Physics 1910

JOHANNES  DIDERIK  VAN  DER  WAALS

*<<for his work on the equation of state for gases and liquids>>*

# Physics 1910

*Presentation Speech by the Rector General of National Antiquities, Professor O. Montelius, President of the Royal Swedish Academy of Sciences*

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen,

The Academy of Sciences has resolved to award this year's Nobel Prize for Physics to the world-famous Dutch physicist, Johannes Diderik van der Waals for his studies of the physical state of liquids and gases.

As far back as in his inaugural dissertation <<The relationship between the liquid and the gaseous state>>, Van der Waals indicated the problem to which he was to devote his life's work and which still claims his attention today. In the dissertation to which I have referred he sought to account for the discrepancies from the simple gas laws which occur at fairly high pressures. He was led to the assumption that these discrepancies are partly associated with the space occupied by the gas molecules themselves, and partly with the attraction which the molecules exert on one another, owing to which the pressure acting on the interior of the gas is greater than the external pressure. These two factors become more and more pronounced with increasing compression of the gas. At a sufficiently high pressure, however, the gas becomes liquid, unless the temperature exceeds a certain value, the critical temperature as it is termed. Van der Waals showed that it is possible to apply the same considerations and calculations to liquids as to gases. When the temperature of a liquid is raised to beyond the critical temperature without the liquid being allowed to volatilize, it is in fact converted continuously from the liquid to the gaseous form; and close to the critical temperature it is impossible to distinguish whether it is liquid or gas.

The force preventing the separation of the molecules in a liquid is their mutual attraction, owing to which a high pressure prevails in the interior of the liquid. Van der Waals calculated this pressure, the existence of which had already been vaguely perceived by Laplace, for water. It amounts to not less than about 10,000 atmospheres at normal temperature. In other words the internal pressure, as it is called, of a drop of water would be about ten times greater than the water pressure at the greatest depth of the sea known to us.

However, this was not the most important result of Van der Waals

studies. His calculations led him to consider that once we are acquainted with the behaviour of a single type of gas and the corresponding liquid, e.g. that of carbon dioxide, at all temperatures and pressures, we are able by simple proportioning to calculate for any gas or liquid its state at any temperature and pressure, provided that we know it at only one, i.e. the critical, temperature.

On the basis of this law of what are known as <<corresponding states>> for various gases and liquids Van der Waals was able to provide a complete description of the physical state of gases and, more important, of liquids under varying external conditions. He showed how certain regularities can be explained which had earlier been found by empirical means, and he devised a number of new, previously unknown laws for the behaviour of liquids.

It appeared, however, that not all liquids conformed precisely to the simple laws formulated by Van der Waals. A protracted controversy arose around these discrepancies which were ultimately found to be attributable to the molecules in these liquids not all being of the same character; the older Van der Waals laws apply only to liquids of uniform composition. Van der Waals then extended his studies to mixtures of two or more types of molecules and here too he managed to find the laws and these, of course, are more complex than those which apply to substances composed of molecules of a single type. Van der Waals is still occupied with working out the details of this great investigation.

Nevertheless, he has successfully surmounted the difficulties that were initially in his path.

Van der Waals' theory has also been brilliantly successful through its predictions which made it possible to calculate the conditions for converting gases to liquids. Two years ago Van der Waals' most prominent pupil, Kamerlingh Onnes, in this way succeeded in compelling helium-the last previously uncondensed gas-to assume the liquid state.

Yet Van der Waals' studies have been of the greatest importance not only for pure research. Modem refrigeration engineering, which is nowadays such a potent factor in our economy and industry, bases its vital methods mainly on Van der Waals' theoretical studies.

Professor Van der Waals.   The Royal Academy of Sciences has awarded you this year's 'Nobel Prize for Physics in recognition of your pioneering studies on the physical state of liquids and gases.

Hamurabi's and Moses' laws are old and of great importance. The laws of Nature are older still and even more important. They apply not just to certain regions on this Earth, but to the whole world. However, they are difficult to interpret. You, Professor, have succeeded in deciphering a few paragraphs of these laws. You will now receive the Nobel Prize, the highest reward which our Academy can give you.

JOHANNES D. VAN DER WAALS

# The equation of state for gases and liquids

*Nobel Lecture, December 12, 1910*

Now that I am privileged to appear before this distinguished gathering to speak of my theoretical studies on the nature of gases and liquids, I must overcome my diffidence to talk about myself and my own work. Yet the thought that you are entitled to expect that of me leads me to hope that you will forgive me if I state my views in this field with utter conviction, even in regard to aspects which are not yet universally known and which have so far not achieved universal recognition. I intend to discuss in sequence:
(1) the broad outlines of my equation of state and how I arrived at it;
(2) what my attitude was and still is to that equation;
(3) how in the last four years I have sought to account for the discrepancies which remained between the experimental results and this equation;
(4) how I have also sought to explain the behaviour of binary and ternary mixtures by means of the equation of state.

(1) The first incentive to this my life's work came to me when, after my studies at university, I learned of a treatise by Clausius ( 1857) on the nature of the motion which we call heat. In this treatise, which is now taught with negligible modifications in every highschool in Holland, he showed how Boyle's law can very readily be derived on the assumption that a gas consists of material points which move at high velocity, that this velocity is of the order of that of sound and increases in proportion to the square root of the absolute temperature. It was subsequently realized that this is only the root mean square of the velocities and that, as Maxwell stated, although he erroneously considered to have proved it, there is a law for the distribution of the velocities known as the Maxwell law. Boltzmann was the first to give the correct proof for this velocity distribution law. Clausius' treatise was a revelation for me although it occurred to me at the same time that if a gas in the extremely dilute state, where the volume is so large that the molecules can be regarded as points, consists of small moving particles, this is obviously still so when the volume is reduced; indeed, such must still be the case down to the maximum compression and also in liquids, which can only be re-

garded as compressed gases at low temperature. Thus I conceived the idea that there is no essential difference between the gaseous and the liquid state of matter - that the factors which, apart from the motion of the molecules, act to determine the pressure must be regarded as quantitatively different when the density changes and perhaps also when the temperature changes, but that they must be the very factors which exercise their influence throughout. And so the idea of continuity occurred to me. I then also asked myself how the solid state behaved. Although I have not as yet seriously gone into that question I do think that in the amorphous state the close proximity of the molecules impedes their mutual displacement. The crystalline state definitely behaves in a slightly different way. Actually I should still be silent on this question. Nevertheless it can now scarcely be doubted that continuity exists between the other two states of aggregation.

As you are aware the two factors which I specified as reasons why a non-dilute aggregate of moving particles fails to comply with Boyle's law are firstly the attraction between the particles, secondly their proper volume. Turning first to the second factor I should like to point out the following : originally I had anticipated that simply the total volume must be decreased with the total volume of the molecules to find the volume remaining for the motion. But closer examination showed me that matters were not so simple. To my surprise I realized that the amount by which the volume must be reduced is variable, that in the extremely dilute state this amount, which I have notated $b$, is fourfold the molecular volume - but that this amount decreases with decreasing external volume and gradually falls to about half. But the law governing this decrease has still not been found. This very point has proved to be the most difficult in the study of the equation of state. Korteweg, Lorentz, Boltzmann, Jeans, and of my pupils, Van Laar, my son, and Kohnstamm have subsequently worked on it. I had thought that it was simply a matter of studying how the mean free path decreases between the collisions of the molecules which are the consequence of their extensiveness, i.e. of the fact that they must not be considered material points but small particles with a real volume in common with all bodies known to us, and so I arrived at this formula:

$$ b = b_g \left\{ 1 - \alpha \frac{b_g}{v} + \beta \left( \frac{b_g}{v} \right)^2 \text{etc.} \right\} \tag{A} $$

where $b_g$ is fourfold the molecular volume.

Boltzmann has shown, however, that this is inadequate and later on Kohnstamm proved that the formula will be more complex and that for $b/b_g$ a quotient will be obtained of two series in which powers of $b_g/v$ occur. It is so difficult to determine the coefficients $\alpha, \beta$ etc. that Van Laar was compelled to carry out fearfully long calculations when determining the second coefficient $\beta$ by my method ($\alpha$ gave rise to far less trouble). This prevented me from proceeding further. And here I have come to the weak point in the study of the equation of state. I still wonder whether there is a better way. In fact this question continually obsesses me, I can never free myself from it, it is with me even in my dreams.

As regards the other cause underlying the non-compliance of real gases and liquids with Boyle's law, i.e. the mutual attraction of the molecules, the situation is somewhat better although here again the last word has not yet been spoken. Using the procedure adopted by Laplace in his capillarity theory, in my continuous theory I have reduced this attraction, which acts in the whole volume, to a surface force which acts towards the interior and thus, together with the external pressure, holds together the moving molecules. Laplace regards his liquid actually as a continuum; at the time he was still unaware of molecules. And if we were dealing with stationary molecules it would have been inadmissible to reduce the attracting forces in the interior to just a surface force. Yet since the molecules are in motion each point in the interior will certainly not be filled with matter at every moment. But space may be regarded as continuously filled with matter of mean-normal - density. I shall return to this point however when I speak of my studies in recent years. The above considerations brought me to the following formula:

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \qquad\qquad (B)$$

which became universally known only as a result of Eilhard Wiedemann's efforts.

(2) Having reached the second part of my lecture I must now mention my own attitude to this equation. It will be abundantly plain from my earlier comments that I never expected this equation, with a and $b$ assigned a constant value, to give results numerically in agreement with experiment and yet people almost always act as though that were my opinion. This astonishes me as in my treatise of 1873 not only did I expressly emphasize the variability

of $b$ but also quoted a series of $b$- values from Andrews' experiment in which for small volumes the change in $b$ with the volume is calculated. For carbon dioxide I moved from the limiting value $b_g = 0.0023$ down to $b = 0.001565$. In this series of values the volumes of the liquid even go below the limiting value of $b_g$ for infinite volume.

Perhaps the reason why my opinion that $b$ is variable has rarely been regarded as seriously intended is to be found in the manner in which I calculated the critical parameters. In this calculation I had to assume $b$ as invariable. But that was because I believed that Andrews' values justified still assigning the limiting value $b_g$ to $b$ in the critical volume. But as I later showed that was a mistake; the value of $b$ in the critical volume has, of course, slightly decreased. Yet to determine the critical volume when $b$ changes with the volume, the first and second differential quotients $\mathrm{d}b/\mathrm{d}v$ and $\mathrm{d}^2b/\mathrm{d}v^2$ also need to be known. To determine the critical volume, as I later showed, we obtain the equation:

$$\frac{v}{v-b}\left(1 - \frac{\mathrm{d}b}{\mathrm{d}v}\right) + \frac{1}{2}\frac{v\,\dfrac{\mathrm{d}^2b}{\mathrm{d}v^2}}{1 - \dfrac{\mathrm{d}b}{\mathrm{d}v}} = \frac{3}{2} \tag{C}$$

Only when we neglect $\mathrm{d}b/\mathrm{d}v$ and $\mathrm{d}^2b/\mathrm{d}v^2$ do we find $v_k = 3b$. And it can again be seen from this equation that what I have termed the weak point of my theory is actually responsible for the theoretical impossibility of calculating accurately the critical volume. Using an approximation formula for $b$ I was able to determine $v_k$ as about 2.2 $b_g$. This equation for determining the critical volume I gave and used in my paper in honour of Boltzmann; it was repeated in part in my 1910 treatises. When I had realized this large deviation in the critical volume I also feared a large deviation in the other critical data, i.e. non-compliance with the formulae:

$$RT_k = \frac{8}{27}\frac{a}{b_g} \text{ and } p_k = \frac{1}{27}\frac{a}{b_g{}^2} \tag{D}$$

To my great joy, however, and not without astonishment, I found that the two equations used to calculate $a$ and $b$ from the critical data remain unchanged. That I was able to conclude from the results of Sydney Young's admirable experiments on the volumes of co-existing vapour and liquid

phases and on the saturation pressure level at various temperatures. I showed this recently in a treatise to which I shall refer again in the present lecture. However I can explain it as follows: Sydney Young determines inter alia the value of

$$\frac{pv}{RT} \tag{D′}$$

at the critical point and finds $1/3.77$. If $p$ and $T$ have the same values as in my theory, providing b is imagined to be constant, the difference from $3/8$, the value which I found for $pv/RT$, can be ascribed wholly to the volume. And this, we can say, is entirely correct. The critical volume is not 3 $b_g$ but $(3/h)$ $b_g = 2.125\ b_g$ (approximately). And the product $pv/RT$ is not $3/8$ but $3/8\ \sqrt{2}$. For the value of

$$\left(\frac{T}{p}\frac{\mathrm{d}p}{\mathrm{d}T}\right)_k - \mathrm{I}$$

my equation gives $a/pv^2$. A value of about 6 is found for this value from Sydney Young's experiments. Therefore for $p_k$ we have the value: $p_k = a/6vk^2$, and with $v_k = (3/d/2)bg$ the value $p_k = (I/27)a/b_g^2$, as was originally found, is again obtained for $p_k$.

It will thus be seen that I have never been able to consider that the last word had been said about the equation of state and I have continually re-turned to it during other studies. As early as 1873 I recognized the possibility that $a$ and $b$ might vary with temperature, and it is well known that Clausius even assumed the value of a to be inversely proportional to the absolute temperature. Thus he thought he could with probability account for the equation

$$\left(\frac{T}{p}\frac{\mathrm{d}p}{\mathrm{d}T} - \mathrm{I}\right)_k = 6$$

only the half being found when a and $b$ are held constant. The foregoing remarks signify that this value does not arise from a change in a with tem-perature, but merely from the change in $b$ with the volume.

For a long time I searched for a definite characteristic to find whether just making $b$ variable is sufficient to bring about complete agreement between

my formula and experiment, and in the case of remaining discrepancies, whether perhaps it is necessary to assume variability of $a$ and $b$ with temperature; and now I come to my latest studies on the equation of state.

(3) In 1906 before the Royal Academy of Sciences in Amsterdam I gave a lecture entitled: pseudo association. At the time, however, I contented myself with an oral communication. But one of my pupils, Dr. Hallo, took it down in shorthand and later Dr.Van Rij incorporated it in his inaugural dissertation and developed the theme further. As the criterion whether the variability of $b$ with the volume would be sufficient to bring about agreement between my formula and Sydney Young's experimentally determined liquid and vapour volumes I used in my lecture the Clapeyron principle which, with $b$ varying only with $v$ and not with $T$, and with a constant, leads to the equation

$$\left(\frac{T}{p}\frac{dp}{dT} - 1\right) p = \frac{\dfrac{a}{v_1} - \dfrac{a}{v_2}}{v_2 - v_1} = \frac{a}{v_1 v_2}$$

or

$$\left(\frac{T}{p}\frac{dp}{dT} - 1\right) p v_1 v_2 = a$$

To ensure that only parameters are involved which are directly determinable by experiment, we may also write

$$\frac{\left(\dfrac{T}{p}\dfrac{dp}{dT} - 1\right) p v_1 v_2}{\left(\dfrac{T}{p}\dfrac{dp}{dT} - 1\right)_k p_k v_k^2} = 1 \tag{E}$$

All the parameters on the left of this equation were accurately determined by Sydney Young for a series of substances. At the critical temperature the value of the left-hand side is, of course, equal to unity; but what is the value at temperatures that are only a fraction of $T_k$? Here it appears that as the temperature decreases the value of the left-hand side increases, very rapidly at first, then at an imperceptible rate.

Sydney Young's experiments only go as far as a value of $T/T_k = 2/3$. The right-hand side has then increased to 1.4 and seems to be approaching asymptotically the value 1.5. The value of the right-hand side may very accurately be represented by the empirical formula

$$1 + \sqrt{1 - m} - \frac{1 - m}{2} \qquad\qquad (F)$$

where $T/T_k = m$.

At a temperature very close to the critical, e.g. $m = 0.99$, the increase in this expression is as much as 0.1 whereas if the square root of 1 - $m$ did not occur in the formula and the increase were only to be represented by $1 - m$, it would be less by a factor of ten.

I then had to examine whether the assumption that a or b is temperature-dependent could account correctly for this increase of the right-hand side; and were such not the case, whether another expression for the internal pressure, which I have always written as $a/V^2$, could explain it. As a result of this examination it was found that each temperature function for a and b compatible with such a rapid initial increase of the right-hand side, must contain $\sqrt{1 - m}$. Yet above the critical temperature that would give imaginary values for a and b and is obviously at variance with the whole behaviour of gases. It also appeared that no other assumption for the internal pressure can lead to such a rapid initial increase as the one under discussion. It should not be forgotten that the critical temperature is actually not a special temperature. At this temperature the co-existing densities are equal in magnitude. That alone gives this temperature a meaning which under all other circumstances it does not have. An abrupt jump, a rapid increase either in a or b would make the temperature quite a special one at any level of compression and its determination would then be possible at any density level. In fact, bluntly speaking, the result would be: an equation of state compatible with experimental data is totally impossible. No such equation is possible, unless something is added, namely that the molecules associate to form larger complexes; this year, therefore, I have given two treatises at the Academy in Amsterdam on this possible association. I have termed it <<pseudo association >> to differentiate it from the association which is of chemical origin. The possible formation of larger molecular complexes, particularly in the liquid state, has frequently been emphasized and the finding that the assumption is necessary to achieve agreement between the state equation

and experiment will hence cause no surprise. Unfortunately my examination is still incomplete. I have found it arduous. And I have had to make use of every piece of evidence to derive something concrete. Nevertheless so much has emerged that it will have to be assumed that a large number of single molecules are required to form a new group which holds together and behaves as a new, larger unit in the molecular motion.

What is the origin of this complex formation, this pseudo association? I was compelled to assume it because it seemed to me the only way to make an equation of state - whichever it is - compatible with the results of measurements. However, as a result of a remark by Debye in last month's *An den der Physik,* I remembered a phrase of Boltzmann's. When a few years ago I was privileged to have him with me for some days, among the many matters which we discussed he told me in passing that he was unable to reduce the attraction of molecules to a surface force. At the time the significance of this remark of Boltzmann's did not dawn on me- only now do I think I appreciate what he meant. As far back as in my treatise of 1873 I came to the conclusion that the attraction of the molecules decreases extremely quickly with distance, indeed that the attraction only has an appreciable value at distances close to the size of the molecules. At the time this even prompted me to state that in the case of gases the collisions alone are responsible for their exhibiting an attraction. And it must have been Boltzmann's view that it is only admissible to adopt Laplace's procedure and assume a surface force as a consequence of the attraction provided it does not fall off so rapidly.* Debye's remark implied that Boltzmann had predicted the formation of a complex. Thus, so I believe, the assumption of pseudo association is justified from the theoretical standpoint. And now I think I may state how I proceeded in my latest treatise whichappeared in November of this year. Pseudo association differs from true association in that the latter is the result of new chemical forces which arise only when molecules are combined to form e.g. double molecules, whereas pseudo association must be ascribed wholly to the normal molecular forces. Now, since this force diminishes so quickly, it has two consequences. Firstly it results in the formation of a complex, but that is not all. Secondly it leads to a surface pressure, although a lower one. And this is precisely what I was compelled to assume in my calculations were I to have some prospect of accounting for the cited differences. I thus sought to make this clear in the following manner. Let the number of molecules that have combined into a complex be so large that it

* Cf. L. Boltzmann, *Gastheorie,* I I, p.176.

is possible to speak of a molecule at the centre surrounded by a single layer containing almost as many other molecules as is possible simultaneously. Then, for the surrounding molecules the attraction directed towards the interior acts only to maintain the complex; and this part of its attraction is lost for the surface pressure. Only the forces acting outwards from these molecules can contribute to the formation of the internal pressure. But of course, for pseudo association as for true association the number of formed complexes increases with decreasing temperature and volume. At the critical point, so I was compelled to conclude, only a very small part of the weight is present as complexes.

If pseudo association exists in a substance, there are at least two types of molecules, namely simple and complex. I say at least two types because it cannot be assumed that all complexes are of equal size. But as a first step I have assumed only two types, i.e. simple molecules and n-fold molecules. For a really scientific treatment, of course, it would be necessary to assume all values of $n$ as possible and to seek the law of distribution for these values. For the time being, however, I have confined myself to assuming only a single type of complex. We then have a binary mixture. It was very fortunate that for many years I had made a serious study of the laws of binary mixtures - and so I come to the fourth point of my lecture. Not to demand too much of your attention, however, I promise to be quite brief.

(4) When I first conceived the idea of utilizing my equation to study the properties of binary mixtures I can no longer say. But even 20 years ago, at the insistence of my friend Kamerlingh Onnes, I was able to publish a complete theory for binary mixtures. My <<Théorie moléculaire d'une substance composée de deux matiéres différentes>> (Molecular theory of a substance made up of two different constituents) appeared in the *Archives Néerlandaises* for 1890. I had written it in Dutch but my esteemed friend Bosscha undertook the difficult task of rendering it into French, a task which was all the more exacting as I had written it in an extremely concise form and the mathematical treatment led to particular points (plait points) and particular curves which at the time had rarely been examined in detail. Previously, however, my friend Korteweg, to whom I had communicated in broad outlines the outcome of my examinations, had studied the mathematical properties of these points and curves, a study which I have often found of great use. The reasons why I hesitated so long over publication were many and it would serve little purpose to enumerate them here. But one of the

reasons of scientific importance was the question which I kept asking my-
self: is it any use, until the study of the equation of state has been completed,
applying it to mixtures ? I appreciated in advance that as long as I was ignorant
of the law governing the variability of *b* and hence had to assume that *b* did
not vary with the volume, the results for many parameters would yield
values exhibiting numerically large differences as compared with the values
of these parameters as determined by experiment. Nevertheless, the consid-
eration that even with *b* constant my theory had not been unimportant in
the case of a single substance gave me the hope that many phenomena would
be explained qualitatively provided that a suitable value for *a* and *b* were
introduced for mixtures. It was of great importance for me to be acquainted
with Gibbs' treatises on the equilibrium of heterogeneous substances which
he had sent me immediately after their appearance. I made use inter alia of
his principle that for a given amount of substance equilibrium sets in if the
free energy is minimum for the given temperature and volume. In his
honour I named the equilibrium surface for a binary system the y-surface.
For, the free energy whose significance for the equilibrium he was the first
to recognize, he always represents by the sign ψ.

   The phenomena are really not complex in the case of a simple substance
and it is an easy matter to obtain a general picture of them. It is therefore
very surprising that in a mere binary mixture they become so complex that
they have often been compared with a labyrinth. This is particularly so
where three-phase pressure can exist. And it has now become clear that they
are at least qualitatively in agreement with the <<Théorie moléculaire, etc.>>
from which they can be derived and indeed often predicted. Owing to the
many experimental studies to which it has given rise I have frequently found
the opportunity of discussing it closely in special communications. Thus in
the years 1907 to 1909 about 15 treatises of this nature have appeared in the
proceedings of the Academy at Amsterdam. It would be an impressive
number were I just to mention the names of the physicists and chemists who,
guided by this theory, have studied and still are studying binary mixtures.
It begins with Kuenen and ends with Dr. Jean Timmermans of Belgium
whose studies have still to be completed but which have already been pub-
lished in part.

And if now I may be permitted to look back on the way I have come, I
must confess that it may fairly be called a detour. Immediately the necessity
of assuming association became clear to ,me I extended my equation of state

analogously to the formula for a binary mixture and introduced a new para-
meter, the degree of association. This degree of association is determined by
means of Gibbs' equation to which I have referred. The degree of association
thus determined must then be introduced into the equation of state. And I
confess that this is a detour. Perhaps there is a direct way. That this way is
seriously being sought I know from those in direct contact with me. In the
search for this way Gibbs' *Elementary Principles of Statistical Mechanics* will be
a necessary guide. In this lecture, I have only given the history of the origin
and further elaboration of my theoretical studies and therefore had to speak
of the difficulties that had to be surmounted. Consequently I could not, or
only meagrely, discuss how they have assisted in correctly understanding the
phenomena. One of the main conclusions, which I have termed the <<Law
of corresponding states>>, has, I may say, become universally known. Nor
have I discussed how this law was a potent contributory factor in Dewar's
determination of the method of liquefying hydrogen, and particularly in
Kamerlingh Onnes' determination of the method of liquefying helium. I
have also forgone detailed discussion of the temperature at which, to use
Regnault's nomenclature, a gas starts to behave like a <<pluperfect gas>> (gaz
plus que parfait), which temperature has been found to have a value of
$(27/8)$ $T_k$ - besides the   temperature at which it may be stated that the Joule-
Kelvin effect reverses: its value is found to be $(27/4)$ $T_k$

Neither have I spoken of my perhaps somewhat overhasty efforts to
determine the equation of state of the molecule itself. I have even omitted
to say why I thought I had to go to such trouble to determine the relation
between *p, v* and *T* for a substance. The formulae of thermodynamics are
effective and can actually be applied in all problems, even to determining
thermal parameters, only when this relation is known, otherwise they can
be regarded as just one equation between two unknowns. I have explicitly
emphasised this in the book in commemoration of Kamerlingh Onnes pub-
lished in 1904.

But it was not my intention to discuss all that and I would not have had
sufficient time. Yet it does not seem to me superfluous, perhaps it is even
necessary, to make a general observation. It will be perfectly clear that in
all my studies I was quite convinced of the real existence of molecules, that
I never regarded them as a figment of my imagination, nor even as mere
centres of force effects. I considered them to be the actual bodies, thus what we
term <<body>> in daily speech ought better to be called <<pseudo body>>. It is
an aggregate of bodies and empty space. We do not know the nature of a

molecule consisting of a single chemical atom. It would be premature to seek to answer this question but to admit this ignorance in no way impairs the belief in its real existence. When I began my studies I had the feeling that I was almost alone in holding that view. And when, as occurred already in my 1873 treatise, I determined their number in one gram-mol, their size and the nature of their action, I was strengthened in my opinion, yet still there often arose within me the question whether in the final analysis a molecule is a figment of the imagination and the entire molecular theory too. And now I do not think it any exaggeration to state that the real existence of molecules is universally assumed by physicists. Many of those who opposed it most have ultimately been won over, and my theory may have been a contributory factor. And precisely this, I feel, is a step forward. Anyone acquainted with the writings of Boltzmann and Willard Gibbs will admit that physicists carrying great authority believe that the complex phenomena of the heat theory can only be interpreted in this way. It is a great pleasure for me that an increasing number of younger physicists find the inspiration for their work in studies and contemplations of the molecular theory. The crowning of my studies by the esteemed Royal Swedish Academy affords me satisfaction and fills me with gratitude, a gratitude which I cannot call eternal and in my old age I cannot even promise that it will be of long duration, but perhaps for this very reason my gratitude is all the more intense.

# Biography

Johannes Diderik van der -Waals was born on November 23, 1837 in Leyden, The Netherlands, the son of Jacobus van der Waals and Elisabeth van den Burg. After having finished elementary education at his birthplace he became a schoolteacher. Although he had no knowledge of classical languages, and thus was not allowed to take academic examinations, he continued studying at Leyden University in his spare time during 1862-65. In this way he also obtained teaching certificates in mathematics and physics.

In 1864 he was appointed teacher at a secondary school at Deventer; in 1866 he moved to The Hague, first as teacher and later as Director of one of the secondary schools in that town.

New legislation whereby university students in science were exempted from the conditions concerning prior classical education enabled Van der Waals to sit for university examinations. In 1873 he obtained his doctor's degree for a thesis entitled Over de *Continuiteit van den Gus- en Vloeistoftoestand* (On the continuity of the gas and liquid state), which put him at once in the foremost rank of physicists. In this thesis he put forward an <<Equation of State>> embracing both the gaseous and the liquid state; he could demonstrate that these two states of aggregation not only merge into each other in a continuous manner, but that they are in fact of the same nature. The importance of this conclusion from Van der Waals' very first paper can be judged from the remarks made by James Clerk Maxwell in Nature, <<that there can be no doubt that the name of Van der Waals will soon be among the foremost in molecular science>> and <<It has certainly directed the attention of more than one inquirer to the study of the Low-Dutch language in which it is written>> (Maxwell probably meant to say <<Low-German>>, which would also be incorrect, since Dutch is a language in its own right). Subsequently, numerous papers on this and related subjects were published in the *Proceedings of the Royal Netherlands Academy of Sciences* and in the *Archives Néerlandaises,* and they were also translated into other languages.

When, in 1876, the new Law on Higher Education was established which promoted the old Athenaeum Illustre of Amsterdam to university status, Van

der Waals was appointed the first Professor of Physics. Together with Van
'␣t Hoff and Hugo de Vries, the geneticist, he contributed to the fame of the
University, and remained faithful to it until his retirement, in spite of en-
ticing invitations from elsewhere.

The immediate cause of Van der Waals' interest in the subject of his thesis
was R. Clausius' treatise considering heat as a phenomenon of motion, which
led him to look for an explanation for T. Andrews' experiments (1869) re-
vealing the existence of <<critical temperatures>> in gases. It was Van der Waals'
genius that made him see the necessity of taking into account the volumes
of molecules and the intermolecular forces <<Van der Waals forces>>, as they
are now generally called) in establishing the relationship between the pres-
sure, volume and temperature of gases and liquids.

A second great discovery - arrived at after much arduous work - was pub-
lished in 1880, when he enunciated the Law of Corresponding States. This
showed that if pressure is expressed as a simple function of the critical pres-
sure, volume as one of the critical volume, and temperature as one of the
critical temperature, a general form of the equation of state is obtained which
is applicable to all substances, since the three constants $a, b,$ and $R$ $in$ the
equation, which can be expressed in the critial quantities of a particular sub-
stance, will disappear. It was this law which served as a guide during experi-
ments which ultimately led to the liquefaction of hydrogen by J. Dewar in
1898 and of helium by H. Kamerlingh Onnes in 1908. The latter, who in
1913 received the Nobel Prize for his low-temperature studies and his pro-
duction of liquid helium, wrote in 1910 <<that Van der Waals' studies have
always been considered as a magic wand for carrying out experiments and
that the Cryogenic Laboratory at Leyden has developed under the influence
of his theories>>.

Ten years later, in 1890, the first treatise on the <<Theory of Binary Solu-
tions>> appeared in the *Archives Néerlandaises* - another great achievement of
Van der Waals. By relating his equation of state with the Second Law of
Thermodynamics, in the form first proposed by W. Gibbs in his treatises
on the equilibrium of heterogeneous substances, he was able to arrive at a
graphical representation of his mathematical formulations in the form of a
surface which he called <<$\psi$ -surface>>  in honour of Gibbs, who had chosen the
Greek letter $\psi$ as a symbol for the free energy, which he realised was signifi-
cant for the equilibrium. The theory of binary mixtures gave rise to numer-
ous series of experiments, one of the first being carried out by J. P. Kuenen,
who found characteristics of critical phenomena fully predictable by the

theory. Lectures on this subject were subsequently assembled in the *Lehrbuch dev Thermodynamik* (Textbook of thermodynamics) by Van der Waals and Ph.Kohnstamm.

Mention should also be made of Van der Waals' thermodynamic theory of capillarity, which in its basic form first appeared in 1893. In this, he accepted the existence of a gradual, though very rapid, change of density at the boundary layer between liquid and vapour - a view which differed from that of Gibbs, who assumed a sudden transition of the density of the fluid into that of the vapour. In contrast to Laplace, who had earlier formed a theory on these phenomena, Van der Waals also held the view that the molecules are in permanent, rapid motion. Experiments with regard to phenomena in the vicinity of the critical temperature decided in favour of Van der Waals' concepts.

Van der Waals was the recipient of numerous honours and distinctions, of which the following should be particularly mentioned. He received an honorary doctorate of the University of Cambridge ; was made honorary member of the Imperial Society of Naturalists of Moscow, the Royal Irish Academy and the American Philosophical Society; corresponding member of the Institut de France and the Royal Academy of Sciences of Berlin; associate member of the Royal Academy of Sciences of Belgium ; and foreign member of the Chemical Society of London, the National Academy of Sciences of the U.S.A., and of the Accademia dei Lincei of Rome.

In 1864, Van der Waals married Anna Magdalena Smit, who died early. He never married again. They had three daughters and one son. The daughters were Anne Madeleine who, after her mother's early death, ran the house and looked after her father; Jacqueline Elisabeth, who was a teacher of history and a well-known poetess; and Johanna Diderica, who was a teacher of English. The son, Johannes Diderik Jr., was Professor of Physics at Groningen University 1903-08, and subsequently succeeded his father in the Physics Chair of the University of Amsterdam.

Van der Waals' main recreations were walking, particularly in the country, and reading. He died in Amsterdam on March 8, 1923.

Physics 1911

WILHELM  WIEN

<<for *his discoveries regarding the laws governing the radiation of heat*>>

# Physics  1911

*Presentation Speech by the Librarian of the National Library, Dr. E. W. Dahlgren, President of the Royal Swedish Academy of Sciences*

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen.

The Royal Academy of Sciences has awarded the Nobel Prize for Physics, for the year 1911, to Wilhelm Wien, Professor at the University of Würzburg, for his discoveries concerning the laws of heat radiation.

Ever since the beginning of the last century and, in particular, since spectrum analysis, reached an advanced stage of development as a result of the fundamental work by Bunsen and Kirchhoff, the problem of the laws of heat radiation has occupied the attention of physicists to an exceptionally high degree.

The solution of this problem has presented immeasurable difficulties both in the theoretical and experimental respects, and it would hardly seem possible to solve this task without a knowledge of certain laws which embrace a wide diversity of radiating bodies.

One of these is the famous Kirchhoff law of the relationship between the ability of substances to emit and to absorb radiation energy. It relates the laws of radiation of all bodies so far as their radiation is dependent on temperature to those laws which are valid for the radiation emitted by a completely black body.

The search for the latter laws has therefore been one of the most fundamental problems of radiation theory. These laws have been discovered in the last decades and, by virtue of the great importance that attaches to them, belong to the major achievements of modern physics.

The  difficulty in investigating the laws of radiation of black bodies was, firstly, that no completely black body exists in nature. In accordance with Kirchhoff's definition, such a body would reflect no light at all, nor allow light to pass. Even substances such as soot, platinum black etc. reflect part of the incident light.

This difficulty was only removed in 1895, when Wien and Lummer stated the principles according to which a completely black body could be constructed, and showed that the radiation which issues from a small hole in a hollow body whose walls have the same temperature behaves in the same

manner as the radiation emitted by a completely black body. The principle of this arrangement is based on the views of Kirchhoff and Boltzmann and had already been applied in part by Christiansen in 1884.

With the assistance of this apparatus it now became possible to investigate black body radiation. In this manner, Lummer, together with Pringsheim and Kurlbaum, succeeded in substantiating the so-called Stefan-Boltzmann law which indicates the relationship between the quantity of heat radiated by a black body and its temperature.

This solved in a highly satisfactory manner one of the major problems of radiation theory, i.e. that which touches total black body radiation.

However, the thermal energy that radiates from a body contains rays of different wavelengths whose intensities differ and change with the temperature of the body. It therefore remained to investigate the manner of change in intensity with wavelength and temperature.

An important step towards the solution of this question had been taken as early as 1886 by Langley who, with his famous spectrobolometer, investigated the distribution of radiation in the spectrum of a number of heat sources of high and low temperature. Inter alia these classical researches showed that the radiation had a maximum for a certain wavelength and that the maximum shifted in the direction of the shorter waves with increasing temperature.

In 1893 Wien published a theoretical paper which was destined to acquire the utmost importance in the development of radiation theory. In this paper he presented his so-called displacement law which provides a very simple relationship between the wavelength having the greatest radiation energy and the temperature of the radiating black body.

The importance of Wien's displacement law extends in various directions. As we shall see, it provides one of the conditions which are required for the determination of the relationships between energy radiation, wavelength and temperature for black bodies, and thus represents one of the most important laws in the theory of heat radiation. Wien's displacement law has however acquired the greatest possible importance in other contexts as well. Lummer and Pringsheim have shown that the radiation of bodies other than black bodies obeys the displacement law, with the sole difference that the constant which forms part of the formula has a different value.

Thus it became possible to determine the temperature of bodies, within fairly narrow limits, simply by seeking the wavelength at which radiation is greatest. The method has successfully been applied to the determination

of the temperature of our light sources, of the sun and of some of the fixed stars, and has yielded extremely interesting results.

The Stefan-Boltzmann law and the Wien displacement law are the most penetrating statements on a secure theoretical foundation that have been discovered with respect to thermal radiation. They do not solve the central problem, i.e. the question as to the distribution of radiation energy over the various wavelengths at different black body temperatures. We can however say that Wien's displacement law provides half the answer to the problem. We have one condition for determining the desired function. One more would be sufficient for solving the problem.

It was only natural that Wien who had contributed so much to the advancement of radiation theory should make an attempt to find an answer to the last remaining question also, i.e. that of the distribution of energy in radiation. In 1894 he indeed deduced a black body radiation law. This law has the virtue that, at short wavelengths, it agrees with the above-mentioned experimental investigations by Lummer and Pringsheim.

By a different approach from that used by Wien, Lord Rayleigh also succeeded in discovering a law of radiation. By contrast with that discovered by Wien, it agrees with experiment for long wavelengths.

The problem now became to bridge the gap between these two laws each of which had been shown to be valid in a specific context. It was Planck who solved this problem; as far as we are aware, his formula provides the long sought-after connecting link between radiation energy, wavelength and black body temperature.

These remarks show that we now know, with considerable accuracy, the laws that govern thermal black body radiation.

A magnificent and unique task has thus been undertaken and brought to a certain conclusion - a task which has claimed the liveliest interest and energy of the leading physicists of our time.

Among the researchers in this field now living it was Wilhelm Wien who made the greatest and most significant contribution, and the Academy of Sciences has therefore decided to award to him the Nobel Prize for Physics for the year 1911.

Professor Wien.   The Swedish Academy of Sciences has awarded to you this year's Nobel Prize for Physics for your discoveries concerning the laws of thermal radiation. You have devoted your researches to one of the most difficult and spectacular problems of physics, and among the researchers now

living it is you who has succeeded in making the greatest and most significant contributions to the solution of the problem. In admiration of the completed task and with the wish that further success may be granted to you in future work, the Academy now calls upon you to receive the prize from the hands of his Majesty the King.

Wilhelm Wien

# On the laws of thermal radiation

*Nobel Lecture, December 11, 1911*

The kind recognition which my work on thermal radiation has received in the views of your ancient and famous Academy of Sciences gives me particular pleasure to speak to you about this subject which is again attracting the attention of all physicists because of the difficulty of the problems involved. As soon as we step beyond the established boundaries of pure thermodynamic theory, we enter a trackless region confronting us with obstacles which even the most astute of us are almost at a loss to tackle.

If, as is the custom, I speak mainly about my own researches, I must say that I was fortunate in finding that not everything had yet been gleaned in the field of general thermodynamic radiation theory. Using known physical laws it was possible to derive a general law of radiation theory which has, under the name of the displacement law, been acclaimed by fellow workers. In applying thermodynamics to the theory of radiation, we make use of the ideal processes which have been found so fruitful elsewhere. These are mental experiments whose realization is frequently impracticable and which nevertheless lead to reliable results. Such deliberations can only be undertaken if all the processes on which, governed by laws, the mental experiments are based, are known, so that the effect of any change can be stated accurately and completely. Further, to be allowed to idealize, we must neglect all non-essential secondary phenomena, while considering only everything indissolubly connected with the processes under examination. In the application of mechanical heat theory, this method has proved to be extremely fruitful. Helmholtz used it in the theory of concentration flows, Van 't Hoff used it in applying thermodynamics to the theory of solutions. It is necessary, in these deliberations, to presuppose the existence of a so-called semi-permeable membrane which permits the solvent to pass, but not the substance dissolved. Although it is impossible to prepare membranes which strictly satisfy this requirement, we can assume them as possible in the ideal processes, because the laws of Nature set no limit to approximation to semipermeability. The conclusions drawn from these assumptions have in any case always been in agreement with experience. In radiation theory,

analogous deliberations can be made if we assume perfectly reflecting bodies as possible in the ideal processes. Kirchhoff used them for proving his famous theorem of the constancy of the ratio of emission and absorption power. This theorem has become one of the most general of radiation theory and expresses the existence of a certain temperature equilibrium for radiation. According to it, there must exist, in a cavity surrounded by bodies of equal temperature, a radiation energy that is independent of the nature of the bodies. If in the walls surrounding this cavity a small aperture is made through which radiation issues, we obtain a radiation which is independent of the nature of the emitting body, and is wholly determined by the temperature. The same radiation would also be emitted by a body which does not reflect any rays and which is therefore designated as completely black, and this radiation is called the radiation of a black body or black-body radiation.

The Kirchhoff theorem is not limited to radiation caused by thermal processes. It seems to be valid for most, if not all luminous processes. That the temperature concept can be applied to all luminous processes is beyond doubt. Since we can produce all types of light by means of hot bodies, we can ascribe, to the radiation in thermal equilibrium with hot bodies, the temperature of these bodies, and thus every radiation, even that issueing from a phosphorescent body, has a certain temperature for every colour. This temperature has however no connection whatever with that of the body, nor is it possible as yet to state how e.g. a phosphorescent body comes into equilibrium with radiation. These conditions are bound to be very complicated, in particular in the case of bodies which convert the absorbed radiation and emit it after a long interval of time.

Again using ideal processes and assuming radiation pressure, which at that time had been deduced from the electromagnetic theory of light, Boltzmann derived from thermodynamics the law, previously empirically formulated by Stefan, that the radiation of a black body is proportional to the fourth power of the absolute temperature.

This did not exhaust the conclusions to be drawn from thermodynamics. There remained the determination of the changes undergone by the colours present in radiation with changes of temperature. Computation of this change is again based on an ideal process. For this, we must assume wholly reflecting bodies as possible that scatter all incident radiation and which can therefore be described as completely white. If we allow the radiation coming from a black body to enter a space of this kind, it will in the end propagate

exactly as if the walls of the space were themselves radiant and had the same temperature as the black body. If we then seal off the black body from the white space, we obtain the unrealisable case of a radiation permanently reciprocated between mirroring walls. In our thoughts, we continue the experiment. We imagine the volume of our space to be reduced by movement of the walls, so that the entire radiation is concentrated in a smaller space. Since radiation exercises a certain pressure, the pressure of light, on the walls it strikes, it follows that some work must have been expended in size reduction, as if we had compressed a gas. Because of the low magnitude of the pressure of light, this work is very small, but it can be computed accurately, which is all that matters in the case under discussion. In accordance with the principle of the conservation of energy, this work cannot be lost, it is converted into radiation, which further increases the radiation concentration. This change of radiation density due to the movement of the white walls is not the only change to which the radiation is subjected. When a light ray is reflected by a moving mirror, it undergoes a change of the colour dictated by the oscillation frequency. This change in accordance with the so-called Doppler principle plays a substantial part in astrophysics. The spectrum line emitted by an approaching celestial body appears to be displaced in the direction of shorter wavelengths in the ratio, its velocity : the velocity of light. This is also the case when a ray is reflected by a moving mirror, except that the change is twice as great. We are therefore able to calculate completely the change undergone by the radiation as a result of the movement of the walls. The pressure of light which is essential to these deliberations was demonstrated at a much later date, Lebedev being the first to do so. Arrhenius used it to explain the formation of comet tails. Before that, it was only a conclusion drawn from Maxwell's electromagnetic theory. We now calculate both the change ofradiation density due to movement, and the change of the various wavelengths. From this mental experiment, we can draw an important conclusion. We can conclude from the second law of mechanical heat theory that the spectral composition of the radiation which we have changed by compression in the space with mirror walls is exactly the same as it would be had we obtained the increased density of radiation by raising the temperature, because we would otherwise be able to produce, by means of colour filters, unequal radiation densities in the two spaces, and to generate work from heat without compensation. Since we can calculate the change of individual wavelengths due to compression, we can also derive the manner in which the spectral composition of black-body radiation varies

with temperature. Without discussing this calculation in detail, let me give you the result: the radiation energy of a certain wavelength varies with changing temperature so that the product of temperature and wavelength remains  constant.

   Using this displacement law it is easy to calculate the distribution of the intensity of thermal radiation over the various wavelengths for any temperature, as soon as it is known for one temperature.

   The shift of the maximum of intensity in particular is directly accessible to observation. Since the wavelength at which the maximum intensity lies also defines the principal area of the wavelength which is most intense at this temperature, we can, by changing the temperature, shift the principal area of radiation in the direction of short or long wavelengths of any desired magnitude. Of the other derivations of the displacement law, I shall only mention that by H. A. Lorentz. If, in the electromagnetic equations of Maxwell, we imagine all spatial dimensions as being displaced in time in the same ratio, these equations show that the electromagnetic energy must decrease in proportion to the fourth power of displacement. Since, according to the Stefan-Boltzmann law, energy increases with the fourth power of absolute temperature, the linear dimensions must vary inversely proportionately to the absolute temperature. Each characteristic length must vary in this ratio, from which the displacement law follows.

   From the displacement law, we can calculate the temperature of the sun if we are entitled to assume that the radiation of the sun must be ascribed to heat, and if we know the position of the maximum of the energy of solar radiation. Different figures are given for this position by different observers, i.e. $0.532\,\mu$ according to Very, and $0.433\,\mu$ according to Abbot and Fowle. Depending on the figure used, the temperature of the sun works out at $5,530°$ and $6,790°$. However much the observers may differ, there can be no doubt that the maximum of solar radiation is situated in the visible range of wavelengths. This is to say that the temperature of the sun is the most favourable utilization of the radiant energy of a black body for our illumination and that, in our artificial light sources which utilize thermal radiation we must aim at achieving this temperature, from which we are admittedly far removed as yet.

   I wish to discuss yet another application of the displacement law, i.e. the possibility of calculating the wavelength of X-rays. As we know, X-rays are produced by the impact of electrons on solid bodies, and their wavelength must be a function of the velocity of the electrons. According to the

kinetic theory of gases, the mean kinetic energy of a molecule is a measure of absolute temperature. If, as is done in the theory of electrons, we assume that this is also valid for the kinetic energy of the electrons, the electric energy of the cathode rays would be a measure of their temperature. If we substitute the temperature thus calculated in the displacement law, we find that the wavelength of the maximum of the intensity indicates a wavelength range of X-rays which agrees well with the wavelengths found by other arguments. It might be objected that we must not ascribe a temperature to the electrons. The permissibility of our procedure can however be justified by an inversion of the above argument. Radiation in an enclosed space must necessarily release electrons whose velocity according to Einstein's law is proportional to the oscillation frequency. The energy maximum of radiation generates electrons whose velocity is so great that their kinetic energy comes very close to the temperature associated with the maximum of energy.

The displacement law exhausts the conclusions that can be drawn from pure thermodynamics with respect to radiation theory. All these conclusions have been confirmed by experience. The individual colours present in the radiation are mutually wholly independent. The manner in which at a given temperature the intensity of radiation is distributed over the individual wavelengths cannot be determined from thermodynamics. For this, one must examine the mechanism of the radiation process in detail. Similar conditions obtain in the theory of gases. Thermodynamics can tell us nothing about the magnitude of the specific heat of the gases; what is required, is to examine molecular motion. But the kinetic theory of gases which is based on probability calculations has made much greater progress than the corresponding theory of radiation. The statistical theory of gases has set itself the task of accounting also for the laws of thermodynamics. I do not wish to discuss here the extent to which the task may be considered as having been solved, and whether we are entitled to consider the reduction of the second law to probability as a wholly satisfactory theory. It has in any case been very successful, in particular since a theoretical explanation has been found of the deviations from the thermodynamic state of equilibrium, the so-called fluctuations, e.g. in Brownian movement. None of the statistical theories of radiation has however as yet even attempted to derive the Stefan-Boltzmann law and the displacement law, which must always be introduced into theory from outside. Quite apart from this, we are as yet far removed from a satisfactory theory to account for the distribution of radiation energy over the individual   wavelengths.

I myself made the first attempt in this direction. I endeavoured to by-pass the problem of applying probability calculation to radiation theory by imagining radiation as resulting from gas molecules moving according to laws of probability. Instead of these we could also imagine electrons generating radiation on striking molecules. What is essential is the further assumption that such a particle will only emit radiation of a certain wavelength dictated by velocity, and that the velocity distribution of the particles obeys Maxwell's law. With the assistance of the radiation laws derived from thermodynamics we obtain a radiation law which shows good agreement with experience for a wide range of wavelengths, i.e. for the range in which the product of temperature and wavelength is not unduly large.

Imperfect as this first attempt was, a formula had been obtained which considerably deviates from reality for large wavelengths only. Since observations however establish these deviations beyond doubt, it was clear that the formula had to be modified.

Lord Rayleigh was the first to approach the problem from an entirely different angle. He made the attempt to apply to the radiation problem a very general theorem of statistical mechanics, i.e. the theorem of the uniform distribution of energy over the degrees of freedom of the system in the state of statistical equilibrium. The meaning of this theorem is as follows:

In the state of thermal equilibrium, all movements of the molecules are so completely irregular that there exists no movement which would be preferred over any other. The position of the moving parts can be established by geometrical parameters which are mutually independent and in the direction of which the movement falls. These are called the degrees of freedom of the system. As regards the kinetic energy of movement, no degree of freedom is preferred over another, so that each contains the same amount of the total energy.

Radiation present in an empty space can be represented so that a given number of degrees of freedom is allocated to it. If the waves are reflected back and forth by the walls, systems of standing waves are established which adapt themselves to the distances between two walls. This is most easily understood if we consider a vibrating string which can execute an arbitrary number of individual vibrations, but whose half wavelengths must be equal to the length of the string divided by an integer.

The individual standing waves possible represent the determinants of the processes and correspond to the degrees of freedom. If we allocate to each degree of freedom its proper amount of energy, we obtain the Rayleigh

radiation law, according to which the emission of radiation of a given wavelength is directly proportional to the absolute temperature, and inversely proportional to the fourth power of the wavelength. The law agrees with observation at exactly the point where the law discussed above failed, and it was at first considered to be a radiation law of limited validity. But if the process of radiation obeys the general laws of electromagnetic theory or of the theory of electrons, we must necessarily arrive at Rayleigh's radiation law, as Lorentz has shown. Viewed as a general radiation law, it directly contradicts all experience, because, according to it, energy would have to accumulate increasingly at the shortest wavelengths. The possibility that we are not dealing in reality with a true state of equilibrium of radiation, but that it very gradually approaches the state where all energy is only present in the shortest wavelengths, is also contradicted by experience. In the case of the visible rays, to which the Rayleigh formula no longer applies at attainable temperatures, we can easily calculate, according to the Kirchhoff law, that the state of equilibrium must be attained in the shortest time, which state however remains far removed from the Rayleigh law. We thus obtain an inkling of the extraordinary difficulties which confront exact definition of the radiation formula. The knowledge that current general electromagnetic theory is insufficient, that the theory of electrons is inadequate, to account for one of the most common of phenomena, i.e. the emission of light, remains purely negative as yet. We only know how the thing cannot be done, but we lack the signposts that would enable us to find our way. We do however know that none of the models whose mode of action is based on purely electromagnetic principles can lead to correct results.

