UNLIMITED

BR52557

1873

FEBRUARY

1976

ROYAL AIRCRAFT ESTABLISHMENT

LIBRARY TRANSLATION No. 1873

CONTRIBUTIONS TO THE OPTICS OF TURBID MEDIA, PARTICULARLY OF COLLOIDAL METAL SOLUTIONS

by

G. Mie

(RAE-Lib-Trans-1873) CONTRIBUTIONS TO THE OPTICS OF TURBID MEDIA, PARTICULARLY OF COLLOIDAL METAL SOLUTIONS (Royal Aircraft Establishment) 60 p HC $5.00 N76-27998

Unclas H2/74 45164

JUL 1976
RECEIVED
NASA STI FACILITY
INPUT BRANCH

RECEIVED BY
NASA STI FACILITY
DATE: 7/16/76
DCAF NO. 070239
PROCESSED BY
☒ NASA STI FACILITY
☐ ESA - SDS ☐ AIAA

UNLIMITED

UDC 551.593.54 : 546.3-145 : 541.182.6

ROYAL AIRCRAFT ESTABLISHMENT

Library Translation 1873

Received for printing 2 February 1976

CONTRIBUTIONS TO THE OPTICS OF TURBID MEDIA, PARTICULARLY OF COLLOIDAL METAL SOLUTIONS

(BEITRÄGE ZUR OPTIK TRÜBER MEDIEN, SPEZIELL KOLLOIDALER METALLÖSUNGEN)

by

G. Mie

Annalen der Physik, 25, 3, 377-445 (1908)

Translator
Barbara Crossland

Translation editor
D.J. Rowley

EDITOR'S SUMMARY

Over the years, a number of theories had been submitted to explain the colouration of metals in a colloidal state. However, none of these proved satisfactory and it was not until 1908 that Mie proposed a theory in an exact form.

This paper considers the simplest case, the spherical particle, where the particles in suspension are small compared to the illuminating wavelength.

CONTENTS

1 INTRODUCTION

The varied colours exhibited by metals in the colloidal state have, over the years, been explained in many different ways. Initially, the inclination was very much towards the view that the metals concerned (particularly silver) existed in several different coloured modifications. Later, the opinion was held that the colours could be attributed to optical resonance. This opinion was, above all, due to F. Ehrenhaft[1]. Finally, J.C. Maxwell-Garnett[2] has recently demonstrated* that the colours of colloidal metals can, if the suspended particles of metal are very small, be satisfactorily explained by the theory developed by L. Lorenz[3] for optically inhomogeneous media. The theory, for a fine metal suspension in which the dimensions of particles are very small in comparison with the wavelength and also with the distances between particles, gives a well-defined absorption curve which can be determined from the optical constants of the metals; accordingly, although the pattern of these absorption curves is quite different from the pattern of absorption curves of the solid metals, they have nothing at all to do with resonance in the sense in which Ehrenhaft, Wood and others use this word. Thus Maxwell-Garnett, among others, was able, quite naturally, to derive the red colour of many gold solutions, which Ehrenhaft had taken to be a resonance effect, from the Lorenzian theory. The theory explains other colours, when the particles are pressed more closely together, and it is possible, as Maxwell-Garnett demonstrated by calculation, to obtain all possible colour transitions from that of the infinitely dilute metal suspension to that of the solid metal. In this way, the interesting colour changes observed by F. Kirchner and R. Zsigmondy[4] in dried gelatine containing colloidal gold can be explained.

In very many other cases, however, this explanation of the strange optical properties of colloidal metals so successfully applied by Maxwell-Garnett on numerous occasions, does not fit. Even with very dilute solutions of one and the same metal, it is possible to obtain the most varied colours, whereas, according to Lorenz's theory, they should always show the same absorption curve. Now, on the other hand, the view advanced by Ehrenhaft concerning the resonance of particles rests on the quite unacceptable assumption that the metals can be

---

* Where indices of refraction of gelatine-silver emulsions are concerned, F. Kirchner in his Leipzig dissertation, also demonstrates the validity of Lorenz's formula as given in Ann. d. Phys., 13, 239 (1904).

regarded, from an optical standpoint also, as perfect conductors. Apart from the objections which must be raised against such an assumption from the point of view of the theory[5], its incorrectness can be demonstrated directly, firstly from the fact that solutions containing the very smallest particles do not predominantly reflect violet and blue diffusely and do not appear yellowish-red in transmitted light, but show other colours characteristic of the metal concerned both in transmitted and in incident light; secondly, in solutions containing very fine particles, the diffusely-scattered light has its polarisation maximum not at 120^{0} as asserted in the theory advanced by Ehrenhaft, but at 90^{0}, just as in the case of cloudiness produced by non-conducting materials, where the light is almost completely polarised.

In order to answer decisively the question as to whether, in colloidal solutions of metals exhibiting different colours, various allotropic modifications of the substance are present, but not in a compact form, or whether these colours can be explained on the basis of particles having the same physical properties as the compact metal but differing from each other only in size and shape, it is absolutely necessary both to obtain still more experimental material and to develop the theory in a more exact form.

For this reason, in the Greifswalder Institut, accurate measurements were carried out by Herr Steubing on various colloidal gold solutions. I have provisionally reported the results of a few of these measurements to the Dresden Naturforscherversammlung. The completed work will be published in the very near future.

The optical theory, in any case, requires to be developed in several directions. Although, of course, metals, in general, crystallise regularly, predominantly in the octahedral form, it is nevertheless quite possible that, upon rapid separation from solution, highly distorted crystals are formed which are suspended in the liquid as platelets or little bars. On the other hand, very regular crystals can certainly also be formed, as observed, for example, in the case of so-called aventurine glass with its beautiful copper octahedra. The theory now makes it possible to substitute, first of all, simple spheres for crystals of such structure as regular octahedral, cubic and so on, and also for platelets and little bars, flattened or elongated ellipsoidals. It may be mentioned, however, that Herr Steubing has carried out certain observations in connection with the polarisation of diffusely-scattered light which suggest that, in fact we are not dealing at all with spheres or similar simple bodies; I shall return to these observations in section 20.

This paper will deal only with the simplest case, in which spherical shape can be attributed to the particles.

2 POLAR COORDINATES

For the sake of simplicity, we shall consider the three axes of coordinates (x,y,z) to be numbered (1,2,3). The coordinate system is taken to be a right-handed one. Furthermore, let the radius vector of a point (x,y,z) be denoted by r; let the angle formed by r and axis 1 be ϑ, and the angle of the projection of r on the (2,3) plane with axis 2 be ϕ (Fig.1). Then (r,ϑ,φ) are the polar coordinates of the point. The components of the electrical and magnetic field intensity in this polar system of coordinates may be denoted by E_r, E_ϑ, E_φ and H_r, H_ϑ, H_φ. It can then easily be shown that the Maxwell equations take the following form:

$$\left.\begin{aligned}
r^2 \sin\vartheta \left(k\frac{\partial E_r}{\partial t} + \Lambda E_r\right) &= \frac{\partial(r\sin\vartheta\, H_\varphi)}{\partial\vartheta} - \frac{\partial(rH_\vartheta)}{\partial\varphi}\,,\\
r\sin\vartheta\left(k\frac{\partial E_\vartheta}{\partial t} + \Lambda E_\vartheta\right) &= \frac{\partial H_r}{\partial\varphi} - \frac{\partial(r\sin\vartheta\, H_\varphi)}{\partial r}\,,\\
r\left(k\frac{\partial E_\varphi}{\partial t} + \Lambda E_\varphi\right) &= \frac{\partial(rH_\vartheta)}{\partial r} - \frac{\partial H_r}{\partial\vartheta}\,,\\
-r^2\sin\vartheta\,\mu\frac{\partial H_r}{\partial t} &= \frac{\partial(r\sin\vartheta\, E_\varphi)}{\partial\vartheta} - \frac{\partial(rE_\vartheta)}{\partial\varphi}\,,\\
-r\sin\vartheta\,\mu\frac{\partial H_\vartheta}{\partial t} &= \frac{\partial E_\vartheta}{\partial\varphi} - \frac{\partial(r\sin\vartheta\, E_\varphi)}{\partial r}\,,\\
-r\mu\frac{\partial H_\varphi}{\partial t} &= \frac{\partial(rE_\vartheta)}{\partial r} - \frac{\partial E_r}{\partial\vartheta}\,.
\end{aligned}\right\} \qquad (1)$$

Here, k, Λ, μ are the dielectric constant, the conductivity and permeability in the same system of measurement. In a non-conducting medium, $k\mu = 1/v^2$, where v is the velocity of electromagnetic waves in the medium.

It would be easy to establish, by appropriate elimination, a differential equation of the second order for both E_r and H_r which would no longer contain remaining unknowns. We shall deal with this, however, only when we have transformed the equations especially for the problem of uniform oscillations. For this purpose we take:

$$\mathcal{E}_r = E_r e^{2\pi int} , \qquad \mathcal{H}_r = H_r e^{2\pi int} \text{ etc.,} \tag{2}$$

where E_r and H_r depend only on the coordinates and not on the time and where n is the number of oscillations per second. Moreover,

$$4\pi^2 n^2 \mu k - 2\pi in\mu\Delta = \frac{4\pi^2 m^2}{\lambda^2} \tag{3}$$

and in fact here λ is the wavelength of the oscillation concerned in a vacuum, while m is the complex index of refraction of the medium for light of wavelength λ. In a non-absorbing medium (e.g. water), m is identical with the usual index of refraction; in metals, on the other hand, $m = \nu(1 - i\varkappa)$, where ν is the real value generally taken as the index of refraction, and $\varkappa$ is the absorption coefficient.

Finally, we introduce the following equations:

$$-\frac{in\mu\lambda}{m} H_r = M_r \text{ etc.,} \tag{4}$$

$$\frac{2\pi mr}{\lambda} = x . \tag{5}$$

We then obtain the following equations in which the values E and M occur in a quite similar way:

$$\left.\begin{aligned}
x^2 \sin\vartheta\, E_r &= \frac{\partial(x \sin\vartheta\, M_\varphi)}{\partial\vartheta} - \frac{\partial(xM_\vartheta)}{\partial\varphi} ,\\
x \sin\vartheta\, E_\vartheta &= \frac{\partial M_r}{\partial\varphi} - \frac{\partial(x \sin\vartheta\, M_\varphi)}{\partial x} ,\\
xE_\varphi &= \frac{\partial(xM_\vartheta)}{\partial x} - \frac{\partial M_r}{\partial\vartheta} ,\\
x^2 \sin\vartheta\, M_r &= \frac{\partial(x \sin\vartheta\, E_\varphi)}{\partial\vartheta} - \frac{\partial(xE_\vartheta)}{\partial\varphi} ,\\
x \sin\vartheta\, M_\vartheta &= \frac{\partial E_r}{\partial\varphi} - \frac{\partial(x \sin\vartheta\, E_\varphi)}{\partial x} ,\\
xM_\varphi &= \frac{\partial(xE_\vartheta)}{\partial x} - \frac{\partial E_r}{\partial\vartheta} .
\end{aligned}\right\} \tag{6}$$

We now consider a small spherical particle of radius ρ, the centre of which coincides with the origin of coordinates; this is surrounded by the solvent (e.g. water). The field values for the sphere and the solvent will be distinguished by suffixes i and a; the two indices of refraction will be denoted by m and m_0. Where the permeability is concerned, we shall assume that it is the same externally and internally; $\mu_i = \mu_a$. The variable x jumps in value at the surface of the sphere; since

$$x_i = \frac{2\pi m}{\lambda} r \, , \qquad x_a = \frac{2\pi m_0}{\lambda} r = \frac{2\pi}{\lambda'} r \, , \tag{6a}$$

where λ' is the wavelength in the solvent. The following boundary conditions must be fulfilled at the surface of the sphere:

$$\left.\begin{aligned} E_{\vartheta a} &= E_{\vartheta i} \, , & E_{\varphi a} &= E_{\varphi i} \, , \\ (xM_\vartheta)_a &= (xM_\vartheta)_i \, , & (xM_\varphi)_a &= (xM_\varphi)_i \, . \end{aligned}\right\} \tag{7}$$

3 SOLUTIONS OF THE MAXWELL EQUATIONS

In order to solve equations (6), it is simply necessary to apply the method developed by Lord Rayleigh in the 'Theory of Sound'. It has, for example, already been used for other purposes on one occasion by Fr. Hasenöhrl[6].
I shall, in following paragraphs, again give a brief derivation of the integral in the interests of summarising, as completely as possible, all formulae introduced in the discussion.

As already mentioned earlier, it is possible, by appropriate elimination, to establish an equation of second order both for E_r and M_r from equations (6):

$$\left.\begin{aligned} \frac{\partial^2 (x^2 E_r)}{\partial x^2} + \frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta} \left(\sin\vartheta \frac{\partial E_r}{\partial\vartheta} \right) + \frac{1}{\sin^2\vartheta} \frac{\partial^2 E_r}{\partial\varphi^2} + x^2 E_r &= 0 \, , \\ \frac{\partial^2 (x^2 M_r)}{\partial x^2} + \frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta} \left(\sin\vartheta \frac{\partial M_r}{\partial\vartheta} \right) + \frac{1}{\sin^2\vartheta} \frac{\partial^2 M_r}{\partial\varphi^2} + x^2 M_r &= 0 \, . \end{aligned}\right\} \tag{8}$$

We can now divide all solutions of equation system (6) into three groups. The first group represents waves which result from electrical vibrations of the sphere; it is characterised by:

$$E_r \neq 0 \; , \qquad M_r = 0 \; .$$

The second group represents waves which results from magnetic vibrations of the sphere. For these:

$$E_r = 0 \; , \qquad M_r \neq 0 \; .$$

The third group contains all integrals of Maxwell equations, which represent uniform, periodic vibrations. They can be obtained by adding of Group I and integrals of Group II.

Assuming that a solution of the differential equation for E_r has been found, then the remaining components corresponding to the case of Group I can readily be obtained by the following method: in the second and third equations of system (6), M_r is put $= 0$, and values found for M_φ and M_ϑ using the fifth and sixth equations of this system are then substituted. This gives immediately the equations which serve for the calculation of E_ϑ and E_φ from the known value of E_r. If now E_r, E_ϑ and E_φ are known, then M_ϑ and M_φ can of course be found from the last two equations of system (6). In this way, the following equation system is obtained:

$$\left.\begin{aligned} & E_r \; , & & M_r = 0 \; , \\ & \frac{\partial^2 (xE_\vartheta)}{\partial x^2} + xE_\vartheta = \frac{\partial^2 E_r}{\partial\varphi\partial x} \; , & & \frac{\partial (xM_\vartheta)}{\partial x} = xE_\varphi \; , \\ & \frac{\partial^2 (x \sin\vartheta \, E_\varphi)}{\partial x^2} + x \sin\vartheta \, E_\varphi = \frac{\partial^2 E_r}{\partial\varphi\partial x} \; , & & \frac{\partial (xM_\varphi)}{\partial x} = - xE_\vartheta \; . \end{aligned}\right\} \quad (9)$$

The calculation for Group II is carried out in a similar way. Moreover, E_r can generally be calculated as a sum of terms, each of which individually fulfils the conditions of equation (8) and is a product of a function of x and a function of the angle ϑ, φ. The νth term will be

$$E_r^{(\nu)} = \frac{K_\nu(x)}{x^2} P_\nu(\vartheta,\varphi) \; .$$

K_ν and P_ν must then fulfil the following two equations:

$$\frac{d^2K_\nu}{dx^2} + \left(1 - \frac{c_\nu}{x^2}\right)K_\nu = 0 \quad , \tag{10}$$

$$\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left[\sin\vartheta\,\frac{\partial P_\nu}{\partial\vartheta}\right] + \frac{1}{\sin^2\vartheta}\frac{\partial^2 P_\nu}{\partial\varphi^2} + c_\nu P_\nu = 0 \quad , \tag{11}$$

where c_ν could be any real or complex number. We shall use only such functions K_ν and P_ν for which:

$$c_\nu = \nu(\nu + 1) \quad . \tag{12}$$

P_ν is then a spherical function of the two variables ϑ, φ of the whole number order ν ; K_ν is a function used as an approximation for the cylindrical functions having a fractional index (denominator 2). Equations (9) now give the following solution of the Maxwell equations:

$$\left.\begin{aligned}
E_r^{(\nu)} &= \frac{K_\nu(x)}{x^2}\,P_\nu(\vartheta,\varphi) \quad ,\\
E_\vartheta^{(\nu)} &= \frac{1}{\nu(\nu+1)}\,\frac{K_\nu'(x)}{x}\,\frac{\partial P_\nu}{\partial\vartheta} \quad ,\\
E_\phi^{(\nu)} &= \frac{1}{\nu(\nu+1)}\,\frac{K_\nu'(x)}{x\sin\vartheta}\,\frac{\partial P_\nu}{\partial\varphi} \quad ,\\
M_r^{(\nu)} &= 0 \quad ,\\
M_\vartheta^{(\nu)} &= \frac{1}{\nu(\nu+1)}\,\frac{K_\nu(x)}{x\sin\vartheta}\,\frac{\partial P_\nu}{\partial\varphi} \quad ,\\
M_\phi^{(\nu)} &= -\frac{1}{\nu(\nu+1)}\,\frac{K_\nu(x)}{x}\,\frac{\partial P_\nu}{\partial\vartheta} \quad .
\end{aligned}\right\} \tag{13}$$

Thus we have found the solutions for the first group ($M_r = 0$). However, because of the symmetry of the differential equations (6) in respect of E and M , it is now possible to write down straight away the solutions for Group II ($E_r = 0$) also:

$$\left.\begin{aligned}
E_r^{(\nu)} &= 0 \;, \\
E_\vartheta^{(\nu)} &= \frac{1}{\nu(\nu+1)} \frac{K_\nu(x)}{x \sin \vartheta} \frac{\partial P_\nu(\vartheta,\varphi)}{\partial \varphi} \;, \\
E_\varphi^{(\nu)} &= -\frac{1}{\nu(\nu+1)} \frac{K_\nu(x)}{x} \frac{\partial P_\nu(\vartheta,\varphi)}{\partial \vartheta} \;, \\
M_r^{(\nu)} &= \frac{K_\nu(x)}{x^2} P_\nu(\vartheta,\varphi) \;, \\
M_\vartheta^{(\nu)} &= \frac{1}{\nu(\nu+1)} \frac{K_\nu'(x)}{x} \frac{\partial P_\nu}{\partial \vartheta} \;, \\
M_\varphi^{(\nu)} &= \frac{1}{\nu(\nu+1)} \frac{K_\nu'(x)}{x \sin} \frac{\partial P_\nu}{\partial \varphi} \;,
\end{aligned}\right\} \qquad (14)$$

where K_ν and P_ν are any solutions of equations (10) and (11), in which $c_\nu = \nu(\nu + 1)$ is to be introduced.

