

*The Conditions for Statistical Equilibrium between Atoms,
Electrons and Radiation.*

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§ 1. *Introduction.*

The principle of the reversibility of atomic processes was introduced by Klein and Rosseland* for the case of non-radiative encounters between atoms and free electrons. These authors pointed out that it is necessary for thermodynamic equilibrium in an enclosure in which the transference of atoms to higher stationary states takes place by collisions with free electrons without the emission or absorption of radiation, that the reverse process by which an atom falls from a higher to a lower stationary state, the whole of the surplus energy being spent in increasing the kinetic energy of a colliding electron, must occur to just a sufficient extent to balance the first process. It cannot, however, be proved from thermodynamic considerations alone that every process that occurs in an assembly in statistical equilibrium is exactly balanced by the reverse process taking place with the same frequency, since, as has been shown by Fowler,† there may be cycles of inseparable processes, each of which does not balance individually, although the whole cycle forms a "unit mechanism" which balances by itself in any assembly in statistical equilibrium.

It seems plausible, however, to suppose that all atomic processes are reversible, or, more exactly, that if after any encounter all the velocities are reversed, then the whole process would just repeat itself backwards, the systems finally leaving the scene of action being the same as the original systems in the first process and having the reverse velocities. With this assumption, to which there are no known exceptions, each kind of encounter must be just as likely to occur as its converse in which every velocity has changed sign, the whole process taking place backwards, since there is now perfect symmetry between past and future time. This converse is not the same as the reverse process referred to above, in which the velocities before and after the encounter are the *same* as the velocities after and before the original encounter respectively. What have been called the converse and reverse encounters are, however, related in such a way that one can be obtained from the other by successive reflections in three

* Klein and Rosseland, 'Zeits. f. Phys.,' vol. 4, p. 46 (1921).

† Fowler, 'Phil. Mag.,' vol. 47, p. 263 (1924).

mutually perpendicular mirrors at rest relative to the assembly as a whole, and so their frequencies of occurrence must be equal, since the assembly is everywhere isotropic. This proves that every kind of encounter occurs with the same frequency as the reverse encounter, the two together leaving unaltered both the numbers of the various kinds of systems, and also their distributions in velocity or momentum. This condition is sufficient for statistical equilibrium, and on the above-made assumption of the reversibility of the encounters, it is necessary.

This principle of the detailed balancing of atomic encounters with their reverse encounters has been used, without reference to the distribution of the atoms in momentum, by Kramers* and Milne† for the process of ionisation by the absorption of radiation and its reverse, and by Fowler‡ for the process of ionisation by collision and its reverse. It has also been applied, with reference to the distribution in momentum of the systems concerned, by W. Pauli, jun.,§ for the process of scattering of radiation by free electrons, and by Einstein and Ehrenfest,|| without going into details, for the most general processes of absorption and emission of radiation by atoms.

It is possible, however, to apply the principle quite simply, and at the same time exactly, to the general case of encounters between an arbitrary number of systems, for processes which may or may not involve radiation. This will give the general conditions for statistical equilibrium, which can then easily be applied to any special process, all the relations between the probabilities of the processes which the principle can give being at once obtained.

§ 2. *Law of Transformation of Density-in-Momentum.*

In order not to interrupt the argument later, we shall here deduce the law of transformation of the density-in-momentum per unit volume of an assembly of similar particles moving in any manner, but such that the law of distribution of velocity is constant in space and time.

We consider only that group of particles, the components of whose momenta lie between the arrow limits M_x, M_y, M_z and $M_x + dM_x, M_y + dM_y, M_z + dM_z$. Let there be $\rho(M_x M_y M_z) dM_x dM_y dM_z$ such particles per unit volume, so that ρ is the density-in-momentum per unit volume, and let M_t be the mass of any one of them multiplied by c .

* Kramers, 'Phil. Mag.', vol. 46, p. 836 (1923).

† Milne, 'Phil. Mag.', vol. 47, p. 209 (1924).

‡ Fowler, 'Phil. Mag.', vol. 47, pp. 257, 416 (1924).

§ Pauli, 'Zeits. f. Phys.', vol. 18, p. 272 (1923).

|| Einstein and Ehrenfest, 'Zeits. f. Phys.', vol. 19, p. 301 (1923).

