission. On the other hand, let n be distributed statistically, so that the density of atoms for which $n = n_i$ is

$$\tau_i = C w_i e^{-\epsilon_i \; kT} \qquad (9)$$

where ϵ_i = energy and w_i = statistical weight of the quantum state characterized by $m = m_1$ and $n = n_i$, k = gas constant for one particle, T = temperature, C = a constant. Let the material be illuminated with radiation of density $\rho_{ab} = \rho_x$ and frequency $\nu_{ab} = \nu_x$ such that on absorption m changes to m_2 and n changes from a certain value n_a to another value n_b. For generality and convenience we shall assume that the

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[6] **This view of the matter supersedes that developed in the author's earlier paper (loc. cit.).**

material is also bathed by thermal radiation corresponding to its temperature, although the effects of this radiation will usually be of the same order as the secondary effects which are neglected under the hypothesis of weak excitation. Then $B_{ab}\rho_{ab}\tau_a$ quanta will be absorbed from the incident beam in unit volume per second, and the coefficient of absorption for this frequency, defined as fraction of the incident energy in unit volume that is absorbed per second, will be $B_{ab}\rho_{ab}\tau_a h\nu_x/\rho_x$ or, by (9),

$$\alpha_x = Cw_a h\nu_x B_{ab}\, e^{-\epsilon_a/kT} \tag{10}$$

(B depends also, of course, on m but for simplicity only the values of n are indicated in the notation.)

Now let us assume further that upon particles thus excited thermal agitation and thermal radiation act either (1) relatively slowly, so that very few changes are thereby effected in n before re-emission occurs, or (2) relatively rapidly, so that most of the excited particles, before re-emission, become re-distributed statistically as to the quantum-number n. Then in case (2) the density of excited particles with $n=n_s$ will be

$$\tau_s' = C'w_s' e^{-\epsilon'_s/kT}\ , \tag{11}$$

C' being a new constant and w_s' the statistical weight and ϵ_s' the energy of the state in which $m=m_2$ and $n=n_s$. The same equation will serve also for case (1) provided we understand that in this case s can have only one value, namely, $s=b$.

Jumps will now occur in which m returns to m_1 and n changes from n_s to some other value, n_r. There will be $(A_{sr}+B_{sr}u_{sr})\tau_s'$ of these in unit volume per second, u_{sr} denoting the density of thermal radiation, and there will be a resulting fluorescent emission, of frequency $\nu_{rs}=\nu_y$, equal per unit volume to

$$F_{yx} = C'w_s' h\nu_y(A_{sr}+B_{sr}u_y)e^{-\epsilon'_s/kT} \tag{12}$$

The constant C' must be such that the total loss of excited atoms balances the gain, hence

$$C'S = C'\sum_r\sum_s w_s'(A_{sr}+B_{sr}u_{sr})e^{-\epsilon'_s/kT} = B_{ab}\rho_x\tau_a\ , \tag{13}$$

s being restricted in case (1) to the value $s=b$. Let us define as the exciting power, ψ_{yx}, for frequencies y and x the fluorescent emission from unit volume of frequency ν_y excited by unit radiation density of frequency ν_x. Then $\psi_{yx}=F_{yx}/\rho_x$ and, by (9), (12) and (13),

$$\psi_{yx} = Cw_a w_s' B_{ab} S^{-1} h\nu_y (A_{sr}+B_{sr}u_y)e^{-(\epsilon_a+\epsilon'_s)/kT}. \tag{14}$$

We can now draw two interesting conclusions that do not require a knowledge of the constants A and B.

Corresponding to (10) we have, using (5),

$$\alpha_y = Cw_r h\nu_y B_{rs} e^{-\epsilon_r/kT} = Cw_s' h\nu_y B_{sr} e^{-\epsilon_r/kT}. \tag{15}$$

Combining this equation with (14), (10), and (6) and putting $\epsilon_s' - \epsilon_r = h\nu_y$, we obtain

$$\psi_{yx} = \kappa \frac{\alpha_x}{\nu_x} \alpha_y u_y, \quad \kappa = \frac{1}{hCS}. \tag{16}$$

Since κ is independent of the choice of frequencies for x and y, we have the double result that *for a fixed frequency of fluorescence the exciting power is proportional to the coefficient of absorption for the exciting light divided by its frequency*; *whereas for fixed excitation at any point in the spectrum the fluorescent emission is proportional to the product of the coefficient of absorption and the black-body intensity at the temperature of the substance*, both taken for the same frequency as the fluorescence.