Now all that remains is to express a plane wave, namely the wave striking the spherical particle, using equations (13) and (14). However, it is first necessary to recognise the most important properties of the solutions of (10) and (11) to be applied for this purpose.

4 THE FUNCTIONS K_ν AND I_ν

The differential equation (10):

$$\frac{d^2K_\nu}{dx^2} + \left(1 - \frac{\nu(\nu+1)}{x^2}\right)K_\nu = 0$$

can immediately be solved for the case $\nu = 0$. Two particular integrals are:

$$K_0(x) = e^{ix} \;,$$

$$K_0(-x) = e^{-ix} \;.$$

If, further, a solution of the equation of order number ν, K_ν is known, it can readily be shown by substitution, that a solution $K_{\nu+1}$ of the equation of order number $(\nu + 1)$ can readily be calculated in the following way:

$$K_{\nu+1}(x) = i\left((\nu + 1)\frac{K_\nu}{x} - \frac{dK_\nu}{dx}\right) . \tag{15}$$

This recurrance formula gives, if one takes $K_0(x) = e^{ix}$;

$$K_\nu(x) = e^{ix} \sum_{0}^{\nu} {}_{\mu} \frac{(\nu + \mu)!}{\mu!(\nu - \mu)!} \frac{i^\mu}{2^\mu x^\mu} . \tag{16}$$

From (15), differentiating once to obtain dK_ν/dx , and using equation (10) to help eliminate d^2K_ν/dx^2

$$K_{\nu-1}(x) = -i\left(\nu\frac{K_\nu}{x} + \frac{dK_\nu}{dx}\right) . \tag{17}$$

Furthermore, from (15) and (17), the following frequently applied relationships are obtained:

$$\left.\begin{aligned} (2\nu + 1)\frac{K_\nu(x)}{x} &= iK_{\nu-1} + \frac{1}{i}K_{\nu+1} \\ (2\nu + 1)\frac{dK_\nu}{dx} &= (\nu + 1)iK_{\nu-1} - \nu\frac{1}{i}K_{\nu+1} . \end{aligned}\right\} \tag{18}$$

A second particular solution of (10) is obtained directly, since, in (10), only the second power of x or dx occurs if the sign is reversed, $K_\nu(-x)$, in the first solution. The general solution is then:

$$AK_\nu(x) + BK_\nu(-x) .$$

Since, in future, it is that very solution $K_\nu(-x)$ which we shall use, it would be a good thing to write down once more the relationships which are obtained by reversing the sign of x in (15), (16), (17), (18):

$$K_\nu(-x) = e^{-ix} \sum_{0}^{\nu} {}_{\mu} \frac{(\nu + \mu)!}{\mu!(\nu - \mu)!} \frac{(-i)^\mu}{2^\mu x^\mu} . \tag{19}$$

$$\left.\begin{aligned} K_{\nu+1}(-x) &= -i\left((\nu+1)\frac{K_\nu(-x)}{x} - K'_\nu(-x)\right) , \\ K_{\nu-1}(-x) &= +i\left(\nu\frac{K_\nu(-x)}{x} + K'_\nu(-x)\right) . \end{aligned}\right\} \quad (20)$$

$$\left.\begin{aligned} -(2\nu+1)\frac{K_\nu(-x)}{x} &= iK_{\nu-1}(-x) + \frac{1}{i}K_{\nu+1}(-x) , \\ -(2\nu+1)K'_\nu(-x) &= i(\nu+1)K_{.}(-x) - \frac{\nu}{i}K_{\nu+1}(-x) . \end{aligned}\right\} \quad (21)$$

If, in expressions (16) and (19), e^{ix} and e^{-ix} are expanded in potential series, multiplying out for this purpose and arranging according to powers of x, then one obtains the power series expansions for $K_\nu(x)$ and $K_\nu(-x)$, which naturally contain an infinite number of powers with negative, whole-number exponents. In fact, it is found that:

$$K_\nu(x) = \sum_{r=-\nu}^{r=+\infty} ri^r x^r \sum_{0}^{\nu} \mu \frac{(\nu+\mu)!(-1)^\mu}{(\mu+r)!\mu!(\nu-\mu)!2^\mu} . \quad (21a)$$

Now, however, it can be shown that:

$$\sum_{0}^{\nu} \mu \frac{(-1)^\mu(\nu+\nu)!}{2^\mu(\mu+r)!\mu!(\nu-\mu)!} = \frac{(r-\nu+1)(r-\nu+3)\ldots(r+\nu-1)}{(r+\nu)!} . \quad (21b)$$

This expression is remarkable for the fact that, up to $r = \nu$, it is alternately different from zero and equal to zero. Up to the power x^ν, therefore, only terms of the form $x^{-\nu+2\mu}$ remain. If, in the coefficients, we put $r = -\nu + 2\mu$, then we obtain:

$$\frac{(r-\nu+1)(r-\nu+3)\ldots(r+\nu-1)}{(r+\mu)!}$$

$$= (-1)^{\nu+\mu+1}\frac{1\times3\times5\ldots(2\nu-2\mu-1)\times1\times3\ldots(2\mu-1)}{(2\mu)!} . \quad (21c)$$

Thus:

$$\left.\begin{aligned} K_\nu(x) &= -i^\nu \sum_0^\nu \mu \frac{1 \times 3 \ldots (2\nu - 2\mu - 1) \times 1 \times 3 \ldots (2\mu - 1)}{(2\mu)!} x^{-\nu+2\mu} \\ &+ \sum_{r=\nu+1}^{r=+\infty} r \frac{(r - \nu + 1)(r - \nu + 3) \ldots (r + \nu - 1)}{(r + \nu)!} i^r x^r \quad . \end{aligned}\right\} \quad (22)$$

Similarly:

$$\left.\begin{aligned} K_\nu(-x) &= -(-i)^\nu \sum_0^\nu \mu \frac{1 \times 3 \ldots (2\nu - 2\mu - 1) \times 1 \times 3 \ldots (2\mu - 2)}{(2\mu)!} x^{-\nu+2\mu} \\ &+ \sum_{r=\nu+1}^{r=+\infty} r \frac{(r - \nu + 1)(r - \nu + 3) \ldots (r + \nu - 1)}{(r + \nu)!} (-i)^r x^r \quad . \end{aligned}\right\}$$

...... (23)

From this it can be seen that the differential equation (10) has also one solution which has to be expanded about the zero point into a power series without negative powers. We shall denote this by the letter I_ν and take:

$$I_\nu(x) = \frac{1}{2i} \left(\frac{K_\nu(x)}{i^\nu} - \frac{K_\nu(-x)}{(-i)^\nu} \right) . \quad (24)$$

The power series for I_ν has only real coefficients, and is given by:

$$I_\nu(x) = \sum_0^\infty \mu \frac{(-1)^\mu x^{\nu+2\mu+1}}{(2\mu + 1)!(2\mu + 3)(2\mu + 5) \ldots (2\mu + 2\nu + 1)} \quad . \quad (25)$$

From (18) and (19), two important relationships are found:

$$\left.\begin{aligned} (2\nu + 1) \frac{I_\nu}{x} &= I_{\nu-1} + I_{\nu+1} \quad , \\ (2\nu + 1) \frac{dI_\nu}{dx} &= (\nu + 1) I_{\nu-1} - \nu I_{\nu+1} \quad . \end{aligned}\right\} \quad (26)$$

In order to calculate the functions $K_\nu(-x)$, $I_\nu(x)$ and their first derivatives (which occur only in the final equations), it is best to use the following expressions:

$$\left.\begin{aligned}
K_1(-x) &= -\frac{i}{x}\,e^{-ix}(1+ix)\;,\\
K_2(-x) &= -\frac{3}{x^3}\,e^{-ix}\left(\left(1-\frac{1}{3}x^2\right)+ix\right)\;,\\
K_3(-x) &= +\frac{15i}{x^3}\,e^{-ix}\left(\left(1-\frac{2}{5}x^2\right)+ix\left(1-\frac{1}{15}x^2\right)\right)\;,\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
K_\nu(-x) &= (-i)^\nu\,\frac{1\times 3\ldots(2\nu-1)}{x^\nu}\,e^{-ix}\;\times\\
&\times\left\{\left(1+\sum_{1}^{\frac{\nu(-1)}{2}}\sigma\,\frac{(\nu-\sigma)_\sigma(-1)^\sigma}{(2\nu-1)(2\nu-3)\ldots(2\nu-2\sigma+1)}\,\frac{x^{2\sigma}}{1\times 3\ldots(2\sigma-1)}\right)\right.\\
&\qquad\left.+\,ix\left(1+\sum_{1}^{\frac{\nu(+1)}{2}-1}\sigma\,\frac{(\nu-\sigma-1)_\sigma(-1)^\sigma}{(2\nu-1)(2\nu-3)\ldots(2\nu-2\sigma+1)}\,\frac{x^{2\sigma}}{1\times 3\ldots(2\sigma+1)}\right)\right\}.
\end{aligned}\right\}$$

...... (27)

$$\left.\begin{aligned}
K_1'(-x) &= +\frac{i}{x^2}\,e^{-ix}\Big((1-x^2)+ix\Big)\;,\\
K_2'(-x) &= +\frac{6}{x^3}\,e^{-ix}\left(\left(1-\frac{1}{2}x^2\right)+ix\left(1-\frac{1}{6}x^2\right)\right)\;,\\
K_3'(-x) &= -\frac{45i}{x^4}\,e^{-ix}\left(\left(1-\frac{7}{15}x^2+\frac{1}{45}x^4\right)+ix\left(1-\frac{2}{15}x^2\right)\right)\;,\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
K_\nu'(-x) &= -(-i)^\nu\,\nu\,\frac{1\times 3\ldots(2\nu-1)}{x^{\nu+1}}\,e^{-ix}\times\\
&\quad\times\left\{\left(1+\sum_{1}^{\frac{\nu(+1)}{2}}\sigma(-1)^\sigma\,\frac{(\nu-\sigma)_\sigma+\frac{2\sigma-1}{\nu}(\nu-\sigma)_{\sigma-1}}{(2\nu-1)(2\nu-3)\ldots(2\nu-2\sigma+1)}\,\frac{x^{2\sigma}}{1\times 3\ldots(2\sigma-1)}\right)\right.\\
&\qquad\left.+\,ix\left(1+\sum_{1}^{\frac{\nu(-1)}{2}}\sigma(-1)^\sigma\,\frac{(\nu-\sigma-1)_\sigma+\frac{2\sigma+1}{\nu}(\nu-\sigma-1)_{\sigma-1}}{(2\nu-1)(2\nu-3)\ldots(2\nu-2\sigma+1)}\,\frac{x^{2\sigma}}{1\times 3\ldots(2\sigma+1)}\right)\right\}.
\end{aligned}\right\}\quad\ldots\ldots\ (28)$$

$$\left.\begin{aligned}
I_1(x) &= \frac{x^2}{3}\left(1-\frac{3}{5}\,\frac{x^2}{3!}+\frac{3}{7}\,\frac{x^4}{5!}-\frac{3}{9}\,\frac{x^6}{7!}+\ldots\right)\;,\\
I_2(x) &= \frac{x^3}{15}\left(1-\frac{3}{7}\,\frac{x^2}{3!}+\frac{3\times 5}{7\times 9}\,\frac{x^4}{5!}-\frac{3\times 5}{9\times 11}\,\frac{x^6}{7!}+\ldots\right)\;,\\
I_3(x) &= \frac{x^4}{105}\left(1-\frac{3}{9}\,\frac{x^2}{3!}+\frac{3\times 5}{9\times 11}\,\frac{x^4}{5!}-\frac{3\times 5\times 7}{9\times 11\times 13}\,\frac{x^6}{7!}+\ldots\right)\;,\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
I_\nu(x) &= \frac{x^{\nu+1}}{1\times 3\ldots(2\nu+1)}\left(1-\frac{3}{2\nu+3}\,\frac{x^2}{3!}+\frac{3\times 5}{(2\nu+3)(2\nu+5)}\,\frac{x^4}{5!}\right.\\
&\qquad\left.-\,\frac{3\times 5\times 7}{(2\nu+3)(2\nu+5)(2\nu+7)}\,\frac{x^6}{7!}+\ldots\right)\;.
\end{aligned}\right\}\quad(29)$$

$$\left.\begin{aligned}
I_1'(x) &= \frac{2x}{3}\left(1 - 2\,\frac{3}{5}\,\frac{x^2}{3!} + 3\,\frac{3}{7}\,\frac{x^4}{5!} - 4\,\frac{3}{9}\,\frac{x^6}{7!} + \ldots\right) ,\\
I_2'(x) &= \frac{3x^2}{15}\left(1 - \frac{5}{7}\,\frac{x^2}{3!} + \frac{5}{9}\,\frac{x^4}{5!} - \frac{5}{11}\,\frac{x^6}{7!} + \ldots\right) ,\\
I_3'(x) &= \frac{4x^3}{104}\left(1 - \frac{3}{2}\,\frac{3}{9}\,\frac{x^2}{3!} + \frac{4}{2}\,\frac{3 \times 5}{9 \times 11}\,\frac{x^4}{5!}\right.\\
&\qquad\qquad \left. - \frac{5}{2}\,\frac{3 \times 5 \times 7}{9 \times 11 \times 13}\,\frac{x^6}{7!} + \ldots\right) ,\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\\
I_\nu'(x) &= \frac{(\nu + 1)x^\nu}{1 \times 3 \ldots (2\nu + 1)}\left(1 - \frac{\nu + 3}{\nu + 1}\,\frac{3}{2\nu + 3}\,\frac{x^2}{3!}\right.\\
&\qquad\qquad \left. + \frac{\nu + 5}{\nu + 1}\,\frac{3 \times 5}{(2\nu + 1)(2\nu + 5)}\,\frac{x^4}{5!} - \ldots\right) .
\end{aligned}\right\}\qquad(30)$$

These series are far more convenient generally for numerical calculations than the final expressions obtained for I_ν and I_ν' according to (24). For other purposes, however, these must also be known:

$$\left.\begin{aligned}
I_1(x) &= -\cos x + \frac{\sin x}{x} ,\\
I_2(x) &= -\sin x - \frac{3\cos x}{x} + \frac{3\sin x}{x^2} ,\\
I_3(x) &= +\cos x - \frac{6\sin x}{x} - \frac{15\cos x}{x^2} + \frac{15\sin x}{x^3} ,\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\\
I_\nu(x) &= \sin\left(x - \frac{\nu\pi}{2}\right) + \sum_1^\nu r\sin\left(x - \frac{(\nu - r)\pi}{2}\right)\frac{(\nu + r)!}{(\nu - r)!\,r!}\,\frac{1}{2^r x^r} .
\end{aligned}\right\}\qquad(29a)$$

$$\left.\begin{aligned}
I_1'(x) &= +\sin x + \frac{\cos x}{x} - \frac{\sin x}{x^2} \ , \\
I_2'(x) &= -\cos x + \frac{3\sin x}{x} + \frac{6\cos x}{x^2} - \frac{6\sin x}{x^3} \ , \\
I_3'(x) &= -\sin x - \frac{6\cos x}{x} + \frac{21\sin x}{x^2} + \frac{45\cos x}{x^3} - \frac{45\sin x}{x^4} \ , \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
I_\nu'(x) &= \cos\left(x - \frac{\nu\pi}{2}\right) + \sum_1^{\nu+1} r \cos\left(x - \frac{(\nu - r)\pi}{2}\right) \times \\
&\qquad \times \frac{(\nu + r - 1)!}{(\nu - r + 1)!\,r!} \, \frac{\big(\nu(\nu + 1) + r(r - 1)\big)}{2^r x^r} \ .
\end{aligned}\right\} \qquad (30a)$$

5 THE SPHERICAL FUNCTIONS

The usual spherical functions, which depend only on one variable (the zonal spherical functions) are not used in the problem involved here. We shall, later in this section, see that functions of the following two forms are necessary to the solution:

$$\mathrm{P}_\nu(\vartheta,\varphi) = \Pi_\nu(v) \cos\vartheta \ , \qquad (31)$$

$$P_\nu(\vartheta,\varphi) = \Pi_\nu(v) \sin\vartheta \cos\varphi \ , \qquad (32)$$

$$v = \sin\vartheta \sin\varphi \ . \qquad (33)$$

The function Π_ν must, as may be seen by substitution of the expressions for P_ν and P_ν in (11), obey the following differential equation:

$$\frac{d^2}{dv^2}\left((1 - v^2)\Pi_\nu\right) + \nu(\nu + 1)\Pi_\nu = 0 \ . \qquad (34)$$

The geometrical significance of the three angular functions occurring in (31), (32), (33):

$$\cos\vartheta \ , \qquad \sin\vartheta \sin\varphi \ , \qquad \sin\vartheta \cos\varphi$$

is clear without further explanation. If we call the angles formed by the radius vector of the point under consideration and the axes 1, 2, 3 (see Fig.2) ϑ_1, ϑ_2, ϑ_3, then, as can be seen immediately from Fig.2:

$$\left.\begin{aligned} \cos\vartheta_1 &= \cos\vartheta \ , \\ \cos\vartheta_2 &= \sin\vartheta\cos\varphi \ , \\ \cos\vartheta_3 &= \sin\vartheta\sin\varphi = \nu \ . \end{aligned}\right\} \qquad (35)$$

We shall now summarise the most important formulae for the functions Π_ν. It is well known that there is a particular solution of the differential equation of the spherical function which is rational and whole-numbered in trigonometric functions of the angular coordinates ϑ, φ. Only this solution is of interest to us. If we have found it for one order number (e.g. $\nu = 1$), then we can calculate it for all other order numbers with the help of the following recurrence formula:

$$\frac{d\Pi_{\nu+1}}{d\nu} = \nu\frac{d\Pi_\nu}{d\nu} + (\nu + 2)\Pi_\nu \ . \qquad (36)$$

This formula can be verified at once by substitution in (34). A solution of (34) for the case $\nu = 1$ is now:

$$\Pi_1(\nu) = 1 \ . \qquad (37)$$

From this, using (36), it is found that:

$$\left.\begin{aligned} \Pi_0(\nu) &= 0 \ , \qquad \Pi_1(\nu) = 1 \ , \\ \Pi_2 &= 3\nu \ , \\ \Pi_3 &= \frac{15}{2}\nu^2 - \frac{3}{2} \ , \\ \Pi_4 &= \frac{35}{2}\nu^3 - \frac{15}{2}\nu \ , \\ \Pi_\nu &= \frac{1}{2^\nu}\sum_0^{\frac{\nu(+1)}{2}-1} s(-1)^s\frac{(2\nu - 2s)!}{(\nu - s)!s!}\frac{\nu^{\nu-2s-1}}{(\nu - 2s - 1)!} \ . \end{aligned}\right\} \qquad (38)$$

Another series expansion for Π_ν is the following:

$$\Pi_\nu = \sum_{0}^{\frac{\nu(+1)}{2}-1} s(-1)^s \frac{(\nu+1)!}{s!(s+1)!} \frac{v^{\nu-2s-1}(1-v^2)^s}{(\nu-2s-1)!2^{2s+1}} . \qquad (39)$$

For the special value $v = 0$, equation (38) gives:

$$\left.\begin{aligned} \Pi_\nu(0) &= 0 , && \text{if } \nu \text{ is an even number} \\ \Pi_\nu(0) &= (-1)^{\frac{\nu-1}{2}} \frac{(\nu+1)!}{2^\nu\left(\frac{\nu+1}{2}\right)!\left(\frac{\nu-1}{2}\right)!} , && \text{if } \nu \text{ is an odd number} \end{aligned}\right\} \qquad (40)$$

and, for the first derivative:

$$\left.\begin{aligned} \left(\frac{d\Pi_\nu}{dv}\right)_{v=0} &= (-1)^{\frac{\nu}{2}-1} \frac{(\nu+1)!}{2^{\nu-1}\left(\frac{\nu}{2}\right)!\left(\frac{\nu}{2}-1\right)!} , && \text{if } \nu \text{ is an even number} \\ \left(\frac{d\Pi_\nu}{dv}\right)_{v=0} &= 0 , && \text{if } \nu \text{ is an odd number .} \end{aligned}\right\} \qquad (41)$$

Similarly, from (39), the values of the function Π_ν and their derivatives for $v = 1$ can be calculated.

