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INDEX SLIP.

GARNETT, J. C. M.—Colours in Metal Glasses and in Metallic Films.
Phil. Trans., A, vol. 203, 1904, pp. 385–420.

"Allotropic" Silver—Constitution, Origin of Colour of.
GARNETT, J. C. M. Phil. Trans., A, vol. 203, 1904, pp. 385–420.

Coloration of Glass by Reduced Metals; Action of Radium.
GARNETT, J. C. M. Phil. Trans., A, vol. 203, 1904, pp. 385–420.

Coloured Metallic Films—Cause of Change on Annealing.
GARNETT, J. C. M. Phil. Trans., A, vol. 203, 1904, pp. 385–420.

Nascent Crystals of Metal, Spherical Form.
GARNETT, J. C. M. Phil. Trans., A, vol. 203, 1904, pp. 385–420.

XII. *Colours in Metal Glasses and in Metallic Films.*

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Introduction.

§ 1. The present paper contains a discussion of some optical properties of a medium containing minute metal spheres. The discussion is divided into two Parts: the first Part dealing with colours in metal glasses, in which the proportion of volume occupied by metal is small; the second Part dealing with metal films, in which this proportion may have any value from zero to unity.

In Part I. the observations of Siedentopf and Zsigmondy beyond the limit of microscopic vision ('Ann. der Phys.,' January, 1903) are discussed. It is shown that the particles seen in a gold ruby glass are particles of gold which, when their diameters are less than $0{\cdot}1\mu$, are accurately spherical. I have endeavoured to show that the presence of many of these minute spheres to a wave-length of light in the glass will account for all the optical properties of "regular" gold ruby glass, and that the irregularities in colour and in polarisation effects sometimes exhibited by gold glass are due to excessive distance between consecutive gold particles or to excessive size of such particles, the latter, however, involving the former. It is also shown that the radiation from radium is capable of producing in gold glass the ruby colour which is generally produced by re-heating. The method adopted enables us to predict from a knowledge of the metal present in metallic form in a glass what colour that glass will be in its "regular" state.

In Part II. the optical properties, and the changes in colour on heating, of the silver and gold films observed by Mr. G. T. Beilby ('Roy. Soc. Proc.,' vol. 72, p. 226), and of the potassium and sodium films deposited on glass by Professor R. W. Wood ('Phil. Mag.,' p. 396, 1902), are discussed, with a view to showing that they can be accounted for by supposing the films to be composed of minute metal spheres of varying sizes.

PART I.

§ 2. Consider the incidence of light of wave-length λ on a sphere of metal of radius a. Suppose the constants of the metal relative to the surrounding medium, which we may first suppose to be æther, are n, the coefficient of refraction, and κ, the coefficient of absorption. Let us write

$$N \equiv n(1 - \iota\kappa) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

where, as usual, ι denotes $\sqrt{-1}$.

We shall use the following notation to denote the electric vector :—

Incident light . . . . . $\mathbf{E}_0 \{X_0 = \exp\{\iota p(t - z/c)\},\ Y_0 = 0,\ Z_0 = 0\}$.

Transmitted + reflected light . . $\mathbf{E}_1 \{X_1,\ Y_1,\ Z_1\}$.

Here $p = 2\pi c/\lambda$, c being the velocity of light *in vacuo*.

Hertz ('Ausbreitung der electrischen Kraft,' Leipzig, 1892, p. 150) has shown that the electric and magnetic forces at any point (x, y, z) due to an oscillating electric doublet of moment $Ae^{\iota pt}$ along the axis of x are given by

$$\mathbf{E} = \nabla \frac{\partial \Pi}{\partial x} - (\nabla^2 \Pi,\ 0,\ 0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

$$\mathbf{H} = \frac{1}{c}\left(0,\ \frac{\partial^2 \Pi}{\partial z\, \partial t},\ -\frac{\partial^2 \Pi}{\partial y\, \partial t}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

where

$$\Pi = A/r . \exp\{\iota p(t - r/c)\},$$

for these expressions satisfy Maxwell's equations

$$\frac{d\mathbf{E}}{dt} = c \operatorname{curl} \mathbf{H}, \quad \frac{d\mathbf{H}}{dt} = -c \operatorname{curl} \mathbf{E} \quad \text{and} \quad \operatorname{div} \mathbf{E} = \operatorname{div} \mathbf{H} = 0,$$

and when r is very small compared with the wave-length ($\lambda = 2\pi c/p$) of the emitted waves the expression for $\mathbf{E}$ reduces to

$$\mathbf{E} = \nabla(\partial \Pi/\partial x),$$

which is at any time the electric force which would be electrostatically due to the doublet if its moment remained constant and equal to its value at that time.

Lord Rayleigh ('Phil. Mag.,' XLIV., pp. 28–52, 1897, and 'Collected Papers,' vol. 4, p. 321) has extended this theorem to the case of a very small sphere. In the region for which the distance, r, from the centre of a small sphere of radius a excited

by an electric field $\mathbf{E} = (e^{\iota pt}, 0, 0)$, is small compared with the wave-length, the electri force due to the sphere is

$$\mathbf{E}_1 = \nabla \frac{\partial}{\partial x}\left(\frac{\mathrm{K}-1}{\mathrm{K}+2}\frac{a^3}{r}\right).e^{\iota pt}.$$

By omparing this with HERTZ'S corresponding result

$$\mathbf{E} = \nabla \frac{\partial}{\partial x}\left(\frac{e^{\iota pt}}{r}\right)$$

for an oscillating doublet of moment $e^{\iota pt}$, as given above, it appears from (2) and (3) that the electric and magnetic forces at any point, due to waves emitted by the sphere must be given by the equations

$$\mathbf{E}_1 = \nabla \frac{\partial \Pi}{\partial x} - (\nabla^2\Pi,\ 0,\ 0), \qquad \mathbf{H}_1 = \frac{1}{c}\left(0,\ \frac{\partial^2\Pi}{\partial x\,\partial t},\ -\frac{\partial^2\Pi}{\partial y\,\partial t}\right) \quad . \quad . \quad (4, 5),$$

where now

$$\Pi = \frac{\mathrm{K}-1}{\mathrm{K}+2}.\frac{a^3}{r}.\exp\{\iota p\,(t - r/c)\}.$$

Replacing K by N^2, where N is the quantity defined by equation (1), we conclude that when a metal sphere is excited by a periodic electric force $\mathbf{E}_0$, it emits the waves which would be emitted by a Hertzian doublet which at time t was of moment equal to

$$\frac{\mathrm{N}^2-1}{\mathrm{N}^2+2}a^3\mathbf{E}_0.$$

The same result can be proved directly by adapting the analysis given by L. LORENZ ('Vidensk. Selsk. Skr.,' Copenhagen, 1890) to the electromagnetic theory. The problem has also been treated by STOKES ('Camb. Trans.,' vol. 9, p. 1, 1849, and 'Papers,' vol. 4, p. 245, p. 262).

At a great distance from the origin, *i.e.*, when r is great compared with λ, equation (4) reduces to [*cf.* RAYLEIGH, *loc. cit.*, equation (106)]

$$\mathbf{E}_1 = \frac{4\pi^2a^3}{\lambda^2 r}\frac{\mathrm{N}^2-1}{\mathrm{N}^2+2}\exp\{\iota p\,(t - r/c)\}\left\{\frac{y^2+z^2}{r^2},\ -\frac{xy}{r^2},\ -\frac{xz}{r^2}\right\} \quad . \quad . \quad (6).$$

If we transform to spherical co-ordinates $\overline{\mathrm{X}}$, $\overline{\mathrm{Y}}$, $\overline{\mathrm{Z}}$ in the respective directions of increase of r, θ, ϕ (fig. 1) we obtain, at a great distance from the origin,

$$\overline{\mathrm{X}}_1 = 0,\ \overline{\mathrm{Y}}_1 = \frac{4\pi^2a^3}{\lambda^2 r}\frac{\mathrm{N}^2-1}{\mathrm{N}^2+2}.\exp\{\iota p\,(t - r/c)\}\cos\theta\cos\phi,$$

$$\overline{\mathrm{Z}}_1 = -\frac{4\pi^2a^3}{\lambda^2 r}\frac{\mathrm{N}^2-1}{\mathrm{N}^2+2}\exp\{\iota p\,(t - r/c)\}\sin\phi. \quad . \quad . \quad . \quad . \quad . \quad (7).$$

It appears from equations (6) or (7) that such a small sphere, in common with any other minute system whose moment is proportional to the electric vector of the incident light, emits light with an intensity proportional to the inverse fourth power of the wave-length, provided that N is independent of λ. It is this property which, as Lord RAYLEIGH has shown, accounts for the blue colour of the light received from the sky.

