

## Radiation Theory and the Quanta\*

### 1. INTRODUCTION

The first Solvay Conference on Physics took place in Brussels from 30 October to 3 November 1911. Its general theme was 'The Theory of Radiation and the Quanta'. The President of the Conference was H. A. Lorentz (Leyden, Holland), and the participants were:

*Germany*: W. Nernst (Berlin), M. Planck (Berlin), H. Rubens (Berlin), A. Sommerfeld (Munich), E. Warburg (Berlin-Charlottenburg), W. Wien (Würzburg).

*England*: J. H. Jeans (Cambridge), E. Rutherford (Manchester).

*France*: M. Brillouin, Madame Curie, P. Langevin, J. Perrin, H. Poincaré (all from Paris).

*Austria*: A. Einstein (Prague), F. Hasenöhrl (Vienna).

*Holland*: H. Kamerlingh Onnes (Leyden).

*Denmark*: Martin Knudsen (Copenhagen).

The Scientific Secretaries of the Conference were: R. Goldschmidt (Brussels), M. de Broglie (Paris), and F. A. Lindemann (Berlin).

As we have already noted, the theme of the first Solvay Conference in 1911, Radiation Theory and the Quanta, indicated the central question in physics in those days. The most important advances in physics in the 19th century were perhaps the development of Maxwell's electromagnetic theory, which offered a far-reaching explanation of radiative phenomena, and the statistical formulation and interpretation of thermodynamics which culminated in Boltzmann's relation between the entropy and probability of the state of a complex mechanical system. However, as Rayleigh's analysis of black-body radiation had shown, the physical and mathematical description of the spectral distribution of cavity radiation in thermal equilibrium presented unsuspected difficulties.

Planck's discovery of the universal quantum of action in 1900 was a turning point in the development. It revealed a feature of 'discreteness' in atomic processes, which was completely foreign to classical physics. Einstein not only emphasized the apparent paradoxes which had arisen in the detailed description of the interaction between matter and radiation, but provided support for Planck's ideas by his investigation of the specific heat of solids at low temperature. Einstein also introduced the idea of light

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quanta or photons as carriers of energy and momentum in elementary radiative processes, and successfully used it in his explanation of the photoelectric effect.

The purpose of the first Solvay Conference was thus two-fold: first, there was the need to examine whether classical theories (molecular-kinetic theory and electrodynamics) could, in some undiscovered ways, provide an explanation of the problem of black-body radiation and of the specific heat of polyatomic substances at low temperatures; secondly, to consider phenomena in which the theory of quanta could be successfully used.

The discussions at the Conference were initiated after the report of H. A. Lorentz. He developed the arguments based on classical ideas leading to the principle of the equipartition of energy between the various degrees of freedom of a physical system, including not only the motion of its constituent material particles but also the normal modes of vibration of the electromagnetic field associated with the electric charge of the particles. These arguments, which followed the lines of Rayleigh's analysis of thermal radiative equilibrium, led to the well-known paradoxical result that no temperature equilibrium was possible since the whole energy of the system would be gradually transferred to electromagnetic vibrations of steadily increasing frequencies.

James Jeans suggested that the only way to reconcile radiation theory with the principles of statistical mechanics was that under experimental conditions one did not have to deal with a true equilibrium but with a quasi-stationary state, in which the production of high frequency radiation would escape notice. The acuteness with which the difficulties in radiation theory were felt was brought home by a letter from Lord Rayleigh, which was read at the conference, in which he recommended that Jeans' suggestion should be given careful consideration. But on closer examination it became evident that Jeans' argument could not be upheld.

After the reports of Warburg and Rubens on the experimental evidence supporting Planck's law of temperature radiation, Planck himself gave an exposition of the arguments which had led him to the discovery of the quantum of action. Planck was deeply concerned with the problems of harmonizing this new feature with the conceptual framework of classical physics. He emphasized that the essential point was not the introduction of a new hypothesis of energy quanta, but rather a reformulation of the very concept of action. Planck expressed the conviction that the principle of least action, which had also been upheld in the theory of relativity, would serve to guide the further development of quantum theory.

Walther Nernst, in his report on the application of quantum theory to various problems of physics and chemistry, considered the properties of matter at very low temperatures. Nernst remarked that his theorem regarding the entropy at absolute zero, of which he had made important applications since 1906, now appeared as a special case of a more general law derived from the theory of quanta.

Kamerlingh Onnes reported on the discovery of superconductivity of certain metals at very low temperatures. This phenomenon presented a great puzzle, and would find its explanation only several decades later.

Nernst's idea of the quantized rotation of gas molecules, which would receive

confirmation in the measurements of the fine structure of infra-red absorption lines, was commented upon from various sides at the conference.

Paul Langevin reported on the variation of the magnetic properties of matter with temperature. He made special reference to the idea of the magneton, which had been introduced by Pierre Weiss to explain the remarkable numerical relations between the strength of the elementary magnetic moments of atoms deduced from the analysis of his measurements. Langevin showed that the value of the magneton could be approximately derived on the assumption that the electrons in atoms were rotating with angular momenta corresponding to a Planck quantum of action.

Arnold Sommerfeld discussed the production of X-rays by high speed electrons as well as problems involving the ionization of atoms in the photoelectric effect and by electronic impact. Sommerfeld considered the existence of Planck's quantum of action as fundamental for any approach to questions of the constitution of atoms and molecules.

Martin Knudsen reported on kinetic theory and the experimental properties of perfect gases, while Jean Perrin gave a detailed report on the proofs of molecular reality and the counting of atoms by the use of statistical fluctuations.

The last report of the conference was given by Albert Einstein. He summarized many applications of the quantum concept and dealt in particular with the fundamental arguments used in his explanation of the anomalies of specific heats at low temperatures.

We shall now treat the individual reports presented at the first Solvay Conference.

## 2. APPLICATION OF THE ENERGY EQUIPARTITION THEOREM TO RADIATION

(H. A. Lorentz)

In the first scientific lecture at the conference, Lorentz declared right away that among physical phenomena there were hardly any more mysterious ones than those of thermal and light radiation. He discussed Kirchhoff's empirical laws of black-body radiation and the 'felicitous' application of the principles of thermodynamics by Boltzmann and Wien, which had led to experimentally verifiable general laws. 'But, in spite of all this', said Lorentz, 'the ideas which prevailed until the end of the last century could not explain why a piece of iron, for instance, [certainly absorbs but] does not emit radiation at ordinary temperatures.' With this he undertook to point out the difficulties which arise in the classical theory of radiation.