Just as in the case of the functions K_ν and L_ν considered above, there is for Π_ν also a second relationship in addition to recurrence formula (36), which, like (36), can be proved:

$$\frac{d\Pi_{\nu-1}}{dv} = v\frac{d\Pi_\nu}{dv} - (\nu-1)\Pi_\nu . \qquad (42)$$

From (36) and (42) can be obtained formulae which are often very useful; these are:

$$\left.\begin{aligned} (2\nu+1)\Pi_\nu &= \frac{d\Pi_{\nu+1}}{dv} - \frac{d\Pi_{\nu-1}}{dv} , \\ (2\nu+1)v\Pi_\nu &= \nu\Pi_{\nu+1} + (\nu+1)\Pi_{\nu-1} , \end{aligned}\right\} \qquad (43)$$

Finally, the differential quotients of P_ν and P_ν which occur in formulae (13) and (14) may be noted here:

$$\left.\begin{aligned} \mathrm{P}_\nu &= \Pi_\nu \cos\vartheta \;, \\ \frac{\partial \mathrm{P}_\nu}{\partial\vartheta} &= -\frac{d(\nu\Pi_\nu)}{d\nu}\sin\vartheta + \frac{d\Pi_\nu}{d\nu}\sin\varphi \;, \\ \frac{1}{\sin\vartheta}\frac{\partial \mathrm{P}_\nu}{\partial\varphi} &= \frac{d\Pi_\nu}{d\nu}\cos\vartheta\cos\varphi \;, \end{aligned}\right\} \tag{44}$$

$$\left.\begin{aligned} P_\nu &= \Pi_\nu \sin\vartheta\cos\varphi \;, \\ \frac{\partial P_\nu}{\partial\vartheta} &= \frac{d(\nu\Pi_\nu)}{d\nu}\cos\vartheta\cos\varphi \;, \\ \frac{1}{\sin\vartheta}\frac{\partial P_\nu}{\partial\varphi} &= -\frac{d(\nu\Pi_\nu)}{d\nu}\sin\varphi + \frac{d\Pi_\nu}{\nu}\sin\vartheta \;. \end{aligned}\right\} \tag{45}$$

For the first two order numbers specially we find:

$$\left.\begin{aligned} \mathrm{P}_1 &= \cos\vartheta \;, & \mathrm{P}_2 &= 3\sin\vartheta\cos\vartheta\sin\varphi \;, \\ \frac{\partial \mathrm{P}_1}{\partial\vartheta} &= -\sin\vartheta \;, & \frac{\partial \mathrm{P}_2}{\partial\vartheta} &= 3\cos 2\vartheta\sin\varphi \;, \\ \frac{1}{\sin\vartheta}\frac{\partial \mathrm{P}_1}{\partial\varphi} &= 0 \;, & \frac{1}{\sin\vartheta}\frac{\partial \mathrm{P}_2}{\partial\varphi} &= 3\cos\vartheta\cos\varphi \;, \\ P_1 &= \sin\vartheta\cos\varphi \;, & P_2 &= 3\sin^2\vartheta\sin\varphi\cos\varphi \;, \\ \frac{\partial P_1}{\partial\vartheta} &= \cos\vartheta\cos\varphi \;, & \frac{\partial P_2}{\partial\vartheta} &= 3\sin 2\vartheta\sin\varphi\cos\varphi \;, \\ \frac{1}{\sin\vartheta}\frac{\partial P_1}{\partial\varphi} &= -\sin\varphi \;, & \frac{1}{\sin\vartheta}\frac{\partial P_2}{\partial\varphi} &= 3\sin\varphi\cos 2\varphi \;. \end{aligned}\right\} \tag{45a}$$

6 INTEGRAL VALUES OF THE SPHERICAL FUNCTION

It is now necessary to solve the problem of the calculation of the total radiation reflected by the sphere. We shall see that this problem involves finding the surface integrals:

$$\int_0^{\pi}\int_0^{2\pi} \mathrm{P}_\nu \mathrm{P}_\mu \sin\vartheta \, d\vartheta d\varphi \qquad \text{and} \qquad \int_0^{\pi}\int_0^{2\pi} P_\nu P_\mu \sin\vartheta \, d\vartheta d\varphi \ .$$

These integrals can readily be calculated, for example by the method given in Maxwell's Treatise on Electricity (Vol.I, p.200 of the German translation). It is found that:

$$\left.\begin{aligned} \int_0^{\pi}\int_0^{2\pi} \mathrm{P}_\nu \mathrm{P}_\mu \sin\vartheta \, d\vartheta d\varphi &= \int_0^{\pi}\int_0^{2\pi} P_\nu P_\mu \sin\vartheta \, d\vartheta d\varphi = 0 \ , \\ \int_0^{\pi}\int_0^{2\pi} \mathrm{P}_\nu^2 \sin\vartheta \, d\vartheta d\varphi &= \int_0^{\pi}\int_0^{2\pi} P_\nu^2 \sin\vartheta \, d\vartheta d\varphi = 2\pi \frac{\nu(\nu+1)}{2\nu+1} \ . \end{aligned}\right\} \qquad (46)$$

7 PLANE WAVE

The problem involved is considered to be solved when the plane wave striking the sphere has successfully been broken down into expressions of the form (13) and (14).

As the direction of propagation of the plane wave, we choose axis 3 and its negative direction. The light is considered to be linearly polarised; axis 1 is taken as the direction of the electrical oscillation and axis 2 as the direction of the magnetic vibration.

If we call the coordinate of a point in the direction of axis 3 temporarily z again, then, according to (35):

$$z = r \cos\vartheta_3 = rv \ .$$

The plane wave is thus represented by the following values:

$$\left.\begin{aligned} E_1 &= e^{2\pi int+\frac{2\pi iz}{\lambda'}}\,, \qquad E_2 = E_3 = 0\,, \\ H_1 &= 0\,, \qquad H_2 = -\sqrt{\frac{k}{\mu}}\,e^{2\pi int+\frac{2\pi iz}{\lambda'}}\,, \qquad H_3 = 0\,. \end{aligned}\right\} \qquad (46a)$$

Here k and μ are the dielectric constant and permeability in the sense used in equation (1); the conductivity of the medium (water) through which the ray passes is taken as zero, and λ' is the wavelength in the medium (water). If now we put (*cf.* (5)):

$$\frac{2\pi iz}{\lambda'} = \frac{2\pi irv}{\lambda'} = ixv\,,$$

then we can immediately write down the values E_r ... and M_r ... introduced earlier (equations (2) and (4)):

$$\left.\begin{aligned} E_r &= e^{ixv}\cos\vartheta\,, & M_r &= ie^{ixv}\sin\vartheta\cos\varphi\,, \\ E_\vartheta &= -\,e^{ivx}\sin\vartheta\,, & M_\vartheta &= ie^{ixv}\cos\vartheta\cos\varphi\,, \\ E_\varphi &= 0\,, & M_\varphi &= -\,ie^{ixv}\sin\varphi\,. \end{aligned}\right\} \qquad (47)$$

However, one can easily expand the exponential function which occurs here in terms of I and Π-functions. In fact:

$$e^{ixv} = \sum_{\nu=1}^{\nu=\infty} \nu(2\nu+1)i^{\nu-1}\frac{I_\nu(x)}{x^2}\Pi_\nu(v)\,. \qquad (48)$$

The correctness of this formula is most readily shown by differentiation with respect to x and v. According to (26) and (43), if first of all we regard the series as $f(x,v)$:

$$\left.\begin{aligned}
\frac{\partial f}{\partial x} &= \frac{1}{x^2}\left\{\sum_1^\infty \nu i^{\nu-1}(2\nu+1)\frac{dI_\nu}{dx} - 2\frac{I_\nu}{x}\Pi_\nu(v)\right\} \;, \\
&= \frac{i}{x^2}\sum_1^\infty \nu\Big((\nu-1)i^{\nu-2}I_{\nu-1} + (\nu+2)i^\nu I_{\nu+1}\Big)\Pi_\nu(v) \;, \\
&= i\sum_1^\infty \nu i^{\nu-1}\frac{I_\nu}{x^2}\Big(\nu\Pi_{\nu+1} + (\nu+1)\Pi_{\nu-1}\Big) \;, \\
&= iv\sum_1^\infty \nu(2\nu+1)i^{\nu-1}\frac{I_\nu}{x^2}\Pi_\nu(v) \;, \\
&= ivf(x,v) \;.
\end{aligned}\right\} \tag{48a}$$

Similarly, it can be shown that:

$$\frac{\partial f}{\partial v} = ixf(x,v) \;.$$

Finally,

$$(f(x,v))_{x=0} = 1 \;.$$

Thus,

$$f(x,v) = e^{ixv} \;.$$

Accordingly, for E_r and M_r we have the desired series expansion:

$$\left.\begin{aligned}
E_r &= \sum_1^\infty \nu(2\nu+1)i^{\nu-1}\frac{I_\nu}{x^2}\mathrm{P}_\nu \;, \\
M_r &= \sum_1^\infty \nu(2\nu+1)i^{\nu}\frac{I_\nu}{x^2}P_\nu \;,
\end{aligned}\right\} \tag{48b}$$

where P_ν and P_ν are the functions defined in (31) and (32).

Starting with the value of E_r, found, and with the help of formula (13), it is now possible to find a solution for Group I; moreover, starting with M_r and using (14), a solution for Group II can be obtained. The sum of these two solutions must then be that same integral of the Maxwell equation which reproduces the plane wave. It can easily be shown by direct calculation that the series expansions obtained in this way are in fact identical with the expressions (47).

It is in fact possible, from equations (26) and (43), if differential equation (10):

$$\frac{1}{\nu(\nu+1)}\left(\frac{d^2 I_\nu}{dx^2} + I_\nu\right) = \frac{I_\nu}{x^2}$$

is taken into consideration, to derive the following two equations:

$$\left.\begin{aligned}
&\sum_1^\infty \nu\,\frac{2\nu+1}{\nu(\nu+1)}\left(i^{\nu-1} I_\nu \frac{d(\nu\Pi_\nu)}{dv} + i^\nu \frac{dI_\nu}{dx}\frac{d\Pi_\nu}{dv}\right) = 0 \;, \\
&\sum_1^\infty \nu\,\frac{2\nu+1}{\nu(\nu+1)}\left(i^{\nu-1} I_\nu \frac{d\Pi_\nu}{dv} + i^\nu \frac{dI_\nu}{dx}\frac{d(\nu\Pi_\nu)}{dv}\right) \\
&\qquad\qquad = \sum_1^\infty \nu(2\nu+1)\,i^{\nu-1}\,\frac{I_\nu}{x^2}\,\frac{d\Pi_\nu}{dv} \;, \\
&\qquad\qquad = \sum_1^\infty \nu(2\nu+1)\,i^{\nu}\,\frac{I_\nu}{x}\,\Pi_\nu \\
&\qquad\qquad = ixe^{ixv} \;.
\end{aligned}\right\} \qquad (49)$$

If now, in accordance with the conditions laid down in formulae (13) and (14), e.g.

$$E_\vartheta = \sum_1^\infty \nu\,\frac{2\nu+1}{\nu(\nu+1)}\,i^{\nu-1}\,\frac{I'_\nu}{x}\,\frac{\partial P_\nu}{\partial\vartheta} + \sum_1^\infty \frac{2\nu+1}{\nu(\nu+1)}\,i^\nu\,\frac{I_\nu}{x\sin\vartheta}\,\frac{\partial P_\nu}{\partial\varphi} \;, \qquad (49a)$$

then, using equations (44), (45) and (49), it is found that:

$$E_\vartheta = -e^{ixv}\sin\vartheta \ ,$$

Similarly

$$\left.\begin{aligned} E_\varphi = \sum_1^\infty \nu \frac{2\nu+1}{\nu(\nu+1)} i^{\nu-1} \frac{I_\nu}{x\sin\vartheta}\frac{\partial P_\nu}{\partial\varphi} \\ - \sum_1^\infty \nu \frac{2\nu+1}{\nu(\nu+1)} i^{\nu} \frac{I_\nu}{x}\frac{\partial P_\nu}{\partial\vartheta} = 0 \ . \end{aligned}\right\} \quad (49b)$$

In the same way, M_ϑ and M_φ are found. Thus, instead of expressions (47), it is also possible to use the following formulae for the plane wave:

$$\left.\begin{aligned}
E_r &= \sum_1^\infty \nu(2\nu+1) i^{\nu-1} \frac{I_\nu}{x^2} P_\nu \ , \\
E_\vartheta &= \sum_1^\infty \nu \frac{2\nu+1}{\nu(\nu+1)} i^{\nu-1} \frac{I'_\nu}{x}\frac{\partial P_\nu}{\partial\vartheta} + \sum_1^\infty \nu \frac{2\nu+1}{\nu(\nu+1)} i^{\nu} \frac{I_\nu}{x\sin}\frac{\partial P_\nu}{\partial\varphi} \ , \\
E_\varphi &= \sum_1^\infty \nu \frac{2\nu+1}{\nu(\nu+1)} i^{\nu-1} \frac{I'_\nu}{x\sin\vartheta}\frac{\partial P_\nu}{\partial\varphi} - \sum_1^\infty \frac{2\nu+1}{\nu(\nu+1)} i^{\nu} \frac{I_\nu}{x}\frac{\partial P_\nu}{\partial\vartheta} \ , \\
M_r &= \sum_1^\infty \nu(2\nu+1) i^{\nu} \frac{I_\nu}{x^2} P_\nu \ , \\
M_\vartheta &= \sum_1^\infty \nu \frac{2\nu+1}{\nu(\nu+1)} i^{\nu-1} \frac{I_\nu}{x\sin\vartheta}\frac{\partial P_\nu}{\partial\varphi} + \sum_1^\infty \nu \frac{2\nu+1}{\nu(\nu+1)} i^{\nu} \frac{I'_\nu}{x}\frac{\partial P_\nu}{\partial\vartheta} \ , \\
M_\varphi &= -\sum_1^\infty \nu \frac{2\nu+1}{\nu(\nu+1)} i^{\nu-1} \frac{I_\nu}{x}\frac{\partial P_\nu}{\partial\vartheta} + \sum_1^\infty \nu \frac{2\nu+1}{\nu(\nu+1)} i^{\nu} \frac{I'_\nu}{x\sin\vartheta}\frac{\partial P_\nu}{\partial\varphi} \ .
\end{aligned}\right\} \quad (50)$$

8 REFRACTED AND REFLECTED WAVES

If now we proceed to the representation also of waves within the sphere and of the waves radiated outwards from it by means of expressions of the form (13) and (14), then we must take two facts into consideration: firstly, only the integral of equation (10) which is denoted by I_ν is used inside the sphere, since all other particular integrals for $x = 0$, i.e. in the centre of the sphere, must be infinite; secondly, in the outer space, $K_\nu(-x)$ is used, since only this has the factor:

$$e^{-ix} = e^{-\frac{2\pi i r}{\lambda'}}$$

so that the components of the electrical and magnetic forces take time into consideration only in the combination:

$$e^{2\pi i\left(nt-\frac{r}{\lambda'}\right)} ,$$

which is the characteristic feature of radiation emitted by the sphere.

The radiation within the sphere can thus be represented in the following way:

$$\left.\begin{aligned}
E_{ri} &= \sum_1^\infty \nu i b_\nu \frac{I_\nu}{x^2} P_\nu , \\
E_{\vartheta i} &= \sum_1^\infty \nu\left(\frac{b_\nu i}{\nu(\nu+1)} \frac{I'_\nu}{x} \frac{\partial P_\nu}{\partial\vartheta} + \frac{q_\nu}{\nu(\nu+1)} \frac{I_\nu}{x \sin\vartheta} \frac{\partial P_\nu}{\partial\varphi}\right) , \\
E_{\varphi i} &= \sum_1^\infty \nu\left(\frac{b_\nu i}{\nu(\nu+1)} \frac{I'_\nu}{x \sin\vartheta} \frac{\partial P_\nu}{\partial\varphi} - \frac{q_\nu}{\nu(\nu+1)} \frac{I_\nu}{x} \frac{\partial P_\nu}{\partial\vartheta}\right) , \\
M_{ri} &= \sum_1^\infty \nu q_\nu \frac{I_\nu}{x^2} P_\nu , \\
M_{\vartheta i} &= \sum_1^\infty \nu\left(\frac{b_\nu i}{\nu(\nu+1)} \frac{I_\nu}{x \sin\varphi} \frac{\partial P_\nu}{\partial\vartheta} + \frac{q_\nu}{\nu(\nu+1)} \frac{I'_\nu}{x} \frac{\partial P_\nu}{\partial\vartheta}\right) ,
\end{aligned}\right\} \qquad (51)$$

$$M_{\varphi i} = \sum_{1}^{\infty} \nu \left(- \frac{b_\nu i}{\nu(\nu+1)} \frac{I_\nu}{x} \frac{\partial P_\nu}{\partial \vartheta} + \frac{q_\nu}{\nu(\nu+1)} \frac{I'_\nu}{x \sin \vartheta} \frac{\partial P_\nu}{\partial \varphi} \right) . \Bigg]$$

The coefficients b_ν and q_ν, to which is added a coefficient of the factor i simply to make the later formulae rather more elegant, are, together with a_ν and p_ν which appear in the following expressions (52), determined from the boundary conditions (7).