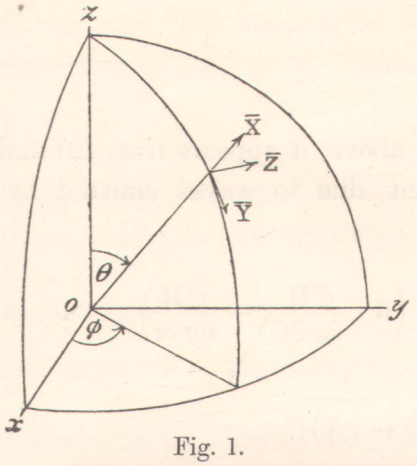


Fig. 1.

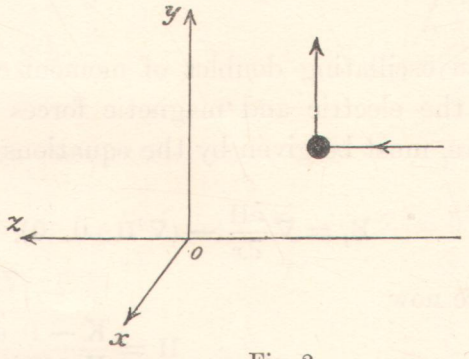


Fig. 2.

§ 3. In the 'Annalen der Physik' for January, 1903, H. SIEDENTOPF and R. ZSIGMONDY publish some observations on the metal particles in gold ruby glasses. By their method of illumination they were able to see particles whose dimensions were of the order of from 4 to 7 $\mu\mu$, where $\mu\mu$ represents 10^{-6} millim.

The arrangement consisted of a system of lenses following a strongly illuminated and very narrow slit. The system of lenses, of which the last is a low power microscopic objective, serves as a condenser and forms a very narrow image of the slit inside the glass under observation. This image of the slit may not be more than one or two wave-lengths thick.

The observation is made with a microscope having the tube perpendicular to the incident light, so that only the light emitted by the metallic particles travels up the tube. This is the light the electric vector of which has been distinguished by the suffix unity in the preceding analysis. The image of the slit, which is parallel to $0x$ in fig. 2, comes directly under the microscope tube, which is in the direction $0y$; thus only the particles illuminated at the image of the slit send light up the tube. The diffraction discs do not pile up on top of one another if the average distance between two metal particles is greater than the thickness of the image of the slit. In this case, then, the number of particles per unit area can be counted.

On pp. 11 and 12 of the paper referred to, SIEDENTOPF and ZSIGMONDY discuss the appearances in the second focal plane of the microscope when the light incident in the glass is plane polarised. The figs. 3–6 above are reproduced from their paper. In fig. 3 the plane of polarisation of the incident light was that of incidence, the plane of incidence being the plane containing the axis of the microscope and that of

the incid nt pencil of light; in figs. 4 and 5 the plane of polarisation of the incident light wa inclined at 45° to the plane of incidence; while in fig. 6 the two planes were per endicular.

In th figs. 3–6 the upper diagram represents the second focal plane of the microsco e when the diameters of the particles of metal in the glass are less than 0·1 μ, th small lines being parallel to the planes of polarisation of the emergent light in arious parts of the field, the "emergent light" here meaning the light sent up the m icroscope tube by the metal particles in the glass under observation. The

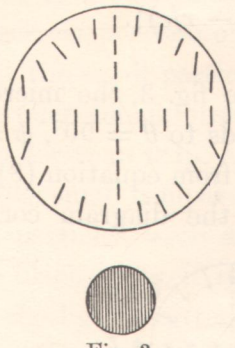


Fig. 3.

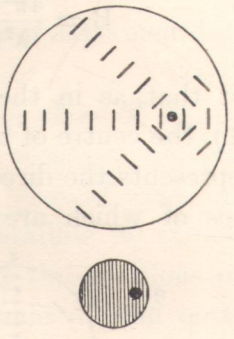


Fig. 4.

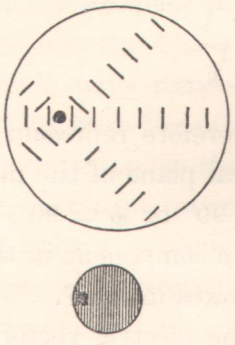


Fig. 5.

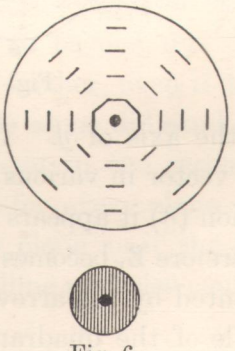


Fig. 6.

lower d agrams in the same figures represent the appearances of a diffraction disc for the sam e respective positions of the plane of polarisation of the incident light.

It is to be noticed that the light emitted in any particular direction comes to a focus a a corresponding point in the second focal plane of the microscope. Consequently a black spot in that plane means that no light is emitted in the corresponding directio n.

If al the particles are spheres sending up no light in some particular direction, there w ll thus be a black spot in the second focal plane, as well as in each diffraction disc, at the point corresponding to that direction.

Supp ose now, as in § 2, that the incident light travels in the direction $0z$ and is polaris d in plane $y0z$, fig. 1. Instead of conceiving this plane to alter as we consider the va ious cases of figs. 3–6, we shall imagine the microscope tube to move in the plane $x0y$.

Thus in fig. 3 the microscope is along $0y$, in fig. 6 along $0x$, while in figs. 5 and 4 the tube lies in the intermediate positions, namely, $\theta = 90°$, $\phi = \pm 45°$ respectively.

It will now be shown that the figs. 3–6 are completely accounted for if the particles are spheres small compared with a wave-length, *i.e.*, appreciably smaller than $0{\cdot}1\ \mu$.

From equations (7) the character of the light emitted by such a sphere in the direction θ, ϕ (fig. 1) is determined by the electric force $\mathbf{E}_1$ whose composition is:

$$\overline{X}_1 = 0, \quad \overline{Y}_1 = B\cos\theta\cos\phi, \quad \overline{Z}_1 = -B\sin\phi \quad . \quad . \quad . \quad . \quad . \quad (8),$$

where

$$B = \frac{4\pi^2 a^3}{\lambda^2 r} \cdot \frac{N^2 - 1}{N^2 + 2} \cdot \exp\{ip(t - r/c)\}.$$

Suppose first that, as in the case corresponding to fig. 3, the microscope tube is along $0y$ (fig. 1), the centre of the field then corresponds to $\theta = 90°$, $\phi = 90°$.

The fig. 7 represents the direction of $\mathbf{E}_1$, as deduced from equation (8), for positions, the co-ordinates of which are θ, ϕ, the centre of the diagram corresponding to

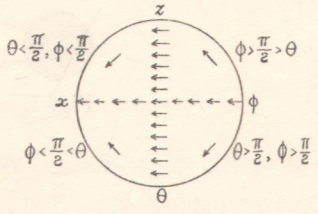


Fig. 7.

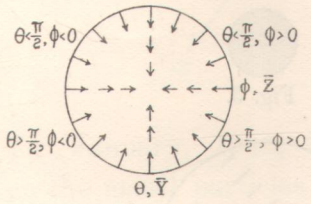


Fig. 8.

$\theta = \phi = 90°$, the axis of y. The same figure will therefore represent the directions of the electric vector in various parts of the second focal plane of the microscope.

From equation (8) it appears that when either $\theta = 90°$ or $\phi = 90°$, we shall have $\overline{Y}_1 = 0$, and therefore $\mathbf{E}_1$ becomes $(0, 0, \overline{Z}_1)$ and only has a component in the direction ϕ. This is represented by the arrows for positions on the axes in fig. 7.

In the middle of the quadrants the directions of the electric vector are no longer parallel to the axis of ϕ but are tilted as in the figure, being tilted in the same manner in opposite quadrants.

Now the planes of polarisation are perpendicular to the electric vector, and the small lines in fig. 3 are perpendicular to the arrows in fig. 7. When, therefore, the incident light is polarised in the plane of incidence, the appearances are accounted for if the particles are small spheres.

