

It is easy to see that this equals

$$\left\{ \frac{(A\nu + N\nu)!}{A\nu! N\nu!} \right\}^{d\nu} \dots (11)$$

or in other words,

$$S_{\nu} d\nu = d\nu \cdot k \log \frac{(A\nu + N\nu)!}{A\nu! N\nu!} \dots (12)$$

$S_{\nu} d\nu$ now denoting entropy of radiation having their frequency between ν and $\nu + d\nu$.

The value of S_{ν} , U_{ν} can be calculated with the aid of the above expression, and the relation $\frac{dS_{\nu}}{dU_{\nu}} = \frac{1}{T}$, but as these calculations are to be found in every standard text-book on radiation, they are not reproduced here.

33. ON THE INFLUENCE OF RADIATION ON IONIZATION EQUILIBRIUM*

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1.

The chief desideratum of the present theories of thermal ionization of gases is that they fail to take any account of the influence of radiation on ionization equilibrium. Yet it can easily be shown, and it has been pointed out by many investigators, that radiation plays an essential role in many physical and astrophysical phenomena. Russell¹ pointed out the possible influence of radiation in the barium-sodium anomaly in the solar photosphere, where barium is found to be almost completely ionized, while sodium is only partially ionized, though both elements possess identical ionization potentials. He traced the phenomena to the fact that Ba^{+} -atoms are susceptible to photospheric radiation, because the resonance lines lie at 4934, 4554, while Na^{+} -atoms are not so, because their resonance lines probably lie far in the ultra-violet. Milne² points out that radiation pouring out through the solar atmosphere is at a higher temperature than the atmosphere itself, and hence the observed ionization is at least partly due to radiation. In recent years, experiments³ have been done in which comparatively cool vapours of alkalis have been ionized by ultra-violet radiation lying beyond the convergence frequency of the principal series of the element. In such cases, the ionization is a purely radiation effect. To the same class of phenomena belong the familiar absorption experiments of Wood and others, where vapours of metals are illuminated by continuous light. In this case the atoms are not ionized, but as a result of the interaction between matter and radiation the valency electron is lifted to higher orbits. There is, in fact, no essential difference between this class of phenomena and phenomena known as photo-chemical reactions, only in the latter case the unit mechanism of reaction is rather obscure.

The treatment of this class of phenomena from the theoretical side is fraught with several difficulties, viz. (1) the mechanism of absorption of a pulse of light by an atom has not yet been tackled successfully on the quantum-mechanical basis; (2) in a reaction of this type, the reacting pulses do not all have the same frequency, *i.e.* the absorption lines have a finite breadth. This means that when pulses slightly differing from the resonance lines collide with the atom, there is a probability of their being absorbed, but the value of this probability factor varies from a maximum for the centre of the absorption line to rapidly decreasing values on both sides of the centre. Again, the maximum absorption varies from line to line. Thus Füchtbauer found that for the same intensity D_2 is twice as strongly absorbed as D_1 .

Up to the present time neither the physical basis of fine width of absorption lines has been cleared up, nor are we in possession of any formula for absorption applicable to all the lines of a series.

2.

The attempts which have been made to deal with the interaction between matter and radiation⁴ may be broadly subdivided into two classes—(1) those based on the methods used in the kinetic theory of gases; (2) those based on thermodynamical methods. To the first category belong the works of Milne⁵ "On the Statistical Equilibrium in relation to Photoelectric Effect," and of R. H. Fowler⁶ "On Statistical Equilibrium and the Mechanism of Ionization by Electronic Impacts." In these cases some knowledge or some assumption regarding the details of the unit mechanism of reaction is essential. Milne assumes that high temperature ionization is largely a volume photoelectric phenomenon, while Fowler treats the case where

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¹ Russell, *Astrophysical Journal*, lvi. May 1922.

² Milne, in a note to 'Nature', see *Month. Notices R. A. S.* June 1925.

³ Foote & Mohler, *Physical Review*, xxvi. p. 195 (1925).

⁴ See *Month. Notices R. A. S.* lxxxv. June 1925; the controversy between Milne and Stewart.

⁵ Milne, *Phil. Mag.* (6) xlvii. p. 200.