In the outer space, in addition to the plane wave (50) which strikes the sphere, there is the reflected radiation:

$$\left.\begin{aligned}
E_{ra} &= \sum_{1}^{\infty} \nu a_\nu i \frac{K_\nu(-x)}{x^2} P_\nu , \\
E_{\vartheta a} &= \sum_{1}^{\infty} \nu \left(\frac{a_\nu i}{\nu(\nu+1)} \frac{K'_\nu(-x)}{x} \frac{\partial P_\nu}{\partial \vartheta} + \frac{p_\nu}{\nu(\nu+1)} \frac{K_\nu(-x)}{x \sin \vartheta} \frac{\partial P_\nu}{\partial \varphi} \right) , \\
E_{\varphi a} &= \sum_{1}^{\infty} \nu \left(\frac{a_\nu i}{\nu(\nu+1)} \frac{K'_\nu(-x)}{x \sin \vartheta} \frac{\partial P_\nu}{\partial \varphi} - \frac{p_\nu}{\nu(\nu+1)} \frac{K_\nu(-x)}{x} \frac{\partial P_\nu}{\partial \vartheta} \right) \\
M_{ra} &= \sum_{1}^{\infty} \nu p_\nu \frac{K_\nu(-x)}{x^2} P_\nu , \\
M_{\vartheta a} &= \sum_{1}^{\infty} \nu \left(\frac{a_\nu i}{\nu(\nu+1)} \frac{K_\nu(-x)}{x \sin \vartheta} \frac{\partial P_\nu}{\partial \varphi} + \frac{p_\nu}{\nu(\nu+1)} \frac{K'_\nu(-x)}{x} \frac{\partial P_\nu}{\partial \vartheta} \right) , \\
M_{\varphi a} &= \sum_{1}^{\infty} \nu \left(- \frac{a_\nu i}{\nu(\nu+1)} \frac{K_\nu(-x)}{x} \frac{\partial P_\nu}{\partial \vartheta} + \frac{p_\nu}{\nu(\nu+1)} \frac{K'(-x)}{x \sin \vartheta} \frac{\partial P_\nu}{\partial \varphi} \right) .
\end{aligned}\right\} \quad (52)$$

9 DETERMINATION OF COEFFICIENTS

The radius of the small sphere is denoted by ρ, the index of refraction of the medium (water) by m_0, and the complex refractive index of the material of the sphere by m. Moreover, the values of x_a and x_i for the special value $r = \rho$ we denoted by α and β, and the relative index of refraction m/m_0 by m', when:

$$\left.\begin{aligned} \alpha &= \frac{2\pi m_0 \rho}{\lambda} = \frac{2\pi\rho}{\lambda'} \ , \\ \beta &= \frac{2\pi m \rho}{\lambda} = \frac{m}{m_0}\alpha = m'\alpha \ . \end{aligned}\right\} \tag{53}$$

Finally, we use the abbreviations:

$$\left.\begin{aligned} I_\nu(\alpha) &= A_\nu & I'_\nu(\alpha) &= A'_\nu \ , \\ I_\nu(\beta) &= B_\nu & I'_\nu(\beta) &= B'_\nu \ , \\ K_\nu(-\alpha) &= C_\nu & K'_\nu(-\alpha) &= C'_\nu \ . \end{aligned}\right\} \tag{54}$$

We now introduce expressions (50), (52) and (51) in the boundary conditions:

$$\left.\begin{aligned} (E_\vartheta + E_{\vartheta a})_{r=\rho} &= (E_{\vartheta i})_{r=\rho} \ , \\ (E_\varphi + E_{\varphi a})_{r=\rho} &= (E_{\varphi i})_{r=\rho} \ , \\ \alpha(M_\vartheta + M_{\vartheta a})_{r=\rho} &= \beta(M_{\vartheta i})_{r=\rho} \ , \\ \alpha(M_\varphi + M_{\varphi a})_{r=\rho} &= \beta(M_{\varphi i})_{r=\rho} \ , \end{aligned}\right\} \tag{54a}$$

and obtain, since two pairs of these equations can be shown to be identical, the following conditions for a_ν, b_ν, p_ν and q_ν :

$$\left.\begin{aligned} -(2\nu+1)i^\nu \frac{A'_\nu}{\alpha} + a_\nu \frac{C'_\nu}{\alpha} &= b_\nu \frac{B'_\nu}{\beta} \ , \\ -(2\nu+1)i^\nu A_\nu + a_\nu C_\nu &= b_\nu B_\nu \ , \\ (2\nu+1)i^\nu \frac{A_\nu}{\alpha} + p_\nu \frac{C_\nu}{\alpha} &= q_\nu \frac{B_\nu}{\beta} \ , \\ (2\nu+1)i^\nu A'_\nu + p_\nu C'_\nu &= q_\nu B'_\nu \ . \end{aligned}\right\} \tag{54b}$$

From this, it is found that:

$$\left.\begin{aligned} a_\nu &= +(2\nu+1)i^\nu \frac{A'_\nu B_\nu \beta - B'_\nu A_\nu \alpha}{C'_\nu B_\nu \beta - B'_\nu C_\nu \alpha} \ , \\ p_\nu &= -(2\nu+1)i^\nu \frac{A_\nu B'_\nu \beta - B_\nu A'_\nu \alpha}{C_\nu B'_\nu \beta - B_\nu C'_\nu \alpha} \ . \end{aligned}\right\} \tag{55}$$

10 FORMULAE FOR PRACTICAL CALCULATIONS

Formulae (55) appear so simple at first sight, but are so difficult to discuss. A particular difficulty, where metallic spherules are concerned, lies in the fact that β and hence B_ν, B'_ν are complex quantities. However, even in the case of non-absorbing spherules, when β is real, two complex quantities, namely C_ν and C'_ν, still remain in the expressions under all circumstances.

For quite small spherules, it is always most convenient to carry out the calculation using equations (27), (28), (29) and (30). Accordingly, we can write:

$$\left.\begin{aligned}
A_\nu &= \frac{\alpha^{\nu+1}}{1 \times 3 \ldots (2\nu + 1)} f_\nu \quad , \\
B_\nu &= \frac{\beta^{\nu+1}}{1 \times 3 \ldots (2\nu + 1)} g_\nu \\
C_\nu &= (-i)^\nu \frac{1 \times 3 \ldots (2\nu - 1)}{\alpha^\nu} e^{-i\alpha} (h_\nu + i\alpha k_\nu) \quad ; \\
A'_\nu &= -\frac{(\nu + 1)\alpha^\nu}{1 \times 3 \ldots (2\nu + 1)} f'_\nu \quad , \\
B'_\nu &= \frac{(\nu + 1)\beta^\nu}{1 \times 3 \ldots (2\nu + 1)} g'_\nu \quad , \\
C'_\nu &= -\nu(-i)^\nu \frac{1 \times 3 \ldots (2\nu - 1)}{\alpha^{\nu+1}} e^{-i\alpha} (h'_\nu + i\alpha k_\nu) \quad .
\end{aligned}\right\} \qquad (56)$$

The factors f_ν, f'_ν are sharply converging power series in α^2 while g_ν, g'_ν are factors of the same series in β^2 ; h_ν, k_ν, h'_ν and k'_ν are finite power sums in α^2 and so all are expressions which can be calculated relatively easily. They can be taken directly from formulae (27) to (30). All these sums, f_ν, f'_ν etc. begin with the term 1, so that, in the case of spherules having a diameter which is small in comparison with the wavelength of the light internally and externally they all lie very close to a value of 1 and very simple expressions can be obtained for A_ν, A'_ν and so on.

If (56) is introduced in (55) and if the abbreviations:

$$u_\nu = e^{i\alpha} \frac{f'_\nu}{h'_\nu + i\alpha k'_\nu} \quad , \qquad v_\nu = \frac{f_\nu}{f'_\nu} \frac{g'_\nu}{g_\nu} \quad , \qquad w_\nu = \frac{h_\nu + i\alpha k_\nu}{h'_\nu + i\alpha k'_\nu} \frac{g'_\nu}{g'} \quad . \qquad (57)$$

$$\frac{\beta^2}{\alpha^2} = \frac{m^2}{m_0^2} = m'2 \quad , \tag{58}$$

are written, the following practical formulae result:

$$\left.\begin{aligned} a_\nu &= (-1)^{\nu-1}\,\frac{\nu+1}{\nu}\,\frac{\alpha^{2\nu+1}}{1^2 \times 3^2 \ldots (2\nu-1)^2}\,u_\nu\,\frac{m'^2 - v_\nu}{m'^2 + \frac{\nu+1}{\nu}\,w_\nu} \quad , \\ p_\nu &= (-1)^{\nu}\,\frac{\nu+1}{\nu}\,\frac{\alpha^{2\nu+1}}{1^2 \times 3^2 \ldots (2\nu-1)^2}\,u_\nu\,\frac{1 - v_\nu}{1 + \frac{\nu+1}{\nu}\,w_\nu} \quad . \end{aligned}\right\} \tag{59}$$

It is not difficult to evaluate approximately the way in which a_ν varies with increasing particle size. For small values of α, the values of f_ν, g_ν etc. are all fairly close to 1 and consequently one can use the approximation formula:

$$\left.\begin{aligned} a_\nu &\sim \alpha^{2\nu+1}\,\frac{\nu+1}{\nu}\,\frac{C_\nu}{1^2 \times 3^2 \ldots (2\nu-1)^2} \quad , \\ C_\nu &= \frac{m'^2 - 1}{m'^2 + \frac{\nu+1}{\nu}}\,(-1)^{\nu-1} \quad . \end{aligned}\right\} \tag{60}$$

Here C_ν is a complex number whose absolute value does not differ too greatly from 1*. Whereas a_ν, as (60) shows, at first increases with the $(2\nu + 1)$th power of α, the curve of the a_ν values bends away for larger values of α and never exceeds a certain value. This can be seen if, from (29a) and (19), one takes the values for I_ν and K_ν for very large arguments. Since α is real and $\beta = \beta' - i\beta'$, then:

$$\left.\begin{aligned} K_\nu(-\alpha) &\sim e^{-i\alpha} \quad , & K'_\nu(-\alpha) &\sim -ie^{-i\alpha} \quad , \\ I_\nu(\alpha) &\sim \sin\left(\alpha - \frac{\nu\pi}{2}\right) \quad , & I'_\nu(\alpha) &\sim \cos\left(\alpha - \frac{\nu\pi}{2}\right) \quad , \\ I_\nu(\beta) &\sim \frac{i}{2}\,e^{\beta''}e^{i\left(\beta' - \frac{\nu\pi}{2}\right)} \quad , & I'_\nu(\beta) &\sim \frac{1}{2}\,e^{\beta''}e^{i\left(\beta' - \frac{\nu\pi}{2}\right)} \quad . \end{aligned}\right\} \tag{60a}$$

---

* In the case of gold spherules, for example, the absolute value of C_1 lies between 0.9 and 2.5, depending on the colour of the light.

Thus, if this is introduced in (55), then, as the limiting value for very large values of α :

$$\left.\begin{aligned} a_\nu &\sim (2\nu+1)c_\nu \;, \\ c_\nu &= \frac{i^\nu e^{i\alpha}}{1+m'}\left(\sin\left(\alpha-\frac{\nu\pi}{2}\right)+im'\cos\left(\alpha-\frac{\nu\pi}{2}\right)\right) \;, \end{aligned}\right\} \qquad (61)$$

is obtained. Here c_ν is a complex quantity which varies periodically with α and which has an absolute value lying always in the region of 1.

Since, in (6) the power $\alpha^{2\nu+1}$ is constant but the denominator increases rapidly with ν , initially a_1 must far exceed all other coefficients. When a_1 tends towards its limiting value, however, (61), a_2 joints it as the second coefficient, while all others remain small. Later, a_3 is added to the first two coefficients and so on. From the formula for f_ν, g_ν etc., it can further be seen that, for the coefficients which follow later, formula (60) remains approximately valid for longer and longer.

From these considerations, it follows that, however large α might be, from a certain value of ν all coefficients remain so small in comparison with the first that they can be completely disregarded.

The radiation reflected by a small sphere is essentially always comprised of an infinite number of partial waves, although the number of partial waves increases as the sphere becomes larger.

This statement is, in the main, applicable only to 'electrical vibrations' of particles associated with the coefficients a_ν ; however, it is also valid for 'magnetic vibrations' which excite the incident waves, i.e. the coefficients p_ν to be discussed later in this section.

In the numerical examples introduced below in order to gain a closer insight into the optical properties of colloidal metal solutions, the diameter considered will have a value of up to $2\rho = 180\mu\mu$. This value already lies at the limit of microscopic resolution and thus corresponds to the extreme size of the particles of colloidal solutions. Even with the large diameter $2\rho = 180\mu\mu$, higher 'electrical partial vibrations' are already vanishingly small in comparison with the first two from $\nu = 3$, so that only a_1 and a_2 need be calculated.

On the other hand, it is necessary, for example in the case of the problem of the rainbow, which could be approached by the method used here, that a fairly large number of partial waves should be considered and very great difficulties as regards the calculation would then be encountered.

The first two coefficients are:

$$\left.\begin{aligned} a_1 &= 2\alpha^3 u_1 \frac{m'^2 - v_1}{m'^2 + 2w_1} , \\ a_2 &= -\frac{1}{6}\alpha^5 u_2 \frac{m'^2 - v_2}{m'^2 + \frac{3}{2} w_2} . \end{aligned}\right\} \qquad (62)$$

If α is very small, u, v and w can be taken as being equal to 1, whereupon:

$$\left.\begin{aligned} a_1 &= 2\alpha^3 \frac{m'^2 - 1}{m'^2 + 2} , \\ a_2 &= -\frac{1}{6}\alpha^5 \frac{m'^2 - 1}{m'^2 + \frac{3}{2}} . \end{aligned}\right\} \qquad (63)$$

Of course, for small values of α, a_2 is already vanishingly small in comparison with a_1 and so only each first partial wave remains, the existence of which was originally demonstrated theoretically by Lord Rayleigh; for this reason, I shall sometimes refer to this, for short, as Rayleigh radiation.

We may also consider briefly the special case in which the spherules are made of a perfectly conducting material. It is well known that this case was first discussed by J.J. Thomson, while F. Ehrenhaft had the idea that the theory developed by Thomson could be applied to the optics of colloidal solutions. Although, for the reasons given in section 1, this idea did not work, the case is of a certain historical and general theoretical interest. We put:

$$m'^2 = -i\infty \qquad (cf.\ (3)) ,$$

and accordingly disregard in equation (55) terms with the factor α in comparison with those having the factor β. Thus it is found that:

REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR

$$a_\nu = (2\nu + 1)i \frac{A'_\nu}{C'_\nu} .$$

For small values of α, therefore:

$$a_\nu = (-1)^{\nu-1} \frac{\nu + 1}{\nu} \frac{\alpha^{2\nu+1}}{1^2 \times 3^2 \ldots (2\nu - 1)^2} e^{i\alpha} \frac{f'_\nu}{h'_\nu + i\alpha k'_\nu} . \tag{63a}$$

For large values of α, (19) and (30a) give:

$$a_\nu = (2\nu + 1) i^{\nu+1} e^{i\alpha} \sin\left(\alpha - \frac{\nu - 1}{2} \pi\right) . \tag{63b}$$

The absolute value of this quantity varies uniformly and periodically between 0 and $(2\nu + 1)$.

Of particular interest here also is the Rayleigh wave; the accurate value of a_1 is:

$$a_1 = 3e^{i\alpha} \frac{\alpha \cos \alpha - (1 - \alpha^2) \sin \alpha}{i\alpha + (1 - \alpha^2)} . \tag{64}$$

For an infinitely small value of α, it is found that:

$$a_1 = 2\alpha^3 .$$

The characteristic difference between this formula and (63) is the fact that there the factor $(m'^2 - 1)/(m'^2 + 2)$ is involved which, as we shall see, cannot be taken as approximately equal to 1 in the case of metals, and which, above all, varies sharply with the wavelength. Another very important difference is the fact that, in (65), a_1 is a pure real quantity whereas the correct a_1 calculated from (63) has a very considerable imaginary part. This part governs the absorption in the colloidal metal solution, as we shall see.

We now proceed to the discussion of the 'magnetic vibrations', i.e. of the coefficients p_ν. For extremely small particles, formula (59) is not used, since $(1 - v_\nu)$ then approaches zero. Moreover, according to (57) and to (29) and (30):

$$\left.\begin{aligned}
1 - v_\nu &= \frac{1}{f'_\nu g_\nu}\,(f'_\nu g_\nu - f_\nu g'_\nu) \quad , \\
1 - v_\nu &= \frac{\beta^2 - \alpha^2}{(\nu + 1)(2\nu + 3)}\,\frac{1}{f'_\nu g_\nu} \\
&\quad \left(1 - \frac{1}{2\nu + 5}\,\frac{\alpha^2 + \beta^2}{2!} + \frac{1 \times 3}{(2\nu + 5)(2\nu + 7)}\,\frac{\alpha^4 + 2\,\frac{2\nu + 5}{2\nu + 3}\,\alpha^2\beta^2 + \beta^4}{4!} + \dots\right) \\
&= \frac{\beta^2 - \alpha^2}{(\nu + 1)(2\nu + 3)}\,\frac{\ell_\nu}{f'_\nu g_\nu} \quad .
\end{aligned}\right\}$$

...... (66)

Here ℓ_ν denotes, in a manner similar to the case of f_ν, f'_ν and so on, a rapidly converging power series in α^2 and β^2, which is equal to 1 for small particle diameters. Furthermore, now putting:

$$s_\nu = e^{i\alpha}\,\frac{\ell_\nu}{g_\nu}\,\frac{1}{h'_\nu + i\alpha k'_\nu} = u_\nu\,\frac{\ell_\nu}{f'_\nu g_\nu} \quad . \tag{67}$$

equation (59) gives, for p_ν:

$$p_\nu = \frac{(-1)^\nu}{\nu(2\nu + 3)}\,\frac{\alpha^{2\nu+3}}{1^2 \times 3^2 \dots (2\nu - 1)^2}\,s_\nu\,\frac{m'^2 - 1}{1 + \frac{\nu + 1}{\nu}\,w_\nu} \quad . \tag{68}$$

For very small diameters, one can approximately take:

$$p_\nu = \frac{(-1)^\nu}{(2\nu + 1)(2\nu + 3)}\,\frac{\alpha^{2\nu+3}}{1^2 \times 3^2 \dots (2\nu - 1)^2}\,(m'^2 - 1) \quad . \tag{69}$$

For large diameters, if the values of A_ν, A'_ν, etc. of equation (54) are calculated according to (29a) and (19), then equation (55) gives:

$$p_\nu \sim (2\nu + 1)\,i^\nu e^{i\alpha}\,\frac{m' \sin\left(\alpha - \frac{\nu\pi}{2}\right) + i \cos\left(\alpha - \frac{\nu\pi}{2}\right)}{m' + 1} \quad . \tag{70}$$

It is thus possible to describe the behaviour of p_ν in the same way as a_ν was dealt with in (15).