Now transform to a frame of reference which moves with velocity $(V, 0, 0)$ relative to the original one, and use dashed letters to denote the values of the corresponding quantities for the same group of particles measured in this new frame of reference. Then

$$M_x' = \beta \left(M_x - \frac{V}{c} M_t \right), \quad M_y' = M_y, \quad M_z' = M_z, \quad M_t' = \beta \left(M_t - \frac{V}{c} M_x \right),$$

where

$$\beta = \left(1 - \frac{V^2}{c^2} \right)^{-\frac{1}{2}}.$$

The variables M_x, M_y, M_z, M_t are not independent, but are connected by the formula

$$M_t^2 - (M_x^2 + M_y^2 + M_z^2) = M_0^2 c^2,$$

where M_0 is the invariant-mass of a particle. Hence

$$\frac{\partial (M_x' M_y' M_z')}{\partial (M_x M_y M_z)} = \frac{\partial M_x'}{\partial M_x} = \beta \left(1 - \frac{V}{c} \frac{\partial M_t}{\partial M_x} \right) = \beta \left(1 - \frac{V}{c} \frac{M_x}{M_t} \right) = \frac{M_t'}{M_t}.$$

Now $\rho (M_x M_y M_z) dM_x dM_y dM_z$, being the number per unit volume of a certain group of specified particles, transforms according to the same law as the reciprocal of a volume moving with the velocity of the particles, that is, the same law as M_t . Hence

$$\frac{\rho (M_x M_y M_z) dM_x dM_y dM_z}{M_t} = \frac{\rho' (M_x' M_y' M_z') dM_x' dM_y' dM_z'}{M_t'},$$

so that

$$\rho (M_x M_y M_z) = \rho' (M_x' M_y' M_z').$$

Therefore the density-in-momentum per unit volume is invariant under a Lorentz transformation.

It is on account of the simplicity of this result that we shall use densities-in-momentum instead of densities-in-velocity in the following investigations.

§ 3. Equilibrium Conditions for Non-Radiative Processes.

Let us first take the case of an n -body process in which no radiation is either emitted or absorbed. We consider only those encounters between the n systems in which (for each value of r) the r th system has initially a momentum lying within an infinitesimal three-dimensional region δM_r about a certain specified value, and in which, as a result of the process, n' systems leave the scene of action, the r th having finally a momentum lying within an infinitesimal three-dimensional region $\delta M_r'$ about another specified value. The word system is here used to denote any molecule, atom, or ion in any stationary

state, or a free electron, or anything else that can take part in an atomic process except a quantum of radiation. Two atoms or molecules of the same kind, but in different stationary states, are counted as two different kinds of system. The n' systems after the process may be of an entirely different nature from the original n , subject only to the condition that they are composed of the same constituents. It is assumed that the density is sufficiently small for the systems to be practically outside each other's sphere of influence except during an encounter.

Let the velocity of the centre of gravity of one set of systems taking part in the process and having momenta lying within the specified regions be the vector V . Transform to a frame of reference (which we shall call the normal frame of reference) in which this centre of gravity is at rest, and use the suffix $_0$ to denote quantities measured in it. The frequency in this normal frame of reference with which the encounters under consideration occur, is proportional to the product of the concentrations (*i.e.*, the numbers per unit volume) in this frame of reference of the systems of each type that take part in them and have their momenta within the specified domains. If we assume for the present that the momenta before and after an encounter are independent, this frequency must be of the form

$$\rho_{10}\delta M_{10} \cdot \rho_{20}\delta M_{20} \dots \rho_{n0}\delta M_{n0} \cdot \phi \cdot \delta M_{10}'\delta M_{20}' \dots \delta M_{n'0}', \quad (A)$$

where the ρ 's are the densities-in-momentum per unit volume of the systems before the encounter, and ϕ is a probability coefficient, which is necessarily independent of the temperature T .

We shall now take, for the variables which determine the encounters under consideration, the momenta of the systems relative to the normal frame of reference and the domains δM_{r0} and $\delta M_{r0}'$, together with the velocity V ; so that, provided these latter momentum domains are kept fixed, ϕ will be independent of V and a function only of the momenta of the systems relative to the normal frame of reference, since the velocity of the original frame of reference no longer has anything to do with the question.

In the same way the frequency of the reverse encounter must be of the form

$$\rho_{10}'\delta M_{10}' \cdot \rho_{20}'\delta M_{20}' \dots \rho_{n0}'\delta M_{n'0}' \cdot \phi' \cdot \delta M_{10}\delta M_{20} \dots \delta M_{n0}, \quad (B)$$

where the ρ 's are the densities-in-momentum per unit volume of the systems taking part in the reverse encounter, and ϕ' is a probability coefficient having the same properties as ϕ .