⁶ R. H. Fowler, *Phil. Mag.* (6) xlvii. p. 257.

ionization is promoted by collision, in particular by electronic impacts. It may be mentioned that these methods follow on the lines initiated by Guldberg and Waage, Boltzmann, and J. J. Thomson in dealing with the problems of dissociation equilibrium and molecular aggregation⁷. In the thermodynamical method, as developed by van't Hoff, Nernst, Sackur⁸, and others, a knowledge of the detailed mechanism is not so indispensable.

The result is obtained by a treatment of the initial and final states, provided the net charge in energy-content is known. The theory thereby loses somewhat in definiteness, but it has the compensating advantage of being free from the vagueness of the assumptions involved in the kinetic methods.

In the present paper we have followed Ehrenfest's method of dealing with dissociation equilibrium. Attempts in this direction have already been made by R. H. Fowler⁹, Fowler and Milne¹⁰ and by Becker¹¹. But they confined their attention to the production of metastable states.

Ehrenfest¹² has shown that the behaviour of a mixture of gases in thermodynamical equilibrium can be defined by a function $\{\gamma\}$ which may be regarded as the total phase-space described by the system. The function $\{\gamma\}$ is allied to the familiar entropy function, but Ehrenfest did not trace the connexion between the two. In two previous papers¹³, we have shown that $\{\gamma\}$ is connected with Boltzmann's probability function W , by the relation:

$$W = \{\gamma\}/\{\gamma\}_0,$$

where $\{\gamma\}_0$ =value of $\{\gamma\}$ when the system is reduced to absolute zero of temperature.

This theorem holds not only for matter, but we showed in the second paper that it also holds for radiation. The entropy of radiation can be calculated from formula (1) by an extension of S. N. Bose's method¹⁴.

This is equivalent to treating radiation as a new component in chemical equilibrium. A similar view has already been expressed by Smit; according to him the familiar phase-rule

$$F = C+2-P$$

has to be replaced in photochemical reactions by the rule $C+3-P$. The photochemically active light plays the role of a new component.

Turning to the present case, it is easy to see that a sodium atom with its electron in the $2p$ -orbits or any higher orbit may be regarded as a chemical entity different from a normal Na-atom. The Na_{2p} atom may, for practical purposes, be regarded as compound of Na-(normal) and D_1, D_2

pulses. Thus the lines of the sodium spectrum, Na^+ -ion and the electron may be regarded as the independent components out of which the whole system, consisting of normal atom Na^+ and the metastable states of Na, are evolved.

3.

Let us now consider a system consisting of

- n_1 neutral atoms,
- n_2 ionized atoms,
- n_3 free electrons.

Let $n_1+n_2+n_3=n$, and K =kinetic energy of the material particles. Let $N_\nu d\nu$ =total number of quanta of frequency comprised within the range $d\nu$. Then, according to the methods described in the previous papers,

$$W_{\nu} \text{ for radiation} = \Pi \left\{ \frac{(A_s+N_s)!}{(A_s! N_s!)} \right\}^{d\nu} \quad \dots(1)$$

For the material particles

$$W_p = \frac{\mu_1^{n_1}}{h^{3n_1} \cdot n_1!} \cdot \frac{\mu_2^{n_2}}{h^{3n_2} \cdot n_2!} \cdot \frac{\mu_3^{n_3}}{h^{3n_3} \cdot n_3!} \quad \dots(2)$$

We shall here ignore the motion of an electron about its nucleus, and suppose that each material particle has only three degrees of freedom, viz. those corresponding to the motion of translation along three mutually perpendicular axes. Therefore, we have,

$$\left. \begin{aligned} \mu_1 &= \int \dots dx dy dz \cdot dp_x dp_y dp_z \\ &= V \int \dots dp_x dp_y dp_z \\ \mu_2 &= V \int \dots dp_x' dp_y' dp_z' \\ \mu_3 &= V \int \dots dp_x'' dp_y'' dp_z'' \end{aligned} \right\} \quad \dots(3)$$

V =total volume of the gas, and p_x, p_y, p_z , etc. represent the momenta coordinates of the particles.