For small particles, p_ν increases with increasing particle size p_ν approximately in accordance with:

$$\left.\begin{aligned} p_\nu &\sim \alpha^{2\nu+3} \frac{C'_\nu}{1^2 \times 3^2 \ldots (2\nu - 1)^2 (2\nu + 1)(2\nu + 3)} \\ C'_\nu &= (m'^2 - 1)(-1)^\nu \end{aligned}\right\} \tag{71}$$

The absolute value of C'_ν is not far removed from 1. For large values of α, the curve of the p_ν-values bends away and finally, for very large values of α, it changes periodically as the particle diameter increases further:

$$p_\nu \sim (2\nu + 1)c'_\nu \; . \tag{72}$$

Here c'_ν is a complex quantity, varying periodically; its amplitude is not far from 1.

Where the magnetic partial vibrations are concerned, the same considerations apply as those advanced in the case of electrical ones; in fact, the νth magnetic vibration runs approximately parallel to the $(\nu + 1)$th electrical vibration.

From a comparison of formulae (69) and (70) with (60) and (61), it can be seen that the absolute value of p_ν in general lies somewhat below that of $a_{\nu+1}$.

The first magnetic partial vibration is for example, always of the same order of magnitude as the second electrical one for all particle sizes.

Very small particles always radiate laterally only the Rayleigh wave; with quite coarse particles in colloidal solution, the second electrical and the first magnetic partial vibration come into the picture.

Thus, in the numerical examples below, I have considered, in all, just three coefficients, namely a_1, a_2 and p_1. I shall calculate p_1 for coarser particles from the following equation:

$$p_1 = -2\alpha^3 u_1 \frac{1 - v_1}{1 + 2w_1} \; , \tag{73}$$

where u_1, v_1 and w_1 are the same quantities as in (62). For smaller particles, the approximation formula:

$$p_1 = -\frac{\alpha^5}{15}(m^2 - 1) \quad , \tag{74}$$

applies.

Whereas the assumption of perfect conductivity in the case of electrical partial vibrations leads to results which nevertheless agree with those given by exact theory, for magnetic vibrations, this assumption leads to widely deviating results. If β in (55) is taken as being infinitely large, then we obtain:

$$p_\nu = -(2\nu + 1)i^\nu \frac{A_\nu}{\mathfrak{C}_\nu} \quad .$$

Therefore, for small diameters, according to (27) and (29) we obtain:

$$p_\nu = (-1)^{\nu-1} \frac{\alpha^{2\nu+1}}{1^2 \times 3^2 \ldots (2\nu - 1)^2} e^{i\alpha} \frac{f_\nu}{h_\nu + i\alpha k_\nu} \quad , \tag{74a}$$

a value which is of quite the same order of magnitude as the value of a_ν found under the same assumption.

If we accept that the spherules suspended in the medium are perfect conductors, then we find the reverse result that the magnetic partial vibration of the νth order runs parallel to the electrical partial vibration of the same order number (instead of the next-highest order number). Particularly in the case of very fine particles, therefore, we arrive at the false result that, in addition to the Rayleigh wave, the first magnetic vibration is involved in approximately the same order of magnitude.

J.J. Thompson, who first proved the last part of this sentence, showed, as already known, that the investigation of the polarisation of light scattered laterally by colloidal metal solutions revealed the falseness of the result. The strange polarisation phenomena which F. Ehrenhaft[7] and E. Müller[8] later observed, in no way indicate a partial validity of the assumption of perfect conductivity. We shall see later that the exact theory explains it quite spontaneously.

In view of the later numerical discussion, the value of p_1 should be noted:

$$p_1 = 3e^{i\alpha}\frac{\sin\alpha - \alpha\cos\alpha}{1 + i\alpha} , \qquad (75)$$

For very small values of α :

$$p_1 = \alpha^3 . \qquad (76)$$

If (76) is compared with (65), it is seen that the amplitude of the magnetic vibration for very small, perfectly conducting spherules, must be exactly half that of the electrical vibration.

11 PARTIAL WAVES

For purposes of the following discussion, it will be useful to have a representation showing how the intensity and direction of vibration of the individual partial waves (particularly the first) vary from point to point on a large sphere at the centre of which the spherule under consideration lies.

The components E_r and H_r does not have to be considered, since they hardly take part in the transfer of energy into the outer space according to Poynting's law. Thus, only the components tangential to the surface of the sphere remain. However, for each partial wave, in accordance with (13) and (14):

$$E_\vartheta M_\vartheta + E_\varphi M_\varphi = 0$$

applies; that is, the magnetic lines of force on the face of the sphere everywhere run perpendicular to the electrical ones. It is therefore sufficient, to obtain a clear representation of the radiation, if one depicts the pattern of the electrical lines of force on the face of the sphere.

In Figs.3-10, the electrical field lines on a sphere surrounding the particle are shown for the first four electrical and the first four magnetic partial vibrations. The plane of the drawing is the 1 × 3 plane, that is, the vibration plane of the light beam which excites the waves. It is a plane of symmetry of the process, and it is easy to complete the figures by adding, to the front half-sphere represented, the hemisphere lying behind the plane of the drawing, since the curves on both are quite congruent. In the case of magnetic vibrations, $E_r = 0$; the lines therefore run as closed spherical curves, and, in fact, for each of the two hemispheres, there are ν central points on the equator ($\vartheta = \pi/2$) at which the force is zero and around which the lines of the field wind in ν different groups. In the case of electrical vibrations, on the other hand, the lines of the field run in certain conical surfaces which all go through ν conical diameters lying in the plane of the drawing. The curves shown are the lines of intersection of these conical surfaces with the sphere. These curves all run towards the ν poles which are marked out by the ν diameters. In fact, the lines of the field bend away from the spherical surface in order to close up either internally or externally, depending on the phase of the vibration, since they can naturally have neither beginning nor end (apart from the lines directly on the radiating particles).

It is now easy to form a picture of the magnetic field lines also. The figures of Group I give, straight away, the magnetic field lines of Group II and vice versa, if they are rotated by 90°, i.e. axes 1 and 2 are exchanged.

12 THE DIFFUSE LATERAL RADIATION

If observations are carried out at an infinite distance from the particle, we then have to introduce in (52):

$$K_\nu(-x) = e^{-ix} ,$$

as obtained from equation (19). Then, moreover:

$$K'_\nu(-x) = -ie^{-ix} ,$$

hence:

$$\left.\begin{aligned}
E_{\vartheta a} &= +iM_{\varphi a} = -i\,\frac{\lambda'}{2\pi}\,\frac{e^{-\frac{2\pi i\nu}{\lambda'}}}{r} \\
&\qquad \sum_1^\infty \nu\left(\frac{a_\nu}{\nu(\nu+1)}\,\frac{\partial P_\nu}{\partial\vartheta} + \frac{p_\nu}{\nu(\nu+1)}\,\frac{1}{\sin\vartheta}\,\frac{\partial P_\nu}{\partial\varphi}\right) , \\
E_{\varphi a} &= -iM_{\vartheta a} = -i\,\frac{\lambda'}{2\pi}\,\frac{e^{-\frac{2\pi ir}{\lambda'}}}{r} \\
&\qquad \sum_1^\infty \left(\frac{a_\nu}{\nu(\nu+1)}\,\frac{1}{\sin\vartheta}\,\frac{\partial P_\nu}{\partial\varphi} - \frac{p_\nu}{\nu(\nu+1)}\,\frac{\partial P_\nu}{\partial\vartheta}\right) .
\end{aligned}\right\} \qquad (77)$$

It is thereby assumed, that the light passing through the solution is linearly polarised, in such a way that the direction of electrical vibration forms axis 1. According to (47):

$$E_1 = -iM_2 = e^{\frac{2\pi i z}{\lambda'}} .$$

Relative to the intensity of the light passing through as the unit, the intensity of the diffusely-scattered light is:

$$\left.\begin{aligned} J_\vartheta &= \frac{\lambda'^2}{4\pi^2 r^2}\left|\sum_1^\infty \nu\left(\frac{a_\nu}{\nu(\nu+1)}\frac{\partial P_\nu}{\partial\vartheta} + \frac{p_\nu}{\nu(\nu+1)}\frac{1}{\sin\vartheta}\frac{\partial P_\nu}{\partial\varphi}\right)\right|^2 , \\ J_\varphi &= \frac{\lambda'^2}{4\pi^2 r^2}\left|\sum_1^\infty \nu\left(\frac{a_\nu}{\nu(\nu+1)}\frac{1}{\sin\vartheta}\frac{\partial P_\nu}{\partial\varphi} - \frac{p_\nu}{\nu(\nu+1)}\frac{\partial P_\nu}{\partial\vartheta}\right)\right|^2 . \end{aligned}\right\} \qquad (78)$$

In these formulae, the straight lines indicate that the absolute value of the complex quantities between them is to be taken. From (78), it can be seen that intensity is inversely proportional to the square of the distance r; this was clear previously. The two intensities J_ϑ and J_φ denote the vibration components parallel to the meridian (J_ϑ) and to the parallel of latitude (J_φ). Both components have, in general, a quite definite phase difference which can be found by calculating the phases of the two complex quantities in (77) in the usual way. If therefore the solution is viewed at an angle to the beam passing through it, one must, in general, receive polarised light, assuming that the beam passing through is linearly polarised and that the suspended particles are so large that, in addition to the Rayleigh radiation (which is, in itself, linearly polarised), still higher partial waves are also observed.

However, all directions lying in the two planes of symmetry 1.3 and 2.3 are exempted from this. From the figures of section 19, it can be seen at once that: if the colloidal solution is illuminated with linearly polarised light and is observed in a direction at right angles to its electrical vibration, then the light scattered laterally is linearly polarised and the direction of its electrical vibration is in fact parallel to that of the beam passing through the solution. If the direction of vibration of the beam passing through the solution is rotated by 90° without alteration in the viewing direction, then linearly polarised light is again obtained, but its direction of vibration is also rotated by 90° in relation to the former direction.

The first case is characterised in our formulae by $\vartheta = \pi/2$ and the second case by $\varphi = \pm \pi/2$.

Although the statement just made may appear to be a simple one, it can nevertheless acquire great importance. The observations which Herr Steubing (see section I) made on the polarisation of light scattered laterally showed that, if illumination is carried out in the way specified with perfectly linearly polarised light, the lateral radiation always contains, although to a very small extent, some unpolarised light in addition to the predominating linearly polarised light. I am very much inclined, from this, to draw the conclusion that the particles suspended in colloidal solutions cannot be spheres, even if the remaining optical properties should support this assumption.

The case in which illumination is carried out with unpolarised light can now be readily dealt with. One can simply imagine the unpolarised light to be dissociated into two incoherent beams of equal intensity, which are linearly polarised; of these beams, one is considered to have its direction of electrical vibration perpendicular to the plane fixed by the direction of the beam and the radius of vision and the other to have its direction of electrical vibration in this plane. Two incoherent, linearly polarised components at right angles to each other are then also obtained in the light transmitted, but having in general, different intensities. This therefore means that the light transmitted is partly linearly polarised.

If an unpolarised beam of light is passed through the colloidal solution, then the light scattered laterally is always partly linearly polarised (never elliptically). In fact, the direction of electrical vibration of the polarised component is either perpendicular to the plane fixed by the direction of the beam and the radius of vision or in this plane, depending on the particle size and the direction of vision.

This statement is naturally valid here only under the assumption that the particles are spherical, but there is no doubt that is always applied in the case of amorphous (hence non-dichroic) colloidal solutions.

When solutions containing very small particles are involved, it is known that only the first direction of polarisation mentioned is observed; with large particles, however, as we shall see, the second direction is also present.

13 INTENSITY OF THE LIGHT SCATTERED AT RIGHT ANGLES TO THE TRANSMITTED LIGHT

Since, in general, observations are carried out using unpolarised light, only the two main cases (I) $\vartheta = \pi/2$ and (II) $\varphi = \pm\pi/2$ are of interest to us. In both cases, $E_\varphi = M_\vartheta = 0$, so that only J_ϑ remains; we shall denote this as J_I and J_{II} in the two cases. J_I is the intensity of the radiation which has its direction of vibration perpendicular to the plane of vision, as we may say for short. J_{II} is the intensity of the beam vibrating in the plane of vision. Firstly, (44) and (45) give for the two cases:

$$\left.\begin{aligned} &(I) \quad \vartheta = \frac{\pi}{2}, \qquad \sin\varphi = v, \\ &\frac{\partial P_\nu}{\partial\vartheta} = -\Pi_\nu(v), \qquad \frac{1}{\sin\vartheta}\frac{\partial P_\nu}{\partial\vartheta} = (1 - v^2)\Pi'_\nu(v) - v\Pi_\nu)(v) \quad . \end{aligned}\right\} \qquad (79)$$

$$\left.\begin{aligned} &(II) \quad \varphi = \pm\frac{\pi}{2}, \qquad \sin\vartheta = \pm v, \\ &\frac{\partial P_\nu}{\partial\vartheta} = \pm\left\{(1 - v^2)\Pi_\nu(v) - v\Pi_\nu(v)\right\}, \qquad \frac{1}{\sin\vartheta}\frac{\partial P_\nu}{\partial\varphi} = \mp\Pi_\nu(v) \quad . \end{aligned}\right\} \qquad (80)$$

This must be introduced in (78). Initially, we shall now restrict discussion to the case where observation is carried out only perpendicular to the beam. We thus put $\nu = 0$ and then use formulae (40) and (41). It is found that:

$$\left.\begin{aligned} J_1 &= \frac{\lambda'^2}{4\pi^2 r^2}\left|-\frac{a_1}{2} + \sum_1^\infty \sigma(-1)^{\sigma+1}\frac{(2\sigma)_\sigma}{2^{2\sigma}}\left(\frac{a_{2\sigma+1}}{2(\sigma+1)} + p_{2\sigma}\right)\right|^2 \quad , \\ J_{II} &= \frac{\lambda'^2}{4\pi^2 r^2}\left|\sum_1^\infty \sigma(-1)^{\sigma+1}\frac{(2\sigma)_\sigma}{2^{2\sigma}}\left(a_{2\sigma} - \frac{p_{2\sigma-1}}{2\sigma-1}\right)\right|^2 \quad . \end{aligned}\right\} \qquad (81)$$

These equations are written in such a way that each summand contains two coefficients having the same order of magnitude (*cf.* section 10). In the numerical example it is possible, as mentioned several times previously, to restrict considerations to the coefficients a_1, a_2 and p_1. The following formulae is thus used for the calculation:

$$\left.\begin{aligned} J_I &= \frac{\lambda'^2}{4\pi^2 r^2}\left|\frac{a_1}{2}\right|^2 , \\ J_{II} &= \frac{\lambda'^2}{4\pi^2 r^2}\left|\frac{a_2 - p_1}{2}\right|^2 . \end{aligned}\right\} \qquad (82)$$

J_{II} has a significant value only in the case of the very largest particles and even then, J_I still predominates. This is the intensity of the Rayleigh radiation and its maximum occurs in fact at right angles to the electrical vibration which excites it. At other angles, its intensity is:

$$J = J_1 \sin^2\vartheta$$

and its total radiation is accordingly:

$$R = J_1 2\pi r^2 \int_0^\pi \sin^3\vartheta \, d\vartheta = \frac{8\pi}{3} r^2 J_1 . \qquad (82a)$$

Consequently, it is thus possible, if one measures the Rayleigh radiation in the principal direction (J_I), to calculate its total value, i.e. therefore, the loss experienced by the transmitted beam of light due to this radiation. In the following discussion, the quantity:

$$R = \frac{2}{3\pi} \lambda'^2 \left|\frac{a_1}{2}\right|^2 \qquad (83)$$

will always be given; this is also a measure of J_1 :

$$J_1 = \frac{3}{8\pi} \frac{R}{r^2} . \qquad (84)$$

How the total value of radiation II is found we shall see in section 17.

14 RADIATION OF MANY PARTICLES

So far, we have always restricted ourselves to the calculation of the light scattered diffusely by a single spherule. We shall now proceed to the case where a large number of spherules are finely dispersed in the medium, all of the same diameter 2ρ and of the same optical behaviour m'. Each individual spherule is then struck not merely by the beam passing directly through it, but also by the light diffusely scattered by the other spherules. The effect of this second other vibration on the process within each spherule and the resulting change in the total lateral radiation thereby incurred has been theoretically investigated for extremely small particles by L. Lorenz, while J.C. Maxwell-Garnett has followed the consequences of the Lorenz theory mathematically in relation to the optics of colloidal metal solutions (*cf.* section 1). It is seen there that the suspended particles must lie very close together if the interaction between the lateral radiation and the radiation process itself is to be observable.

We shall regard aqueous colloidal solutions of metals in the following discussion as being optically infinitely dilute and we shall calculate the total lateral radiation simply by multiplication of radiation diffusely scattered due to the existence of an individual particle, by the number of particles present.

If one has remaining objections concerning the validity of this assumption, it can readily be checked experimentally, whereupon the solution is diluted still further. If our assumption is correct, the colour of the solution must thereby remain unchanged and the absorption must be shown to be proportional to the concentration in all parts of the spectrum. On the other hand, if the assumption were false, then a colour change would thereby occur, as observed by Kirchner and Zsigmondy in investigations on concentrated gold solutions in gelatine (*cf.* section 1). So far as I know, such concentrated aqueous solutions have not yet been achieved. In any case, I restrict myself to the usual dilute solutions.

In the following discussion, we shall give the concentration of the solution in cubic millimetres of metal per cubic millimetre of water. If the number of particles in a cubic millimetre is N, their diameter 2ρ, so that the volume $V = 4\pi\rho^3/3$, then the concentration is:

$$C = NV = \frac{\lambda'^3}{6\pi^2} N\alpha^3 . \qquad (85)$$

On the other hand, according to (83), the total value of the Rayleigh radiation is:

$$R = N \frac{2}{3\pi} \lambda'^2 \left|\frac{a_1}{2}\right|^2 ,$$

hence:

$$R = F_1 C \quad , \tag{86}$$

where F_1 is a quantity which is independent of the concentration but which depends on the particle size and the wavelength. For this quantity F_1, we shall use two different formulae according to whether the particles are small or large:

$$F_1 = \frac{24\pi^3}{\lambda'^4} V \left| \frac{a_1}{2\alpha^3} \right|^2 \quad , \tag{87}$$

$$F_1 = \frac{4\pi}{\lambda'} \frac{1}{\alpha^3} \left| \frac{a_1}{2} \right|^2 \quad . \tag{88}$$

The first formula is particularly suitable for small particles, since, as we already know, for very small spherules a_1 increases proportionally with α^3. According to (62):

$$\frac{a_1}{2\alpha^3} = u_1 \frac{m'^2 - v_1}{m'^2 + 2w_1} \quad , \tag{88a}$$

where u_1, v_1 and w_1 assume the value 1 for very small particle diameters. Thus:

$$F_1 = \frac{24\pi^3}{\lambda'^4} V \left| u_1 \frac{m'^2 - v_1}{m'^2 + 2w_1} \right|^2 \tag{89}$$

and, for extremely small particles:

$$F_1 = \frac{24\pi^3}{\lambda'^4} V \left| \frac{m'^2 - 1}{m'^2 + 2} \right|^2 \quad . \tag{90}$$

This equation (90) is none other than the familiar Rayleigh formula[9]. It indicates that, at constant concentration, the radiation of a solution is all the greater, the coarser are the particles. In fact, the intensity of the radiation is directly proportional to the particle volume. Moreover, in general, short-wave rays predominate if the factor $(m'^2 - 1)/(m'^2 + 2)$ which is dependent on the optical properties of the spherules, does not greatly vary with the colour of the light. This last statement does not actually hold absolutely true in the case of metals; the light diffusely radiated by colloidal metal solutions containing the finest particles is, for this reason, generally not blue like other turbid solutions, but has a colour characteristic of the metal involved. If $(m'^2 - 1)/(m'^2 + 2)$ is constant, then the familiar Rayleigh law applies, according to which, for different colours under otherwise similar conditions, the radiation is proportional to λ'^{-4}.