The principle of detailed balancing allows us to equate these two expressions, with the result

$$\rho_{10}\rho_{20} \dots \rho_{n0}\phi = \rho_{10'}\rho_{20'} \dots \rho_{n'0'}\phi'. \quad (1)$$

The provisional assumption that we made concerning the independence of the momenta of the systems before and after the encounter is, of course, not true. The law of conservation of energy will provide one relation between them, and, since the resultant momentum in the normal frame of reference is infinitesimal, there must be six more relations between the momenta of the individual systems in this frame of reference. There may also be other such relations for particular types of processes. The effect of this will be that the frequency of the encounters will vanish for all values of the initial and final momenta which do not satisfy these conditions, so that we must suppose ϕ (and ϕ') to vanish for these values of the momenta; while for values of the momenta which do satisfy all the conditions, there will be fewer differentials occurring in the value of the frequency than there are in expression (A), which must, therefore, be corrected. This will not, however, affect the validity of equation (1) since, whichever are the differentials which are necessary and sufficient to define the encounters, and which, therefore, appear in the corrected expression (A), the same differentials may be taken as defining the reverse encounters, owing to our assumption of complete reversibility, and will thus be the only ones appearing in the corrected expression (B), so that they will just cancel out of equation (1). Even if we did not take the same momenta as independent variables for the direct and reverse processes, the Jacobian connecting the differentials in the corrected expressions (A) and (B) would be independent of the temperature and of the velocity V , so that it could be absorbed in ϕ or ϕ' , and equation (1) would still be formally true. Hence, this equation may be taken to be true quite generally for any radiationless encounter.

If we now transform back to the original frame of reference in which the assembly as a whole is at rest and in statistical equilibrium, then owing to the invariance of density-in-momentum per unit volume, equation (1) becomes

$$\rho_1\rho_2 \dots \rho_n\phi = \rho_1'\rho_2' \dots \rho_{n'}'\phi'. \quad (2)$$

If the systems are distributed in momentum according to Maxwell's law, then we can put

$$\rho_r = A_r e^{-(E_r + \epsilon_r)/kT}, \quad \rho_r' = A_r' e^{-(E_r' + \epsilon_r')/kT}, \quad (3)$$

where E_r and ϵ_r are the internal and kinetic energies of the r th system respectively, and the A 's are coefficients which are independent of the momenta but functions of the temperature. Two A 's and E 's are, of course, equal when they refer to systems of the same kind.

The law of conservation of energy gives

$$\Sigma (E_r + \varepsilon_r) = \Sigma (E_r' + \varepsilon_r'),$$

provided the zero energies relative to which the internal energies of the systems are measured are properly chosen. Hence, substituting the values of ρ given by (3) in (2), we get

$$A_1 A_2 \dots A_n \phi = A_1' A_2' \dots A_n' \phi'. \quad (4)$$

The fact that the velocity V has disappeared from this equation means that Maxwell's law is satisfied. The most general distribution law which makes V disappear is that obtained from Maxwell's law by substituting for the temperature an arbitrary function of the temperature, which must be the same for all the kinds of system. The present method does not enable us to tell what this function is.

Since the A 's are independent of the momenta, it follows from (4) that the ratio of ϕ to ϕ' must be independent of the momenta of the systems relative to the normal frame of reference, provided they satisfy the necessary conditions for the encounter to be possible. Hence ϕ and ϕ' in (4) may, if desired, be taken to represent the average values of the probability coefficients for all values of the momenta, the average being calculated according to any law. This result is true, of course, only for the particular definitions of ϕ and ϕ' that we have chosen.

The concentrations of the various kinds of systems are given by formulæ of the type

$$c_r = A_r e^{-E_r/kT} \iiint e^{-\varepsilon_r/kT} \delta M_r. \quad (5)$$

The exact evaluation of the triple integrals involves Bessel functions, and has been done by F. Jüttner in his paper on Maxwell's velocity distribution law in the theory of relativity.* At all ordinary temperatures, however, the relativity correction of Newtonian mechanics is entirely negligible, so that we may put the triple integral equal to $(2\pi m_r kT)^{\frac{3}{2}}$ where m_r is the mass of the system considered. With this approximation, we obtain from (4) and (5) the reaction equilibrium condition

$$\frac{c_1' c_2' \dots c_n'}{c_1 c_2 \dots c_n} = \frac{\phi}{\phi'} \left\{ \frac{m_1' m_2' \dots m_n'}{m_1 m_2 \dots m_n} \right\}^{\frac{3}{2}} (2\pi kT)^{\frac{3}{2}(n'-n)} e^{(\Sigma E_r - \Sigma E_r')/kT}. \quad (6)$$

The left-hand side is the equilibrium constant K of the reaction. For certain elementary processes its value is immediately obvious; for example,

* Jüttner, 'Ann. der Phys.,' vol. 34, p. 856 (1911).

if the process is a simple collision which leaves the systems in the same state as they were before, then K is equal to unity, while if the process is an inelastic or superelastic collision between an atom and an electron, then by Boltzmann's law

$$K = \frac{q_2}{q_1} e^{-(E_2 - E_1)/kT}$$

where q_1 and q_2 are the statistical weights, and E_1 and E_2 the internal energies of the atom before and after the process respectively. Whenever K is known and one of the probability coefficients is known, then the other can be calculated from equation (6), this being all the information that the principle of detailed balancing can supply. There is, of course, one equation (6) for every kind of encounter that can take place.