Hence

$$W_p = \frac{V^n}{h^{3n} n_1! n_2! n_3!} \int \dots dp_{1x} dp_{1y} dp_{1z} \dots dp_{1x}' dp_{1y}' dp_{1z}' \dots dp_{1x}'' dp_{1y}'' dp_{1z}''$$

the integrals being taken for all molecules of each class. The total kinetic energy K being given, the integration is to be performed subject to the condition

$$\frac{\sum^{n_1} p_{1x}^2 + p_{1y}^2 + p_{1z}^2}{2M} + \frac{\sum^{n_2} p_{1x}'^2 + p_{1y}'^2 + p_{1z}'^2}{2M} + \frac{\sum^{n_3} p_{1x}''^2 + p_{1y}''^2 + p_{1z}''^2}{2m} = K, \quad \dots(4)$$

where M =mass of a neutral atom and m =mass of an electron.

⁷ For a summary, see Jeans, 'Dynamical Theory of Gases,' chap. 7, 209-219.

⁸ See Sackur, 'Thermodynamics,' chap. 9.

⁹ Fowler, Phil. Mag. (6) xiv. p. 1.

¹⁰ Fowler & Milne, Month. Notices Roy. Ast. Soc. lxxxiii. p. 403.

¹¹ Becker, Zs. für Physik, xviii. p. 325.

¹² Ehrenfest & Trkal, Proc. Amst. xxi. (1920); Ann. der Physik, lxxiii.

¹³ Saha & Sur, Phil. Mag. Jan. 1926, p. 279.

¹⁴ S. N. Bose, Zs für Physik, xxvi. p. 178 (1924); xxvii. p. 384.

Thus

$$W_p = \frac{V^n}{h^{3n}} \cdot \frac{1}{n_1! n_2! n_3!} \cdot \frac{(2\pi K)^{\frac{3n}{2}}}{\left(\frac{3n}{2}\right)} \cdot (\sqrt{M^3})^{n_1} (\sqrt{M^3})^{n_2} (\sqrt{m^3})^{n_3} \dots (5)$$

For the total system, consisting of radiation and material particles,

$$W = W_{dv} \cdot W_p,$$

or

$$W = \Pi \left\{ \frac{(A_s + N_s)!}{A_s! N_s!} \right\}^{dv} \cdot \frac{V^n}{h^{3n}} \cdot \frac{1}{n_1! n_2! n_3!} \cdot \frac{(2\pi K)^{\frac{3n}{2}}}{\left(\frac{3n}{2}\right)} \cdot (\sqrt{M^3})^{n_1} (\sqrt{M^3})^{n_2} (\sqrt{m^3})^{n_3} \dots (6)$$

Let us now consider a unit process in which a neutral atom is dissociated into a free electron and a positively charged atom by the absorption of a quantum $h\nu$. Then

$$\begin{array}{ll} n_1 & \text{changes to } n_1 - 1 \\ n_2 & \text{,, ,, } n_2 + 1 \\ n_3 & \text{,, ,, } n_3 + 1 \\ n & \text{,, ,, } n + 1 \\ N_s dv & \text{,, ,, } N_s dv - 1. \end{array}$$

The total energy E of the combined system, however, remains unaltered, *i.e.* $dE = 0$,

$$dE = dK + \chi - h\nu_3 = 0,$$

or

$$dK = h\nu - \chi, \dots (7)$$

where χ represents the ionization potential per atom. The probability of the system now is

$$W' = \Pi \frac{(A_s dv + N_s dv - 1)!}{A_s dv! (N_s dv - 1)!} \cdot \frac{V^{n+1}}{h^{3(n+1)}} \cdot \frac{\{2\pi(K+dK)\}^{\frac{3(n+1)}{2}}}{(n_1-1)! (n_2+1)! (n_3+1)!} \cdot \frac{(\sqrt{M^3})^{n_1-1} (\sqrt{M^3})^{n_2+1} (\sqrt{m^3})^{n_3+1}}{\left(\frac{3(n+1)}{2}\right)} \dots (8)$$