Lorentz gave a brief account of Rayleigh's radiation law<sup>1</sup>, which had been established by assuming the validity of the equipartition theorem. But this law, which is quite satisfactory for long wavelengths (up to infra-red), is in complete disagreement with observations in the short wavelength region of the black-body spectrum. Lorentz asked if there was any means of avoiding the equipartition theorem in this particular case or, for that matter, generally.

In order to answer such questions Lorentz was led to analyze the assumptions made

all velocities, one obtains for  $f(\chi/\lambda)$  a limiting form which vanishes not as  $e^{-\chi/\lambda}$  but as  $e^{-\sqrt{\chi/\lambda}}$ , a result which is contrary to observation.

As a result of these considerations, Jeans concluded that any such extension of the Maxwell–Boltzmann theory cannot account for the phenomena of radiation on the assumption of the proposed mechanism of radiation, and that the theory could not be tested further until some other mechanism of radiation were suggested.

## DISCUSSION

The comments of Lorentz, Rutherford, Langevin, Lindemann and Wien emphasized the difficulties present in Jeans' extension of the Maxwell–Boltzmann theory. Referring to Jeans' hydrodynamical analogy, with his use of pipes, tanks, and leakages, Poincaré remarked sharply that with all this 'Mr Jeans could account for any experimental result. However, that is not the role of physical theories. One must not introduce as many arbitrary constants as there are phenomena to be explained. The goal of physical theory is to establish a connection between diverse experimental facts, and above all to predict.'

## 5. THE LAW OF BLACK-BODY RADIATION AND THE HYPOTHESIS OF THE ELEMENTARY QUANTUM OF ACTION

(M. Planck)

The laws of classical mechanics, electrodynamics and electron theory, have been found to apply with remarkable accuracy to all phenomena in which they have been tested experimentally. The statistical methods and results of the kinetic theory of gases seem to apply even in the domain of atoms and electrons. But the application of laws of classical theory, even with the extension provided by the Lorentz–Einstein principle of relativity, encounters insurmountable difficulties for understanding the experimental laws of black-body radiation.

### 5.1. CLASSICAL THEORY AND RADIATION LAWS

If  $u_\lambda$  is the energy density of black-body radiation within the wavelengths  $\lambda$  and  $\lambda + d\lambda$ , then the Stefan–Boltzmann law for total radiation states that,

$$\int_0^\infty u_\lambda d\lambda = CT^4, \quad (1)$$

where  $C$  is a constant and  $T$  the absolute temperature. Wien's displacement law requires that,

$$u_\lambda d\lambda = \frac{1}{\lambda^5} f(\lambda, T) d\lambda, \quad (2)$$

and the Rayleigh–Jeans law gives,

$$u_\lambda d\lambda = \frac{CT}{\lambda^4} d\lambda. \quad (3)$$

However, the results of measurements [of F. Paschen, O. Lummer, E. Pringsheim,

H. Rubens and F. Kurlbaum]\* are best represented by Planck's formula,

$$u_\lambda d\lambda = \frac{C_1}{\lambda^5} \frac{d\lambda}{e^{C_2/\lambda T} - 1}. \quad (4)$$

Planck thought that his formula (4), even if it were not exact, did possess sufficient validity as to be in agreement with experimental results. For large values of the product  $\lambda T$ , the expressions (3) and (4) become identical; while for small values, they disagree completely with each other.

The question arises as to how to bring the theory into accord with facts, and Planck addressed himself to this question. He briefly discussed the different approaches that had been made in this direction. Thus Jeans' theory<sup>1</sup> had sought to remove the contradiction between the formulas (3) and (4) by not admitting that the measured quantity (4) corresponds to the normal black-body radiation. According to Jeans, the radiant energy escaping from a small opening in a cavity at uniform temperature does not correspond to the equilibrium radiation of a completely isolated cavity – because, in the latter, the density of radiation according to the formula (3) must increase indefinitely as the wavelength  $\lambda$  diminishes. According to this idea, the question does not arise of a given spectral distribution of a finite quantity of radiant energy in equilibrium, because the integral in (3) over all the wavelengths is infinite.

According to the theory of Jeans, one would have to assume that the observed phenomena correspond to a continuous transformation in which the radiant energy inside the cavity passes continuously from long toward the small wavelengths so slowly that the newly formed radiations always have the time to escape across the walls of the cavity, leading to the establishment of a kind of stationary state of the transformation whose character varies from one case to another. No available experimental evidence justifies such a conception – while many contradict this, among them the almost perfect opacity of the cavity walls [used in the measurements] for the radiation of very small wavelengths, as well as the complete independence of the observed radiation of the nature of the substance inside the cavity or the material of the cavity walls.

For these reasons, Jeans' hypothesis was not received favourably among the physicists. Almost all the investigations of the theory of radiation are based on the supposition – introduced by Kirchhoff and Boltzmann, and verified by Wien and Lummer – of a veritable state of equilibrium, in the thermodynamic sense, inside a cavity at uniform temperature. Planck accepted this point of view.

An especially important confirmation is supplied by the experimental verification of all the consequences obtained by the laws of thermodynamics and electrodynamics at equilibrium. Some of these consequences are particularly remarkable and fruitful: among them, other than Kirchhoff's law of the proportionality of the powers of emission and absorption, are the Stefan–Boltzmann law of total radiation, Equation (1), and Wien's displacement law, Equation (2). The latter is compatible with Equa-

\* E. Warburg and H. Rubens gave brief reports on the experimental verification of Planck's black-body radiation formula (4) at the first Solvay Conference, just prior to Planck's report.

tions (3) and (4), while the Stefan–Boltzmann law is in contradiction with Equation (3).

The application of the general principles of thermodynamics and electrodynamics does not lead beyond Wien's displacement law. The form of the function  $f$  in Equation (2) can only be determined by a detailed analysis of the [molecular] mechanism of the emission and absorption of radiation. For instance, Lorentz<sup>2</sup> had calculated, for a metallic conductor, the emissivity on the basis of the acceleration of the electrons, and the absorptivity by considering the electrical conductivity as being due to the motion of the same electrons. By dividing the quantities thus obtained, one by the other, Lorentz had obtained the emissive power of the black body.

In any case, one can almost certainly foresee that all methods analogous to the foregoing must lead to the Rayleigh–Jeans radiation law, particularly since the motions of and forces between the molecules and the electrons are calculated by means of classical dynamics and electrodynamics. In Planck's view, this would apply also to the radiation law given by J. J. Thomson<sup>3</sup>, in which he had introduced the special hypothesis of a repulsion between the electrons and the molecules proportional to the inverse cube of the distance [the dipole interaction]. It applies also to Ritz' theory of retarded potentials<sup>4</sup> to the extent that this theory is compatible with classical dynamics.