It is the merit of Planck to have introduced new hypotheses which enable us to avoid Rayleigh's radiation law. For long waves, this law is undoubtedly correct, and the right radiation formula must have a form such that, for very long waves, it passes into Rayleigh's law, and for short waves into the law formulated by me. Planck therefore retains as starting point the distribution of energy over the degrees of freedom of the system, but he subjects this distribution of energy to a restriction by introducing the famous hypothesis of elements of energy, according to which energy is not infinitely divisible, but can only be distributed in rather large quantities which cannot be divided further. This hypothesis would probably have been accepted without difficulty, if unchangeable particles, e.g. atoms of energy had been involved. It is an assumption that has proved inevitable for matter and electricity. The energy elements of Planck are however no atoms of energy; on the contrary,

the displacement law requires that they are inversely proportional to the wavelength of a given vibration. This represents great difficulty for the understanding of these energy elements. Once we accept the hypothesis, we arrive at an entirely different distribution of energy over the radiating centres, if we search for them according to the laws of probability. This does not however give us the radiation law. All we know is how much energy the radiating molecules possess on average at a certain temperature, but not how much energy they emit. To derive emission at a given energy, we need a definite model which emits radiation. We can only construct such a model on the foundation of the known electromagnetic laws, and it is at this early point that the difficulty of the theory starts. On the one hand we relinquish the electromagnetic laws by introducing the energy elements; on the other hand we make use of these same laws for discovering the relationship between emission and energy. It could admittedly be argued that the electromagnetic laws are only valid for mean values taken over extended periods, whereas the energy elements relate to the elementary radiation process itself. An oscillator radiating in accordance with the electromagnetic laws will indeed have little similarity with the real atoms. Planck however rightly argues that this does not matter precisely because radiation in the equilibrium state is independent of the nature of the emitting bodies. It will however be required of a model which is to stand for the real atoms that it should lack none of the essential characteristics of the event under consideration. Every body that emits thermal rays has the characteristic that it is able to convert thermal rays of one wavelength into thermal rays of a different wavelength. It is on this that there rests the possibility of a specific spectral composition being established in the radiation at all times. The Planck oscillator lacks this ability, and doubts are bound to be raised as to whether it can properly be used for establishing the relationship between energy and emission. This difficulty can be avoided, and the oscillator can be done without, if, with Debye, we decompose the radiation energy in a hollow cube into Planck energy elements and distribute these energy elements over the oscillation frequencies of the standing waves formed in the cube according to the laws of probability. The logarithm of this probability will then be proportional to entropy, and the law of radiation results, if we search for the maximum of this entropy. This result is proof of the extremely general nature of Planck's concepts.

There are however further difficulties. The energy elements increase with decreasing wavelength, and an oscillator exposed to incident radiation will,

at low intensity, need a very long time before it absorbs a full energy element. What happens if the incident radiation ceases, before an entire energy element has been absorbed? The difficulties implicit in answering this question have recently induced Planck to reformulate his original theory. He now assumes of emission only that it can occur exclusively by whole energy elements. Absorption is assumed to occur continuously according to the electromagnetic laws, and the energy content of an oscillator is assumed to have energy values capable of continuous change. The difficulty of the long absorption time is indeed avoided in this manner. On the other hand the close relationship between emission and absorption for the elementary process is relinquished, and this relationship now becomes valid statistically only. Every atom which only emits whole energy elements and absorbs continuously would therefore in the event of emission suddenly expend energy from its own reserve and would supplement this but little in the event of short irradiation. The special hypothesis must be made that, taken as a whole for many atoms in the stationary state, the absorbed energy after all becomes equal to that emitted. Whereas in the original form of the Planck theory the introduction of the hypothesis of energy elements was sufficient to permit the radiation laws to be derived, the new theories include uncertainties which can only be removed by further hypotheses. On the other hand the new fundamental hypothesis provides the possibility of further application, e.g. to electron emission.

It will be seen from the few observations I am able to offer in this context how great are the difficulties that remain in radiation theory. But the reference to these difficulties which it is the duty of the scientific approach to emphasize must not prevent us from paying tribute to the great positive achievements which the Planck theory has already accomplished.

It has produced a law of radiation which accomodates all observed data and includes the Rayleigh formula and my own formula as limiting cases. In addition, it has thrown unexpected light on an entirely different subject, i.e. the theory of specific heats.

It has long been known that the specific heats do not strictly obey the Dulong-Petit law and that they decrease at low temperatures. Diamonds do not obey the Dulong-Petit law even at normal temperatures. This law can be derived from the theorem of the distribution of kinetic energy over the degrees of freedom and states that, in solid bodies, every atom possesses, in accordance with its three degrees of freedom, three times the amount of energy, and, because of the potential energy, altogether six times the amount

of energy of a degree of freedom. If however we apply Planck's distribution of energy by energy elements, we obtain, according to Einstein, a formula for the specific heat which does in fact show the drop of temperature. This result is characteristic of the Planck theory. This theory of specific heats is not derived from the radiation formula, but from the formula for the mean energy of an oscillator which is based directly on the hypothesis of the energy elements. Unfortunately, difficulties are beginning to appear. The exact measurements of specific heats at low temperatures made in Nernst's laboratory have shown that the Einstein formula does not agree with observation. The formula which satisfies the experimental data contains half energy elements in addition to the whole energy elements, which cannot be interpreted satisfactorily as yet. There can however be no doubt that the Planck radiation theory provides the first step to the theory of specific heats.

That the theory should remain in many respects incomplete and provisional, is in the nature of the problem which is perhaps the most difficult which has ever confronted theoretical physics. What is involved is to leave behind the laws of theoretical physics confirmed by direct observation, which alone have been applied in the past, and to enter areas which are beyond the reach of direct observation.

The difficulties which beset radiation theory also emerge in an entirely different approach. Einstein investigated the fluctuations to which radiation is continuously subjected even in the state of equilibrium as a result of the irregularities of the thermal processes. If we imagine a small plate in a cavity filled with radiation, this plate will be subjected to a radiation pressure which is the same on average on both sides of the plate. Since the radiation must contain irregularities, the pressure will alternately be greater on one or the other side so that the plate will execute small irregular movements, similar to the Brownian movement of a dust particle suspended in a liquid. These fluctuations can be derived from probability calculations. According to the Boltzmann theorem there is a simple relationship between entropy and probability. The entropy of radiation is known from the radiation law, so that the probability of state is also known, from which the fluctuations can be calculated. The mathematical expression for these fluctuations consists, in a peculiar manner, of two members. The first is readily understandable: it is due to irregularities which arise as a result of the mutual interference of the many independent beams which meet in one point. Where the density of radiation energy is high, this term alone predominates; it corresponds to the radiation range that obeys Rayleigh's law.

The other term, which cannot be directly explained by the undulation theory, predominates at low density of radiation energy, where the radiation obeys the law formulated by me. It would be understandable if the radiation consisted of the Planck energy elements which would be localized even in an empty space. We cannot however pursue this line of thought. We cannot shake the undulation theory of light, which is one of the most firmly established constructions in the whole of physics. Moreover, the term to be explained by localized energy elements, is not present by itself, and it is a priori impossible to introduce a dualistic approach into optics, e.g. to assume simultaneously Huyghens' wave theory and Newton's emanation theory. All we can do is to relinquish the Boltzmann method of applying probability calculations to this type of fluctuations, or to assume that a new irregularity is introduced into radiation with the process of reflection.

In view of the magnitude of the difficulties it is natural that opinions about the path to be pursued should differ greatly. Some are of the opinion that the fundamental principles of electrodynamics must be changed. And yet, previous theory embraces a vast range of facts, it accounts for events even in the most rapid movements of the $\beta$ -rays, it has proved itself in the most precise optical measurements. In my view, all the signs suggest that the deviations from current theory are due to events within the atom. None of the processes in which the interior of the atom participates are amenable to current theory.

Sommerfeld made an attempt in this direction: He would ascribe to the constant $h$ of the radiation law, which together with the oscillation frequency dictates the magnitude of the energy element, a simple significance for the interior of the atom. It is alleged to determine the period in which an electron entering the atom comes to a stop, as a function of its velocity. On this view, the constant $h$ expresses a universal characteristic of the atoms. This theory permits calculation of the wavelength of X-rays, and it connects two previously independent attempts made by me to carry out this calculation. One method is based on the Planck theory of energy elements in that it assumes that the energy of the so-called secondary electrons released by X-rays is dictated by the energy element. The second method is based on the theory of electrons by means of which it calculates the energy radiated in the X-rays by sudden braking of an electron. From the determination of the energy of the cathode rays and the X-rays we can then calculate the brake path of the electrons and consequently the wavelength of the X-rays. The Sommerfeld theory connects these two theories. It has the great advantage

of explaining the generation of X-rays with the aid of electromagnetic theory. A number of conclusions can then be drawn from this which are in complete agreement with observation, e.g. the polarisation of X-rays, the diversity of emission and of hardness in various directions.

The Sommerfeld theory has the great advantage that it attempts to invest the universal constant h of the Planck radiation theory with physical significance. It has the disadvantage that it has been applied so far only to electron emission and absorption, but cannot yet solve the problem of thermal radiation.

We must admit that the result of radiation theory todate is not a very good one for theoretical physics. As we have seen, only the general thermodynamic theories have proved satisfactory as yet. The theory of electrons has come to grief over the radiation problem, the Planck theory has not yet been brought into a definite form. Research is faced with exceptional difficulties and we cannot discern when and how they can be overcome. In science, the redeeming idea often comes from an entirely different direction, investigations in an entirely different field often throw unexpected light on the dark aspects of unresolved problems. We must base our hope in the future in the expectation that the present era which has proved so fruitful for physics may not pass without a complete solution being found for the problem of thermal radiation. Far-reaching and new thoughts will have to set to work, but the result will be great, because we shall obtain a profound insight into the world of the atom and the elementary processes within it.

# Biography

Wilhelm Wien was born on January 13, 1864 at Fischhausen, in East Prussia. He was the son of the landowner Carl Wien, and seemed destined for the life of a gentleman farmer, but an economic crisis and his own secret sense of vocation led him to University studies. When in 1866 his parents moved to Drachstein, in the Rastenburg district of East Prussia, Wien went to school in 1879 first at Rastenburg and later, from 1880 till 1882, at the City School at Heidelberg. After leaving school he went, in 1882, to the University of Göttingen to study mathematics and the natural sciences and in the same year also to the University of Berlin. From 1883 until 1885 he worked in the laboratory of Hermann von Helmholtz and in 1886 he took his doctorate with a thesis on his experiments on the diffraction of light on sections of metals and on the influence of materials on the colour of refracted light.

His studies were then interrupted by the illness of his father and, until 1890, he helped in the management of his father's land. He was, however, able to spend, during this period, one semester with Helmholtz and in 1887 he did experiments on the permeability of metals to light and heat rays. When his father's land was sold he returned to the laboratory of Helmholtz, who had been moved to, and had become President of, the Physikalisch-Technische Reichsanstalt, established for the study of industrial problems. Here he remained until 1896 when he was appointed Professor of Physics at Aix-la-Chapelle in succession to Philipp Lenard. In 1899, he was appointed Professor of Physics at the University of Giessen. In 1900 he became Professor of the same subject at Würzburg, in succession to W. C. Röntgen, and in this year he published his *Lehrbuch der Hydrodynamik* (Textbook of hydrodynamics).

In 1902 he was invited to succeed Ludwig Boltzmann as Professor of Physics at the University of Leipzig and in 1906 to succeed Drude as Professor of Physics at the University of Berlin; but he refused both these invitations.

In 1920 he was appointed Professor of Physics at Munich, where he remained throughout the rest of his life.

In addition to the early work already mentioned, Wien worked, at the

Physikalisch-Technische Reichsanstalt, with Holborn on methods of measuring high temperatures with the Le Chatelier thermoelements and at the same time did theoretical work on thermodynamics, especially on the laws governing the radiation of heat.

In 1893 he announced the law which states that the wavelength changes with the temperature, a law which later became the law of displacement.

In 1894 he published a paper on temperature and the entropy of radiation, in which the terms temperature and entropy were extended to radiation in empty space. In this work he was led to define an ideal body, which he called the black body, which completely absorbs all radiations. In 1896 he published the formula of Wien, which was the result of work undertaken to find a formula for the composition of the radiation of such a black body. Later it was proved that this formula is valid only for the short waves, but Wien's work enabled Max Planck to resolve the problem of radiation in thermal equilibrium by means of quantum physics. For this work Wien was awarded the Nobel Prize for Physics for 1911. An interesting point about it is that this theoretical work came from an Institute devoted to technical problems and it led to new techniques for illumination and the measurement of high temperatures.

When Wien moved, in 1896, to Aix-la-Chapelle to succeed Lenard, he found there a laboratory equipped for the study of electrical discharges *in vacuo* and in 1897 he began to work on the nature of cathode rays. Using a very high vacuum tube with a Lenard window, he confirmed the discovery that Jean Perrin had made two years earlier, that cathode rays are composed of rapidly-moving, negatively-charged particles (electrons). And then, almost at the same time as Sir J. J. Thomson in Cambridge, but by a different method, he measured the relation of the electric charge on these particles to their mass and found, as Thomson did, that they are about two thousand times lighter than the atoms of hydrogen.

In 1898 Wien studied the canal rays discovered by Goldstein and concluded that they were the positive equivalent of the negatively-charged cathode rays. He measured their deviation by magnetic and electric fields and concluded that they are composed of positively-charged particles never heavier than electrons.

The method used by Wien resulted some 20 years later in the spectrography of masses, which has made possible the precise measurement of the masses of various atoms and their isotopes, necessary for the calculation of the energies released by nuclear reactions.

In 1900 Wien published a theoretical paper on the possibility of an electromagnetic basis for mechanics. Subsequently he did further work on the canal rays, showing, in 1912, that, if the pressure is not extremely weak, these rays lose and regain, by collision with atoms of residual gas, their electric charge along their course of travel. In 1918 he published further work on these rays on the measurement of the progressive decrease of their luminosity after they leave the cathode and from these experiments he deduced what classical physics calls the decay of the luminous vibrations in the atoms, which corresponds in quantum physics to the limited duration of excited states of atoms.

In this, and other, respects Wien's work contributed to the transition from Newtonian to quantum physics. As Max von Laue wrote of him, his <<nmortal glory >> was that <<he led us to the very gates of quantum physics>>.

Wien was a member of the Academies of Sciences of Berlin, Göttingen, Vienna, Stockholm, Christiania and Washington, and an Honorary member of the Physical Society of Frankfurt-on-Main.

In 1898 he married Luise Mehler of Aix-la-Chapelle. They had four children. He died in Munich on August 30, 1928.

Physics    1912


# NILS GUSTAF DALÉN


*<<for his invention of automatic regulators for use in conjunction with gas accumulators for illuminating lighthouses and buoys>>*

# Physics 1912

*Presentation Speech by Professor H. G. Söderbaum, President of the Royal Swedish Academy of Sciences*

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen.

The Royal Academy of Sciences believes it is acting in strict accordance with Alfred Nobel's will in awarding the Physics Prize to Chief Engineer Gustaf Dalén in recognition of his remarkable invention of automatic valves designed to be used in combination with gas accumulators in lighthouses and light-buoys.

The ever-growing use of maritime communication creates an increased demand for navigational safety devices. Amongst these devices lighthouses and light-buoys are of great importance, and their number has become several times greater during the last few decades. At the same time efforts have been made to find ways of making their lights more powerful and their different lights more easily distinguishable. As far as possible, work has been directed towards finding a system which would regulate these lights automatically. This is a very important point, for no country is wealthy enough to maintain a continuous inspection of all its necessary lighting equipment.

In Sweden, a country with a long coastline and large archipelagos, the problem of a reliable and fairly inexpensive lighting organisation has for a long time been more pressing than elsewhere.

About 1895, for the first time it was discovered how to prepare acetylene from calcium carbide on a commercial scale. Acetylene is a gaseous hydrocarbon which, when burnt, produces an extremely bright and white light.

The first attempt to use this gas for lighting in lighthouses did not have very satisfactory results. The petroleum gas in use for similar purposes up to this time had been compressed and enclosed in large iron containers. It was found extremely dangerous to treat acetylene in the same manner, as this gas, when under the pressure of one or more atmospheres, explodes at the slightest shock. It was also attempted to store calcium carbide in light-buoys and to let the acetylene escape under the action of water supplied automatically. Unfortunately this method proved to be inconvenient, not very reliable, and unusable in cold weather.

In 1896, two French chemists, Claude and Hess, discovered that acetone

possesses the property of dissolving large quantities of acetylene. This solu-
tion is not explosive. However, it cannot be used as it is to store acetylene,
because, even if the container is filled to the brim with a saturated solution
under high pressure, the volume of the liquid is reduced by consumption
or by cooling, and explosive acetylene gas is produced in the space above
the surface of the liquid.

It was then discovered that its explosive nature disappears if the acetylene
solution is compressed in a porous mass. Numerous unsuccessful attempts
were made to prepare such a porous mass which would be sufficiently resis-
tant and elastic to withstand the shocks encounteredin transportation, with-
out cracking and crumbling and thus producing cavities filled with explosive
acetylene  gas.

The credit for the eventual discovery of such a mass, called *aga* or porous
substance, belongs to Gustaf Dalén.

By a complicated and carefully developed process, this substance is en-
closed in steel containers which thus become practical accumulators for the
acetylene gas. The porous mass in the container is half-filled with acetone,
and acetylene is then introduced by compressing it to a pressure of ten
atmospheres. Under this pressure, and at a temperature of $15°$C, the con-
tainer contains one hundred times its own volume of acetylene. The con-
tainer is then ready for supplying to a lighthouse or light-buoy the acetylene
necessary for lighting.

The advantage of this arrangement would not be great if the acetylene
light had to burn uninterruptedly. On the one hand, this form of lighting
would be quite costly, and, on the other hand, it would be difficult to distin-
guish the lights ofvarious lighthouses from one another and from other light-
sources. True, several methods of producing an intermittent light were al-
ready known. For example, the flame can be surrounded by moving screens,
or the lighting device itself can be made to rotate. But such arrangements
need continual inspection and consequently involve considerable expense.

Where compressed petroleum gas was used as the source of light, eclips-
ing or flashing lighting devices had also been constructed using the escaping
gas as motive power. The flashes lasted 5 to 7 seconds, which was perhaps
necessary because of the weak light output of petroleum gas. But with the
intense brightness of acetylene light, such a long flash becomes unnecessary.
Furthermore, long flashes offer insufficient variation of the signal. Accord-
ingly the big lighthouses have generally replaced them with lights giving
flashes lasting from $\frac{1}{10}$ to $\frac{3}{10}$ of a second.

It was about 1904 that Dalén started to study this problem. With a petroleum gas apparatus it was impossible to divide one litre of gas into more than fifty flashes. So Dalén constructed an apparatus, based on an entirely new principle, which by instantaneous opening and closing of the gas pipe, enabled one litre of gas to provide several thousand very rapid but distinct flashes. After a considerable trial period, this ingenious device proved to be extremely reliable. Dalén then provided a brilliant solution for the supplementary problems arising from the use of aga light in the lighthouse service, and an ever increasing number of lighthouses and light-buoys in Sweden have been adapted to this form of lighting. The burner is fitted with a small permanent flame which, in the most usual arrangement, lights a flash every three seconds lasting $\frac{3}{10}$ of a second.

In 1907 Dalén crowned his achievement with a further refinement by designing a kind of valve, called the <<solar valve>> which extinguishes the light at sunrise and re-lights it when night falls. This valve is controlled by four metal rods enclosed in a glass tube. The lower one is blackened, while the others are gilded and highly polished. Daylight is absorbed by the blackened rod which is heated and consequently expands, closing the gas valve. As the daylight decreases, the black rod reaches the temperature of the other three rods: it contracts and allows the gas valve to reopen.

The device can be regulated in such a way as to act with more or less sensitivity. To be on the safe side, it is usually regulated so that it lights as soon as mist or clouds cover the sun.

The solar valve combined with an intermittent light produces a saving of gas of 93 per cent, and even greater economy might be achieved by prolonging the periods between the flashes.

The use of aga light facilitates the placing of lighthouses and lightbuoys in the most inaccessible places such as archipelagos and seas with dangerous reefs. With the use of one or more of the easily transportable gas accumulators, such lights can give their warning or guiding signals for a whole year or more without the need of inspection or the fear of failure.

The result is an entirely new standard of safety in navigation and an enormous economy. For example, one shoal in Swedish waters previously required a lightship costing approximately 200,000 Kronor and maintained at a cost of about 25,000 Kronor a year. Now, in many cases, navigation is adequately served by establishing an aga buoy with optical and audio-signalling apparatus, the cost of which is 9,000 Kronor, and the annual maintenance of which costs about 60 Kronor.

Most of the maritime nations have now started to install these Dalén devices, and they are to be found operating from Spitzberg, the Varanger Fjord, Iceland and Alaska in the north, to the Straits of Magellan and Kerguelen Island in the south. The annual benefit to navigation can be expressed in terms of saving of thousands of human lives and of hundreds of millions of Kronor.

The aga flame has proved to be extremely useful in other fields, such as the lighting of railway coaches, railway signalling apparatus, car head-lights, soldering, the casting and cutting of metals and so on.

The Academy of Sciences recognizes the true value of all these applications and wishes to emphasize those which contribute to the progress of navigation, because it is uncontestably these that have rendered the greatest benefit to humanity.

The sciences that were especially favoured in the will of the great explosives technician Alfred Nobel, i.e. Physics, Chemistry, and Medicine, have one common feature of involving and sometimes demanding the sacrifice of the experimenter's personal safety. We all know that this year's Physics Prize winner was the victim of a serious accident which prevents him from being here to receive the award from the hands of his King.

He is represented by his brother, Professor Albin Dalén, of the Caroline Institute. Professor, when handing over to your brother the medal and the diploma, I beg you also to convey to him from the Royal Academy of Sciences, our sincere congratulations on the distinction he has merited, and our best wishes for a complete and speedy recovery.

*No Lecture was delivered by Mr. N. G. Dalén*

# Biography

Nils Gustaf Dalén was born at Stenstorp in Skaraborg, Sweden on November 30, 1869, the son of a farmer. After his preliminary education, he entered a School of Agriculture to study dairy farming but he was later advised by Gustaf de Laval, who recognized his natural gift for mechanics, to seek a technical education. He prepared himself for the Chalmers Institute at Gothenburg and gained admission in 1892. He graduated as an engineer in 1896 and spent a year in Switzerland, studying under Professor Stodola at the Eidgenössisches Polytechnikum.

On his return to Sweden, Dalén carried out some research at Gothenburg and set up as a consulting engineer. He became Technical Chief of the Svenska Karbid- och Acetylen A.B. (Swedish Carbide and Acetylene, Ltd.) in 1901 and he later joined the Gas Accumulator Company where he became Chief Engineer in 1906. In 1909, the company was reorganized as Svenska Aktiebolaget Gasaccumulator (AGA) (Swedish Gas Accumulator Ltd.) with Dalén as Managing Director.

Dalén's inventiveness first showed in his early days on his father's farm when he built a threshing machine powered by an old spinning wheel. He contrived a device to indicate the butterfat content of milk and thereby made his contact with de Laval. On completion of his advanced education, he worked on the construction of a hot-air turbine and related air compressors and pumps. He also invented a pasteurization apparatus and a milking machine.

In 1901, Dalén's company purchased the patent rights of the French invention of dissolved acetylene and he began his work on automatic flashing beacons for lighthouses. His subsequent invention of the sun-valve, which causes a beacon to light automatically at dusk and extinguish itself at dawn, enabled lighthouses to function perfectly and unattended for periods of up to a year. His invention of cylinder filled with a porous mass of asbestos and diatomaceous earth for storage of acetylene reduced considerably the hazards in handling this material and its use in welding became safe. He also invented a mixer for providing a constant and correct balance of gas and

air for use in the incandescent mantle and a device for removing broken mantles and replacing them by new ones.

In 1912, whilst testing safety devices on cylinders of acetylene in an outdoor location, and when satisfactory safety precautions had been taken, a sudden explosion seriously injured Dalén and caused the loss of his eyesight. He recovered from his other injuries and overcoming his great incapacity, continued his researches. He was awarded the contract for lighting the Panama Canal and later turned to the field of thermal technics to invent a stove, now in universal use, which maintains cooking heat for 24 hours using only eight pounds of coal.

Dalén's writings were few, but he left his mark in a practical way by the provision of light, and therefore safety, for the benefit of travellers by land, sea and air.

Amongst the many distinctions conferred upon Dalén are membership of the Swedish Royal Academy of Sciences, 1913, and the Academy of Science and Engineering, 1919. He was made Honorary Doctor of Lund University in 1918 and received the Morehead Medal of the International Acetylene Association. He took part in debates at the National Society of Economics and served on the Lidingö City Council for almost twenty years.

Dalén married Elma Persson in 1901. They had two sons and two daughters. Their eldest son, Gurmar, qualified as an engineer and followed his father as a Director of AGA; their younger son, Anders, became a Doctor of Medicine; Gustaf's brother Albin, a famous ophthalmologist, was a Professor at the Caroline Institute.

Dalén died on December 9, 1937, in his villa at Lidingö.

# Physics 1913


# HEIKE KAMERLINGH ONNES


*<<for his investigations on the properties of matter at low temperatures which led, inter alia, to the production of liquid helium>>*

# Physics 1913

*Presentation Speech by former Councillor Th. Nordström, President of the Royal Swedish Academy of Sciences*

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen.

At its meeting on the 11th November the Royal Academy of Sciences decided to award the Nobel Prize for Physics for the year 1913 to Dr.Heike Kamerlingh Onnes, Professor at the University of Leyden <<for his investigations on the properties of matter at low temperatures which led, *inter alia,* to the production of liquid helium>>.

As early as 100 years ago research into the behaviour of gases at various pressures and temperatures gave a great impetus to physics. Since this time the study of the connection between the pressure, the volume and the temperature of gases has played a very important part in physics, and particularly in thermodynamics - one of the most important disciplines of modem physics.

In the years 1873 and 1880 Van der Waals presented his famous laws governing gases which, owing to their great importance for thermodynamics, were rewarded by the Royal Academy of Sciences in 1910 with the Nobel Prize for Physics.

The thermodynamic laws of Van der Waals were laid down on a theoretical basis under the assumption that certain properties could be attributed to molecules and molecular forces. In the case of gases the properties of which are changed by pressure and temperature, or in one way or another do not agree with Van der Waals' hypothesis, deviations from these laws occur.

A systematic experimental study of these deviations and the changes they undergo due to temperature and the molecular structure of the gas must therefore contribute greatly to our knowledge of the properties of the molecules and of the phenomena associated with them.

It was for this research that Kamerlingh Onnes set up his famous laboratory at the beginning of the 1880's, and in it he designed and improved, with unusual success, the physical apparatus needed for his experiments.

It is impossible to report briefly here on the many important results of this work. They embrace the thermodynamic properties at low temperatures of a series of monatomic and diatomic gases and their mixtures, and have

contributed to the development of modern thermodynamics and to an elu-
cidation of those associated phenomena which are so difficult to explain.
They have also made very important contributions to our knowledge of the
structure of matter and of phenomena related to it.

Whilst important onits own account, this research has gamed greater sig-
nificance because it has led to the attainment of the lowest temperatures so
far reached. These lie in the vicinity of so-called absolute zero, the lowest
temperature in thermodynamics.

The attainment of low temperatures in general was not possible until we
learnt to condense the so-called permanent gases, which, since Faraday's pio-
neer work in this field in the middle of the 1820's, has been one of the most
important tasks of thermodynamics.

After Olszewski, Linde, and Hampson had prepared liquid oxygen and
air in a variety of ways, and after Dewar, having overcome great experi-
mental difficulties, had succeeded in condensing nitrogen, all temperatures
down to -259°C, i.e. all temperatures down to 14° from absolute zero,
could be attained.

At these low temperatures all known gases can easily be condensed, except
for helium, which was discovered in the atmosphere in the year 1895.

Thus, by condensing this it would be possible to reach still lower tem-
peratures. After both Olszewski and Dewar, Travers, and Jacquerod had
tried in vain to prepare liquid helium, using a variety of methods, it was gen-
erally assumed that it was impossible.

The question was solved in 1908, however, by Kamerlingh Onnes, who
then prepared liquid helium for the first time.

I should have to cover too much ground if I were to report here on the
experimental equipment with which Kamerlingh Onnes was at last success-
ful in liquefying heliurn, and on the enormous experimental difficulties which
had to be overcome. I would only mention here that the liquefaction of he-
lium represented a continuation of the long series of investigations into the
properties of gases and liquids at low temperatures which Kamerlingh Onnes
has carried out in so praiseworthy a manner. These investigations finally led
to the determination of the so-called isotherms of helium and the knowledge
gained here was the first step towards the liquefaction of helium. Kamerlingh
Omres has constructed cold baths with liquid helium which permit research
to be done into the properties of substances at temperatures which he be-
tween 4.3° and 1.15° from absolute zero.

The attainment of these low temperatures is of the greatest importance to

physics research, for at these temperatures both the properties of the substances and also the course followed by physical phenomena, are generally quite different from those at our normal and higher temperatures, and a knowledge of these changes is of fundamental importance in answering many of the questions of modem physics.

Let me mention one of these particularly here.

Various principles borrowed from gas thermodynamics have been transferred to the so-called theory of electrons, which is the guiding principle in physics in explaining all electrical, magnetic, optical, and many heat phenomena.

The laws which have been arrived at in this way also seem to be confirmed by measurements at our normal and higher temperatures. That the situation is at very low temperatures not the same, however, has, amongst other things, been shown by Kamerlingh Onnes' experiments on resistance to electrical conduction at helium temperatures and by the determinations which Nernst and his students have carried out in relation to specific heat at liquid temperatures.

It has become more and more clear that a change in the whole theory of electrons is necessary. Theoretical work in this direction has already been begun by a number of research workers, particularly by Planck and Einstein.

In the meantime new supports had to be created for these investigations. These could only be obtained by a continued experimental study of the properties of substances at low temperatures, particularly at helium temperatures, which are the most suitable for throwing light upon phenomena in the world of electrons. Kamerlingh Onnes' merit lies in the fact that he has created these possibilities and at the same time opened up a field of the greatest consequence and significance to physical science.

Owing to the great importance which Kamerlingh Onnes' work has been seen to have for research in physics, the Royal Academy of Sciences has found ample grounds for bestowing upon him the Nobel Prize for Physics for the year 1913.

HEIKE KAMERLINGH ONNES

# Investigations into the properties of substances at low temperatures, which have led, amongst other things, to the preparation of liquid helium

*Nobel Lecture, December 11, 1913*

Since you have done me the honour of describing to you my investigations into the properties of substances at low temperatures, which have also led me, amongst other things, to the preparation of liquid helium, I must first of all express my deepest thanks to your old and famous Academy for distinguishing me in this manner. This has happened at a time when the continuation of my work will make great demands upon me. Nothing could make me more able than your good will does to meet new problems with the same hopeful confidence with which, 30 years ago, I met difficulties now overcome.

The main aim in investigations at low temperatures has greatly changed since then. When I first turned to this field of work the aim was still to liquefy statically the gases which up to then had not been mastered and to pour into open containers those gases which it is most difficult to liquefy.

What has given a character of its own to the Leyden work from the very beginning is that I allowed myself to be led by Van der Waals' theories, particularly by the law of corresponding states which at that time had just been deduced by Van der Waals.

This law had a particular attraction for me because I thought to find the basis for it in the stationary mechanical similarity of substances and from this point of view the study of deviations in substances of simple chemical structure with low critical temperatures seemed particularly important.

I was greatly drawn to making the necessary precision measurements at low temperatures. To this end large measuring instruments had to be maintained at constant temperatures, and one had also to construct suitable temperature baths - which would also be very useful for other investigations - to cover the whole field of low temperatures.

Just as I was thinking about how to do this, the basic classic work of Wroblewski and Olszewski appeared on the static liquefaction of oxygen. This meant that the determination of isotherms of hydrogen in a bath of

liquid oxygen was of great value, particularly with regard to liquefaction of hydrogen. These determinations were not carried out until the second ten-year period of the cryogenic institute and the results could not be published until many years after Dewar had already liquefied hydrogen. The first great stage in the development of the cryogenic laboratory, which made measurements in a bath of liquid oxygen possible, was likewise not reached until after ten years. Olszewski and Dewar had by then already solved the problem of pouring oxygen into open containers.

The Leyden process differed from the others as follows : in order to have a permanent bath available, the evaporated oxygen was liquefied again and conducted through a closed circulation system. When the apparatus in the Leyden laboratory was further developed the production of circulation systems of the same type was considered, although the investigations to be carried out were directed towards still lower temperatures. Earlier experience could thus be used in attacking a later problem and this was decisive for the liquefaction of helium. Thus the whole cryogenic laboratory still bears the marks left on it by its early problems.

The range of low temperatures now available to us far exceeds what I ever dreamt of at the beginning, for helium was not discovered until later and this allows us to get five to ten times nearer to absolute zero than is possible with hydrogen.

At the same time the aim of the cryogenic laboratory, which had originally been a limited one, became much more diverse.

This was the case as early as ten years ago, when I discussed in my rectorial address the programme of the laboratory at that time. Besides thermodynamic questions, questions relating to other fields were dealt with.

Thermodynamic problems were then in the forefront as far as the cryogenic section of the laboratory was concerned, because it was particularly work on the equation of state which was concentrated on low temperatures. But questions of other types, which demanded investigations at low temperatures, had become so numerous and important that I had felt it indicated that I should continue the other groups of work also exclusively at low temperatures, and dedicate the Leyden institute entirely to a study of the general character of the influence of low temperatures.

It is due to having specialized in this way that I was able to co-operate with a number of learned men who accepted the hospitality of the laboratory. The decision to make the Leyden institute an institute which co-operated with other larger ones, being a special institute for the more difficult

work in the field of low temperatures, has been found to be well worth as the scientific basis of this collaboration.

During the specialization in the Leyden institute, which is now completed, I was of course convinced that the investigations into the properties of substances at low temperatures would provide explanations for many of these properties. But my expectations were far surpassed by the reality. Not only has it been generally desirable - and to a far greater extent than was foreseen - to simplify as far as possible the conditions under which the phenomena occur, via extensive suppression of thermal motion, but it has also been shown that with liquid helium one can take an unexpectedly long step in this direction, as it permits temperatures to be reached which, for certain phenomena, represent practically absolute zero. Further discoveries in another field have made necessary, in an unexpected connection, the examination of many properties in the neighbourhood of absolute zero. The Nernst heat theorem and, especially, Planck's quantum theory and zero-point energy theory have made measurements at low temperatures of prime interest to physicists.

It is true that Faraday's problem as to whether all gases can be liquefied has been solved step by step in the sense of Van der Waals' words <<matter will always show attraction>>, and thus a fundamental problem has been removed. At the same time, however, the question asked by Planck introduces a problem which is probably no less fundamental, to the solution of which investigations into the properties of substances at low temperatures can contribute.

I would now ask you to follow me into the Leyden laboratory.

As I have already briefly explained, the measurements are made in baths of liquid gases, which are maintained as long as is required in cryostats (equipment for maintaining constant low temperatures), the evaporated gas being allowed to circulate-it is sucked up and liquefied again.

The cycles for the various gases, as in Pictet's famous experiment, are joined in cascades, so that the, cold bath, which can be maintained by a previous cycle, also serves to liquefy at a lower temperature the gas which circulates in the following cycle. In Fig. 1 is shown diagrammatically the various cycles with the exception of that for helium. They are shown by various sorts of lines.

The first cycle contains methyl chloride. The liquid methyl chloride is in a condenser cooled by water. From the condenser it passes into a refrigerator, where it evaporates under a pressure corresponding to the temperature necessary to liquefy ethylene. The vapour is sucked up by a large vacuum pump
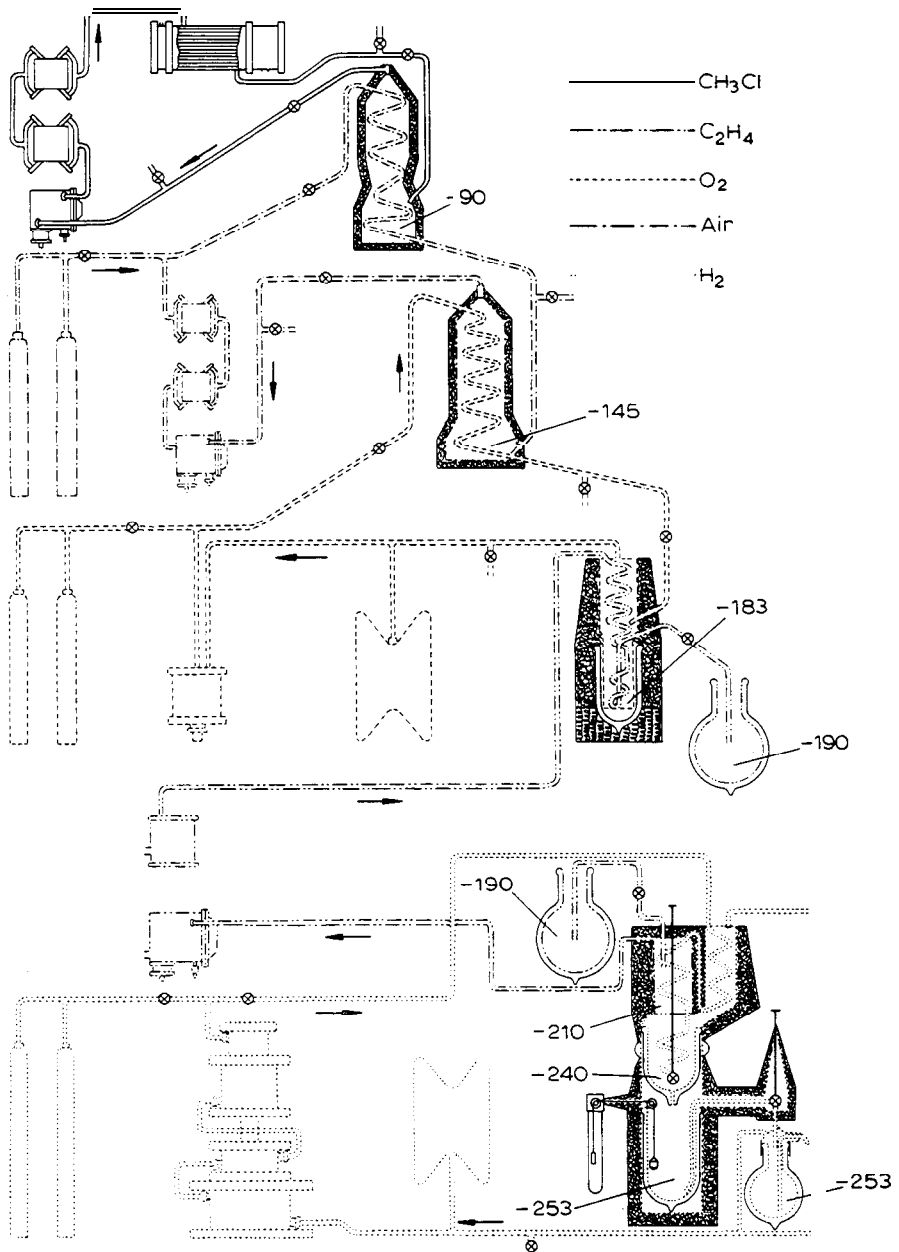
Fig.1.

through a regenerator (in which, according to the counter-current principle, it flows past the ethylene which is being cooled), and is led by a conjugated compressor back to the condenser where it is liquefied.

In the second cycle is the ethylene. Circulation proceeds in the same way as in the first cycle.

In the third cycle the oxygen circulates in the same way. The liquefied oxygen can also serve to produce liquid air in the oxygen refrigerator.

The cryostat with the bath of liquid oxygen, of which I spoke before, was erected without using vacuum glass vessels. It was connected to the liquefying apparatus and the measurements could thus only be made in the immediate neighbourhood of this apparatus. Dewar revolutionized working at low temperatures by introducing his silvered vacuum glass vessels. The liquid oxygen could be stored in these vessels and transported in them from the liquefying apparatus to the point where one wished to use it. When working the cycles and in my subsequent work I found Dewar's ingenious idea very useful.

The liquid air is prepared in the fourth cycle. The other cycles are closed but this can be broken into. Air is sucked up from the room and a supply of liquid air can be stored in open vacuum glass vessels.

Shortly after success had been achieved in making available a permanent bath of liquid oxygen, the great master of refrigeration technique, Linde, discovered the process by means of which he created the liquid-air industry. This ingenious discovery permits the air, starting from normal temperature, to be liquefied without intermediate stages. You will see that the preparation of liquid hydrogen and liquid helium in the following cycles, which demands each time a similarly large temperature drop without an intermediate stage, is based on the principles of the Linde process. We, however, still always prepare the liquid air by means of cycles joined in cascade, as already described. When considering this arrangement, which is also very economical and supplies about 14litres per hour, it must be borne in mind that all the relevant cycles here must be ready for continuous work so that during experiments in the laboratory the whole temperature range down to -217°C is always freely available.

Fig.2 shows a view of the four first cycles of the Leyden cascade. The conjugated pumps for the methyl chloride and ethylene circulation systems and the Brotherhood compressor for the oxygen cycle can clearly be seen. (Many pieces of equipment can also be seen which are used for taking various measurements; the figure does not show either the Brotherhood air compressor
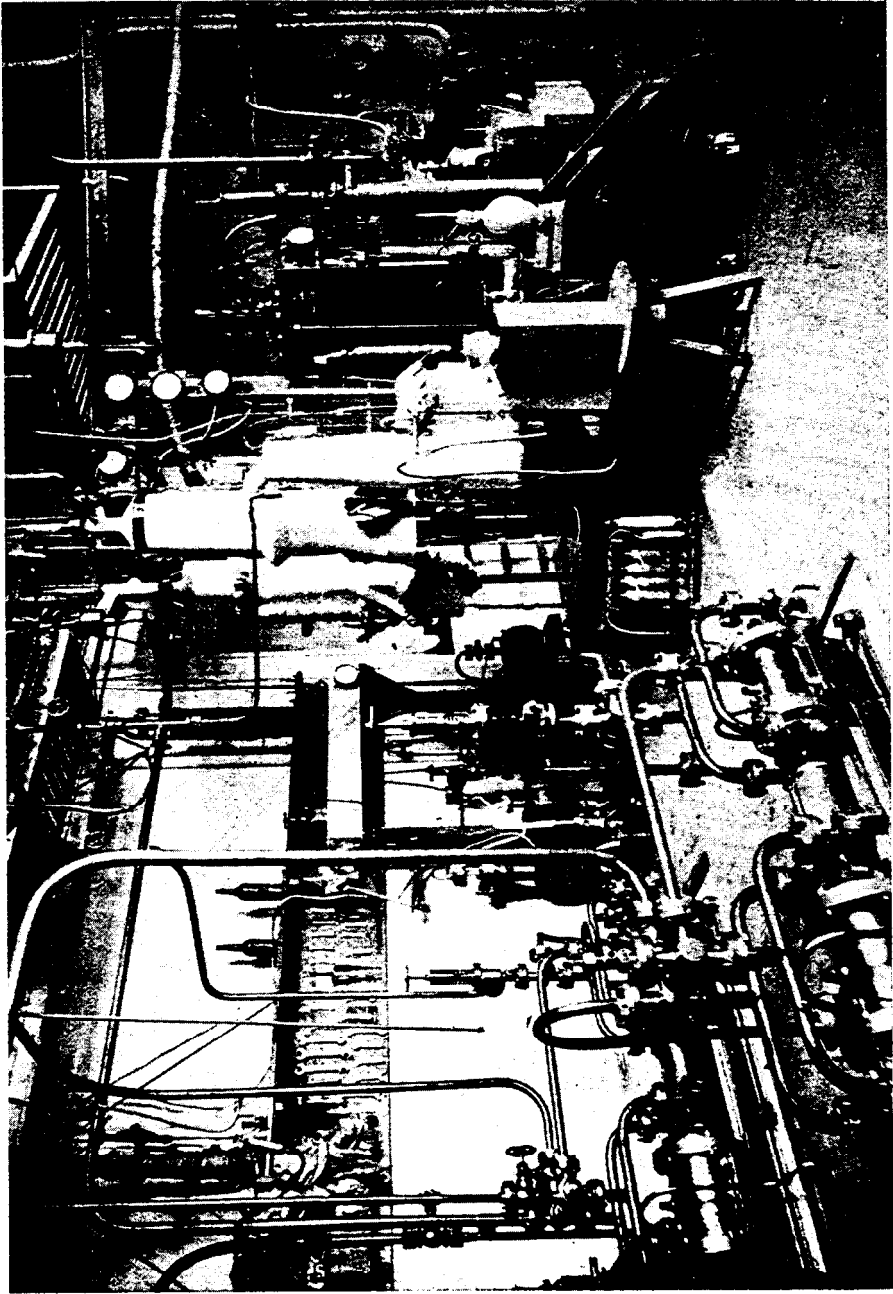
Fig.2.
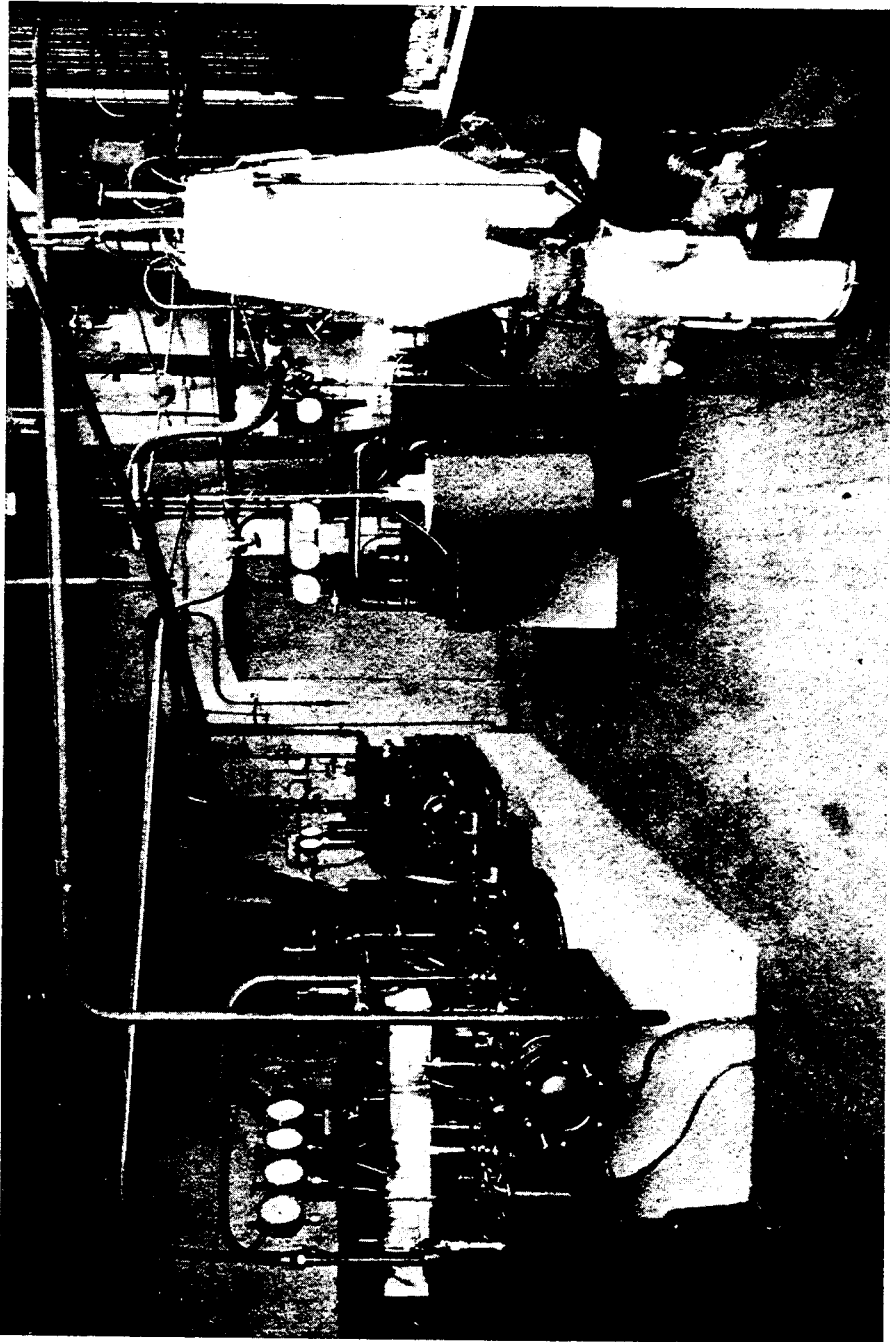
Fig.3.

or the vacuum pumps which are so important to the working of the apparatus and which make evaporation possible under very low pressure. These are particularly important to the measurements because it is with their help that a wide temperature range can be covered with the same liquid gas.)

Let us now consider the hydrogen cycle. When I began to consider liquefying hydrogen, I started from the principle of mechanical similarity, already mentioned. From this and the critical data determined in such a masterly way by Olszewski it could be concluded that if one were successful in constructing an apparatus suitable as a model, which liquefies oxygen starting from a normal temperature, it would also be possible, with apparatus based on this model, to liquefy *hydrogen* starting from the temperature of the *liquid* oxygen. Long before I had the opportunity of using this principle, hydrogen had already been liquefied by Dewar. I have already discussed the great importance of Dewar's brilliant triumph for physics measurements in the rectorial address referred to above. In the liquid hydrogen we have at our disposal a freezing agent which leads us five times nearer to absolute zero than does liquid air. In Leyden a cycle which worked continuously was set up to make use of this. (Owing to the great demands made by the precision measurements which were envisaged at hydrogen temperatures, this did not come into being until many years later.) The circulation system is shown diagrammatically in Fig. I.

The compressed hydrogen comes out of the refrigerator in which air is evaporating at the air pump, into a regenerator spiral with a throttle valve, which, following Dewar's example, is placed in a silvered vacuum glass. The spiral itself is modelled on the extremely practical Hampson apparatus for air liquefaction.

The liquid hydrogen collects in a Dewar glass and (as indicated by a float) is siphoned over into transportable, silvered vacuum glass vessels, which are connected to the container for pure hydrogen. The liquid hydrogen is siphoned out of the vacuum glass vessels in a similar way into the cryostats. It is clear that very pure hydrogen, a carefully closed cycle and special pumps must be used to circulate $40m^3$ per hour continuously, since only a little admixture of air will block up the fine ducts and valves through which the hydrogen has to flow.

The circulation is shown in the accompanying Fig.3. The compressors, the liquefying apparatus and the vacuum pump for evaporating the liquid air in the refrigerator can easily be recognized. Much more apparatus is necessary to ensure the regular supply of 10litres of liquid hydrogen per hour

which we now obtain and to enable the larger supplies, necessary when work-
ing with liquid helium, to be collected.

Tubing to suck the gas out of the cryostats connects the cycles described
with all the working rooms. Thus, by means of liquefied gases, which evap-
orate under suitable pressure and which are, so to speak, as freely available as
water, it is possible to maintain constant temperatures down to the freezing
point of hydrogen in all parts of the laboratory.

Let us now turn to the experiments which have been carried out by this
method.

Generally speaking the first task was to suit the measuring apparatuses to
the method of working chosen. They had to be enclosed in an air-tight
chamber, which was not always easy. It was, however, often important. For,
once a cryostat of this type suitable for the experiments had been constructed,
there was the advantage that one could pour the various gases one after an-
other into the same cryostat and thus run through the whole range of low
temperatures without the measuring apparatus having to be altered at all.

I cannot spend much time over this equipment (nor can I linger over that
for the handling of baths, although this was often decisive for the success of
difficult measurements, since it permitted the observer to concentrate all his
attention on the measurements). I would prefer to put forward that the in-
vestigations in which they were used have led to a knowledge of the tem-
perature dependence of properties of very different type. In mentioning some
of these I will limit myself to those investigations which went down as far as
the freezing point of hydrogen. May I first mention a few people who have
collaborated with me.