If Wien's formula can be employed with sufficient accuracy for u,

$$\psi_{yx} = \kappa' \frac{\alpha_x}{\nu_x} \alpha_y \nu_y^3 e^{-h\nu_y/kT}. \tag{17}$$

We can also eliminate all unknown factors by interchanging y and x in (16) and then dividing the equation thus obtained into (16); the result is a remarkably simple relation between the reciprocal exciting powers for any two frequencies and the corresponding black-body intensities, namely:

$$\frac{\psi_{yx}}{\psi_{xy}} = \frac{\nu_y u_y}{\nu_x u_x}, \tag{18}$$

or approximately, if Wien's formula be used for u,

$$\frac{\psi_{yx}}{\psi_{xy}} = \frac{\nu_y^4}{\nu_x^4} e^{-h(\nu_y - \nu_x)/kT}. \tag{18a}$$

Let us consider now the extent to which the assumptions underlying these results can be generalized. The same equations are easily obtained if the quantum state is characterized by three or more quantum numbers of which each is of the type either of m or of n as above defined. Eq. 18, but not (16), can also be deduced very plausibly without the restrictions touching thermal agitation.

For this purpose we need only draw from the principle of "detailed balance" the inference that, under conditions of thermal equilibrium, as many excited atoms or molecules are transferred in one direction between any two quantum states as are transferred in the opposite direction. Let the quantum states, which may be of any sort, be numbered as before from 1 to ω and let τ_i be the number of particles per unit volume that are in the i-state in thermal equilibrium; let p_{ij} denote the probability per second for the passage of a given particle from the i-state to the j-state under the combined influences of thermal agitation and thermal radiation. Then by the principle just stated

$$p_{ij}\tau_i = p_{ji}\tau_j \tag{19}$$

for all i and all $j \neq i$. The assumption of weak excitation will, however, be retained, with the added proviso that all changes of density shall be small relative to the general density of the particles; from the assumption as thus extended it follows that the values of the p's themselves are little affected by the excitation.

Now let the material be weakly illuminated from the outside with density $\rho_{ab}=\rho_x$ of frequency $\nu_{ab}=\nu_x$. A steady state will be set up, with slightly modified densities $\tau_i'=\tau_i(1+\sigma_i)$, such that "loss equals gain" or, for each value of i,

$$\sum_j (p_{ij}+B_{ij}\rho_{ij})\tau_i(1+\sigma_i) = \sum_j (p_{ji}+B_{ji}\rho_{ij})\tau_j(1+\sigma_j)$$

or, by (19),

$$\sum_j (p_{ij}\sigma_i\tau_i + B_{ij}\rho_{ij}\tau_i') = \sum_j (p_{ji}\sigma_j\tau_j+B_{ji}\rho_{ij}\tau_j')$$

where the value $j=i$ is to be omitted in the sums, and $\rho_{ij}=0$ except that it equals ρ_x when either $i=a$ and $j=b$ or else $i=b$ and $j=a$; or, if we put $p_{ii}=-\sum_{j}{}_i^{i-1} p_{ij}-\sum_{j}{}_{i+1}^{\omega} p_{ij}$ and replace τ' by τ in the coefficients of ρ because of the assumption of weak excitation,

$$\sum_{j=1}^{\omega} p_{ji}\tau_j\sigma_j = \sum_{j=1}^{\omega} (B_{ij}\tau_i - B_{ji}\tau_j)\rho_{ij}, \quad (i=1, 2, \cdots, \omega). \tag{20}$$

Solving these equations simultaneously for the σ's, we find

$$\sigma_j=\frac{1}{\Delta}(M_{aj}-M_{bj})(B_{ab}\tau_a-B_{ba}\tau_b)\rho_x, \tag{21}$$

Δ being the determinant of the coefficients and M_{ij} the minor of the element in the ith row and jth column.

