To sum up, the thermodynamic probability in Planck's sense is given by

$$W = \frac{\{\gamma\}}{h^{f N} \cdot \lfloor N} \qquad \ldots (20 \cdot 1)$$

This will cover all cases.

On the basis of this law we shall now calculate the entropy of a system consisting of diatomic molecules.

§ 4. *Entropy of a Gas consisting of Diatomic Molecules.*

In this case we shall ignore the rotation of molecules about the axis of symmetry and also all internal motions of atoms in the molecule. Therefore, each molecule has only five degrees of freedom, three of these being translational and two rotational.

Thus
$$\{\gamma\}_0 = h^{f N} \lfloor N$$
$$= h^{5N} \, N, \qquad \ldots (24)$$

where N denotes the total number of molecules considered.

Now, for a single molecule,

$$\{\mu\} = \int \ldots dx \, dy \, dz \, d\theta \, d\psi \, dp_1 dp_2 dp_3 dp_4 dp_5$$
$$= V . 4\pi . \int \ldots dp_1 \ldots dp_5 \qquad \ldots (25)$$

Therefore γ-space for the total system is given by

$$\{\gamma\} = \mathop{\Pi}_{N} \{\mu\}$$

$$= V^N . (4\pi)^N . \int \ldots dp_{1r} dp_{2r} \ldots dp_{5r} \ldots \qquad \ldots (26)$$

the integrals being taken for all molecules, dp_{1r}, dp_{2r}, etc. denote the momenta of the different molecules.

The total kinetic energy of the molecules being given, the integration is to be taken over all possible values of the momenta which are consistent with it. If E be the kinetic energy given, we have

$$\Sigma \frac{p_{1r}^2}{2m} + \frac{p_{2r}^2}{2m} + \frac{p_{3r}^2}{2m} + \frac{p_{4r}^2}{2a} + \frac{p_{5r}^2}{2b} = E, \qquad \ldots (27)$$

where m is the molecular mass and a and b represent the

moments of inertia. The molecules being all similar, these quantities (m, a, and b) have the same values for all the molecules. The total number of terms in the left-hand side of equation (27) is 5N.

Hence

$$\{\gamma\} = V^N . (4\pi)^N . \int \ldots dp_{1r} dp_{2r} \ldots dp_{5r} \ldots$$

$$= V^N . (4\pi)^N . \sqrt{\pi}^{5N} . \frac{\sqrt{E^{5N-1}}}{\left(\dfrac{5N}{2}\right)} . \{(2m)^{3/2} . (2a)^{1/2} . (2b)^{1/2}\}^N \qquad \ldots (28)$$

since N is very large, we may put 5N for 5N—1.

$$\{\gamma\} = V^N . (4\pi)^N . \frac{\sqrt{2\pi E}^{5N}}{\left(\dfrac{5N}{2}\right)} . (m^{3/2} . a^{1/2} . b^{1/2})^N$$

$$= \frac{V^N . (4\pi)^N . \sqrt{2\pi E}^{5N} . (m^{3/2} . a^{1/2} . b^{1/2})^N}{\left(\dfrac{5N}{2}\right)!} . \qquad \ldots (28 \cdot 1)$$

Hence

$$W = \frac{\{\gamma\}}{\{\gamma\}_0} = \frac{\{\gamma\}}{h^{5N} . N!} \qquad \ldots (29)$$

$$= \frac{V^N . (4\pi)^N . \sqrt{2\pi E}^{5N} . (m^{3/2} . a^{1/2} . b^{1/2})^N}{h^{5N} . N! \left(\dfrac{5N}{2}\right)!} . \qquad \ldots (29 \cdot 1)$$

Using Stirling's formula and putting $E = \frac{5}{2} N k T$, we obtain

$$W = \left\{ \frac{e^{7/2} . 4\pi V . (2\pi k T)^{5/2} . m^{3/2} . a^{1/2} . b^{1/2}}{N . h^5} \right\}^N . \qquad \ldots (29 \cdot 2)$$

$$S = k \log W$$

$$= Nk \log \left\{ \frac{e^{1/2} . 4\pi V . m^{3/2} . a^{1/2} . b^{1/2} . (2\pi k T)^{5/2}}{N . h^5} \right\} \qquad \ldots (30)$$

It may be emphasized here that the theorems $E = \frac{3}{2} N k T$ for monatomic gases and $E = \frac{5}{2} N k T$ for diatomic gases have not been assumed here, but followed directly from the theory. The calculations have not been reproduced here.

32. ON ENTROPY OF RADIATION II*

MEGHNAD SAHA & RAMANI KANTA SUR

In a previous paper, it has been shown that the thermodynamical probability of a system is given by the law,

$$W = \{\gamma\} / \{\gamma\}_0 \qquad \ldots (1)$$

Where $\{\gamma\}$ = phase-space described by the system at temperature T_0, $\{\gamma\}_0$ = phase-space described at absolute

zero. It was shown that the absolute value of entropy of perfect gases could be deduced from this theorem.