Next consider the case corresponding to fig. 6, when the microscope tube is above $0x$. The centre of the field is then $\theta = 90°$, $\phi = 0$. The arrows represent the direction of $\mathbf{E}_1$ in various parts of the field. All these arrows point nearly towards the centre. Along the two axes they point accurately towards the centre. There is no force at the centre, for then both $\overline{Y}_1$ and $\overline{Z}_1$ vanish. Consequently, a black spot should appear at the centre, if the particles were spheres. Finally, lines perpendicular to the arrows in fig. 8 are parallel to the lines in fig. 4. Consequently, in this case also the appearances are explained by supposing the particles to be spheres.

In his case, namely, when the incident light is polarised perpendicular to the plane of incidence, it further appears that if an analysing nicol be introduced so as to polarise the emergent light in the plane of incidence, then the analysing nicol removes the Y component of E_1 and the vanishing of Z_1 also, for $\phi = 0$ causes a dark band to cross the field over the diffraction disc if there be only one particle sending light up the tube, the dark band lying along the axis of θ in fig. 8, *i.e.*, in the plane of incidence, and this also was observed by SIEDENTOPF and ZSIGMONDY for the particles in gold glass (*loc. cit.*, p. 12).

The discussion of the cases of figs. 4 and 5 presents no difficulty. The phenomena, including the correct position of the black spot, are again explained, by means of the hypothesis that the small particles are spheres.

Thus all the phenomena, observed in the second focal plane of the microscope, due to particles smaller than $0{\cdot}1\mu$, are exactly those which would be produced by spheres of metal of radius small compared with the length of a wave of light in the glass.

If now the particles were small spheroids, or crystalline in structure, then the position of the black spots, if indeed any existed, and the positions of the plane of polarisation of the light emitted from the particles, would depend on the orientation of the particles. Unless, therefore, the orientation of all the particles were the same, we should, if many particles were sending light up the tube, get no black spot in the focal plane, because the black spot, supposing there to be one, due to one particle, would not coincide with that due to another. And further, even if the orientation of all the particles were the same, and if every particle alone did send off no light in some particular direction, so that there were a black spot in the second focal plane, then, unless the common orientation were such that, for every plane of polarisation of the incident light, the black spot were in the same plane as if the particles were spheres, which is an impossibility, spheroidal or crystalline particles could not account for the effect observed.

These considerations show, therefore, that the small particles in gold ruby glass are really spheres of gold, so long as their dimensions are considerably smaller than $0{\cdot}1\mu$ (10^{-} centim.).

This result is of considerable interest in connection with the formation of crystals. When a metal crystallises out of a vitreous solution, it appears that until the dimensions have increased beyond a certain limit, the forces of surface tension overcome the crystallic forces, and the particles of metal are spherical and not crystalline.*

Mr. G. T. BEILBY has arrived at the same conclusion from microscopic examination

* [*Note added* 14*th May*, 1904.—The presence of crystals, whether of silicates or of reduced metal, in many pottery glazes suggests that minute spheres of the same material as the crystals were present before the formation of these crystals, and that some may co-exist with the crystals. The colours of the glazes may therefore be wholly or in part due to the presence of these minute spheres, in the same manner as a gold ruby glass depends for its colour on the presence of minute spheres of gold.]

of the films of metal deposited from solutions ('Proc. Roy. Soc.,' vol. 72, 1903, p. 223).

In the manufacture of gold and copper ruby glasses and of silver glass, the gold or copper or silver is mixed with the other ingredients of the glass before the first firing. If, when the glass is formed in the furnace, the whole be quickly cooled, the glass with the metal in it is colourless and exactly resembles clear glass. I have had in my possession several pieces of such clear gold glass, and some of clear silver glass. One of the former was used in an experiment with the emanation from radium, to be described later.

In this clear glass the gold or silver is probably in solution in the glass. But when the glass is re-heated the metal "crystallises" out of solution, or, as we shall say, is "excreted" from the glass and appears in the small particles observed by Siedentopf and Zsigmondy. These particles of metal, as we shall show, account for the colour of the glass.

I have seen a piece of copper glass which was allowed to cool down slowly in the glass pot along with the furnace, taking a week or more in the process. The glass formed a dark brown, nearly opaque, mass with minute crystals of bright, shining copper scattered throughout its substance, the crystals being large enough to be easily distinguishable with the naked eye, while the appearance of the whole mass somewhat resembled that of the well-known African stone, aventurine.

It is suggested that the second heating, without melting the glass, confers sufficient freedom on the molecules of the glass to enable the forces of surface tension to exert themselves in bringing the molecules of the metal, which have been distributed amongst those of the glass, together into heaps, the phenomenon being similar to that exhibited when a metal film is heated to 300° or 400° without being melted, when, as will be described later, the metal forms itself into minute granules, which, in the light of what we have proved for the particles in gold glass, must be spheres or spheroids with axes normal to the film. The latter form is possible for the films of metal, though not for the metal in the gold glass, because a thin film, as opposed to a piece of glass, is not subjected to similar conditions in all directions.

§ 4. We have thus to consider the problem of light traversing a medium containing many small metal spheres to a wave-length of light.

It has been seen (§ 2) that a small metal sphere produces in all surrounding space the same effect as would be produced by a Hertzian doublet placed at its centre. We may therefore imagine the spheres replaced by such electric doublets and thus avoid considering their finite size.

Let the average (for a large number of doublets) moment of a doublet be, at time t, $\mathbf{f}(t) \equiv \{f_1(t), f_2(t), f_3(t)\}$.

Then if there be $\mathfrak{N}$ spheres per unit volume, the polarisation of the medium will be $\mathbf{f}'(t) = \mathfrak{N}\mathbf{f}(t)$. If $\mathbf{E}'$, due to the regular force $\mathbf{E}_0$ together with forces due to the

neighbouring doublets, be the force causing the polarisation $\mathbf{f}(t)$, then we have proved (§ 2) that

$$\mathbf{f}(t) = \alpha^3 \frac{N^2 - 1}{N^2 + 2} \mathbf{E}'.$$

Now by means of the analysis given by H. A. LORENTZ ('Wied. Ann.,' 9, 1879, p. 641) and by LARMOR ('Phil. Trans.,' A, 1897, p. 238), and which has been fully verified in LORENTZ's own paper and by others, it can be proved that (see § 7 below)

$$\mathbf{E}' = \mathbf{E}_0 + \frac{4\pi \mathbf{f}'}{3} = \mathbf{E}_0 + \frac{4\pi}{3} \mathfrak{N}\alpha^3 \frac{N^2 - 1}{N^2 + 2} \mathbf{E}' \quad \ldots\ldots (9),$$

provided the medium under consideration extends throughout a space of dimensions which in no direction are of an order of magnitude so small as a wave-length of light. This provision is satisfied except in the case of very thin films. When dealing with such films in a later portion (§ 7) of this paper we shall return to the consideration of this point.

From equation (9) we obtain

$$\mathbf{E}' = \mathbf{E}_0 \Big/ \left\{ 1 - \frac{4\pi}{3} \mathfrak{N}\alpha^3 \frac{N^2 - 1}{N^2 + 2} \right\},$$

so that

$$\mathbf{f} = \mathbf{E}_0 \frac{N^2 - 1}{N^2 + 2} \alpha^3 \Big/ \left\{ 1 - \frac{4\pi}{3} \mathfrak{N}\alpha^3 \frac{N^2 - 1}{N^2 + 2} \right\}.$$

CLERK MAXWELL'S equations written with Hertzian units for this medium, now, therefore, are

$$\epsilon' \frac{d\mathbf{E}}{dt} = c \operatorname{curl} \mathbf{H} \quad \text{and} \quad \frac{d\mathbf{H}}{dt} = -c \operatorname{curl} \mathbf{E},$$

where

$$\epsilon' = (\mathbf{E} + 4\pi \mathbf{f}')/\mathbf{E} = 1 + 4\pi \mathfrak{N}\alpha^3 \frac{N^2 - 1}{N^2 + 2} \Big/ \left\{ 1 - \frac{4\pi}{3} \mathfrak{N}\alpha^3 \frac{N^2 - 1}{N^2 + 2} \right\}.$$

We have therefore proved that a medium consisting of small metal spheres distributed *in vacuo*, many to a wave-length of light, is optically equivalent to a medium of refractive index n' and absorption κ' given by $N' \equiv n'(1 - \iota\kappa') \equiv \sqrt{\epsilon'}$, where

$$\epsilon' = 1 + \frac{4\pi \mathfrak{N}\alpha^3 \dfrac{N^2 - 1}{N^2 + 2}}{1 - \dfrac{4\pi}{3} \mathfrak{N}\alpha^3 \dfrac{N^2 - 1}{N^2 + 2}} \quad \ldots\ldots (10).$$

We shall throughout use the symbol μ to denote the volume of metal per unit

volume of the medium (except when μ is evidently used to denote the thousandth part of a millimetre). Thus $\mu \equiv \frac{4\pi}{3} \mathfrak{N} a^3$, and equation (10) becomes

$$\epsilon' = 1 + \frac{3\mu \dfrac{N^2 - 1}{N^2 + 2}}{1 - \mu \dfrac{N^2 - 1}{N^2 + 2}} \quad \ldots \ldots \ldots \quad (10').$$

If the metal spheres be situated in glass of refractive index ν instead of *in vacuo*, this equation becomes

$$\{n'(1 - \iota\kappa')\}^2 = \epsilon' = \nu^2 + \frac{3\mu\nu^2 \dfrac{N^2 - \nu^2}{N^2 + 2\nu^2}}{1 - \mu \dfrac{N^2 - \nu^2}{N^2 + 2\nu^2}} \quad \ldots \ldots \quad (11).^*$$

The constants n' and κ' of the medium thus depend only on μ, the relative volume of metal, and not on the radii of the individual spheres. It is clear that the spheres may now be supposed to be of quite various radii, provided only that there be many spheres to a wave-length of light in the medium.