Equation (88) can serve to follow Rayleigh's radiation law up into the range of very coarse particles. As we have seen (in section 10), a_1 for very large particles varies as a periodic function of the particle diameter with constant amplitude. From equation (88), it is accordingly found that, at constant concentration, the Rayleigh radiation decreases with increasing particle diameter as soon as the particles become large. Indeed, apart from periodical variations, the Rayleigh radiation is finally inversely proportional to the particle volume.

(I) At constant concentration, the Rayleigh radiation increases, for a very fine dispersion, as the particle diameter increases, roughly in proportion to the particle volume, but reaches a maximum once the particles have already become quite large and from then on decreases continually and rapidly if the distribution grows still coarser; actually, maxima can be established periodically which become weaker and weaker.

(II) If the spherules consist of perfectly conducting material or of material which, to all intents and purposes is perfectly white, the particle diameter for which the maximum of the radiation is achieved is proportional to the wavelength and the maximal value of the radiation itself is inversely proportional to the wavelength.

The second statement which is derived directly from equation (88) naturally does not apply to colloidal metal solutions.

It would be possible, perhaps with certain reservations, to define as optical resonance the occurrence of this radiation maximum, which must also arise in the case of turbidity produced by non-conducting bodies (mastic turbidity, steam jet, etc.), although at a different position, as it does in the case of conductors. However, it must be borne in mind that this 'optical resonance' is associated only with quite flat maxima and that, consequently, the energy spectrum of the diffuse radiation will show only slight increases

$$\frac{\mathrm{a}_1}{2\alpha^3} = a_1 \quad . \tag{91}$$

The Rayleigh radiation is then calculated, according to (87) as:

$$\left.\begin{aligned} F_1 &= \frac{24\pi^3}{\lambda'^4} V|a_1|^2 \quad , \\ a_1 &= u_1 \frac{m'^2 - v_1}{m'^2 + 2w_1} \quad . \end{aligned}\right\} \tag{92}$$

The radiation for infinitely fine particles is found by setting u_1, v_1 and w_1 equal to 1 in all three cases. For gold, the following values are obtained for $(a_1)_0 = (m'^2 - 1)/(m'^2 + 2)$:

$\lambda =$	420	450	500	525
	$0.579 - i \times 0.675$	$0.602 - i \times 0.666$	$0.807 - i \times 1.180$	$1.330 - i \times 1.440$

$\lambda =$	550	600	650
	$1.925 - i \times 1.211$	$1.880 - i \times 0.391$	$1.545 - i \times 0.180$.

In each case, these values are quite different from those which one would find in the case of infinitely high conductivity. For perfect conductors, formula (65) gives, in fact:

$$(a_1)_0 = 1$$

quite independently of the wavelength. In general, for metals, a_1 has the form:

$$a_1 = a_1' - ia_1''$$

and:

$$|a_1|^2 = a_1' + a_1''^2 \quad .$$

In order to emphasise clearly the difference compared with the perfect conductor, for which $|a_1|^2 = 1$, when radiation is considered, I shall also write down the values of $|a_1|^2$ for gold:

above a mean value, even with a high degree of uniformity of the particles forming the turbidity, if the particles have become coarse. The radiated light in the case of turbid bodies containing non-conducting particles (steam jet, mastic turbidity) is therefore finally almost white with only a weak tinge of colour. Colloidal metal solutions behave similarly; as we shall see, in the case of gold, for example, the yellow is, in general, rather conspicuous, corresponding to the natural yellow colour.

15 RAYLEIGH RADIATION OF GOLD SOLUTIONS

I now begin the calculation of the optical properties of a suspension of extremely small gold spherules in water, taking first of all the Rayleigh radiation. As a basis, the following figures are obtained when the smoothest possible curve is drawn through the measured values recorded by Hagen and Rubens[10]. Only values of the reflection coefficient in the violet region have been changed somewhat, since those given by Hagen and Rubens[11] are certainly too small.

λ	R (H and R)	$\nu\chi$ (H and R)	R (taken)	$\nu\chi$ (taken)	m	m'^2	λ'
420	0.293	1.72	0.332	1.70	$1.70 - i \times 1.70$	$0.00 - i \times 3.20$	313
450	0.331	1.73	0.338	1.72	$1.73 - i \times 1.72$	$-0.017 - i \times 3.32$	336
500	0.470	2.07	0.480	2.02	$1.10 - i \times 2.02$	$-0.160 - i \times 2.49$	374
525	-	-	0.613	2.23	$0.79 - i \times 2.23$	$-2.45 - i \times 1.98$	393
550	0.740	2.32	0.730	2.45	$0.57 - i \times 2.45$	$-3.20 - i \times 1.57$	412
600	0.844	2.91	0.850	2.96	$0.38 - i \times 2.96$	$-4.84 - i \times 1.26$	450
650	0.889	3.58	0.888	3.54	$0.41 - i \times 3.54$	$-6.97 - i \times 1.63$	487

In this table, the first column contains the wavelengths of the colours concerned in vacuum, the next two columns show the reflection coefficient and the absorption factor according to Hagen and Rubens, the third and fourth columns give the values which I chose for the calculation, m is the complex index of refraction of the gold relative to a vacuum calculated from these values, m'^2 is the square of the complex refractive index relative to water $\left(m'^2 = m^2/m_0^2\right)$ and finally λ' is the wavelength in water.

Furthermore, I shall introduce a practical abbreviation in the following discussion:

λ =	420	450	500	525	550	600	650
$\|a_1\|^2$ =	0.790	0.805	2.05	3.84	5.18	3.70	2.42

We can now already form a picture of the energy spectrum of the lateral radiation by very small particles, since this is equal to the product of the concentration, particle volume and the value $24\pi^3|a_1|^2/\lambda'^4$.

The following table gives these values, both for perfectly conducting spherules and for gold spherules:

	420	450	500	525
$\frac{24\pi^3}{\lambda'^4} \times 1$	7.76×10^{16}	5.85×10^{16}	3.81×10^{16}	3.13×10^{16}
$\frac{24\pi^3}{\lambda'^4}\|a_1\|^2$	6.12×10^{16}	4.71×10^{16}	7.77×10^{16}	11.95×10^{16}

	550	600	650
$\frac{24\pi^3}{\lambda'^4} \times 1$	2.59×10^{16}	1.82×10^{16}	1.315×10^{16}
$\frac{24\pi^3}{\lambda'^4}\|a_1\|^2$	13.37×10^{16}	6.70×10^{16}	3.17×10^{16}

As the unit of length, I have here and in the following discussion, chosen the millimetre.

With the exception of the extreme blue and the violet, the radiation by gold spherules is stronger than that which perfectly conducting spherules would emit.

One could then perhaps say that the atoms of gold resonate in response to light waves, best of all to green-yellow ones. However, it is then necessary to suppose that, in larger particles, they are better coupled with the vibrating ether than in small particles, since the radiation increases with the volume of the particles.

Fig.11 represents the radiation of small gold particles and of small, perfectly conducting particles again in graph form. (The dotted curve gives the radiation of the latter following the addition of the first magnetic vibration (*cf.* section 10).) The last-mentioned radiation follows the Rayleigh law quite accurately (proportional to λ'^{-4}).

In order to find the radiation for coarser dispersions also, it is necessary to calculate u_1, v_1 and w_1 which are comprised of series in α^2 (or $\beta^2 = m'^2\alpha^2$). I carried out the calculation for the values of α^2 given in the first column of Table 1 and, at the same time, I calculated a_1 also for the case of a perfect conductor, taking the same value of α^2. Thereupon I calculated the radiation (87):

$$F_1 = \frac{24\pi^3}{\lambda'^4} V \left| \frac{a_1}{2\alpha^3} \right|^2 = \frac{4\pi}{\lambda'} \alpha^3 |a_1|^2 . \qquad (92a)$$

The particle diameter associated with any value of α^2 :

$$2\rho = \frac{\lambda'}{\pi} \sqrt{\alpha^2}$$

can be taken from the following table:

Particle diameter in μμ

α^2	λ = 420	450	500	525	550	600	650
0.2	44.6	47.8	53.2	55.9	58.6	64.0	69.3
0.4	63.1	67.6	75.2	79.1	82.9	90.5	98.1
0.6	77.3	82.9	92.2	96.8	101.5	110.8	120.1
0.8	89.3	95.8	106.5	111.8	117.2	128.0	138.7
1.0	99.8	107.0	119.0	125.0	131.0	143.0	155.0
1.5	122.2	131.1	145.8	153.1	160.5	175.2	190.0
2.0	141.1	151.3	168.3	176.8	185.3	202.2	219.2
2.5	157.7	169.1					

The curves illustrating the dependence of the radiation on the particle diameter are shown in Fig.12. The abscissa gives the particle diameter in μμ, while the ordinate gives the total intensity of the radiation R emitted by a cubic millimetre of a solution having a concentration of 10^{-6} (1mm^3 of gold per litre of water), the values being expressed in parts per thousand of the intensity of the beam of light transmitted by a square millimetre.

The value F_1 is thus obtained from the figures given on the ordinate by multiplication by 10^3. For purposes of comparison, the corresponding curves (only of the Rayleigh radiation) are shown on the same scale in Fig.13 for spherules of a perfect conductor. The diameters for which the maximum of the radiation is achieved are here proportional to the wavelengths λ' ; in fact:

$$2\rho_{max} = 0.324\lambda' \ .$$

The maxima decrease with increasing wavelength in proportion to $1/\lambda'$.

The radiation emitted by gold particles is, apart from the blue and violet, considerably greater throughout than that emitted by perfectly conducting particles. As stated earlier, it is as though the resonance of the gold atoms in the yellow had been added to the 'resonance' of the particles. The curve rises to its highest point for 600μμ (hence in the orange-yellow). The diameters of the particles giving rise to the most intense radiation are:

	420	450	500	525	550	600	650
$2\rho_{max}$	105	111	110	100	96	113	131
λ'	113	336	374	393	412	450	487
$\frac{2\rho_{max}}{\lambda'}$	0.336	0.331	0.294	0.255	0.233	0.252	0.269

Thus $2\rho_{max}$ lies, in general, between $\lambda'/4$ and $\lambda'/3$.

From the curves in Fig.12, one can readily obtain the energy spectrum of the radiation for given particle sizes. From these curves, the following values are found:

2ρ	420	450	500	525	550	600	650
20	0.262	0.199	0.338	0.546	0.637	0.299	0.139
40	2.10	1.60	2.72	4.62	5.90	2.92	1.35
60	6.2	5.0	8.0	13.7	19.7	12.3	5.9
80	10.4	9.1	14.1	22.9	37.8	33.0	14.7
100	13.2	12.0	17.2	27.1	42.3	55.5	29.0
120	12.5	12.0	17.1	25.0	36.0	57.5	45.0
140	10.0	10.5	15.0	20.8	27.9	44.5	46.2
160	7.9	8.5	12.4	17.1	22.5	33.3	36.8
180	6.3	7.2	10.4	13.8	17.7	25.0	28.0

Using these values, the curves in Fig.14 can be constructed. From the curves, it is seen that small spherical gold particles must appear yellow-green in the ultramicroscope. The larger they become, the more their colour changes to yellow and red-yellow. At constant concentration, the most intense radiation is emitted by solutions containing particles with a diameter of between 100 and 140μμ which emit mainly light of an orange colour. The solutions emitting the most intense radiation therefore appear brown in incident light.

That these colour phenomena are governed by the special optical behaviour of the gold is apparent if the corresponding radiation curves are constructed from the 'resonance curves' of perfectly conducting spherules. This has been illustrated in Fig.15 for the particle sizes $2\rho = 100$, 120, 140, 160 and 180μμ. These are therefore all quite coarse turbidities. Whereas for $2\rho = 100$, the curve climbs quite steeply towards the violet, with increasing particle size, the curve becomes flatter and flatter and shows a rather weak maximum which, for a particle size of 180μμ, already lies at a wavelength greater than 650μμ. Light transmitted by particles larger than 100μμ is thus in fact quite white, with a weak tinge of colour which can be blue, green, yellow or red, depending on the size of the particle. Actually, at 180μμ, according to Fig.15, an orange tinge must have been fairly clear, but for the fact that here we restricted ourselves to Rayleigh radiation. If the following partial waves had also been taken into consideration, then all curves, and particularly the last, would have flattened off still more, as a simple, rough calculation shows.

Colours similar to those transmitted by the imaginary, perfectly conducting particles would also be obtained for colourless particles. From the formulae which I have used, it is readily possible, for example, to evaluate the phenomena of coloured vapour jets and curves like those in Fig.15 will thereby be obtained, but for other particle sizes.

16 POLARISATION OF LIGHT DIFFUSELY SCATTERED BY GOLD SOLUTIONS

We now proceed to the calculation of the coefficients a_2 and p_1. For convenience, we introduce here some new expressions:

$$\mathfrak{a}_2 = -\frac{a_2}{2\alpha^3}, \qquad \mathfrak{p}_1 = \frac{p_1}{2\alpha^3}. \tag{93}$$

From (62), (73) and (74), it follows that:

$$\mathfrak{a}_2 = \frac{\alpha^2}{12} u_2 \frac{m'^2 - v_2}{m'^2 + 1.5w_2}, \qquad \mathfrak{p}_1 = u_1 \frac{v_1 - 1}{1 + 2w_1}, \tag{94}$$

and, for small values of α:

$$\mathfrak{a}_2 = \frac{\alpha^2}{12} \frac{m'^2 - 1}{m'^2 + 1.5}, \qquad \mathfrak{p}_1 = \frac{\alpha^2}{30}(1 - m'^2). \tag{95}$$

Here u_1, v_1 and w_1 are the functions of α^2 already used in the calculation of a_1 and u_2, v_2 and w_2 are obtained from equations (57) and (27) to (30).

From the values of a_1 and p_1 given in Tables 2 and 3, it can be seen that the second electrical and the first magnetic partial wave can only occur for a very coarse distribution emitting the Rayleigh radiation. They occur most strongly at about 550μμ. If the ratio J_{II}/J_I is calculated for 550μμ according to (82) for the radiation emitted perpendicular to the transmitted beam:

$$\frac{J_{II}}{J_I} = \frac{|a_2 - p_1|^2}{|a_1|^2} = \frac{|a_2 + p_1|^2}{|a_1|^2} , \qquad (96)$$

then it is found that:

α^2	small	1	2
J_{II}/J_I	$0.016\alpha^4$	0.059	0.642
2ρ	-	131μμ	185.3μμ .

With the help of these figures, the one curve in Fig.16 is constructed. It is now possible and is quite usual to give the polarised light content of the radiation in percent; this is:

$$P = \frac{J_I - J_{II}}{J_I + J_{II}} .$$

In our example, we have:

α^2	1	2
P	0.885	0.22
2ρ	131μμ	185.3μμ .

The value P is represented by the second curve in Fig.16.

If the radiation of a colloidal gold solution at 90° to the beam passing through it is not completely polarised, it follows from this that the solution contains particles having a diameter well above 100μμ. For a particle size of 130μμ, the amount of polarisation is still about 90%.

Solutions containing particles with a diameter above 100μμ are precisely those which emit mainly yellow and red radiation. We shall see in the following discussion that they are always transparent to blue light.

Only particles of blue gold solutions radiate light which is polarised to only a small extent at 90° to the transmitted beam.

The statement is to be made only with reservations, however, since it rests on the assumption of spherical particles. In any case, there are also blue solutions which, at 90°, to all intents and purposes radiate polarised light completely. Nevertheless, it can certainly be said that there are no red solutions which fail, at 90°, to give completely polarised light. If observations lead to any other result (see, for example, Ref.12), then it follows that the solutions used were undoubtedly inhomogeneous and contained many weakly-radiating, but strongly absorbing, red particles and relatively few strongly-radiating blue particles.

