It is easy to see that this equals
\[
\frac{\left(\frac{A}{A'} + \frac{N}{N'}\right)!}{A'! \cdot \frac{N}{N'}!} \quad \text{... (11)}
\]
or in other words,
\[
Sd\nu = d\nu \cdot k \log \frac{\left(\frac{A}{A'} + \frac{N}{N'}\right)!}{A'! \cdot \frac{N}{N'}!} \quad \text{... (12)}
\]

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. Russell\(^1\) 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. Milne\(^2\) 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. It recent years, experiments\(^3\) have been done in which comparatively cool vapours of alkalies 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.

\(^*\)Communicated by the Authors.


\(^2\) Milne, in a note to 'Nature', see Monthly Notices R. A. S. June 1925.


\(^4\) See Monthly 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 aggregation. In the thermodynamical method, as developed by van't Hoff, Nernst, Sackur, 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 J. H. Fowler, Fowler and Milne, and by Becker. But they confined their attention to the production of metastable states.

Ehrenfest has shown that the behaviour of a mixture of gases in thermodynamical equilibrium can be described 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 papers, we have shown that \( \{ \gamma \} \) is connected with Boltzmann's probability function \( W \), by the relation:

\[
W = \{ \gamma \}/\{ \gamma \}_0,
\]

where \( \{ \gamma \}_0 \) is the 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 method.

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-orbit 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\(_2\).

3.

Let us now consider a system consisting of

\[
\begin{align*}
n_1 & \text{ neutral atoms}, \\
n_2 & \text{ ionized atoms}, \\
n_3 & \text{ free electrons}.
\end{align*}
\]

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

\[
W = \Pi \left( \frac{(A_1 + N_s)!}{(A_1)! (N_s)!} \right)^{n_1} \left( \frac{(A_2 + N_s)!}{(A_2)! (N_s)!} \right)^{n_2} \left( \frac{(A_3 + N_s)!}{(A_3)! (N_s)!} \right)^{n_3} 
\]

For the material particles

\[
W_p = \frac{\mu_1^{n_1}}{h^{n_1} n_1!} \frac{\mu_2^{n_2}}{h^{n_2} n_2!} \frac{\mu_3^{n_3}}{h^{n_3} n_3!} \quad \text{(2)}
\]

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,

\[
\begin{align*}
\mu_1 &= \int dx dy dz dp_x dp_y dp_z \\
\mu_2 &= \int dp_x dp_y dp_z \\
\mu_3 &= \int dp_x dp_y dp_z
\end{align*}
\]

\[
= V \left[ \int dp_x dp_y dp_z \right] ^{n_1} \left[ \int dp_x dp_y dp_z \right] ^{n_2} \left[ \int dp_x dp_y dp_z \right] ^{n_3} \quad \text{(3)}
\]

\[
V = \text{total volume of the gas,}
\]

\[
p_x, p_y, p_z, \text{ etc. represent the momenta coordinates of the particles.}
\]

The kinetic energy \( K \) being given, the integration is to be performed subject to the condition

\[
\frac{n_1 p_x^2 + p_y^2 + p_z^2}{2M} + \frac{n_2 p_x'^2 + p_y'^2 + p_z'^2}{2M} + \frac{n_3 p_x''^2 + p_y''^2 + p_z''^2}{2m} = K, \quad \text{(4)}
\]

where \( M \) = mass of a neutral atom and \( m \) = mass of an electron.
Thus
\[ W = \frac{V^n}{\hbar^m \cdot n_1 \cdot n_2 \cdot n_3} \cdot \frac{1}{\left( \frac{3n}{2} \right)^{3n}} \cdot (\sqrt{M^3})^{n_1} \cdot (\sqrt{M^3})^{n_2} \cdot \frac{1}{\left( \frac{3n}{2} \right)^{3n}}. \]  