From the foregoing it follows that in order to escape from the [Rayleigh–Jeans] radiation law (3) it is indispensable to make a fundamental modification of the classical theory. One can easily recognize that, above all, it is necessary to introduce a completely new notion of the dynamical significance of the temperature. In fact, according to (1), the energy of radiation, for all wavelengths, is proportional to the temperature, while according to (4) when the temperature [in the first order] becomes infinitely small the energy of radiation becomes infinitesimal.

The most general relation between energy and temperature, Planck concluded, can only be obtained by considerations of probability. Consider two physical systems capable of exchanging energy, whose state is determined by a large number of independent variables. They shall be in statistical equilibrium if further exchange of energy would not correspond to an increment of probability. If  $W_1 = f(E_1)$  is the probability that the first system has an energy  $E_1$ , and  $W_2 = \varphi(E_2)$ , the probability that the second system has energy  $E_2$ , then the probability that the two systems have the energies  $E_1$  and  $E_2$  respectively is  $W_1 W_2$ ; and the condition that this be a maximum is

$$d(W_1 W_2) = 0,$$

or

$$\frac{dW_1}{W_1} + \frac{dW_2}{W_2} = 0$$

under the condition

$$dE_1 + dE_2 = 0.$$

Thus, the general condition for statistical equilibrium is

$$\frac{1}{W_1} \frac{dW_1}{dE_1} = \frac{1}{W_2} \frac{dW_2}{dE_2}.$$

If this condition of statistical equilibrium is identified with the thermodynamic condition according to which the two systems have the same temperature, then the general definition of temperature is given by

$$\frac{1}{T} = k \frac{d \log W}{dE} \quad (5)$$

where the universal constant  $k$  depends only on the units of energy and temperature.

Thus, for Planck, the problem of the black-body radiation reduced itself to the calculation of the probability  $W$  for which the energy of radiation has a given value  $E$ .

## 5.2. DOMAINS OF PROBABILITY AND THE QUANTUM OF ACTION

The probability for a given value of a continuously variable quantity can be obtained if one can define the *independent elementary domains of equal probability*. The probability that a physical system described by a large number of variables possesses an energy  $E$  is thus represented by the number of ways of distributing [complexions] compatible with the energy  $E$ , of the independent variables of the system among the different elementary domains of equal probability.

In order to determine these domains, one employs, in classical mechanics, the theorem that two states of a system, which succeed each other according to the laws of motion, have equal probability. If the state of a system is defined by the independent coordinates,  $q$ , and their corresponding momenta,  $p$ , then Liouville's theorem states that the domain given by  $\iint dq dp$  remains invariant with time provided the evolution of  $q$  and  $p$  obeys Hamilton's equations. Moreover, at a given instant,  $q$  and  $p$  may attain all possible values independently of each other. Consequently, the infinitesimally small elementary domain of probability is given by

$$dq dp. \quad (6a)$$

The new hypothesis must therefore be chosen in such a manner as to introduce certain limitations in the system of the variables  $q$  and  $p$ , whether one considers discontinuous variation for these quantities or whether one regards them to some extent related to each other. In any case, one is led to a diminution in the number of independent domains of equal probability, and obtains the extension of each of these domains. The hypothesis of the elementary quanta of action obtains this change in a precise manner by introducing, in place of infinitesimally small elementary domains, the domains of finite extension,

$$\iint dq dp = h. \quad (6b)$$

The quantity  $h$ , the elementary quantum of action, is a universal constant of the dimension of energy multiplied by time. If, for the calculation of the probability,  $W$ , of an energy density,  $u_\lambda$ , one employs the finite value  $\iint dq dp$  instead of the infinitesimally small value  $dq dp$ , one obtains – with the help of Equations (5) and (2) – the formula (4) [i.e. Planck's formula] in place of Equation (3). Thus the theoretical radiation law is made to agree with the results of measurements.

One has to content oneself with the principle that the elementary domain of probability has an extension  $h$ , and put aside all questions concerning the physical significance of this remarkable constant. J. Larmor<sup>5</sup> had accepted this phenomenological point of view, and P. Debye<sup>6</sup> had also taken this attitude. Planck thought that this was indeed how one should introduce the essential content of the hypothesis of quanta. However, it seemed to Planck that one would not know thereby how to stick to it without endangering the further development of the theory, and it was of the utmost importance to look for relations which might exist between the quantum of action and the other physical constants in order to determine and extend its significance.

### 5.3. CALCULATION OF PROBABILITY AND THE PHYSICAL NATURE OF THE CONSTANT $h$

Planck, therefore, tried to examine closely the physical nature of the constant  $h$ . First of all there arises a question of principle: Does this element of action possess a physical significance for the propagation of radiant energy in the vacuum, or – because of its nature – it plays a role only in the processes of emission and absorption of light? The further development of the theory would certainly follow completely different routes depending upon the answer to this question.

The former point of view had been adopted by A. Einstein<sup>7</sup> in his hypothesis of the light quanta, and J. Stark<sup>8</sup> had followed him. According to this hypothesis, the energy of a light ray of frequency  $\nu$  is not distributed continuously in space, but propagates in a straight line in quanta of magnitude  $h\nu$  in the same manner as the light corpuscles in the emission theory of Newton. As a confirmation of this hypothesis, one invokes the fact that the velocity of secondary cathode rays produced by Röntgen rays is independent of the intensity of the latter.

J. J. Thomson<sup>9</sup> had been led to an analogous conclusion from a study of photoelectric phenomena. He found that the small number of emitted electrons and the independence of their velocities from the intensity of the incident light could only be explained by admitting local accumulations of this energy, rather than a uniform distribution of energy, in the wavefronts of light.

It goes without saying that such hypotheses are irreconcilable with Maxwell's equations and all the electromagnetic theories of light that have been proposed. All of them suppose, in effect, that the smallest luminal perturbation propagates itself throughout all space, if not in all directions with the same intensity then at least with a continuous distribution over concentric spheres whose radius increases with the speed of light. Planck noted that, 'If one considers the complete experimental confirmation which Maxwell's electrodynamic theory obtained by means of the most delicate interference phenomena, and if one considers the extraordinary difficulties which its abandonment would entail for the entire theory of electric and magnetic phenomena, then one senses a certain repugnance in ruining its very fundamentals.' For this reason, Planck thought, 'We shall leave aside the hypothesis of light quanta, especially since it is still quite early in the development of this notion.'