If any system is unchanged except in kinetic energy by the encounter, such as the electron in an inelastic or superelastic collision, then this system may be omitted from consideration in the application of equation (6) since its contribution to either side cancels.

If equation (6) is differentiated logarithmically with respect to T , then the probability coefficients disappear, leaving the equation

$$\begin{aligned} \frac{d}{dT} \log K &= \frac{1}{kT^2} (\Sigma E_r' - \Sigma E_r) + \frac{3}{2} \frac{n' - n}{T} \\ &= \frac{1}{kT^2} \{ \Sigma (E_r' + \bar{\epsilon}_r') - \Sigma (E_r + \bar{\epsilon}_r) \} \end{aligned}$$

where $\bar{\epsilon}_r = \frac{3}{2}kT$ and is the mean kinetic energy of translation of the r th kind of system. This is just the van't Hoff isochore, the expression in the bracket on the right being the "heat of reaction per molecule."

It is interesting to notice that this equation is still exactly true with relativity mechanics. To prove this, differentiate (4) and (5) logarithmically with respect to T , obtaining

$$\Sigma \frac{d}{dT} \log A_r = \Sigma \frac{d}{dT} \log A_r'$$

$$\begin{aligned} \text{and} \quad \frac{d}{dT} \log c_r &= \frac{d}{dT} \log A_r + \frac{E_r}{kT^2} + \frac{1}{kT^2} \frac{\iiint \epsilon_r e^{-\epsilon_r/kT} \delta M_r}{\iiint e^{-\epsilon_r/kT} \delta M_r} \\ &= \frac{d}{dT} \log A_r + \frac{E_r + \bar{\epsilon}_r}{kT^2}. \end{aligned}$$

$$\begin{aligned} \text{Hence} \quad \frac{d}{dT} \log K &= \sum \frac{d}{dT} \log c_r' - \sum \frac{d}{dT} \log c_r \\ &= \frac{1}{kT^2} \left\{ \sum (E_r' + \bar{\epsilon}_r') - \sum (E_r + \bar{\epsilon}_r) \right\} \end{aligned}$$

as before.

In the preceding investigation we supposed that the encounters considered were defined by the condition that the systems taking part in them must have momenta lying within certain specified regions relative to a frame of reference of given velocity V , such that the resultant momentum in it of all the systems taking part in an encounter lies within a small domain about the value zero. This last condition is not really necessary. Any other frame of reference would do equally well instead, the encounters considered being defined by the values of the momenta relative to it, together with its velocity (V' say) relative to the assembly as a whole, so as to make the probability coefficients independent of V^1 . This remark applies also to the following investigations of radiative processes, although, for definiteness, it is convenient to think in terms of the normal frame of reference, this being the one in which the resultant momentum of the systems and the radiation taking part in an encounter is infinitesimal.

§ 4. *Equilibrium Conditions for Processes Involving the Absorption of Radiation.*

We shall now consider what modifications are necessary in the expressions (A) and (B) for the frequencies of certain encounters and their converses when the process takes place with absorption of radiation. To define the encounters to be considered it is necessary to specify, in addition to all the preceding quantities, the infinitesimal solid angle $d\Omega$ in which the direction of the radiation must lie, and also, for certain processes such as the photo-electric effect, the limits between which the frequency ν of the radiation must lie. This latter specification is unnecessary for other processes, such as the transference of an atom to a higher stationary state by incident radiation, in which only radiation of one particular frequency can be absorbed. These additional specifications must be made relative to the normal frame of reference, and the new differentials $d\Omega_0$ and perhaps $d\nu_0$ must appear (provisionally) in (A) and (B). The same remarks as before apply concerning the redundancy of some of the variables: whichever differentials are omitted from the new expression (A) to correct for this, the same differentials may be chosen as the ones to be

omitted from the new (B), and the result obtained by equating the new (A) and (B) will be unaffected.