We have given the general result which holds for all values of μ, as we shall require it later. But in the case of metal glasses, by which name we shall describe glasses in which a metal is present in metallic form, the value of μ varies from about 10^{-4} for a silver glass down to about 10^{-6} for a soda glass coloured by radium. The last equation giving the optical constant $N' = n'(1 - \iota\kappa')$ of the metal glass may be written

$$\{n'(1 - \iota\kappa')\}^2 - \nu^2 = 3\mu\nu^2 \frac{N^2 - \nu^2}{N^2 + 2\nu^2} \equiv 3\mu\nu^2(\alpha - 2\beta\iota), \text{ say} \quad \ldots \quad (12),$$

where N is the optical constant of the metal and ν the index of refraction of the glass by itself.

§ 5. Equation (12) may now be written

$$n'^2(1 - \kappa'^2) - \nu^2 - 2\iota n'^2\kappa' = 3\mu\nu^2 \frac{n^2(\kappa^2 - 1) + \nu^2 + 2\iota n^2\kappa}{n^2(\kappa^2 - 1) - 2\nu^2 + 2\iota n^2\kappa} \equiv 3\mu\nu^2(\alpha - 2\iota\beta).$$

Thus, equating real and imaginary parts, we find, after some reduction,

$$\left.\begin{aligned} \alpha &\equiv \frac{n'^2(1 - \kappa'^2) - \nu^2}{3\mu\nu^2} = \frac{\{n^2(\kappa^2 - 1)\}^2 - n^2(\kappa^2 - 1)\nu^2 + 4n^4\kappa^2 - 2\nu^4}{\{n^2(\kappa^2 - 1) - 2\nu^2\}^2 + 4n^4\kappa^2} \\ \beta &\equiv \frac{n'^2\kappa'}{3\mu\nu^2} = \frac{3n^2\kappa\nu^2}{\{n^2(\kappa^2 - 1) - 2\nu^2\}^2 + 4n^4\kappa^2} \end{aligned}\right\} \quad (13).$$

* [*Note added 16th May*, 1904.—This equation may be written $\dfrac{N'^2 - \nu^2}{N'^2 + 2\nu^2} = \mu \dfrac{N^2 - \nu^2}{N^2 + 2\nu^2}$.]

We have now to see whether by means of these equations (13), and of the values of n and κ for various metals, we shall be able to predict the colour of a glass which contains a number of small metal spheres, whose linear dimensions and distances apart are small compared with a wave-length of visible light.

In the annexed table the refractive index of the glasses has been taken to be $\nu = 1{\cdot}56$.

The values of $n^2(\kappa^2 - 1)$ and of $n^2\kappa$ for the metal are those given by DRUDE ('Physikalische Zeitschrift,' January, 1900), for yellow light ($\lambda = {\cdot}0000589$ centim.), and for red light ($\lambda = {\cdot}0000630$ centim.). For the potassium-sodium amalgam, however, blue and yellow light were used instead of yellow and red.

Now let us suppose that μ, the quantity of metal per unit volume, is very small If, then, α and β represent the numbers in the penultimate and last columns of Table I. respectively, we have

$$n'^2(1 - \kappa'^2) = \nu^2 + 3\mu\nu^2\alpha, \qquad n'^2\kappa' = 3\mu\nu^2\beta.$$

Hence

$$n'^2(1 + \kappa'^2) = \{\nu^4 + 2\nu^2 . 3\mu\nu^2\alpha + 9\mu^2\nu^4\alpha^2 + 36\mu^2\nu^4\beta^2\}^{\frac{1}{2}}$$
$$= \nu^2 + 3\mu\nu^2\alpha + 9\mu^2\nu^2 2\beta^2 + 27\mu^3(\ldots) + \ldots$$

Hence, neglecting higher powers of μ,

$$n'\kappa' = 3\mu\nu\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14).$$

Now, suppose that light of wave-length λ *in vacuo* travels through this composite medium, whose constants are n' and κ'. The light *in vacuo* being given by

$$X = A \exp\{2\pi\iota(t/T - z/\lambda)\},$$

in this medium it is given by

$$X = A' \exp\{2\pi\iota(t/T - N'z/\lambda)\}$$
$$= Ae^{-\frac{2\pi n'\kappa' z}{\lambda}} \exp\{2\pi\iota(t/T - n'z/\lambda)\},$$

so that $n'\kappa'$ measures the absorption. In fact, the intensity of the light sinks to e^{-2} (= $\frac{1}{7{\cdot}4}$ nearly) of its original value in traversing a distance

$$d = \frac{\lambda}{2\pi n'\kappa'} = \frac{\lambda}{6\pi\mu\nu\beta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

of the medium.

We have now to apply the formulæ to the observations, in order to test the validity of our analysis as regards the actual phenomena. SIEDENTOPF and ZSIGMONDY give ('Ann. der Physik,' January, 1903, pp. 33, 34) a table of various gold glasses examined by them. This table is reproduced in Table II.

Table I

λ yellow = ·0000589 centim. λ red = ·0000630 centim.

Metal.	Coloured.	$\{n^2(\kappa^2-1)\}^2$.	$n^2(\kappa^2-1)\nu^2$.	$4n^4\kappa^2$.	Numerator of first fraction in (2).	$3n^2\kappa\nu^2$.	$\{n^2(\kappa^2-1)-2\nu^2\}^2$.	Denominator.	$\frac{n'^2(1-\kappa'^2)-\nu^2}{3\mu\nu^2}\equiv\alpha$	$\frac{n'^2\kappa'}{3\mu\nu^2}\equiv\beta$.
Silver* . .	Yellow .	182·25	32·8536	1·7956	139·3472	4·8915	74·5287	76·3243	1·826	·0641
	Red . .	246·49	38·2075	2·6244	199·0631	5·9136	78·0219	80·6463	2·468	·0733
Copper . .	Yellow .	42·25	15·8184	11·56	26·1468	12·4114	2·6667	14·2267	1·838	·8724
	Red . .	90·25	23·1192	12·99	58·2760	13·1414	21·4647	34·4547	1·691	·3814
Gold* . . .	Yellow .	60·84	18·9821	4·2436	34·2567	7·5198	8·6025	12·8461	2·667	·5854
	Red . .	96·04	23·8493	3·6864	64·0323	7·0088	24·3345	28·0209	2·285	·2501
Potassium-sodium. .	Blue . .	9·61	7·5442	·2704	− 9·5086	1·8982	3·1223	3·3927	−2·803	·5594
	Yellow .	22·09	11·4379	·2916	− ·9011	1·9712	·0286	·3196	−2·819	6·1678

$\nu = 1{\cdot}56$. $\nu^2 = 2{\cdot}4336$. $2\nu^2 = 4{\cdot}8672$. $2\nu^4 = 11{\cdot}8448$.

* See also Appendix.

TABLE II.