Planck insisted that all phenomena which take place in vacuum are governed exactly by Maxwell's equations, which have no connection of any kind with the

constant  $h$ . From this he was led to the following conclusions: Thermal radiation, enclosed in an evacuated cavity with perfectly reflecting walls, will indefinitely conserve its initial distribution of energy in the spectrum. One cannot admit that this distribution would slowly evolve toward that of black-body radiation. A fundamental difference manifests itself here between the theory of radiation and kinetic gas theory. For a gas enclosed in a cavity, an initial arbitrary distribution of velocities transforms itself with time into the most probable distribution determined by Maxwell's law. This difference arises because the molecules of the gas collide with each other, while thermal radiation merely traverses through the cavity. The results of the collisions can only be calculated by the methods of probability, while these methods cannot be applied to the radiation in vacuum because each ray always conserves its initial energy. This energy is given to it forever at the moment of emission and can only be modified by absorption or by a new emission. If an arbitrary distribution of the energy is conserved indefinitely in an absolute vacuum, then, on the other hand, the introduction [into the cavity] of the smallest quantity of a substance capable of absorbing or emitting suffices to modify progressively the composition of the radiation and to transform it into the indefinitely stable black-body radiation. From this point of view it is not possible to evaluate the probability for the energy of radiation without taking into account the phenomenon of emission itself, and one is therefore obliged to examine in detail the mechanism of the emission and absorption of radiant energy.

Since, according to Kirchhoff, the intensity of black-body radiation enclosed in a cavity is independent of the emitting and absorbing substance, one must conclude that all mechanisms compatible with the principles of thermodynamics and electrodynamics would provide a correct expression for the [spectral] composition of black-body radiation. The simplest radiating system is a linear oscillator of a given period. Its energy is of the form

$$E = \frac{1}{2}Kq^2 + \frac{1}{2}L\left(\frac{dq}{dt}\right)^2, \quad (7)$$

where  $q$  is the dielectric moment of the oscillator, and  $K$  and  $L$  are positive constants. The frequency of the oscillations is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{L}}. \quad (8)$$

This, together with the relation (6b), allows one to calculate the magnitude of the energy corresponding to the elementary domain of probability, i.e. the magnitude of the element of action  $h$ . Thus,

$$h = \int_{E}^{E+\epsilon} dq dp,$$

and, since,

$$p = L \frac{dq}{dt},$$

one obtains,

$$E = \frac{1}{2}Kq^2 + \frac{1}{2}\frac{1}{L}p^2. \quad (9)$$

The double integral giving  $h$  represents the surface in the  $qp$ -plane between the ellipse  $E=\text{const}$ , and the ellipse  $E+\varepsilon=\text{const}$ . With this, one has

$$h = 2\pi \sqrt{\frac{L}{K}} \varepsilon = \frac{\varepsilon}{v}.$$

Hence, for an oscillator of a given proper frequency  $v$ , there exist elements of energy,

$$\varepsilon = hv, \quad (10)$$

in the sense that the probability of a given value of the energy depends only on the number of energy elements which it contains.

The question now arises as to how to interpret the elements of energy physically or, in other words, which dynamical law should be taken as the basis for the vibrations of the oscillator in order to obtain the statistical law that has been enunciated. The simplest assumption is that the energy of the oscillator is always an integral multiple of the energy element  $hv$ . Thus it becomes relatively simple to calculate the probability such that a system consisting of a large number  $N$  of identical oscillators possesses a given energy  $E_N$ . If

$$P = \frac{E_N}{\varepsilon} = \frac{E_N}{hv} \quad (11)$$

represents the number of energy elements contained in the total energy  $E_N$ , then the probability  $W$  is measured by the number of complexions in which the oscillators may be distributed among the domains of energy corresponding to the integral multiples of  $\varepsilon$ . This number is equal to the number of ways of distributing  $P$  energy elements among  $N$  oscillators, if one takes into account only the number and not the individuality of the energy elements which appertain to each oscillator in each distribution considered. One obtains<sup>10</sup>

$$W = \frac{(N+P)!}{N! P!} = \frac{(N+P)^{N+P}}{N^N P^P}, \quad (12)$$

and by using Equations (6) and (11),

$$E_N = \frac{Nhv}{e^{hv/kT} - 1}. \quad (13)$$

The calculation can be made in other ways which are not different in principle from the preceding one. One can represent each complexion of the system of oscillators by a point in the  $2N$ -dimensional phase space of Gibbs. The probability  $W$  is then represented by an extension of the surface in this space, determined by the condition

$$E = E_N. \quad (14)$$

The calculation is notably simplified if one considers a canonical distribution of the system of oscillators in phase space with an average energy  $E_N$ . This is because one can easily identify, without appreciable error, the number of systems which possess an average energy  $E_N$  with the total number of systems of the canonical distribution; and the modulus of this distribution is  $kT$ . Thus, for the energy of the system of oscillators considered, one obtains,

$$E_N = \frac{\int E e^{-E/kT} d\sigma}{\int e^{-E/kT} d\sigma}, \quad (15)$$

where  $d\sigma = dq_1 dp_1 dq_2 dp_2 \dots dq_N dp_N$ , and the integration is over the entire extension in the phase space of  $2N$ -dimensions; moreover, the energy  $E$  must be expressed as a function of the variables  $q, p, \dots$

If we now introduce the hypothesis that  $E$  can only be an integral multiple of  $\varepsilon = h\nu$ , the integrations may be transformed into summations and we finally obtain<sup>11</sup>,

$$\begin{aligned} E_N &= N \frac{0 + \varepsilon e^{-\varepsilon/kT} + 2\varepsilon e^{-2\varepsilon/kT} + \dots}{1 + e^{-\varepsilon/kT} + e^{-2\varepsilon/kT} + \dots} \\ &= \frac{Nh\nu}{e^{h\nu/kT} - 1}. \end{aligned} \quad (16)$$

A third way of calculating the probability  $W$  proceeds from the first one in a manner opposite to that of Gibbs. Thus, in the canonical distribution one introduces not only the complexions compatible with the given energy  $E_N$ , but also all the complexions relative to the energies comprised between  $E=0$  and  $E=\infty$ ; while, following Boltzmann, the sought for probability,  $W$ , is determined by only one part of the complexions compatible with the energy  $E_N$ , i.e. one which corresponds to the most probable distribution of this energy among different oscillators. The latter definition leads to the same expression for  $W$  as the two preceding ones, since, compared to the most probable distribution, the other distributions comprising all ensembles correspond merely to a negligible number of complexions.