Concerning the other factors in the new expressions (A) and (B), the most natural assumptions to make are that the frequency of the absorption process is directly proportional to the intensity of the radiation of the right frequency and in the right direction to be absorbed, and that the frequency of the reverse emission process is independent of the intensity of the incident radiation. With these assumptions the expression (A) must be multiplied by $I_0(\nu_0)$, the intensity in the normal frame of reference, and then no more changes are required in (A) or (B). The probability coefficients ϕ and ϕ' are, as before, independent of T and V , and they are also independent of the intensity of the radiation, though they may depend on the direction of the radiation absorbed, since this comes in the specification of the encounters under consideration.

The equation (1) now becomes

$$I_0(\nu_0) \rho_{10} \rho_{20} \dots \rho_{n0} \phi = \rho_{10}' \rho_{20}' \dots \rho_{n0}' \phi'. \quad (1A)$$

Since $I(\nu) \nu^{-3}$ is invariant under a Lorentz transformation,* equation (2) becomes

$$I(\nu) \nu^{-3} \nu_0^3 \rho_1 \rho_2 \dots \rho_n \phi = \rho_1' \rho_2' \dots \rho_n' \phi'. \quad (2A)$$

Substituting the values for the ρ 's given by (3), and using the fact that the energy equation is now

$$\Sigma(E_r + \epsilon_r) + h\nu = \Sigma(E_r' + \epsilon_r'),$$

we find that

$$I(\nu) \nu^{-3} \nu_0^3 e^{h\nu/kT} A_1 A_2 \dots A_n \phi = A_1' A_2' \dots A_n' \phi'. \quad (4A)$$

The only terms occurring in this equation that depend on the velocity V are $I(\nu)$ and ν , so that, by varying V and keeping T constant, we see that $I(\nu) \nu^{-3} e^{h\nu/kT}$ is independent of ν , and from Wien's displacement law it must also be independent of the temperature. The assumptions that we made have thus led to Wien's radiation formula.

In order to obtain Planck's law of black-body radiation, we must assume that the reverse emission process is stimulated by incident radiation of the same frequency and in the same direction as the emitted radiation. To take this effect into account we must multiply the expression (B) for the frequency of the reverse process by the additional factor $[1 + \alpha I_0(\nu_0)]$, where the "stimulation coefficient" α is, like ϕ and ϕ' , independent of T and V . This

* See, for example, Pauli, *loc. cit.*, p. 282.

additional factor should occur on the right-hand side of equation (1A), and so (2A) will become

$$I(\nu) \nu^{-3} \nu_0^3 \rho_1 \rho_2 \dots \rho_n \phi = \rho_1' \rho_2' \dots \rho_n' [1 + \alpha I(\nu) \nu^{-3} \nu_0^3] \phi' \quad (2B)$$

and (4A) will become

$$I(\nu) \nu^{-3} \nu_0^3 e^{h\nu/kT} A_1 A_2 \dots A_n \phi = A_1' A_2' \dots A_n' [1 + \alpha I(\nu) \nu^{-3} \nu_0^3] \phi'$$

or

$$e^{h\nu/kT} A_1 A_2 \dots A_n \phi = \left[\frac{\nu^3}{\nu_0^3 I(\nu)} + \alpha \right] A_1' A_2' \dots A_n' \phi'. \quad (4B)$$

Planck's radiation formula may be written in the form

$$e^{h\nu/kT} = \frac{2h}{c^2} \frac{\nu^3}{I(\nu)} + 1.$$

This will agree with (4B) provided

$$\frac{2h\nu_0^3}{c^2} A_1 A_2 \dots A_n \phi = A_1' A_2' \dots A_n' \phi' \quad (7B)$$

and

$$\alpha = \frac{c^2}{2h\nu_0^3}. \quad (8B)$$

If we introduce the concentrations c_r given by equation (5) and neglect the modifications of ordinary mechanics required by the theory of relativity, then equation (7B) becomes

$$\frac{c_1' c_2' \dots c_n'}{c_1 c_2 \dots c_n} = \frac{\phi}{\phi'} \frac{2h\nu_0^3}{c^2} \left\{ \frac{m_1' m_2' \dots m_n'}{m_1 m_2 \dots m_n} \right\}^{\frac{1}{2}} (2\pi kT)^{\frac{1}{2}(n'-n)} e^{(\Sigma E_r - \Sigma E_r')/kT}. \quad (6B)$$

This is the reaction equilibrium condition corresponding to equation (6) for a process involving the absorption of radiation. It differs only through having, on the right-hand side, the additional factor $\frac{2h\nu_0^3}{c^2}$. Since this does not involve the temperature, on differentiating by the temperature the usual van't Hoff isochore will be obtained, which therefore holds for photo-chemical reactions. If a reaction can take place either with or without the absorption of radiation, we get the following relation from (6) and (6B):—

$$\frac{\phi_1}{\phi_1'} = \frac{\phi_2}{\phi_2'} \frac{2h\nu_0^3}{c^2},$$

where ϕ_1 and ϕ_1' refer to the non-radiative process, and ϕ_2 and ϕ_2' to the radiative process.