Mr. J. Becquerel came to examine the absorption spectra of rare earths with
and without magnetic field (Zeeman phenomenon), Messrs. Becquerel, fa-
ther and son, to examine the phosphorescence of the uranyl compounds, Mr.
Lenard and Mr.Pauli to examine the long-lasting phosphorescence of the
alkaline earth sulphides, Mme. Curie to examine the penetrating radiation of
radium, Mr. Weber to determine the viscosity of gaseous hydrogen and he-
lium. I am particularly glad to mention that the deserving Swedish research
worker Mr. Bengt Beckman and his wife came to Leyden to work on a num-
ber of problems mainly connected with his Uppsala experiments, from
amongst which I name the Hall effect of alloys and the increase in resistance
brought about 'by pressure in lead. I would like to show here (in Fig. 4) a
diagram taken from a work by Dr.Beckman, in which baths of ethylene,
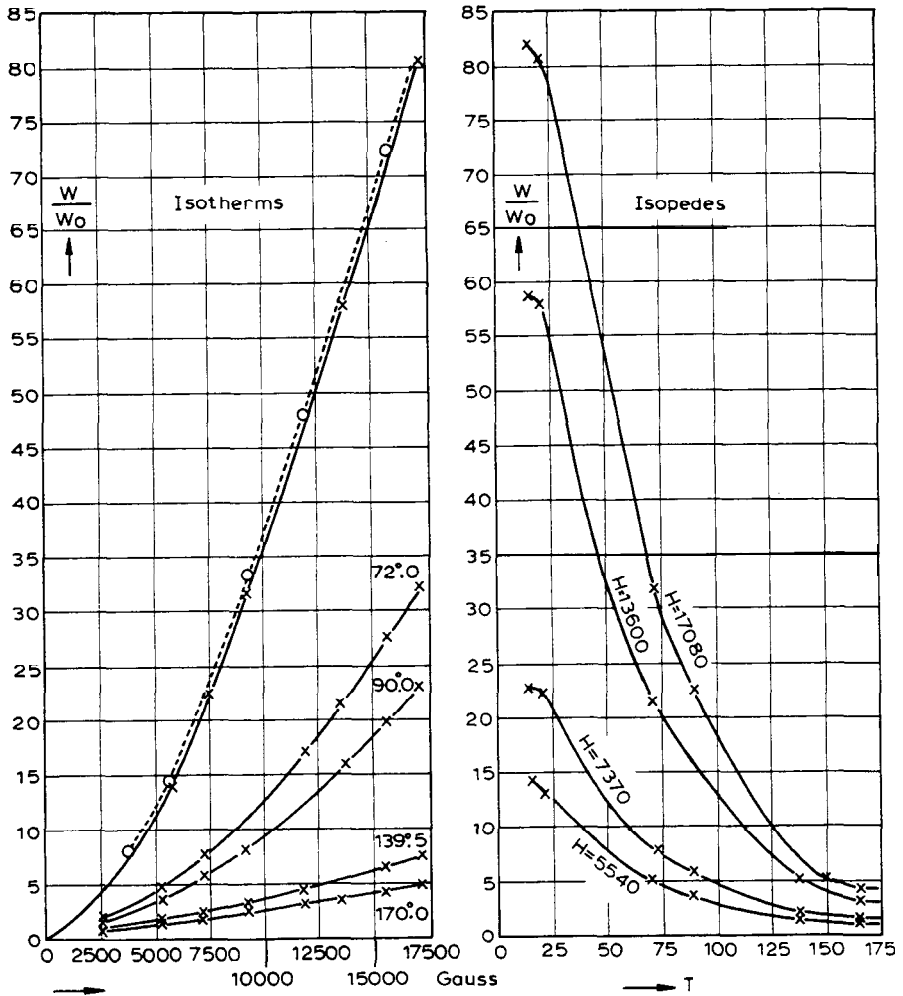
Fig.4.

oxygen and hydrogen were used. The diagram shows to what high values the magnetic increase in resistance of bismuth rises at hydrogen temperatures.

A group particularly closely connected with the experiments last mentioned is made up of those concerned with magnetism.

Mr. Weiss came to determine the magnetic moment of the molecular magnets of ferromagnetic substances by means of saturation measurements at the melting point of hydrogen. Later, when Weiss discovered the magneton,

the results contributed to the determination of its value, which is probably fundamental to the magnetic moments of all atoms. The experiment undertaken by Mr.Perrier and myself on liquid and solid oxygen led to deviations from the Curie law, which we then found also with paramagnetic salts. During the continuation of the work with Mr. Oosterhuis it was found that one class of these deviations can be explained by assuming a Weiss molecular field with a negative sign, which then - according to investigations by Mr.Perrier and myself into the susceptibility of liquid mixtures of oxygen and nitrogen and following up Weiss' theory - could be conceived as a function of the spacing of the molecules.

The continuation of measurements on paramagnetism at helium temperatures, which has been in course of preparation for some time, is also important in connection with the theory of zero-point energy. The fact is that attempts have been made to explain deviations from the Curie law without assuming a negative field. This was on the part of Oosterhuis, in that he introduces into the Langevin theory of rotational energy, which Langevin puts as proportional to the temperature, the expression of Einstein and Stem which contains zero-point energy. If the unchanged theory of Langevin is right, however, this would be shown very clearly at helium temperatures. Also the influence of the external field on the susceptibility, which is according to the Langevin theory inversely proportional to temperature, would become clearly visible at helium temperatures in attainable fields, whilst at hydrogen temperatures it cannot be expected to the same extent until fields are reached which are ten times greater and thus far exceeding what it is possible to expect. (See Addendum I.)

The study of the equation of state related to the monumental theories of Van der Waals has always been a main item of research in the Leyden laboratory. In particular, the exact study of the equation of state of simply constructed gases belongs to the low temperature field. Here also belong the determination of the absolute scale of temperatures below the freezing point of water. For help with the extensive precision measurements which are dealt with here I must thank my many talented co-workers. In recent times particularly Messrs. Braak, Clay, Crommelin and Dorsman, Mr. and Mrs. de Haas-Lorentz, and Messrs. Holst and Keesom have supported me and of these I have been indebted to Mr. Crommelin also for the technical running of the laboratory.

I owe much to the distinguished theoretical knowledge of Mr.Keesom and to the thorough and ingenious way in which he has worked on the the-

oretical problems connected with the equation of state, the study of which also fell mostly to his lot.

As far as the experimental work is concerned, various conditions needed to be fulfilled, each with great precision. (The law of corresponding states is roughly valid and thus only those observations are of real value the accuracy of which makes it possible to determine deviations from this law.) The pressure under which the gas is compressed, the volume which it occupies and the temperature at which the experiment takes place must be known with suitable accuracy. The volume which had to be assigned to the measuring apparatus demanded that the baths in the cryostats should sometimes have a capacity of up to 1 1/2 litres, even when working with liquid hydrogen. The temperature also had to be held evenly and constantly to within 1/100 degree in such cases.

(The layout of a piezometer for high pressures is shown diagramatically in
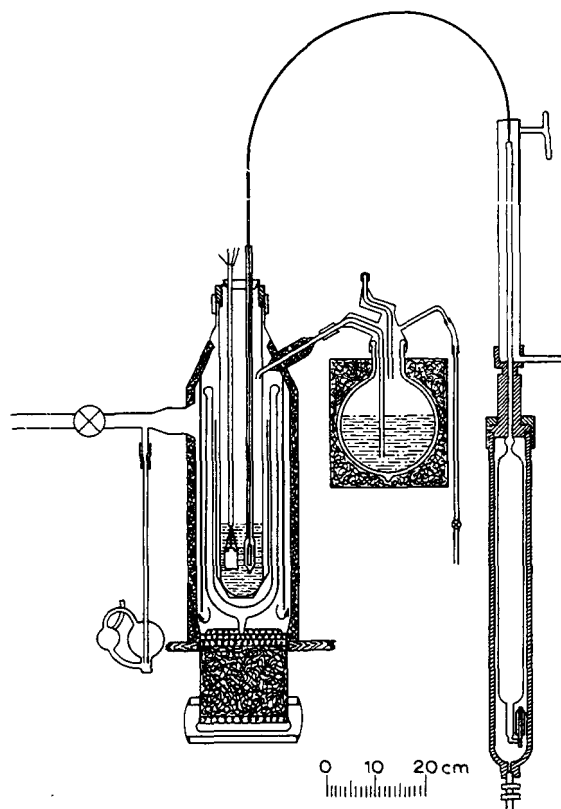


Fig.5.

Fig.5. The large reservoir filled with the gas to be examined is dipped into a Cailletet block and connected by a steel capillary tube to the small reservoir. The latter is in the cryostat in which the bath is maintained by one of the cycles. The gas in the piezometer is pressed by the mercury into the small reservoir. The amount of gas which is transferred is measured by the mercury rising in the calibrated column.)

In order to have a basis for pressure measurement, which would guarantee the necessary accuracy, the pressure was transferred from one to the next and so on in a series of mercury differential manometers, as shown in Fig.6, by suitably compressed gas, so that a height of 45metres of mercury column can be accommodated in the working room, and pressures up to 60 atmospheres measured to the nearest millimetre. (The apparatus was later extended to 90 atmospheres.)

As far as thermometry is concerned I must limit myself to mentioning that its standard was a hydrogen thermometer to which more recently a helium thermometer was also added. From the simultaneous study of all types of auxiliary thermometers down to the melting point of hydrogen it seems certain that in the absolute determination of temperatures an accuracy of 1/50 degrees is reached.

The volume gauge which was used amongst other things in the investigations into rectilinear diameter for which Mr.Mathias came to Leyden, belongs to the apparatus which serves to determine the equation of state. I must pass this by, along with much other auxiliary equipment, although I should have liked to give a better picture than is possible in this short report of the work which had to be done to determine an equation of state. Still less can I linger over the evaluation of observations. I should like, however, to mention that I obtained the virial coefficients for hydrogen with the help of Mr. Braak and Mr. de Haas, and those for argon with the help of Mr. Crommelin. Using these coefficients Mr.Keesom then did some fine work in testing various theoretical conceptions and found, amongst other things, that, as far as deviations from Boyle's law at low pressures are concerned, hydrogen behaves at low temperatures in a similar way to monatomic argon, just as was found for specific heat by Eucken.

Determination of the isotherms of helium was of the greatest importance in the liquefaction of this gas. From them information could be obtained as to whether helium, like other substances, follows the law of corresponding states, and if so what the critical data of helium are. With this information it
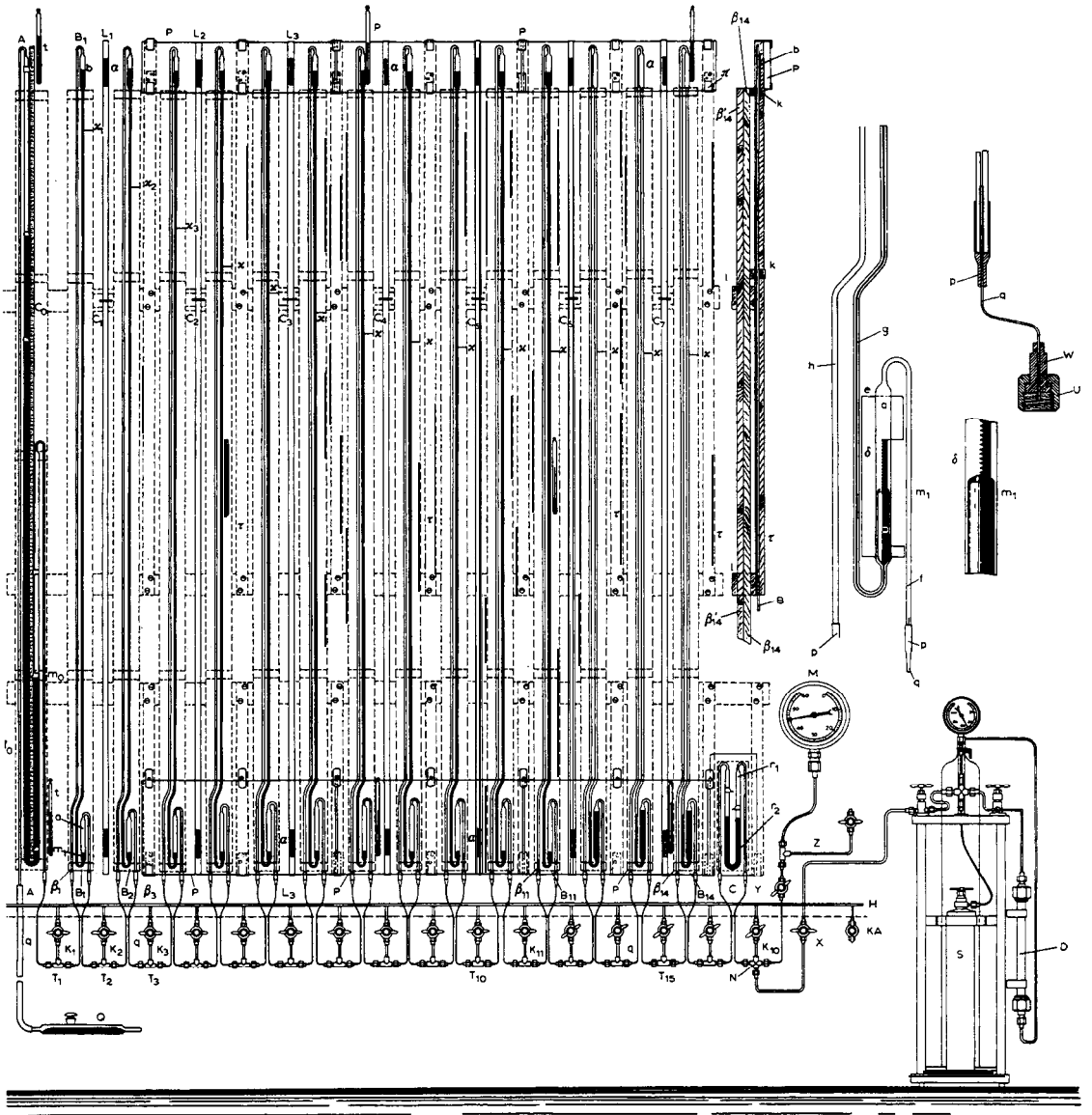
Fig.6.

would be possible to judge whether the gas, starting from the freezing point of hydrogen, the lowest temperature to which it could be cooled, could be liquefied by means of Linde's process. If so then the principle of similarity could again be applied to the setting up of a helium cycle, just as the hydrogen liquefier had been built according to Hampson's model for an air liquefier. It became clear that it had to be found out whether the temperature at which the initial compression of the helium follows Boyle's law - the Boyle point - lies above the melting point of hydrogen. In this case one could hope for static liquefaction, if a closed helium cycle on the model of the hydrogen cycle were set up and operated in a suitable way. The question was answered in the affirmative by isotherm determination. Moreover, the compression pressure, the time the experiment would take, the cooling action to be brought about by the hydrogen cycle and also the quantity of helium necessary, were assessed as being not beyond what might be attained. As far as the helium was concerned, my brother Mr. O. Kamerlingh Onnes, the Director of the Department of Foreign Trade Relations in Amsterdam, was able to help me to obtain the necessary monazite. I am glad to be able to thank him here also.

Carrying out the experiment in the manner stated meant that the usual intermediate stage in the liquefaction of a gas would have to be by-passed by one great effort, although this bordered on the impossible. This seemed, however, the only thing to do since helium, then still such a mystery, had already so greatly disappointed me.

The accompanying Fig.7 gives a diagram of the equipment for the experiment. The compressed helium comes, after suitable pre-cooling, into the refrigerator, where hydrogen is evaporating at the air pump, runs through the regenerator spiral and expands at the throttle valve. The liquid formed according to the Linde process gathers in the lower portion of the vacuum glass vessel. In order to be able to observe the liquid helium this portion is transparent and is surrounded by a vacuum glass vessel which is kept filled with liquid hydrogen, which is again protected by a transparent vacuum glass vessel containing liquid air, and this again by a vessel in which heated alcohol circulates.

The helium cycle, as set up, is shown again in Fig.8 in more detail, but still in diagrammatic form, and here we find again the liquefaction apparatus; the compressors, storage flasks and regulating gas bells floating on oil are also shown. The liquefier itself is shown in more detail in Fig.9, where the liquefying spiral built on the Hampson model can again easily be recognized.
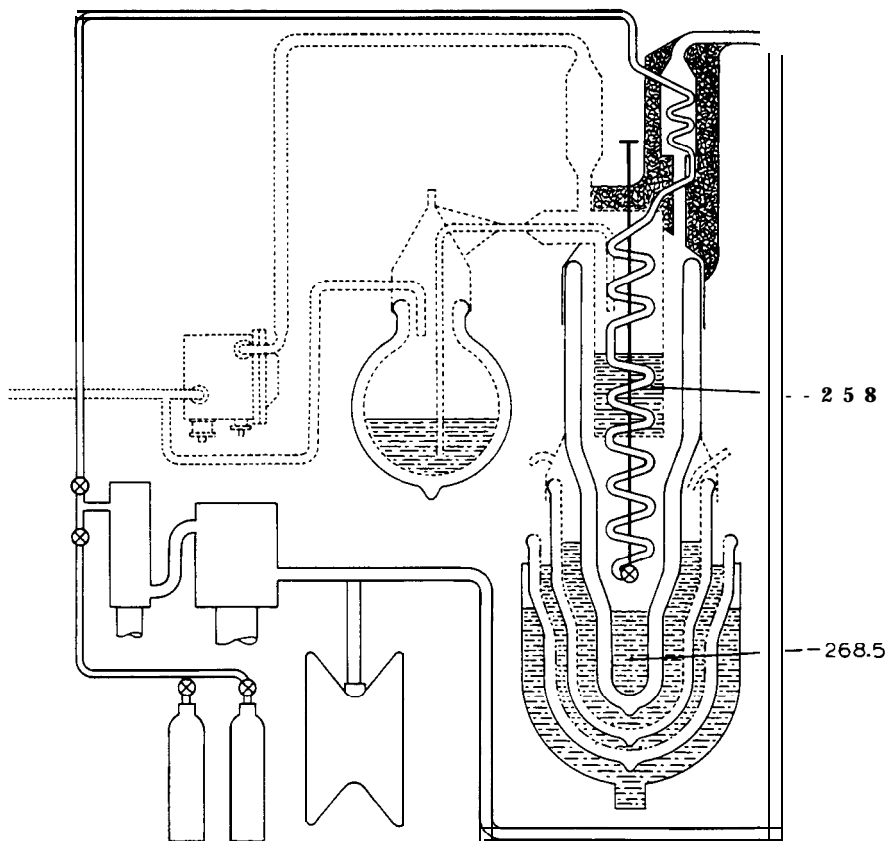
Fig.7.

The refrigerator is supplied with liquid hydrogen from a transparent inter-
mediate reservoir, into which the liquid hydrogen is siphoned from the
storage flasks. The helium, before being cooled in the hydrogen refrigerator,
runs through a tube cooled in liquid air, with carbon to free it from traces
of air which might have contaminated it during circulation. We owe the
application of this property of carbon to Dewar. I have already stressed the
great importance of his work, but would like to emphasize here that it has
been of greatest use to me in the liquefaction of helium.

The temperature of the helium is measured with a helium gas thermom-
eter, the reservoir of which is in the liquefying chamber and is connected
by a steel capillary tube to the manometer portion.

The accompanying Fig. 10 gives a view of the whole apparatus. The trans-
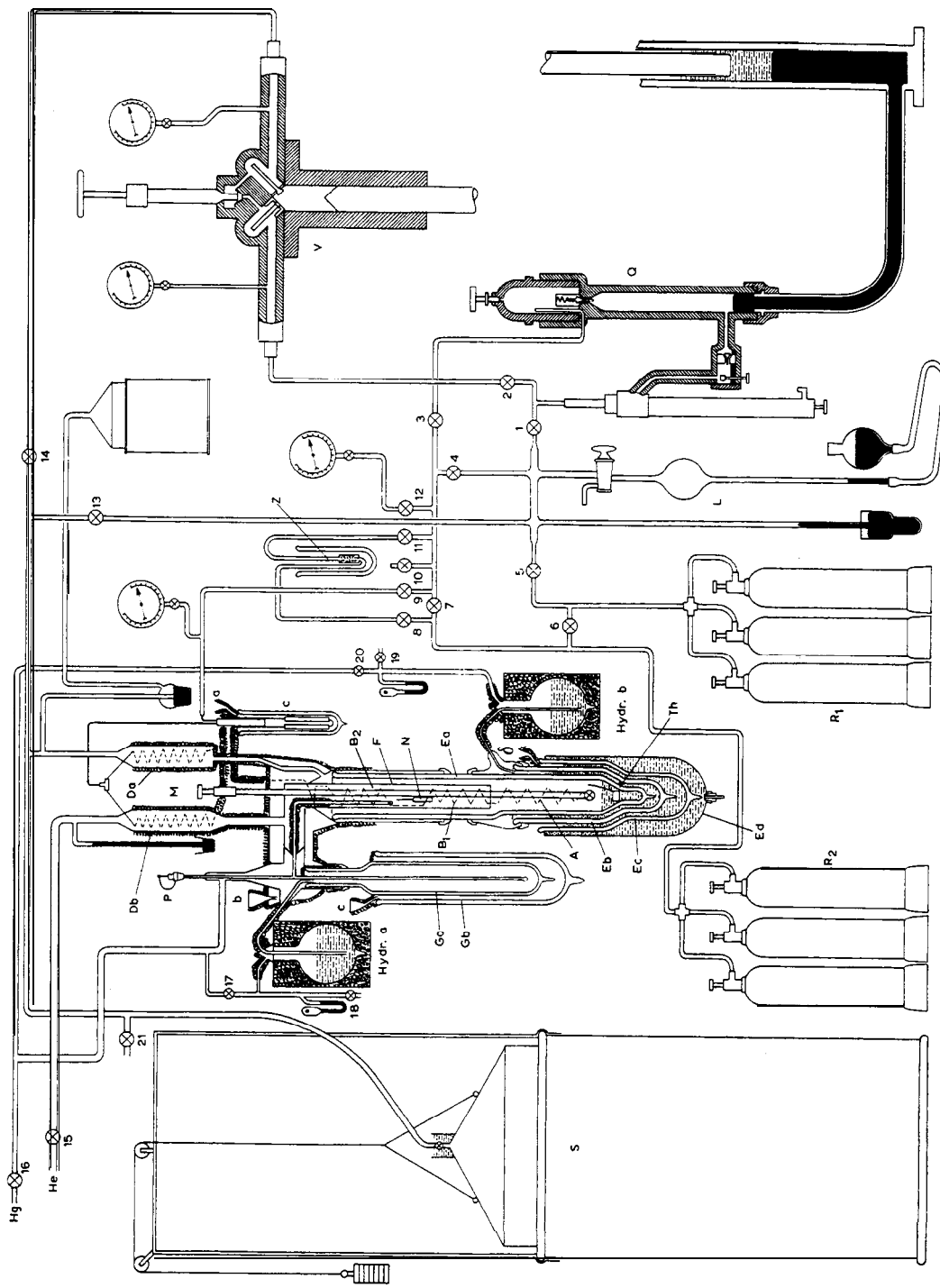
Fig.8.
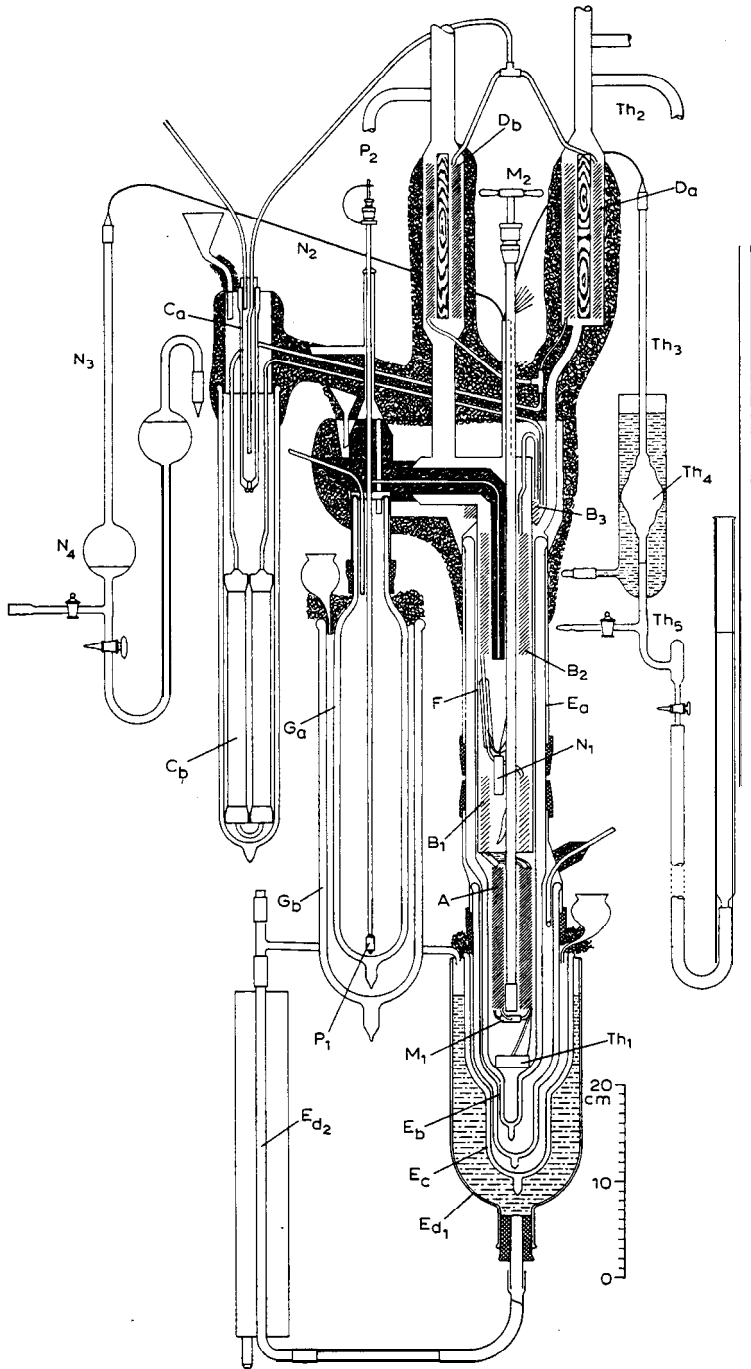
Fig.9.
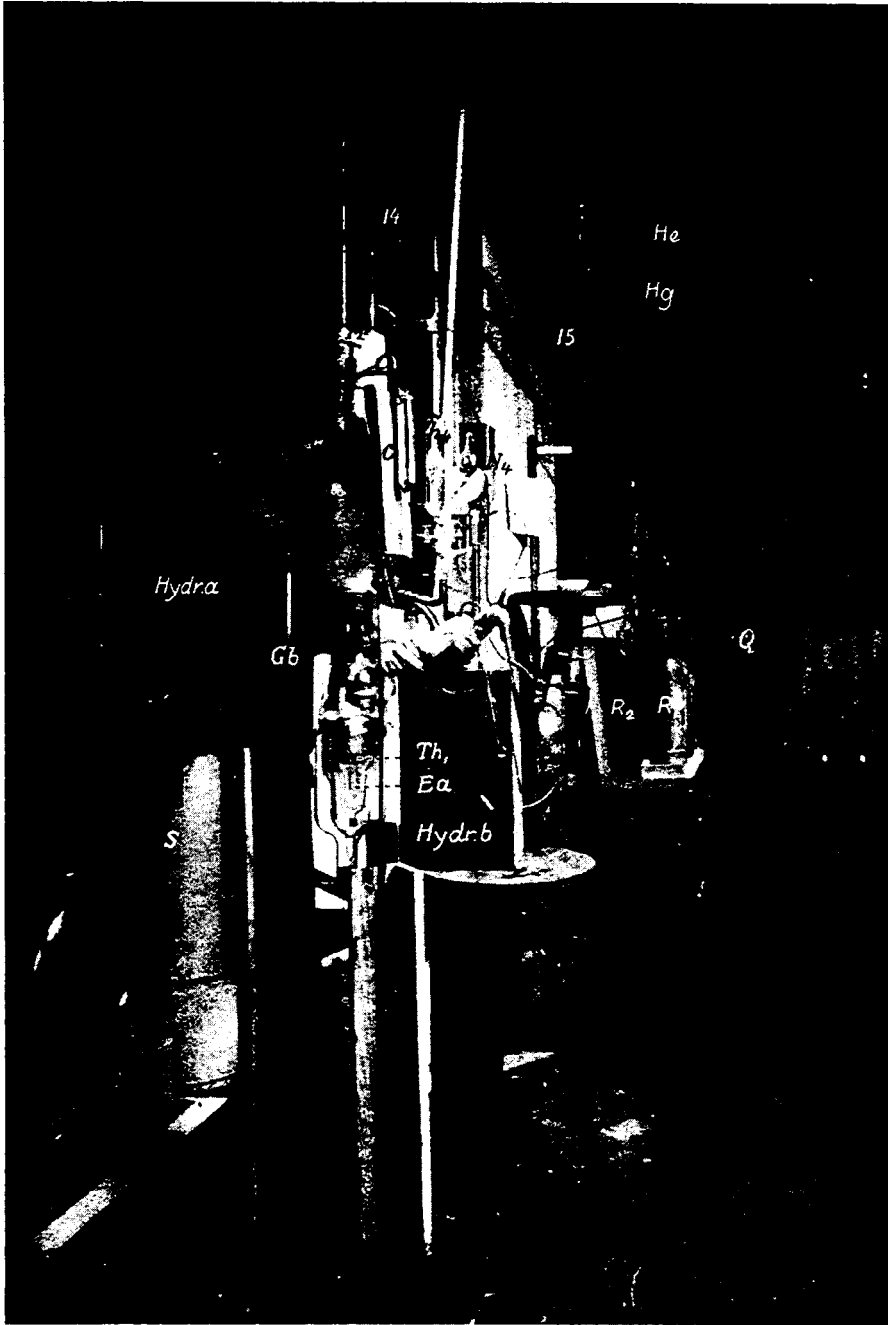
Fig.10.

parent liquefying chamber, with three-fold protection, can be easily recognized.

As had been foreseen when the experiments were planned, their execution bordered on the impossible. By the time the experiment, which began at half past five in the morning, had ended at half past nine at night, the first helium having been seen at half past six, everyone had done everything that could possibly be demanded of him. This is particularly true of my loyal co-worker G. J. Flim, the mechanic, to whom I am also deeply grateful for help in setting up the other experiments and apparatuses discussed here.

It was a wonderful sight when the liquid, which looked almost unreal, was seen for the first time. It was not noticed when it flowed in. Its presence could not be confirmed until it had already filled up the vessel. Its surface stood sharply against the vessel like the edge of a knife.

How happy I was to be able to show condensed helium to my distinguished friend Van der Waals, whose theory had guided me to the end of my work on the liquefaction of gases.

The boiling temperature of the helium was found at 4.25°K, the critical temperature assessed as 5°K. The low critical pressure to which we had to conclude and which fell between 2 and 3 atmospheres was remarkably small.

Now that we had arrived at this elucidation of the properties of helium the next target was already indicated.

Using our knowledge, we had to make measurements and to this end, on the basis of the information obtained, to decide on arrangements which would simplify the preparation of liquid helium and make it available in a cryostat. This problem I also solved step by step. I will indicate these steps by mentioning some of the investigations already carried out with liquid helium. In these I was supported by Mr. Dorsman in the thermodynamic work and by Mr.Holst in the electrical work. I am most grateful to them.

First of all somewhat difficult conditions were encountered in the liquefying chamber. In the experiments shown in Fig. II considerable progress had already been made in various directions.

The experimental chamber also for these experiments is still closed off at the top by the liquefying spiral and the experiments are thus made difficult (since it is only possible to penetrate into the experimental chamber with the help of steel capillary tubes or insulated wires led past the liquefying spiral), yet a whole collection of instruments is already placed in the liquid helium. We see here a helium thermometer, the pressure of which (at 0°C 145mm)
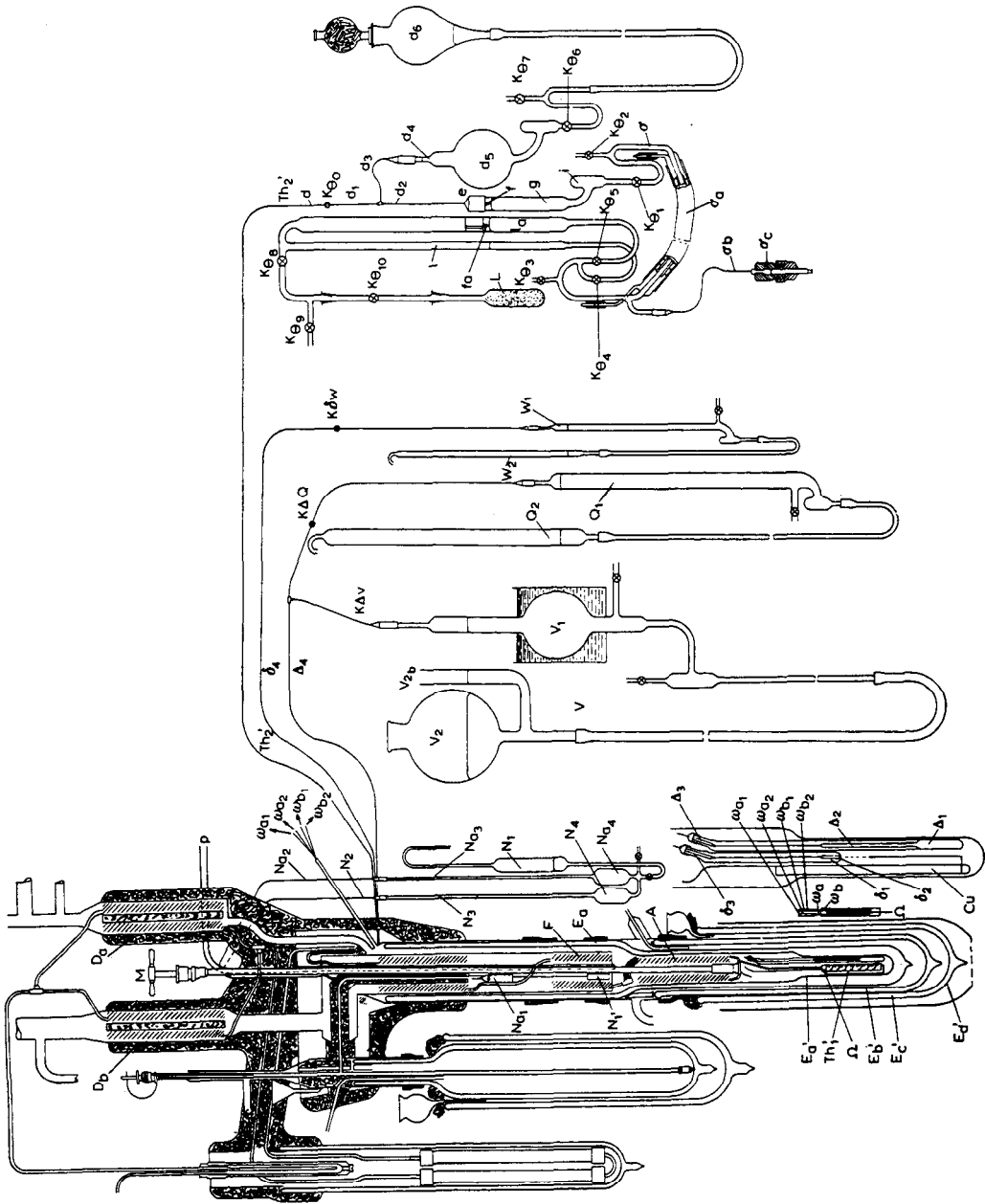
Fig.11.

amounts to only 3mm at the boiling point of helium, so that temperatures down to 1.5°K approximately could be measured with it. Here the accuracy of the measurement was suited to the smallness of the pressure.

The simultaneous measurement of the pressure in the chamber in which the liquid helium evaporates yielded the law of vapour pressure. To measure how the density of the liquid helium changes with the temperature there was also in the helium bath a differential dilatometer (into which volumetrically measured quantities of helium were brought through two identical steel capillary tubes).

It is very noticeable that the experiments indicate that the density of the helium, which at first quickly drops with the temperature, reaches a maximum at 2.2°K approximately, and if one goes down further even drops again. Such an extreme could possibly be connected with the quantum theory. At any rate, closer examination of the equation of state of the helium in relation to deviations from the law of corresponding states is very promising, as it is the critical temperature precisely of this gas which approaches absolute zero so closely.

Naturally the question arose as to whether helium can also be converted into the solid state. An experiment aimed at lowering the temperature of helium sufficiently by evaporating it without supply of heat was not successful, and only served to reach the lowest temperature recorded up to that time. The helium (see Fig. **12)** evaporating in a vacuum glass vessel was protected against heat supply, the vessel itself being dipped in a bath of liquid helium. The bath was obtained, as the figure shows, by the liquid helium flowing out of the liquefying apparatus into a cryostatic vessel.

The evaporation of even a very small quantity, when the pressure of the vapour is small, demands the continuous carrying away of colossal volumes of vapour. With vacuum pumps of very large capacity we succeeded in lowering the pressure to 0.2millimetre. The temperature then reached was 1.15°K according to the law of vapour pressure found. ( Of course we can only make an estimate here. The working out of the thermometry of these low temperatures with, amongst other things, the aid of the Knudsen hot wire manometer is still in its initial stages.) Since it would have needed new equipment, I deferred the question as to whether helium can be made to freeze in favour of other, more urgent problems, which could be tackled with the equipment  available.

The handling of these questions was very considerably facilitated when we succeeded in getting the cryostat shown in Fig.13 to work. The liquid he-
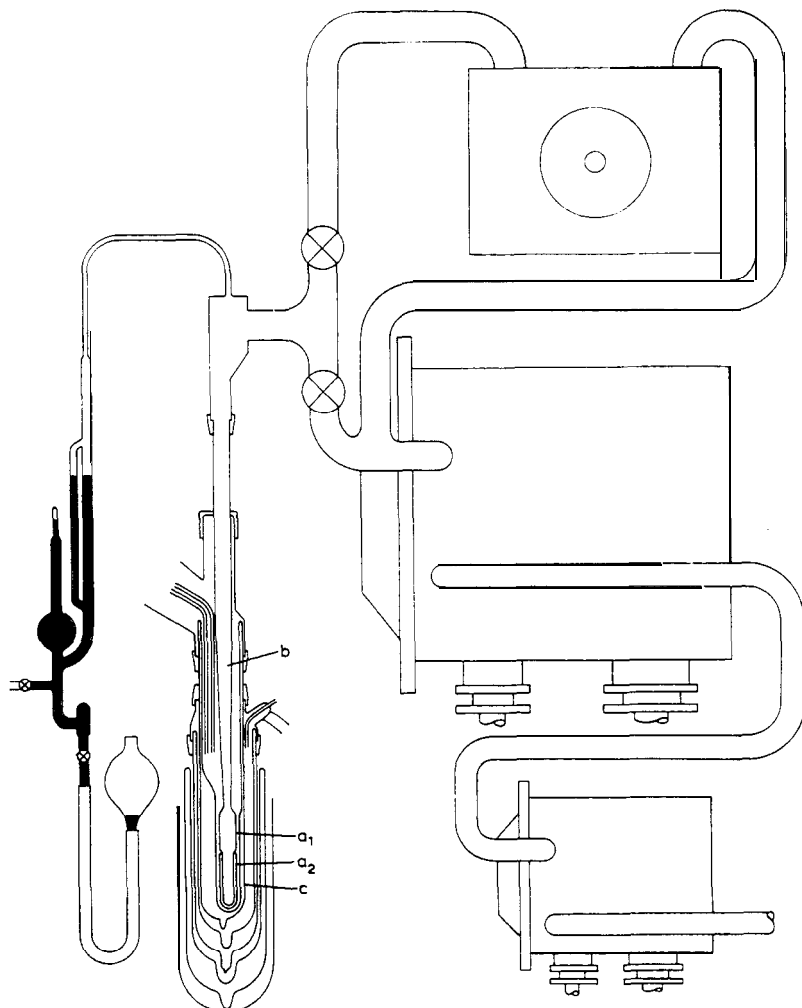
Fig.12.

lium is siphoned over from the liquefier into a cryostatic vessel open at the
top (through a vacuum tube cooled with liquid air). The liquefier can be
shut off from the cryostat by a valve. In this way continuous working of the
liquefier was possible. The bath is stirred vigorously by an electromagneti-
cally-driven  pump.

With this cryostat, investigations into the extraordinarily great conduc-
tivity of somemetals at low temperatures were possible, and I wish now to
report on these;

Even the very first experiments on the resistance of metals had brought
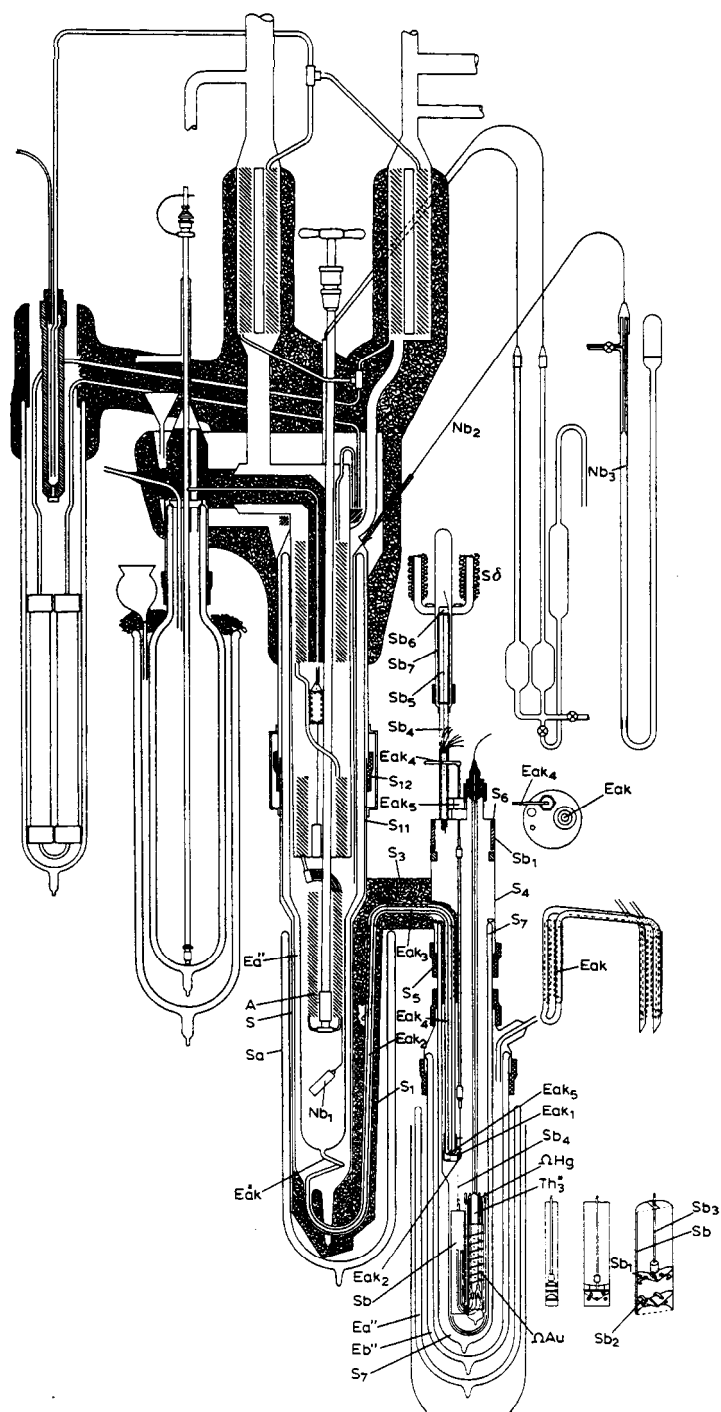
Fig.13.

very surprising results. With platinum wire there was no re-rise in resistance
after reaching a minimum, as would be expected, if the electrons which pro-
vide the conduction were firmly frozen to the atoms at low temperatures,
but on the contrary resistance became independent of temperature. The con-
clusion drawn from the results of an experiment carried out with Mr. Clay
down to the freezing point ofhydrogen was that for absolutely pure platinum
resistance would disappear at the boiling point of helium. At the lowest tem-
perature therefore the conduction electrons are not bound but the factors
which hinder their movement disappear. The obvious thing was to look for
these hindering factors in the energy of Planck's vibrators, so that here the
theory of resistance agrees very well with that of specific heat.

I attributed the fact that the resistance had become constant and not zero
to the slight impurities which remain even in pure gold. I could only hope
to get the mercury purer than gold, and the observations just made permit
one to conclude that its resistance at the boiling point of helium would still
be observable but that at the lowest temperature that could be reached with
helium it would disappear. The possibility of confirming this caused me to
think of little account all the difficulties which were attached to the experi-
ment. These were overcome and the results are, as Fig.14 shows, convincing.
The resistance, in fractions of the resistance at zero Centigrade, is shown as
the ordinate and the temperature as the abscissa. The figure contains, as well
as the results obtained in helium, which are marked II, also those, marked I,
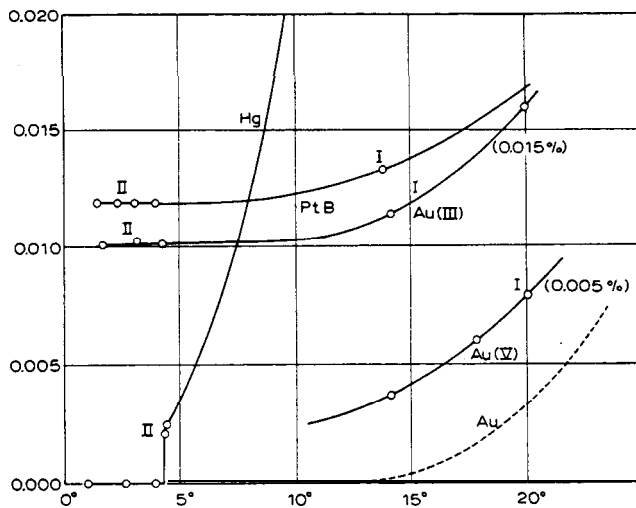


Fig.14
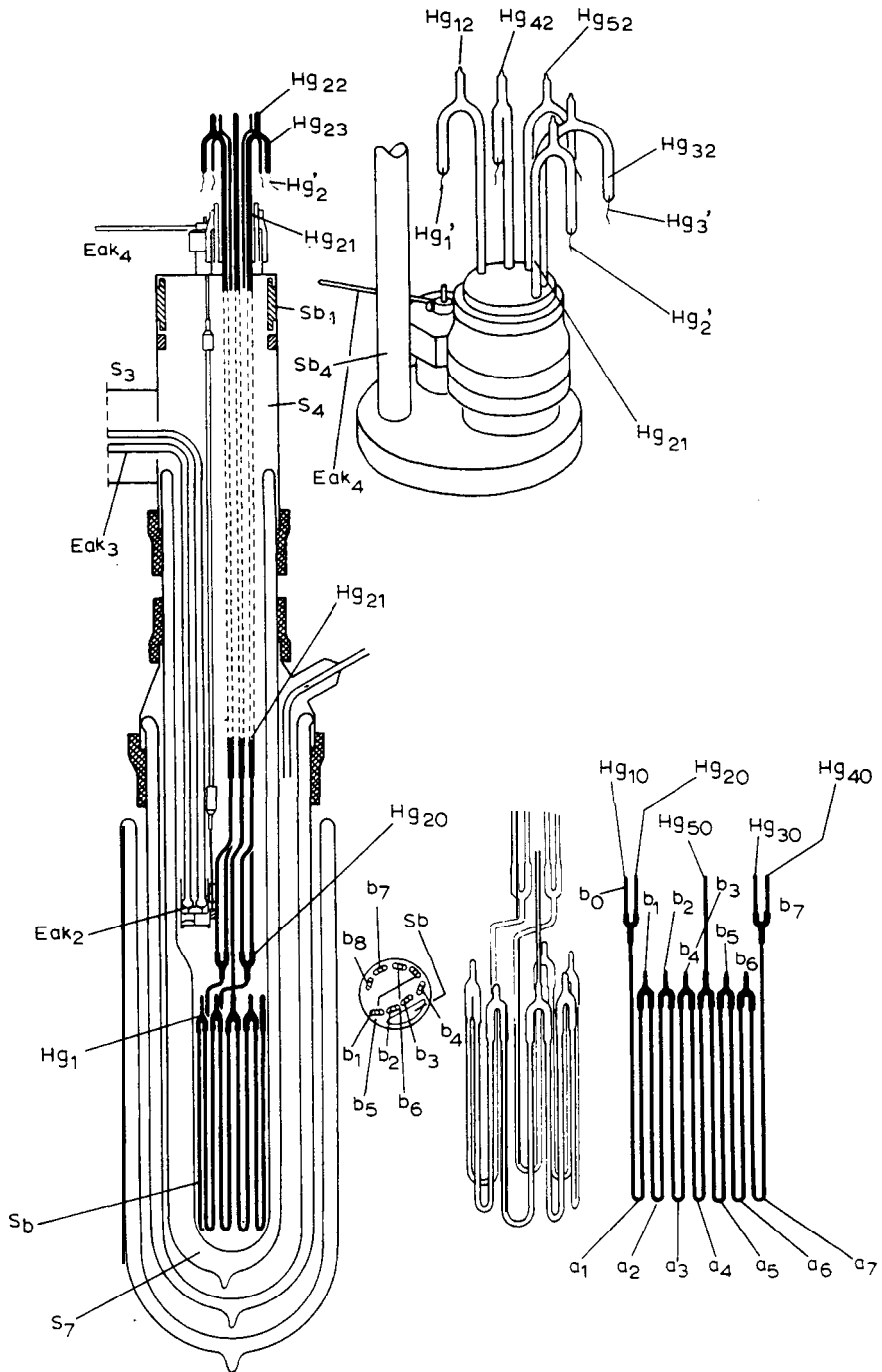
Fig.15.

which had been found in the course of investigations carried out by Mr. Clay down to the melting point of hydrogen. The resistance of the mercury is indicated by *Hg*. The results for platinum and for gold are also given in the figure, as well as the hypothetical curve for pure gold, the latter shown as a dashed line.

I would like to spend a little time on the arrangement of the experiment.

The thread of mercury, the resistance of which was measured, is shown in the accompanying Fig.15. The mercury, which had been painstakingly purified, is poured off into a series of U-shaped capillary tubes of only 1/20 millimetre diameter in vacuo and frozen in them during the experiment. At the upper ends of the U there are (see Fig. 16) reservoirs to deal with the change in the volume of the mercury. It is, however, difficult to avoid the
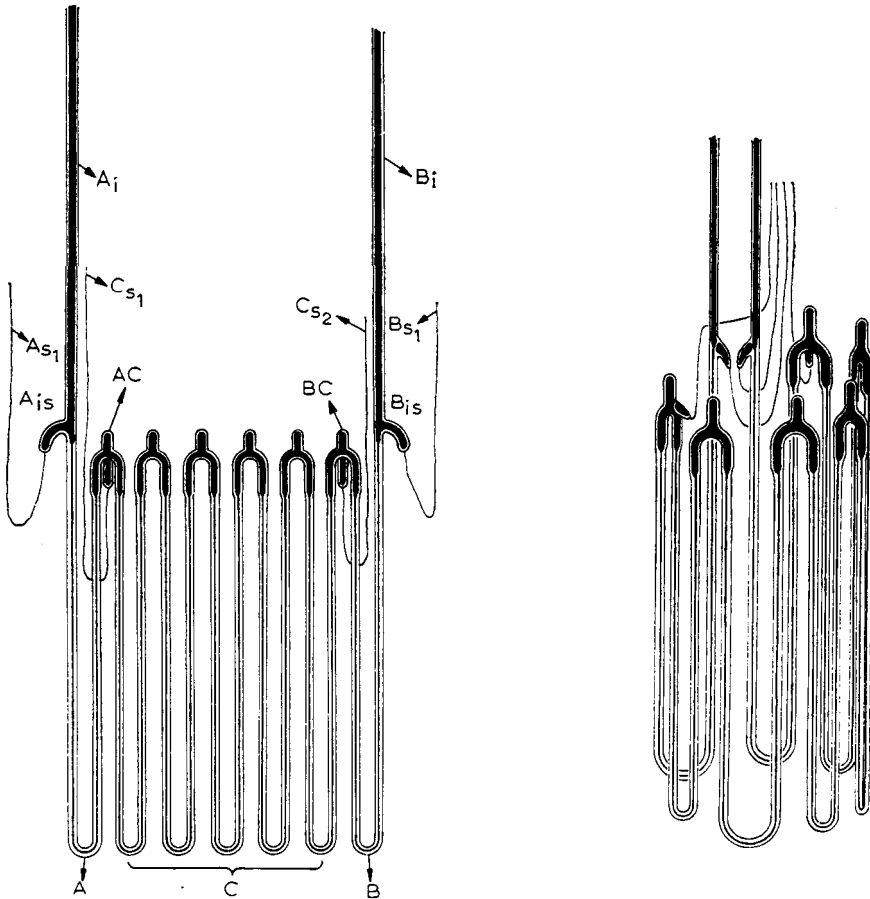
Fig.16.

tubes bursting or the thread breaking either during thawing or freezing. At the ends of the resistances there are mercury wires to conduct the current and to measure potential differences. (This is the most simple model theoretically : a branched wire system all of the same metal. In the following model, see Fig. 16, the lower portions of the voltage wires are replaced by platinum wires.)