Let  $N_0, N_1, N_2 \dots$  be the number of oscillators of the system which, for an arbitrary distribution of the quantity of energy  $E_N$ , possess the energies,  $0, \varepsilon, 2\varepsilon, \dots$ . Following Boltzmann, the probability of this distribution is

$$W = \frac{N!}{N_0! N_1! N_2! \dots} = \frac{N^N}{N_0^{N_0} N_1^{N_1} N_2^{N_2} \dots}. \quad (17)$$

The condition that  $W$  be a maximum, keeping in mind that  $E_N = Ph\nu$ , gives the following values for the most probable distribution:

$$\begin{aligned} N_0 &= N^2 \frac{1}{N + P}, & N_1 &= N^2 \frac{P}{(N + P)^2}, \\ N_2 &= N^2 \frac{P^2}{(N + P)^3}, & \dots, \end{aligned} \quad (18)$$

and these values, introduced in the expression for  $W$ , again lead to the formula (12).

A fourth manner of obtaining the formula (12), less exact but with a more concrete physical significance, was proposed by Nernst.<sup>12</sup> He looked for a distribution of energy in a system of oscillators having a circular vibration, subject to collisions of molecules of an ideal gas and in statistical equilibrium with it. The hypothesis that the energy of an oscillator is necessarily an integral multiple of the quantum,  $\varepsilon$ , is then introduced. One assumes further that in the most probable stationary distribution the number of oscillators which possess the energy,  $n\varepsilon$ , is equal to the number of oscillators whose energy, for the same temperature, would comprise between  $n\varepsilon$  and  $(n+1)\varepsilon$  if the ordinary Maxwellian distribution were applicable. This then gives, for the numbers  $N_0, N_1, N_2$ , etc. of the oscillators which possess 0, 1, 2, ... quanta of energy, the values

$$\begin{aligned} N_0 &= N(1 - e^{-\varepsilon/kT}), & N_1 &= N(e^{-\varepsilon/kT} - e^{-2\varepsilon/kT}), \\ N_2 &= N(e^{-2\varepsilon/kT} - e^{-3\varepsilon/kT}), & \dots, \quad \text{etc.} \end{aligned} \quad (19)$$

The total energy of the system of oscillators,

$$E_N = N_0 \cdot 0 + N_1 \cdot \varepsilon + N_2 \cdot 2\varepsilon + \dots,$$

then takes the form given by Equation (13).

As the concordant results of the different procedures of calculation show, the relations (12) and (13) necessarily follow from the hypothesis that the energy of an oscillator is an integral multiple of the element of energy  $\varepsilon$ .

In order to pass from formula (13) to a law of radiation capable of experimental verification, one must again know the relation between the average energy of the oscillator,  $E_N/N = E$ , and the density,  $u_\nu$ , corresponding to the frequency of radiation present in space. Maxwell's electrodynamics leads to the equation<sup>13</sup>

$$u_\nu \, dv = \frac{8\pi\nu^2}{V^3} \, E \, dv. \quad (20)$$

In combination with Equation (13) one obtains for the law of black-body radiation,

$$\begin{aligned} u_\nu \, dv &= u_\lambda \, d\lambda = \frac{8\pi h\nu^3}{V^3} \frac{dv}{e^{h\nu/kT} - 1} \\ &= \frac{8\pi hV}{\lambda^5} \frac{d\lambda}{e^{hV/k\lambda T} - 1}, \end{aligned} \quad (21)$$

which is exactly of the same form as the experimental law (4), in agreement with the measurements.

If, in order to calculate the two constants  $k$  and  $h$ , one employs the number used by Lummer and Pringsheim,

$$\lambda_{\max} T = 0.294 \text{ cm deg}, \quad (22)$$

and Kurlbaum's number

$$S_{100} - S_0 = 7.31 \times 10^5 \text{ ergs/cm}^2 \text{ sec}, \quad (23)$$

where  $S_t$  represents the total energy radiated per second per  $\text{cm}^2$  of a black-body at temperature  $t$  degrees, one obtains<sup>14</sup>

$$k = 1.346 \times 10^{-16} \text{ erg degree} \quad (24)$$

and

$$h = 6.548 \times 10^{-27} \text{ erg sec.} \quad (25)$$

The quantity  $k$ , since it results from an application of Equation (5) to the statistical equilibrium of the molecules of an ideal gas, is equal to the *gas constant*, related not to a gram molecule but really to a single isolated molecule. Thus there results a method of calculating the number of molecules which is much more precise than all others employed earlier. Since, however, these other methods had been perfected only just prior to Planck's calculations, the agreement of their results with Planck's provided a remarkable confirmation of the considerations developed by him.

Planck thought that in spite of its apparent success, the new theory of radiation could not in any way be considered satisfactory, since the hypotheses on the basis of which Equations (13) and (20), respectively, have been derived are mutually contradictory. In order to obtain the former, one assumes that the energy of the oscillator is an integral multiple of  $h\nu$ , while the reasoning which leads to the second supposes that this energy is continuously variable. It is not possible to decide in favour of one of these cases without noting, at least on a first consideration, that the equation based on the other alternative becomes illusory.

Planck pointed out that all models which had been proposed for representing the properties of an oscillator, capable of emitting and absorbing radiant energy in agreement with the theory of quanta, suffered from the same inner contradiction. A. E. Haas<sup>15</sup>, for instance, considered as the oscillator the uniform sphere of J. J. Thomson, inside which an electron can oscillate around a centre. The maximum energy for this oscillation, which is attained when the amplitude becomes equal to the radius of the sphere, must be equal to the quantum of energy  $\epsilon = h\nu$ . For larger amplitudes, periodic oscillation is impossible because the electron leaves the sphere completely; while for smaller amplitudes, the oscillation is periodic and its energy is continuously variable. The grounds on which the demonstration of Equation (13) is based do not admit these conditions, and this equation is no longer applicable. This is particularly evident if one considers the oscillations of Haas' system of oscillators in a stationary field of radiant energy, sufficiently weak, such that the average energy of an oscillator is small compared with the quantum  $\epsilon$ . Each oscillator, in a stationary state, vibrates with a small amplitude like a dipole governed by the laws of Maxwell's electrodynamics, emitting and absorbing radiant energy in a continuous manner. None of these oscillations obtains the energy  $\epsilon$ , the radius of the sphere becomes immaterial, and the elements of energy play no role. The existence of the fluctuations of free radiation caused by interference do not affect this conclusion, because these fluctuations are too feeble to explain the distribution (18) of energy among the oscillators corresponding to the correct laws of radiation. The same difficulties occur in the modification introduced by A. Schidlof<sup>16</sup> in Haas' oscillator.

#### 5.4. ATOMIC MODELS AND THE LAW OF RADIATION

In Planck's view, the models of Schidlof or Haas led necessarily to the Rayleigh-Jeans law of radiation for the simple reason that these models rigorously admitted all the laws of classical dynamics. In order that an oscillator should provide radiation according to Equation (4), it is necessary to introduce in the law of its behaviour a special physical hypothesis which, at a fundamental point, is in contradiction with classical mechanics, either explicitly or tacitly.