The other condition necessary for equilibrium with a field of radiation

obeying Planck's law, namely, equation (8B), gives the value of the stimulation coefficient α , which is seen to be independent of the nature of the atomic process concerned, and to vary inversely as the cube of the frequency of the radiation, measured in the same frame of reference as that in which α is measured.

§ 5. Equilibrium Conditions for General Radiative Processes.

Up to the present, the only radiative processes we have considered are those in which radiation is either emitted or absorbed. There are, however, processes by which a quantum is absorbed and another quantum (or perhaps the same one, if this has any meaning) is emitted, in general in a different direction and with a different frequency. The scattering of radiation by atoms or free electrons is an example of such a process. Also there may be more complicated processes by which more than one quantum is absorbed and more than one is emitted. The theory can easily be extended to include all such cases.

We shall assume that every process is stimulated by external incident radiation whose frequency is equal to that of any of the quanta emitted by the process, the stimulation coefficient being given in each case by equation (8B). Expression (A) for the frequency of the encounters must now be multiplied by a factor $I_0(\nu_0)$ for each quantum absorbed, and a factor $[1 + \alpha I_0(\nu_0)]$ for each quantum emitted by the process, ν_0 taking successively the values of the frequencies of each of these quanta in the normal frame of reference. Similarly, expression (B) must be multiplied by the corresponding factors for the reverse encounter. These two sets of factors must be multiplied into the left and right sides of equation (1) respectively, and the corresponding sets of factors in which $I_0(\nu_0)$ has been replaced by $I(\nu) \nu^{-3} \nu_0^3$ must be multiplied into the left and right sides of equation (2). If we substitute as before the values for the ρ 's given by (3), and use the fact that the energy equation is now

$$\Sigma (E_r + \varepsilon_r) + \Sigma h\nu = \Sigma (E_r' + \varepsilon_r') + \Sigma h\nu',$$

where the ν 's are the frequencies of the absorbed quanta, and the ν 's those of the emitted quanta, we shall obtain the following equation, corresponding to (4B):—

$$\begin{aligned} \Pi \left[\frac{\nu'^3}{\nu_0^3 I(\nu')} + \alpha' \right] e^{\Sigma h\nu/kT} A_1 A_2 \dots A_n \phi \\ = \Pi \left[\frac{\nu^3}{\nu_0^3 I(\nu)} + \alpha \right] e^{\Sigma h\nu'/kT} A_1' A_2' \dots A_n' \phi', \end{aligned} \quad (4c)$$

where the symbol Π before a factor means the product of all the factors like

that one for all the frequencies of the emitted (or absorbed) quanta. From Planck's law of radiation

$$\frac{\nu^3}{I(\nu)} = \frac{c^2}{2h} (e^{h\nu/kT} - 1),$$

so that, using (8B)

$$\frac{\nu^3}{\nu_0^3 I(\nu)} + \alpha = \frac{c^2}{2h\nu_0^3} e^{h\nu/kT}.$$

If this is substituted in (4c) the ν 's will disappear, leaving the equation

$$\Pi \left[\frac{2h\nu_0^3}{c^2} \right] A_1 A_2 \dots A_n \phi = \Pi \left[\frac{2h\nu_0'^3}{c^2} \right] A_1' A_2' \dots A_n' \phi', \quad (7c)$$

which is the equilibrium conditions corresponding to (7B) for processes in which more than one quantum take part.

The assumptions made have thus enabled us to satisfy all the conditions necessary for thermodynamic equilibrium. They are the same as those made by Einstein and Ehrenfest* for processes in which only one system takes part. (Their method can, however, easily be extended to the general case.) Einstein and Ehrenfest do not consider the relations which must exist between the probability coefficients for two encounters of which one is the same as the other except for a uniform translational velocity superposed on everything. It would be necessary to show that these relations are satisfied in order to prove that statistical equilibrium is possible with the assumptions made.†

By the present method it can easily be shown that there are no reasonable alternative assumptions. For each absorbed quantum, the ratio of the additional factors required in expressions (A) and (B) must be $e^{h\nu/kT}$ multiplied by something independent of ν (and so of the velocity V) in order that V may disappear from equation (4c), leaving an equation like (7c). Now if T is eliminated from this expression for the ratio by means of Planck's radiation formula, the only rational result it is possible to obtain is

$$1 + \frac{2h}{c^2} \frac{\nu^3}{I(\nu)} \quad \text{or} \quad \frac{\alpha I_0(\nu_0) + 1}{\alpha I_0(\nu_0)}$$