Glass.	Colour by transmitted light. (Layer about 4 millims. thick).	Colour of cone of light.	Behaviour of cone of light when examined with a Nicol.		Total gold content, μ in cub. millims.; gold per cub. millim., glass.	Colorimetrically found gold content, μ.	Size of particles in $\mu\mu$.	
			Nicol parallel to plane of incidence.	Nicol perpendicular to plane of incidence.			(*a*) From gold content.	(*b*) From colorimetrical gold content.
A*	Colourless . . .	Gold-yellow . .	White-yellow	Red-yellow, rather lessened	$12 \cdot 6 . 10^{-6}$	—	487–791	—
B*	Dirty reddish, "lebrig" cloudy	Gold-yellow, very intense	White-yellow	Red-yellow, rather lessened	$10 \cdot 1 . 10^{-6}$	—	131–173	—
Ca*	Almost colourless	Green, intense .	Green, scarcely lessened	Green, much lessened .	$13 \cdot 3 . 10^{-6}$	—	115–145	—
Cb*	Pink.	Green	Green, scarcely lessened	Green, much lessened .	$13 \cdot 3 . 10^{-6}$	—	63–106	—
Cc*	Pink.	Green	Green	Green, almost extinguished	$13 \cdot 3 . 10^{-6}$	$1 \cdot 34 . 10^{-6}$†	20·6–32·8	9·6–15·3
Da	Clear blue . . .	Pink, copper-red	As without Nicol . .	Brown, lessened . . .	$6 \cdot 8 . 10^{-6}$	—	68·8–103	—
Db	Clear blue to violet	Brass-yellow . .	As without Nicol . .	Brown-red, lessened .	$6 \cdot 8 . 10^{-6}$	—	68–74	—
E	Blue-violet with pink films	Brown with green films	As without Nicol, the green films rather brighter than the brown	Brown, lessened; green extinguished	$9 \cdot 05 . 10^{-6}$	$4 \cdot 5 . 10^{-6}$	13·2–17·4	10·5–13·9
F	Clear red . . .	Green, slight intensity	As without Nicol . .	Almost extinguished .	$8 \cdot 0 . 10^{-6}$	$4 \cdot 4 . 10^{-6}$	9·3–12·5	7·6–10·2
G	Deep red, intense	Green, feeble intensity	As without Nicol . .	Extinguished in places.	$14 \cdot 0 . 10^{-6}$	$7 \cdot 2 . 10^{-6}$	10·5–13·2	8·4–10·6
H	Pink.	Green, slight intensity	As without Nicol . .	Extinguished in places.	—	$1 \cdot 0 . 10^{-6}$	—	3·9–6·9‡

* Distances of particles apart fully resolvable. † This value is probably too small. ‡ Distribution was very uniform in this glass.

If l^3 denote the volume of the gold particles, so that l is given in the 8th or 9th column of the Table II., according as μ, the gold content, is taken from the 6th or 7th column, then the number $\mathfrak{N}$ of gold particles per cubic (10^{-4} centim.) is given by $\mathfrak{N} = 10^9\mu/l^3$.

We have said that for our analysis to be applicable there must be many spheres to a wave-length. Since the spheres in glasses A, B, Ca, Cb, Cc (Table II.) can be separated by a Zeiss $\frac{1}{12}$th objective, they must be at a distance apart greater than $\cdot 2\mu$, or half a wave-length of violet light. We shall therefore not expect our analysis to apply to them. It is further apparent that the particles are more widely separated in Da than Db. If we take for l the mean of the two numbers given, we have

$$\mathfrak{N}_{\mathrm{Db}} = \cdot 019, \quad \mathfrak{N}_{\mathrm{E}} = 2\cdot 48, \quad \mathfrak{N}_{\mathrm{F}} = 6\cdot 24, \quad \mathfrak{N}_{\mathrm{G}} = 8\cdot 40, \quad \mathfrak{N}_{\mathrm{H}} = 6\cdot 35,$$

so that, since $\mathfrak{N}_{\mathrm{F}}$, $\mathfrak{N}_{\mathrm{G}}$, and $\mathfrak{N}_{\mathrm{H}}$ are larger than $\mathfrak{N}_{\mathrm{Db}}$ and $\mathfrak{N}_{\mathrm{E}}$, the glasses F, G, H satisfy our condition best.

But here we are presented with a difficulty. The wave-length of the yellow light, $\lambda = \cdot 0000589$ centim., is in our glass ($\nu = 1\cdot 56$) only, $\lambda' = \cdot 00003775$ centim. or $\cdot 3775\mu$. Thus to find the number of gold particles in λ'^3, we must multiply $\mathfrak{N}$ by $(\cdot 3775)^3 = \cdot 0538$. We shall thus, even for glass G, have less than one particle to a wave-length. On the other hand, SIEDENTOPF warns us (*loc. cit.*, p. 27) that the linear dimensions of the particles are only to be taken as upper limits and may be three times too large.

Suppose this is the case, then the number of particles in a yellow wave-length in the glass is $27 \times \cdot 0538$ ($= 1\cdot 45$) times the above numbers, $\mathfrak{N}$, with of course a still greater value for red light.

On this hypothesis then the glasses F, G, H alone of the series satisfy our condition. If, therefore, the theory is correct, it should explain the colour and other optical properties of these three glasses as set out in the first five columns of Table II.

Let us, for instance, consider the colour of glass G. From equation (15) we have as the distance d in which the intensity of light of wave-length λ is reduced to $1/7\cdot 4$ of its original value $\lambda/6\pi\mu\nu\beta$ given by (15).

From the Table I. we have, supposing $\nu = 1\cdot 56$,

$$\beta = \cdot 5854, \quad \text{for yellow light } \lambda = 10^{-7}\ \cdot 589 \text{ centim.}$$
$$\beta = \cdot 2501, \quad \text{for red light } \quad \lambda = 10^{-7}\ \cdot 630 \quad ,,$$

The value of μ found by colorimetry is 72.10^{-7}. Consequently we have

$$\text{Yellow, } d = \cdot 48 \text{ centim., nearly.}$$
$$\text{Red, } \quad d = 1\cdot 19 \text{ centims.} \quad ,,$$

Since the latter number is greater than the former, it follows that this glass, and

indeed all gold glasses for which our condition is satisfied, should be much more red than yellow. Presumably, therefore, they are still more yellow than green, and more green than blue.* We should therefore expect the gold glasses F, G, H, which satisfy our condition, to be *red*, as in fact they are.

The above values for d are certainly of the right order, but they may be somewhat too large. If we had taken the value of μ, called the Total Gold Content in Table II., the corresponding values of d would have been only half those given above.

It is to be remembered that manufacturers, in making gold ruby glass for "flashing" on to clear glass, use much more gold. A common value for the total gold content is about 3.10^{-5}.

By means of equation (15) and Table I. we can in this way predict whether a gold, silver, or copper glass for which $\nu = 1{\cdot}56$ will transmit more red or more yellow light, and whether such a glass containing small spheres of "potassium-sodium" will transmit more yellow or more blue.

We thus find that when there are several metal spheres to a wave-length

Silver glass transmits yellow (β/λ yellow $<$ β/λ red),

Copper ,, ,, red (β/λ red $<$ β/λ yellow),

Gold ,, ,, ,, (β/λ ,, $<$ β/λ ,,),

Potassium-sodium glass transmits blue (β/λ blue $<$ β/λ yellow).

From the values of β on Table I., p. 396, we see that for a silver glass to absorb as much red light as a gold glass does yellow, μ would have to be $\frac{5854}{733}$, or, roughly, eight times as great for the silver glass as for the gold. And, since the values of β for yellow and red light are more nearly equal for silver than for gold, in order to produce the same coloration there would have to be even more than eight times as much silver (by volume) as gold. I am told that manufacturers put in ten times as much silver by weight into a silver glass as they put gold into a gold glass.

Again, the very large value of β for yellow light in a potassium-sodium glass shows that such a glass would absorb as much yellow light as a gold glass with only $\frac{1}{10}$ of the amount of metal excreted.

Thus a very slight excretion of the potassium-sodium metal would give a very strong blue or violet coloration. This probably explains the colouring of soda glass by radium, the radiation causing the excretion of the metal.

In order to test this hypothesis I asked Mr. F. Soddy, on 9th November, 1903, at University College, London, to examine whether the emanation from radium was capable of colouring quartz glass in which there could evidently be no possibility of the excretion of metal. He stated that he and Professor Ramsay had already made this experiment and had found no coloration.

At my request Mr. Soddy then placed a small piece of colourless gold glass in a

* See Appendix.

tube containing some emanation. Within two days an unmistakable ruby tint appeared in the glass.*

It seems probable that the violet coloration of soda glass bulbs used in the production of Röntgen rays may be due to the excretion of metal caused by the β rays from the cathode.