For equilibrium,

$$dW = W' - W = 0, \dots (9)$$

whence we obtain,

$$\frac{1}{n_1} \cdot \frac{A_s dv + N_s dv}{N_s dv} \cdot \frac{(2\pi K)^{\frac{3n}{2}}}{\left(\frac{3n}{2}\right)} = \frac{V}{h^3} \cdot \frac{1}{n_2 n_3} \cdot \frac{\{2\pi(K+dK)\}^{\frac{3(n+1)}{2}}}{\left(\frac{3(n+1)}{2}\right)} \cdot m^{3/2}.$$

Replacing $\left(\frac{3n}{2}\right)$ by $\left(\frac{3n}{2}\right)!$ and using Stirling's formula,

$$\frac{n_2 \cdot n_3}{n_1} = \frac{N_s}{A_s + N_s} \cdot \frac{V}{h^3} \cdot \left\{ \frac{2\pi m K}{2} \right\}^{3/2} \cdot \left(1 + \frac{dK}{K}\right)^{\frac{3n}{2}},$$

$$\frac{n_2 \cdot n_3}{n_1} = \frac{N_s}{A_s + N_s} \cdot \frac{V}{h^3} \cdot \left\{ \frac{2\pi m K}{2} \right\}^{3/2} \cdot \left(1 + \frac{3n dK}{2K}\right). \dots (11)$$

Putting $K = \frac{3n}{2} kT$, and using (7), we have, after taking logarithms,

$$\log \frac{n_2 \cdot n_3}{n_1} = \frac{h\nu - \chi}{kT} + \log \left\{ \frac{N_s}{A_s + N_s} \cdot \frac{V}{h^3} \cdot (2\pi m kT)^{3/2} \right\} \dots (12)$$

Now

$$\frac{N_s}{A_s + N_s} = \frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu} \dots (13)$$

Using partial pressures, we have, after some reduction,

$$\log \frac{p_2 \cdot p_3}{p_1} = \frac{N h\nu - U}{RT} + \log \frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{3/2}}{h^3} \right\}, \dots (14)$$

where N = Avogadro number,

U = Ionization potential for a mol.

If the temperature of radiation be the same as that of the gaseous system

$$\rho_\nu = 8\pi \frac{h\nu^3}{c^3} \cdot \frac{1}{e^{\frac{h\nu}{kT}} - 1}, \dots (15)$$

the quantity $\frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu}$ reduces to $e^{-\frac{h\nu}{kT}}$ and the equation

(14) reduces to the familiar form

$$\log \frac{p_2 \cdot p_3}{p_1} = -\frac{U}{RT} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h} \right\} \dots (16)$$

If, within the reaction-space, the density of radiation be the same as that given within black-body chamber,

$$\frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu} = e^{-\frac{h\nu}{kT_s}},$$

where T_s = temperature of radiation.

Then

$$\log \frac{p_2 \cdot p_3}{p_1} = \frac{N h\nu}{RT} \left(\frac{1}{T} - \frac{1}{T_s} \right) - \frac{U}{RT} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right\} \dots (17)$$

This formula is practically identical with one given earlier by Einstein¹⁵. Einstein's formula was deduced from photo-chemical reactions, and runs thus:

$$\log \frac{n_2 \cdot n_3}{n_1} = \frac{Nh\nu}{R} \left(\frac{1}{T} - \frac{1}{T_s} \right) + \frac{1}{R} \Sigma \delta n \left\{ c_v \log T + c_1 - (c_v + R) - \frac{b}{T} \right\}. \quad (17')$$

It is easy to see that we can apply this formula directly to the present case and arrive at (17).

Formula (14) is, however, quite general and can be adapted to the circumstances of the case. In place of ρ_ν we have now to use I_ν , where I_ν is the intensity of light from the source in the reaction-space. The formula then takes the form:

$$\log \frac{p_2 \cdot p_3}{p_1} = \frac{Nh\nu - U}{RT} + \log \frac{I_\nu}{2 \frac{h\nu^3}{c^2} + I_\nu} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right\}.$$

As a special case, let the radiation proceed from a black-body radiator at temperature T_s , and let the radiation confined within a solid angle w . Let F_ν be its residual intensity in the reaction-space, i.e. $F_\nu = r \cdot I_\nu$, r being a fraction and

$$I_\nu = 2 \frac{h\nu^3}{c^2} \cdot \frac{1}{e^{\frac{h\nu}{kT_s}} - 1}.$$

The quantity $\frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu}$ is to be replaced by $\frac{r \frac{w}{4\pi} \cdot I_\nu}{2 \frac{h\nu^3}{c^2} + r \frac{w}{4\pi} I_\nu}$,

or to a first approximation by $r \frac{w}{4\pi} e^{-\frac{h\nu}{kT_s}}$.