* Einstein and Ehrenfest, *loc. cit.*

† The equilibrium conditions for simple emission and absorption have been considered, in a way similar to that of Einstein and Ehrenfest, in a paper by O. Halpern ('Zeits. f. Phys.,' vol. 21, p. 151 (1924)). This author has his probability coefficients for the emission and absorption depending on the temperature, instead of *making* them independent of the temperature as the principles of statistical mechanics demand. The conclusion to which he comes, that the stimulated radiation need not be emitted in the same direction as the stimulating radiation, can hardly be correct, since unless they are in the same direction, their frequencies will not be equal in all systems of co-ordinates.

multiplied by something independent of $I_0(\nu_0)$, in agreement with the ratio actually assumed; from which, using the experimental fact that the absorption is always proportional to the intensity of the incident radiation, the probability of the emission process must be proportional to $[1 + \alpha I_0(\nu_0)]$. In general it is possible to obtain other results owing to the arbitrary function of T in the expression for the ratio, but these will all contain $I(\nu)$ under a logarithm, and it is very unlikely that a probability would be of that form.

Hence it is a general law that:—

Any atomic process which results in the emission of one or more quanta of radiation is stimulated by external incident radiation of the same frequency as that of any of the emitted quanta, the ratio of the amount of stimulated emission to the amount of spontaneous emission being proportional to the intensity of the incident radiation divided by the cube of its frequency and independent of the nature of the process concerned, and the direction of the stimulated radiation being the same as that of the incident radiation.

This law must be true even for radioactive processes, provided they are not exceptions to the rule that all processes are reversible. This means that the rate of disintegration of any radioactive substance that emits γ -rays will be increased by the incidence of external γ -rays of the same frequency. The effect will, however, be very small owing to the fact that the stimulation coefficient varies inversely as the cube of the frequency.

The general reaction equilibrium condition for any radiative process with non-relativity mechanics is similar to (6B), there being a factor like $\frac{2h\nu_0^3}{c^2}$ in the numerator of the right-hand side for each absorbed quantum, and one in the denominator for each emitted quantum. If the probability coefficients are unknown, then the conditions for equilibrium, for radiative or non-radiative processes, take the form that

$$\frac{c_1' c_2' \dots c_n'}{c_1 c_2 \dots c_n} e^{(\sum E_r' - \sum E_r) / kT} T^{\frac{1}{2}(n-n')}$$

must be independent of the temperature and concentrations for any two sets of n and n' systems in the assembly that are composed of the same constituents, a constituent being an electron or a nucleus of an atom. This follows from the fact that there must be processes or series of processes by which one set is changed into the other, or it could not be known that they were composed of the same constituents. These conditions are satisfied if, for each system,

$$c_r e^{E_r/kT} T^{-\frac{1}{2}} = e^{i_r} \cdot \Pi_r f_k(T),$$

i_r being a constant (related to the chemical constant of the r th system), and there being one $f(T)$ for each constituent in the assembly, the symbol Π_r meaning the product of the $f(T)$'s for all the constituents of the r th system. The $f(T)$'s must be chosen so as to make the concentration of each constituent have an assigned value. Hence the concentrations of the systems are completely determined by the above equation when the chemical constants are known.

For the discussion of equilibrium problems, quanta of radiation cannot be regarded as very small particles of matter moving with very nearly the speed of light. There are two important points in which this picture is inadequate. In the first place the small particles could not (according to ordinary statistical theory) have any stimulating effect on processes by which they are emitted, and they would therefore be distributed in momentum according to Maxwell's law, which is the same as being distributed in energy (or frequency) according to Wien's radiation law. Secondly, the concentration of quanta in thermodynamic equilibrium is not arbitrary, as is the case with all kinds of material particles, but is a definite function of the temperature.

§ 6. *Application to the Process of Ionisation of a Gas.*

As an illustration of the method, we shall obtain formulæ for the degree of ionisation of a monatomic gas in statistical equilibrium. For simplicity we shall neglect relativity effects, and also, to begin with, we shall suppose that the atoms when not ionised have only one stationary state, whose ionisation potential is χ_1 . Let c and c_1 be the concentrations of ions and neutral atoms, and M and M_1 their masses, and let m be the mass of an electron. Since the gas as a whole is electrically neutral, the concentration of the free electrons is the same as that of the ions, *i.e.*, c .