We shall now proceed to the calculation of the polarisation of the light at different angles in relation to the transmitted beam. We shall denote the angle made with the direction of the incident beam by γ. In the two main cases I and II (section 13), we then have:

$$\left.\begin{aligned}
&\text{I}\quad \vartheta = \frac{\pi}{2}\,, \qquad \varphi = \frac{\pi}{2} - \gamma\,, \qquad v = \cos\gamma \\
&J_{I} = \frac{\lambda'^2}{4\pi^2 r^2}\left|\sum_{1}^{\infty} \nu\left\{\frac{a_\nu}{\nu(\nu+1)}\Pi_\nu + \frac{p_\nu}{\nu(\nu+1)}\left(v\Pi_\nu - (1-v^2)\Pi'_\nu\right)\right\}\right|^2 . \\
&\text{II}\quad \varphi = \frac{\pi}{2}\,, \qquad \vartheta = \frac{\pi}{2} - \gamma\,, \qquad v = \cos\gamma\,. \\
&J_{II} = \frac{\lambda'^2}{4\pi^2 r^2}\left|\sum_{1}^{\infty} \nu\left\{\frac{a_\nu}{\nu(\nu+1)}\left(v\Pi_\nu - (1-v^2)\Pi'_\nu\right) + \frac{p_\nu}{\nu(\nu+1)}\Pi_\nu\right\}\right|^2 .
\end{aligned}\right\} \qquad (96a)$$

Since, in the following discussion, we are concerned only with the relative values $J_{II}:J_I$, we shall calculate only the values:

$$\mathcal{J}_I = \frac{4\pi^2 r^2}{\lambda'^2}\,\frac{J_I}{\alpha^6}\,, \qquad \mathcal{J}_{II} = \frac{4\pi^2 r^2}{\lambda'^2}\,\frac{J_{II}}{\alpha^6}\,. \qquad (96b)$$

Moreover, we shall, as always, restrict ourselves to the first terms. It is found that:

$$\left.\begin{aligned} J_{\mathrm{I}} &= \left|a_1 - (a_2 - p_1)\cos\gamma\right|^2 , \\ J_{\mathrm{II}} &= \left|a_1 \cos\gamma - a_2 \cos 2\gamma + p_1\right|^2 . \end{aligned}\right\} \tag{97}$$

Here a_1, a_2, p_1 are the quantities for which values are given in Tables 1, 2 and 3. By graphical interpolation, from these tables one obtains

$$\begin{array}{lcll} 2\rho & = & 160\mu\mu & 180\mu\mu \\ a_1 & = & -0.08 - i \times 0.63 & -0.03 - i \times 0.47 \\ a_2 & = & 0.15 - i \times 0.22 & 0.12 - i \times 0.30 \\ p_1 & = & 0.09 + i \times 0.03 & 0.09 + i \times 0.03 \end{array}$$

$$\text{for } \lambda = 550\mu\mu .$$

If this is introduced in (97), then $J_{\mathrm{I}} + J_{\mathrm{II}}$ gives the total radiation in dependence on the angle γ, and $J_{\mathrm{I}} - J_{\mathrm{II}}$ gives the excess of polarised light over the unpolarised; $\mathrm{P} = (P_{\mathrm{I}} - P_{\mathrm{II}})/(P_{\mathrm{I}} + P_{\mathrm{II}})$ is the percentage content of polarised light. Since we are only concerned with the relative value, I have divided the individual value J by $(J_{\mathrm{I}} + J_{\mathrm{II}})_{90^\circ}$; that is to say, I have related everything to the radiation occurring below $\gamma = 90^\circ$ as the unit. The calculated values are:

$2\rho = 160\mu\mu$

	0°	20°	40°	60°	80°	90°
Total radiation	0.64	0.67	0.75	0.88	0.97	1.00
Polarised	0	0.02	0.06	0.18	0.44	0.62
P	0	0.03	0.09	0.21	0.46	0.62

	100°	120°	140°	160°	180°
Total radiation	1.06	1.35	2.01	2.76	3.17
Polarised	0.80	0.97	0.72	0.29	0
P	0.76	0.72	0.36	0.10	0

$2\rho = 180\mu\mu$

	0°	20°	40°	60°	80°	90°
Total radiation	0.12	0.17	0.37	0.68	0.95	1.00
Polarised	0	-0.02	-0.10	-0.15	+0.06	0.31
P	0	-0.11	-0.27	-0.22	+0.06	0.31

	100°	120°	140°	160°	180°
Total radiation	1.04	1.33	2.16	3.30	3.85
Polarised	0.62	1.10	0.65	0.35	0
P	0.60	0.82	0.30	0.10	0

In both cases, the maximum of the polarisation is thus displaced from 90° to the side of increasing γ, in the one case ($2\rho = 160\mu\mu$) roughly towards $\gamma = 110^\circ$ and in the other case ($180\mu\mu$) towards $\gamma = 120^\circ$. The fact that these particular angles are involved probably lies in the special optical nature of the gold, since, for other metals, smaller angles have usually been found experimentally. The negative sign in front of certain numbers in the case: $2\rho = 180\mu\mu$, indicates that here there is an excess of polarised light which vibrates at right angles to the Rayleigh radiation. The most striking feature of the figures found, however, is the wide variability of values with the angle of radiation. In the case of large particles, lateral radiation predominates to a quite extraordinarily high degree, the light beam passing through the solution going towards the side. I have attempted to clarify these conditions by preparing some radiation diagrams in which I plotted the intensity of the radiation as lengths along the radius vectors originating from the particle. The outer curves in Figs.17-20 cut off, from the radii, sections which are proportional to the total radiation, while the inner curves similarly give the unpolarised radiation, so that the intermediate section of the radius vector is proportional to the polarised radiation.

Summarising, we can say that: if the polarisation maximum of the light scattered laterally by a turbid solution is displaced towards the side of increasing γ, this is a sure sign that the solution contains very coarse particles. At the same time, the lateral radiation on the side towards which the light beam which excites it travels ($\gamma > 90^\circ$) must then be very much more intense than on the other side ($\gamma < 90^\circ$).

For purposes of comparison, the radiation diagram for very fine particles and also for very fine particles of an imaginary perfect conductor has been constructed (Figs.17, 20). If one looks at the latter diagram, it can be seen that the intensity ratios are just the inverse of those for coarse gold particles. If there had been any possible doubt that the explanation given here of the polarisation phenomena observed by Herr F. Ehrenhaft[7] and Herr E. Muller[8] is correct, then one could very easily have decided the matter by comparing, probably even with the naked eye, the intensities of light emitted at different angles.

The curves for the quantity P (Figs.21-24) require no further explanation.

17 THE ABSORPTION OF TURBID MEDIA

In order to calculate the absorption, we shall ascertain how much energy a particle would dissipate if it alone were present. The coefficient of absorption of the solution is obtained from this energy by multiplication by the number of particles in a cubic millimetre.

We imagine a spherical surface of radius r about the centre of the spherule and let $x = 2\pi r/\lambda'$ be a very large number. The current density of the energy current through this spherical surface outwards is, at any instant:

$$E_\vartheta H_\varphi - E_\varphi H_\vartheta \quad .$$

We must now integrate this instantaneous energy flow over a one second period in order to obtain the intensity of the light. However, according to (2):

$$E_\vartheta = R[\mathrm{E}_\vartheta e^{2\pi int}] \ , \qquad H_\vartheta = R[\mathrm{H}_\vartheta e^{2\pi int}]$$

and so on; where $R[\,]$ means: the 'real part of'. If this is introduced, the time integral sought is then found:

$$\int_{t=1}^{t=1} (E_\vartheta H_\varphi - E_\varphi H_\vartheta)dt = \tfrac{1}{2}[(\mathrm{E}_\vartheta \mathrm{H}_\varphi) - (\mathrm{E}_\varphi \mathrm{H}_\vartheta)] \quad . \tag{97a}$$

Here the round brackets indicate that the 'scalar product' of the two complex factors is to be formed, i.e. the product of the two absolute values and the cosine of the phase difference. If:

$$\mathrm{E}_\vartheta = \mathrm{E}'_\vartheta + i\mathrm{E}''_\vartheta \ , \qquad \mathrm{H}_\varphi = \mathrm{H}'_\varphi + i\mathrm{H}''_\varphi \ , \tag{97b}$$

where E'_ϑ, E''_φ etc. signify real values, then:

$$(\mathrm{E}_\vartheta \mathrm{H}_\varphi) = \mathrm{E}'_\vartheta \mathrm{H}'_\varphi + \mathrm{E}''_\vartheta \mathrm{H}''_\varphi \quad . \tag{97c}$$

Since, for the scalar multiplication of two quantities, just the same rules apply as for usual multiplication, we shall simply omit the round brackets in future. When two complex quantities E and H are multiplied by each other, in the following discussion this always refers to the scalar product. According to (4), the complex quantities H_ϑ and H_φ can be replaced by $i\mathrm{M}_\vartheta$

and iM_φ . The intensity of the normal component of the light passing through the spherical surface is then

$$E_\vartheta iM_\varphi - E_\varphi iM_\vartheta$$

up to a certain numerical factor.

This numerical factor is so chosen that the intensity of the light passing through the solution is equal to 1. For E_ϑ, M_φ etc. from (51) and (52), we have to write the values $E_\vartheta + E_{\vartheta a}$, $M_\varphi + M_{\varphi a}$ etc. The integral over the spherical surface, which represents the total quantity of light passing through the spherical surface towards the outside, breaks down into three parts:

$$\left.\begin{aligned}
I &= \int_0^\pi \int_0^{2\pi} \left(E_\vartheta iM_\varphi - E_\varphi iM_\vartheta\right) r^2 \sin\vartheta \, d\vartheta d\varphi \ , \\
II &= \int_0^\pi \int_0^{2\pi} \left(E_{\vartheta a} iM_\varphi + E_\vartheta iM_{\varphi a} - E_{\varphi a} iM_\vartheta - E_\varphi iM_{\vartheta a}\right) r^2 \sin\vartheta \, d\vartheta d\varphi \ , \\
III &= \int_0^\pi \int_0^{2\pi} \left(E_{\vartheta a} iM_{\varphi a} - E_{\varphi a} iM_{\vartheta a}\right) r^2 \sin\vartheta \, d\vartheta d\varphi \ .
\end{aligned}\right\} \qquad (97d)$$

Part I contains the energy current of the transmitted light beam; if it were barely affected by the particle, then it is immediately obvious that the value of part I would be zero. Part III is a positive quantity, namely the total amount of energy radiated laterally; it thus gives that part of the coefficient of absorption which is to be used in the calculation of the diffuse radiation. Part II is negative; it is the total loss in energy of the transmitted beam and thus gives the full coefficient of absorption governed both by the diffuse radiation and by the actual absorption of radiant energy in the particle.

Since we have assumed that $x = 2\pi r/\lambda'$ is infinitely large compared to 1, then, according to (29a) and (19), we can write:

$$\left.\begin{aligned} I_\nu(x) &= \sin\left(x - \frac{\nu\pi}{2}\right) , \qquad & I'_\nu(x) &= \cos\left(x - \frac{\nu\pi}{2}\right) ; \\ K_\nu(-x) &= e^{-ix} , & K'_\nu(-x) &= -ie^{-ix} . \end{aligned}\right\} \tag{97e}$$

If, further, we introduce the following abbreviations:

$$\left.\begin{aligned} A_\nu &= \frac{\lambda'}{2\pi}\,\frac{2\nu+1}{\nu(\nu+1)}\, i^{\nu-1} \cos\left(x - \frac{\nu\pi}{2}\right) , \\ B_\nu &= -\frac{\lambda'}{2\pi}\,\frac{2\nu+1}{\nu(\nu+1)}\, i^{\nu} \sin\left(x - \frac{\nu\pi}{2}\right) , \\ C_\nu &= \frac{\lambda'}{2\pi}\,\frac{a_\nu}{\nu(\nu+1)}\, e^{-ix} , \\ D_\nu &= -\frac{\lambda'}{2\pi}\,\frac{P_\nu}{\nu(\nu+1)}\, e^{-ix} , \end{aligned}\right\} \tag{97f}$$

then, for the factors of the scalar products to be calculated, it is found that:

$$\left.\begin{aligned} E_\vartheta + E_{\vartheta a} &= \sum_1^\infty \nu\,\frac{A_\nu + C_\nu}{r}\,\frac{\partial P_\nu}{\partial\vartheta} - \sum_1^\infty \nu\,\frac{B_\nu + D_\nu}{r}\,\frac{1}{\sin\vartheta}\,\frac{\partial P_\nu}{\partial\varphi} , \\ E_\varphi + E_{\varphi a} &= \sum_1^\infty \nu\,\frac{A_\nu + C_\nu}{r}\,\frac{1}{\sin\vartheta}\,\frac{\partial P_\nu}{\partial\varphi} + \sum_1^\infty \nu\,\frac{B_\nu + D_\nu}{r}\,\frac{\partial P_\nu}{\partial\vartheta} , \\ -i(M_\vartheta + M_{\vartheta a}) &= \sum_1^\infty \nu\,\frac{B_\nu + C_\nu}{r}\,\frac{1}{\sin\vartheta}\,\frac{\partial P_\nu}{\partial\varphi} + \sum_1^\infty \nu\,\frac{A_\nu + D_\nu}{r}\,\frac{\partial P_\nu}{\partial\vartheta} , \\ i(M_\varphi + M_{\varphi a}) &= \sum_1^\infty \nu\,\frac{B_\nu + C_\nu}{r}\,\frac{\partial P_\nu}{\partial\vartheta} - \sum_1^\infty \nu\,\frac{A_\nu + D_\nu}{r}\,\frac{1}{\sin\vartheta}\,\frac{\partial P_\nu}{\partial\varphi} . \end{aligned}\right\} \tag{97g}$$

The light intensity itself can now be calculated:

$$\left.\begin{aligned}
&(E_\vartheta + E_{\vartheta a}) i (M_\varphi + M_{\varphi a}) - (E_\varphi + E_{\varphi a}) i (M_\vartheta + M_{\vartheta a}) \\
&= \sum_1^\infty \nu \sum_1^\infty \mu \, \frac{(A_\nu + C_\nu)(B_\mu + C_\mu)}{r^2} \left(\frac{\partial P_\nu}{\partial \vartheta} \frac{\partial P_\mu}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \frac{\partial P_\nu}{\partial \varphi} \frac{\partial P_\mu}{\partial \varphi} \right) \\
&\quad - \sum_1^\infty \nu \sum_\lambda^\infty \mu \, \frac{(A_\nu + C_\nu)(A_\mu + D_\mu) + (B_\nu + C_\nu)(B_\mu + D_\mu)}{r^2} \frac{1}{\sin \vartheta} \\
&\qquad \qquad \left(\frac{\partial P_\nu}{\partial \vartheta} \frac{\partial P_\mu}{\partial \varphi} + \frac{1}{\sin^2 \vartheta} \frac{\partial P_\nu}{\partial \varphi} \frac{\partial P_\mu}{\partial \vartheta} \right) \\
&\quad + \sum_1^\infty \nu \sum_1^\infty \mu \, \frac{(B_\nu + D_\nu)(A_\mu + D_\mu)}{r^2} \left(\frac{\partial P_\nu}{\partial \vartheta} \frac{\partial P_\mu}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \frac{\partial P_\nu}{\partial \varphi} \frac{\partial P_\mu}{\partial \varphi} \right) .
\end{aligned}\right\} \qquad (97h)$$

We can now carry out the integration over the spherical surface. This is:

$$\left.\begin{aligned}
\int_0^{2\pi} \int_0^\pi \frac{\partial P_\nu}{\partial \vartheta} \frac{\partial P_\mu}{\partial \vartheta} \sin \vartheta \, d\vartheta d\varphi &= - \int_0^{2\pi} \int_0^\pi P_\nu \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial P_\mu}{\partial \vartheta} \right) d\vartheta d\varphi \\
\int_0^{2\pi} \int_0^\pi \frac{\partial P_\nu}{\partial \varphi} \frac{\partial P_\mu}{\partial \varphi} \frac{d\vartheta d\varphi}{\sin \vartheta} &= - \int_0^{2\pi} \int_0^\pi P_\nu \frac{\partial^2 P_\mu}{\partial \varphi^2} \frac{d\vartheta d\varphi}{\sin \vartheta} .
\end{aligned}\right\} \qquad (97i)$$

Using equation (11), it is found that:

$$\begin{aligned}
&\int_0^{2\pi} \int_0^\pi \left(\frac{\partial P_\nu}{\partial \vartheta} \frac{\partial P_\mu}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \frac{\partial P_\nu}{\partial \varphi} \frac{\partial P_\mu}{\partial \varphi} \right) \sin \vartheta \, d\vartheta d\varphi \\
&\qquad = \mu(\mu + 1) \int_0^{2\pi} \int_0^\pi P_\nu P_\mu \sin \vartheta \, d\vartheta d\varphi .
\end{aligned} \qquad (97j)$$

Hence, according (46):

$$\left.\begin{aligned} &= 0 \,, && \nu \neq \mu \,, \\ &= 2\pi \frac{\nu^2(\nu+1)^2}{2\nu+1} \,, && \nu = \mu \,, \end{aligned}\right\} \tag{97k}$$

The same result is obtained if $\mathcal{P}_\nu, \mathcal{P}_\mu$ are substituted for P_ν, P_μ. Finally:

$$\int_0^{2\pi}\int_0^{\pi}\left(\frac{\partial P_\nu}{\partial\vartheta}\frac{\partial \mathcal{P}_\mu}{\partial\varphi} - \frac{\partial P_\nu}{\partial\varphi}\frac{\partial \mathcal{P}_\mu}{\partial\vartheta}\right)d\vartheta d\varphi$$

$$= \int_0^{2\pi}\left[P_\nu \frac{\partial \mathcal{P}_\mu}{\partial\varphi}\right]_{\vartheta=0}^{\vartheta=\pi} d\varphi - \int_0^{\pi}\left[P_\nu \frac{\partial \mathcal{P}_\mu}{\partial\vartheta}\right]_{\varphi=0}^{\varphi=2\pi} d\vartheta = 0 \,. \tag{97m}$$

The energy current flowing from the spherical surface is accordingly:

$$2\pi \sum_1^\infty \nu\Big((A_\nu + C_\nu)(B_\nu + C_\nu) + (A_\nu + D_\nu)(B_\nu + D_\nu)\Big)\frac{\nu^2(\nu+1)^2}{2\nu+1} \,. \tag{97n}$$

This expression is now broken down into the three parts mentioned above:

$$\left.\begin{aligned} \mathrm{I} &= 4\pi \sum_1^\infty \nu(A_\nu B_\nu)\frac{\nu^2(\nu+1)^2}{2\nu+1} = 0 \,, \\ \mathrm{II} &= 2\pi \sum_1^\infty \nu(A_\nu + B_\nu)(C_\nu + D_\nu)\frac{\nu^2(\nu+1)^2}{2\nu+1} \\ &= \frac{\lambda'^2}{2\pi}\sum_1^\infty \nu(-1)^{\nu-1}\left(ie^{-ix} \times (a_\nu - p_\nu)e^{-ix}\right) \\ &= \frac{\lambda'^2}{2\pi}\,\mathcal{Im}\left(\sum_1^\infty \nu(-1)^{\nu-1}(a_\nu - p_\nu)\right) \,. \\ \mathrm{III} &= 2\pi \sum_1^\infty \nu\left(C_\nu^2 + D_\nu^2\right)\frac{\nu^2(\nu+1)^2}{2\nu+1} = \frac{\lambda'^2}{2\pi}\sum_1^\infty \nu\,\frac{|a_\nu|^2 + |p_\nu|^2}{2\nu+1} \,. \end{aligned}\right\} \tag{97p}$$

If the number of particles in a cubic millimetre is N, then II gives, for the coefficient of absorption per millimetre of solution:

$$k = N \frac{\lambda'^2}{2\pi} Jm\left(\sum_1^\infty \nu(-1)^\nu (a_\nu - p_\nu)\right) . \qquad (98)$$

The loss through radiation alone amounts, according to III, to:

$$k' = N \frac{\lambda'^2}{2\pi} \sum_1^\infty \nu \frac{|a_\nu|^2 + |p_\nu|^2}{2\nu + 1} \qquad (99)$$

per millimetre.

The symbol $Jm(\ )$ in equation (98) denotes that the imaginary part is to be taken from the complex quantity in brackets. The vertical lines in (99) signify that the absolute value of the quantity between them is to be found.

18 ABSORPTION OF COLLOIDAL GOLD SOLUTIONS

For colloidal solutions, we can restrict ourselves to the coefficients a_1, a_2, p_1. We shall, moreover, as above, introduce the three values:

$$a_1 = \frac{a_1}{2\alpha^3} , \qquad a_2 = -\frac{a_2}{2\alpha^3} , \qquad p_1 = \frac{p_1}{2\alpha^3} . \qquad (99a)$$

Since, further, the concentration of the solution is:

$$C = NV , \qquad V = \frac{4\pi\rho^3}{3} = \frac{\alpha^3\lambda'^3}{6\pi^2} ,$$

then:

$$\left.\begin{aligned} k &= CK , \\ K &= \frac{6\pi}{\lambda'} Jm(-a_1 - a_2 + p_1) . \end{aligned}\right\} \qquad (100)$$

The value K varies only slowly as the particles become larger when very small particle diameters are involved.