The observations of ELSTER and GEITEL, 'Wied. Ann.,' 59, p. 487, 1896, quoted by J. J. THOMSON, 'Conduction of Electricity through Gases,' p. 496, that salts of the alkali metals coloured by exposure to cathode rays exhibit photo-electric effects, suggestive of the presence of traces of the free metal, support this view as to the cause of the coloration of metal glasses exposed to the radiation from radium.

From equation (6), as modified for the case when the metal sphere is surrounded by glass of refractive index ν, it appears that the amplitude at any point of the light emitted from the sphere is proportional to $\left|\frac{N^2-\nu^2}{N^2+2\nu^2}\right|\frac{a^3}{\lambda^2}$, where $|u+iv|$ denotes the modulus, $+\sqrt{u^2+v^2}$. Using α and β as defined in equation (13), we have $\left|\frac{N^2-\nu^2}{N^2+2\nu^2}\right|^2 \equiv \alpha^2+4\beta^2$, where α and β are to be found from the table on p. 396, where $\nu = 1{\cdot}56$. Thus at any point the intensity of light emitted by a sphere of radius a is proportional to $(\alpha^2+4\beta^2)/\lambda^4 \equiv I$, say. Measuring λ in millim./1000, the Table I. gives the following values of I:—

		Silver.	Copper.	Gold.
Yellow ($\lambda = {\cdot}589$) I_y	=	27·95	62·11	70·88
Red ($\lambda = {\cdot}630$) I_x	=	38·81	21·75	34·79.

From these values of I it appears that when white light falls on a small sphere the light emitted is, for

Silver, more red than yellow, $I_z > I_y$,
Copper ,, yellow ,, red, $I_y > I_z$,
Gold ,, ,, ,, ,, $I_y > I_z$.

The presumption is that for the two latter the light may be more green than yellow.

In the table given by SIEDENTOPF and ZSIGMONDY (*loc. cit.*), of which a copy is given (Table II., p. 397), it is seen that of the five glasses Cc, E, F, G, H, whose particles are small compared with a wave-length of light in the glass, the four glasses Cc, F, G, H contain particles which send out a *green* cone of light, and the glass E contains some particles which send out *green* and some which send out *brown*.

Thus far we have confined attention to glasses for which the condition of having

* [*Note added* 14*th May*, 1904.—Sir WILLIAM RAMSAY has lately exposed some clear silver glass and some soda glass at the same time to the emanation from radium. After a fortnight's exposure the silver glass had turned a faint yellow and the soda glass a deep blue-violet.]

man metal particles to a wave-length is satisfied. We have shown that when the meta is gold such glasses should be pink (*cf.* column 3 of Table II.) by transmitted ligh ; and that the small gold spheres should send up the microscope light which is pre- minently yellow or green (*cf.* columns 4 and 5); and we have remarked that for the ame reason that explains the polarisation of sky light, such small spheres send no li ht directly up the microscope tube when the electric vector of the incident light is in that direction, so that in this case the cone of light as examined with the low- pow r objective will be cut off (*cf.* column 5), although the large numerical aperture of t e Zeiss $\frac{1}{12}$th oil immersion lens will allow some light to go up the tube, but so as t leave a black spot in the centre of the focal plane of the microscope as shown in fi . 6.

A these deductions from our analysis are confirmed in every detail by the three glass s F, G, H (Table II.). And it is these very glasses, of all the glasses in that tabl , for which, according to the numbers there given, the particles are both smallest and losest together.

§ . Let us now briefly notice the remaining glasses of Table II. For these glasses the umber of metal particles to a wave-length, measured by (gold content)$^{\frac{1}{3}}$ ÷ size of p rticle, as determined from the 6th and 8th or from the 7th and 9th columns of that table, is smaller than for the glasses F, G, H, which show the regular pink colou . For the glasses A to E this number is greatest for the glasses Cc and E, of whic the former and parts of the latter *do* show the regular pink colour.

E en glasses which do not satisfy the condition of many particles to a wave-length, and which consequently do not exhibit the "regular" (pink) colour of gold glass, have many of their properties co-ordinated by the results we have obtained for regu ar glasses.

Ta e, for instance, the glasses A and B (Table II.). Comparison of the gold cont nt μ with the size of the *observed* particles shows that those particles at any rate are so far apart as not to satisfy our condition. The fact that glass A is colou less shows that if there are also minute spheres present which escaped obse vation, they also lie so far apart as not to be many to a wave-length. On the othe hand the pink colour of glass B suggests the presence of minute unobserved sphe es which are sufficiently close together to satisfy our condition, the absorption of th glass being proportional to that small part of the gold content (μ) which is asso ated with the minute spheres.

In both glasses the large particles reflect much more light than is emitted by the minu e spheres. The colour of this reflected light is the usual yellow-red metallic refle ion from gold. Therefore the colour of the cone of light should be gold- yello (i).

W en the Nicol is introduced parallel to the plane of incidence, presumably half the ncident light is cut off. Consequently the large particles send only half the yello -red light up the tube that they previously sent. Owing, however, to the fact

hat the minute spheres send no light directly up the tube when the electric vector f the incident light is parallel to the microscope tube (Nicol perpendicular to plane of ncidence), less than half the green light from any small spheres will be cut off. The one of light will therefore have more green in proportion to the yellow-red than efore the introduction of the Nicol. Therefore the colour of the cone of light will be ore white than before (ii).

When the Nicol is perpendicular to the plane of incidence, the green light from the nall spheres is cut off, so the colour of the cone of light will be more red than ith no Nicol, and therefore the total quantity of light sent up the tube will be ther lessened (iii). The conclusions (i), (ii), (iii) are in accordance with the henomena tabulated in the 3rd, 4th, and 5th columns of Table II.

The glasses Ca, Cb, Cc present no special difficulties. We have seen (§ 3) that hose metal particles in a gold glass whose diameters are less than $0{\cdot}1\mu$ (10^{-5} centim.) re spherical, and (§ 5) that small gold spheres send *green* light up the microscope ube. In the above-named glasses the figures in the 7th column of Table II. show hat the particles are so small as to approximate to the spherical form. This is onfirmed by the green cone of light and its approximate extinction when the electric ector of the incident light is in the direction of the microscope tube.

As here, too, the observed particles are far enough apart to be distinguished under he microscope, it is necessary to postulate additional minute spheres to explain the ink colours of these glasses.

In glasses D and E the blue and violet colours of the transmitted light present a ifficulty which I have not yet been enabled completely to surmount.* It is probable hat the particles in this glass are not sufficiently thickly distributed to satisfy the ondition of there being many particles to a wave-length of blue light. When the ncident light is blue, the absorption that we have investigated is therefore not resent. When, however, the incident light is red, there are sufficient particles to a vave-length for absorption to take place. Thus, although if light of all wave-lengths vere absorbed, the red would be least absorbed; yet here it is only the larger wave-engths that suffer the absorption whose nature we have investigated.

PART II.

§ 7. With a view to examining whether these principles apply to the colour changes xhibited by translucent films of metal when heated, observed by Mr. G. T. Beilby ('Roy. Soc. Proc.,' vol. 72, 1903, p. 226) and by Professor R. W. Wood ('Phil. Mag.,' vol. 3, 1902, p. 396), we proceed to consider the transmission of light by films of netal, the metal being in the form of small spheres, many to a wave-length of light n the film.

* See Appendix added July 8th for explanation of Blue and Violet Colours.

We shall first confine attention to very thin films, defining very thin films to be such that $\pi d/\lambda'$ may be treated as small, d being the thickness of the film, and λ' the wave-length of light in the film.

It has already been noticed that equation (9), p. 393, does not hold for very thin films. That equation is obtained by observing that the *average* action of its neighbours on a particle is that due to a medium which is perfectly uniformly polarised in the neighbourhood of the particle, and whose external boundary is that of the actual medium, and whose internal boundary is a sphere of radius r_0, equal to the smallest distance between the centres of two particles. Poisson has shown that the effect of such a uniformly polarised medium is equivalent to that of a surface distribution over its internal and external boundaries.

The medium actually present here can only be treated as uniformly polarised throughout the region inside a sphere whose radius, r_1, is small compared with the wave-length of light in the medium. When the outer boundary of the medium is in all directions many wave-lengths distant from the particle under consideration, the effect of the periodically varying polarisation outside $r = r_1$ can be allowed for by neglecting the Poisson distribution on the outer boundary of the medium. Consequently, in this case, the effect on any particle of the remaining particles is that due to a Poisson distribution over the sphere $r = r_0$, which leads to equation (9).