As has been said, the experiment left no doubt that, as far as accuracy of measurement went, the resistance disappeared. At the same time, however, something unexpected occurred. The disappearance did not take place gradually but (compare Fig.17) *abruptly.* From 1/500 the resistance at 4.2°K drops to a millionth part. At the lowest temperature, 1.5°K, it could be established that the resistance had become less than a thousand-millionth part of that at normal temperature.

Thus the mercury at 4.2°K has entered a new state, which, owing to its particular electrical properties, can be called the state of superconductivity.

It is very important to the study of the properties of this state that tin and lead can also become superconductive. The transition point of tin lies at 3.8°K, that of lead probably at 6°K. Now that we are able to use these metals, which are easy to work, all types of electrical experiments with resistance-free apparatus have become possible. To take one example : a self-contained coil, cooled in the magnetic field, should, when the field is removed,
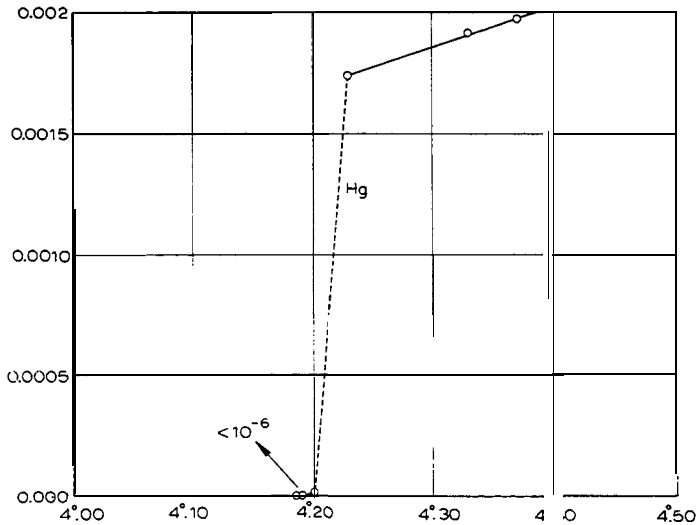


Fig.17.

be able to simulate for some time an Ampere molecular current. (See Addendum 2.) There is also the question as to whether the absence of Joule heat makes feasible the production of strong magnetic fields using coils without iron, * for a current of very great density can be sent through very fine, closely wound wire spirals. Thus we were successful in sending a current of 0.8 amperes, i.e. of 56 amperes per square millimetre, through a coil, which contained 1,000 turns of a diameter of 1/70 square mm per square centimetre at right angles to the turns.

All that I have said so far about superconductors applies only to currents below a certain threshold value, which lies all the higher the lower one drops in temperature. Up to this threshold value of current intensities no potential differences are found at the ends of the resistance within the degree of accuracy reached so far. The wire has at the most only a residual microresistance. As soon, however, as the threshold value is exceeded, a potential difference is necessary to maintain the current. Then, in a way as yet unexplained, normal resistance occurs in the wire, and at the great rate at which the potential difference is increased at the ends, there can be a considerable rise in temperature. Thus a bright lead wire which had been dipped in liquid helium and which remained superconductive up to a current density of 4.20 amps. per square millimetre, melted at a current density of 940. It appears

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* Shortly before this lecture I still felt that further experiments would lead to this question being answered in the affirmative. For if the contrary were the case new phenomena would have to be found. It seems possible that the potential phenomena which will be further discussed in the text can be suppressed by improving the material and the construction of the coil. Then only the resistance would be need to be considered which, owing to the characteristic magnetic field of the coil, can be produced in the resistanceless wire. After the experiment with the small coil mentioned in the text, it seemed that even this resistance would not come into the picture very much, even when strong fields are produced. From analogy it was to be assumed that it rises regularly with the field and even when it is proportional to the square of the field it would not be of very great importance even in fields of 100,000 Gauss, as the resistance produced in the coil by its own field was anyway still unnoticeable. Only experiments, however, could make certain of this. The experiments then planned were carried out after this lecture was given and produced surprising results. In fields below a threshold value (for lead at the boiling point of helium 600 Gauss), which was not reached during the experiment with the small coil mentioned in the text, there is no magnetic resistance at all. In fields above this threshold value a relatively large resistance arises at once, and grows considerably with the field. Thus in an unexpected way a difficulty in the production of intensive magnetic fields with coils without iron faced us. The discovery of the strange property which causes this made up for the difficulties involved.

that, generally speaking, when the threshold value of the current intensity is exceeded, local heating of the conductor through which the current is passing occurs above the transition temperature and this is why normal resistance at this point originates. When the current intensity increases the Joule heat produced at this point soon brings the whole resistance above the transition point.

The great question still not solved is whether this first impulse proceeds from bad sections of the wire or is also produced in pure, tension-free, evenly crystallized metal. If the potential phenomena are to be attributed to bad spots, we shall learn to eliminate them and then it is perhaps possible that the conductivity could be increased still higher than to the value reached at present, which is thousand million times that at normal temperature. The potential phenomena may, however, depend upon the nature of the metal in that the resting vibrators of the now superconductive metal are not made to move until the electron wind which blows past them has reached a certain strength, just as the surface of water is not ruffled until the wind has reached a certain strength. Ohm's law would have lost its validity for these phenomena.

Rather than immersing myself in a possible explanation based on the quantum theory, I should like to consider one of the experimental questions raised by the superconductors. According to ordinary theory of electrons one finds, for the free paths of the electrons, which at normal temperature are about of molecular size, values for the superconductive state going up to a metre. Will superconductive foils be passed through more easily, or with less deflection, by electric rays of various types than are ordinary conductive ones? This question has been raised by Mr. Lenard and myself. Mr. Becker and I are already busy with the relevant preliminary experiments.

I have already said that this is only one of the many questions which the superconductors raise. From each field of physics further questions push their way to the fore which are waiting to be solved by measurements at helium temperatures.

In the future I see all over the Leyden laboratory measurements being made in cryostats, to which liquid helium is transported just as the other liquid gases now are, and in which this gas also, one might say, will be as freely available as water.

In the meantime there is plenty of work which can already be done, albeit with difficulty (as when we began to use liquid oxygen), in the neighbourhood of the liquefying apparatus, and which can contribute towards lifting the veil which thermal motion at normal temperature spreads over the inner world of atoms and electrons.

*Added in proof*

1. In May 1914 the qualitative validity of the Langevin theory in both the connections mentioned in the text was established in gadolinium sulphate by experiments at helium temperatures.

2. The following was achieved during the experiments carried out in April-June 1914 relating to currents persisting in superconductors in the absence of electromotive force. The current, once produced, lasted for hours practically unchanged in the superconductive coil. Heating the latter above the transition point immediately destroys the electromagnetic field borne by the circuit. The experiments evidently demonstrate the frictionless mechanism as envisaged by Maxwell in the ether around a circuit and the absorption of its kinetic energy by a resistance introduced into the circuit.

# Biography

Heike Kamerlingh Onnes was born on September 21, 1853, at Groningen, The Netherlands. His father, Harm Kamerlingh Onnes, was the owner of a brickworks near Groningen; his mother was Anna Gerdina Coers of Arnhem, the daughter of an architect.

After spending the allotted time at the <<Hoogere Burgerschool>> in his native town (secondary school without classical languages), the director of which was the later Professor of Chemistry at Leyden J. M. van Bemmelen, he received supplementary teaching in Greek and Latin. In 1870 he entered the University of Groningen, obtained his <<candidaats>> degree (approx. B. Sc.) the following year, and then went to Heidelberg as a student of Bunsen and Kirchhoff from October 1871 until April 1873. Thereafter he returned to Groningen, where he passed his <<doctoraal>> examination (approx. M.Sc.) in 1878 and obtained the doctor's degree in 1879 with a remarkable thesis *Nieuwe bewijzen voor de aswenteling der aarde* (New proofs of the rotation of the earth).

Meanwhile in 1878 he had become assistant at the Polytechnicurn at Delft, working under Bosscha, in whose place he also lectured in 1881 and 1882, the year in which he was appointed Professor of Experimental Physics and Meteorology at Leyden University, in succession to P. L. Rijke.

Kamerlingh Onnes' talents for solving scientific problems was already apparent in 1871, when at the age of 18 he was awarded a Gold Medal for a competition sponsored by the Natural Sciences Faculty of the University of Utrecht, followed the next year by a Silver Medal for a similar event at the University of Groningen. When working with Kirchhoff he also won the <<Seminarpreis>>, entitling him to occupy one of the two existing assistantships under Kirchhoff.

In his doctor's thesis theoretical as well as experimental proof was given that Foucault's well-known pendulum experiment should be considered as a special case of .a large group of phenomena which in a much simpler fashion can be used to prove the rotational movement of the earth. In 1881 he published a paper *AIgemeene theorie deer vloeistoffen* (General theory of liquids),

which dealt with the kinetic theory of the liquid state, approaching Van der Waals' law of corresponding states from a mechanistic point of view. This work can be considered as the beginning of his life-long investigations into the properties of matter at low temperatures. In his inaugural address *De be-teekenis van het quantitatief onderzoek in de natuurkunde* (The importance of quantitative research in physics) he arrived at his well-known motto <<Door meten tot weten>> (Knowledge through measurement), an appreciation of the value of measurements which concerned him throughout his scientific career.

After his appointment to the Physics Chair at Leyden, Kamerlingh Onnes reorganized the Physical Laboratory (now known as the Kamerlingh Onnes Laboratory) in a way to suit his own programme. His researches were mainly based on the theories of his two great compatriots J. D. van der Waals and H. A. Lorentz. In particular he had in mind the establishment of a cryogenic laboratory which would enable him to verify Van der Waals' law of corresponding states over a large range of temperatures. His efforts to reach extremely low temperatures culminated in the liquefaction of helium in 1908. Bringing the temperature of the helium down to $0.9^{\circ}$K, he reached the nearest approach to absolute zero then achieved, thus justifying the saying that the coldest spot on earth was situated at Leyden. It was on account of these low-temperature studies that he was awarded the Nobel Prize. Later, his pupils W. H. Keesom and W. J. de Haas (Lorentz' son-in-law) conducted experiments in the same laboratory which led them still closer to absolute zero.

Other investigations in his laboratory which gradually gained in importance and international fame, included thermodynamics, the radioactivity law, and observations on optical, magnetic and electrical phenomena, such as the study of fluorescence and phosphorescence, the magnetic rotation of the polarization plane, absorption spectra of crystals in the magnetic field; also the Hall effect, dielectric constants, and especially the resistance of metals. A momentous discovery (1911) was that of the *superconductivity* of pure metals such as mercury, tin and lead at very low temperatures, and following from this the observation of *persisting currents.*

The results of Kamerlingh Onnes' investigations were published in the *Proceedings of the Royal Academy of Sciences of Amsterdam* and also in the *Communications from the Physical Laboratory at Leyden.* Many foreign scientists came to Leyden to work in his laboratory for shorter or longer periods, not only those mentioned on pp. 314 and 315 but others as well.

The laboratory gained additional fame throughout the world through the training school for instrument-makers and glass-blowers housed in it, founded by Kamerlingh Onnes in 1901.

At the early age of 30, Kamerlingh Onnes was appointed a member of the Royal Academy of Sciences of Amsterdam. He was one of the founders of the Association (now Institut) International du Froid. He was a Commander in the Order of the Netherlands Lion, the Order of Orange-Nassau of the Netherlands, the Order of St. Olaf of Norway, and the Order of Polonia Restituta of Poland. He held an honorary doctorate of the University of Berlin, and was awarded the Matteucci Medal, the Rumford Medal, the Baumgarten Preis and the Franklin Medal. He was Member of the Society of Friends of Science in Moscow, and of the Academies of Sciences in Copenhagen, Uppsala, Turin, Vienna, Göttingen and Halle; Foreign Associate of the Académie des Sciences of Paris; Foreign Member of the Accademia dei Lincei of Rome and the Royal Society of London; and Honorary Member of the Physical Society of Stockholm, the Société Helvéque des Sciences Naturelles, the Royal Institution of London, the Sociedad Española da Física y Química of Madrid, and the Franklin Institute of Philadelphia.

Outside his scientific work, Kamerlingh Onnes' favourite recreations were his family life and helpfulness to those who needed it. Although his work was his hobby, he was far from being a pompous scholar. A man of great personal charm and philanthropic humanity, he was very active during and after the First World War in smoothing out political differences between scientists and in succouring starving children in countries suffering from food shortage. In 1887 he married Maria Adriana Wilhelmina Elisabeth Bijleveld, who was a great help to him in these activities and who created a home widely known for its hospitality. They had one son, Albert, who became a high-ranking civil servant at The Hague.

Kamerlingh Onnes' health had always been somewhat delicate, and, after a short illness, he died at Leyden on February 21, 1926.

# Physics 1914

# MAX VON LAUE

*<< for his discovery of the diffraction of Röntgen rays by crystals>>*

# Physics   1914

*Presentation Speech by Professor G. Granqvist, Chairman of the Nobel Committee
for Physics of the Royal Swedish Academy of sciences*

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen.

Seldom indeed can a discovery in the field of physics have given rise to such intensive research work as did that of Röntgen in 1896, when he proved the existence of a new form of rays which had hitherto been unknown and which, owing to their remarkable characteristics, have since achieved a position of the greatest importance, not only in the field of pure physics but also in connection with research work throughout the other sciences.

Notwithstanding the considerable number of tests which have been carried out since their discovery and directed toward investigation of the true nature of X-rays, it was not until over a decade had passed that their true nature had finally been elucidated.

Already during the first tests it was established that not even the strongest magnetic fields were able to alter the direction of the rays. It was equally impossible to prove the existence of a refraction on transfer of the rays from one medium to another. If the X-rays were of a corpuscular nature they could not, therefore, be carriers of an electrical charge, as is the case with other known rays of corpuscular nature. If, therefore, we wish to disregard matter which has no electrical charge, it is necessary to assume that the particles, whose motion is characteristic for the X-rays, bear two charges of opposite sign, one of which neutralizes the other. On the other hand, from the fact that there was no evidence of refraction of the X-rays, it was possible to assume that, should they consist of a transverse wave motion-as is the case with light waves-the relevant wavelength would have to be very small, as for very small wavelengths, according to the theory of dispersion of light, the refractive index would approach unity.

After hurriedly discarding an hypothesis which had been expounded initially, according to which X-rays were believed to consist of longitudinal wave motions in ether, opinions as to their actual nature were divided according to the above two alternatives. Nevertheless an objective presentation could only describe them as a type of impulse of an unknown nature.

On the basis of an hypothesis expounded as early as 1896 by Stokes and

Wiechert this impulse was believed to consist of a disturbance which occurs in the ether when the cathode-ray particle, i.e. a forward-rushing electron, is impeded on colliding with molecules of matter. This disturbance or impulse was believed to propagate in all directions at the speed of light from the ether surrounding the electron. In each part of the space this disturbance was maintained for a period of identical duration to that in which the electron was impeded. This period of time, multiplied by the speed of light, was described as the impulse width, a quantity which, if the nature of the X-rays were the same as that of the light rays, would coincide with the wavelength.

According to that theory the X-ray impulse, which originates perpendicular to the cathode-ray bundle by which it is excited, is alleged to be completely polarized. The evidence of this type of polarization was first produced by Barkla in 1905, but, contrary to the theory, the polarization was not complete but only partial. While it was possible to explain the causative factors of this aberration the characteristics of the polarization were not adequate to prove the existence of a transverse undulation.

Once Dorn had succeeded, in 1897, in determining the fraction of the energy of the impeded electrons which is converted to X-rays, W. Wien was able to calculate the impulse width which, according to his figures, amounted to approximately $10^{-10}$ cm, or only one hundred-thousandth of the shortest known wavelengths of light. The short impulse width thus determined could explain the lack of success with previous diffraction tests which had been carried out on slits with X-rays, for even with the narrowest slit the diffraction phenomenon, which is produced by such small impulse widths or wavelengths, would have to lie just about at the limits of possible observation. And it may, in actual fact, only be said even of the most accurate of these tests conducted by Walter and Pohl that they render diffraction highly probable. From the research carried out by these scientists it would meanwhile seem to follow that the upper limit for the impulse width of X-rays lies at $4 \times 10^{-9}$.

This was the situation when von Laue placed a research medium of the highest import at the disposal of science by virtue of his epoch-making discovery of the interference of X-rays and, at the same time, proved that X-rays, as is the case with light rays, consist of progressive transversal waves.

Previous research had indicated, as is mentioned in the foregoing, that it was highly probable that, if X-rays are wave motions of the same type as light rays, then their wavelengths would have to be of an order of $10^{-9}$ cm. In order to obtain clear interference phenomena of the same type as those

which are caused when light rays pass a grating it was necessary for the distance between the grating slits to be of an order of $10^{-8}$ cm. But this is approximately the distance between the molecules of a solid body and it was in this manner that von Laue arrived at the idea of employing, as a diffraction grating, a solid body with regularly-arranged molecules, e.g. a crystal. As early as 1850 Bravais had introduced into crystallography the assumption that the atoms composing the various crystals are arranged in regular groups, so-called three-dimensional lattices or space-lattices, whose constants could be calculated with the aid of crystallographic data.

However, the theoretical basis of a space-lattice was unknown and thus it was first necessary for von Laue to develop this theory if else the investigation were to have a value. This he did mainly according to the same approximations as those conventional to the science of optics as applied to normal one-dimensional lattices.

Von Laue left the execution of the experimental work in the hands of W. Friedrich and P.Knipping. The apparatus which they employed consisted of a lead box into which they admitted a thin bundle of X-rays which they directed so as to fall upon a precisely oriented crystal. Sensitized film was positioned both behind and at the sides of the crystal. Already the preparatory tests showed that the intensity maxima which had been anticipated by von Laue became evident in the form of blackened spots on the film positioned behind the crystal.

From the grouping shown by these intensity maxima in accordance with the requirements of the theory, as established, for such photograms of various crystals and from the degree of clarity with which they have been reproduced, it follows that they are an interference phenomenon. Absorption tests have shown that the rays which give rise to the points of interference are actually X-rays, and from this von Laue has deduced with a high degree of certainty that the X-rays which cause intensity maxima on irradiation of a crystal have the character of a wave motion. However, the same is required also for those rays employed for irradiation purposes, for, as he says, were they of a corpuscular nature, coherent oscillations could only arise from those atoms set into motion by the identical corpuscle and these atoms would have to form together one whole agglomerate whose dimensions would be largest in the direction of radiation. However, contrary to what was indicated in the experiment, this would result in the intensity maxima consisting of irregular concentric circles.

As a result of von Laue's discovery of the diffraction of X-rays in crystals

proof was thus established that these light waves are of very small wave-lengths. However, this discovery also resulted in the most important discoveries in the field of crystallography. It is now possible to determine the position of atoms in crystals and much important knowledge has been gained in this connection. We can anticipate further discoveries of equal note in the future. It is thus rendered likely that experimental research into the influence of temperature upon diffraction will provide the solution to the question of a zero-point energy, or will at least be of some assistance in arriving at a solution to this problem, as the temperature factor assumes a different value according to whether a zero-point energy exists or not. However, the direct results of this discovery of diffraction are of no less importance: it is now possible to subject the X-ray spectra to direct examination, their line spectra can even be photographed, and science has thus been enriched by a method of research whose full implications can not yet be fully appreciated.

If it is permissible to evaluate a human discovery according to the fruits which it bears then there are not many discoveries ranking on a par with that made by von Laue. If one reflects further on the fact that only a few years have passed since his discovery was first published it may surely be said that, when awarding the Nobel Prize for Physics, the Royal Academy of Sciences will presumably seldom, if ever, be in a position of such close agreement with the letter of the Testament as on this occasion in deciding to award the Nobel Prize for Physics for the year 1914 to Professor Max von Laue, for his discovery of the diffraction of X-rays in crystals.

M AX VON L A U E

# Concerning the detection of X-ray interferences

*Nobel Lecture, November 12, 1915*

If other Nobel Prize winners express their thanks for this high honour at this juncture by recounting the history of their discovery they are able to report how, at the outset, they envisaged a high, but nevertheless attainable, objective and how they strove toward that objective by many paths, most of which proved initially to be false and how then, after many years of protracted endeavour, they finally achieved their objective. In my eyes the credit to which they are entitled increases in direct proportion to the magnitude of the difficulties which they finally surmounted. By comparison, what I have to say here differs somewhat from those examples. There is no doubt that I, also, had long been aware of the problem, i.e. producing X-ray interferences, before the inherent difficulties had finally been surmounted. But I never believed that it would be my personal good fortune to make a contribution in that direction, and it was for that reason that I did not concern myself unduly in that respect until suddenly I perceived the way which subsequently proved to be the shortest path to success. I am not, therefore, able to recount many details in connection with my personal preparatory work, so I shall confine my comments to explaining the combination of scientific and personal circumstances from which the idea first arose.

In the case of X-rays their discoverer had already made efforts to locate diffraction or interference phenomena in order to solve the question of whether or not they represent a wave phenomenon or the ejection of any small particles. But in this quest his research, which had otherwise been so successful, met with failure. Nevertheless, from the outset there were supporters for the former opinion; for Stokes and Wiechert could point out with complete justification that, according to Maxwell-Lorentz electrodynamics, electromagnetic waves must be produced whenever electricity carriers alter their velocity; one was also aware that cathode rays, which induce X-rays on striking an obstacle, are made up of electrons. W. Wien endeavoured to reconcile this consideration with what was, at that time, the very young quantum theory in order thus to arrive at an estimate of the relevant wavelengths. He arrived

at a value lying between $10^{10}$ and $10^{-9}$cm, which was in accordance with the fact that, if they were at all made up of waves, the X-rays could only have a shorter wavelength than visible light. For in 1900 all electromagnetic radiation of longer wavelengths was already known at least to the extent that one could not seek in it the more striking characteristics of X-rays such as, for example, the strong penetrating power.

If diffraction or interference phenomena were to be sought it was therefore necessary, in accordance with the basic principles of wave theory, to select for the test arrangement far smaller decisive dimensions than those employed in corresponding tests with visible light. Thus Haga and Wind, as well as Walter and Pohl, selected a wedge-shaped pointed slit at the pointed end of which they were able to prove a broadening of the transmitted X-ray bundles which could be attributed to diffraction. The conclusive force of these tests has frequently been a subject of dispute; for example there was one school of thought which tried to explain the broadening as a subjective optical illusion. However, the photometric measurement carried out by P. P. Koch on the best photograms of this type and the estimated wavelength of $4 \times 10^{-9}$ cm which Sommerfeld connected with those results would appear to prove that there is an objective basis for the broadening theory. For now that the relevant wavelengths have been confirmed we must regard this value as representing a very good determination for such tests.

Further evidence in support of the wave theory of X-rays was provided by Barkla's discovery of polarisation. Barkla permits rays, such as those originating from the anticathode of an X-ray tube, to fall upon a substance such as, for example, carbon, after which he then carries on working with those secondary X-rays as result from scattering, which emanate from the substance in question perpendicular to the original direction of radiation. If the secondary radiation is again permitted to fall upon such a substance this causes a production, as a result of repeated scattering, of a tertiary radiation of X-rays; but this has, at the plane perpendicular to the secondary radiation, an intensity maximum in one direction, and perpendicular to that a minimum at which it may even disappear completely. This indicates most clearly that, for the secondary radiation, the direction of propagation is not a symmetry axis and that it is thus polarised. This fact can be explained only with extreme difficulty by a corpuscular theory - of this we are only too well aware from the history of optics. Conversely it is quite possible to explain this by wave theory based upon the fact that all electromagnetic waves oscillate transversally and are therefore generally polarised. This theory also readily

explains the further fact that the direction of the vanishing intensity is parallel to the direction of the primary rays.

Notwithstanding these major arguments the wave theory initially did not meet with complete acceptance. For experts like W. H. Bragg maintained until 1912 the corpuscular view and, in support of that view, they were able to quote a series of phenomena which, in actual fact, have remained inaccessible to explanation by the wave theory. If X-rays do, in fact, fall upon a body, they not only excite the aforementioned secondary X-rays, they also free electrons. The velocities of these electrons do not now depend upon the temperature and other conditions obtaining with the body in question and one might therefore assume that their kinetic energy is derived from the incident X-ray radiation. But this is where the difficulty is encountered. For the velocities which have been observed are not dependent upon the intensity of radiation but, in fact, upon their degree ofhardness, and specifically in such a manner that these velocities increase with increasing hardness. If the intensity is weakened this will result in a decrease in the number of electrons released, but it will have no effect upon their velocities. The greatest velocity which occurs is always that which was possessed by the cathode radiation by which the X-rays have been excited; it is almost as if X-ray radiation retains a <<memory>> of the process of its creation and expresses this fact when, for its part, it releases electrons.

This would be quite easy to comprehend if the energy of the X-ray radiation were to accumulate and remain accumulated at certain points, as would, for example, be the case with the motion of individual corpuscles. But in agreement with the wave theory it expands progressively over increasing areas. This poses us with a complete puzzle, which is merely rendered the more complex by the further observation that the electrons which have been released would appear to prefer the direction taken by the incident X-rays. And it is a source of only qualified comfort if we make clear to ourselves that with the short-wave visible and ultraviolet light rays the same phenomena occur in the photoelectric effect. In this case also, where we most certainly have before us a wave process, they are simply incomprehensible.

We can only understand the reasons why our understanding fails at this juncture. Einstein has provided us with a rule on the dependency of the greatest existing electron velocity upon the frequency of light waves; in this the decisive role is played by the universal constant *h,* designated by Planck, its discoverer, as the elementary quantum of action. Conversely, more recent measurements - among which particular accuracy was achieved in those

made by Ernst Wagner in Munich - have shown that with the reverse process, specifically the excitation of X-rays by cathode rays, the same constant appears. This same Einstein law, namely, also links the greatest frequency in the X-ray spectrum with the kinetic energy of cathode rays. We are confronted here with just one special case of the great quantum mystery, the solution of which one may justly term the most important objective currently confronting the entire field of physics. However, it was quite understandable that before this relationship with the quantum theory had been ascertained researchers had based their arguments against the wave theory on the facts of electron emission.

But let us turn once again to the situation which obtained before 1912. For as far back as I can recall having had an interest in physics - and that goes back to the days in which I was privileged to receive first-class instruction at the famous old Protestant Gymnasium in Strassburg, Alsatia - my particular attention was drawn to the field of optics, and within that field the wave theory of light. The lectures which I heard during my student days from Voigt, Planck and Lummer provided me at that time, and especially in the afore-mentioned field, with thorough experimental and theoretical knowledge; and as I had finally been able to cultivate what one could almost term a special feeling or intuition for wave processes, it was quite natural that my first independent work should be concerned with the propagation of natural radiation in dispersing substances and the thermodynamics of interference phenomena. It turned out to be a matter of great good fortune that Sommerfeld passed to me the article <<Wellenoptik>> (Wave optics) at that time to work upon for the *Encyclopedia of Mathematical Sciences.* For it was during that project that I was obliged to seek a mathematical presentation of the lattice theory which - while it was not exactly what one might term an innovation - could be applied with considerable simplicity to lattice grids. Already at that juncture I was devoting considerable thought to the further transfer to space-lattices; but I did not pursue the matter further owing to the fact that they do not, after all, play any actual part in the field of optics.

On my arrival in Munich in 1909 my attention was drawn constantly - first owing to the influence of Röntgen's work at this University and subsequently by Sommerfeld's active interest in X-rays and y-rays, which he had also testified in several works-back to the question of their actual nature. To this was added a further important circumstance. Since the times of Hauy and Bravais the basic crystallographic law of rational indices had been explained simply and visually by the mineralogists through space-lattice arrangement of

the atoms. Sohncke, Federow and Schoenflies had brought the mathematical theory of possible space-lattices to the greatest possible degree of perfection. But no more far-reaching physical conclusion had evolved from this line of thought and thus, in the form of a questionable hypothesis, it remained a somewhat unknown quantity to physicists. But in Munich, where models of the Sohncke space-lattices were to be found in more than one university institute, it was P. Groth who expressed his defence of it, both orally and in writing, and I, also, thus learned from him. My interest in the theories which he was expounding increased progressively as, already at an early time, I had made sure-and contrary to the doubts which, in my day, were maintained by only a few philosophers concerning the reality of atoms - that there existed no watertight epistemological arguments which might contradict this fact, while practical experience was constantly providing fresh confirmation in support of it.

Such was the state of affairs as, one evening in February 1912, P. P. Ewald came to visit me. On Sommerfeld's instigation he was working on a mathematical investigation into the behaviour of long electromagnetic waves in a space-lattice and subsequently he published a dissertation on the theory of crystal optics which was based upon that work. But he was faced at that time with certain difficulties and came to me with a request for advice. Now it was not, however, possible for me to assist him at that time. But during the conversation I was suddenly struck by the obvious question of the behaviour of waves which are short by comparison with the lattice-constants of the space-lattice. And it was at that point that my intuition for optics suddenly gave me the answer: lattice spectra would have to ensue. The fact that the lattice-constant in crystals is of an order of $10^{-8}$cm was sufficiently known from the analogy with other interatomic distances in solid and liquid substances, and, in addition, this could easily be argued from the density, molecular weight and the mass of the hydrogen atom which, just at that time, had been particularly well determined. The order of X-ray wavelengths was estimated by Wien and Sommerfeld at $10^{-9}$cm. Thus the ratio of wavelengths and lattice-constants was extremely favourable if X-rays were to be transmitted through a crystal. I immediately told Ewald that I anticipated the occurrence of interference phenomena with X-rays.

It was not long before W. Friedrich also heard of this. While he immediately expressed his willingness to carry out a relevant test, the acknowledged masters of our science, to whom I had the opportunity of submitting it, entertained certain doubts about this viewpoint. A certain amount of diplomacy

was necessary before Friedrich and Knipping were finally permitted to carry out the experiment according to my plan, using very simple equipment at the outset. Copper sulphate served as the crystal, since large and regular pieces of it can easily be obtained. The irradiation direction was left to chance. Immediately from the outset the photographic plate located behind the crystal betrayed the presence of a considerable number of deflected rays, together with a trace of the primary ray coming directly from the anticathode. These were the lattice spectra which had been anticipated (Fig. I).

In continuation of the work, Friedrich and Knipping, with the aid of the considerable amount of equipment then placed at their disposal by the Institute of Theoretical Physics of the Munich University, substituted random irradiation of triclinic copper sulphate with irradiation, in the crystallographically-indicated axial directions, of crystals of maximum possible symmetry, i.e. regular crystals. In principle the theory had already been completed by transfer from the ordinary and from the grid lattice, and, on June 8, 1912, Sommerfeld was able to submit to the Munich Academy the joint work of Friedrich, Knipping, and myself on X-ray interferences, which work, apart from the theory itself, also contained a series of very characteristic exposures (Figs.2 and 3). Four weeks later followed the first application of the theory for interpreting the points ofinterference, produced by a regular crystal after irradiation along a four-fold axis (Fig. 2). Each point of interference corresponds with three integral numbers, originating from the three space-lattice periodicities, the ratios of which determine its position. I have attributed these numbers to the points of interference in the second publication which appeared simultaneously with the first. And said numbers, or their ratios, have proven thoroughly reliable, even after re-checking by the Braggs and other researchers. Thus the initial probe into the rightness of the interference theory proved favourable for this new phenomenon. This benefitted not only the wave conception of X-rays but also the lattice theory of crystals.

The wavelength can also be determined from the three specified numbers and the latter publication contains therefore also information in that connection. Nevertheless I made no secret of the fact that I could not attribute to these values the same degree of reliability as to the ratios of the numbers. For this there were two reasons. On the hand there may occur in each interference maximum - as has been adequately known in the science of optics - apart from a basic wavelength, in addition its half, third, etc. For as long as one has no further point of reference, apart from the position of the maximum, the wavelength thus remains uncertain by an integral factor. The wavelengths

Fig.I.
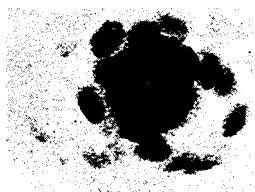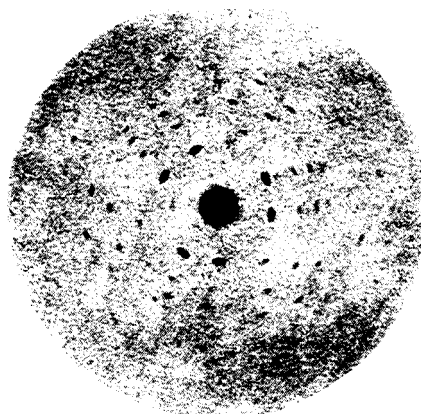


Fig.2.
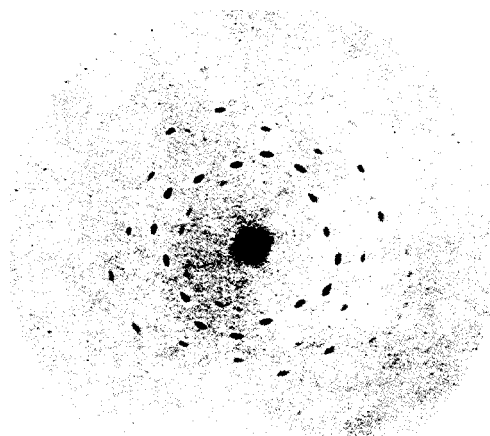


Fig.3.

were then measured by the dimensions of the space-lattice. As has already been mentioned, these could certainly be estimated by the order of magnitude; but in order to compute them with some degree of accuracy it would be necessary to know the molecular structure of the crystals down to the last detail. Instead of that one was aware, solely from the research carried out by the mathematicians, that, apart from the simple space-lattices, many other types of lattice were possible, for example, face- and body-centred lattices. The type of structure which is found in certain crystals was first determined by the Braggs after they had made a daring guess in producing an accurate

hypothesis as to the structure of sodium chloride. And it was thus that only they were also able to carry out the final measurements on the wavelengths.

But in reference to the manner in which the mathematical theory is to be generalised for such more complex types of structure, this I set forth almost one year later, when the necessity of that step had been shown with all urgency. The changes are minimal. The position of the points of interference remains the same as with a simple lattice of identical lattice-constants; it is only in the expression of their intensity that a new factor appears which is now designated as the structural factor. However, this factor can occasionally reduce to zero and then the relevant point is suppressed completely. It is due to this factor when an irradiation exposure plate gives some indication of the lower symmetry of the actual crystal instead of the full symmetry of the simple space-lattice.

The considerable interest which had been caused by the initial investigations was soon reflected in a large number of subsequent works. At first cercain doubts were expressed as to whether, in this instance, an interference phenomenon really did exist. But these were soon overcome. In my opinion the most complete rebuff was embodied in the proof produced by Wagner and Glocker that the X-ray radiation at the points of interference contained only one wavelength, even if many of them should exist in the original ray. The experimental research diverged essentially into two branches. The crystals were either investigated with the aid of the interferences, which examined the crystals' space-lattices, or they were employed in spectroscopy in the X-ray range. Since 1912 much has been done in both fields, and in both sectors W. L. Bragg and W. H. Bragg have taken the first important step beyond the investigations carried out at Munich. It would range far too wide if I were, at this juncture, to compile a fairly comprehensive list of all the researchers who have gained distinction in that research work. I can mention here only the transformation of the process, which proved to be of great importance for the further conduct of the experiments and in which Debye transferred the examination of beautiful, well-formed crystal fragments-which sometimes are obtainable only with considerable difficulty - to research into the finest possible crystal powder. Mention should also be made here of the extremely painstaking and accurate determination of the characteristic spectra which, commenced by Moseley, have been carried on - especially here in Sweden by Manne Siegbahn and Stenström-on the great majority of chemical elements. This research, as is known, has become of fundamental importance for the further knowledge of the structure of the atom. Neither

should I neglect to mention the fact that also the theory has been successfully extended. The important question as to why the thermal motion of the atoms does not result in any great amount of disturbance to the interference phenomena, has been settled by Debye, while H. A. Lorentz showed the manner in which the interference points which originate from the continuous spectrum obtain their intensity from the energy of many neighbouring wavelengths. For both reasons, owing to the thermal motion and to the working together of various wavelengths, factors arise which, in a similar manner to the structural factor, exert some influence upon the brightness of the interference points but not upon their location.

I would finally like to deal with a question which is still pending and to which, I trust, X-rays will shortly bring the answer. There are two contradictory opinions in respect of the mixed crystals. Opinions are united in respect of the fact that atoms form space-lattices, as is the case with chemically uniform crystals. There is also agreement in respect of the fact that in a mixed crystal of, e.g., potassium chloride and rubidium chloride the chlorine atoms lie in precisely the same position in relation to each other as in pure potassium chloride or pure rubidium chloride. (From the work carried out by the Braggs we are already aware of the fact that these two salts have the identical space-lattice.) But how are the potassium and rubidium atoms distributed over the positions reserved for the metal atoms ? According to the one viewpoint, which probably originated from Van 't Hoff, this occurs entirely by chance, while the other viewpoint maintains that it occurs regularly, thus permitting the space-lattices to be composed of equal-sized parallelepipeds of molecular dimensions which are identical in every respect, including the atomic occupation. For purely theoretical reasons the former opinion would appear to me to be the more probable. If, as in the example given, every mixing ratio is possible, it is indeed difficult to conceive, in every case, of atomic distributions which observe crystallographic symmetry, and, in addition, leave sufficiently small dimensions for the specified elementary parallelepipeds. Also the irradiation tests conducted by Vegard and Skjeldrup on the above-mentioned mixtures would appear to have resulted in an even stronger contradiction of the second opinion than these researchers themselves had originally thought. Nevertheless during recent years Tammarm has conducted chemical tests on mixed crystals of various metals such as, for example, copper and gold, which appear at first sight to support the second view. This should provide a further field of endeavour for a new application of X-ray interferences.

# Biography

Max Theodor Felix von Laue was born on October 9, 1879 at Pfaffendorf, near Koblenz. He was the son of Julius von Laue, an official in the German military administration, who was raised to hereditary nobility in 1913 and who was often sent to various towns, so that von Laue spent his youth in Brandenburg, Altona, Posen, Berlin and Strassburg, going to school in the three last-named cities. At the Protestant school at Strassburg he came under the influence of Professor Goering, who introduced him to the exact sciences.

In 1898 he left school and for a year did his military service. He then went to the University of Strassburg where he studied mathematics, physics and chemistry; but soon he moved to the University of Göttingen, where he worked under Professor W. Voigt and Professor W. Abraham, who greatly influenced him. After a semester at the University of Munich he went, in 1902, to the University of Berlin to work under Professor Max Planck. Here he attended lectures by O.Lummer on interference spectroscopy and heat radiation, the influence of which was shown in von Laue's dissertation on interference phenomena in plane-parallel plates.

After obtaining his doctorate at Berlin in 1903, von Laue went for two years to the University of Göttingen. In 1905 he was offered the post of assistant to Max Planck at the Institute for Theoretical Physics at Berlin. Here he worked on the application of entropy to radiation fields and on the thermodynamic significance of the coherence of light waves.

In 1909 he went as Privatdozent to the University of Munich, where he lectured on optics, thermodynamics and the theory of relativity and in 1912 he became Professor of Physics at the University of Zurich. In 1914 he moved, as Professor of physics, to Frankfurt-on-Mains and from 1916 he was engaged in war work at the University of Würzburg on high vacuum tubes used for telephony and wireless communication. In 1919 he was appointed Professor of Physics at the University of Berlin, a post which he held until 1943. From 1934 onwards he acted as consultant to the Physikalisch-Technische Reichsanstalt at Berlin-Charlottenburg.

In 1917, when the Institute for Physics was established at Berlin-Dahlem with Einstein as its Director, von Laue had charge, as Second Director, of most of the administrative work of this Institute, which was in close touch with German scientific research. Von Laue exerted, during this period and also later, considerable influence on the development of scientific research in Germany. When Berlin was bombed, this Institute moved to Hechingen, in Württemberg and von Laue accompanied it there. He remained at Hechingen from 1944 until 1945 and here, to distract his thoughts from the war, he wrote a History of Physics, which went into four editions and was translated into seven other languages. Here he welcomed the arrival of the French troops and was taken by an Anglo-American mission, together with nine other German scientists, to England where he remained until 1946. During his confinement in England he wrote a paper on the low absorption of X-rays during diffraction, which he contributed in 1948, to the International Union of Crystallographers at Harvard University. In 1946 he went to Göttingen as Acting Director of the Max Planck Institute and Titular Professor in the University there.

In 1951 he was elected Director of the Fritz Haber Institute for Physical Chemistry at Berlin-Dahlem and here he did much work on X-ray optics in collaboration with Borrmann and others.

In 1958 he retired and in 1959 his 80th birthday was celebrated in Berlin-Dahlem. He lived on, still actively at work, for another six months.

Apart from his earlier work already mentioned, von Laue's scientific work extended over a wide field. Early in his career he was greatly excited by Einstein's theory of relativity and between 1907 and 1911 he published eight papers on the application of this theory. In 1911 he published a book on the restricted theory and in 1921 another on the general theory, both books going into several editions.

His best known work, however, for which he received the Nobel Prize for Physics for 1914, was his discovery of the diffraction of X-rays on crystals. This discovery originated, as he related in his Nobel Lecture, when he was discussing problems related to the passage of waves of light through a periodic, crystalline arrangement of particles. The idea then came to him that the much shorter electromagnetic rays, which X-rays were supposed to be, would cause in such a medium some kind of diffraction or interference phenomena and that a crystal would provide such a medium. Although his colleagues Sommerfeld, W. Wien and others, with whom he discussed the idea on a skiing expedition, raised objections to the idea, W. Friedrich, one of

Sommerfeld's assistants and P. Knipping tested it out experimentally and, after some failures, succeeded in proving it to be correct. Van Laue worked out the mathematical formulation of it and the discovery was published in 1912. It established the fact that X-rays are electromagnetic in nature and it opened the way to the later work of Sir William and Sir Lawrence Bragg. Subsequently von Laue made other contributions to this subject.

Also prominent in von Laue's work were his contributions to the problems of superconductivity which he made when he was Professor of Theoretical Physics at Berlin University. At this time Walther Meissner was studying at the Physikalisch-Technische Reichsanstalt in Berlin, the remarkable disappearance of ohmic resistance shown by many metals at temperatures of the order of that of liquid helium. An especially valuable contribution then made by von Laue was his explanation, in 1932, of the fact that the threshold of the applied magnetic field which destroys superconductivity varies with the shape of the body because, when the magnetic field is established after the state of superconductivity has been established, the magnetic field is deformed by the supercurrents induced at the surface of the metal being used. This explanation was confirmed and it opened the way to Meissner's subsequent discovery that a superconductor eliminates the whole magnetic field in its interior and this became the basic idea of F. and H. London's theory of superconductivity. Von Laue published one paper in collaboration with F. and H. London and between 1937 and 1947 he published a total of 12 papers and a book on this subject.

Among the many honours and distinctions which he was awarded were the Ladenburg Medal, the Max-Planck Medal and the Bimala-Chum-Law Gold Medal of the Indian Association at Calcutta. He held Honorary Doctorates of the Universities of Bonn, Stuttgart, Munich, Berlin, Manchester and Chicago, was a member of the Russian Academy and the Academy of Sciences of Berlin, the German Physical Society and Mathematical Society, the Kant Society, the Academy of Sciences of Vienna, the American Physical Society, the Société Française de Physique and the Société Française de Minéralogie et Crystallographic. He was also Honorary Senator of the Max-Planck Society and Honorary Member of the German Röntgen Society, and Corresponding Member of the Academies of Sciences of Göttingen, Munich, Turin, Stockholm, Rome (Papal), Madrid, the Academia dei Lincei of Rome, and the Royal Society of London. In 1948 he became Honorary President of the International Union of Crystallographers, in 1952 he was made a Knight of the Order Pour le Merite, in 1953 he received the Grand Cross with Star

for Federal Services, and in 1957 he became an Officer of the Legion of Honour of France.

Much esteemed by his contemporaries for his character and sound judgment, von Laue's opinions were often sought and during his life he exerted great influence on the direction and development of German scientific work. Among his characteristics were a deep love and admiration of Prussia and a strong sense of justice and fair play. When Hitler and the National Socialist Party were in power, he defended, even at the risk of reprimand or personal injury, scientific views, such as the theory of relativity, which were not approved by the Party or by such strong adherents to it as the physicist Lenard. When Einstein resigned from the Berlin Academy and the Vice-President of this Academy stated that this was no loss, von Laue was the only member of the Academy who protested.

Chief among his recreations were sailing, skiing, mountaineering and motoring. Von Laue was not a rock-climber, but preferred to tour the Alpine glaciers with his scientific friends. As a motorist he was famous in Berlin, first on the motor bicycle on which he went at high speed to his lectures; and later in a car. He loved high speeds, but never, until the fatal collision that ended his life, had any accident.

In his later years he suffered from attacks of depression and a feeling of being persecuted by scientists and by the military authorities, whom he disliked intensely. Usually, however, he successfully overcame these attacks and regained his sense of humour and joy in life. He did not practise any art, but he took an interest in many arts, especially in classical music; and he read widely history and the philosophy of science. He thought of the stars, the mountain peaks and the achievements of the human with awe and humility and was at heart a deeply religious man. He asked that his tombstone should bear the statement that he died trusting firmly in the mercy of God.

In 1910 von Laue married Magdalena Degen.

On April 8, 1960, when he was driving alone to his laboratory, a motor cyclist, who had only received his licence two days previously, collided with von Laue's car. The motor cyclist was instantly killed and von Laue's car overturned in the Berlin speedway and he was taken from beneath it by the Fire Brigade. Although he showed at first some signs of recovery from his injuries, he died of them on April 24, at the age of 80.

# Physics 1915

# WILLIAM HENRY BRAGG

# WILLIAM LAWRENCE BRAGG

*<<for their services in the analysis of crystal* structure by means
of *Röntgen rays>>*

# Physics 1915

*The following account of the work of the Braggs\* is by Professor G. Granqvist, Chairman of the Nobel Committee for Physics of the Royal Swedish Academy of Sciences*

Von Laue's epoch-making discovery of the diffraction of the X-rays in crystals, on the one hand established wave motion as the essential quality of those rays and, on the other, afforded the experimental proof of the existence of molecular gratings in the crystals. The problem, however, of calculating the crystal structures from von Laue's formulae was an exceedingly complicated one, inasmuch as not only the space lattices, but also the wavelengths and the intensity-distribution over the various wavelengths in the spectra of the X-rays, were unknown quantities. It was consequently a discovery of epoch-making significance when W. L. Bragg found out that the phenomenon could be treated mathematically as a reflection by the successive parallel planes that may be placed so as to pass through the lattice points, and that in this way the ratio between the wavelengths and the distances of the said planes from each other can be calculated by a simple formula from the angle of reflection.

It was only by means of that simplification of the mathematical method that it became possible to attack the problem of the crystal structures, but to attain the end in view it was further necessary that the photographic method employed by von Laue should be replaced by an experimental one, based on the reflection principle, which admitted of a definite, even though at first unknown, wavelength being made use of. The instrument requisite for the said purpose, the so-called X-ray spectrometer, was constructed by Professor W. H-Bragg, W.L.Bragg's father, and it has been with the aid of that instrument that father and son have carried out, in part conjointly, in part each on his own account, a series of extremely important investigations respecting the structure of crystals.

If a number of cubes are laid on and beside each other in such a way that one cube face coincides in every case with the face of an adjoining cube, whereby consequently eight vertices always meet in one point, those angular points give a visual picture of the lattice points in the so-called simple cubic

lattice. If again a lattice point is placed so as to coincide with the central point of each cube face, the so-called face-centred cubic lattice is obtained, whereas the centred cubic lattice has one lattice point in every cube-centre. With the exception of these three cases there is no cubic lattice that fufils the condition that parallel planes placed in any direction whatever so as to pass through all the lattice points, shall also be at a constant distance from each other. The space lattice in the regular or cubic system must therefore coincide with one of those three, or constitute combinations of them. In such lattice combinations, on the other hand, in which the condition just mentioned is not fulfilled, where consequently parallel planes placed to pass through all the lattice points in certain directions are not equidistant, that circumstance is revealed by an abnormal intensity distribution among spectra of different orders, when the reflection takes place by those planes.

From crystallographical data it is always known how the face of a cube is situated in any given regular crystal, and there is consequently no difficulty in fixing the crystal on the spectrometer table in such a way that the reflection shall take place by planes with any prescribed orientation.

The rays falling on the crystal were produced by X-ray tubes, platinum being at first used for the anticathode. The characteristic X-radiation of the metals consists, as is well known, of a few strong lines or narrow bands, and the very first experiments with the spectrometer revealed the X-radiation that is characteristic of platinum. However, in the research undertaken to find out the nature of complicated space lattices, in which an abnormal intensity distribution among spectra of varying orders constitutes one of the most important of the results observed, it soon proved desirable to have available an X-radiation of approximately half the wavelength of the strongest platinum-line. From theoretical considerations W. H. Bragg regarded it as probable that a metal whose atomic weight was somewhere near the figure 100, would give a characteristic radiation of the desired wavelength. Accordingly anticathodes of palladium and rhodium were produced, which fully answered the purpose in view, so that spectra even of the fifth order could be obtained and measured. In order to take practical advantage, however, of those results, it was essential to have a method for calculating the intensity in the case of a complicated space lattice, that would prove simpler than the one given by von Laue's theory, and W. L. Bragg developed one.

The above is a brief sketch of the methods discovered by the two Braggs for investigating crystal structures. The results of their investigations em-

brace a large number of crystals belonging to various systems and can only
be cursorily summarized in this place.

To begin with, the two investigators applied themselves to the simplest
types of the regular system, represented by the alkaline haloid salts. It then
proved that potassium bromide and potassium iodide showed the spectra
that are characteristic of a face-centred cubic lattice, while the spectra of
potassium chloride represented a simple cubic lattice, sodium chloride oc-
cupying an intermediate position. As it must be assumed, on the strength of
the analogy of these salts, both in a chemical and a crystallographical sense,
that they are possessed of a corresponding space lattice, which could also be
corroborated in another way, it was proved by those researchers that the lat-
tice of the crystals in question consists of two face-centred cubic lattices cor-
responding to the two atoms, which interpenetrate in such a way that they
together constitute one single cubic lattice.

From these investigations it follows that a metal atom in the crystals of the
alkaloid salts is situated at one and the same distance from the six haloid
atoms nearest to it, and vice versa - a relationship that was found to prevail,
*mutatis mutandis,* in all the crystals examined. That means the exceedingly
important discovery, both for molecular physics and chemistry, that the crys-
tals consist of atomic lattices and not, as has been always imagined, of molec-
ular ones.

Two face-centred cubic lattices can also interpenetrate in such a way that
every point belonging to the one lattice is at the centre of gravity of a tetra-
hedron whose vertices are points belonging to the other lattice. That structure
was found by the two Braggs in the diamond, and afforded an experimental
support for the tetrahedral arrangement that chemists postulate for the four-
co-ordinate carbon. On the other hand, the explanation became evident of
why crystallographers have not been able to agree regarding the class in the
regular system to which the diamond should be referred.

It would carry us too far and be quite too complicated a proceeding to
give an account here of the further investigations into the space lattices of the
crystals. It will suffice to add that, in the course of their investigations, the
two Braggs have also discovered important relations between the amplitude
and the phase difference of the diffracted rays on the one hand and the atomic
weights on the other, and have also shown experimentally the influence
of heat on the space lattice.

Finally it may be mentioned that the two investigators have also deter-
mined the wavelengths of the X-rays and the distances between the succes-

sive planes placed to pass through the lattice points with such exactitude, that the error, if any, is probably at most some few units per cent and is more due to the general physical constant entering into the calculations than to the measurements themselves.

Thanks to the methods that the Braggs, father and son, have devised for investigating crystal structures, an entirely new world has been opened and has already in part been explored with marvellous exactitude. The significance of these methods, and of the results attained by their means, cannot as yet be gauged in its entirety, however imposing its dimensions already appear to be. In consideration of the great importance that these methods possess for research in the realm of physics, the Swedish Royal Academy of Sciences decided that the 1915 Nobel Prize in Physics should be divided between Professor W. H. Bragg and his son W. L. Bragg, in recognition of their services in promoting the investigation of crystal structures by means of X-rays.