There will now be a differential or fluorescent emission due to the disturbance in the atomic distribution; its amount per unit volume for a frequency $\nu_{rs}=\nu_y$, divided by ρ_x, is the exciting power for these two frequencies, ψ_{yx}. Hence

$$\psi_{yx}=\left[(A_{sr}+B_{sr}u_y)\sigma_s\tau_s-B_{rs}u_y\sigma_r\tau_r\right]\frac{h\nu_y}{\rho_x}\cdot$$

But, since the τ's refer to the equilibrium state, $(A_{sr}+B_{sr}u_y)\tau_s=B_{sr}u_y\tau_r$. Hence

$$\psi_{yx}=\frac{1}{\Delta}B_{rs}u_y\tau_r(M_{as}-M_{bs}-M_{ar}+M_{br})(B_{ab}\tau_a-B_{ba}\tau_b)h\nu_y.$$

Similarly, interchanging the roles of ν_x and ν_y,

$$\psi_{xy}=\frac{1}{\Delta}\,B_{ab}u_x\tau_a(M_{rb}-M_{sb}-M_{ra}+M_{sa})(B_{rs}\tau_r-B_{rs}\tau_s)h\nu_x.$$

Now because of (19) $M_{ij}=M_{ji}$; furthermore, $\tau_i=Cw_ie^{-\epsilon_i/kT}$. Hence, using (5), we find

$$\frac{\psi_{yx}}{\psi_{xy}}=\frac{\nu_yu_y}{\nu_xu_x}\,\frac{1-e^{-(\epsilon_b-\epsilon_a)/kT}}{1-e^{-(\epsilon_s-\epsilon_r)/kT}}. \tag{22}$$

This equation is more general in form than (18). It should hold for instance, for the fluorescence, or increment of emission, excited by throwing an additional beam of radiation into a furnace at a high temperature. We obtain (18) as a first approximation if we now assume further that the temperature of the material is low enough so that the two higher quantum states, b and s, associated with the two frequencies in question are rare in the absence of excitation; for the exponentials are then small. This condition is satisfied in all ordinary cases of fluorescence.

Another restriction to be removed is that all of the results obtained so far in this paper have had reference to a line spectrum, ψ referring to the total energy and α to the integrated absorption for an entire line (i. e. if α' = absorption per unit of frequency, $\alpha=\int\alpha'd\nu$). If, however, we have an approach to a continuous spectrum in the form of many unresolved lines close together,—and it seems probable that any continuous spectrum is at least equivalent to such,—then one easily sees that the results obtained in Part I of the paper will still hold. Eq. (18) and (22), which are linear in the ψ's with coefficients depending only on the frequencies, will also hold, ψ_{yx} denoting now the fluorescent emission from unit volume per unit of frequency due to unit density of exciting radiation at frequency ν_x.

On the other hand, Eqs. (16) or (17) will hold, with a similar change in the meaning of ψ and with α denoting simply the absorption referred to energy density, only provided the constant κ is the same for all lines. This appears to mean that either there must be only one undistributed quantum number of the type of m, or, if there are several, then only one mode of simultaneous change of them must be involved within the spectral region under consideration. *Under these conditions* it will also follow that the *shape of the fluorescence band is independent of the frequency of excitation*, for quantities referring to the latter frequency enter in (16), relative to y, only in the constant of proportionality.

For complete accuracy the effect of refractive index ought also to be considered, but that will not be done here.