The oscillator model proposed by M. Reinganum<sup>17</sup> was much closer to this condition. In it, an electron was assumed to be completely immobile until it had absorbed a whole quantum of energy. This at least guaranteed that the energy of the oscillator was always an integral multiple of  $\epsilon$ .

However, in this case also, as in all cases where the energy of an isolated oscillator is supposed to vary in a discontinuous manner, it is impossible to understand where the energy absorbed by the oscillator comes from since (as it should often happen at low temperatures) its energy increases suddenly from 0 to  $h\nu$ . The intensity of the thermal radiation in space, below a certain wavelength, is too feeble at low temperatures to supply the necessary energy. According to the laws of Maxwell's electrodynamics, the time required for an oscillator placed in a radiation field to absorb the energy,  $\epsilon = h\nu$ , corresponding to its frequency, is

$$t = \frac{e^{h\nu/kT} - 1}{2\sigma\nu}, \quad (26)$$

where  $\sigma$  is the average decrease of the oscillations. This value of the time,  $t$ , increases so rapidly as  $T$  decreases, that at relatively low temperatures one could hardly speak of a sudden absorption of an element of energy.

This difficulty becomes still more serious if one considers an oscillator subject to the action of non-stationary radiation. In this case, one has in effect no possibility of knowing whether the oscillator would start to absorb at all, because one does not know whether the duration of radiation would be sufficiently long enough to allow the oscillator to extract a whole quantum.

The hypothesis that the absorbed energy does not come from absorbed radiation, but from the electrons encountered, for instance, does not offer any help here. If, indeed, the free radiation is not absorbed by virtue of the laws of the stationary state, then it can also not be emitted, and the fundamental hypothesis of an exchange of energy between the oscillator and free radiation cannot be preserved.

#### 5.5. CONTINUOUS ABSORPTION

Faced with these difficulties, it seemed inevitable to Planck to renounce the supposition that the energy of the oscillator should be an integral multiple of the element of energy  $\epsilon = h\nu$ . He concluded that *the phenomenon of the absorption of free radiation is essentially continuous*. From this point of view, one could preserve the fundamental hypothesis of quanta by supposing that the emission of thermal radiation by an

oscillator of frequency  $\nu$  is discontinuous, and is produced in integral multiples of the elements of energy  $\epsilon = h\nu$ .

Even though the energy of an oscillator is continuously variable, one can still define the domains of elementary probability by means of the finite quantum of action  $h$ . Let the energy of the oscillator be expressed in the form

$$E = n\epsilon + \varrho \quad (27)$$

in such a way that the oscillator possesses  $n$  whole quanta,  $\epsilon$ , and the remaining  $\varrho < \epsilon$ ; the integral number  $n$  alone is subject to the law of chance while  $\varrho$ , which naturally assumes different values for different oscillators in a field of stationary radiation, increases continuously and uniformly as a function of time. The probability of the energy  $E$  does not depend on the quantity  $\varrho$ , which is continuously variable in a regular and familiar manner, but only on the integral number  $n$  which alone is subject to the law of chance. If  $n=0$  and  $E < \epsilon$ , the oscillator does not emit at all and its energy increases constantly by absorption until it becomes equal to the first quantum, after which emission occurs sooner or later.

This hypothesis of the quanta of emission<sup>18</sup> also leads to formula (21) for the radiation, but the relation between the average energy of the oscillator and the temperature is no longer given by (13), but by the equation,

$$\bar{E} = \frac{E_N}{N} = \frac{h\nu}{2} \frac{e^{h\nu/kT} + 1}{e^{h\nu/kT} - 1}. \quad (28)$$

At very low temperatures,  $\bar{E}$  is equal to  $h\nu/2$ , i.e. almost all of the oscillators possess only the energy  $\varrho$  which cannot be lost, and its average value is

$$\frac{\epsilon}{2} = \frac{h\nu}{2}.$$

Equation (20) is thus replaced by,

$$u_v dv = \frac{8\pi v^2}{v^3} dv \left( \bar{E} - \frac{\epsilon}{2} \right). \quad (29)$$

The consequence that the energy of an oscillator does not tend to zero as the temperature decreases indefinitely, but only remains less than  $\epsilon$ , seems to offer a satisfactory solution of the difficulty mentioned earlier, which led J. J. Thomson, Einstein and Stark to the hypothesis of a discontinuous structure of free radiation.

When light waves or Röntgen rays fall on a metal and release electrons, it is not necessary that radiation should supply, according to the hypothesis of the quanta of emission, the total energy which comes into play. The radiation would only have to complete the energy,  $\varrho$ , of an oscillator up to a whole quantum,  $\epsilon$ , in order that the emission of an electron becomes possible. The more feeble the intensity of the external radiation, the less will be the number of oscillators whose energy will thus be completed, and consequently the smaller will be the number of electrons emitted. On the other hand, one understands readily that the velocity of the electrons depends only on

the frequency of light or the duration of Röntgen rays, if one assumes that the emission of electrons, just as that of radiation, is produced by quanta of energy whose magnitude depends only on the oscillators which emit and, consequently, on the nature of the radiation absorbed by these oscillators.

### 5.6. QUANTUM OSCILLATORS AND THE SPECIFIC HEAT

One obtains a new verification of the theory of quanta by taking the derivative, with respect to the temperature, of Equations (13) or (28) which express the energy of the oscillator as a function of the temperature. In both cases one obtains, for the specific heat of the oscillators,

$$\frac{dE_N}{dT} = Nk \frac{(hv/kT)^2 e^{hv/kT}}{(e^{hv/kT} - 1)^2}. \quad (30)$$

From this A. Einstein<sup>19</sup> had derived a formula giving the variation with temperature of the specific heat of solids, by identifying the latter with systems of oscillators capable of vibrating with the same frequency along the three directions of the axes, and his formula agreed [at least roughly] with the results of measurements. The deviations which persist may well be because the simple hypothesis admitted by Einstein does not correspond exactly to the facts. Since the laws of black-body radiation are completely independent of the type of oscillator employed, it is probable that simple oscillators, convenient for establishing the law of radiation, differ notably from more complex ones which exist in nature and which determine the specific heat of solids.

### 5.7. THEORY OF RADIATION AND APERIODIC PHENOMENA

Finally, Planck mentioned that a completely satisfactory theory of radiation would necessarily have to explain non-stationary phenomena, the discussion of which lay beyond the limits of his report. He made only some general remarks in this connection.