*No Lecture was delivered by Professor W. H Bragg*

# Biography

William Henry Bragg was born at Westward, Cumberland, on July 2,1862. He was educated at Market Harborough Grammar School and afterwards at Ring William's College, Isle of Man. Elected a minor scholar of Trinity College, Cambridge, in 1881, he studied mathematics under the well-known teacher, Dr. E. J. Routh. He was Third Wrangler in the Mathematical Tripas, Part I, in June 1884, and was placed in the first class in Part II in the following January. He studied physics in the Cavendish Laboratory during part of 1885, and at the end of that year was elected to the Professorship of Mathematics and Physics in the University of Adelaide, South Australia. Subsequently he became successively Cavendish Professor of Physics at Leeds (1909-1915), Quain Professor of Physics at University College, London (1915-1925), and Fullerian Professor of Chemistry in the Royal Institution.

His research interests embraced a great many topics and he was an adept at picking up a subject, almost casually making an important contribution, then dropping it again. However, the work of Bragg and his son Lawrence in 1913-1914 founded a new branch of science of the greatest importance and significance, the analysis of crystal structure by means of X-rays. If the fundamental discovery of the wave aspect of X-rays, as evidenced by their diffraction in crystals, was due to von Laue and his collaborators, it is equally true that the use of X-rays as an instrument for the systematic revelation of the way in which crystals are built was entirely due to the Braggs. This was recognized by the award of the Nobel Prize jointly to father and son in 1915.

During the First World War, Bragg was put in charge of research on the detection and measurement of underwater sounds in connection with the location of submarines. It was probably in acknowledgement of his work, as well as of his scientific eminence, that Bragg was made a C.B.E. in 1917 and was knighted in 1920. The Order of Merit followed in 1931. After having been a Fellow since 1907, he was elected President of the Royal Society in 1935.

He was an honorary doctor of some sixteen-universities, and a member of the leading foreign societies. Many other medals and awards were bestowed

upon him among which may be mentioned the Rumford Medal in 1916 and the Copley Medal (its premier award) in 1930.

He was the author of many books, including *Studies in Radioactivity; X-Rays and Crystal Structure; The World of Sound; Concerning the Nature of Things; Old Trades and New Knowledge; An Introduction to Crystal Analysis;* and *The Universe of light.* His favorite recreation was golf.

In 1889 he married Gwendoline Todd, daughter of Sir Charles Todd, F.R.S., Postmaster General and Government Astronomer of South Australia. Their son William Lawrence Bragg shared the Nobel Prize with his father.

After a life of astonishing productiveness, Sir William Bragg died on March 10, 1942.

W ILLIAM  L AWRENCE  B RAGG

# The diffraction of X-rays by crystals

*Nobel Lecture, September 6, 1922\**

It is with the very greatest pleasure that I take this opportunity of expressing my gratitude to you for the great honour which you bestowed upon me, when you awarded my father and myself the Nobel Prize for Physics in the year 1915. In other years scientists have come here to express their thanks to you, who have received this great distinction for the work of an illustrious career devoted to research. That you should have given me, at the very outset of my scientific career, even the most humble place amongst their ranks, is an honour of which I cannot but be very proud.

You invited me here two years ago, after the end of the war, but a series of unfortunate circumstances made it impossible for me to accept your invitation. I have always profoundly regretted this, and it was therefore with the very greatest satisfaction that I received the invitation of Prof. Arrhenius a few months ago, and arranged for this visit. I am at last able to tell you how deeply grateful I am to you, and to give you my thanks in person.

You have already honoured with the Nobel Prize Prof. von Laue, to whom we owe the great discovery which has made possible all progress in a new realm of science, the study of the structure of matter by the diffraction of X-rays. Prof von Laue, in his Nobel Lecture, has described to you how he was led to make his epochal discovery. In trying to think of some way in which diffraction effects with X-rays might be found, and the question of their true nature answered, he came to the realization that Nature had provided, in a crystal, a diffraction grating exactly suited for the purpose. It had already been surmised that the X-rays, if they were in truth electromagnetic waves, would be found to have a very short wavelength, of the order of $10^{9}$ centimetre. The work of Sohnke, Fedorov, and others on the geometry of crystal structure had shown that the atoms or molecules in a crystal must be arranged in a geometrical pattern with perfect regularity, and it was possible to calculate that the spacing of the pattern must be of the order of $10^{8}$

centimetre. The relation between this spacing and the conjectured wavelength of the X-rays was precisely that required to give diffraction effects. Von Laue, in collaboration with Friedrich and Knipping, tried the experiment of passing a narrow beam of X-rays through a crystal, and they were immediately successful in obtaining undoubted evidence of regular diffraction. The lines of investigation which this discovery opened up have been so numerous and fruitful that Prof. von Laue could only give the briefest review of them in his address to you. When we consider the advances in our knowledge of the structure of matter which have been made by means of the von Laue effect, this discovery must surely be regarded as occupying a unique position in the history of science.

In saying something about the work for which we were awarded the Nobel Prize, I feel that I cannot but speak for both my father and myself. It was with his inspiration and under his guidance that any contributions of my own were made, and it was one of the proudest moments of my life when I heard that you had associated my name with his and awarded the prize to us jointly.

Prof. von Laue had made some of his earliest experiments with a crystal of zinc sulphide, and had obtained results which proved that the diffracted pencils showed the symmetry of the underlying crystal structure, which in this case was cubic. He developed a mathematical theory of diffraction by a space lattice, and proved that these diffracted pencils were in directions which were to be expected for a series of diffracting points arranged on a cubic space lattice. In pursuing the analysis still further, he tried to account for the fact that, whereas there were a large number of directions in which one would expect to find a diffracted beam, only a certain number of these appeared on the photographic plate used to record the effect. He suggested that this might be accounted for by the existence, in the X-ray beam, of certain wavelengths alone; and that a diffracted beam only appeared when conditions were right for diffracting these wavelengths. In studying his work, it occurred to me that perhaps we ought to look for the origin of this selection of certain directions of diffraction in the peculiarities of the crystal structure, and not in the constitution of the X-ray beam; this might be of the nature of white light and be composed of a continuous range of wavelengths. I tried to attack the problem from a slightly different point of view, and to see what would happen if a series of irregular pulses fell on diffracting points arranged on a regular space lattice. This led naturally to the consideration of the diffraction effects as a reflexion of the pulses by the planes of the crystal structure. The

points of a space lattice may be arranged in series of planes, parallel and equidistant from each other. As a pulse passes over each diffracting point, it scatters a wave, and if a number of points are arranged on a plane the diffracted wavelets will combine together to form a reflected wave front, according to the well-known Huygens construction.

The pulses reflected by successive planes build up a wave train, which analysis shows to be composed of the wavelengths given by the formula

$$n\lambda = 2d \sin \vartheta$$

In this expression, $n$ is an integer, $\lambda$ is the wavelength of the X-rays, $d$ the spacing of the planes, and $\vartheta$ the glancing angle at which the X-rays are reflected.

To regard the diffraction as a reflexion of the X-rays involved no new principle that was not already contained in von Laue's mathematical treatment. It still left open the question why certain planes in the zinc blende structure appeared to reflect strongly, while others which were apparently equally well adapted to do so were not represented by diffracted pencils. In analysing von Laue's result, however, I found that the selection of the effective planes could be accounted for by assuming that the diffracting centres were arranged in a face-centred cubic lattice, and not on a simple cubic lattice. The structural unit of the face-centred cubic lattice is a cube with a point at each comer and at the centre of each face. When the planes of such a lattice are arranged in the order of those most densely packed with atoms, and so most effective for reflexion, this order is rather different to that for a simple cubic lattice. By assigning a face-centred cubic structure to zinc blende, it seemed possible to explain satisfactorily the von Laue photograph as due to the diffraction of white radiation with a maximum intensity in a certain part of the spectrum. I made a further test of two simple cubic crystals, sodium chloride and potassium chloride. While the von Laue photographs obtained with sodium chloride indicated a face-centred lattice, those obtained with potassium chloride were of a simpler nature, and were such as one would expect from an arrangement of points at the corners of cubes. Since it seemed probable that these two crystals had a similar structure, I was led to conjecture that the atoms were arranged as shown in Fig. I, where every comer of the cube is occupied by an atom, whereas the atoms of one kind considered alone are arranged on a face-centred lattice. In potassium chloride the atoms are so nearly equal in their weight that they act as equivalent diffracting centres and the structure may be regarded as a simple cubic one.
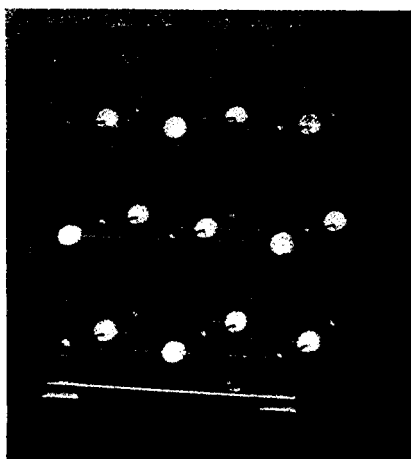
Fig.1.
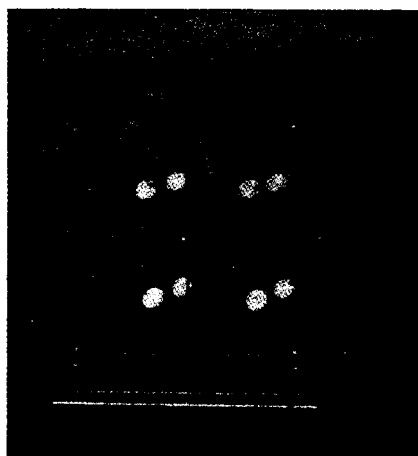


Fig.2.
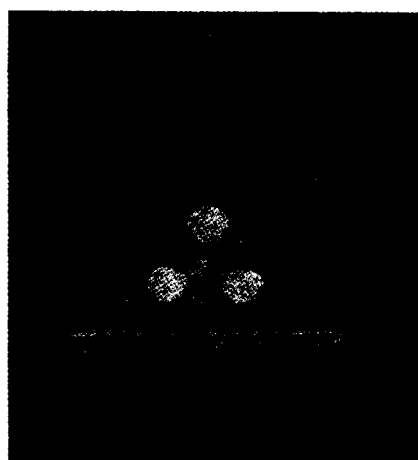


Fig.3.

Fig. I. *Rocksalt type (NaCl, KCl, LiF, etc.).* The *white balls* represent sodium (or chlorine); the *black balls,* chlorine (or sodium).

Fig.2. *Fluorspar (CaF$_2$).* The *black balls* represent calcium; the *white balls, fluo-rine.*

Fig.3. *Diamond.* Both *black* and *white balls* represent carbon atoms. Each ball is at the centre of gravity of four others.

Although it seemed certain that the von Laue effect was due to the diffraction of very short waves, there remained the possibility that there might not be the X-rays. My father, in order to test this, examined whether the beam reflected by a crystal ionized a gas; this he found to be the case. He examined the strength of the reflexion at various angles, and the instrument which was first used for the purpose was developed later into the X-ray spectrometer with which we have done the greater part of our work. In this instrument the X-rays coming from a tube are limited to a narrow beam by slits, and fall on a crystal at the centre of the spectrometer table by which they are

reflected; the reflected beam is received and measured in an ionization chamber.

In examining the effect for varying angles of incidence my father discovered that a very strong reflexion appeared when a given crystal face was set at certain definite angles. Since the relationship which has been mentioned above must hold between glancing angle and wavelength, this constituted the first evidence of the existence of characteristic <<lines>> in the radiation given off by the anticathode. These same lines could be recognized in the reflexions from other faces, and the measurement of the angles at which they appeared proved a most powerful method of finding the arrangement of the atoms in the crystal. The structures of sodium chloride and potassium chloride, which had been suggested by the von Laue photographs, were established on a firm basis by means of the spectrometer, and more complex struc-
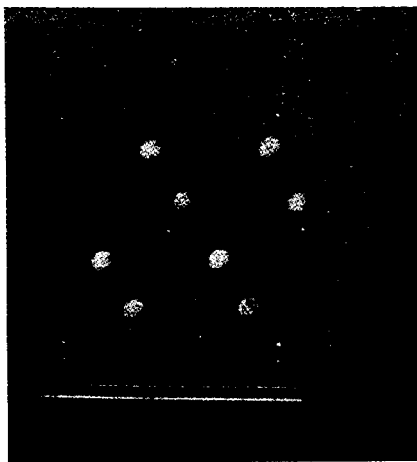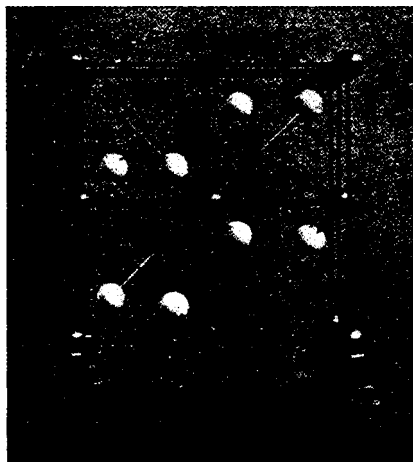


Fig.4.                                      Fig.5.

Fig.4. *Iron pyrites (FeS$_2$).* The arrangement may be considered as a modification of CaF$_2$. The *black balls* are the iron atoms. Each *white ball,* now representing a sulphur atom is displaced from the centre of the cube as in CaF$_2$ along a diagonal: the diagonal is chosen in a special way, best grasped from the model. A trigonal axis passes through the two white balls which lie close together and near the centre of the whole figure.

Fig.5. *Iron pyrites.* Viewed from a different angle, which shows the disposition of the sulphur atoms in horizontal lines. These are parallel to the well-known markings on the FeS$_2$ crystal. If the viewpoint is altered, as by turning the model through a right angle about a vertical axis, or au axis in the plane of the paper, the disposition of the sulphur atoms appears vertical instead of horizontal: just as the marking do.
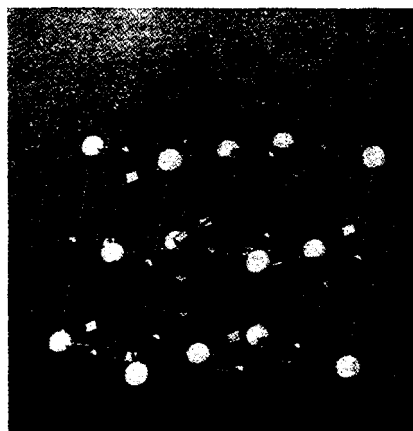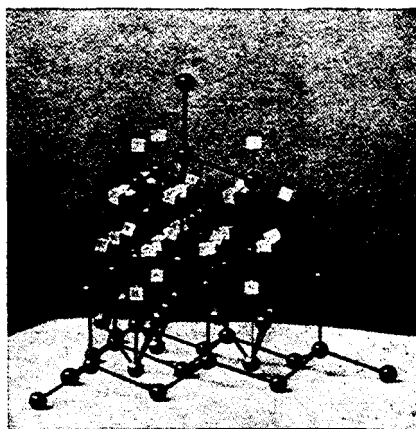
Fig.6.                                    Fig.7.

Fig.6. *Calcite (CaCO₃).* The *white balls* represent calcium; the *black balls,* carbon; and the *cubes,* oxygen.

Fig.7. *Spinel structure (spinel MgAl₂O₄; magnetite FeFe₂O₄; gahnite ZnAl₂O₄; etc.).* The divalent atoms (Mg, Fe, Zn, etc.) are placed with respect to each other in the same way as the carbon atoms in a diamond and are represented by the *black balls.* The *grey balls* represent the trivalent atoms (Al, Fe, etc.) A grey ball lies at the centre of every hexagonal (benzene) ring of black balls. The *light cubes* are the oxygen atoms. Every divalent atom touches four oxygen atoms and nothing else. Every trivalent atom touches six oxygen atoms and nothing else. Every oxygen atom touches one divalent and three trivalent atoms. The distance between the centres of two neighbouring divalent atoms in magnetite is 3.60Å.

tures such as calcite, zinc blende, fluorspar, and iron pyrites, were analysed. On the other hand, since the arrangement of atoms in these crystals was known, it was possible to calculate the spacings of the reflecting planes and so to assign a definite wavelength to the characteristic lines in the spectrum. By using tubes with anticathodes of platinum, osmium, tungsten, nickel, and other metals, it became clear that each gave off a radiation containing characteristic lines which agreed in their properties with the K- or L-radiations first discovered by Barkla. Further, Whiddington had measured the energy of the cathode rays required to excite Barkla's K- and L-radiations. The results obtained with the spectrometer gave the frequency of these radiations, and my father was able to show that the product, of the frequency and Planck's constant *h,* was equal to the cathode-ray energy required to excite the rays; this was a first proof of the quantum law as applied to X-rays.
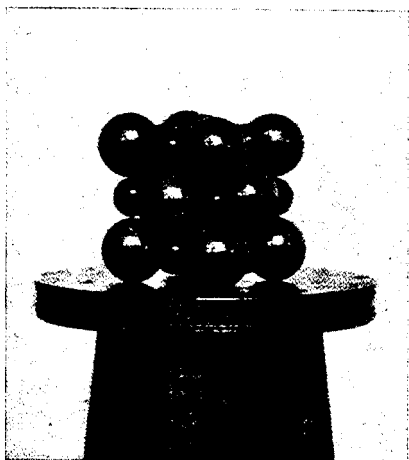
Fig.8.
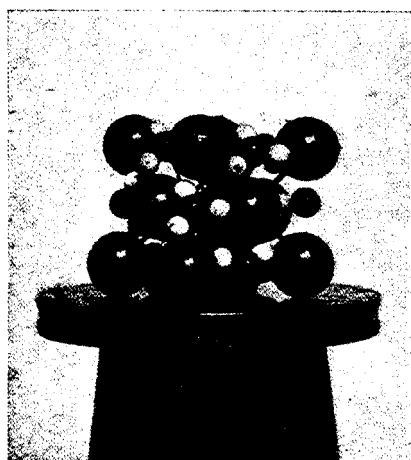


Fig.9.
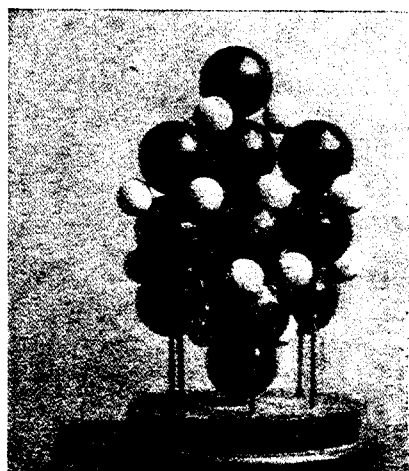
Fig.8. *Rocksalt (See also* Fig. I).
Fig.9. *Calcite.* The *large dark ball* is the
calcium atom; *the small dark ball,* carbon;
and the *white ball,* oxygen.



Fig. IO.

Fig.10. *Corundum  (Al₂O₃).* The type of
symmetry is the same as that of calcite.
The axis is vertical. The *dark balls* repre-
sent aluminium, the white *balls,* oxygen.

These two lines of investigation, into X-ray spectra and into crystal struc-
ture, are the two great branches of research to which von Laue's discovery
led. Moseley was the first to make a survey of X-ray spectra. His famous
researches established the law which governs the number and order of the
elements. He found that, in passing from one element to the next in the
Periodic Table, there was a regular progression of the frequency in the K-and
L-radiations given out by the elements, and that its regularity was so great
that it was possible to assign with absolute certainty each element to its prop-
er place in the list, and to find the gaps where an element was not known.
Moseley's death in the war cut short his brilliant career at its outset. Since

then the technique of X-ray spectrometry has been very highly developed. No one has done more in this line than Prof. Siegbahn at your University of Lund, who has attained such a marvellous accuracy and delicacy in his measurement of X-ray spectra. The establishment of the origin of the K-, L-, and M-radiations first indicated by Kossel's relationships, and the examination of the absorption edges, where the absorbing power of an element, for different wavelengths, passes through a critical value, have been of vital importance in the study of atomic structure since they furnish direct evidence as to the amount of energy-change, when an electron passes from one stationary state to another in the interior of the atom. The refinement to which wavelength measurement can now be pushed has even made it possible to discover that there are small differences in the position of these absorption edges, when different chemical compounds of an element are used as absorbers, as Dr. Lindh has shown, and this suggests a new and most powerful method of examining the chemical composition of substances and the potential energy of valency bonds.

The examination of crystal structure, with the aid of X-rays has given us for the first time an insight into the actual arrangement of the atoms in solid bodies. The study of structure by means of a microscope is limited by the coarseness of the light which illuminates the object, for we can never hope
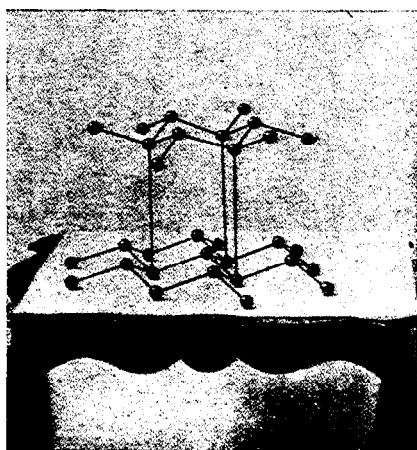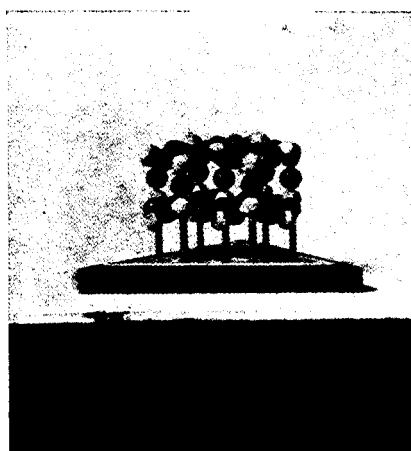


Fig.II.                                          Fig.12.

Fig. II. *Graphite.*

Fig.12. Ice ($H_2O$). Th*e white balls* represent the oxygen atoms, the *black balls* the hydrogen atoms. The oxygen atoms are arranged like those of carbon in diamond. Each hydrogen atom is situated midway between two oxygen atoms.

to see details smaller than the wavelength of the light. By using X-rays with their very short wavelengths, this limit of minuteness has at one step been decreased ten thousand times, for the wavelength of the X-rays is of a smaller order than the dimensions of the atomic structure. We are actually looking into the interior of the molecule and the atom with this fine-grained form of light.

The limits of the crystal pattern are arranged on a space lattice. Each limit is repeated over and over again in an identical fashion throughout the structure, at regular intervals in all directions. In analysing a crystal structure by X-rays, it is first necessary to find the dimensions of the unit cell of this space lattice, which has for its sides the primitive translation which the structure may be supposed to undergo in order so be brought into self-coincidence. It is a simple matter to achieve this. We find the angle at which a monochromatic beam of X-rays of known wavelength is reflected by the various faces of the crystal. Reflexion takes place only when the relation

$$n\lambda = 2d \sin \vartheta$$

is satisfied, and so the spacing $d$ of the planes parallel to any face under examination can be found by measuring the angle $\vartheta$. The dimensions of the unit cell can be found by measuring $d$ for several faces. Having determined the dimensions of the unit cell, we can calculate how many atoms or molecules are contained within it, using as data the density of the crystal and the mass of each molecule.

The second step in analysis consists in the determination of the manner in which the atoms are grouped together to form each unit of the structure. It is here that the principal difficulty is experienced. The way in which the analysis is pursued may be illustrated by an analogy with the spectra obtained with a diffraction grating. It is well known that the form of the lines ruled on a grating has an influence on the relative intensity of the spectra which it yields. Some spectra may be enhanced, or reduced, in intensity as compared with others. Indeed, gratings are sometimes ruled in such a way that most of the energy is thrown into those spectra which it is most desirable to examine. The form of the line on the grating does not influence the positions of the spectra, which depend on the number of lines to the centimetre, but the individual lines scatter more light in some directions than others, and this enhances the spectra which lie in those directions.

The structure of the group of atoms which composes the unit of the crystal

grating influences the strength of the various reflexions in exactly the same way. The rays are diffracted by the electrons grouped around the centre of each atom. In some directions the atoms conspire to give a strong scattered beam, in others their effects almost annul each other by interference. The exact arrangement of the atoms is to be deduced by comparing the strength of the reflexions from different faces and in different orders.

In our early work we made certain assumptions in order to unravel the complex tangle which the reflexions from some crystals represented. We supposed that the diffraction took place at the centre of each atom, as if the whole effect were localized there. Further, we supposed that the effect of an atom was proportional to its atomic weight. Neither of these assumptions is more than very approximately true, as deeper analysis has shown. However, theory shows that the strength of the scattered beams varies so greatly with slight changes in the relative positions of the atoms, that these assumptions will serve to give an accurate determination of these positions. We analysed a number of simple crystals in this way, examples of which are given in the plates at the end of this address.

A single crystal is employed in the X-ray spectrometer. We used large crystals in our first experiments, reflecting from natural or artificially prepared faces. It is not essential to do this, however, for the ionization chamber is so sensitive a detector of X-radiation that small crystals a millimetre or two in breadth can be examined. In this case the rays are reflected throughout the whole volume of the crystal, which is not sufficiently thick to absorb them too much. A small crystal can be set at the centre of the instrument, adjusted so that a zone is parallel to the axis, and then turned round so that the reflexion of various faces is observed in turn. The X-ray spectrometer may be thus used in a manner very similar to that employed by a crystallographer when he measures a crystal with a goniometer. It is a more searching method, however. The goniometer can only measure the angles between faces which have been developed on the crystal, whereas the X-ray spectrometer measures the angles between planes of the crystal structure, and the spacings of the planes, although the crystal may have no regular external form.

In many cases it is impossible to obtain even small perfect crystals. The beautiful method of analysis initiated by Debye and Scherrer in Germany, and by Hull. in America, has overcome this difficulty. In their method a monochromatic beam of X-rays is allowed to fall on a mass of crystalline powder. Some of the minute crystals will be set so as to reflect the rays for

every face and order, and so to give rise to a series of diffracted haloes which are recorded on a photographic plate. By means of this method, Hull has analysed the structure of a very large number of elements, including most of the metals. The method is admirably adapted to the study of compounds which do not form large crystals, but whose structure is very simple. By itself, it is not so well adapted to the analysis of complex crystals, since there is nothing to indicate which planes have given rise to the diffracted beams observed on the plate. Very often, however, a clue to the unravelling of the data can be got by examining the reflexion from an identified plane of a single small crystal; this gives us the key which enables us to assign the lines on the Debye photograph to the correct crystal planes.

The Debye method of crystal analysis has possibilities of development which have hardly been touched on as yet. A complex mixture of different crystals can be analysed, since each substance gives its characteristic series of haloes. This is an entirely new way of attacking such problems as the structure of alloys, or of minerals, since it tells us, not only what are the constituents, but how they are built up into solids; their crystallographic as well as their chemical structure.

A further development of the powder method which has proved to be most interesting is the study of colloidal particles. Scherrer has shown that particles of metals in the colloidal state consist of minute crystals, with a structure like that of large crystals; he has even formed an estimate of the size of the particles by observing the broadening of the haloes, this being due to a loss of resolving power owing to the small number of reflecting planes in any one particle.

There seems to be hardly any type of matter in the condition of a true solid which we cannot attempt to analyse by means of X-rays. For the first time the exact arrangement of the atoms in solids has become known; we can see how far the atoms are apart and how they are grouped. The importance of this consists in the light it throws on chemical composition. Very few crystals have yet been analysed by means of X-rays, and those that have been done are of simple composition, but as the knowledge of crystal structure increases we ought to get a far deeper insight into the nature of the forces which bind atoms together. One type of chemical binding has been already confirmed. In a structure such as that of sodium chloride (Fig. I) the atoms of sodium and chlorine are not associated into chemical molecules, but are arranged alternately equidistant from several neighbours. This is explained by supposing that these atoms are ionized in the crystal structure, and that

the whole is held together by the attraction of oppositely charged ions. This is in accordance with the theories of Kossel on the constitution of compounds, and the work of Born and Landé has shown that we can make quantitative comparisons between the electrical potential energy of such an assemblage of ions, and the heat of formation of the solid from its elements. This is one of the first steps towards an explanation of chemical affinity in terms of familiar physical forces.

On the other hand, the chemical composition of a compound aids in the determination of its crystal structure. So many dispositions of the atoms are possible, in the more complex crystals, that one is at a loss where to begin in trying various arrangements in order to explain the X-ray diffraction effects. A knowledge of the most probable configuration of the atoms, and of the distances between them, is of the greatest assistance, however approximate it may be. This may perhaps be illustrated by the structures of the aromatic organic compounds, some of which my father has lately succeeded in analysing. The symmetry of the crystals of such substances as naphtalene, anthracene, and their derivatives is low, and there are a large number of atoms in the molecule, so that the analysis of their structures would be very difficult from first principles. However, it was assumed that the size of the benzene
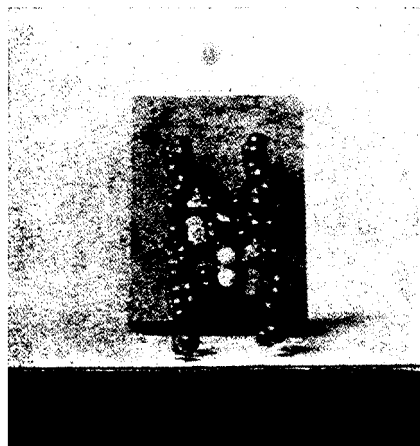


Fig.13.                                    Fig.14.

Fig.13. *Naphthalene* $(C_{10}H_8)$. The double rings of *grey balls* represent the double benzene rings of carbon atoms. The positions of the hydrogen atoms are indicated by the *black* and *white balls.*

Fig.14. *Naphthalene* $(C_{10}H_8)$. The same model as in Fig.13, viewed perpendicularly to the C-axis.

rings in these crystals was approximately the same as that of the corresponding rings in diamond and graphite. With this assumption, the data on the size of the unit cell for all these compounds fell into relationship with each other. The benzene ring could be treated as a single unit, and space had to be found in the crystal structure for one or more to be packed into each unit cell. Probably the solutions of many other complex crystals, which appear almost hopeless at present, will be made along similar lines.

Finally, there is a still deeper application of the X-ray analysis, to the structure of the atom itself Since the wavelength of the X-rays is less than the <<atomic diameter>>, as it is somewhat vaguely termed, and since the rays are presumably diffracted by the electrons in the atom, we ought to be able to get some idea of the distribution of these electrons in the same way that we draw conclusions as to the grouping of the atoms. Interference between the waves scattered by the electrons must take place. In order to study this question, a much closer analysis of the mechanism of X-ray reflexion must be made. Many workers have attacked this problem, amongst them Darwin in England, Debye in Germany, Compton in America. We have been trying to make some accurate quantitative determinations of the strength of X-ray reflection, the object in view being the measurement of the amount of radiation scattered by an atom in all directions when an X-ray beam passes over it. The whole subject bristles with difficulties, and the assumptions on which the theory of reflexion rests have not been exhaustively proved. On the other hand there seems to be a prospect that the method will prove a valid way of testing various models proposed for the atom, since the way, in which these models should diffract the rays, can be calculated, and compared with that which is actually observed.

I have only given in this account a very brief description of the many lines of investigation which have arisen from von Laue's discovery. I wish that there were more contributions of my own to this subject which I could have described to you, to justify the supreme compliment which you paid me in giving me your award, but the war interrupted work for so many years, and since then there has been so much reorganization of all university work in England that research has been difficult to achieve. I will conclude, then, in expressing my thanks to you for giving me this opportunity of addressing you, and my gratitude for all which I owe to you.

# Biography

William Lawrence Bragg, son of William Henry Bragg, was born in Adelaide, South Australia, on March 31, 1890. He received his early education at St. Peter's College in his birthplace, proceeding to Adelaide University to take his degree in mathematics with first-class honours in 1908 He came to England with his father in 1909 and entered Trinity College, Cambridge, as an Allen Scholar, taking first-class honours in the Natural Science Tripos in 1912. In the autumn of this year he commenced his examination of the von Laue phenomenon and published his first paper on the subject in the *Proceedings of the Cambridge Philosophical Society* in November.

In 1914 he was appointed as Fellow and Lecturer in Natural Sciences at Trinity College and the same year he was awarded the Barnard Medal. From 1912 to 1914 he had been working with his father, and the results of their work were published in an abridged form in *X-rays and Crystal Structure* (1915). It was this work which earned them jointly the Nobel Prize for Physics in 1915, and from this year to 1919 W. L. Bragg served as Technical Advisor on Sound Ranging to the Map Section, G.H.Q., France, receiving the O.B.E. and the M.C. in 1918. He was appointed Langworthy Professor of Physics at Manchester University in 1919, and held this post till 1937.

W. Lawrence Bragg, who had been elected Fellow of the Royal Society in 1921, was Director of the National Physical Laboratory in 1937-1938 and Cavendish Professor of Experimental Physics, Cambridge, from 1938 to 1953. He was Chairman of the Frequency Advisory Committee from 1958 to 1960.

Knighted in 1941, Sir Lawrence holds the degree of M.A. (Cambridge), Honorary D.Sc. (Dublin, Leeds, Manchester, Lisbon, Paris, Brussels, Liege, and Durham), honorary Ph.D. (Cologne), and honorary LL. D. (St.Andrews). He has many honorary fellowships and is an honorary or foreign member of American, French, Swedish, Chinese, Dutch, and Belgian Scientific Academies, besides being Membre d'Honneur de la Société Française de Minéralogie et Cristallographie.

He was awarded the Hughes Medal of the Royal Society in 1931; the

Royal Medal of the same Society in 1946, and the Roebling Medal of the Mineral Society of America in 1948.

Together with his father, he has published various scientific papers on crystal structure after their joint publication of 1915: *The Crystalline State* (1934), *Electricity* (1936), and *Atomic Structure of Minerals* (1937).

Sir Lawrence's chief interests at the present time are the application of X-ray analysis to the structure of protein molecules, which are being investigated in the Davy-Faraday Laboratory of the Royal Institution, in continuation of similar work at the Cavendish Laboratory, Cambridge. This collaboration has succeeded in determining for the first time the structure of the highly complex molecules of living matter.

Having been awarded the Nobel Prize at the very early age of 25, W. Lawrence Bragg was the youngest-ever laureate. The very rare opportunity of celebrating a golden jubilee as a Nobel Laureate was given special attention during the December ceremonies at Stockholm in 1965, when Sir Lawrence, at the invitation of the Nobel Foundation, delivered a lecture-the first Nobel Guest Lecture-m retrospect on developments in his field of interest during the last fifty years.

In 1921 he married Alice Grace Jenny (née Hopkinson) of Cambridge, and they have two sons (the elder of whom became chief scientist with Rolls Royce, while the younger entered a Cambridge instrument-making firm), and two daughters (the elder of whom married an official of the Foreign Office, while the second married the son of the Master of Corpus Christi College, Cambridge).

# Physics 1916

Prize not awarded

Physics *1917*


CHARLES  GLOVER  BARKLA


*<<for his discovery of the characteristic Röntgen radiation of the elements>>*

# Physics 1917

*The following account of Barkla's work\* is by Professor G. Granqvist, Chairman of the Nobel Committee for Physics of the Royal Swedish Academy of Sciences*

When X-rays fall on any substance, whether solid, liquid, or gaseous, they cause a secondary radiation. That was discovered by Sagnac in 1897 and it has since then been studied by a long series of investigators. Professor Barkla of Edinburgh, however, has carried out the most fundamental and exhaustive researches into the nature of this radiation, and in doing so he has discovered a new and unanticipated phenomenon, which has turned out to possess the utmost importance for physical investigation.

The secondary radiation consists of two varieties of radiation wholly different from each other. One is a corpuscular radiation of the same character as cathode rays and as the analogous b -rays of radioactive substances, being an emission of electrons. The other, on the contrary, is of the same character as X-rays.

Barkla has made a long series of very careful investigations into the nature of the latter of the two types of radiation. In the first place he discovered that there are two different kinds of X-rays in the secondary radiation. The absorption coefficients of one of these two varieties are the same as those of the incident X-rays. Thus the rays have the same penetrability as the primary rays, and, as they prove in other respects to have the same qualities as the primary rays, they must be regarded as a diffused primary radiation.

The intensity of this diffuse radiation varies in different directions in relation to that of the incident primary radiation. By measuring the distribution of intensity of the diffuse radiation, Barkla was able to determine the total emission of a series of substances under varying conditions. One very important result among others that his investigations led to, enabled Barkla at an early stage to estimate approximately the number of electrons contained in an atom.

The other variety of X-rays is wholly independent of the character of the incident radiation. Barkla showed that this radiation is homogeneous, that its absorption coefficient is not dependent on the incident radiation, but is determined by the irradiated substance. Further, he made the important dis-

l Owing to war conditions Professor Barkla was unable to attend the ceremony.

covery that the character of the rays is solely dependent on the qualities of
the atoms constituting the substance, irrespective of their grouping and in-
fluence upon each other, that is to say, independent of the chemical composi-
tion of the substance. Every chemical element yields a secondary radiation
that is characteristic of that element. Hence Barkla named this variety of
radiation the characteristic X-radiation.

   This variety of radiation may be most conveniently studied in elements of
relatively high atomic weight, for in them it is stronger than the diffuse radia-
tion. The characteristic radiation, however, being, in contrast to the diffuse
radiation, perfectly homogeneous, can be distinguished from the latter, and
thus Barkla could trace the characteristic radiation down to elements of the
atomic weight of 27.

   The characteristic radiation is furthermore, in contrast to the diffuse radia-
tion, wholly unpolarized and is not dissymmetrical in respect to the direction
of incidence of the primary radiation, but spreads uniformly in all directions.

   As the characteristic radiation originates from X-rays, the emission of this
radiation must be accompanied by an absorption of X-rays. For this reason
Barkla made a very thorough investigation of the absorption of X-rays by
various substances. The result was that all such factors as density, temper-
ature, state of aggregation and chemical composition proved to be with-
out essential importance. The qualities of the atoms alone determine the
amount of the absorption. The absorption is furthermore selective, and, just
as with regard to light, those rays are by preference absorbed that the sub-
stance emits at the same temperature, so it is here, the atoms absorbing by
preference those X-rays that they themselves emit in the form of characteristic
radiation.

   Another striking resemblance between light and the X-rays has been dis-
covered by Barkla. Just as, in agreement with Stokes' law, fluorescence can
only be generated by light of a higher frequency, so too the characteristic ra-
diation requires for its origination a greater penetrability of the primary rays.

   Barkla's discovery that two domains of differing hardness are to be dif-
ferentiated in the characteristic radiation, is of fundamental importance as
regards the modern conception of the structure of atoms. Barkla has named
the two domains the K-series and the L-series respectively. Thus every chem-
ical element, when irradiated by X-rays, emits two rays of different pen-
etrability, that is to say, every element can by fluorescence emit an X-ray
spectrum of two lines or line-groups, the so-called K-series and L-series. Of
these, the K-series have the greater penetrability. Barkla succeeded in fol-

lowing the K-series from calcium to cerium, the L-series from silver to bismuth.

If these rays are defined, for instance, in terms of their absorption in aluminium, the said absorption for rays belonging to one and the same series proves to be, approximately, a linear function of the atomic weight of the element that emits the radiation. By arriving at that conclusion Barkla had on the one hand furnished the most indisputable proof that every chemical element possesses a characteristic X-ray spectrum of its own, while on the other hand it was made manifest by these investigations that the said characteristic spectra, in contrast to all other spectra hitherto known, do not display any periodic qualities in connection with the places of the elements in the periodic system.

Barkla's discovery of the characteristic X-radiation has proved to be a phenomenon of extraordinary importance as regards physical research, a fact which has been made increasingly manifest by the subsequent researches of other investigators.

The discovery of the diffraction of X-rays in crystals gave a means of measuring their wavelengths, and since then the further investigation of the K-series and the L-series has yielded results of fundamental importance as regards our conception of the inner structure of atoms. It would, however, carry us too far to enter upon that topic here. Suffice it to say that those investigations have shown that it is the electrical charge of the nucleus of the atom that determines its place in the periodic system, not, as has been hitherto assumed, its atomic weight. The former is in general half the latter, but the divergences from the rule are due to irregularities in the distribution of the atomic weight amongst the elements, the charge of the nucleus being the factor that determines the chemical attributes of the atom. It has also been possible to establish the fact that of the chemical elements there are now not more than six that are unknown. Barkla's discovery of the characteristic X-radiation of the elements reveals a phenomenon of the utmost importance for the study of the inner structure of atoms and has already led to such far-reaching and significant conclusions, that it may with justice be asserted that no such important discovery in spectroscopy has been made since that of the discontinuous spectra from flames and electric sparks and the subsequent differentiation of those spectra in series, line and band spectra.

In consideration of this fact the Royal Swedish Academy of Sciences decided to award the 1917 Nobel Prize in Physics to Professor Barkla for his discovery of the characteristic X-radiation of the elements.

Charles G. Barkla

# Characteristic Röntgen radiation

*Nobel Lecture, June 3, 1920*

I have had some difficulty in deciding what to speak about to-day. Much of my work on characteristic radiation is already comparatively old and may be familiar to many of you, as it has been summarized in such works as the *Jahrbuch der Radioaktivität und Elektronik* and Professor Stark's *Atomdynamik*. I shall therefore choose two, and only two, points which are of more recent interest - firstly, the results of my own experiments which have a bearing on the Quantum Theory of Radiation; secondly, the evidence for another series of characteristic radiations - a *J* series*.

## *The quantum theory of radiation*

*Phenomena of scattering* - The results of experiments on the scattering of X-rays, which have an obvious bearing on the Quantum Theory of Radiation, may be briefly summarized.

When X-rays traverse matter of any kind, this matter becomes a source of a radiation similar in character to that of the primary radiation falling upon it. A variation in the intensity of this scattered radiation with direction around the primary beam shows slight polarization of the primary radiation proceeding direct from an X-ray tube.

The scattered radiation proceeding in a direction at right angles to that of propagation of the primary radiation is highly polarized in the manner of light scattered from the sky.

The variation in intensity of the scattered radiation with direction relative to the axis of the primary radiation agrees within certain limits very closely with the theoretical distribution as given by the equation

$$I_0 = I_{\pi/2}\ (1 + \cos^2\theta)$$

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* References to the original papers by the author will be found in the Bakerian Lecture, 1916, published *in Philosophical Transactions of the Royal Society,* 1917.

an equation readily derived on the orthodox electromagnetic wave theory. These experimental results were looked for as necessarily following from such a theory.

Difficult as the first two results would be to explain on any entity or quantum theory, that is, on any theory assuming radiation itself to exist in definite indivisible bundles or quanta, perhaps the strongest evidence against this is provided by the experimental verification, within limits, of the above equation. The derivation of this equation depends essentially on a steady variation with direction, not of a number of indivisible entities, but of the energy density around a single radiating charge - an electron in this case.

Further, measurement of the energy of radiation scattered furnishes one of the most searching and critical of tests that could be applied to any theory. The writer early concluded that neither atoms, molecules nor gaseous ions were the scattering units, but that these were the constituent electrons in matter, and that in general the number of electrons per atom, for light atoms at any rate, was proportional to the atomic weight.* The fraction of a beam lost by scattering per centimetre of substance traversed was shown by J. J. Thomson to be given by the expression

$$f = \frac{8\pi}{3} N \frac{e^4}{m^2} \mu^2$$

where N is the number per cubic centimetre of particles of charge e and mass *m.* Applying this to the experimental data, it at first appeared that the number of electrons per atom was several times the atomic weight. As the data available for the values of *N,* e/m, and e were more accurately determined, the calculated value for the number of electrons per atom became smaller, until with the most recent values the number indicated is one electron per atom of hydrogen, 6 per atom of carbon, 7 per atom of nitrogen, 8 for oxygen, 15 or 16 for sulphur, and so on.

As these conclusions regarding the number of electrons (outer electrons) within the atom have been confirmed by the researches of Rutherford, Bohr and Moseley, it is perfectly legitimate to use the agreement as evidence in support of the theory of radiation upon which it was based. The chances of such an agreement being arrived at accidentally are almost infinitesimal, for, apart from the orthodox theory of electromagnetic radiation, the intensity of scattered radiation might have been anything between - say - one thou-

* Hydrogen excepted.

sandth part and a thousand times what was experimentally observed. Yet the value experimentally determined in 1904 agrees with the calculated value to a degree of accuracy as close as it is now possible to estimate the pressure of the air upon which the experiments were performed!

This confirmation is very remarkable. The theory on which it is based is the spreading wave theory. It assumes that the scattered radiation is the radiation resulting from the disturbance in electrons while under the influence of the electrostatic field in the primary radiation.

The theory assumes that radiation can take place from these electrons in any quantity whatever, and is not confined to units or quanta; that the radiation is a continuous process not depending on any limiting or critical condition.

Again, I have found that the intensity of the radiation scattered from light elements over considerable ranges varies little with the wavelength of the primary radiation. This is in perfect agreement with the theory based on the assumption of independent action of the electrons. Further experiments have shown that the intensity of scattered radiation from the heavy atoms in which the constituent electrons are more closely packed, increases rapidly and apparently continuously with the wavelength of the radiation, unless this is fairly small. Also, in general, the rate of increase of intensity with wavelength is greater, the heavier the atom from which the scattered radiation proceeds. Such results are, again to be expected on the wave theory when the wavelength becomes comparable with the size of the atom, for there is very close agreement in phase of the radiations set up by neighbouring electrons; ultimately a group of electrons and not an individual electron moves as a whole and becomes the scattering unit. (When the group comprises all the electrons in the atom, the scattering per atom becomes on this theory proportional to the atomic number squared, instead of to the atomic number, when the electrons scatter independently.)

There is thus in the phenomena of scattering, not only no suggestion of a quantum or entity of radiation, or of any discontinuity in the process of radiation involved, but there is some of the strongest positive evidence against any such theory. The results appear conclusive, for the tests which have been applied are the most searching and sensitive. The phenomena observed become meaningless on any quantum or entity theory. This conclusion is true also of absorption, for in the transmission of X-rays, particularly of short wavelength through matter consisting of light elements only, the energy absorbed is practically all re-emitted as scattered radiation. The quantities

radiated by each electron are approximately identical with those absorbed. It follows that *this* process of absorption is also a process which takes place in any quantity whatever, and is unlimited by any critical condition.

*Characteristic radiation* - Each element when traversed by X-rays emits X-radiations characteristic of the element; each characteristic radiation is in-affected by changes in the physical condition or state of chemical combination of the radiating element, and its quality is independent of that of the exciting primary radiation. But only primary radiations of shorter wavelength are able to excite the characteristic X-radiations - an extension of Stokes's fluorescence law.

All the radiations hitherto definitely observed have fallen into three series, the *K, L,* and *M* series (the *M* series was discovered by Siegbahn and his collaborators). There is also strong evidence of a higher frequency series - a *J* series. This will be discussed later. The absorption method of analysing a radiation showed the radiation of the *K* series from a particular element to be so homogeneous, that it was regarded as giving a spectral line, the Kline; but the possibility of the *L* radiation consisting of more than one line was suggested by an obvious heterogeneity in the *L* radiation.

The interference experiments of Bragg, Moseley and others have shown, however, that both the *K* and *L* radiations give spectra consisting of a number of neighbouring lines.

The uniformity in the distribution of the characteristic radiation around the radiating substance, even when the primary beam is polarized, shows that, in contrast with the process of emission of scattered radiation, the emission of a characteristic radiation is absolutely uncontrolled by the primary radiation exciting it. The phenomena of emission is not an immediate consequence of the passage of the primary beam, but arises only indirectly from it; the process is dependent on some critical condition, as evidenced by Stokes' law. Here we see the possibility of the applicability of some kind of quantum theory. The most significant evidence as to the origin of the characteristic radiation comes from the study of the accompanying phenomena of the absorption of the exciting primary radiation and the emission of electrons by the radiating substance in the form of a corpuscular radiation. I have shown that the total absorption of a primary radiation in the substance traversed can be analysed into what are apparently independent absorptions, each - with the exception of that due to the process of scattering - definitely associated with the emission of a characteristic X-radiation. Thus there are

the *J, K, L, M* absorptions. Similarly, a corpuscular radiation may be ana-
lysed into *J,* K, *L, M* corpuscular radiations, each associated* with the emis-
sion of the corresponding characteristic X-radiation.

    The results obtained from a study of the energy of the primary beam ab-
sorbed, of the energy of the characteristic radiation emitted, and of the cor-
puscular radiation emitted, are very significant. In certain substances - bro-
mine and probably substances of high atomic weight - nearly all the energy
of the primary beam absorbed in association with the emission of *K* char-
acteristic radiation is re-emitted partly as characteristic X-radiation of the *K*
series, and partly as corpuscular radiation of the *K* series. Not only this, but
there is a definite relation between the intensity of the *K* radiation and the
number of electrons emitted in the associated corpuscular radiation. For va-
rious wavelengths of the primary radiation it appears that the number of
quanta of *κ* fluorescent radiation per *κ* electron emitted is approximately I.
The numbers actually obtained are 1.09, 0.95, 0.85, 0.81, 0.90. The max-
imum variation of 19% from unity is exceedingly small, considering the
number and nature of the experimental determinations involved. Apart from
the quantum theory, the range of possible values is so enormous, in com-
parison with the variation observed, that the emission of one quantum of
characteristic X-radiation for each electron in the associated corpuscular ra-
diation must be regarded as an experimentally established fact. If the two *K*
secondary radiations, the corpuscular and the characteristic X-radiations,
together accounted for the whole of the *K* energy absorbed, we should have
of the energy of the primary beam absorbed ( *K* absorption) the fraction
$n/(n+n_k)$, re-emitted as *K* corpuscular radiation, and fraction $n_k/(n + n_k)$,
re-emitted as *K* fluorescent X-radiation, where *n* and $n_k$ are the fre-
quencies of the primary and the characteristic radiation respectively. As a
matter of fact, when *n* is slightly greater than $n_k$, the two secondary radia-
tions together account for about 88% of the primary radiation. As *n* in-
creases the two energies of fluorescent and corpuscular radiations remain ap-
proximately complementary, the energy of the former diminishing while
that of the other increases. There is indeed very close agreement between the
fractions observed and those given by the above expressions. It may be, how-
ever, that one quantum of *L* radiation, in addition to one quantum of *L* ra-
diation, is emitted for each *K* electron ejected. There is even closer agree-
ment between the observed and the calculated values, based on this assump-
tion. Whatever the process of radiation may be, there can be little doubt that
* Probably in the case of *T* radiation.

characteristic radiation is emitted in quanta by those atoms merely from which an electron has been ejected.

The same energy relations, however, show us that absorption is not in quanta of primary radiation. Each absorbing atom, that is each atom which ultimately emits an electron, absorbs the energy of one quantum of primary radiation plus the energy of one quantum of characteristic radiation, which is $(I + n_k/n)$ quanta of primary radiation. This may be anything from I to 2 quanta. All the evidence suggests that the characteristic radiation is emitted immediately after the ejection of the electron from the atom.

Summarizing, we may say that all the available evidence shows that X-radiation may be, and is, emitted by electrons, probably in certain cases by groups of electrons, or even atoms - as a continuous process and in any quantity whatever. It is frequently emitted in quantities almost infinitesimal in comparison with a quantum. It is, however, emitted in quanta from atoms, when certain critical conditions resulting in the ejection of certain electrons are reached, the process of radiation then taking place in a perfectly definite manner, involving the radiation of a definite amount of energy which is proportional to the frequency of vibration (Planck's Law: $E = hn$).

Absorption, too, normally takes place in very minute quantities - very small in comparison with a quantum. But in certain processes, which usually account for nearly the whole absorption, the radiation is absorbed in quantities greater than a quantum of the primary radiation, quantities varying with the conditions from one to two quanta approximately. There is no evidence of absorption of X-radiation in whole quanta, though the conditions are frequently such as to give an approximation to this.