The same formula can be applied for deducing the entropy of radiation. Since the time when Bartoli deduced the existence of radiation pressure from thermodynamical reasoning, it has been customary to look upon radiation as

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*Communicated by the Authors.

a sort of perfect gas. But the analogy is often misleading, for the energy of gaseous molecules is capable of continuous variation, while according to Planck, radiant energy or energy of light pulses can vary only in multiples of $h\nu$. If $E\nu$ = total energy of frequency ν, then

$$E\nu = N\nu \cdot h\nu \qquad \ldots(2)$$

$$N\nu = \text{number of energy elements.}$$

In calculating the probability, we have further to find out the number of ways in which a quantum can be contained within unit volume. This is equal to $A = \frac{8\pi\nu^2}{c^3}$. The deduction of this theorem forms the greatest difficulty in the theory of black body radiation. In the original method of deduction by Jeans and others, $\frac{8\pi\nu^2}{c^3}$ represents the total number of stationary waves in unit volume having their frequency between ν and $\nu+1$. It is deduced in a most complicated way from electromagnetic considerations.

Bose has recently given a very elegant and simple method of deducing the theorem

$$A = \frac{8\pi\nu^2}{c^3}, \qquad \ldots(3)$$

which is reproduced here.

According to modern conceptions, a pulse of light carries with it the momentum $\frac{h\nu}{c}$ in the direction of its motion. It has got the components

$$p_x, \ p_y, \ p_z, \ \text{where } p_x{}^2 + p_y{}^2 + p_z{}^2 = \frac{h^2\nu^2}{c^2}.$$

The phase-space described by the pulse in its translatory motion is, according to Planck,

$$\ldots \iint dp dq \ldots = \ldots \overset{\nu+1}{\underset{\nu}{\iiint}} dx dy dz dp_x dp_y dp_z = \frac{4\pi h^3\nu^2}{c^3} V. \qquad \ldots(4)$$

According to the quantum theory, the phase-space can be split up into cells each of volume h^3, hence the total number of cells

$$= \frac{4\pi h^3\nu^2}{c^3} \ V/h^3 = \frac{4\pi\nu^2}{c^3} V, \text{ or } \frac{8\pi\nu^2}{c^3} \ V, \qquad \ldots(5)$$

when we take both the polarized pulses. The number $P = \frac{8\pi\nu^2}{c^3}$ represents the total number of ways in which a quantum $h\nu$ can be contained within unit volume. The idea is therefore the same as the number of stationary waves.

The essential point in the above argument is that the *translatory motion* of a pulse of light can be treated according to the quantum theory, viz., $\int dp \ dq = h$ for any one of the degrees of freedom of the pulse of light.

We can now calculate the entropy of radiation by using the relation

$$W = \{\gamma\}/\{\gamma\}_0.$$
$$\text{Now} \qquad \{\gamma\} = \Pi \ (\mu) \ P, \qquad \ldots(6)$$

where (μ) = phase-space described by one pulse in its internal electromagnetic vibrations, P = permutability of the pulses. We are not yet acquainted with any method for expressing the internal vibrations within a light-pulse in terms of Hamiltonian coordinates. Planck and other authors, e.g. Darwin and Fowler, identify the pulse with some resonator—Hertzian oscillator, or the Bohr-vibrator. But we think it may be possible, in the case of a free pulse, to avoid this appeal to material carriers. At any rate, we assume that the pulse is subject to Hamilton's equation

$$\iint dp dq = h,$$

for each of its degrees of vibrations.

$$\text{Then} \qquad \Pi(\mu) = h^{3N}\nu,$$

which means that the pulses do not interchange energy, like gas-molecules, but are independent of each other.

$$P = \frac{A+N!}{A! \ N!}, \qquad \ldots(7)$$

because any one of the cells may contain 0, 1, 2 ... $N\nu$ pulses.

$$\text{Thus} \qquad \{\gamma\} = h^{3N}\nu \frac{A+N!}{A! \ N!} \qquad \ldots(8)$$

We have now to find out the value of $\{\gamma\}_0$. This brings us to the point: how we can reach the absolute zero by using radiation as the working substance in a Carnot reversible engine as was first done by Bartoli. Wien showed that we can pass from a radiation space at temperature T to a space at temperature T' by a virtual slow displacement of the walls. The wave-lengths of radiation enclosed within the space are changed according to the relation

$$\lambda T = \lambda T',$$

$$\text{or} \qquad \nu = \alpha T.$$

Hence at T = 0, ν = 0, *i.e.* at absolute zero, it is not possible to have any radiation at all.

This brings us to an interesting analogy. We have seen in the previous paper that if we use a gas as a working substance in the Carnot cycle, absolute zero can be attained only when all matter has been annihilated. The present theorem tells us that if we use radiation as a working substance, absolute zero can be attained in a space where all radiation has been completely annihilated.

We thus obtain $A = 0$, $P = 1$,

$$\text{and} \qquad \{\gamma\}_0 = \Pi(\mu) \ P = h^{3N}\nu, \qquad \ldots(9)$$

$$\therefore \quad W = \{\gamma\}/\{\gamma_0\} = \frac{A+N!}{A! \ N!}, \qquad \ldots(10)$$

from which the value of S can be easily deduced.

If we use $A\nu d\nu$, $N\nu d\nu$ instead of A and N, we obtain

$$\text{Probability} \quad W = \frac{(A d\nu + N d\nu)!}{A d\nu! \ N d\nu!}.$$

It is easy to see that this equals

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

or in other words,

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

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

The value of $S\nu$, $U\nu$ 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*

MEGHNAD SAHA & RAMANI KANTA SUR

(Phil. Mag., Sr. VII, 1, 1025, 1926)

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.

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 radiation[4] may be broadly subdivided into two classes—(1) those based on the methods used in the knetic theory of gases; (2) those based on thermodynamical methods. To the first category belong the works of Milne[5] "On the Statistical Equilibrium in relation to Photoelectric Effect," and of R. H. Fowler[6] "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

*Communicated by the Authors.

[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.