For the total system, consisting of radiation and material particles,
\[ W = W_0. \]

or
\[ W = \Pi \left( \frac{(A_s + N_s)!}{A_s \cdot N_s!} \right)^d \cdot \frac{V^n}{\hbar^m \cdot n_1 \cdot n_2 \cdot n_3} \cdot \frac{1}{\left( \frac{3n}{2} \right)^{3n}} \cdot (\sqrt{M^3})^{n_1} \cdot (\sqrt{M^3})^{n_2} \cdot \frac{(2\pi K)^{3n}}{2}. \]

Replacing \( \frac{(3n)}{2} \) by \( \frac{(3n)}{2} ! \) and using Stirling's formula,
\[
\begin{align*}
   n_2 \cdot n_3 & = \frac{N_s}{A_s + N_s} \times \frac{V}{\hbar^3} \left( \frac{2\pi mK}{\frac{3n}{2}} \right)^{\frac{3n}{2}} \cdot \left( 1 + \frac{dK}{K} \right)^{\frac{3n}{2}}, \\
   \left( \frac{n_2 \cdot n_3}{n_1} \right) & = \frac{N_s}{A_s + N_s} \times \frac{V}{\hbar^3} \left( \frac{2\pi mK}{\frac{3n}{2}} \right)^{\frac{3n}{2}} \cdot \left( 1 + \frac{3n \cdot dK}{2K} \right). 
\end{align*}
\]

Putting \( K = \frac{3n}{2} K_T \), and using (7), we have, after taking logarithms,
\[ \log \frac{n_2 \cdot n_3}{n_1} = \frac{h \nu - \chi}{kT} + \log \left\{ \frac{N_s}{A_s + N_s} \times \frac{V}{\hbar^3} \left( \frac{2\pi mK}{\frac{3n}{2}} \right)^{\frac{3n}{2}} \right\}. \]

Now
\[ \frac{N_s}{A_s + N_s} = \frac{\rho_\nu}{8\pi \frac{h^3}{c^3} + \rho_\nu}. \]

Using partial pressures, we have, after some reduction,
\[ \log \frac{p_2}{p_1} = \frac{N h \nu - U}{RT} + \log \frac{\rho_\nu}{8\pi \frac{h^3}{c^3} + \rho_\nu} + \frac{1}{2} \log T + \log \left\{ \left( \frac{2\pi m}{\frac{3n}{2}} \right)^{\frac{3n}{2}} \right\}. \]

where \( N \) = Avogadro number, 
\( U \) = Ionization potential for a mol.

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

\[ \rho_\nu = \frac{8\pi \frac{h^3}{c^3}}{e^\frac{h \nu}{kT} - 1}, \]

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

\[ \log \frac{p_2}{p_1} = -\frac{U}{RT} + \frac{h \nu}{kT} \log T + \log \left\{ \left( \frac{2\pi m}{\frac{3n}{2}} \right)^{\frac{3n}{2}} \right\}. \]

(14) reduces to the familiar form

\[ \log \frac{p_2}{p_1} = -\frac{U}{RT} + \frac{h \nu}{kT} \log T + \frac{1}{2} \log T + \log \left\{ \left( \frac{2\pi m}{\frac{3n}{2}} \right)^{\frac{3n}{2}} \right\}. \]

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

\[ \frac{\rho_\nu}{8\pi \frac{h^3}{c^3} + \rho_\nu} = \frac{1}{e^\frac{h \nu}{kT} - 1}, \]

where \( T_s \) = temperature of radiation.

Then
\[ \log \frac{p_2}{p_1} = \frac{N h \nu}{RT} \left( \frac{1}{T} - \frac{1}{T_s} \right) - \frac{U}{RT} + \frac{1}{2} \log T \]

\[ + \log \left\{ \left( \frac{2\pi m}{\frac{3n}{2}} \right)^{\frac{3n}{2}} \right\}. \]
This formula is practically identical with one given earlier by Einstein\textsuperscript{15}. Einstein’s formula was deduced from photo-chemical reactions, and runs thus:

\[
\log \frac{n_2 \cdot n_3}{n_1} \cdot \frac{N h v}{R} \left( \frac{1}{T} - \frac{1}{T_v} \right) + \frac{1}{R} \sum n \left\{ c_v \log T + c_3 - (c_v + R) - \frac{b}{T} \right\}. \tag{17'}
\]