All this evidence seems to indicate that a quantum of radiation in the sense in which it has frequently been used, i.e. as an indivisible bundle of radiation energy, does not exist. The process of radiation may be, and is, continuous - at any rate within limits extending to far smaller quantities than the quantum. The quantum is a unit of atomic energy which must be absorbed in order to change the configuration of the atom, and is radiated when that configuration returns to its original state. It thus of necessity appears in certain processes of absorption and radiation.

*Probable* 3 *series  of  radiation*

Recent investigations have led me to the conclusion that a characteristic radiation of higher frequency than the *K* radiation (forming a *J* series in the various elements) is probably emitted by each of the light elements. For experiments on ( I) the absorption of X-rays, (2) the ionization of gases by X-rays, and (3) the intensity of corpuscular (electronic) radiation from plates exposed to X-rays, all show that a decrease in the wavelength of the primary X-radiation is accompanied by a sudden increase in the particular effect measured - an increase such as has invariably been found to accompany the emission of a characteristic X-radiation, and such as has hitherto not been observed except in association with such emission.

There is also close agreement between the values of the critical wavelengths found by the three methods.

Further, as with the phenomena accompanying *K, L* or *M* characteristic radiation, an increase in the atomic weight of the element is accompanied by a decrease in the critical wavelength in that element.

Direct evidence of the emission of] characteristic radiations has proved to be less easily obtained than appeared probable from preliminary experiments. Certain experimental results appeared to indicate that, though the *J* radiations might not be separable from the body of scattered radiation, their existence could readily be demonstrated. They have, however, proved more elusive than early experiments led us to believe. Experiments at present in progress are being gradually improved, and will, we hope, succeed in providing the direct evidence for which we are looking. It should, however, be pointed out that the evidence obtained from experiments on the *K* characteristic radiation would lead us to expect only a very weak characteristic radiation from these light elements, for of the energy of a primary beam absorbed in association with the emission of a particular *K* fluorescent characteristic radiation - i.e. *K* absorption - the fraction transformed into that characteristic X-radiation becomes rapidly smaller, as the atomic weight of the element decreases, so that even of the << *K* absorption>> only a very small fraction appears as *K* characteristic radiation from these light elements. Thus the fraction *K* radiation (energy)∕ *K* absorption (energy) at its maximum value in copper is about 40%, in iron 30%, in chromium 20%. There is every indication of it becoming very small indeed in the lightest elements. In addition, the <<absorption>> in these light elements is only a small fraction of the absorption by scattering - say of the order of magnitude of 15%.

Consequently, from aluminium, oxygen, nitrogen and carbon we might reasonably expect the energy of the fluorescent radiation to be something much less than 3% - 15% of 2% - of the energy of the scattered radiation; how much less it would be impossible to predict, but the probability is however, that it is less than 1%. We are, however, reasoning from our experience of << $K$ radiations a: this might be regarded as unsafe ground if it did not find confirmation in our experimental results, obtained in investigations of $J$ radiations.

Duane and others have been unable to detect any $J$ characteristic radiation excited in *aluminium* when bombarded by cathode rays. This may mean either that the] characteristic radiation is very weak in comparison with the heterogeneous X-radiation produced in aluminium - for it must be remembered that by analogy with the other characteristic radiations, $J$ radiation is produced only in association with the emission of J electrons, and these may be very few or difficult to displace - or it may just possibly indicate that $J$ radiation cannot be excited at all or only in the most exceptional cases by the impact of cathode particles. This is not at all unlikely, if the $J$ electrons are closely bound with other electrons, positive and negative, as they may be in a nucleus. For the cathode particle may come under the influence of this minute system as a whole and be deflected by it, without ever coming into such intimate relationship with any constituent electron as to disturb its stability. Thus it is quite conceivable that the negative and positive components of such a system are influenced separately by X-radiation, and that equilibrium is disturbed and] electrons are ejected and succeeded by the emission of $J$ characteristic X-radiation; whereas an electron of the corpuscular radiation is unable to produce the necessary displacement of the] electron. Further experiments alone can decide this point.

One important feature of the discovery of a $J$ series of characteristic X-radiations lies in the fact that there is no room for it in Bohr's theory of radiation as applied to $K$ and $L$ radiations. It may, however, be that a $J$ radiation is emitted by electrons in a system of different kind, as for instance in the nucleus itself instead of outside it. But the association of other phenomena - an association similar to that observed with $K$ and $L$ characteristic radiations - suggests a close similarity in the whole process involved. Experiments on this subject are at present in progress.

# Biography

Charles Glover Barkla was born on June 7, 1877 at Widnes, Lancashire, England, where his father, J. M. Barkla, was Secretary to the Atlas Chemical Company. He was educated at the Liverpool Institute and entered University College, Liverpool, in 1894 to study mathematics and physics, the latter under Oliver Lodge. He graduated with First Class Honours in Physics in 1898 and in the following year he obtained his master's degree. Also in 1899, he was awarded a research scholarship by the Royal Commissioners for the Exhibition of 1851 and he proceeded to Trinity College, Cambridge, to work in the Cavendish Laboratory with J.J.Thomson. He migrated to King's College during 1900 and in 1902 returned to Liverpool as Oliver Lodge Fellow. From 1905 to 1909 he was successively demonstrator, assistant lecturer in physics and special lecturer in advanced electricity at the University, and in 1909 he succeeded H. A. Wilson as Wheatstone Professor of Physics in the University of London. In 1913, Barkla accepted the Chair in Natural Philosophy in the University of Edinburgh and he held this position until his death.

Barkla's first researches concerned the velocity of electric waves along wires but in 1902 he commenced his investigations on Röntgen radiation which were to occupy almost his whole life. His discovery of homogeneous radiations characteristic of the elements showed that these elements had their characteristic line spectra in X-ray and he was the first to show that secondary emission is of two kinds, one consisting of X-rays scattered unchanged, and the other a fluorescent radiation peculiar to the particular substance. He discovered the polarisation of X-rays, an experimental result of considerable importance for it meant that X-radiation could be regarded as similar to ordinary light. Barkla made valuable contributions to present knowledge on the absorption and photographic action of X-rays and his later work demonstrated the relation between the characteristic X-radiation and the corpuscular radiation accompanying it. He has also shown both the applicability and the limitation of the quantum theory in relation to Röntgen radiation. The results of his findings are recorded in various papers which have ap-

peared mainly *in* the *Transactions* and *Proceedings of the Royal Society.* He had a considerable reputation as an examiner in physics.

Barkla, a Fellow of the Royal Society, had several honorary degrees. He was appointed Bakerian Lecturer (Royal Society) in 1916 and he was awarded the Hughes Medal in the following year.

Charles Glover Barkla married Mary Esther, the eldest daughter of John T. Cowell of Douglas, Receiver-General of the Isle of Man, in 1907. They had two sons and one daughter. Their youngest son, Flight Lieutenant Michael Barkla, a brilliant scholar, was killed in action in 1943. Barkla's chief recreation was singing - he had a powerful baritone voice and he was a member of the King's College Chapel Choir, 1901-1902. Latterly, he had also become fond of golf.

Barkla died at his home, Braidwood, Edinburgh, on October 23, 1944.

Physics 1918


# MAX  PLANCK


*<<in recognition of the services he rendered to the advancement of Physics by his discovery of energy quanta>>*

# Physics 1918

*Presentation Speech by Dr. Å. G. Ekstrand, President of the Royal Swedish Academy of Sciences*

Ladies and Gentlemen.*

The Royal Academy of Sciences has decided to award the Nobel Prize for Physics, for the year 1918, to Geheimrat Dr. Max Planck, professor at Berlin University, for his work on the establishment and development of the theory of elementary quanta.

From the time that Kirchhoff enunciated the principle <<that the intensity of radiation from a black body is dependent only upon the wavelength of the radiation and the temperature of the radiating body, a relationship worth while investigation>>, the theoretical treatment of the radiation problem has provided a rich, fertile source of fresh discoveries. It is only necessary here to recall the fertile Doppler principle, and further, the transformation of our concept of the nature of light as seen now in the electromagnetic theory of light formulated by that great man, Maxwell, the deduction of Stefan's Law by Boltzmann, and Wien's Law of Radiation. Since it was clear, however, that this did not correspond exactly with the reality, but was rather, like a radiation law propounded by Lord Rayleigh, only a special case of the general radiation law, Planck sought for, and in 1900 found, a mathematical formula for the latter, which he derived theoretically later on. The formula contained two constants; one, as was demonstrated, gave the number of molecules in a gram molecule of matter. Planck was also the first to succeed in getting, by means of the said relation, a highly accurate value for the number in question, the so-called Avogadro constant. The other constant, the so-called Planck constant, proved, as it turned out, to be of still greater significance, perhaps, than the first. The product *hv,* where v is the frequency of vibration of a radiation, is actually the smallest amount of heat which can be radiated at the vibration frequency *v.* This theoretical conclusion stands in very sharp opposition to our earlier concept of the radiation phenomenon. Experience had to provide powerful confirmation, therefore, before Planck's

* Owing to the sudden decease of the Royal Princess, no member of the Royal Family was present at the ceremony.

radiation theory could be accepted. In the meantime this theory has had un-heard-of success. The specific heat of substances, Stokes' Law for phosphor-escence and fluorescence phenomena and the photoelectric effect provide, as Einstein has first suggested, most powerful support for Planck's radiation theory as against the older, usual concept. A still greater triumph was en-joyed by Planck's theory in the field of spectral analysis, where Bohr's basic work, the work of Sommerfeld and Epstein, and other complementary ef-forts provided an explanation for the enigmatic laws ruling within this part ofscience. Recently, basic physico-chemical phenomena, such as the effect of temperature upon speed of reaction and the heat of reaction, have also had a new light shed upon them as a result of the work of W. C. McCullagh, Lewis, Perrin and others, using Planck's theory.

Planck's radiation theory is, in truth, the most significant lodestar for modern physical research, and it seems that it will be a long time before the treasures will be exhausted which have been unearthed as a result of Planck's genius.

Professor Planck.    The Swedish Academy of Sciences has awarded you the Nobel Prize for 1918 in recognition of your epoch-making investigations into the quantum theory. This theory, which was originally connected with black-body radiation, has now demonstrated its validity for other fields and relationships of Nature, and the constant number, named after you, is a proportionality factor which describes a common, but until now unknown, property of matter. The Academy now begs you, Professor, to receive the prize from the President of the Nobel Foundation.

M AX P LANCK

# The genesis and present state of development of the quantum theory

*Nobel Lecture, June 2, 1920*

If I take it correctly that the duty imposed upon me today is to give a public lecture on my writings, then I believe that this task, the importance of which I am well aware through the gratitude felt towards the noble-minded founder of our Foundation, cannot be more suitably fulfilled than by my trying to give you the story of the origin of the quantum theory in broad outlines and to couple with this, a picture in a small frame, of the development of this theory up to now, and its present-day significance for physics.

When I look back to the time, already twenty years ago, when the concept and magnitude of the physical quantum of action began, for the first time, to unfold from the mass of experimental facts, and again, to the long and ever tortuous path which led, finally, to its disclosure, the whole development seems to me to provide a fresh illustration of the long-since proved saying of Goethe's that man errs as long as he strives. And the whole strenuous intellectual work of an industrious research worker would appear, after all, in vain and hopeless, if he were not occasionally through some striking facts to find that he had, at the end of all his criss-cross journeys, at last accomplished at least one step which was conclusively nearer the truth. An indispensable hypothesis, even though still far from being a guarantee of success, is however the pursuit of a specific aim, whose lighted beacon, even by initial failures, is not betrayed.

For many years, such an aim for me was to find the solution to the problem of the distribution of energy in the normal spectrum of radiating heat. Since Gustav Kirchhoff has shown that the state of the heat radiation which takes place in a cavity bounded by any emitting and absorbing substances of uniform temperature is entirely independent upon the nature of the substances, a universal function was demonstrated which was dependent only upon temperature and wavelength, but in no way upon the properties of any substance. And the discovery of this remarkable function promised deeper insight into the connection between energy and temperature which is, in fact, the major problem in thermodynamics and thus in the whole of molecular physics. To

attain this there was no other way but to seek out from all the different sub-
stances existing in Nature one of known emissive and absorptive power, and
to calculate the properties of the heat radiation in stationary energy exchange
with it. According to Kirchhoff's Law, this would have to prove independent
of the nature of the body.

Heinrich Hertz's linear oscillator, whose laws of emission, for a given fre-
quency, Hertz had just previously completely developed, seemed to me to
be a particularly suitable device for this purpose. If a number of such Hertzian
oscillators are set up within a cavity surrounded by a sphere of reflecting walls,
then by analogy with audio oscillators and resonators, energy will be ex-
changed between them by the output and absorption of electromagnetic
waves, and finally stationary radiation corresponding to Kirchhoff's Law,
the so-called black-body radiation, should be set up within the cavity. I was
filled at that time with what would be thought today naively charming and
agreeable expectations, that the laws of classical electrodynamics would, if
approached in a sufficiently general manner with the avoidance of special
hypotheses, be sufficient to enable us to grasp the most significant part of
the process to be expected, and thus to achieve the desired aim. I, therefore,
developed first the laws of emission and absorption of a linear resonator on
the most general basis, in fact I proceeded on such a detour which could
well have been avoided had I made use of the existing electron theory of
H. A.Lorentz, already basically complete. But since I did not quite trust the
electron hypothesis, I preferred to observe that energy which flowed in and
out through an enclosing spherical surface around the resonator at a suitable
distance from it. By this method, only processes in a pure vacuum came into
account, but a knowledge of these was sufficient to draw the necessary con-
clusions however, about the energy changes in the resonator.

The fruit of this long series ofinvestigations, of which some, by comparison
with existing observations, mainly the vapour measurements by V. Bjerknes,
were susceptible to checking, and were thereby confirmed, was the estab-
lishment of the general connection between the energy of a resonator of
specific natural period of vibration and the energy radiation of the corre-
sponding spectral region in the surrounding field under conditions of sta-
tionary energy exchange. The noteworthy result was found that this con-
nection was in no way dependent upon the nature of the resonator, partic-
ularly its attenuation constants - a circumstance which I welcomed happily
since the whole problem thus became simpler, for instead of the energy of
radiation, the energy of the resonator could be taken and, thereby, a complex

system, composed-of many degrees of freedom, could be replaced by a simple system of one degree of freedom.

Nevertheless, the result meant no more than a preparatory step towards the initial onslaught on the particular problem which now towered with all its fearsome height even steeper before me. The first attempt upon it went wrong, for my original secret hope that the radiation emitted from the resonator can be in some characteristic way or other distinguished from the absorbed radiation and thereby allow a differential equation to be set up, from the integration of which one could gain some special condition for the properties of stationary radiation, proved false. The resonator reacted only to those rays which it also emitted, and was not in the slightest bit sensitive to the adjacent spectral regions.

Furthermore, my hypothesis that the resonator could exercise a unilateral, i.e. irreversible, effect upon the energy in the surrounding radiation field, was strongly contested by Ludwig Boltzmann, who, with his riper experience in these problems, proved that according to the laws of classical dynamics each of the processes observed by me can proceed in exactly the opposite direction, in such a way, that a spherical wave emitted from the resonator, returns and contracts in steadily diminishing concentric spherical surfaces inwards to the resonator, and is again absorbed by it, thereby allowing the formerly absorbed energy to be re-transmitted into space in the direction from which it came. And when I excluded this kind of singular process, such as an inwardly directed wave, by means of the introduction of a limiting definition, the hypothesis of natural radiation, all these analyses still showed ever more clearly that an important connecting element or term, essential for the complete grasp of the core of the problem, must be missing.

So there was nothing left for me but to tackle the problem from the opposite side, that of thermodynamics, in which field I felt, moreover, more confident. In fact my earlier studies of the Second Law of Heat Theory stood me in good stead, so that from the start I tried to get a connection, not between the temperature but rather the entropy of the resonator and its energy, and in fact, not its entropy exactly but the second derivative with respect to the energy since this has a direct physical meaning for the irreversibility of the energy exchange between resonator and radiation. Since I was, however, at that time still too far oriented towards the phenomenological aspect to come to closer quarters with the connection between entropy and probability, I saw myself, at first, relying solely upon the existing results of experience. In the foreground of interest at that time, in 1899, was the energy

distribution law established by W. Wien shortly before, whose experimental proof was taken up, on the one hand, by F. Paschen at the Technische Hochschule in Hannover, and, on the other hand, by O. Lummer and E. Pringsheim at the State Institution in Charlottenburg. This law brought out the dependence of the radiation intensity on the temperature, representing it by an exponential function. If one calculates the connection between the entropy and the energy of a resonator, determined by the above law, the remarkable result is obtained that the reciprocal value of the above-mentioned differential coefficient, which I will call $R$, is proportional to the energy. This extremely simple relationship can be considered as the completely adequate expression of Wien's energy distribution law; for with the dependence upon the energy, the dependence upon the wavelength is always directly given through the general, well-established displacement law by Wien.

Since the whole problem concerned a universal law of Nature, and since at that time, as still today, I held the unshakeable opinion that the simpler the presentation of a particular law of Nature, the more general it is-though at the same time, which formula to take as the simpler, is a problem which cannot always be confidently and finally decided-I believed for a long time that the law that the quantity $R$ is proportional to the energy, should be looked upon as the basis for the whole energy distribution law. This concept could not be maintained for long in the face of fresh measurements. Whilst for small values of the energy and for short waves, Wien's law was satisfactorily confirmed, noteworthy deviations for larger wavelengths were found, first by O. Lummer and E. Pringsheim, and finally by H. Rubens and F. Kurlbaum, whose measurements on the infrared residual rays of fluorite and rock salt revealed a totally different, though still extremely simple relationship, characterized by the fact that the quantity $R$ is not proportional to the energy, but to the square of the energy, and in fact this holds with increasing accuracy for greater energies and wavelengths.

So, through direct experiment, two simple limits were determined for the function $R$: for small energies, proportionality with the energy; for greater energies, proportionality with the square of the energy. There was no better alternative but to make, for the general case, the quantity $R$ equal to the sum of two terms, one of the first power, and one of the second power of the energy, so that for small energies the first is predominant, whilst for the greater energies the second is dominant. Thus the new radiation formula was found, which, in the face of its experimental proof, has stood firm to a reasonable

extent until now. Even today, admittedly, we cannot talk of final exact confirmation. In fact, a fresh attempt at proof is urgently required.

However, even if the radiation formula should prove itself to be absolutely accurate, it would still only have, within the significance of a happily chosen interpolation formula, a strictly limited value. For this reason, I busied myself, from then on, that is, from the day of its establishment, with the task of elucidating a true physical character for the formula, and this problem led me automatically to a consideration of the connection between entropy and probability, that is, Boltzmann's trend of ideas; until after some weeks of the most strenuous work of my life, light came into the darkness, and a new undreamed-of perspective opened up before me.

I must make a small intercalation at this point. According to Boltzmann, entropy is a measure for physical probability, and the nature and essence of the Second Law of Heat Theory is that in Nature a state occurs more frequently, the more probable it is. Now one always measures in Nature the difference in entropies, never the entropy itself, and to this extent one cannot speak of the absolute entropy of a state, without a certain arbitrariness. Nevertheless, it is useful to introduce the suitably defined absolute value of entropy, namely for the reason that with its help certain general laws can be particularly easily formulated. The case seems to be parallel, as I see it, with that of energy. Energy itself cannot be measured, only its difference. For that reason one used to deal, not with energy, but with work, and even Ernst Mach, who had so much to do with the Law of Conservation of Energy, and who in principle kept away from all speculations beyond the field of observation, has always avoided speaking of energy itself. Likewise, in thermochemistry, one has always stuck to the thermal effect, that is, to energy differences, until Wilhelm Ostwald in particular emphatically showed that many detailed considerations could be significantly abbreviated if one dealt with energy itself instead of with calorimetric numbers. The additive constant which was at first still undetermined in the expression for energy, has later been finally determined through the relativistic law of the proportionality between energy and inertia.

In a similar way to that for energy, an absolute value can be defined also for entropy and, as a result thereof, for the physical probability too, e.g. by so fixing the additive constant that energy and entropy disappear together. On the basis of a consideration of this kind a specific, relatively simple combinatorial method was obtained for the calculation of the physical probability of a specified energy distribution in a system of resonators, which led

exactly to that entropy expression determined by the radiation law, and it brought me much-valued satisfaction for the many disappointments when Ludwig Boltzmann, in the letter returning my essay, expressed his interest and basic agreement with the train of thoughts expounded in it.

For the numerical treatment of the indicated consideration of probability, knowledge of two universal constants is required, both of which have an independent physical meaning, and whose subsequent evaluation from the law of radiation must provide proof as to whether the whole method is to be looked upon as a mere artifice for calculation, or whether it has an inherent real physical sense and interpretation. The first constant is of a more formal nature and is connected with the definition of temperature. If temperature were to be defined as the average kinetic energy of a molecule in an ideal gas, that is, as a tiny, little quantity, then the constant would have the value $\frac{2}{3}$. In conventional temperature measure, on the contrary, the constant has an extremely small value which stands, naturally, in close association with the energy of a single molecule, and an exact knowledge of which leads, therefore, to the calculation of the mass of a molecule and those parameters related to it. This constant is often referred to as Boltzmann's constant, although, to my knowledge, Boltzmann himselfnever introduced it - *a* peculiar state of affairs, which can be explained by the fact that Boltzmann, as appears from his occasional utterances, never gave thought to the possibility of carrying out an exact measurement of the constant. Nothing can better illustrate the positive and hectic pace of progress which the art of experimenters has made over the past twenty years, than the fact that since that time, not only one, but a great number of methods have been discovered for measuring the mass of a molecule with practically the same accuracy as that attained for a planet.

At the time when I carried out the corresponding calculation from the radiation law, an exact proof of the number obtained was quite impossible, and not much more could be done than to determine the order of magnitude which was admissible. It was shortly afterward that E. Rutherford and H. Geiger succeeded in determining, by direct counting of the alpha particles, the value of the electrical elementary charge, which they found to be 4.65 *x* $10^{-10}$ electrostatic units; and the agreement of this figure with the number calculated by me, *4.69* x $10^{-10}$, could be taken as decisive confirmation of the usefulness of my theory. Since then, more sophisticated methods have led to a slightly higher value, these measurements being carried out by E. Regener, R. A. Millikan, and others.

The explanation of the second universal constant of the radiation law was not so easy. Because it represents the product of energy and time (according to the first calculation it was $6.55 \times 10^{-27}$ erg set), I described it as the elementary quantum of action. Whilst it was completely indispensable for obtaining the correct expression for entropy - since only with its help could the magnitude of the <<elementary regions>> or << free rooms for action>> of the probability, decisive for the assigned probability consideration, be determined-it proved elusive and resistant to all efforts to fit it into the framework of classical theory. As long as it was looked upon as infinitely small, that is, for large energies or long periods of time, everything went well; but in the general case, however, a gap yawned open in some place or other, which was the more striking, the weaker and faster the vibrations that were considered. The foundering of all efforts to bridge the chasm soon left little doubt. Either the quantum of action was a fictional quantity, then the whole deduction of the radiation law was in the main illusory and represented nothing more than an empty non-significant play on formulae, or the derivation of the radiation law was based on a sound physical conception. In this case the quantum of action must play a fundamental role in physics, and here was something entirely new, never before heard of, which seemed called upon to basically revise all our physical thinking, built as this was, since the establishment of the infinitesimal calculus by Leibniz and Newton, upon the acceptance of the continuity of all causative connections.

Experiment has decided for the second alternative. That the decision could be made so soon and so definitely was due not to the proving of the energy distribution law of heat radiation, still less to the special derivation of that law devised by me, but rather should it be attributed to the restless forward-thrusting work of those research workers who used the quantum of action to help them in their own investigations and experiments. The first impact in this field was made by A. Einstein who, on the one hand, pointed out that the introduction of the energy quanta, determined by the quantum of action, appeared suitable for obtaining a simple explanation for a series of noteworthy observations during the action of light, such as Stokes' Law, electron emission, and gas ionization, and, on the other hand, derived a formula for the specific heat of a solid body through the identification of the expression for the energy of a system of resonators with that of the energy of a solid body, and this formula expresses, more or less correctly, the changes in specific heat, particularly its reduction with falling temperature. The result was the emergence, in all directions, of a number of problems whose more accurate

and extensive elaboration in the course of time brought to light a mass of valuable material. I cannot give here even an approximate report on the abundance of the work carried out. Only the most important and characteristic steps along the path of progressive knowledge can be high-lighted here.

First come thermal and chemical processes. As far as the specific heat of solid bodies is concerned, Einstein's theory, which rested upon the assumption of a single natural vibration of the atom, was extended by M. Born and Th. von Kármán to the case of various kinds of natural vibrations, which approached more nearly to the truth. P. Debye succeeded, by means of a bold simplification of the stipulations for the character of natural vibrations, in producing a relatively simple formula for the specific heat of solid bodies which, particularly for low temperatures, not only satisfactorily reproduces the measurements obtained by W. Nernst and his pupils, but is also compatible with the elastic and optical properties of these substances. The quantum of action also comes to the fore in considering the specific heat of gases. W. Nernst had earlier suggested that to the quantum of energy of a vibration there must also correspond a quantum of energy of a rotation, and accordingly it was to be expected that the rotational energy of the gas molecules would disappear with falling temperature. The measurements by A. Eucken on the specific heat of hydrogen confirmed this conclusion, and if the calculations of A. Einstein and O. Stem, P. Ehrenfest and others have not until now afforded any completely satisfactory agreement, this lies understandably in our, as yet, incomplete knowledge of the model of a hydrogen molecule. The fact that the rotations of the gas molecules, as specified by quantum conditions, do really exist in Nature, can no longer be doubted in view of the work on absorption bands in the infrared by N. Bjerrum, E. von Bahr, H. Rubens, G. Hetmer and others, even though it has not been possible to give an all-round exhaustive explanation of this remarkable rotation spectra up to now.

Since, ultimately, all affinity properties of a substance are determined by its entropy, the quantum-theoretical calculation of the entropy opens up the way to all the problems of chemical relationships. The Nemst chemical constant, which O. Sackur calculated directly through a combinatorial method as applied to oscillators, is characteristic for the absolute value of the entropy of a gas. H. Tetrode, in close association with the data to be obtained by measurement, determined the difference in entropy values between vapour and solid state by studying an evaporation process.

Whilst in the cases so far considered, states of thermodynamic equilibrium are concerned, for which therefore the measurements can only yield statis-

tically average values relating to many particles and lengthy periods of time, the observation of electron impacts leads directly to the dynamic details of the process under examination. Thus the determination of the so-called resonance potential carried out by J. Franck and G. Hertz, or that concerning the critical velocity is the minimum an electron must possess in order to cause emission of a light quantum or photon by impact with a neutral atom, supplied a method of measuring the quantum of action which was as direct as could be wished for. The experiments by D. L. Webster and E. Wagner and others resulted in the development of methods suitable for the Röntgen spectrum which also gave completely compatible results.

The production of photons by electron impact appears as the reverse process to that of electron emission through irradiation by light-, Röntgen-, or gamma-rays and again here, the energy quanta, determined by the quantum of action and by the vibration frequency, play a characteristic role, as could be recognized, already at an early time, from the striking fact that the velocity of the emitted electrons is not determined by the intensity of radiation, but only by the colour of the light incident upon the substance. Also from the quantitative aspect, Einstein's equations with respect to the light quantum have proved true in every way, as established by R. A. Millikan, in particular, by measurements of the escape velocity of emitted electrons, whilst the significance of the photon for the initiation of photochemical reactions was discovered by E. Warburg.

If the various experiments and experiences gathered together by me up to now, from the different fields of physics, provide impressive proof in favour of the existence of the quantum of action, the quantum hypothesis has, nevertheless, its greatest support from the establishment and development of the atom theory by Niels Bohr. For it fell to this theory to discover, in the quantum of action, the long-sought key to the entrance gate into the wonderland of spectroscopy, which since the discovery of spectral analysis had obstinately defied all efforts to breach it. And now that the way was opened, a sudden flood of new-won knowledge poured out over the whole field including the neighbouring fields in physics and chemistry. The first brilliant acquisition was the derivation of Balmer's series formula for hydrogen and helium including the reduction of the universal Rydberg constant to merely known numerical quantities, whereby even the small discrepancies for hydrogen and helium were recognized as essentially determined by the weak motion of the heavy atom nucleus. Investigation then turned to other series in the optical and the Röntgen spectrum using the extremely fruitful Ritz

combination principle, which was at last revealed clearly in all its fundamental significance.

Whoever, in view of the numerous agreements which in the case of the special accuracy of spectroscopic measurements could lay claim to particularly striking confirmatory power, might have been still inclined to feel that it was all attributable to the play of chance, would been forced, finally, to discard even his last doubt, as A. Sommerfeld showed that from a logical extension of the laws of quantum distribution in systems with several degrees of freedom, and out of consideration of the variability of the inertial mass in accordance with the relativity theory, that magic formula arose before which both the hydrogen and the helium spectrum had to reveal the riddle of their fine structure, to such an extent that the finest present-day measurements, those of F. Paschen, could be explained generally through it -an achievement fully comparable with that of the famous discovery of the planet Neptune whose existence and orbit was calculated by Leverrier before the human eye had seen it. Progressing further along the same path, P. Epstein succeeded in fully explaining the Stark effect of the electrical splitting up of the spectral lines, P. Debye produced a simple explanation of the K-series of the Röntgen spectrum, which had been investigated by Manne Siegbahn, and now followed a great number of further experiments, which illuminated with more or less success the dark secrets of the construction of the atom.

After all these results, towards whose complete establishment still many reputable names ought essentially to have been mentioned here, there is no other decision left for a critic who does not intend to resist the facts, than to award to the quantum of action, which by each different process in the colourful show of processes, has ever-again yielded the same result, namely, $6.52 \times 10^{-27}$ erg set, for its magnitude, full citizenship in the system of universal physical constants. It must certainly appear a unique coincidence that just in that time when the ideas of general relativity have broken through, and have led to fantastic results, Nature should have revealed an <<absolute>> in a place where it could be least expected, an invariable unit, in fact, by means of which the action quantity, contained in a space-time element, can be represented by a completely definite non-arbitrary number, and thereby divested itself of its

To be sure, the introduction of the quantum of action has not yet produced a genuine quantum theory. In fact, the path the research worker must yet tread to it is not less than that from the discovery of the velocity of light by Olaf Römer to the establishment of Maxwell's theory of light. The difficul-

ties which the introduction of the quantum of action into the well-tried classical theory has posed right from the start have already been mentioned by me. During the course of the years they have increased rather than diminished, and if, in the meantime, the impetuous forward-driving research has passed to the order of the day for some of these, temporarily, the gaps left behind, awaiting subsequent filling, react even harder upon the conscientious systematologist. What serves in Bohr's theory as a basis to build up the laws of action, is assembled out of specific hypotheses which, up to a generation ago, would undoubtedly have been flatly rejected altogether by every physicist. The fact that in the atom, certain quite definite quantum-selected orbits play a special role, might be taken still as acceptable, less easily however, that the electrons, circulating in these orbits with definite acceleration, radiate no energy at all. The fact that the quite sharply defined frequency of an emitted photon should be different from the frequency of the emitting electron must seem to a theoretical physicist, brought up in the classical school, at first sight to be a monstrous and, for the purpose of a mental picture, a practically intolerable demand.

But numbers decide, and the result is that the roles, compared with earlier times, have gradually changed. What initially was a problem of fitting a new and strange element, with more or less gentle pressure, into what was generally regarded as a fixed frame has become a question of coping with an intruder who, after appropriating an assured place, has gone over to the offensive; and today it has become obvious that the old framework must somehow or other be burst asunder. It is merely a question of where and to what degree. If one may make a conjecture about the expected escape from this tight corner, then one could remark that all the signs suggest that the main principles of thermodynamics from the classical theory will not only rule unchallenged but will more probably become correspondingly extended. What the armchair experiments meant for the foundation of classical thermodynamics, the adiabatic hypothesis of P. Ehrenfest means, provisonally, to the quantum theory; and in the same way as R. Clausius, as a starting point for the measurement of entropy, introduced the principle that, when treated appropriately, any two states of a material system can, by a reversible process, undergo a transition from one to the other, now the new ideas of Bohr's open up a very similar path into the interior of a wonderland hitherto hidden from him.

There is in particular one problem whose exhaustive solution could provide considerable elucidation. What becomes of the energy of a photon after

complete emission? Does it spread out in all directions with further propagation in the sense of Huygens' wave theory, so constantly taking up more space, in boundless progressive attenuation? Or does it fly out like a projectile in one direction in the sense of Newton's emanation theory? In the first case, the quantum would no longer be in the position to concentrate energy upon a single point in space in such a way as to release an electron from its atomic bond, and in the second case, the main triumph of the Maxwell theory- the continuity between the static and the dynamic fields and, with it, the complete understanding we have enjoyed, until now, of the fully investigated interference phenomena- would have to be sacrificed, both being very unhappy consequences for today's theoreticians.

Be that as it may, in any case no doubt can arise that science will master the dilemma, serious as it is, and that which appears today so unsatisfactory will in fact eventually, seen from a higher vantage point, be distinguished by its special harmony and simplicity. Until this aim is achieved, the problem of the quantum of action will not cease to inspire research and fructify it, and the greater the difficulties which oppose its solution, the more significant it finally will show itself to be for the broadening and deepening of our whole knowledge in physics.

# Biography

Max Karl Ernst Ludwig Planck was born in Kiel, Germany, on April 23, 1858, the son of Julius Wilhelm and Emma (née Patzig) Planck. His father was Professor of Constitutional Law in the University of Kiel, and later in Göttingen.

Planck studied at the Universities of Munich and Berlin, where his teachers included Kirchhoff and Helmholtz, and received his doctorate of philosophy at Munich in 1879. He was Privatdozent in Munich from 1880 to 1885, then Associate Professor of Theoretical Physics at Kiel until 1889, in which year he succeeded Kirchhoff as Professor at Berlin University, where he remained until his retirement in 1926. Afterwards he became President of the Kaiser Wilhelm Society for the Promotion of Science, a post he held until 1937. The Prussian Academy of Sciences appointed him a member in 1894 and Permanent Secretary in 1912.

Planck's earliest work was on the subject of thermodynamics, an interest he acquired from his studies under Kirchhoff, whom he greatly admired, and very considerably from reading R. Clausius' publications. He published papers on entropy, on thermo-electricity and on the theory of dilute solutions.

At the same time also the problems of radiation processes engaged his attention and he showed that these were to be considered as electromagnetic in nature. From these studies he was led to the problem of the distribution of energy in the spectrum of full radiation. Experimental observations on the wavelength distribution of the energy emitted by a black body as a function of temperature were at variance with the predictions of classical physics. Planck was able to deduce the relationship between the energy and the frequency of radiation. In a paper published in 1900, he announced his derivation of the relationship : this was based on the revolutionary idea that the energy emitted by a resonator could only take on discrete values or quanta. The energy for a resonator of frequency $v$ is $hv$ where $h$ is a universal constant, now called Planck's constant.

This was not only Planck's most important work but also marked a turning point in the history of physics. The importance of the discovery, with

its far-reaching effect on classical physics, was not appreciated at first. However the evidence for its validity gradually became overwhelming as its application accounted for many discrepancies between observed phenomena and classical theory. Among these applications and developments may be mentioned Einstein's explanation of the photoelectric effect.

Planck's work on the quantum theory, as it came to be known, was published in the *Annalen der Physik.* His work is summarized *in* two books *Thermodynamik* (Thermodynamics) (1897) and *Theorie der Wärmestrahlung* (Theory of heat radiation) (1906).

He was elected to Foreign Membership of the Royal Society in 1926, being awarded the Society's Copley Medal in 1928.

Planck faced a troubled and tragic period in his life during the period of the Nazi government in Germany, when he felt it his duty to remain in his country but was openly opposed to some of the Government's policies, particularly as regards the persecution of the Jews. In the last weeks of the war he suffered great hardship after his home was destroyed by bombing.

He was revered by his colleagues not only for the importance of his discoveries but for his great personal qualities. He was also a gifted pianist and is said to have at one time considered music as a career.

Planck was twice married. Upon his appointment, in 1885, to Associate Professor in his native town Kiel he married a friend of his childhood, Marie Merck, who died in 1909. He remarried her cousin Marga von Hösslin. Three of his children died young, leaving him with two sons.

He suffered a personal tragedy when one of them was executed for his part in an unsuccessful attempt to assassinate Hitler in 1944.

He died at Göttingen on October 3, 1947.

Physics 1919

# JOHANNES STARK

*<<for his discovery of the Doppler effect in canal rays and the splitting of spectral lines in electric fields>>*

# Physics 1919

*Presentation Speech by Dr. Å.G. Ekstrand, President of the Royal Swedish Academy*
of Sciences

Ladies and Gentlemen.*

The Royal Academy of Sciences has decided to award the Nobel Prize in Physics for 1919 to Dr. Johannes Stark, professor in the University of Greifswald, for his discovery of the Doppler effect in canal rays and of the splitting of spectral lines in electric fields.

It is only rarely that the study of a physical phenomenon has led to such a brilliant series of important discoveries as that which follows the conducting of an electrical current through a rarefied gas. As long ago as 1869 Hittorf discovered that if a low pressure is set up in a discharge tube, rays are emitted from the negative electrode, the so-called cathode. Although invisible to the eye, they can nevertheless be observed through certain effects peculiar to them. The continued study of these cathode rays, in which Lenard in particular earned great merit, showed that they are composed of a stream of negatively charged particles, the mass of which amounts only to 1/1,800 of the mass of the hydrogen atom. We call these minute particles electrons, and gradually one of the principal theories of modern physics grew from the study of the properties of electrons and of their relationship with matter. The electron theory with its concept of the constitution of matter has become of radical importance to both physics and chemistry.

When cathode rays strike an object, this becomes the source of a new radiation, namely that discovered by Röntgen in 1895 and named by him X-rays, the study of which has led to so many important results for major branches of science, not only within physics. Through von Laue's discovery of the diffraction of X-rays in crystals it was demonstrated that these rays are light waves of very short wavelength. It is now even possible to photograph the spectra of these rays, and science has by this been enriched with a means of research the implications of which cannot yet be fully realized.

Von Laue's discovery also occasioned important discoveries in the field of crystallography. It is possible, now that W. H. Bragg and his son have worked

*Owing to the sudden decease of the Royal Princess, no member of the Royal Family was present at the ceremony.

out theoretic and experimental methods for that purpose, to determine the positions of the atoms in crystals. By these methods a whole new world has been opened up, and has already been partly explored.

Of not less importance was Barkla's discovery in the year 1906 that every chemical element when irradiated with X-rays emits an X-ray spectrum, characteristic of the element in question. This discovery has become of outstanding importance for the theoretical study of the structure of the atom.

In the year 1886 Goldstein discovered a new kind of rays in discharge tubes containing rarefied gas, the study of which has become extremely important to our knowledge of the physical properties of atoms and molecules. In view of the manner of their formation Goldstein called them canal rays. It was proved by the research of W. Wien and J. J. Thomson that the majority of these are composed of positively charged atoms of the gas in the discharge tube, which move along the beam at a very high velocity.

In their course along the beam these canal-ray particles are continually colliding with the gas molecules which are contained in the tube, and thus it may be expected that light is emitted, if the kinetic energy is sufficiently great. As long ago as 1902 Stark predicted that the moving canal-ray particles thus become luminous, and that consequently the lines in the spectrum emitted by them must be displaced to the violet end of the spectrum if the rays are sighted approaching the observer. This takes place in the same way as the displacement of the lines in the spectra of those stars which are moving towards us, and as this displacement, the so-called Doppler effect, increases with the velocity of the light source, it must thus also be possible to determine the velocity of the canal-ray particles.

In 1905 Stark succeeded for the first time in detecting this phenomenon in a canal-ray tube containing hydrogen.

Beside each of the single hydrogen lines belonging to the familiar, so-called Balmer series, a new, broader line appeared, which lay beside the original line, on the violet side of the spectrum if the canal rays were observed approaching the observer, but on the red side of the spectrum if observed from behind. The effect mentioned here has been established for the canal rays of all chemical elements which, in addition to hydrogen, have been investigated in this respect.

This discovery, by which a Doppler effect was recorded for the first time in the case of a terrestrial light source, was instrumental in the proof that canal-ray particles are luminous atoms, or atomic ions. The further study of the Doppler effect in their spectra, which has been pursued principally by

Stark and his pupils, has led to extremely important results, not only concerning the canal rays themselves, their formation, etc., but also concerning the nature of the different spectra which one and the same chemical element can emit in different circumstances.

In the course of an investigation of canal rays in a tube containing hydrogen gas, which passed through a strong electric field, Stark observed, in 1913, a broadening of the lines in the spectrum of the hydrogen. A more thorough examination of this broadening showed that the lines decomposed into several components with characteristic  polarization conditions. Although this splitting can best be observed in canal rays, it has nevertheless nothing to do with the movement of the atoms, but depends solely on the fact that these are present in an extremely strong electric field.

In this, a discovery was made analogous to Zeeman's discovery of the splitting of serial lines by means of an extremely strong magnetic field, which was also in its time crowned with the Nobel Prize by this Academy.

This splitting of lines in electric fields has been detected and measured by Stark in the line spectrum not only of hydrogen, but also of that of a great number of other substances, and the result of these investigations was that (the effect named after him turned out to be in several respects quite different from the Zeeman effect, and that thus) the optical dynamics of the atoms alters, under the influence of an *electric* field, in a manner quite different from that under the influence of a magnetic field.

The effect discovered by Stark has become extraordinarily significant for modem research into the structure of atoms, and has opened up new fields for the study of the effect of atomic ions on each other and on molecules. The extremely complicated conditions which this effect manifests in the spectral series of hydrogen and of helium were successfully explained by a theory which forms one of the strongest pillars on which the modern concept of the internal structure of the atom rests.

In view of the great significance which Stark's work so obviously has for physical research within various fields of great importance, the Royal Academy of Sciences considers it well warranted that the Nobel Prize in Physics for 1919 should be bestowed on this scientist.

Professor Stark.   Our Academy of Sciences has awarded you the Nobel Prize in Physics for 1919 in recognition of your epoch-making research into the so-called Doppler effect in canal rays, which has given us an insight into the reality of the internal structure of atoms and molecules. The Nobel Prize

relates also to your discovery of the splitting of spectral lines in electric fields
- a discovery which is of the greatest scientific importance.

I ask you now, Professor, to receive the Nobel Prize from the President of
the Nobel Foundation.

J OHANNES  S TARK

# Structural and spectral changes
# of chemical atoms

*Nobel Lecture, June 3, 1920*

The question of the composition of perceptible objects is one which already occupied the mind of the ancient Greeks. They formed the concept, as a philosophical speculation, of the indivisible particle, the atom, as the smallest component of perceptible objects. However, they did not pass beyond this stage of the hypothesis; they did not bring it to productivity through experimental research.

It is otherwise with the mind of the Germanic peoples. They proceeded from the experience of their chemical dealings with matter, established the existence of a number of basic substances, or chemical elements, which could not be decomposed further, and proposed the hypothesis that a chemical element consists of homogeneous individuals, or atoms, which are responsible for the peculiar properties of the element, and which with the aid of chemical methods can neither be broken down further nor distinguished from one another.

Towards the end of the last century a certain torpidity fell upon this concept of the chemical atom. Its verification in thousands of chemical experiments led to the belief that the chemical atom not only could not be decomposed into further parts by familiar chemical methods, but that it was completely and absolutely indivisible. Moreover, the abundance of chemical compounds and their importance in daily life hindered the chemist from investigating the question, in what does the individuality of the atoms of different elements consist. In the last three decades the concept of the chemical atom has been set free from this torpidity by our experiences in physics. The discovery of various phenomena has led to a recognition of the fact that the chemical atom is an individual which again is itself made up of several units into a selfcontained whole.

At the head of these new discoveries and insights comes the establishment of the facts that electricity is composed of discrete particles of equal size, or quanta, and that light is an electromagnetic wave motion. It followed necessarily from this that single separate electric quanta must be present in the

composition of a chemical atom. For under certain conditions the chemical atoms emit light waves of a specific length or oscillation frequency- their familiar characteristic spectra- and these can come in the form of electro-magnetic waves only from accelerated electric quanta.

Moreover, the discovery that the negative electron is a component of the chemical atom is of fundamental importance. In cathode rays the physicist became acquainted with free negative electric quanta capable of independent movement, the mass of which is smaller than a thousandth of the mass of the hydrogen atom. In the process of ionization he saw the liberation of such negative quanta or electrons from the chemical atoms. By exerting the influence of a magnetic field on the spectral lines of chemical elements, Zeeman and Lorentz even succeeded in detecting the negative electron in its place in, and as a component of, the atomic whole.

Furthermore, in these last three decades of great physical discoveries, as never before in history, Nature has drawn back the veil from a third un-dreamt-of secret before the eyes of the physicist. The discovery and investigation of radioactivity has made clear even for the most sceptical not only the separability of the parts of an atom, but also the chemical and physical individuality of a chemical atom - particularly of a parent atom, but equally of the atoms arising from its decay.

By recognizing that the chemical atom is composed of single separable electric quanta, humanity has taken a great step forward in the investigation of the natural world. However, this advance has faced us with a new, even greater problem - that of the structure of the atom. How many electric quanta are present in the atom of a chemical element? What are their fields of force? What are their mutual distances? What are their movements? What forces are roused on them if their state of equilibrium is disturbed by external interference ?

We have been faced with these questions for a decade and a half. It is im-probable that speculations will succeed in providing the answer to all these questions at one stroke, by one bold vision. It is more likely that more than a century will pass before we know the structure of the chemical atoms as thoroughly as we do our solar system. The path to this goal will lead, as it has so far, through the difficulties and surprises of experimental research. Many scientists will have to contribute to the solution of the great problem; they will have to follow up and measure all those phenomena in which the atomic structure is directly expressed.

With this in mind, for some twenty years I have set myself as my partic-

ular task the experimental investigation of the connexion between change in the structure and change in the spectra of chemical atoms. First of all, two questions may be posed in this connexion.

The first of them is tied up with the phenomenon of change in the structure of the surface of the atom. In order that we may have clearly set out before us every possibility in this respect, we shall proceed from the single atom, the parts of which are all arranged according to mutual equilibrium. We have learnt through experience that when an electrical ray strikes the surface of an atom, an electron, and in some circumstances a second and even a third electron, can be detached. In place of the structure of the neutral atom we are left with the structure of the corresponding monovalent, divalent, or trivalent atomic ion. We ask ourselves: what are the two spectra which belong to the two atomic structures-to neutral atoms and to positive atomic ions ? And this question may be supplemented by the second question: is a specific spectrum emitted if the positive atomic ion is changed into a neutral atom?

To these questions I had given certain answers, at first in the form of working hypotheses, after a tentative examination of all previous observations known to me, in order to be able to think out a specific series of experiments to test the hypotheses.

The answer to the first of these questions was as follows: the spectral series of a chemical element are peculiar to the structure of the positive atomic ions, and are observed principally in arcs and sparks, and their lines, as Rydberg showed most successfully, can be grouped together, the lines of each group being a function of the integers.

The second hypothesis was as follows : during the attachment of negative electrons on the positive atomic ions of a chemical element its fine-structure band-spectra are emitted, as in numerous different orbits of attachment the potential energy is emitted in multiples of Planck's quantum constant.

These two working hypotheses have met with very different fates. Not long after its postulation I realized that the second of them was wrong, and neither bore it experimental fruit. However, what has been extraordinarily fruitful theoretically is the nucleus of it - that is, the assumption that energy is emitted in accordance with Planck's quantum law through an electron changing orbits about a positive charge. This assumption forms the starting-point of Bohr's theory of the emission of serial lines. Although I myself once stood on the threshold of this theory, and although the final formulae give a series of frequency relationships in the spectral series which agree well with

observed facts, I am nevertheless unable to believe it, because in its provisions it postulates suppositions which contradict, not only Maxwell's theory, but the very spirit of physics. This criticism is directed not at Planck's quantum of action, but at the hypotheses of Bohr which are bound up with it.

But let us return to the hypothesis that the positive atomic ions are responsible for the spectral series. Shortly after it was formed, I was able to make it bear experimental fruit through the following reflection.

By allowing the positive ions to pass through an electric field and thus giving them a certain velocity, it is possible to distinguish them from the neutral, stationary atoms. If it is possible to deduce their velocity from the spectral lines emitted by them, then this deduction implies the assignment of the displaced spectral lines to the moving atomic ions as emitters. The movement of the emitters of the spectral lines may be deduced on the basis of the Doppler principle.

We can in fact first place the beam of rays of moving positive atomic ions in a plane perpendicular to the axis in which we see the spectral lines emitted by them. These only appear in the places in which they are normally situated in the spectrum when their emitters are stationary. Secondly we can allow the beam of positive atomic ions in our axis of vision to approach us, and then their spectral lines appear to us displaced from their normal place in the spectrum towards the shorter wavelengths, by an amount which is proportional to the velocity of the emitting system. And thirdly, if we make the atomic ions in our axis of vision travel away from us, then their spectral lines appear to us displaced from their normal position towards the opposite side.

In the year 1905 I set about proving experimentally the phenomenon just described. The state of research at that time meant that one had to regard as positive ions the canal rays, which approach the cathode of the glow current and emerge on the other side through perforations in it. I directed the axis of the collimator of my spectrograph first perpendicular to the axis of a beam of hydrogen canal rays, and on a second occasion I allowed the canal rays in the axis of the collimator to approach it. During the comparison of the two spectrograms so obtained, the anticipated Doppler effect in the serial lines of hydrogen appeared, and the same result was later obtained on the serial lines of numerous other chemical elements.

Thus at the beginning of 1906 it seemed to be established that the emitters of the spectral series of chemical elements are their positive atomic ions. This interpretation of my observations, it is true, was soon questioned. For, as

particularly W. Wien and J. J. Thomson have shown, canal rays usually contain, beside the positive atomic-ion rays, also neutral rays, so that it was not possible to determine accurately whether the spectral lines showing a Doppler effect should be attributed to the former or the latter. However, cases came to light later in which canal rays containing only positive ions showed a Doppler effect in the spectral lines emitted by them. If even today I still regard the positive atomic ions of a chemical element as the emitters of their spectral series, nevertheless I do not take this concept now as restricted as I did when I only considered free positive atomic ions which owing to their positive total charge are accelerated by the electric field. Rather, in my present opinion, it is possible that the serial lines can in addition be emitted from a positive atomic ion which is not free, and to which a negative electron has already begun to attach itself; only the electron must not yet have come so close to the atomic ion that emission from the latter will already be sensitive to and disturbed by the electric field of the electron.

In this connexion the ultraviolet continuous spectrum of hydrogen may be mentioned. I expected that a continuous spectrum would be emitted when in the course of the attachment of the negative electron to the positive atomic hydrogen ion its encroachment has continued so far that the emission of the serial lines is noticeably disturbed. I therefore looked for - and found - a continuous spectrum in hydrogen canal rays.

Since the discovery of the Doppler effect in canal rays a great number of experiments on this phenomenon have taken place. The following results may, briefly, be deduced from them.

The emitters of the spectral series are without exception single atoms, not compounds of atoms. The spectra of atomic ions of higher valence are different from the spectra of atomic ions of the same element, but of lower valence.

The band-spectra - for example, those of hydrogen and nitrogen - do not as a rule show a canal-ray Doppler effect. Because I expected on the one hand that their emitters were positive molecular ions consisting of more than one atom, and because on the other hand positive molecular ions are also found as canal rays under low pressure, I was led to explain the absence of the Doppler effect in bands by the theory that when stimulation by collision takes place, so that light is emitted, the molecular ions of more than one atom are dissociated after a short period of existence. This concept also makes the canal-ray Doppler effect appear possible in bands, at a small velocity and low pressure. And in fact Mr. Rau of the Würzburg Institute of Phys-

ics has recently succeeded in proving this in the case of negative-nitrogen bands. All his observations, moreover, lead to the conclusion that the emitters of these bands are positive diatomic nitrogen molecular ions.

The announcement of this new step forward bids us recognize that research work on the canal-ray Doppler effect is by no means complete and the question of where the various spectra of chemical elements originate has not yet been conclusively answered.