Above all, it is important to insist that the hypothesis of quanta is not, strictly speaking, a hypothesis of *energy* but could be called an hypothesis of *action*. The fundamental conception is that of an elementary domain of probability of extension *h*. The quantum of energy or radiation, *hv*, is derived from that, and has only a significance for periodic phenomena of a given frequency, *v*. There is no doubt that, to the extent that the hypothesis of quanta possesses a profound significance, the element of action *h* must also have a fundamental importance for non-periodic and non-stationary phenomena. Sommerfeld<sup>20</sup> has shown it directly for some particular cases. It might perhaps be possible, thanks to the introduction of this element of action *h*, to deduce the laws of black-body radiation for all wavelengths starting from non-periodic phenomena, as H. A. Lorentz had done for the large wavelengths starting from electron collisions.

The extension of the theory of quanta to phenomena of ordinary mechanics raises a question of fundamental importance. Do the quanta play no role in these phenomena because the acceleration is too small or because the theory of quanta cannot be

applied? In other words, is the difference between the laws of ordinary mechanical and electrical phenomena and those of emission from the optical oscillator fundamental or merely qualitative?

Planck expressed his preference for the first alternative, i.e. the admission of an essential difference between the phenomena produced by the quantum of action and those which arise in a continuous manner in agreement with the laws of classical dynamics. Planck even felt tempted to see in this the separation or differentiation between physical and chemical phenomena. The atoms and molecules, and also perhaps the free electrons, move according to the laws of classical dynamics; however, the atoms or the electrons subject to a molecular interaction obey the laws of the theory of quanta. Physical forces such as gravitation, electrical and magnetic attractions and repulsions, and cohesion, act in a continuous manner; chemical forces, on the other hand, act through quanta. The physical laws are of the same kind as allow the masses in physics to interact with each other to any extent, while in chemistry they can act only in definite proportions and vary in a discontinuous manner.

Planck thought that a complete understanding of the physical significance of the element of action,  $h$ , will only be obtained by means of the principle of least action, which seems to govern all fundamental phenomena and whose importance has been affirmed even in the theory of relativity. The theory of quanta, in Planck's view, must be brought into harmony with the principle of least action. It would only be necessary to give the latter principle a more general form that would make it applicable to discontinuous phenomena.

Planck concluded that if one considers the general result of the efforts made thus far to interpret theoretically the laws of radiation, one cannot, in any way, regard it as being satisfactory. One should not be surprised by this if one recognizes that the solution of the problem cannot be obtained except by the introduction of a completely new hypothesis which is in direct contradiction with the conceptions accepted hitherto. Still, it is without doubt that one shall, by continued effort, be able to formulate a hypothesis free of contradictions that will preserve in a definitive manner a certain number of the ideas introduced thus far.

#### DISCUSSION

At the conclusion of Max Planck's report Albert Einstein expressed the opinion that the manner in which the probability  $W$  had been introduced by Planck was 'somewhat shocking', because in doing so the Boltzmann principle did not have a physical meaning any longer. Even if one succeeded in defining the probability in a way that the entropy derived from Boltzmann's principle would agree with the empirical definition, it seemed to Einstein that the manner in which Planck had introduced this principle would not allow one to conclude the correctness of the theory by basing it on its [i.e. Boltzmann's principle's] agreement with experimental thermodynamic properties. H. A. Lorentz agreed that it would be desirable to start with a good definition of probability.

Planck was aware of the problem but thought that in the state of knowledge of the day it was not possible to give such a definition. He summed up the problem as follows: What is the method of calculation which, by an application of Boltzmann's principle, leads to an entropy of radiation in agreement with experiment? Once the general solution has been obtained, Planck thought, one would also have a general physical definition of the probability.

F. Hasenöhrl emphasized the difference between the points of view of Boltzmann and Planck by

noting that it arose because Boltzmann took the element of extension in phase as being infinitesimally small, while Planck gave it a finite value.

Henri Poincaré raised questions concerning the elements of action and stated the following difficulty. Since  $h$  is the area of a certain domain of the  $pq$ -plane, the decomposition of the plane can be done in many different ways according to the chosen shape of the area. What would be the influence of this choice on Planck's result? Planck maintained that the process was introduced to evaluate the probability of a given energy, hence the shape of the elements was determined by the lines of constant energy. Poincaré then wondered whether there exists a conservation of the action in the same way as there exists conservation of matter or of electricity.

Lorentz pointed out that historically the element of energy was introduced by Planck *before* the element of action, and wanted to know the relation between the statistical methods of Planck and Gibbs. In Planck's view the difference was that Gibbs had infinitesimal extensions in phase while he himself had introduced finite ones, leading to a limitation in the use of Hamilton's equations.

J. H. Jeans and P. Langevin raised the question concerning the existence of a quantum of ether. Planck thought that if it meant that a finite element of action plays a role in the propagation of electromagnetic disturbances in ether, the answer would be no.

The discussion of Planck's report then concentrated on the question as to how legitimate was the use of statistical methods for radiation and, in general, for ether. W. Wien pointed out that a ray of light emitted by a black body has a temperature and entropy given by the laws of probability.

Poincaré returned to his question concerning the decomposition of the  $pq$ -plane and gave the example of a three-dimensional harmonic oscillator for which different decompositions lead to a contradiction. He wondered how Planck's treatment of the harmonic oscillator and its quantum condition, according to which the equation  $\iint dq dp = h$  determines the elementary region of a priori probability in the  $pq$ -plane, should be extended to systems with more than one degree of freedom. In his reply, Planck expressed the belief that the formulation of a quantum condition for systems with more than one degree of freedom, although it did not exist at that moment, would soon be possible.\*

Lorentz pointed out that the assumption,  $\epsilon = hv$ , made by Planck was the only possible one that was not in contradiction with Carnot's principle. He wondered whether in the new theory it was possible to see that the relation  $\epsilon = hv$  was the only one ensuring agreement with the second law of thermodynamics. Langevin thought that the reason for this agreement had to be sought in Liouville's theorem, which is still valid in the decomposition of Planck, at least for a decomposition in which the definition of probability is still correct.

Lorentz emphasized the importance of Arthur Haas' model which had been rejected by Planck, to which Langevin pointed out that this model would lead to absorption of energy varying with the intensity of radiation.

W. Nernst wondered whether, in addition to Planck's resonator, it would not be important to introduce the assumption of a charged particle forced to remain at a fixed distance from a given point. Hasenöhrl responded that in such a model the period is not independent of the energy; if the elements of extension in phase space are equal, the elements of energy are different, and vice versa.