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 \( \rho_v \) we have now to use \( I_v \), where \( I_v \) is the intensity of light from the source in the reaction-space. The formula then takes the form:

\[
\log \frac{\rho_v \cdot \rho_3}{\rho_1} = \frac{N h v - U}{R T} - \log \frac{I_v}{e^\frac{h v}{k T}} + \frac{1}{2} \log \frac{I_v}{e^\frac{h v}{k T}} + \frac{1}{2} \log \frac{(2 \pi m)^{3/2} h^{5/2}}{k^3}.
\]

As a special case, let the radiation proceed from a black-body radiator at temperature \( T_v \), and let the radiation confined within a solid angle \( \omega \). Let \( F_v \) be its residual intensity in the reaction-space, i.e. \( F_v = r I_v \), \( r \) being a fraction and

\[
I_v = 2 \frac{h v}{e^\frac{h v}{k T_v} - 1}.
\]

The quantity \( \frac{\rho_v}{8 \pi h v} \) is to be replaced by \( \frac{r w}{4 \pi} \cdot I_v \),

or to a first approximation by \( r \frac{w}{4 \pi} \).

The formula (14) then reduces to

\[
\log \frac{\rho_v \cdot \rho_3}{\rho_1} = \frac{N h v - U}{R T} + \log \left( \frac{r w}{4 \pi} \cdot e^\frac{h v}{k T_v} \right) + \frac{1}{2} \log \frac{(2 \pi m)^{3/2} h^{5/2}}{k^3}. \tag{18'}
\]

\textit{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).
- \( n_3 \): number of energy pulses within the frequency region \( \nu \), \( \nu + \nu \). The normal atoms pass to the excited state by the absorption of these pulses.

Then we have

\[
W = \left\{ \frac{(A + N)!}{A! \cdot N!} \right\} \cdot g_v \cdot g_{v_1} \cdot g_{v_1} \cdot \frac{V^n}{(3n)^{3/2}} \cdot \frac{V^n}{(2n)^{3/2}}.
\]

\( g_v \) and \( g_{v_1} \) 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 \( n_1 - 1 \), \( n_3 \) to \( n_3 + 1 \), and \( N d v \) to \( N d v - 1 \), we have

\[
W = \frac{(A d v + N d v - 1)!}{A d v! \cdot N d v - 1!} \cdot \frac{g_v \cdot g_{v_1} \cdot g_{v_1}^{n_1 - 1}}{h^m \cdot (n_1 - 1)! \cdot (n_1 + 1)!} \cdot \frac{V^n}{(3n)^{3/2}} \cdot \frac{V^n}{(2n)^{3/2}}.
\]

where \( d K = h v - \chi \); \( \chi \) now represents the difference in the energy levels of the two states.

Now putting

\[
W' - W' = 0 \quad \text{and} \quad K = \frac{3n}{2} k T,
\]

we have

\[
\frac{n_3}{n_1} = \frac{g_v}{g_1} \cdot \frac{N}{A + N} \cdot \left( 1 + \frac{h v - \chi}{k T} \right),
\]

or

\[
\frac{n_3}{n_1} = \frac{g_v}{g_1} \cdot \frac{N}{A + N} \cdot \frac{e^{h v - \chi}}{e^{k T}}
\]

i.e.

\[
\frac{n_3}{n_1} = \frac{g_v}{g_1} \cdot \frac{N}{\pi^2} \cdot \frac{h v - \chi}{e^{k T}}. \tag{19}
\]

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

\[
\frac{n_3}{n_1} = \frac{g_v}{g_1} \cdot \frac{e^{h v - \chi}}{e^{k T}}. \tag{20}
\]

When \( T \) is sufficiently high

\[
\frac{n_3}{n_1} \rightarrow \frac{g_v}{g_1}. \tag{21}
\]

as is apparent from the definition of weight factor.

\textit{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.

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\textsuperscript{15} Einstein, \textit{Ann. der Physik}, xxxvii. p. 838,