If the experimental physicist has already done a great deal of work in this field, nevertheless the theoretical physicist has still hardly begun to evaluate the experimental material which may lead him to conclusions about the structure of the atom. It has, however, been established that the conversion of the structure of the neutral atom into the structure of the ion involves fundamental changes in the oscillation of the electric quanta which remain in the structure. What conclusions, however, may be drawn from this about the structure of the neutral atom and of the ion remains an unanswered question.

The removal of an electron from the surface of an atom - that is, the ionization of the atom-means a fundamental structural change in its surface layer. That this is accompanied by an equally fundamental change in the spectrum of the surface layer was to be expected from the very first. Matters are different in the case of the second sort of structural change which I made the subject of my experimental research.

We must always bear firmly in mind that the chemical atom is an individual, self-contained structure of positive and negative electric quanta. An external electric field, meeting it and passing through it, affects the negative as much as the positive quanta of the atom, and pushes the former to one side, and the latter in the other direction. Certainly this displacement is soon stopped by the opposing forces which it awakens among the quanta, which are displaced relative to one another, but nevertheless the displacement does take place, and it means a deformation, an alteration of the atomic structure in comparison with its form before the influence of the external electric field. And the question arises whether this sort of alteration of the atomic structure, this deformation by an electric field, manifests itself in an alteration of the spectrum of the atom. In other words, the question of the effect of an electric field on spectral lines has thus arisen.

At the time when I became engaged on this question Voigt had already developed and worked out mathematically a theory of an electric analogue to the Zeeman effect. The result of this theory was not encouraging; because

it implied that the alteration to the oscillation frequency, or wavelength, of spectral lines by an electric field would be so small that it would be immeasurable. And this result seemed to be confirmed by the complete absence of success in research to find this effect extending over a number of years.

However, I was unable to accept the presupposition of the theory - namely, the assumption that the emission of a spectral line on the part of an atom was the work of only one single independently moving electron in the atom. In my view the structure of the whole atom was that of an individual, with all its parts interconnected, and the emission of a spectral line appeared to me to be the result of the coherence and co-operation ofseveral electric quanta. Therefore I expected that from the alteration of the atomic structure by an external electric field there would arise also an alteration of the spectrum of the atomic structure. And I tried to solve my problem by producing a strong electric field in a luminous gas. I achieved this by making canal rays, passing through perforations in the cathode, on the other side travel in a strong electric field between the cathode and a second supplementary electrode placed opposite it.

My very first spectrogram of canal rays in hydrogen and helium revealed the effect of the electric field on a number of spectral lines and gave some hint of the wealth of phenomena in the newly opened-up field. Moreover this discovery also showed again how much richer and more original are the works of Nature than the ideas of Man. In the event of the axis on which the observer views the luminous electric field being perpendicular to the axis of the field, the theory had postulated that every single spectral line would be splitted under the influence of the electric field into two components, both of which would appear, relative to the normal line, displaced towards the longer wavelengths, and of which one would vibrate parallel, the other perpendicular, to the field. How different the reality! For example, the red hydrogen line is splitted symmetrically to the normal line into nine components, of which the electric vibrations of six are parallel, and three perpendicular, to the field.

Since the discovery of the effect of an electrical field on spectral lines in the year 1913, already a great number of experiments on it have taken place. The most common and most important result of them is that the nature and size of the effect on corresponding series of different elements are largely an expression of the peculiarity of their atomic structure - or, at least, of the structure of the surface. Thus the effects on the hydrogen series, on the series

of mono- and bivalent positive atomic helium ions, on the series of lithium, mercury, and aluminium, differ from one another in characteristic ways.

The following results may be of interest in detail.

Along a series of lines running from longer to shorter wavelengths the effect of the electric field becomes greater as the serial numbers increase - that is, as the wavelength decreases.

The proportion of the intensity of various series within a serial system is, in the case of several elements, dependent on the strength of the deforming electric field. Thus under its influence new series may become visible, which outside the electric field possess so little intensity that they are not observable.

The broadening and displacement of spectral lines which accompanies an increase in the pressure of the gas or in the density of ions, originates in the effect of the electric fields of single atoms on neighbouring light-emitting atoms. Connected with this is Haber's highly promising idea of tracing the heterogeneous catalysis in solid surfaces back to the deformation of the molecular structure by the molecular electric field. Perhaps it will be possible to spectro-analyse accurately such electric fields.

But let us leave these details and return to the problem of the structure of the atom. We must ask ourselves whether a conclusion about the structure of the atom, or at least about the process of the emission of serial lines, may be drawn from the effects of an electric field on serial lines. Now, Bohr and Epstein have developed a theory for the effect in question which gives the number and interval for the component lines in electric fields which agree surprisingly well with observed facts, at least in the case of the series of the monovalent atomic hydrogen ion and of the bivalent atomic helium ion-or, rather, in the case of the electron adhering to these ions. This agreement strongly supports Bohr's theory of the emission of spectral lines, and thus also his presupposition, originating from Rutherford, about the structure of the hydrogen and helium atoms.

In spite of my high estimation of this achievement by the theory, nevertheless I am unable to accept it as definitive; apart from the fact that I am unable to believe in some of its presuppositions, it does not fully correspond to our experience. It cannot explain the following observation, which seems to me very important to research into the structure of the atom.

A beam of luminous hydrogen canal rays has, owing to its velocity, exactly the same direction as that of the electric field in which it may be made to move. If the axis of the beam is placed perpendicular to the axis of the field, the intensities of the components of every single line which is splitted

are as symmetrical relative to the normal lint as the intervals at which the components are situated to right and left of it. On the other hand, if the direction of the rays is the same as that of the field, then the intensity of those components which lie on the side towards the longer wavelengths increases. And if the canal rays are made to travel in the opposite direction to that of the field, then vice versa, the components towards the shorter wavelengths appear with greater intensity. It would therefore seem as if a hydrogen atom, or its ion, in an electric field possesses polarity along the axis of the field - that is, two sides may be distinguished in this axis.

This phenomenon is as remarkable as it is important. We may legimately expect to be able to come, from its theoretical implications, to a conclusion about the structure of the hydrogen atom. It may well be successful, if we not only take into account, as has been the case up till now, the effect on a single electron at the surface of the atom, but take as the point of departure for our inferences from the observations the connexion between the parts of an atom which go to make up an individual structure.

Reference to this brings us back to the problem of the structure of the atom. We shall realize the immensity of this problem when we cast a glance behind us at the ground which has already been covered. Research into changes in the spectrum of chemical atoms as a result of changes in their structure has disclosed a whole series of new phenomena. The removal of an electron from the surface of an atom - or its reattachment-leads to fundamental changes in the spectrum of the atomic parts capable of oscillation; and the deformation of the atomic structure by an electric field is expressed by various forms of influence on the oscillation of those atomic parts. But even though these new phenomena have already so richly borne experimental fruit, even though the theories which are beginning to be built on them seem so promising, nevertheless they have hardly begun to clarify the great problem, have only shed light on a small part of the experimental work, and still less on the theoretical field. Research into these phenomena can do no more than contribute a little to the solution of the great problem of the structure of the atom. It will still need the work of many generations to reach that solution. Our advance from the speculative hypothesis of the atom formed by the Greek mind to the discovery of the electric nature of the structure of the atom through the Germanic research of the past century should be an encouragement and a lesson for the century to come.

# Biography

Johannes Stark was born on April 15, 1874 in Schickenhof, Bavaria; his father was a landed proprietor. He was educated at the Gymnasium (grammar school) in Bayreuth and later in Regensburg and proceeded to Munich University in 1894 to read physics, mathematics, chemistry and crystallography. Stark graduated in 1897 on the basis of his doctoral dissertation on Newton's electrochronic rings in a certain type of dim media. He worked as assistant to von Lommel at the Physics Institute at Munich University from 1897 until 1900 and then became unsalaried university lecturer of physics at the University of Göttingen. In 1906 he was appointed extraordinary professor at the Technische Hochschule in Hannover and in 1909 he followed the invitation of the Technische Hochschule in Aachen to become Professor there. A similar appointment at the University of Greifswald followed in 1917. Three years later he moved to the Physics Institute of the University of Wüzburg, where he stayed until 1922.

Stark's scientific works cover three large fields: the electric currents in gases, spectroscopic analysis, and chemical valency. His spectroscopic work deals with the connection between the alteration in the structure and in the spectrum of chemical atoms. In 1919 Stark was awarded the Nobel Prize for Physics for his <<discovery of the Doppler effect in canal rays and the splitting of spectral lines in electric fields>>. The prize enabled him to set up his own private laboratory.

In 1933 Stark was elected President of the Physikalisch-Technische Reichsanstalt (Physico-Technical Institute) as successor to von Paschen, where he remained until his retirement in 1939. At the same time he held the post of President of the Deutsche Forschungsgemeinschaft (German Research Association).

Stark was a prolific writer and published more than 300 scientific papers. His book Die *Elektrizität in Gasen* (Electricity in gases) was published in 1902. This was followed by works on elementary radiation and electrical spectroscopic analysis of chemical atoms. In connection with his work on chemical valency he wrote a book *Die Elektrität im chemischen Atom* (Elec-

tricity in the chemical atom). Stark founded the *Jahrbuch der Radioaktivtät und* Elektronik (The Year-Book of Radioactivity and Electronics) and edited this publication from 1904 until 1913.

Johannes Stark was a corresponding member of the Academies in Göttingen, Rome, Leyden, Vienna and Calcutta, and was awarded the Baumgartner Prize of the Vienna Academy of Sciences in 1910 and Vahlbruch Prize of the Göttingen Academy of Sciences in 1914, and also the Matteucci Medal of the Rome Academy.

During the last years of his life Stark, in his private laboratory on his country estate Eppenstatt near Traunstein in Upper Bavaria, investigated the effect of light deflection in an unhomogeneous electric field.

He was married to Luise Uepler. They had five children. His recreations were forestry and cultivation of fruit trees.

Stark died on June 21, 1957.

Physics 1920

# CHARLES-ÉDOUARD GUILLAUME

*<<in recognition of the service he has rendered to precision measurements in Physics by his discovery of anomalies in nickel steel alloys>>*

# Physics 1920

*Presentation Speech by Dr. Å G. Ekstrand, President of the Royal Swedish Academy of Sciences*

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen.

The Swedish Academy of Sciences has decided to award the Nobel Prize for Physics 1920 to Ch.É. Guillaume, Director of the International Bureau of Weights and Measures, for the services he has rendered to the physical precision technique by his discovery of the properties of nickel steel.

One of Greece's greatest thinkers said that <<things are numbers>> and attempted to explain the origin of everything by numbers. The scientists of today do not take the cult of numbers to quite that extent; yet they recognize nevertheless that every exact knowledge of Nature begins only when we succeed in expressing the phenomena in measures and weights. The development of science has always been in step with the progress in measuring precision. This applies to astronomy, geodesy, chemistry and above all to physics, the special growth of which dates from the time when modern precision began to be applied in observations.

This was the point which had been grasped by the French National Assembly when, in 1790, it instructed the Academy of Sciences of Paris to lay down an invariable base for weights and measures. A committee was set up for that purpose, consisting of Borda, Lagrange, Laplace, Monge and Condorcet, and on their suggestion the National Assembly adopted a decimal system based on a certain part of a quadrant of the Earth's meridian. Thus the principle of the metric system was introduced into France which was then established by a law passed by the Convention held on August 1, 1793.

In the other countries progress was slower. It was not until after a few decades that people in Europe began to realize the advantages of the metric system and that mainly because of the large international exhibitions. During the 1867 international exhibition in Paris a committee was formed by most of the countries represented at the exhibition with a view to preparing the adoption of a single international system for weights and measures. The proposal to that effect, approved by the emperor on September 1, 1869, was submitted to all the states and thus was subsequently founded the International Bureau of Weights and Measures at Breteuil, near Paris.

It was the French nation which not only conceived the idea of this great reform, but which, by its diplomatic skill, was also able to bring about its adoption in the whole civilized world; on this account, therefore, mankind owes France a great debt of gratitude.

All the copies of the standard metre and the standard kilogramme intended for the various countries are meticulously examined and compared in this International Bureau, the head of which, Charles-Édouard Guillaume, is undeniably the foremost metrologist of today. By devoting his entire life to the service of science, this scientist has made a powerful contribution to the progress of the metric system; during his long and painstaking studies he discovered a metal with the most excellent metrological properties. That is the discovery which the Swedish Academy of Sciences has sought to reward by conferring this year's Nobel Prize for Physics, since the discovery is of great significance for the precision of scientific measurements and thereby even for the development of science in general.

Actually the mere fact of possessing an international system for weights and measures and an International Bureau for the application of that system had not done away with the difficulties entailed in each measuring or weighing operation unless it is possible to achieve here the maximum precision. With measurements of length in particular the chief source of errors was dependent on temperature as a result of the well-known property of materials to change their volume with variations in temperature.

It was thus basic to examine with the greatest precision the expansibility of all metals and alloys under the action of heat. During these delicate examinations, and particularly while studying the properties of certain types of steel, Guillaume hit on the apparently paradoxical idea that it should be possible to produce an alloy free from this universal property of materials to change their volume at various temperatures. The long and difficult experiments performed by Guillaume year after year on numerous alloys and above all on nickel steel to determine their expansibility, elasticity, hardness, changeability with age, and stability ultimately led him to the important discovery of the nickel steel alloy known as invar, the temperature coefficient of which is practically zero.

These studies and discoveries by Guillaume have continued to give rise to new and significant practical applications. Instances are the use of invar in the design of physical instruments, and especially in geodesy where Guillaume's discovery has completely transformed the methods of measuring base lines; nickel steel has also supplanted platinum in the manufacture of

incandescent lamps and on the basis of the current price of platinum this represents an annual saving of twenty million francs; lastly chronometry is indebted to Guillaume's discoveries and investigations for a new refinement - the use of the new alloys enables watches to be adjusted more accurately and at less cost than formerly.

From the theoretical standpoint, too, Guillaume's penetrating and systematic studies on the properties of nickel steel have had the greatest significance because they have confirmed Le Chatelier's allotropic theory for binary and ternary alloys. He has thus made an important contribution to our knowledge of the composition of solid matter.

In consideration of the great importance of Mr. Guillaume's work for precision metrology and thus for the development of all modern science and engineering, the Swedish Academy of Sciences has awarded this year's Nobel Prize for Physics to Charles-Édouard Guillaume in recognition of the services which he has rendered to the physical precision technique by his discovery of the properties of nickel steel.

Monsieur Guillaume.   By your persevering studies in thermometry you have deserved well of physics and chemistry; but you have gained your scientific laurels mainly in a different sector. By your studies of metal alloys and their sensitivity to temperature influences, you established that a few of those alloys possess remarkable properties; some scarcely expand on heating which suggested to you the idea of making them into measuring standards. One of the nickel steel alloys in particular, the one containing thirty-six per cent nickel, you considered to fulfil the necessary conditions. Since it is almost invariable under the action of heat and under other influences, you have called it invar. Its potential benefit to science for the construction of standards and of various instruments can readily be appreciated. In geodesy, invar wires give much more accurate base-line values than those formerly obtained.

On behalf of the Royal Swedish Academy of Sciences, I congratulate you on your studies and on your discoveries which have been of the greatest utility and for that very reason deemed worthy of the Nobel Prize. I would now ask you to receive the prize from the hands of His Majesty the King who has been pleased to make the presentation to you.

C HARLES- É. G UILLAUME

# Invar and elinvar

*Nobel Lecture, December 11, 1920*


*The anomaly of nickel steels*

*Discovery of the anomaly* - In 1889 the General Conference on Weights and Measures met at Sèvres, the seat of the International Bureau. It performed the first great deed dictated by the motto inscribed in the pediment of the splendid edifice that is the metric system : <<*A tous les temps, a tous les peuples*>> (For all times, to all peoples); and this deed consisted in the approval and distribution, among the governments of the states supporting the Metre Convention, of prototype standards of hitherto unknown precision intended to propagate the metric unit throughout the whole world.

These prototypes were indeed noteworthy. They were made of a platinum-iridium alloy developed by Henri Sainte-Claire-Deville which combined all the qualities of hardness, permanence, and resistance to chemical agents which rendered it suitable for making into standards required to last for centuries. Yet their high price excluded them from the ordinary field of science; at that time a single metre actually cost 7,000 crowns - and how much more today!

A less costly answer had to be sought since between these precious prototypes and standards affording only uncertain guarantees there was a gap which nothing could fill.

I first examined this problem in 1891 and soon discovered the really excellent properties of pure nickel and still today this is the metal used to make a non-oxidizable standard, unaffected by the passage of time, rigid and of average expansibility. However, one difficulty prevented me generalizing its use. A geodesic standard 4metres long was required, and no nickel-producing factory would undertake to supply, perfectly sound and crack-free, a suitable bar.

Subsequent studies were guided by a few strokes of good luck. In 1895, at the request of the Ordnance Technical Department (Section technique de l'artillerie) in Paris, J. R. Benoit had undertaken the study of a standard made from an iron alloy containing 22% nickel and 3% chromium and found its

expansibility to be close to that of brass. It was a non-magnetic alloy and thus was doubly anomalous.

The very curious phenomena discovered by John Hopkinson had already been known for a few years, notably that after forging certain alloys of iron and nickel containing about 25% of the latter are non-magnetic and not very hard; however, once they have been cooled in, say, solid carbon dioxide, they are hard and strongly magnetic; furthermore, during this transformation, their volume has increased by about 2%.

The phenomena discovered by Hopkinson and Benoit were clearly related. But however interesting they might be for the physical chemist, they were strictly taboo for the metrologist. An alloy that is changeable, and another of high expansibility, are unsuitable for designing length standards.

The matter took on a different aspect when in 1896 I was put on the trail of a new and quite unexpected fact closely connected with those just reported. A bar of steel containing 30% nickel arrived at the International Bureau and I found its expansibility to be about one third less than that of platinum. The continuation of a study so begun augured well and I pursued it with stubborn obstinacy.

For metrology the matter of expansibility is fundamental; as a matter of fact the temperature measuring error relates to the length measurement in proportion to the expansibility of the standard and the constantly renewed efforts of metrologists to protect their measuring instruments against the interfering influence of temperature reveal clearly the importance they attach to the expansion-induced errors.

It is common knowledge, for instance, that effective measurements are possible only inside a building, the rooms of which are well protected against the changes in outside temperature, and the very presence of the observer creates an interference against which it is often necessary to take strict precautions.

Prior to the discovery of the anomaly to which I have just referred, any physicist would have sworn that there was no hope of remedy by means of metals or alloys whose expansibility was much lower than the known values because it had always been considered that the rule of mixtures was complied with in practice.

My first care was to check the direction of the expansions as a function of the composition of the alloys. This was not a vain precaution since between the non-magnetic 22% alloy and the magnetic 30% alloy a discontinuity was apt to occur. Experiments conducted on two alloys, enclosing

the second, and which were reported to me by the Société de Commentry-
Fourchambault & Decazeville, established the continuity.*

*Classification* by *magnetic properties.* - The accurate measurement of expansions
is long and difficult. Since there could be no doubt that the anomaly in-
volved affected all the properties of the new alloys, more readily applicable
methods had to be used. It was self-evident to study the magnetic suscep-
tibility, for if it is merely a question of ascertaining the presence or absence
of ferro-magnetism, the experiments are elementary.

In its early stages this study showed me that there were two distinct trans-
formations. The one is irreversible and this is the one discovered by Hop-
kinson; the other is reversible and its discovery was new. A number of ob-
servers, notably Osmond, Louis Dumas, Pierre Weiss and his pupils, Na-
gaoka and Honda have established its characteristics.

A very simple diagram shows at a glance the over-all pattern of the trans-
formations of ferro-nickels referred to their magnetic properties.

Starting from iron these transformations split into two groups, AB and
AC, which progressively diverge (Fig.1a). When we cross downwards the
lower curve, magnetism appears, then increases up to a certain limit. When
the alloy is reheated the magnetism decreases from a given temperature and
ultimately disappears at the intersection with the upper curve. On the other
hand the behaviour of the single curve indicates, in alloys with a higher
nickel content, both the appearance, on cooling, and the disappearance, on
reheating, of the ferromagnetic properties.

The intersection of the curves for the two categories has a precise signif-
icance: additions of carbon, chromium, and manganese appreciably lower
the temperature of the irreversible transformations but have far less effect
on the reversible transformations. It is thus possible to follow the reversible
transformation into the region of the normally irreversible alloys.

Moreover, to the right of the intersection moderate cooling leaves the
magnetism completely reversible; more intense cooling sets the transforma-
tion and renders it irreversible.

Let us now assume a third axis at right angles to the other two. Along it
we shall plot the susceptibility and in the solid diagram thus obtained we

* Inspired initially by the managing director, Henry Fayol, this firm was not content
to stop there; when submitting to me its analytical reports the firm supplied me with
alloys numbering more than six hundred. It is due to this unstinting collaboration that
my studies were able to carry on for almost a quarter of a century.

make two orthogonal sections, *ab* and *cd.* In the irreversible region the pre-
viously cooled alloy retains along ABC (Fig.Ib) the susceptibility it has
acquired, which reverts to zero along CD. On cooling it will remain zero
until point F is reached where it will start to rise again along line FB.

Cooling may be interrupted at any time, then the alloy reheated and it
will retain the constant magnetic properties shown by the line B'C'.

In the reversible region the susceptibility is represented by the single curve
ABCDEF (Fig.IC).

All the properties of the alloys with which we are concerned are asso-
ciated with these transformations, and the characteristics of those which we
have just traced will also be found in the curves representing the changes in
volume or elasticity modulus.

Having thus found the guide I devoted my full energies to studying the
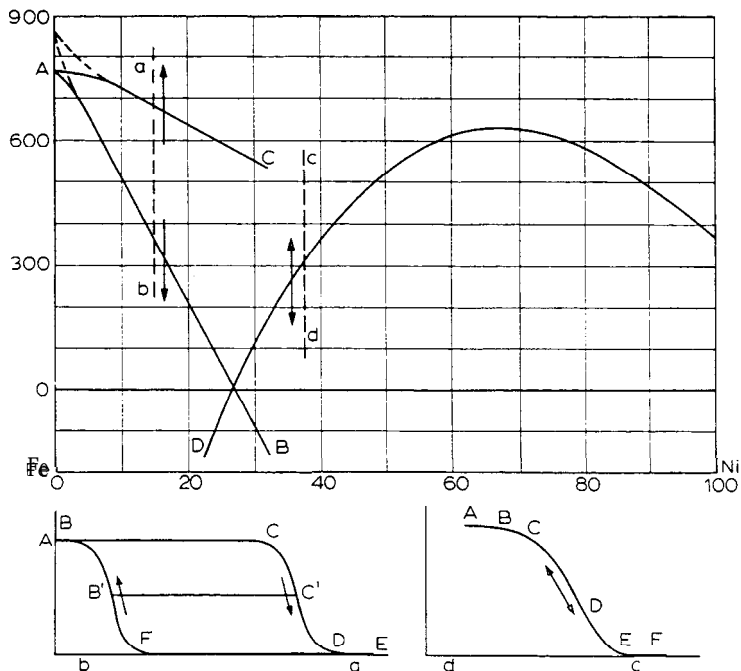


Fig.Ia. Magnetic transformation temperature of nickel steels as a function of their
composition. The branches AB and AC refer to irreversible alloys, branch DE to re-
versible alloys.
Figs. Ib, ɪc. Variations in magnetic susceptibility of nickel steels as a function of
temperature in the irreversible and reversible alloy regions (temperature along abscissae,
susceptibilities along the ordinates).

changes in volume which constitute the main metrological factor associated with the existence of these alloys.

## Changes in volume

Methods-It was during the 18th century that the expansibility of solid materials was clearly demonstrated. The famous French physicist and geodesist Bouguer once wished to exhibit its effects to a large assembly and for this purpose he suspended under the dome of the Hotel des Invalides a metal wire supporting a telescope balanced at two points. The telescope was sighted on a distant levelling rod and when, during the course of the day, the temperature rose then fell, the variations in length of the wire were revealed by the movement of the point on the rod seen in the telescope.

In that case, however, it was merely a verification and not a measurement. Various methods of determining expansions were used during the 19th century; the one which I have used almost exclusively is that of the comparator which Baron Wrede recommended to the International Bureau to be used in the form in which he himself used it and which, perfected over the years, particularly by J.R.Benoit, has resulted in the methods in use today.

Two micrometer microscopes fixed to stone supports are vertically sighted on the marks on a rod immersed in water and measure the changes in its length when it is brought to various temperatures in succession. However, as the distance between the microscopes is not fixed, the procedure is to measure alternately the rod under test and a standard kept at a practically constant temperature in a second trough. This is termed an *absolute* method. For routine work it is replaced by the relative method in which the reference standard is placed in the same bath as the rod under test. The expansibility of the latter is the algebraic sum of the relative expansibility given by the experiment and of that of the standard rod determined beforehand by the absolute method. I used the comparator method in its relative form with an iridium platinum rod as the reference standard.

But the comparator method can be used only over a restricted temperature range the limits of which, in the case of my experiments, were $0°$ and $38°$C. To attain temperatures higher than $200°$C and thus better characterize the transformations, I secured the sample to be studied to a brass rod, the two being coupled at one extremity and free to expand over the remainder of their length. The relative extensions were measured at the free end with a microscope.

   Later P. Chevenard designed a dilatometer whereby the relative extensions
of a small sample of the metal under test (25 to 50 mm) and of a reference
made of a suitably chosen alloy can be measured with high accuracy. His
dilatometer, with photographic recording, enabled the whole range of tem-
peratures from that of liquid air to 1,000°C to be covered. In their common
parts our diagrams coincide, but Chevenard's go far beyond mine.

*Irreversible changes* - Knowledge of the irreversible changes in volume of the
alloys was necessary, especially to ascertain their limit. I studied the various
aspects in binary and ternary ferro-nickel alloys with chromium, copper, etc.
I was only able to trace the low part of the cycle. The complete cycles were
traced much later by P. Chevenard.

   When a bar of an irreversible alloy is heated from a low temperature, it
expands in accordance with the almost rectilinear curve ABC (Fig.2b), then,
at a certain temperature, the rate of extension falls off, then progressive con-
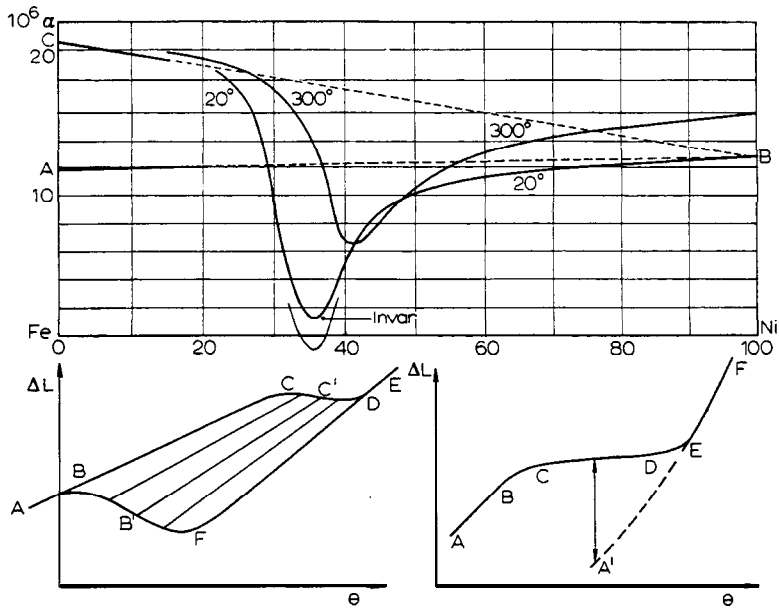


Fig.2a.  Diagram showing the expansibilities of nickel steels as a function of their com-
position. The two straight lines starting from A and C limit the range of the irreversible
alloys, the curves represent the true expansibilities of the reversible alloys at 20° and at
$300°C$ $(\alpha_{20}, \alpha_{300})$.

Figs. 2b, 2c. Diagrams for a reversible and an irreversible alloy.

traction sets in and continues regularly until completion of the transformation, whereupon the expansion resumes its regular course DE.

If the bar is allowed to cool it will be found to contract in accordance with EDF, at which point an expansion sets in which ceases at B and gives place to a contraction along BA.

If the cooling has been suspended at B' and if the bar is reheated, the movement follows the line B'C' and continues along the curve C'DE as in the preceding case. The slope of the straight line AC is between 10 and 11 x $10^{-6}$, that of EF is about 18 x $10^{-6}$.

The former shows the expansibilities of the ordinary irons or steels, the second those of the non-magnetic iron-nickel-chromium alloy mentioned above. Between the two all the intermediate expansibilities can be attained by suspending the transformation at any point along one of the curves CD or FB.

Along the curve ABC the iron is in a state which we shall term <<cold stable>>; along the curve EDF it is in the <<hot stable>>, non-magnetic state.

Collating the expansibilities of the irreversible alloys, we find that they lie between the segments of the straight lines AB and CB in Fig.2a, proper to their particular zone. Contrary to all appearances the rule of mixtures is obeyed but it must be applied to the association of the nickel with that of the varieties of iron present in the alloy within the limits of the zone covered, or else with a proportion of each of the two states of iron which depends on the degree attained by the transformation.

The zone which can be occupied by the high expansibilities is progressively extended to ordinary temperatures by retarding the transformation by additions of manganese, chromium, or carbon, as mentioned when discussing magnetism.

*Reversible changes* - The experiments with the reversible alloys were much more extensive.

A first examination consisted in determining the anomaly curve as a function of the nickel, entirely neglecting the manganese, carbon and silicon additions present in varying amounts in the alloys and which left the curve slightly ambiguous. Next I studied a series of alloys containing up to the maximum possible proportions of manganese and carbon. Having thus determined the coefficients relating to these additions for all the contents of nickel, I was able to convert the results to constant proportions of additions : 0.1% Mn, 0.4% C, and the alloys containing them I have termed *standard*

alloys. Moreover, after hot rolling and cooling in air, these alloys will be referred to as being *in the natural state.*

Since the expansibility of a material is given by the equation

$$l_0 = l_0 \left( \mathrm{I} + \alpha\theta + 2\beta\theta^2 \right)$$

the expression

$$\alpha_0 = \alpha + 2\beta\theta$$

will be termed the true coefficient at θ, which is at the same time the mean coefficient of expansion between 0°C and 2 θ ; β will be the *quadratic coefficient.*

The expansibility of most metals is well represented, over a wide range of temperatures, by an equation of the above form; for the alloys under discussion the same rule is adequately applicable over the narrow range where I used the comparator; but, when it is extended, it soon becomes apparent that a second degree equation is no longer sufficient to represent the phenomenon. Nevertheless it is convenient to retain the same form of the equation, attributing to β a value which varies with the temperature and which indicates the semi-curvature of the expansibility curve at each point.

For normal, reversible nickel steels the values of $\alpha_{20}$ and $\beta_{20}$ are represented by the curves in Figs.2a and 3. The lines AB link together the values of the same coefficients for nickel and steel in the cold stable state and so reveal the magnitude of the anomaly in expansibility. For β this anomaly is undeniably positive, then negative. It appears to be likewise for α but the line CB which starts from the value of the coefficient in gamma iron and limits
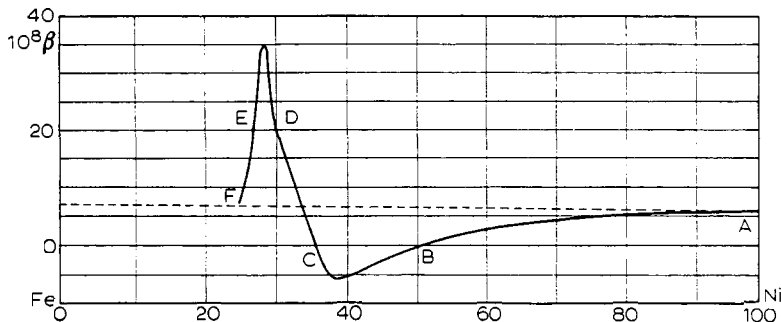


Fig. 3. Values for coefficient b in reversible alloys. The letters marked on the curve correspond to those in Figs. ɪᴄ and 2ᴄ.

the zone of large expansibilities of the irreversible alloys, shows the anomaly as entirely negative. And in fact it has to be referred to this representation.

The anomaly is very great since the expansibility of the alloys varies in the ratio of about 1 to 15 and reaches a value which is only one quarter of the lowest expansibility found in one metal. From a practical standpoint, moreover, it will be noticed that the low expansibilities are achieved here by inexpensive metals and constitute a completely continuous scale in contrast with the discontinuous and costly sequence of the less expansible metals, iridium, tantalum, tungsten.

The generic name *invar,* short for invariable, has been given to the alloy whose expansibility differs little from the minimum. The coordinates of the minimum for the standard alloys in the natural state are: Ni = 35.6; $\alpha =$ $1.2 \times 10^{-6}$.

Great importance need not be attached to the exact value of these coordinates. Actually they relate to an alloy in which the additions have been fixed arbitrarily at about the mean amounts contained in industrial alloys, and we shall soon see that these additions have a considerable effect on the position of the minimum. Moreover, every heat treatment or mechanical treatment modifies the expansibilities, raising them in the case of annealing with slow cooling, reducing them when the cooling is rapid, and more still when the alloys are hammer hardened. By superimposing one reducing treatment on the other it is thus possible to bring the expansibility of an alloy to $1.5 \times 10^{-6}$ below its value corresponding to the natural state and give it a negative value. Then, after this has been achieved, heating for a few hours at 100°C, for instance, raises it again and may bring it very close to zero. In this way a method was elaborated for making several kilometres of invar wire, the expansibility of which can be detected only by very accurate measurements. This result is of great practical importance, as we shall soon see.

The wide margin of variations of the coefficient β is sufficient to suggest that the general curve representing the true expansibility of the alloys as a function of their composition will deform rapidly when the temperature to which it corresponds is altered. Furthermore, comparison of the curves in Figs. 1a and 3 shows that the maximum of β largely corresponds, for the particular case of ordinary temperatures, to the region in which the magnetism appears or disappears. This coincidence is universal, as I was able to demonstrate in 1896, up to the limit of the temperatures which it was possible for me to attain and I immediately concluded that the complete curve for the changes in length specific to a given alloy, transfers its characteristics

to the neighbouring alloys with a simple shift in the scale of temperatures. From that I deduced a rule of corresponding states which assuredly is only a coarse approximation to reality but nevertheless permits generalisation and, consequently, prediction.

It may be formulated by stating that, at a certain temperature, a given alloy is in the same state as another alloy at a temperature which differs from that at which magnetism first appears by the same margin as in the first alloy.

To apply this rule the concomitant values of α and β for the series of alloys which are considered at the same temperature will be compared as belonging to the same alloy for the series of temperatures. In this way it is possible to trace *a priori* the extension curve of a given alloy which has the general shape shown in Fig.2c. Essentially five periods are distinguishable in this curve, the two extremes, AB and EF, with β weakly positive, giving the result obtained from the rule of nickel-iron mixtures in the cold and hot stable states, and three intermediate regions, BC and DE with β weakly negative or very strongly positive, lastly CD which is the region of inflexion where β changes from negative to positive, and where, as a result, the expansibility reaches its minimum.

Between 150° and 200° C the expansibility of invar proper starts to increase, and between 250° and 300° C its expansibility becomes normal.

Since the entire curve shifts towards the high temperatures with increasing nickel content, the alloy will be matched to the temperature range specific to the intended applications. It should not be forgotten, however, that the curve deforms slowly and that at high temperatures there are no alloys with very low expansibility.

The top curve in Fig.2a represents, by way of an example, the expansibilities of nickel steels at 300°C as found in Chevenard's experiments. The anomaly is still very marked but the minimum has shifted considerably towards the high nickel contents as foreshadowed by the trend of the p-values.

The distance between the curve FEA' and the curve EDCBA (Fig. 2c) is the amplitude of the anomaly at each temperature.

## Elastic properties

*Elasticity moduli* - The irreversibility and the reversibility revealed by the study of the magnetic properties of the alloys, or of the variations in their volume, recur, as was to be expected, in their elastic properties. Here again the transformations whose effects we have ascertained bring about changes

which are a function of the prevailing temperature or else which are largely dependent on the thermal influences to which they have previously been exposed.

Generally speaking any expansion of materials lowers the modulus by reducing the intensity of the intermolecular reactions. The irreversible changes in volume also have this result and owing to the transformation undergone by irreversible nickel steels at low temperatures, their elasticity modulus decreases by about one tenth of its original value, the decrease being along the curve FB (Fig.4b). Lastly, I would like to add that the system of which this curve is a part represents all the changes of the modulus in this class of alloys and its analogy with the changes in volume illustrated in Figure 2b is clearly apparent.

Compared with the values specific to iron and nickel, the curve of the moduli as a function of the content is depressed, the maximum depression
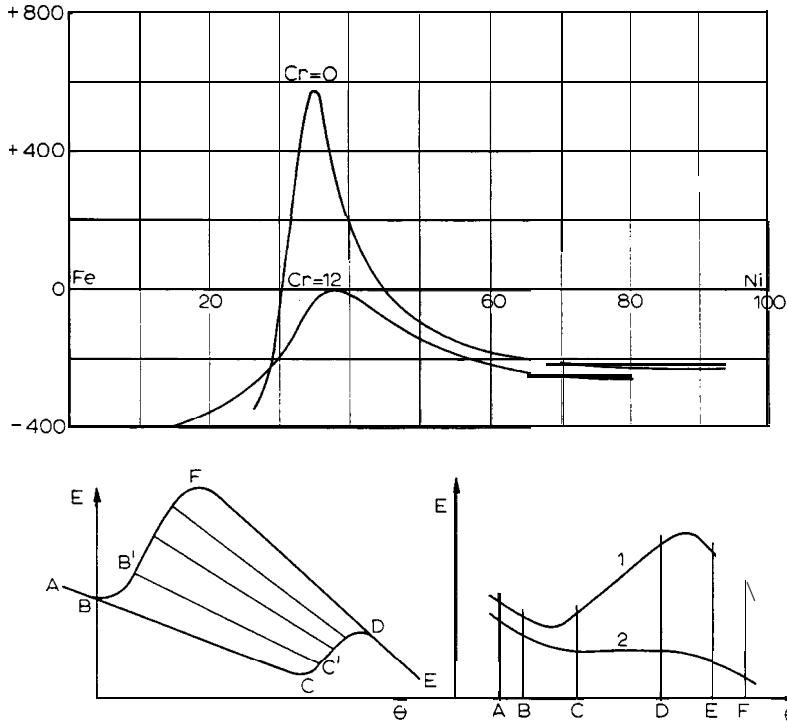


Fig. 4a.  Thermoelastic coefficients of standard iron-nickel alloys and of alloys with 12% additions of chromium.
Figs. 4b, 4c. Changes in elasticity modulus of an irreversible and a reversible alloy. The letters in this diagram correspond to those in diagrams 1, 2 and 3.

occurring in the invar region, where it reaches about one quarter of the value that would be indicated by the rule of mixtures. The minimum modulus at ordinary temperature is thus close to $1.4 \times 10^{12}$ c.g.s.units.

*Variation of modulus with temperature* - Interest centres mainly on studying the variations of the modulus with temperature, whether flexion or torsion is involved.

In the case of the latter I merely performed a rapid examination which showed me how, by an adaptation, it was possible to deduce the thermal coefficients from those which govern the flexion. P. Chevenard went into it very thoroughly. In all cases the torsional pendulum method was used.

To study the thermoelastic coefficient in the case of flexion the instrument chosen is the chronometer, this being readily available, very small, and yielding directly a result that can be used in practice. Its drawback is that successful manufacture and fitting of the balance spring require an expert. For this study I had the valuable assistance of a skilled regulator, Paul Perret, who had taken the initiative in offering me his services soon after my initial publications on invar; later, the experiments were conducted under my control by the technical laboratories of the Sociétè des Fabriques de Spiraux Réunies.

The balance spring is made of the alloy under examination and mounted on a balance of a known metal and the assembly constitutes the regulator of the chronometer.

The thermal changes in the period of oscillation of the balance driven by the balance spring involve the expansions and the variations in bending modulus  simultaneously.

Contrary to a very widespread idea, the expansion of the balance spring alone would reduce the oscillation period, i.e. the chronometer would be fast at high temperatures, the reason being that the transverse dimensional changes occur four times, and the changes in length only once, in determining the elastic moment. For its part, the expansion of the balance causes the chronometer to go slowly at high temperatures in accordance with the generally accepted idea. In the case of a steel balance spring and a brass balance the effects of the expansion largely cancel out each other. But a chronometer so equipped loses II seconds a day for each degree rise in temperature; this loss is due almost entirely to the temperature-induced change in modulus, the. coefficient of which is negative.

For the reversible alloys the values of the thermoelastic coefficient, $dE/d\theta$, exhibit equally as strange an anomaly as that of the expansibility. The trend

is shown by the top curve (Cr = o) in Fig. 4a. Beginning at a negative, i.e. normal value, the thermoelastic coefficient climbs very steeply, concurrently with increasing nickel content, crosses the zero axis, continues to climb, passes through a pronounced maximum in the invar region, then turns down and carries on more slowly to the value proper to nickel. Thus, for a whole category of alloys, the thermoelastic coefficient is positive; when bent at ordinary temperature, these alloys tend to straighten out when heated.

If not Young's modulus but the coefficient of deformability of the alloys had been plotted as a function of temperature, the sign would have altered and the curve, starting from positive values, would have exhibited a minimum. Its shape would then not have been very different from that of the expansibility curve and the common origin of the two anomalies would have been evident.

Owing to the low elastic limit of the metals at high temperatures the study of their bending deformations is very delicate there. Nevertheless, the application of the rule of corresponding states enables us to presume the characteristic of the modulus. Its general trend is shown by curve I, Fig. 4c, where the minimum and maximum relate to the two points at which the over-all curve intersects the zero axis; the regions AB, etc..., which have already appeared in the study of the magnetic properties and expansibility, also occur in this curve.

### Ternary alloys

The alloys whose properties have just been described are not pure mixtures of iron and nickel free from additions. They are, in fact, complexes in which solely the main constituents are entirely predominant since they form more than *99%* of the total mass of the alloy. The additions are close to the indispensable minimum although it is possible to raise the quantity to a second limit and thus obtain ternary or quaternary alloys proper whose properties it is interesting to know.

Apart from the importance of this study considered from the physico-chemical point of view, these alloys may possess properties which render them particularly suitable for practical problems. Thus a sufficient addition of manganese makes the alloys suitable for casting, whereas chromium or carbon, or the two together, raise the elastic limit and make them better for manufacturing into springs.

My studies dealt in most detail with iron-nickel-manganese alloys and they
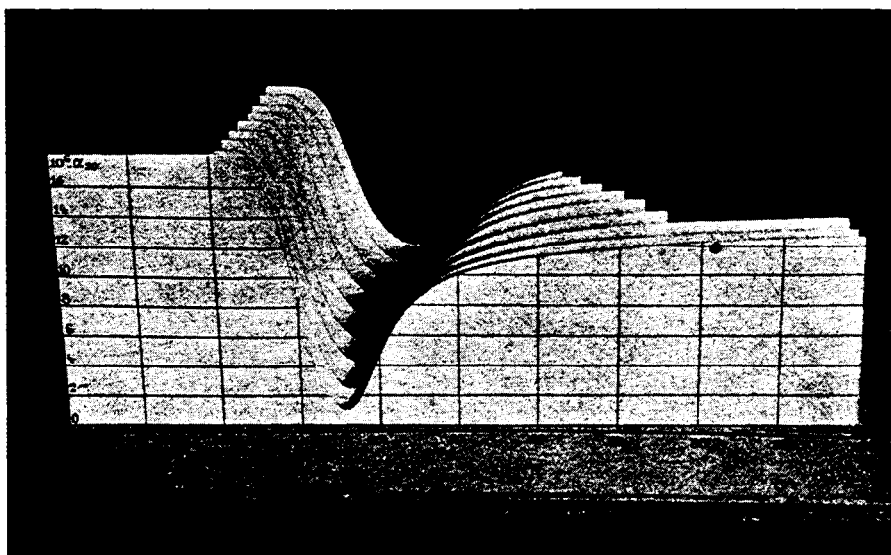
Fig. 5. Triangular diagram of the iron-nickel-manganese alloys.

were sufficiently thorough to enable a family of curves Fig. 5 to be plotted on the principle of Guthrie's triangular diagrams.

The first curve is that of the standard alloys containing 0.4% manganese, the others refer to whole per cents, from 1 to 8. This three-dimensional diagram shows that the minimum rises rapidly, at the same time shifting towards the higher nickel contents.

Studies of the action of chromium, copper and carbon, although less extensive, have enabled an accurate plot to be obtained showing the trend of both value and position of the minimum. The two diagrams Figs. 6a and 6b illustrate this trend. Slight extrapolation to higher manganese content shows that when this metal is present to the extent of 10%, in the alloy of least expansibility, it reduces the anomaly by about a half.

The curves in Fig. 7 represent the true expansibilities at 20°C for the limit contents of the additional constituent. The study of their action was of very special significance in connection with a practical problem, the solution of which I was searching for. Essentially the problem was to improve the conditions under which it was possible to prepare an alloy with a zero thermoelastic coefficient, an alloy with invariable elasticity modulus to which I had given the name *elinvar* in advance to define the programme of its preparation.

The binary alloys provide a double solution to the problem. However,
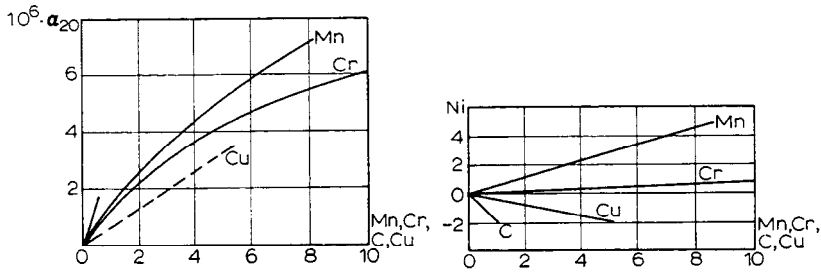
Figs. 6a, 6b.  Trend of minimum for nickel steels containing varying additions of man-
ganese, chromium, copper and carbon.
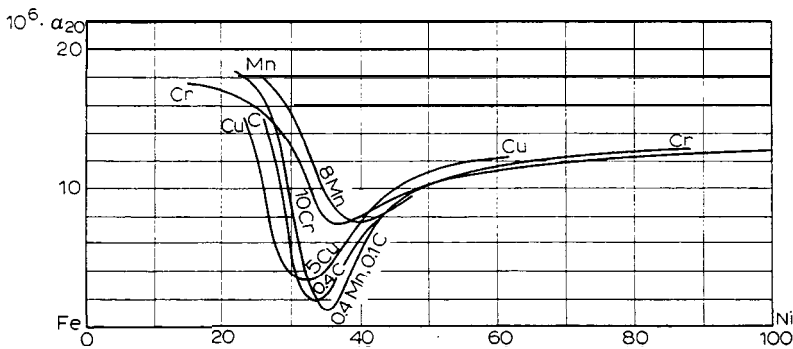


Fig. 7.  True expansibilities at 20°C of nickel steels with additions of manganese, chro-
mium, copper and carbon to the limits attained by the experiments.

on the one hand the thermoelastic coefficient curve cuts the zero axis at a
very steep angle so that the smallest errors in composition, and even mere
defects in the homogeneity of the alloy, lead to a property different from
that sought; on the other hand the zero value is nothing other than the min-
imum or maximum of a variation curve and this value exists practically only
over a small range of temperature.

    Yet if we consider the raising of the expansibility minimum in ternary
alloys and the analogy between the elastic and expansibility anomalies, we
can be certain beforehand that suitable additions will give a thermoelastic
coefficient curve tangential to the zero axis and, hence, leading to the ready
preparation of elinvar. Furthermore, the rule of corresponding states shows
that the whole of the modulus values for one and the same alloy will ex-
hibit neither a maximum nor a minimum, but rather an inflexion, probably
very extensive and almost horizontal.

These two conditions are indicated in the bottom curve (Cr = 12) in Fig. 4a and in curve 2 of Fig. 4c (region CD); they characterize elinvar.

Direct experiments have established the amount of the additions needed to make elinvar. The elastic limit conditions directed research mainly towards the hardening additions: chromium tungsten and carbon. The number of solutions is infinite since to reduce the anomaly the additions can replace one another continuously. In his torsion experiments, Chevenard found true elinvar with a 12% addition of chromium, the other auxiliary substances being kept close to the indispensable minimum.

### Progressive or transient changes

The quite remarkable properties of nickel steels hold much promise for metrology. However, the hopes that had been founded on their use were for long restricted by a real defect which they have, notably a slight instability detected by accurate measurements of the length of test bars repeated over the years or else performed after a variety of heat treatments.

The character of these changes varies from one alloy to another and to describe it effectively it must be related to a particular alloy.

A bar of invar, for example, cooled in air from the forging temperature and kept at ambient temperature extends over the years at rather a fast rate to begin with, then at a progressively slower rate such that after twenty years very accurate measurements can only positively detect the change that occurs in one year.

If the cooling had been interrupted by a period at $100°C$, the bar would have extended at an incomparably higher rate than at ordinary temperatures and, after about a hundred hours, the movement would almost have ceased to be perceptible. Generally speaking, the rapid initial rate is an exponential function of the temperature, such that each time the temperature increases by $20°C$, the rate increases by a factor of about 7. This movement thus obeys the laws formerly established by Arrhenius.

From almost nothing at $100°C$ the movement re-ensues when the bar is brought to ordinary temperature but it is much less than in the absence of an intermediate stage. If after a few months or years have elapsed the bar is reheated to $100°C$ it can be seen to contract rapidly and revert to its length after the first heating.

Thus, at each temperature, the length of the bar tends towards a limit

value; between 0° and 100°C these values lie practically on a curve, the ordinates (negative) of which are proportional to the square of the temperature, starting from common zero. This rule continues beyond 100°C, then the rate of change decreases and when the alloy passes into the non-magnetic state, it undergoes only very slight changes.

The difference between the ultimate lengths of the bars at 0° and 100°C is of the order of 30 millionths for standard invar. The first extension, at 100°C, after the forging temperature, has about the same value. However, the magnitude of these changes is a steep function of the nickel content. Thus, when this content is increased from that corresponding to invar the magnitude of the changes diminishes rapidly and there is no change when the nickel content attains 42%; the change then reverses, passes through a negative minimum then continues to increase and ceases perceptibly when the nickel content reaches 70%.

A number of very significant results recently emerged from my study of ternary alloys in the region of instability.

I found, one after another, that the presence of manganese and of chromium reduces the instability while the presence of carbon aggravates it. By means of experiments in which, through the offices of the Aciéries d'Imphy, the carbon additions were made with the ultimate degree of accuracy, I found that the instability is proportional to the carbon and that consequently alloys from which all carbon had been removed would be perfectly stable.

However, ferric alloys cannot be altogether freed from carbon and it might be thought that invar will always retain a slight degree of instability.

The cause of this instability appeared to me to be probably in the transformations of cementite ($Fe_3C$), a compound which forms almost always when iron and carbon occur together and which, again, undergoes transformations with accompanying change in volume.

The answer to the instability problems will thus be to eliminate the cementite. The method is simple, consisting in introducing into the alloy a constituent having a strong affinity for carbon, e.g. chromium, tungsten or vanadium.

Reducing the carbon content to the minimum lowers the expansibility; the supplementary constituent raises it slightly. The matter is novel and the best conditions have not yet been established nor, more especially, achieved. But even now it has been possible to obtain alloy castings, whose expansibility remained that of a good quality invar and whose instability was reduced to one tenth of that of standard invar.

The slow changes in the elastic properties of the alloys, associated with those of their dimensions, have not been studied systematically. However, it may be taken as almost certain that they obey analogous laws in the sense that any increase in volume entails a reduction in the modulus. The ratio of the relative changes in these two properties, either in the transformation of the irreversible alloys, or else in just the expansion of normal metals and alloys, is of an order of magnitude between 20 and 30, i.e.an increase in length is accompanied by a relative decrease in modulus greater by a factor of twenty to thirty.

In the absence of a direct investigation it is possible with a certain degree of probability to guess the form of the laws governing the progressive or transient changes in elastic properties, and even the order of magnitude of their  parameters.