For a very fine distribution of the metal in the solution, the colour is independent of the particle size while the coefficient of absorption is in simple proportion to the concentration of the solution.

This statement can naturally apply only up to a certain lower limit where the smallness of the particles is concerned, since the gold atoms certainly behave optically in a different way to small gold spheres. It would therefore probably be very interesting to investigate the absorption of solutions with the very smallest amicroscopic particles and to follow the process by which the gold particles are built up from atoms, as it were, using optical methods.

If the gold particles are larger than about 10μμ, then the statement no longer applies. I have taken, from Tables 1, 2 and 3, the values of a_1, a_2 and p_1 and, using these values, have constructed the curve showing the dependence of the absorption on the particle diameter for each colour (similar to the radiation curves in Fig.12). From this diagram, I then read off the absorption coefficients for the particle diameters given in the following table. The figures are in just the same units as those employed for the radiated energy earlier (p.49). They thus indicate the loss of light over a path of 1mm through a solution of concentration 10^{-6} (1mm^3 of gold in the 1 litre of water), that is, in parts per thousand. The value of K is then obtained from them by multiplication by 10^3.

Absorption of colloidal gold solutions

2ρ	420	450	500	525	550	600	650
0	40.5	37.4	59.6	69.0	55.5	16.4	7.0
20μμ	42.7	38.8	62.2	76.6	61.6	18.5	8.0
40μμ	46.5	42.0	66.0	86.5	77.7	25.0	11.3
60μμ	48.8	45.4	67.4	88.4	96.1	37.3	16.4
80μμ	46.5	44.8	62.5	81.0	97.0	65.0	27.1
100μμ	41.0	41.0	52.2	66.3	82.2	85.0	44.5
120μμ	34.6	34.8	42.8	51.2	61.0	77.5	58.7
140μμ	29.4	29.7	35.9	41.9	48.6	57.0	56.1
160μμ	25.7	26.1	30.8	36.0	41.2	45.1	45.6
180μμ	24.0	24.8	28.0	33.0	37.0	37.7	36.5

These series of numbers are reproduced graphically in Fig.25 as the absorption spectra for different particle sizes.

For fine distributions, the familiar steep absorption maximum of ruby-red gold solutions can be seen in the green at a wavelength of ca. 525μμ. If the particle size increases, then, at constant concentration, the absorption initially increases over the whole spectrum; the colour changes but little, but gradually acquires a thrust in the blue region, whereupon the maximum moves somewhat to the right. A sharp change only occurs when the particle diameter becomes about 100μμ. For this particle size, the solution is violet. At 120 and 140, we already see the characteristic spectra of deep-blue gold solutions, while at 160 we see those of indigo-blue and at 180 those of green-blue solutions. In fact, therefore, with change in particle size, one obtains all the colours observed in colloidal gold solutions.

It is immediately clear that the colour of gold solutions depends mainly on the characteristic absorption of the light in the gold particles. If the particles were perfectly conducting, absorption would never be observed. Here the light loss would be due entirely to light scattered laterally and the absorption curves would thus be identical with the radiation curves shown earlier in Fig.15 (if the loss associated with the next highest partial waves, hence the loss corresponding to the coefficients p_1, a_2 and p_2 is added). These curves appear quite different from the absorption curves of the gold solutions; they would always represent only quite matt colours and, for an infinitely fine distribution, the absorption would be zero throughout.

Nevertheless, for large particle diameters, the light loss due to lateral radiation does determine the colour of the gold solutions. Blue solutions are comparable with those which radiate a strong red-yellow radiation. It is, however, of interest to calculate the two summands of the absorption coefficient separately. For the practical calculation, it is found from equation (99) that:

$$\left.\begin{aligned} k' &= CK' \,, \\ K' &= \frac{4\pi}{\lambda'}\,\alpha^3\left(|a_1|^2 + |p_1|^2 + \frac{3}{5}\,|a_2|^2\right) \\ &= \frac{24\pi^2}{\lambda'^4}\,V\left(|a_1|^2 + |p_1|^2 + \frac{3}{5}\,|a_2|^2\right) \,. \end{aligned}\right\} \qquad (101)$$

Up to $2\rho = 100\mu\mu$, K' is identical with the value of F_1 calculated in section 15 (Fig.14). For large particle diameters, the coefficients p_1 and a_2 arise, although Rayleigh radiation still predominates up to 180μμ. The values of p_1 and a_2 for coarser particles have been obtained, by graphical interpolation, from Tables 2 and 3 and K' has been calculated for those particle sizes for which K is already known. Then:

$$K'' = K - K' \tag{102}$$

is the measure of the fraction of the light lost in the particle itself. In the following table, the values of K'' thus calculated are given, omitting the factor 10^3.

Coefficients of pure absorption

2ρ	420	450	500	525	550	600	650
0μμ	40.5	37.4	59.6	69.0	55.5	16.4	7.0
20μμ	42.4	38.6	61.9	76.1	61.0	18.2	7.9
40μμ	44.4	40.4	63.3	81.9	71.8	22.1	9.9
60μμ	42.6	40.4	59.4	74.7	76.4	25.0	10.5
80μμ	35.9	35.6	48.3	58.1	59.2	32.0	12.4
100μμ	27.4	28.7	34.9	39.0	39.8	29.5	25.5
120μμ	21.1	22.0	25.2	25.6	24.5	19.7	13.6
140μμ	17.2	18.0	20.1	19.9	19.1	11.9	9.6
160μμ	14.0	14.8	16.4	16.1	15.2	10.0	8.1
180μμ	11.9	12.9	14.1	14.3	13.3	8.8	6.5

These series of figures are presented graphically in the curves of Fig.26. These curves for pure absorption always have their maximum in the green between $\lambda = 525$ and $\lambda = 550$. If Fig.26 and Fig.14 are compared, moreover, there is no certain parallel between absorption and radiation which can be recognised. Thus, for small particle sizes, when the radiation maximum still lies in the green-yellow, the radiation increases rapidly with growing particle size, whereas the absorption shows a weak increase. Later on, whereas the maximum of the radiation is displaced to the right, the maximum for pure absorption, although also displaced a little to the right, still remains in the green. However, in addition to these relatively small changes, there occurs another which obviously does not depend on the special nature of the gold and which finally predominates over all others; the coarser the particles become, the lower and flatter are the curves. This is also immediately obvious, since, when the particles are quite thick, then finally they are opaque to all colours and the thicker they become, the smaller is the sum of the areas casting shadows. If one were to disregard the effect of diffraction completely, and hence were to calculate only the geometrical shadows, then the absorption coefficient would be $k_0 = Nq$, whereupon, for a concentration of 10^{-6}:

$$N = \frac{10^{-6}}{\frac{4\pi}{3}\rho^3} , \qquad q = \pi\rho^2 , \qquad (102a)$$

whence

$$k_0 = Nq = \frac{3}{4\rho} 10^{-6} . \qquad (102b)$$

Thus, for $2\rho = 180$, the calculation would give: $k_0 = 8.3$ parts per thousand, and, for $2\rho = 160$: $k_0 = 9.4$ parts per thousand. I have plotted these two values of k_0 in Figs.25 and 26 also; naturally, these plots are straight lines since k_0 does not depend on the colour. It can be seen that, as the result of diffraction, the absorption increases considerably. Furthermore, in the yellow and red, by far the greatest part of the light is removed from the particles by reflection, whereas, in the left half of the spectrum, approximately a half of the light lost is absorbed by the particles.

The colours of colloidal gold solutions can be explained by the interaction of two properties of the gold particles. The gold particles have, in fact, a very sharp maximum of the absorptivity in the green, and, secondly, a maximum of the reflectivity in the red-yellow. Very small particles reflect weakly and absorb strongly, so that the solution appears ruby red. Large particles reflect strongly and, at the same time, their pure absorption curves become lower and flatter, so that they make the solution blue. Where the colour of the largest particle is concerned, that property of the gold according to which it strongly reflects the red-yellow part of the spectrum, alone is decisive, so that its less intense blue-green colour arises.

This statement, of course, only applies under the assumption that the particles are spherical. However, also in the case of particles of leaf or bar form, it is necessary to distinguish, in an analogous manner, between the absorptivity and the reflectivity of the particles.

The comparison between theoretical and experimental results contained in the paper was withheld until after the appearance of the work by Herr Steubing. Nevertheless, it may be stated here that, seemingly, the known optical properties of gold in fact also hold where ultramicroscopic particles are concerned and are quite adequate for purposes of explaining the optical properties of colloidal solutions; on the other hand, the theory needs to be completed if all phenomena are to be explained and possibly if it is to be developed to cover ellipsoidal particles (plates or bars) also.

19 RESULTS

(1) The problem of calculating the optical properties of turbid media is solved by making two simplifying assumptions: firstly, that the particles can be regarded as spherical; secondly, that the turbidity is optically infinitely dilute. The second assumption is certainly applicable in the case of the usual colloidal solutions.

(2) Light emitted by small particles can be calculated as a series of "partial waves"; in fact, there are two groups of partial waves corresponding to the electrical and magnetic vibrations of the particles. No matter how large the particles, only a finite number of these partial waves need be considered and actually the vth electrical vibration occurs parallel with the (v - 1)th magnetic vibration.

In the case of colloidal solutions containing very fine particles, only the first electrical vibration, corresponding to 'Rayleigh radiation', makes any significant contribution. For colloidal solutions containing coarser particles, the second electrical and the first magnetic vibration is encountered.

(3) The assumption of perfect conductivity of the spheres, which leads to a quite unacceptable simplification of the formulae, produces another result, namely that the vth magnetic vibration goes in parallel with the vth electrical vibration. Accordingly, even in the case of turbidities produced by the finest particles, in addition to Rayleigh radiation, the first magnetic vibration would have to be observable and Thomson's law of the polarisation maximum at 120° would then ensue. Since the assumption is false, the result cannot, of course, be confirmed experimentally.

(4) If, through the turbid solution, one passes an unpolarised beam of light, then the light emitted laterally is completely or partly polarised (never elliptically polarised).

(5) Up to a particle size of about 100μμ, the light scattered laterally by gold spherules is almost exclusively Rayleigh radiation, with its polarisation maximum (actually 100%) at 90°. If the particles are larger, the contribution of unpolarised light at 90° increases very rapidly and the polarisation maximum advances; for particle sizes of 160 and 180μμ it lies at 110° and 120°. At the same time, the initial symmetry of the Rayleigh radiation is disturbed as the result of the interference of the partial waves; by far the greatest part of the diffuse radiation goes towards the side, after which the excited light ray

continues on its way. In the latter connection, the light reflected by spherules imagined to be very small and perfectly conducting would behave in exactly the opposite way. Large gold spherules which show this anomalous polarisation behaviour have a reddish-yellow diffuse radiation and colour the solution blue. No red-coloured particles can be produced which behave in this way.

(6) When the concentration is maintained constant, the diffuse radiation from very fine turbidity is proportional to the volume of a small particle. In the case of turbidity produced by coarser particles, the diffuse radiation increases more slowly with increasing particle size and finally reaches a maximum, the position of which depends on the wavelength. In fact, for turbidity due to imagined, perfectly-conducting spherules, the particle diameter to which the maximum radiation corresponds is proportional to the wavelength ($0.0324\lambda'$); in the case of gold spherules, there is no such simple law, but the particle diameter encountered always lie between $\lambda'/4$ and $\lambda'/3$.

(7) The colour of the diffusely-scattered light for imagined perfectly-conducting spherules, also, in the main, for perfectly white spherules, when they are very small, is blue-violet, in accordance with the Rayleigh law (radiation proportional to λ'^{-4}). Larger particles would emit approximately white light, with a weak, dull colour tone depending on the size of the particles. Any optical resonance, which would lead to strong emphasis on a certain colour, is excluded, at least in the case of spherical particles, and no explanation of the vivid colours of colloidal solutions on the basis of resonance is possible.

(8) The diffuse radiation of gold particles is, in general, much stronger than that which would be emitted by perfectly-conducting spherules of the same size. Moreover, in finest distributions, they show a very sharp maximum in the green-yellow region. Later, the radiation maximum rises until very high in the red-yellow. If one wishes to introduce resonance, it would then be necessary to speak of a resonance of the gold atoms, giving rise to yellow and superimposed on the phenomena which one would expect to be associated with colourless, conducting particles.

(9) Even infinitely fine suspensions of gold particles show (in very sharp contrast to the behaviour which would be expected of perfectly-conducting particles) a characteristic absorption depending only on the quantity of the suspended metal (the concentration), but not on the degree of fineness of the distribution. It would be interesting to investigate experimentally the way

in which the situation changes as ultimately one comes to extremely fine particles containing only a few atoms.

(10) In general, the absorption of colloidal gold solutions depends on two properties of the metallic gold: the absorbtivity and the reflectivity. Solutions in which the diffuse reflection is weaker than the characteristic absorption show the gold particle absorption maximum in the green and the solutions are therefore ruby red. On the other hand, solutions exhibiting strong diffuse reflection are clear blue, since gold, in the main, reflects red-yellow light.

(11) For the sake of completeness of the theory, it is absolutely necessary to investigate also the behaviour of ellipsoidal particles.

Table 1

VALUES OF THE COEFFICIENT $\alpha = a_1/2\alpha^2$

α^2	Perfect conductor	Gold		
		420	450	500
0	1.00	0.579 − i × 0.675	0.602 − i × 0.666	0.807 − i × 1.180
0.2	1.04 − i × 0.065	0.484 − i × 0.755	0.505 − i × 0.743	0.528 − i × 1.312
0.4	1.04 − i × 0.188	0.343 − i × 0.750	0.368 − i × 0.757	0.216 − i × 1.211
0.6	0.961 − i × 0.318	0.224 − i × 0.699	0.244 − i × 0.706	0.042 − i × 1.029
0.8	0.831 − i × 0.410	0.145 − i × 0.632	0.156 − i × 0.640	−0.047 − i × 0.849
1.0	0.638 − i × 0.437	0.094 − i × 0.559	0.100 − i × 0.566	−0.056 − i × 0.715
1.5	0.405 − i × 0.366	0.038 − i × 0.401	0.043 − i × 0.406	−0.044 − i × 0.480
2.0	0.265 − i × 0.256	0.028 − i × 0.297	0.031 − i × 0.299	−0.015 − i × 0.349
2.6	0.190 − i × 0.176	0.026 − i × 0.225	−	−

α^2	Gold			
	525	550	600	650
0	1.330 − i × 1.440	1.925 − i × 1.211	1.880 − i × 0.391	1.345 − i × 0.180
0.2	0.850 − i × 1.823	1.602 − i × 2.050	2.190 − i × 0.977	1.920 − i × 0.515
0.4	0.263 − i × 1.640	0.975 − i × 2.040	1.750 − i × 1.874	1.767 − i × 1.080
0.6	−0.028 − i × 1.347	0.057 − i × 1.719	0.807 − i × 1.980	1.233 − i × 1.492
0.8	−0.114 − i × 1.061	−0.107 − i × 1.306	0.160 − i × 1.612	0.673 − i × 1.431
1.0	−0.126 − i × 0.855	−0.134 − i × 1.014	0.095 − i × 1.240	0.353 − i × 1.191
1.5	−0.075 − i × 0.554	−0.079 − i × 0.727	0.009 − i × 0.721	0.124 − i × 0.718
2.0	−0.029 − i × 0.395	−0.022 − i × 0.435	0.032 − i × 0.479	0.096 − i × 0.471
2.5		−	−	−

Table 2

VALUES OF $a_2 = \frac{a_2}{2\alpha^3}$

α^2	420	450	500
	$\alpha^2 \times$	$\alpha^2 \times$	$\alpha^2 \times$
small	$0.058 - i \times 0.053$	$0.060 - i \times 0.052$	$0.087 - i \times 0.081$
1	$0.047 - i \times 0.059$	$0.049 - i \times 0.058$	$0.063 - i \times 0.101$
2	$0.053 - i \times 0.118$	$0.057 - i \times 0.119$	$0.038 - i \times 0.188$
2.5	$0.039 - i \times 0.140$		

α^2	525	550	600	650
	$\alpha^2 \times$	$\alpha^2 \times$	$\alpha^2 \times$	$\alpha^2 \times$
small	$0.124 - i \times 0.085$	$0.149 - i \times 0.061$	$0.138 - i \times 0.021$	$0.118 - i \times 0.010$
1	$0.102 - i \times 0.124$	$0.152 - i \times 0.114$	$0.157 - i \times 0.043$	$0.132 - i \times 0.023$
2	$0.052 - i \times 0.258$	$0.108 - i \times 0.322$	$0.264 - i \times 0.261$	$0.260 - i \times 0.151$

Table 3

VALUES OF $p_1 = \frac{P_1}{2\alpha^3}$

α^2	420	450	500
	$\alpha^2 \times$	$\alpha^2 \times$	$\alpha^2 \times$
small	$0.033 + i \times 0.107$	$0.034 + i \times 0.111$	$0.087 + i \times 0.083$
1	$0.045 + i \times 0.065$	$0.045 + i \times 0.066$	$0.063 + i \times 0.042$
2	$0.064 + i \times 0.072$	$0.065 + i \times 0.073$	$0.078 + i \times 0.051$
1.5	$0.065 + i \times 0.071$		

α^2	525	550	600	650
	$\alpha^2 \times$	$\alpha^2 \times$	$\alpha^2 \times$	$\alpha^2 \times$
small	$0.115 + i \times 0.066$	$0.140 + i \times 0.052$	$0.195 + i \times 0.042$	$0.266 + i \times 0.054$
1	$0.072 + i \times 0.031$	$0.081 + i \times 0.025$	$0.100 + i \times 0.020$	$0.117 + i \times 0.021$
2	$0.087 + i \times 0.042$	$0.094 + i \times 0.037$	$0.110 + i \times 0.036$	$0.123 + i \times 0.041$

REFERENCES

No.	Author	Title, etc.
1	F. Ehrenhaft	Wiener Sitzunzsber IIa, 112, 181 (1903); 114, 1115 (1905)
2	J.C. Maxwell-Garnett	Phil. Trans., 203, 385 (1904); 205, 237 (1906)
3	L. Lorenz	Wied. Ann., 11, 70 (1880)
4	R. Zsigmondy	Ann. d. Phys., 15, 573 (1904)
5	-	Physik. Zeitschr., 5, 152, 387, 460 (1904) (see discussion between F. Pockels and F. Ehrenhaft).
6	Fr. Hasenöhrl	Wiener Ber., IIa, 111, 1229 (1902)
7	F. Ehrenhaft	Ann. d. Phys., 11, 489 (1903)
8	E. Müller	Ann. d. Phys., 24, 1 (1907)
9	Lord Rayleigh	Phil. Mag., (5) 47, 379 (1899)
10	E. Hagen H. Rubens	Ann. d. Phys., 8, 1 and 432 (1903)
11		Ibid, 453
12	E. Müller	Ann. d. Phys., 24, 13 and 16 (1907)