The formula (14) then reduces to

$$\log \frac{p_2 \cdot p_3}{p_1} = \frac{Nh\nu - U}{RT} + \log \left(r \frac{w}{4\pi} e^{-\frac{h\nu}{kT_s}} \right) + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right\}. \quad \dots (18')$$

4

Influence of Radiation in producing Higher Quantum States.

By a similar treatment it is possible to deduce the equilibrium between normal and excited states. Let

n_1 = number of atoms in the normal state

(1s in the case of Na, 2p in the case of Al).

n_2 = number in any higher excited state

(2p in the case of Na).

$n_1 + n_2 = n$.

$Nd\nu$ = number of energy pulses within the frequency region $\nu, \nu + d\nu$. The normal atoms pass to the excited state by the absorption of these pulses.

Then we have

$$W = \left\{ \frac{(A+N)!}{A! N!} \right\}^{d\nu} \cdot \frac{g_1^{n_1}}{h^{3n_1} \cdot n_1!} \cdot \frac{g_2^{n_2}}{h^{3n_2} \cdot n_2!} \cdot \frac{V^n}{\left(\frac{3n}{2} \right)} \cdot (2\pi K)^{\frac{3n}{2}} \cdot m^{\frac{3n}{2}};$$

g_1 and g_2 represent the statistical weights of the two states, K the total kinetic energy, and m the mass of the atoms.

If we take a virtual displacement (unit change) in which n_1 changes to $n_1 - 1$, n_2 to $n_2 + 1$, and $Nd\nu$ to $Nd\nu - 1$, we have

$$W' = \frac{(Adv + Nd\nu - 1)!}{Adv! (Nd\nu - 1)!} \cdot \frac{g_1^{n_1 - 1} \cdot g_2^{n_2 + 1}}{h^{3n} \cdot (n_1 - 1)! \cdot (n + 1)!} \cdot \frac{V^n}{\left(\frac{3n}{2} \right)} \cdot \{2\pi K + dK\}^{\frac{3n}{2}} \cdot m^{\frac{3n}{2}},$$

where $dK = h\nu - \chi$; χ now represents the difference in the energy levels of the two states.

Now putting

$$W' - W = 0 \quad \text{and} \quad K = \frac{3n}{2} kT,$$

we have

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot \frac{N}{A+N} \cdot \left(1 + \frac{h\nu - \chi}{kT} \right),$$

or $\frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot \frac{N}{A+N} \cdot e^{\frac{h\nu - \chi}{kT}}$ to an approximation,

$$i.e. \quad \frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot \frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu} \cdot e^{\frac{h\nu - \chi}{kT}} \quad \dots (19)$$

When the radiation is in temperature equilibrium with the gas, it is easy to see that

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot e^{-\frac{\chi}{kT}} \quad \dots (20)$$

When T is sufficiently high

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \quad \dots (21)$$

as is apparent from the definition of weight factor.

Conclusion

It will be seen from an inspection of the formulae deduced that the finite breadth of the absorption band does not occur in any one of them. This shows that the formulae can be regarded only as approximate. This is not unexpected, because the idea of absorption is rather foreign to the thermodynamical methods.

After a short note announcing this result was published in 'Nature' (Nature, April 11, 1923), Woltjer published a note in which he mentioned that the formulae (14) and (19) could be obtained from Milne's method of treatment. We have found that this method gives identical results. But contrary to our expectations, even in this method of treatment the absorption factor does not occur.

October 1, 1925.

¹⁵ Einstein, *Ann. der Physik*, xxxvii. p. 838.