Referred to wave-length throughout, the final equations read:

$$f_{yx}=\frac{\kappa}{v}\lambda_x\alpha_x\alpha_y J_y,\; f_{yx}=\frac{\kappa'}{v}\lambda_x\alpha_x\frac{\alpha_y}{\lambda_y{}^5}e^{-ch/k\lambda T}, \qquad (16', 17')$$

$$\frac{f_{yx}}{f_{xy}}=\frac{\lambda_x}{\lambda_y}\frac{J_y}{J_x}\doteq\frac{\lambda_x{}^6}{\lambda_y{}^6}e^{-ch/kT(1/\lambda_y-1/\lambda_x)}, \qquad (18', 18'\text{a})$$

J denoting spectral black-body intensity, f_{yx}, fluorescent emission per unit of wave-length at λ_y due to unit energy density in the neighborhood of λ_x, and v, the speed of light. If the shape of the fluorescence band is constant, we can write $f_{yx}=\zeta(\lambda_y)\varphi(\lambda_x)$ where φ is "the" exciting power; substituting in (18′) and allowing λ_x to take on all values while λ_y is held fixed, we have the equivalent equation

$$\zeta(\lambda)=k_o\frac{J(\lambda)}{\lambda}\varphi(\lambda), \qquad (23)$$

k_o being a new constant.

The appearance of λ or ν in these equations is a characteristic result of quantum theory; except for this factor, (17′) and (23) agree with results obtained previously on quite a different basis.[6] The difference is due to the fact that here conservation of quanta, instead of energy, is assumed during the double process of emission and absorption, the energy balance being maintained at the expense of heat energy.

COMPARISON WITH EXPERIMENT

The theory here developed ought, if its basis is sound, to apply to band spectra such as that of iodine,[7] the quantum numbers for both intra-molecular vibrations of the atoms and rotation of the molecule playing the role of n while the electronic quantum number plays that of m. In the case of the rotation number, observation[7] suggests that thermal agitation is almost completely ineffective before re-emission occurs, so that we have case (1). Qualitatively, the increase in the number of "anti-Stokes" lines with rise of temperature is in accord with the theory, but quantitative observations are lacking.

Because of the generality of the basis underlying the present theory it seems quite possible, also, that it may apply to fluorescent liquids and solids. Experimental support from observations on eosin and resorufin was adduced in a former paper for Eq. (23) (with the factor λ omitted, which is of little consequence because the spectral range is so

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[6] Loc. cit., Eqs. (10) and (13). The argument there given can be reconstructed in harmony with present assumptions and then yields the results of this paper, but its significance remains doubtful because of the impracticability, pointed out above, of resolving black-body radiation into thermal and fluorescent components.

[7] Cf. W. Lenz, PZS 21, 691–2 (1920).

limited). In these cases it has been thought that band shape was independent of exciting frequency; if that is true, there is a good chance that (16), and (17) will hold for these substances, and evidence that they probably do hold is afforded by observations just published in the Physical Review by E. Merritt. Additional experiments on fluorescein are approaching completion in this laboratory and will be published soon by the present author.

In a qualitative way, it might be said that (16) expresses in mathematical form an explanation of the universal fact that, where a fluorescence band visibly overlaps the associated absorption band, either the former descends steeply or the latter rises steeply toward shorter wave-lengths, and the maximum fluorescence lies at a lower frequency than the maximum absorption. This arises, in the equation, from the extreme steepness of the black-body curve at ordinary temperatures. The physical explanation may be stated as follows. If we fix our attention upon a particular wave-length corresponding to a jump between two given quantum levels, then absorption of this wave-length is favored by abundance of particles in the level of lower energy whereas fluorescence is favored by abundance in the higher level; hence thermal agitation, by favoring abundance in the lower level at the expense of the higher, favors absorption rather than fluorescence at this wave-length. As the wave-length is decreased the difference in energy between the levels is increased and with it the effect of thermal agitation in favoring absorption more than it does fluorescence. The relative position of the two curves is thus accounted for.

Eq. (18) similarly throws light on the fact that Stokes' Law is, probably, never strictly true, and yet the exciting light can never be pushed to much longer wave-lengths than the fluorescence. The physical reason for this, already suggested by other writers, is that at ordinary temperatures quantum states of energy higher than normal by an amount corresponding to a large shift in wave-length very rarely occur as a consequence of thermal influence alone.

A special interest attaches to the question whether exact relations such as these hold for the fluorescence in liquids and solids because, although the breadth of the bands has been vaguely ascribed to the combination of thermal with electronic energy, yet no satisfactory start has yet been achieved toward a detailed theory.

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