\* Planck and Sommerfeld formulated the generalization to many degrees of freedom only *four years later*. [M. Planck, 'Die Quantenhypothese für Moleküle mit mehreren Freiheitsgraden', *Verh. Deut. Phys. Ges.* **17**, 407–418, 438–451 (1915); 'Die Physikalische Struktur des Phasenraumes', *Ann. Physik* **50**, 385–418 (1916); A. Sommerfeld, 'Zur Theorie der Balmerischen Serie', *Münchener Ber.* (1915), 425–458, 'Die Feinstruktur der Wasserstoff und wasserstoffsähnlichen Linien', *Münchener Ber.* (1915), 459–500, 'Zur Quantentheorie der Spektrallinien', *Ann. Physik* **51**, 1–94, 125–167 (1916).]

Planck considered dynamical systems of  $f$  degrees of freedom, the equations of motion of which admit regular intervals. He generalized his treatment of the harmonic oscillator by dividing the phase space by means of surfaces  $F(p_k, q_k) = \text{constant}$ , defined by the integrals, into regions of volume  $h^f$ . Planck postulated that the stationary states correspond to the  $f$ -dimensional intersections of these surfaces.

Paul Epstein showed later on [P. S. Epstein, 'Über die Struktur des Phasenraumes bedingt periodischer Systeme', *Berliner Ber.* (1918), 435–446] that Planck's conditions for characterizing the stationary states were equivalent to the quantum conditions of Sommerfeld. Kneser, who wrote a thesis on quantum theory under David Hilbert in 1921 [H. Kneser, 'Untersuchungen zur Quantentheorie', *Math. Ann.* **84**, 277–302 (1921)] also proved rigorously the equivalence of the quantum conditions of Planck and Sommerfeld for the characterization of stationary states.

Wien thought that the difficulty with Planck's first theory consisted in the great amount of time which would be necessary in order that an oscillator could receive an element of energy in the case of a weak radiation. Wien suggested the introduction of a coupled oscillator. Planck thought that even in the case of a coupled oscillator the absorption time would remain too large.

Poincaré pointed out that if only a fixed resonator and ether were considered, avoiding the Doppler effect, it would be impossible to reach an equilibrium without the presence of matter or of some medium the energy of which varied in an arbitrary manner. Poincaré then asked Planck to justify an assumption which he had introduced in the derivation of the absorption formula – specifically, why the energy between  $n\hbar\nu$  and  $(n+1)\hbar\nu$  had to vary linearly with the time? Planck replied that if the oscillator would only absorb radiant energy, its energy would increase proportionally with the time, but if the exchange of energy were caused by collision with an atom or an electron nothing precise could be said about the mechanism of this exchange.

Madame M. Curie thought that, since in Planck's theory the emission of energy was instantaneous, Maxwell's equations would not hold even in vacuum. Lorentz responded that emission might take place during a large number of vibrations.

Madame Curie then asked how one could imagine a mechanism that would allow this emission to be interrupted. 'It is quite probable', she said, 'that such a mechanism will not exist at our [human] level, but rather be comparable to Maxwell's demon. It would allow one to obtain the deviations based on the laws of radiation as envisaged by statistics just as Maxwell's demon allows one to obtain the deviations following from the consequences of Carnot's principle.' Poincaré gave the example of the discharge of an Hertzian oscillator which starts instantaneously but lasts a certain time.

Planck recognized that if the emission from an oscillator takes place in quanta then Maxwell's equations will have to be modified within the oscillator and its immediate vicinity. Einstein also pointed out that if an oscillator emits in a different manner than the one corresponding to Planck's original theory, Maxwell's equations must be abandoned in the vicinity of the oscillator, because the application of Maxwell's equations to the quasi-static oscillating dipole field necessarily yields the emission of energy in the form of spherical waves.

Nernst drew attention to the fact that Planck's new hypothesis concerning the zero point energy will probably require that, at the absolute zero of temperature, the atoms will still have motions, and thereby solid bodies will still have vapour pressure. Planck, however, thought that the vapour pressure at absolute zero should be null.

Arnold Sommerfeld expressed his belief that the hypothesis of emission quanta, as well as the initial hypothesis of the quanta of energy, should be considered more as a form of explanation [a model] rather than as physical reality.

Lorentz was interested in finding out how Planck would seek to modify the fundamental equations for the electron. Planck did not have a precise answer, but he indicated the direction in which he was searching. For Planck, the equations of the electromagnetic field were exact outside the linear oscillator, but in between two emissions the vibrations were governed by the law,

$$m \frac{d^2x}{dt^2} + nx = efx,$$

where the symbols have their usual significance. However, Lorentz insisted on the fact that one should not attach too much importance to the units of  $\hbar$ , as the quantity  $e^2/V$ , if  $e$  is measured in electrostatic units, has also the dimension of an action.

The discussion that ensued after Planck's report at the first Solvay Conference provided the beginning of a new way of thinking, and increasingly subtle arguments would be pursued in the succeeding decades. With the work of Einstein on light quanta, Niels Bohr's work on the theory of the hydrogen atom and the search for an atomic mechanics, leading finally to the creation of a unified quantum mechanics in 1926, the physical reality of quanta and the statistical laws for the description of atomic phenomena would become central questions in the epistemology of one of the greatest scientific revolutions in history.

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## 6. KINETIC THEORY AND THE EXPERIMENTAL PROPERTIES OF PERFECT GASES

(M. Knudsen)

Martin Knudsen gave an account of the status of kinetic theory and the experimental properties of perfect gases. A pure gas is composed of molecules in motion, all of the same mass  $m$ . The interaction between the molecules is appreciable only when the distance is smaller than a certain limit which, for perfect gases, is negligible compared to the path during which the molecules move freely.

Having stated this fundamental assumption, Knudsen recalled that according to the general laws of collision, and using Avogadro's law, there exists the relation,

$$p = \frac{1}{3} \rho \bar{c}^2, \quad (1)$$

where  $p$  is the pressure,  $\rho$  the density ( $\rho = Nm$ ), and  $\bar{c}^2$  the mean square speed of the particles.

In order to confirm this theory many different quantities can be computed and compared with experimental results. Knudsen discussed the derivation of the law  $c_p/c_v = \frac{5}{3}$  for specific heats, a result which had been verified for monatomic gases but was a little too high for polyatomic gases. He also discussed certain results in which the nature of the particles was irrelevant.

The mass  $G$  of a gas flowing out, through a hole in a surface  $A$ , during a time  $\tau$  at a stationary regime, is given by

$$G = A\tau \frac{1}{\sqrt{2\pi}} \sqrt{\rho_0} \sqrt{\frac{273}{T}} (p' - p''), \quad (2)$$

where  $p'$  and  $p''$  are the pressures on the two sides of the surface, and  $\rho_0$  is the density of the gas before expansion. Knudsen illustrated the validity of this law with experimental examples.

If the mutual collisions between molecules may be neglected, the theory shows that