When the external boundary of the medium is, in any direction, at a very small distance from the average particle, we are not justified in neglecting the Poisson distribution over that boundary. In the case of a thin film of the medium in the plane xy it is, however, clear that when the electric force is parallel to that plane, there is no Poisson distribution over the surfaces of the film. Consequently the film has (complex) dielectric constants in the direction of the axes of x and y, which are the same as for the medium in bulk. Omitting the accent in equation (10′), this constant is given by

$$\epsilon - 1 = 3\mu \frac{N^2 - 1}{N^2 + 2} \Big/ \left\{ 1 - \mu \frac{N^2 - 1}{N^2 + 2} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16).$$

The dielectric constant ϵ', parallel to Oz, may be different from ϵ; if so, the film behaves optically like a uniaxial crystal whose three (complex) dielectric constants are ϵ, ϵ, ϵ', the optic axis being normal to the film.

§ 8. Putting $\nu = 1$ in equations (12) and (13), we have

$$\frac{N^2 - 1}{N^2 + 2} = \alpha - 2\beta\iota \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12'),$$

where

$$\alpha = \frac{\{n^2(\kappa^2 - 1)\}^2 - n^2(\kappa^2 - 1) + 4n^4\kappa^2 - 2}{\{n^2(\kappa^2 - 1) - 2\}^2 + 4n^4\kappa^2}, \quad \beta = \frac{3n^2\kappa}{\{n^2(\kappa^2 - 1) - 2\}^2 + 4n^4\kappa^2} \cdot \quad (13').$$

We shall henceforward find it convenient to use n and κ to denote the constants of the medium containing the spheres. The constants of the metal itself will therefore be denoted by n_1 and κ_1, and it will appear, as is *à priori* evident, that the latter are the values of n and κ when $\mu = 1$. Since therefore $\epsilon \equiv \{n(1 - \iota\kappa)\}^2$, equation (16) gives us on substituting from (12′)

$$n^2(1 - \kappa^2) - 1 - 2\iota n^2\kappa = \epsilon - 1 = 3\,\frac{\mu\alpha - 2\mu\beta\iota}{1 - \mu\alpha + 2\mu\beta\iota} \quad . \quad . \quad . \quad (17),$$

from which, by equating real and imaginary parts,

$$n^2\kappa = \frac{3\mu\beta}{(1 - \mu\alpha)^2 + 4\mu^2\beta^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18),$$

$$n^2(\kappa^2 - 1) = 2 - \frac{3(1 - \mu\alpha)}{(1 - \mu\alpha)^2 + 4\mu^2\beta^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (19),$$

whence

$$\{n^2(\kappa^2 + 1)\}^2 = 3\,\frac{3 - 4(6 - \mu\alpha)}{(1 - \mu\alpha)^2 + 4\mu^2\beta^2} + 4 \quad . \quad . \quad . \quad . \quad . \quad (20).$$

The following table gives the values of α and β as found by means of formula (13′) from the constants n and κ of the solid metal as given by DRUDE (*loc. cit.*) :—

TABLE III.

Metal.	Colour.	α.	β.
Gold	Yellow λ = ·589	1·4593	·0816
	Red λ = ·630	1·3626	·0446
Silver	Yellow λ = ·589	1·2574	·0150
	Red λ = ·630	1·2160	·01277
Potassium-sodium	Blue	3·269	·531
	Yellow	2·068	·107

In order to determine the values of n and κ for various values of μ, the numerical values of the functions ξ, η, ζ, where

$$\frac{\xi}{\mu\beta} = \frac{\eta}{1 - \mu\alpha} = \frac{\zeta}{1} = \frac{1}{(1 - \mu\alpha)^2 + 4\mu^2\beta^2} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

were calculated for gold and for silver for the following values of μ:

$$\mu = \cdot 1, \quad \mu = \cdot 5, \quad \mu = \cdot 6, \quad \mu = \cdot 7, \quad \mu = \cdot 8, \quad \mu = \cdot 9, \quad \mu = 1 \cdot 0.$$

Equations (19) and (20) may be written

$$n^2(\kappa^2 - 1) = 2 - 3\eta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19'),$$

$$n^2(\kappa^2 + 1) = \{3(3\zeta - 4\eta) + 4\}^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20'),$$

whence the values of n and $n\kappa$ for gold and for silver were calculated for the above values of μ. The values of $n^2\kappa$ thence obtained were checked against those obtained by means of equation (18), namely,

$$n^2\kappa = 3\xi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18').$$

In the case of silver with μ less than $\cdot 8$ it was, however, seen to be better to obtain $n\kappa$ as the quotient of the value of $n^2\kappa$ got from (18'), by the value of n got from (19') and (20'), owing to the large probable error when $n\kappa$ was determined directly from (19') and (20').

From equation (13') we find

$$n_1^2\kappa_1 = \frac{3\beta}{(1-\alpha)^2 + 4\beta^2}, \quad n_1^2(\kappa_1^2 - 1) = 2 - \frac{3(1-\alpha)}{(1-\alpha)^2 + 4\beta^2},$$

which are the same as equations (19) and (20) with $\mu = 1$. Consequently, as should be the case, the medium of spheres is equivalent to the solid metal wherein the spheres are of such varied sizes that they fill the whole space. Another check on the tabulated numbers is afforded therefore by a comparison of the calculated and observed values of $n_1^2\kappa_1$, $n_1\kappa_1$ and n_1.

I believe that nearly all the numbers here given for silver and for gold are subject to an error of less than 1 per cent.

The values of $n^2\kappa = 3\xi$ and of η for the potassium-sodium amalgam of DRUDE'S table, 'Phys. Zeitschrift,' January, 1900, are less carefully calculated.

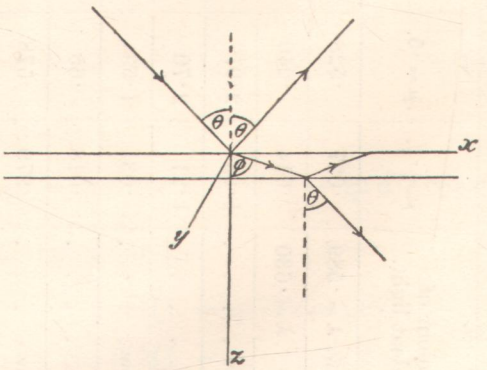


Fig. 10.

§ 9. Consider now the incidence of plane polarised light on a plate of this medium. We shall first suppose the plate to be very thin and therefore optically crystalline.

Suppose the two surfaces of the film are $z = 0$ and $z = d$, and that zx is the plane of incidence.

TABLE IV.—Gold and Silver.

		Colour of incident light.	$\mu = \cdot 1$.	$\mu = \cdot 5$.	$\mu = \cdot 6$.	$\mu = \cdot 7$.	$\mu = \cdot 8$.	$\mu = \cdot 9$.	$\mu = 1 \cdot 0$.	Given value for solid metal.	Value for $\mu = \frac{1}{\alpha}$.
Gold	$n\kappa$.	Yellow, $\lambda = \cdot 589$	·027	·528	1·50	4·07	3·80	3·19	2·82	2·82	3·80 for $\mu = \cdot 685$
		Red, $\lambda = \cdot 630$	·014	·240	·605	2·87	5·01	3·75	3·15	3·15	4·89 for $\mu = \cdot 734$
	n	Yellow	1·23	2·91	3·89	3·12	1·14	·58	·37	·37	3·53 for $\mu = \cdot 685$
		Red	1·21	2·70	3·67	5·40	1·62	·57	·31	·31	4·68 for $\mu = \cdot 734$
	$n^2\kappa$	Yellow	·034	1·53	5·86	12·70	4·34	1·84	1·03	1·03	13·42 for $\mu = \cdot 685$
		Red	·018	·65	2·22	15·53	8·11	2·09	·96	·96	22·9 for $\mu = \cdot 734$
	M_0	Yellow	·979	·578	·406	·374	·695	1·05	1·34	—	·354 for $\mu = \cdot 685$
		Red	·982	·622	·450	·247	·435	·845	1·19	—	·232 for $\mu = \cdot 734$
Silver	$n\kappa$.	Yellow	·0049	·066	·140	·449	8·75	4·91	3·68	3·67	7·99 for $\mu = \cdot 795$
		Red	·0042	·052	·104	·282	3·00	5·69	3·97	3·96	8·51 for $\mu = \cdot 822$
	n	Yellow	1·20	2·46	3·19	4·74	6·74	·46	·18	·18	7·87 for $\mu = \cdot 795$
		Red	1·19	2·38	3·01	4·24	8·81	·64	·20	·20	8·39 for $\mu = \cdot 822$
	$n^2\kappa$	Yellow	·0059	·163	·445	2·13	58·9	2·24	·67	·67	62·9 for $\mu = \cdot 795$
		Red	·0050	·124	·313	1·19	26·5	3·65	·81	·81	71·4 for $\mu = \cdot 822$

Potassium-Sodium.