For the process of ionisation by collision, the equilibrium condition is given by equation (6). Since the ionising atom or electron may be omitted from consideration, we get

$$\frac{c^2}{c_1} = \frac{\phi}{\phi'} \left(\frac{mM}{M_1} \right)^{\frac{3}{2}} (2\pi kT)^{\frac{3}{2}} e^{-\chi_1/kT}. \quad (i)$$

If the ionisation takes place by the absorption of radiation, equation (6B) must be used, which will give an equation the same as (i) except for a constant factor. If both ionisation processes can take place, the two equations must be identical, and this will give a relation between the probability coefficients for the two processes and their reverses.

The fraction x of atoms ionised is given by

$$x = \frac{c}{c + c_1}, \quad (ii)$$

and the total pressure P may be assumed to be given by the perfect gas law

$$P = (2c + c_1) kT. \quad (iii)$$

Hence

$$c = \frac{P}{kT} \frac{x}{1+x}, \quad c_1 = \frac{P}{kT} \frac{1-x}{1+x}, \quad (iv)$$

so that (i) becomes

$$\frac{x^2 P}{1-x^2} = \frac{\phi}{\phi'} \left(\frac{2\pi m M}{M_1} \right)^{\frac{3}{2}} (kT)^{\frac{3}{2}} e^{-x_1/kT}.$$

This is the same as Saha's ionisation formula, except for a constant factor.

For the general case when the neutral atom has several possible stationary states, let the ionisation potential for the r th state be χ_r , and let the concentration of the atoms in the r th state be c_r . Instead of equation (i) we now have a series of equations of the type

$$\frac{c^2}{c_r} = \frac{\phi_r}{\phi'} \left(\frac{m M}{M_1} \right)^{\frac{3}{2}} (2\pi kT)^{-\frac{3}{2}} e^{-\chi_r/kT}.$$

The only change necessary in equations (ii), (iii) and (iv) is to replace c_1 by Σc_r , the summation being taken over all the non-ionised stationary states. The ionisation equation now becomes

$$\begin{aligned} \frac{1-x^2}{x^2 P} &= \frac{\Sigma c_r}{c^2 kT} \\ &= \left(\frac{M_1}{2\pi m M} \right)^{\frac{3}{2}} (kT)^{-\frac{3}{2}} \Sigma_r \frac{\phi_r'}{\phi_r} e^{\chi_r/kT}. \end{aligned}$$

This is of the same form as the formula obtained by Fowler,* which involves statistical weights instead of probability coefficients.

In conclusion, the writer wishes to express his thanks to Mr. R. H. Fowler for his kind interest and assistance in this work.

Summary.

The principle that every process which occurs in an assembly in thermodynamic equilibrium is exactly balanced by the reverse process occurring to the same extent is applied to the general case of n -body encounters, both radiative and non-radiative processes being considered. Reaction equilibrium

* Fowler, 'Phil. Mag.', vol. 45, p. 21 (1923).

conditions are obtained involving the probabilities of the direct and reverse processes. It is shown that van't Hoff's isochore is of universal validity, even for radiative processes and with relativity mechanics.

From Planck's law of radiation it is deduced that every process by which radiation is emitted is stimulated by external radiation of the same frequency, the ratio of stimulated to spontaneous emission being independent of the nature of the process, and inversely proportional to the cube of the frequency.

The method is applied to the deduction of formulæ for the degree of ionisation of a gas.

Absorption and Dispersion of Thallium Vapour.

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[PLATE 8.]

In recent years the study of absorption of light by vapours of metals of Group III of the periodic table has attracted the attention of many physicists. For the chief difference between the spectra of metals of this group and those of the elements of the first two groups is that the convergence frequency of the principal series is smaller than that of the subordinate series, a fact not easily reconciled with the quantum theory, unless the observed principal series is of the second type, as Foote and Mohler have pointed out in "The Origin of Spectra."

Recent experiments of Grotrian* and Carroll† indicate that, in the case of metals of this group, the ground orbit of the valence electron is $1, \pi$ orbit, and not $1, \sigma$ orbit, as in the case of other metals. According to Bohr's theory, for the vapour of an element to absorb lines corresponding to a given series in its spectrum, it is necessary that in the vapour there should be a fairly

* "Absorption Spectra of Tl and in Vapours," W. Grotrian, 'Zeits. f. Physik,' vol. 12, 3 and 4, pp. 218-31 (1922).

† "Note on the Spectra of Al Sub-group," J. A. Carroll, 'Roy. Soc. Proc.,' A, vol. 103, pp. 334-39 (May, 1923). For a good general account of the work done on this subject the reader is referred to Carroll's paper.