*Applications*

The unusual properties of nickel steels afford an approach by entirely new methods to the generally simple solution of technical and scientific problems hitherto regarded as difficult or complex.

The elasticity or expansion anomalies, and even the magnetic transformations of these alloys, have led to certain applications, the enumeration of which will be sufficient to make them immediately evident.

The presence in a magnetic circuit of a component made of an alloy with approximately the composition at which magnetism disappears rapidly alters the properties of that circuit as a function of temperature. If, say, this component is the armature of a magnet, the mutual attraction will decrease with increasing temperature until it disappears altogether. This circuit can thus be applied as an automatic temperature limiter; for that purpose it is sufficient to load the armature with an appropriate mechanical component. With the alloy piece it is also possible to make a shunt across the magnetic field, the value of which decreases with increasing temperature such that the field proper tends to reinforce itself. Proceeding from this idea E.Meylan has equipped measuring instruments with temperature compensation for field variations.

Furthermore, along the expansibility curve there is a region close to 45% Ni in which the successive alloys have the expansibility of all the usual types of glass. These alloys could be used to make constant-grip optical mountings,

or else conductor wires for incandescent lamps. In the latter case the wire, from which the large quantity of occluded gas has first been removed by prolonged heating in vacuo, readily fuses to the glass. The *platinite* so formed has, for this purpose, almost completely supplanted platinum which is thus freed for other applications. The saving achieved in this way is approximately one hundred million crowns.

Elinvar, for its part, is suitable for making monofilar suspensions or, with a slight change in composition, for making tuning-forks, the period of which is independent of temperature. This information, which I announced in 1898, was confirmed in 1912 by Félix Robin who worked extensively on the study of nickel steel thermoelasticity.

This rapid survey clearly demonstrates the diversity of the problems which can be solved with the aid of nickel steels.

We shall now study in detail very refined applications, the method or scientific importance of which prompt a closer examination.

### *Measurement of length*

*General* - To determine the limits to which nickel steels can be used in constructing instruments for the measurement of length, it is necessary to know those of their properties which will have to be involved in each specific case.

These alloys take a wonderful polish; provided the manganese or carbon addition is not too close to the minimum they are generally free from pitting. Perfectly clean traces can be made on them. They are slightly oxidizable and are able to withstand several hours' immersion in cold water. After a few years in a moist atmosphere the polished surfaces are unimpaired or else covered with a very fine film which can be removed simply by rubbing gently with a soft leather; on the other hand acid vapours attack nickel steels quite rapidly and their action must carefully be avoided.

I should mention, however, that the alloys suitable for all the length measuring applications of invar are not exactly the same. Lengths are measured by means of rulers, the marked surfaces of which are observed through a microscope, or else by means of freely suspended wires, as we shall shortly see. The absence of pitting is an essential quality of the metals used for marked standards; for wires a high elastic limit is required. In the first case the manganese content will be increased, in the second a slight amount of chromium will be introduced into the alloy. Carbon would be useful for both but

we have seen that it is the cause of instability; hence it must be used as little as possible.

Although on the one hand it is true that the finished wires must have a high elastic limit, their manufacture on the other hand requires high malleability. These properties appear contradictory to a certain degree. Nevertheless the invar type alloys achieve them in the sense that in the annealed state they are highly extensible but they harden rapidly when mechanically deformed so that if the initial length of an annealed wire has been doubled by drawing, it is capable of quite large elastic deformations.

The instability of nickel steels imposes, as has been stated, a limit to the field of applications for which one might initially be tempted to use them. However, providing that a measuring standard made of, say, invar can from time to time be checked against a perfectly stable standard, it may with almost complete reliability be used as an interpolation instrument; in all cases where its temperature is difficult to determine or cannot be determined with accuracy its value becomes paramount.

The detailed study of the laws governing the changes undergone by invar and the alloys close to it have in the past enabled the results to be freed from most of the effects of these changes. And, for the future, the prospect of making a perfectly stable invar removes most of the objections that might be raised to the use of low expansion alloys in very high precision measurements.

*Geodetic base-lines* - Every geodetic grid relies on one or more base-lines, each comprising a length marked out on the ground between fixed limits, the intervening distance being as large as permitted by the circumstances and generally of the order of about ten kilometres and measured with the maximum accuracy.

The determination of this distance, in the open air and under frequently ill-defined conditions of temperature, calls for careful precautions which geodesists have persistently striven to elaborate during the last century. During the first three-quarters of the century they tried mainly to improve accuracy largely regardless of the cost of the operations. Then a reaction set in; it was realized that there was more to be gained, as regards dividing the work between measuring angles and measuring lengths, by increasing the number of base-lines or extending them at the cost of a slight loss in measuring accuracy.

E. Jäderin, who assembled and codified the sparse methods, invented new

processes and developed a complete technique, was the chief proponent of this reaction which gave rise to a new conception of the organisation of geodetic grids.

In traditional geodesy the measuring instrument was the rigid rod (generally 4metres long) in conjunction with microscopes sighted on the end-marks to fix their distance on the ground; then, after the rod had been moved a distance of its own length, the position of a third microscope was fixed by reference to the second, and so on. The method was accurate but costly. To avoid the action of radiation the instruments and the observers were accommodated in mobile huts. The instruments themselves were heavy and certain preparatory steps were required before they could be placed in position on the ground. The full team required for the measurements thus totalled about sixty men and, on days when everything went off smoothly, one hundred lengths, i.e.400metres, could be measured.

The measuring instrument proposed by Jäderin is a wire under tension at constant load and which is used to determine the relative distances of a series of lightweight marks that are readily transported and placed in position.

The length given to the wire by Jäderin is normally 24metres, which reduces to one sixth the number of spans. The ground no longer needs preparation; with longer wires, if need be, ravines or rivers can be crossed (the longest wire used so far was 168metres), all with 12 to 15 men; in short it is much more economical to use and its rate of measurement is quite different from that of the ruler and microscopes.

Temperature remained a very difficult point, of course.

Jäderin had seen, quite rightly, that the best procedure was to apply the principle adopted by Borda and Lavoisier, namely to measure each of the spans in succession by means of a steel wire and a brass wire, the difference between them giving at each moment the common temperature. However, the method developed before the discovery of invar was substantially less accurate than the ruler and microscope method, since the temperature remained unreliable; but the method as a whole was there in the rational form of a much better balance between the number of base-lines and the number of triangles.

Immediately he knew of the existence of invar, Jäderin, who was busy preparing for the measurement of base-lines for the Swedish-Russian Spitzbergen Expedition requested me to supply him with the necessary wire. I had already given the matter my attention and had had the Aciéries d'Imphy prepare wires suitable for base-line measurements, which wires had been

used in a number of preliminary experiments. The effect of drawing on the expansibility was already partly known and it was possible to supply the Expedition with wires that were practically non-expanding.

The success of the Spitzbergen measurements in 1899 was quite remarkable. A letter from Jäderin dated Treurenberg Bay, September 13, 1899 actually states the following:

<<I am now pleased to inform you that our base-line measurements carried out this summer were completely successful. In both the outward and return directions we measured a base-line of 10,024metres. So far we have made only a single provisional calculation which shows a discrepancy of merely 19 mm. We made no allowance for the expansion of the wires.>>

And the letter closed with these words which, through their infinite melancholy, seem to me full of fine courage:

<<The last of our boats leaves tomorrow for Stockholm and until June 1900 we shall be left completely separated from the world. Only once post has arrived for us; part of it seems to have gone astray.>>

This message from the ends of the inhabitable world was for me the most powerful and the most valued encouragement. Benoit and I performed our own experiments with greater urgency and when, a year later, the Geodetic Association met in Paris, while the results submitted by the Swedish-Russian Expedition created a tremendous sensation, we were able to assert that a very high accuracy ought to be attained by an even greater perfection of the method, to which we were prepared to devote our utmost efforts. The Association passed a resolution to that effect and the committee vested with the permanent authority over the International Bureau finally entered this project on its programme.

A wall base-line which was built at once has been used since 1901 for studies which have been continuously in progress ever since.

The observations which we have made in about twenty years now number some hundreds of thousands. However, our labours have been amply rewarded since we have been able to define the conditions under which invar wires which have first been specially treated, then determined at the Bureau or in any standardization laboratory, can be transported in the form of a coil to the base-line area, then uncoiled and used without their characteristics altering.

By eliminating temperature-induced errors from measurements altogether, the use of invar wire appreciably raised the accuracy of the method. To take advantage of the method's potentialities Benoit and I were led to make

a partly new equipment which now ensures that in the measurement of each span - normally 24metres - errors of the order of a hundred thousandth of the measured length will never be made. In accordance with the principle of the addition of errors, a length of 100 spans will thus not be subject to errors of the order of one millionth as a result of the observations.

A great many base-line measurements have been carried out in recent years using invar wire. The checks obtained either by the determinations performed in the outward and return directions or else by successive measurements with different wires have revealed that an accuracy of one millionth is quite common. Since the equipment is very easily installed it is now possible to use sites which would have been quite unsuitable with the old instruments comprising rigid rulers and microscopes. Moreover, in view of the speedy installation and the long spans coupled with the light weight and ready transportability of the equipment, it has been possible to reduce the number of personnel to about one fifth, and increase the speed tenfold; a well-trained team is capable of measuring up to 5km in a day. Thus, the over-all saving in the measurement of base-lines is about 98%.

The increase in the number of base-lines and their greater length strongly reduce the effects of errors in the measurement of angles and the requirements which traditional geodesy was obliged to impose on them can be relaxed; the result is a second appreciable saving.

*Non-expanding transmissions* - From the point of view of the principle I shall confine myself almost entirely to the matter which has just been discussed by mentioning transmission over a fixed distance by means of an invar wire.

Its specialist applications are many. On railways, for example, there are a great many transmissions between a manoeuvre in a signal box and a movement received by a signal on the track. The expansion of the control wires disturbs the transmission: in the case of a rather severe temperature drop it may cause the signal to operate prematurely, and if the temperature increases rapidly, the expansion may completely neutralize the manoeuvre. Invar wire has afforded a means of overcoming these drawbacks and of guarding against the resultant dangers; however, its use has not been very widely adopted since, except for in special cases, the price of the alloy is considered prohibitive.

In contrast, no such limitation is involved in the acceptance testing of metal structures where a wire, fixed at one end to the structure itself, faithfully transmits its movement to a recording instrument.

The study, interesting in itself, of the vertical movements of the Eiffel Tower, plainly demonstrates the variety of applications of which this technique is capable.

Invar wire has greatly facilitated this operation. A wire of this type, fixed at its lower end to a peg in the ground, was attached at the other to a lever mounted on the second platform of the Tower and which actuated a recording instrument; a damping device integral with the lever compelled the latter to return slowly to the position assigned to it by the straight wire when it had momentarily been bent by a gust of wind. The experiment showed that, however violent the movement of the air, moments of calm occur from time to time which are sufficiently long to allow the lever to return to its rest position. Thus, its limit positions indicated the true movements of the
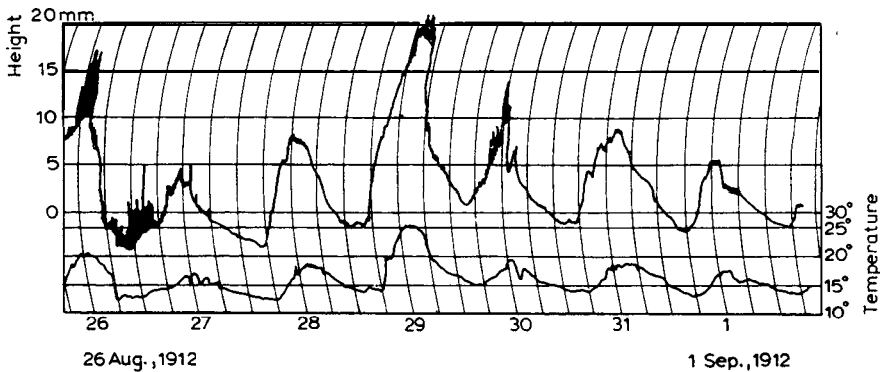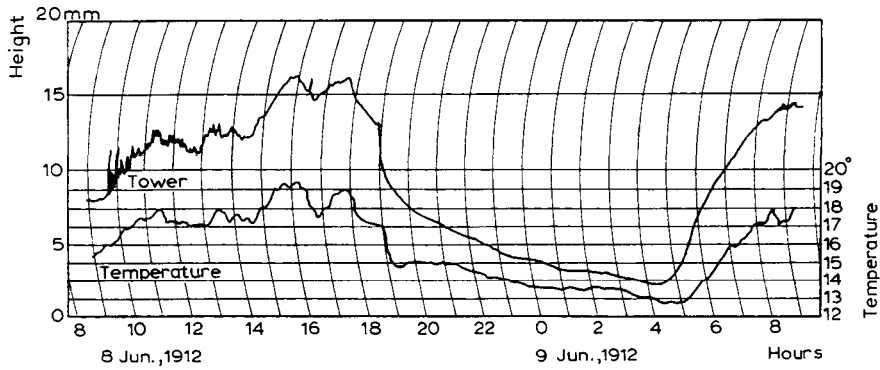




Fig. 8. Daily movements of the Eiffel Tower (a downpour at 19 hours caused a sudden temperature drop).

Fig. 9. Movements of the Tower under variable summer conditions (stormy week).

Tower, while a kind of tail, starting from the envelope, recorded the gusts of wind.

Figs. 8 and 9 show two examples of the movements observed. The first was obtained using a recording drum which rotated once per day, the other with one rotating once weekly. The lower curves are those of the thermograph.

When inspecting the two series of curves it is impossible not to be struck by their extraordinary similarity, which is such that each small inflection of one has its counterpart in the other. Thus the Eiffel Tower appears as a gigantic thermometer of high sensitivity, notwithstanding its enormous mass.

### *Measurement of time*

Once time measuring instruments had become sufficiently accurate it became evident that their action was affected by temperature and attempts were made to guard against this by fitting them with devices known as compensators, the effectiveness of which had been demonstrated by a century and a half of experience, although they complicate the already complex mechanisms of clocks and watches.

Reference has been made earlier to the causes of the temperature-induced changes in the functioning of watches; they are very different from those specific to clocks, so that the two problems have to be treated separately.

The compensated pendulum in clocks - Of the various compensating devices invented to offset the influence of temperature on clock pendulums, the most widespread by far a few years ago was Graham's, which took advantage of the upward expansion of mercury in a vessel suspended from the pendulum rod to cancel out the effects of the rod's downward expansion.

Invar which has been treated in various ways is capable of all possible expansions between two limits close to zero and a bob of any desired metal will, when attached to the nut of the previously selected rod, correct the extensions of the rod by its upward expansion.

The advantages are many. Apart from the presence in the oscillating system of a liquid, Graham's pendulum has the drawback of being actually compensated only provided that the temperature is uniform from top to bottom of the clock case, a condition which is fully satisfied only in competently constructed installations.

It will be noticed that for this specific application, the instability of or-

dinary invar does not matter since the state of a clock must be checked from time to time, so that a slow change in its daily rate entails no error in the time measurement. After a few year's operations, this change will be reduced to two or three hundredths of a second per year.

*The compensating spring of watches* - A watch fitted with a steel balance spring and a brass balance loses, as we have seen, about II seconds per degree per day, almost the whole of this change being attributable to the variation in Young's modulus of the metal from which the spring is made. A correcting mechanism for watches is thus indicated.

In Ferdinand Berthoud's <<marine clocks>> this mechanism comprised a bi-metallic plate which automatically modified the active length of the spring. In 1775 Arnold invented the compensating balance which was soon per-fected by Earnshaw and which consists of a diametral arm, from the two extremities of which project semi-circular, bimetallic plates, steel inside, brass outside, which curve in towards the axis when the temperature rises, so re-ducing the moment of inertia of the assembly in the mean ratio of the change undergone by the elasticity modulus of the balance spring.

If the steel of the spring is replaced by a nickel steel of composition such that the maximum or minimum modulus occurs at ordinary temperatures, the watch, fitted with a monometallic balance, will function alike at two temperatures at either side of the ambient, e.g. 0° and 30°C, and between the two will gain or lose most at 15°C. The trend of the curve is such that the maximum gain (the loss occurs with alloys having a low elastic limit) will be 20 to 25 seconds per day compared to the running at extreme tem-peratures, this being twelve or fifteen times less than the discrepancies ob-served in the case of the steel balance spring. This progress has been considered so important by watchmakers that almost three million watches are equipped annually with the compensator spring.

*Correction of secondary error of chronometers by the integral balance* -Arnold and Earnshaw's balance does not compensate entirely the action of temperature on the rate of watches. Ferdinand Berthoud noticed in 1775 a <<secondary error>> which Dent found in 1832 for the balance, and which consists in the fact that a watch equipped with a steel balance spring compensated by a steel-brass balance gains 2 to 3 seconds per day at 15°C, if it functions correctly at 0°C and 30°C.

Considerable efforts were made with a view to eliminating Dent's error.

We shall see how a rational application of a nickel steel afforded a very simple means to achieve that.

The reason for Dent's error lies in the following fact: the elasticity modulus of the balance spring varies with temperature in accordance with a pronounced curve OS (Fig.10a). The action of the balance, for its part, is controlled by the difference in expansibility between the brass OL and the steel OA, expressed by functions in which the coefficients β are very approximately the same. Their difference OB will hence be linear and the algebraic sum of OS and OB, i.e. OC, will leave a quadratic remainder.
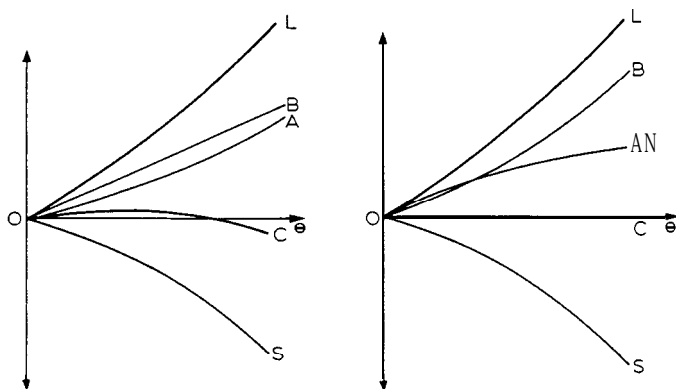


Figs. 10a, 10b. Diagrams showing the cause of the secondary error of chronometers and the principle of its correction.

Let us now replace OA by a curve OAN (Fig. 10b) representing the expansibility of a nickel steel with negative β. The difference with OL will be a curve OB which can be made symmetrical with OS and thus a zero algebraic sum is obtained at all its points.

In 1899 I made the design calculations for such a balance, the low expansion constituent of which was a steel containing 45% Ni, and in 1900 two Swiss chronometer makers, P. D. Nardin and P. Ditisheim, achieved complete temperature compensation by its aid.

From then on the new balance has replaced the old practically everywhere in precision chronometers. Rate logs thus became obsolete, not only owing to the elimination of the secondary error but because once chronometers no longer had this error it became important to attempt to correct the lesser defects. In fact, the rates of the best chronometers today are four to five times less erratic than twenty years ago.

*The complete solution to the problem of compensation by the elinvar balance spring* - For more than ten years I thought that the use of nickel steels had led to all the fundamental improvements in compensating mechanisms of which they were capable. Yet, in about 1912, a faint inkling occurred to me of a means to achieve perhaps the ultimate solution to the compensation problem. When studying ternary alloys I had just had a glimpse of the simultaneous reduction in the anomaly of expansibility and thermoelasticity.

A series of experiments was embarked on during the following year using two series of alloys with varying nickel contents and with 5% and 10% additions of chromium. The maximum thermoelastic coefficient in this second series was already very close to that of elinvar and only a very slight modification of the composition was needed to produce an alloy forming balance springs which in conjunction with monometallic balance wheels vouchsafed that the watches in which they were fitted ran almost the same at various temperatures and were almost free from the secondary error. The problem was hence very close to its solution. Then, after a pause, the experiments could be resumed; they recently resulted in the manufacture of balance springs which, in conjunction with a suitably chosen monometallic balance, constitute a regulating device almost entirely immune to temperature changes.

Such a simple solution as this to a long standing problem is regarded as revolutionary by the most competent chronometer makers. However, its very simplicity, if its retention is insisted upon, conceals a further slight defect.

The particular and immense advantage of the new combination is that of leading very close to perfection at the first attempt by the association of a balance spring having a low, constant thermoelastic coefficient with a balance of suitable expansibility. For industrial manufacture the balance metal will be matched as closely as possible to the requirements of the balance spring; the range of expansions between invar and brass affords ample scope for doing so. Nevertheless once the combination has been found it is not, at least in its immediate form, suitable for those progressive and meticulous small alterations which make the task of the regulator an art at once so difficult and so exciting.

To reduce the scope of this reservation to its correct proportions forthwith, I should state that at the present time it is very common for the combination of a balance spring and monometallic balance to be manufactured. the temperature-induced error of which is less than one hundredth of that which would occur were a steel spring used.

Currently the situation is that whereas the compensating spring used to be restricted to use in ordinary watches, it is now becoming established in the precision watch sector; at present it is still only barred from precision chronometry. However it has only just appeared and it would be presumptuous to think that it has reached the limit of its perfection at the first attempt.

The simplicity of the new compensating mechanism entails many advantages. Bimetallic plates invariably upset regulators slightly who see in them a possible cause of instability; deformations by centrifugal force necessitate ensuring that the large and small arcs are isochronous by slight alterations to the shape of the balance spring; lastly the rectangular shape and the presence of setting screws cause air to be entrained, so giving rise to a <<barometric coefficient>> whose value is sufficiently high for the changes in atmospheric pressure to constitute in certain circumstances the essential cause of rate variations in the present state of chronometry. On the other hand it is easy to taper the cross-section of a monometallic balance wheel, reducing as far as possible the entrainment of air. These various points enhance the relative advantages of the new balance spring and should justify relaxing the stipulations governing the ultimate limits of compensation.

### Conclusion

Let us now glance back to the origins of the studies of which the results have just been reported. The point at issue was essentially to look for a metal having qualities which would enable it to be used to make standards of length that are inexpensive while satisfying metrological requirements. An initial solution had been found which required only slight refinement and it was during the search for this slight refinement that an unsuspected anomaly came to light which was a direct manifestation of the struggle between the various states of iron to which the association of nickel gives an unexpected shape, creating a class of alloys whose properties, unique so far, satisfy in a quite unhoped-for manner the wishes which metrologists would have formulated had it not been assumed that such properties could not exist in metals.

Then the problem broadened: from the measurement of length, which was the only aim of the original programme, the measurement of time arose of its own accord as a direct and to some extent obvious consequence, so true is it that in metrology everything is related and that a carefully executed measurement invariably entails generalizations.

The whole of the research programme required the constant collaboration of a factory and a laboratory. The great advantage of cooperation of this type is nowadays commonly appreciated and it would be superfluous to insist on it except to highlight a particular feature.

When in the spring of 1896, the Société de Commentry-Fourchambault & Decazeville undertook to assist a programme of research which, failing such assistance, would not have advanced beyond its initial stages, they did so without the directors imagining that they would be rewarded with anything but the satisfaction of having lent effective assistance to a task of scientific exploration. But the meticulous examination to which the alloys were subjected, and the increasingly stringent requirements imposed on the company as regards the compositions as well as the treatments, led, in the jointly explored field, to the creation of a kind of precision metallurgy, the result of which has been the manufacture of products considered impossible a few years ago.

That has been a new and unexpected outcome of the scope of precision measurements. Demanding unflagging and occasionally laborious effort of those who apply themselves to it, precision measurement research could not long be pursued without the guidance and illumination of an ideal of perfection. For the research worker himself, this ideal stimulated by a belief in the utility - even afar off - of every unselfish effort is his mainstay at all times and the counsellor of every initiative.

The highest approval which you have just conferred on my work highlights a task stretching back a quarter of a century and for that reason I feel obliged right here to express my deepest gratitude to the illustrious members of the Nobel Committee and of the Swedish Academy of Sciences, as well as to the memory of Alfred Nobel. From generation to generation my descendants will look with pride on the magnificent diploma and the Nobel medal, treasured testimony of your kindness and esteem. But also I wish to express my gratitude to you on behalf of the International Bureau which I have served for thirty-seven years and whose existence reflects at this moment the dramatic changes occurring in the world. Next I am grateful to you on behalf of metrology on which the conferment of a Nobel Prize casts a bright lustre well-fitted to commend it as a vocation. Lastly my gratitude is on behalf of the two countries with which my life is associated: Switzerland, of which I am a citizen and which I left equipped for life, and France, where I have known so many esteemed friendships.

# Biography

Charles-Édouard Guillaume was born at Fleurier, in the Swiss-Jura, on February 15, 1861. His grandfather had left France for political reasons during the Revolution and established a watchmaking business in London. The business was carried on by his three sons but Charles' father, Édouard, eventually returned to settle in Fleurier.

Guillaume received his early education in Neuchâtel before going to the Zurich Polytechnic where he obtained his doctor's degree. He spent a short time as an officer in the artillery before entering the International Bureau of Weights and Measures, as an assistant, in 1883. He became Associate Director in 1902 and from 1915 until his retirement in 1936, he was Director of the Bureau. He remained as Honorary Director from 1936 until his death.

During his brief military career, Guillaume studied mechanics and ballistics but his earliest investigations at the bureau were with thermometry. He carried out important investigations on corrections to mercury-in-glass thermometers and he was responsible for the detailed calibration of thermometers used at the Bureau in the establishment of the thermal expansions of the standards of length. He was concerned in initial work on the International Metre and undertook a determination of the volume of one kilogram of water by the contact method.

A chance observation by Guillaume on the coefficient of expansion of nickel-iron alloys led to a systematic investigation of a whole series of alloys and the discovery of invar, an alloy with a very low coefficient of expansion; elinvar, for which the thermoelastic coefficient is practically zero, i.e. Young's modulus constant, over a considerable temperature range; together with other useful alloys. The applications of invar were quickly recognized and the material was used in rapid methods for the measurement of geodetic baselines. The alloy is widely used in instruments of precision, such as thermostats and pendulums of astronomic clocks. Guillaume's total compensating balance for high-grade watches and chronometers, which eliminates the secondary error, was perfected by an elinvar hair spring.

Guillaume's work is recorded in many papers published by the Bureau

and he has written, amongst other works, *Etudes* thermométriques (Studies on Thermometry, 1886), *Traite' de thermométrie* (Treatise on Thermometry, 1889), *Unités et Étalons* (Units and Standards, 1894), *Les rayons X* (X-Rays, *1896), Recherches sur* le *nickel et* ses *alliages* (Investigations on Nickel and its Alloys, *1898), La vie de la matiére* (The Life of Matter, 1899), *La Convention du Métre et le Bureau international des Poids et Mesures* (Metrical Convention and the International Bureau of Weights and Measures, 1902), *Les applications* des *aciers au nickel* (Applications of Nickel-Steels, *1904), Des états de la matiére* (States of Matter, 1907), *Les récent progrès du systéme métrique* (Recent progress in the Metric System, 1907, 1913). His book *Initiation à la Mécanique* (Introduction to Mechanics) has been translated into several languages.

He was appointed Grand Officer of the Legion of Honour and received honorary Doctor of Science degrees from the Universities of Geneva, Neuchâtel and Paris. He was a President of the Société Française de Physique and a member, honorary member or corresponding member of more than a dozen of the leading scientific academies of Europe.

Charles-Édouard Guillaume married Mlle. A. M. Taufflieb in *1888.* They had three children. He died on May 13, 1938.

Physics 1921

ALBERT  EINSTEIN

*<<for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect>>*

# Physics 1921

*Presentation Speech by Professor S. Arrhenius, Chairman of the Nobel Committee for Physics of the Royal Swedish Academy of sciences*

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen.

There is probably no physicist living today whose name has become so widely known as that of Albert Einstein. Most discussion centres on his theory of relativity. This pertains essentially to epistemology and has therefore been the subject of lively debate in philosophical circles. It will be no secret that the famous philosopher Bergson in Paris has challenged this theory, while other philosophers have acclaimed it wholeheartedly. The theory in question also has astrophysical implications which are being rigorously examined at the present time.

Throughout the first decade of this century the so-called Brownian movement stimulated the keenest interest. In 1905 Einstein founded a kinetic theory to account for this movement by means of which he derived the chief properties of suspensions, i.e. liquids with solid particles suspended in them. This theory, based on classical mechanics, helps to explain the behaviour of what are known as colloidal solutions, a behaviour which has been studied by Svedberg, Perrin, Zsigmondy and countless other scientists within the context of what has grown into a large branch of science, colloid chemistry.

A third group of studies, for which in particular Einstein has received the Nobel Prize, falls within the domain of the quantum theory founded by Planck in 1900. This theory asserts that radiant energy consists of individual particles, termed <<quanta>>, approximately in the same way as matter is made up of particles, i.e. atoms. This remarkable theory, for which Planck received the Nobel Prize for Physics in 1918, suffered from a variety of drawbacks and about the middle of the first decade of this century it reached a kind of impasse. Then Einstein came forward with his work on specific heat and the photoelectric effect. This latter had been discovered by the famous physicist Hertz in 1887. He found that an electrical spark passing between two spheres does so more readily if its path is illuminated with the light from another electrical discharge. A more exhaustive study of this interesting phenomenon was carried out by Hallwachs who showed that under certain con-

ditions a negatively charged body, e.g. a metal plate, illuminated with light
of a particular colour - ultraviolet has the strongest effect-loses its negative
charge and ultimately assumes a positive charge. In 1899 Lenard demon-
strated the cause to be the emission of electrons at a certain velocity from the
negatively charged body. The most extraordinary aspect of this effect was
that the electron emission velocity is independent of the intensity of the il-
luminating light, which is proportional only to the number of electrons,
whereas the velocity increases with the frequency of the light. Lenard stressed
that this phenomenon was not in good agreement with the then prevailing
concepts.

An associated phenomenon is photo-luminescence, i.e.phosphorescence
and fluorescence. When light impinges on a substance the latter will oc-
casionally become luminous as a result of phosphorescence or fluorescence.
Since the energy of the light quantum increases with the frequency, it will
be obvious that a light quantum with a certain frequency can only give rise
to the formation of a light quantum of lower or, at most, equal frequency.
Otherwise energy would be created. The phosphorescent or fluorescent light
hence has a lower frequency than the light inducing the photo-luminescence.
This is Stokes' rule which was explained in this way by Einstein by means of
the quantum theory.

Similarly, when a quantum of light falls on a metal plate it can at most
yield the whole of its energy to an electron there. A part of this energy is
consumed in carrying the electron out into the air, the remainder stays with
the electron as kinetic energy. This applies to an electron in the surface layer
of the metal. From this can be calculated the positive potential to which the
metal can be charged by irradiation. Only if the quantum contains sufficient
energy for the electron to perform the work of detaching itself from the
metal does the electron move out into the air. Consequently, only light
having a frequency greater than a certain limit is capable of inducing a pho-
to-electric effect, however high the intensity of the irradiating light. If this
limit is exceeded the effect is proportional to the light intensity at constant
frequency. Similar behaviour occurs in the ionisation of gas molecules and
the so-called ionisation potential may be calculated, provided that the fre-
quency of the light capable of ionising the gas is known.

Einstein's law of the photo-electrical effect has been extremely rigorously
tested by the American Millikan and his pupils and passed the test brilliantly.
Owing to these studies by Einstein the quantum theory has been perfected
to a high degree and an extensive literature grew up in this field whereby

the extraordinary value of this theory was proved. Einstein's law has become the basis of quantitative photo-chemistry in the same way as Faraday's law is the basis of electro-chemistry.*

* Being too remote from Sweden, Professor Einstein could not attend the ceremony.

A LBERT E INSTEIN

# Fundamental ideas and problems
# of the theory of relativity

*Lecture delivered to the Nordic Assembly of Naturalists at Gothenburg\**
*July 11, 1923*

If we consider that part of the theory of relativity which may nowadays in a sense be regarded as bona fide scientific knowledge, we note two aspects which have a major bearing on this theory. The whole development of the theory turns on the question of whether there are physically preferred states of motion in Nature (physical relativity problem). Also, concepts and distinctions are only admissible to the extent that observable facts can be assigned to them without ambiguity (stipulation that concepts and distinctions should have meaning). This postulate, pertaining to epistemology, proves to be of fundamental importance.

These two aspects become clear when applied to a special case, e.g. to classical mechanics. Firstly we see that at any point filled with matter there exists a preferred state of motion, namely that of the substance at the point considered. Our problem starts however with the question whether physically preferred states of motion exist in reference to *extensive* regions. From the viewpoint of classical mechanics the answer is in the affirmative; the physically preferred states of motion from the viewpoint of mechanics are those of the inertial frames.

This assertion, in common with the basis of the whole of mechanics as it generally used to be described before the relativity theory, far from meets the above <<stipulation of meaning>>. Motion can only be conceived as the relative motion of bodies. In mechanics, motion relative to the system of coordinates is implied when merely motion is referred to. Nevertheless this interpretation does not comply with the <<stipulation of meaning>> if the coordinate system is considered as something purely imaginary. If we turn our attention to experimental physics we see that there the coordinate system is invariably represented by a <<practically rigid>> body. Furthermore it is assumed that such rigid bodies can be positioned in rest relative to one another

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\* The Lecture was not delivered on the occasion of the Nobel Prize award, and did not, therefore, concern the discovery of the photoelectric effect.

in common with the bodies of Euclidian geometry. Insofar as we may think of the rigid measuring body as existing as an object which can be experienced, the <<system of coordinates>> concept as well as the concept of the motion of matter relative thereto can be accepted in the sense of the <<stipulation of meaning>>. At the same time Euclidian geometry, by this conception, has been adapted to the requirements of the physics of the <<stipulation of meaning>>. The question whether Euclidian geometry is valid becomes physically significant; its validity is assumed in classical physics and also later in the special theory of relativity.

In classical mechanics the inertial frame and time are best defined together by a suitable formulation of the law of inertia: It is possible to fix the time and assign a state of motion to the system of coordinates (inertial frame) such that, with reference to the latter, force-free material points undergo no acceleration; furthermore it is assumed that this time can be measured without disagreement by identical clocks (systems which run down periodically) in any arbitrary state of motion. There are then an infinite number of inertial frames which are in uniform translational motion relative to each other, and hence there is also an infinite number of mutually equivalent, physically preferred states of motion. Time is absolute, i.e.independent of the choice of the particular inertial frame; it is defined by more characteristics than logically necessary, although - as implied by mechanics - this should not lead to contradictions with experience. Note in passing that the logical weakness of this exposition from the point of view of the stipulation of meaning is the lack of an experimental criterion for whether a material point is force-free or not; therefore the concept of the inertial frame remains rather problematical. This deficiency leads to the general theory of relativity. We shall not consider it for the moment.

The concept of the rigid body (and that of the clock) has a key bearing on the foregoing consideration of the fundamentals of mechanics, a bearing which there is some justification for challenging. The rigid body is only approximately achieved in Nature, not even with desired approximation; this concept does not therefore strictly satisfy the <<stipulation of meaning>>. It is also logically unjust&able to base all physical consideration on the rigid or solid body and then finally reconstruct that body atomically by means of elementary physical laws which in turn have been determined by means of the rigid measuring body. I am mentioning these deficiencies of method because in the same sense they are also a feature of the relativity theory in the schematic exposition which I am advocating here. Certainly it would be

logically more correct to begin with the whole of the laws and to apply the <<stipulation of meaning>> to this whole first, i.e. to put the unambiguous relation to the world of experience last instead of already fulfilling it in an imperfect form for an artificially isolated part, namely the space-time metric. We are not, however, sufficiently advanced in our knowledge of Nature's elementary laws to adopt this more perfect method without going out of our depth. At the close of our considerations we shall see that in the most recent studies there is an attempt, based on ideas by Levi-Civita, Weyl, and Eddington, to implement that logically purer method.

It more clearly follows from the above what is implied by apreferred states of motion)). They are preferred as regards the laws of Nature. States of motion are preferred when, relative to the formulation of the laws of Nature, coordinate systems within them are distinguished in that with respect to them those laws assume a form preferred by simplicity. According to classical mechanics the states of motion of the inertial frames in this sense are physically preferred. Classical mechanics permits a distinction to be made between (absolutely) unaccelerated and accelerated motions; it also claims that velocities have only a relative existence (dependent on the selection of the inertial frame), while accelerations and rotations have an absolute existence (independent of the selection of the inertial frame). This state of affairs can be expressed thus : According to classical mechanics <<velocity relativity>> exists, but not <<acceleration relativity>>. After these preliminary considerations we can pass to the actual topic of our contemplations, the relativity theory, by characterizing its development so far in terms of principles.

The special theory of relativity is an adaptation of physical principles to Maxwell-Lorentz electrodynamics. From earlier physics it takes the assumption that Euclidian geometry is valid for the laws governing the position of rigid bodies, the inertial frame and the law of inertia. The postulate of equivalence of inertial frames for the formulation of the laws of Nature is assumed to be valid for the whole of physics (special relativity principle). From Maxwell-Lorentz electrodynamics it takes the postulate of invariance of the velocity of light in a vacuum (light principle).

To harmonize the relativity principle with the light principle, the assumption that an absolute time (agreeing for all inertial frames) exists, had to be abandoned. Thus the hypothesis is abandoned that arbitrarily moved and suitably set identical clocks function in such a way that the times shown by two of them, which meet, agree. A specific time is assigned to each inertial frame; the state of motion and the time of the inertial frame are defined, in

accordance with the stipulation of meaning, by the requirement that the light principle should apply to it. The existence of the inertial frame thus defined and the validity of the law of inertia with respect to it are assumed. The time for each inertial frame is measured by identical clocks that are stationary relative to the frame.

The laws of transformation for space coordinates and time for the transition from one inertial frame to another, the Lorentz transformations as they are termed, are unequivocally established by these definitions and the hypotheses concealed in the assumption that they are free from contradiction. Their immediate physical significance lies in the effect of the motion relative to the used inertial frame on the form of rigid bodies (Lorentz contraction) and on the rate of the clocks. According to the special relativity principle the laws of Nature must be covariant relative to Lorentz transformations; the theory thus provides a criterion for general laws of Nature. It leads in particular to a modification of the Newtonian point motion law in which the velocity of light in a vacuum is considered the limiting velocity, and it also leads to the realization that energy and inertial mass are of like nature.

The special relativity theory resulted in appreciable advances. It reconciled mechanics and electrodynamics. It reduced the number of logically independent hypotheses regarding the latter. It enforced the need for a clarification of the fundamental concepts in epistemological terms. It united the momentum and energy principle, and demonstrated the like nature of mass and energy. Yet it was not entirely satisfactory-quite apart from the quantum problems, which all theory so far has been incapable of really solving. In common with classical mechanics the special relativity theory favours certain states of motion-namely those of the inertial frames- to all other states of motion. This was actually more difficult to tolerate than the preference for a single state of motion as in the case of the theory of light with a stationary ether, for this imagined a real reason for the preference, i.e. the light ether. A theory which from the outset prefers no state of motion should appear more satisfactory. Moreover the previously mentioned vagueness in the definition of the inertial frame or in the formulation of the law of inertia raises doubts which obtain their decisive importance, owing to the empirical principle for the equality of the inertial and heavy mass, in the light of the following consideration.

Let K be an inertial frame without a gravitational field, K' a system of coordinates accelerated uniformly relative to K. The behaviour of material points relative to K' is the the same as if K' were an inertial frame in respect

of which a homogeneous gravitational field exists. On the basis of the empirically known properties of the gravitational field, the definition of the inertial frame thus proves to be weak. The conclusion is obvious that any arbitrarily moved frame of reference is equivalent to any other for the formulation of the laws of Nature, that there are thus no physically preferred states of motion at all in respect of regions of finite extension (general relativity principle).

The implementation of this concept necessitates an even more profound modification of the geometric-kinematical principles than the special relativity theory. The Lorentz contraction, which is derived from the latter, leads to the conclusion that with regard to a system K' arbitrarily moved relative to a (gravity field free) inertial frame K, the laws of Euclidian geometry governing the position of rigid (at rest relative to K') bodies do not apply. Consequently the Cartesian system of coordinates also loses its significance in terms of the stipulation of meaning. Analogous reasoning applies to time; with reference to K' the time can no longer meaningfully be defined by the indication on identical clocks at rest relative to K', nor by the law governing the propagation of light. Generalizing, we arrive at the conclusion that gravitational field and metric are only different manifestations of the same physical field.

We arrive at the formal description of this field by the following consideration. For each infinitesimal point-environment in an arbitrary gravitational field a local frame of coordinates can be given for such a state of motion that relative to this local frame no gravitational field exists (local inertial frame). In terms of this inertial frame we may regard the results of the special relativity theory as correct to a first approximation for this infinitesimally small region. There are an infinite number of such local inertial frames at any space-time point; they are associated by Lorentz transformations. These latter are characterised in that they leave invariant the <<distance>> ds of two infinitely adjacent point events - defined by the equation:

$$ds^2 = c^2 dt^2 - dx^2 - d_Y{}^2 - dz^2$$

which distance can be measured by means of scales and clocks. For, $x$, $y$, z, $t$ represent coordinates and time measured with reference to a local inertial frame.

To describe space-time regions of finite extent arbitrary point coordinates in four dimensions are required which serve no other purpose than to pro-

vide an unambiguous designation of the space-time points by four numbers each, $x_1$, $x_2$, $x_3$ and $x_4$, which takes account of the continuity of this four-dimensional manifold (Gaussian coordinates). The mathematical expression of the general relativity principle is then, that the systems of equations expressing the general laws of Nature are equal for all such systems of coordinates.

Since the coordinate differentials of the local inertial frame are expressed linearly by the differentials $dx_v$ of a Gaussian system of coordinates, when the latter is used, for the distance ds of two events an expression of the form

$$\mathrm{d}s^2 = \Sigma g_{\mu\nu}\,\mathrm{d}x_\mu\mathrm{d}x_\nu \quad (g_{\mu\nu} = g_{\nu\mu})$$

is obtained. The $g_{uv}$ which arc continuous functions of $x_v$, determine the metric in the four-dimensional manifold where ds is defined as an (absolute) parameter measurable by means of rigid scales and clocks. These same parameters $g_{uv}$ however also describe with reference to the Gaussian system of coordinates the gravitational field which we have previously found to be identical with the physical cause of the metric. The case as to the validity of the special relativity theory for finite regions is characterised in that when the system of coordinates is suitably chosen, the values of $g_{uv}$ for finite regions are independent of $x_v$.

In accordance with the general theory of relativity the law of point motion in the pure gravitational field is expressed by the equation for the geodetic line. Actually the geodetic line is the simplest mathematically which in the special case of constant $g_{uv}$ becomes rectilinear. Here therefore we are confronted with the transfer of Galileo's law of inertia to the general theory of relativity.

In mathematical terms the search for the field equations amounts to ascertaining the simplest generally covariant differential equations to which the gravitational potentials $g_{uv}$ can be subjected. By definition these equations should not contain higher derivatives of $g_{uv}$ with respect to $x_v$ than the second, and these only linearly, which condition reveals these equations to be a logical transfer of the Poisson field equation of the Newtonian theory of gravity to the general theory of relativity.

The considerations mentioned led to the theory of gravity which yields the Newtonian theory as a first approximation and furthermore it yields the motion of the perihelion of Mercury, the deflection of light by the sun, and the red shift of spectral lines in agreement with experience.*

* As regards the red shift, the agreement with experience is not yet completely assured, however.

To complete the basis of the general theory of relativity, the electro-magnetic field must still be introduced into it which, according to our present conviction, is also the material from which we must build up the elementary structures of matter. The Maxwellian field equations can readily be adopted into the general theory of relativity. This is a completely unambiguous adoption provided it is assumed that the equations contain no differential quotients of $g_{uv}$ higher than the first, and that in the customary Maxwellian form they apply in the local inertial frame. It is also easily possible to supplement the gravitational field equations by electromagnetic terms in a manner specified by the Maxwellian equations so that they contain the gravitational effect of the electromagnetic field.

These field equations have not provided a theory of matter. To incorporate the field generating effect of ponderable masses in the theory, matter had therefore (as in classical physics) to be introduced into the theory in an approximate, phenomenological representation.

And that exhausts the direct consequences of the relativity principle. I shall turn to those problems which are related to the development which I have traced. Already Newton recognized that the law of inertia is unsatisfactory in a context so far unmentioned in this exposition, namely that it gives no real cause for the special physical position of the states of motion of the inertial frames relative to all other states of motion. It makes the observable material bodies responsible for the gravitational behaviour of a material point, yet indicates no material cause for the inertial behaviour of the material point but devises the cause for it (absolute space or inertial ether). This is not logically inadmissible although it is unsatisfactory. For this reason E. Mach demanded a modification of the law of inertia in the sense that the inertia should be interpreted as an acceleration resistance of the bodies against *one another* and not against <<space>>. This interpretation governs the expectation that accelerated bodies have concordant accelerating action in the same sense on other bodies (acceleration induction).

This interpretation is even more plausible according to general relativity which eliminates the distinction between inertial and gravitational effects. It amounts to stipulating that, apart from the arbitrariness governed by the free choice of coordinates, the $g_{uv}$-field shall be completely determined by the matter. Mach's stipulation is favoured in general relativity by the circumstance that acceleration induction in accordance with the gravitational field equations really exists, although of such slight intensity that direct detection by mechanical experiments is out of the question.

Mach's stipulation can be accounted for in the general theory of relativity by regarding the world in spatial terms as finite and self-contained. This hypothesis also makes it possible to assume the mean density of matter in the world as finite, whereas in a spatially infinite( quasi-Euclidian) world it should disappear. It cannot, however, be concealed that to satisfy Mach's postulate in the manner referred to a term with no experimental basis whatsoever must be introduced into the field equations, which term logically is in no way determined by the other terms in the equations. For this reason this solution of the <<cosmological problem>> will not be completely satisfactory for the time being.

A second problem which at present is the subject of lively interest is the identity between the gravitational field and the electromagnetic field. The mind striving after unification of the theory cannot be satisfied that two fields should exist which, by their nature, are quite independent. A mathematically unified field theory is sought in which the gravitational field and the electromagnetic field are interpreted only as different components or manifestations of the same uniform field, the field equations where possible no longer consisting of logically mutually independent summands.

The gravitational theory, considered in terms of mathematical formalism, i.e.Riemannian geometry, should be generalized so that it includes the laws of the electromagnetic field. Unfortunately we are unable here to base ourselves on empirical facts as when deriving the gravitational theory (equality of the inertial and heavy mass), but we are restricted to the criterion of mathematical simplicity which is not free from arbitrariness. The attempt which at present appears the most successful is that, based on the ideas of Levi-Civita, Weyl and Eddington, to replace Riemannian metric geometry by the more general theory of affine correlation.

The characteristic assumption of Riemannian geometry is the attribution to two infinitely adjacent points of a <<distance>> ds, the square of which is a homogeneous second order function of the coordinate differentials. It follows from this that (apart from certain conditions of reality) Euclidian geometry is valid in any infinitely small region. Hence to every line element (or vector) at a point P is assigned a parallel and equal line element (or vector) through any given infinitesimally adjacent point P' (affine correlation). Riemannian metric determines an affine correlation. Conversely, however, when an affine correlation( law of infinitesimal parallel displacement) is mathematically given, generally no Riemannian metric determination exists from which it can be derived.

The most important concept of Riemannian geometry, <<space curvature>> , on which the gravitational equations are also based, is based exclusively on the <<affine correlation>>. If one is given in a continuum, without first proceeding from a metric, it constitutes a generalization of Riemannian geometry but which still retains the most important derived parameters. By seeking the simplest differential equations which can be obeyed by an affine correlation there is reason to hope that a generalization of the gravitation equations will be found which includes the laws of the electromagnetic field. This hope has in fact been fulfilled although I do not know whether the formal connection so derived can really be regarded as an enrichment of physics as long as it does not yield any new physical connections. In particular a field theory can, to my mind, only be satisfactory when it permits the elementary electrical bodies to be represented as solutions free from singularities.

Moreover it should not be forgotten that a theory relating to the elementary electrical structures is inseparable from the quantum theory problems. So far also relativity theory has proved ineffectual in relation to this most profound physical problem of the present time. Should the form of the general equations some day, by the solution of the quantum problem, undergo a change however profound, even if there is a complete change in the parameters by means of which we represent the elementary process, the relativity principle will not be relinquished and the laws previously derived therefrom will at least retain their significance as limiting laws.

# Biography

Albert Einstein was born at Ulm, in Württemberg, Germany, on March 14, 1879. Six weeks later the family moved to Munich and he began his schooling there at the Luitpold Gymnasium. Later, they moved to Italy and Albert continued his education at Aarau, Switzerland and in 1896 he entered the Swiss Federal Polytechnic School in Zurich to be trained as a teacher in physics and mathematics. In 1901, the year he gained his diploma, he acquired Swiss citizenship and, as he was unable to find a teaching post, he accepted a position as technical assistant in the Swiss Patent Office. In 1905 he obtained his doctor's degree.

During his stay at the Patent Office, and in his spare time, he produced much of his remarkable work and in 1908 he was appointed Privatdozent in Berne. In 1909 he became Professor Extraordinary at Zurich, in 1911 Professor of Theoretical Physics at Prague, returning to Zurich in the following year to fill a similar post. In 1914 he was appointed Director of the Kaiser Wilhelm Physical Institute and Professor in the University of Berlin. He became a German citizen in 1914 and remained in Berlin until 1933 when he renounced his citizenship for political reasons and emigrated to America to take the position of Professor of Theoretical Physics at Princeton. He became a United States citizen in 1940 and retired from his post in 1945.

After World War II, Einstein was a leading figure in the World Government Movement, he was offered the Presidency of the State of Israel, which he declined, and he collaborated with Dr. Chaim Weizmann in establishing the Hebrew University of Jerusalem.

Einstein always appeared to have a clear view of the problems of physics and the determination to solve them. He had a strategy of his own and was able to visualize the main stages on the way to his goal. He regarded his major achievements as mere stepping-stones for the next advance.

At the start of his scientific work, Einstein realized the inadequacies of Newtonian mechanics and his special theory of relativity stemmed from an attempt to reconcile the laws of mechanics with the laws of the electro-magnetic field. He dealt with classical problems of statistical mechanics and

problems in which they were merged with quantum theory: this led to an explanation of the Brownian movement of molecules. He investigated the thermal properties of light with a low radiation density and his observations laid the foundation of the photon theory of light.

In his early days in Berlin, Einstein postulated that the correct interpretation of the special theory of relativity must also furnish a theory of gravitation and in 1916 he published his paper on the general theory of relativity. During this time he also contributed to the problems of the theory of radiation and statistical mechanics.

In the 1920's, Einstein embarked on the construction of unified field theories, although he continued to work on the probabilistic interpretation of quantum theory, and he persevered with this work in America. He contributed to statistical mechanics by his development of the quantum theory of a monatomic gas and he has also accomplished valuable work in connection with atomic transition probabilities and relativistic cosmology.

After his retirement he continued to work towards the unification of the basic concepts of physics, taking the opposite approach, geometrisation, to the majority of physicists.

Einstein's researches are, of course, well chronicled and his more important works include *Special Theory of Relativity* (1905), *Relativity* (English translations, 1920 and 1950), *General Theory of Relativity* (1916), *Investigations on Theory of Brownian Movement* (1926), and *The Evolution of Physics* (1938). Among his non-scientific works, *About Zionism* (1930), *Why War? (1933), My Philosophy (1934),* and *Out of My Later Years* (1950) are perhaps the most important.

Albert Einstein received honorary doctorate degrees in science, medicine and philosophy from many European and American universities. During the 1920's he lectured in Europe, America and the Far East and he was awarded Fellowships or Memberships of all the leading scientific academies throughout the world. He gained numerous awards in recognition of his work, including the Copley Medal of the Royal Society of London in 1925, and the Franklin Medal of the Franklin Institute in 1935.

Einstein's gifts inevitably resulted in his dwelling much in intellectual solitude and, for relaxation, music played an important part in his life. He married Mileva Maritsch in 1901 and they had two sons; their marriage was dissolved and in 1917 he married his cousin, Elsa Einstein, who died in 1936. He died on April 18, 1955 at Princeton, New Jersey.

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