	Colour of incident light.	$\mu = \cdot 1$.	$\mu = \cdot 2$.	$\mu = \cdot 4$.	$\mu = \cdot 5$.	$\mu = \cdot 6$.	$\mu = \cdot 7$.	$\mu = \cdot 8$.	$\mu = \cdot 9$.	$\mu = 1 \cdot 0$.	Given value for solid metal.	Value for $\mu = \frac{1}{\alpha}$.
$n^2\kappa$	Blue	·343	1·29	2·32	1·17	·717	·512	·403	·309	·254	·26	4·85, $\mu = \cdot 306$
	Yellow	·051	—	3·45	12·38	3·26	1·10	·59	·48	·270	·27	14·49, $\mu = \cdot 484$

First let the incident light be polarised in the plane of incidence, so that the incident wave is

$$X = 0, \quad Y = \exp[\iota p\{t - (x \sin\theta + z\cos\theta)/c\}], \quad Z = 0,$$

$$\alpha = -\cos\theta \exp[\iota p\{t - (x\sin\theta + z\cos\theta)/c\}], \quad \beta = 0, \quad \gamma = \sin\theta \exp[\iota p\{\ldots\}].$$

The reflected wave is

$$X = 0, \quad Y = B\exp[\iota p\{t - (x\sin\theta - z\cos\theta)/c\}], \quad Z = 0,$$

$$\alpha = B\cos\theta \exp[\iota p\{t - (x\sin\theta - z\cos\theta)/c\}], \quad \beta = 0, \quad \gamma = B\sin\theta\exp[\iota p\{\ldots\}].$$

Inside the film, *i.e.*, between $z = 0$ and $z = d$,

$$X = 0, \quad Y = A'\exp[\iota p\{t - (x\sin\phi + z\cos\phi)/V\}] + B'\exp[\iota p\{t - (x\sin\phi - z\cos\phi)/V\}], \quad Z = 0,$$

$$\alpha = -\frac{c\cos\phi}{V}\{A'\exp[\iota p\{t - (x\sin\phi + z\cos\phi)/V\}] - B'\exp[\iota p\{\ldots\}]\}, \quad \beta = 0,$$

$$\gamma = \sin\theta\{A'\exp[\ldots] + B'\exp[\ldots]\}.$$

Transmitted wave

$$X = 0, \quad Y = C\exp[\iota p\{t - (x\sin\theta + z\cos\theta)/c\}], \quad Z = 0,$$

$$\alpha = -C\cos\theta\exp[\iota p\{t - (x\sin\theta + z\cos\theta)/c\}], \quad \beta = 0, \quad \gamma = C\sin\theta\exp[\ldots].$$

In these expressions we have

$$V^2 = c^2/\epsilon \quad \text{and} \quad \sin\phi/V = \sin\theta/c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(a)}.$$

Since Y and α are continuous at $z = 0$,

$$1 + B = A' + B' \quad \text{and} \quad (1 - B)\cos\theta = (A' - B')\,c/V\cos\phi \quad . \quad . \quad \text{(b)}.$$

Since Y and α are continuous at $z = d$, if we replace

$\exp[\pm \iota p\, d/V\cos\phi]$ by $1 \pm \iota p\, d/V\cos\phi$, and $\exp[-\iota p\, d/c\cos\theta]$ by $1 - \iota p\, d/c\cos\theta$,

we obtain, when the square of $2\pi d/\lambda$ is neglected, the equations

$$\left.\begin{aligned} \{A' + B' - (A' - B')\,\iota p\, d/V\cos\phi\} &= C(1 - \iota p\, d/c\cos\theta) \\ c\cos\phi/V\{(A' - B') - (A' + B')\,\iota p\, d/V\cos\phi\} &= \cos\theta C(1 - \iota p\, d/c\cos\theta) \end{aligned}\right\} \quad \text{(c)}.$$

From the last pair of equations we find, neglecting squares of $p\,d/c$, that

$$A' + B' = C$$

$$\frac{c\cos\phi}{V\cos\theta}(A' - B') = C\left\{1 - \frac{\iota p\, d\sec\theta}{c}\left(\cos^2\theta - \frac{c^2\cos^2\phi}{V^2}\right)\right\} = C\left\{1 - \frac{\iota p\, d\sec\theta}{c}(1 - \epsilon)\right\}. \quad \text{(d)},$$

on using (a); then eliminating A', B', B from the equations (b) and (d), we finally have

$$C = 1 - \iota\pi\, d/\lambda \,.\, \sec\theta \,.\, (\epsilon - 1).$$

On taking the modulus and substituting for ϵ from (17) we obtain

$$|C|^2 = 1 - 4\pi d/\lambda \sec\theta \,.\, n^2\kappa \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22).$$

Secondly, suppose that the incident light is polarised perpendicular to the plane of incidence, α, β, γ being the magnetic force.

The incident wave is

$$\alpha = 0, \quad \beta = \exp\left[\iota p\left\{t - (x\sin\theta + z\cos\theta)/c\right\}\right], \quad \gamma = 0.$$

The transmitted wave is

$$\alpha = 0, \quad \beta = C\exp\left[\iota p\left\{t - (x\sin\theta + z\cos\theta)/c\right\}\right], \quad \gamma = 0.$$

The velocity V inside the film is connected with the angle of refraction by the equations

$$V^2 = c^2\left(\frac{\cos^2\phi}{\epsilon} + \frac{\sin^2\phi}{\epsilon'}\right) = \frac{c^2\epsilon'}{\epsilon\epsilon' + \sin^2\theta\,(\epsilon' - \epsilon)}.$$

The final result after using the two sets of boundary conditions is

$$C = 1 - \frac{\iota\pi d\sec\theta}{\lambda}\left\{\cos^2\theta\,(\epsilon - 1) + \sin^2\theta\,\frac{\epsilon' - 1}{\epsilon'}\right\},$$

whence, using (17), we obtain

$$|C|^2 = 1 - \frac{4\pi d\cos\theta}{\lambda}\left\{n^2\kappa + \tan^2\theta\,\frac{\epsilon' - 1}{\epsilon'}\right\} \quad . \quad . \quad . \quad . \quad . \quad (23).$$

When the light is normally incident, the crystalline character of the film does not manifest itself, and we have from (22) or (23)

$$|C|^2 = 1 - 4\pi d/\lambda \,.\, n^2\kappa \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24).$$

The absorption of directly incident light by a thin film is therefore governed by $n\kappa$.

Owing to the difficulty of knowing whether any particular metal film whose changes of colour have been observed, but whose thickness has not been recorded, for example, the films observed by Professor R. W. Wood or by Mr. G. T. Beilby (*loc. cit.*), is to be regarded as very thin for the purpose of this section, formulæ for thick films will now be found.

We consider here only the case of directly incident plane-polarised light, and proceed to obtain an equation corresponding to (24), reserving the full discussion of the behaviour of thick films under obliquely incident light till later. Using the axes shown in fig. 10, suppose that

Incident wave is

$$\mathbf{E} = 0,\ \exp\left\{\iota p\,(t - z/c)\right\},\ 0\,; \quad \mathbf{H} = -\exp\left\{\iota p\,(t - z/c\right\},\ 0,\ 0.$$

Reflected wave

$$\mathbf{E} = 0, \quad B\exp\left\{\iota p\,(t + z/c)\right\},\ 0\,; \quad \mathbf{H} = B\exp\left\{\iota p\,(t + z/c)\right\},\ 0,\ 0.$$

Wave in film, *i.e.*, between $z = 0$ and $z = d$,

$$\mathbf{E} = 0, \quad A' \exp\{\iota p(t - z/V)\} + B' \exp\{\iota p(t + z/V)\}, \ 0,$$

$$\mathbf{H} = -c/V[A' \exp\{\iota p(t - z/V)\} - B' \exp\{\iota p(t + z/V)\}], \ 0, \ 0.$$

Transmitted wave

$$\mathbf{E} = 0, \quad C \exp\{\iota p(t - z/c)\}, \ 0; \quad \mathbf{H} = -C \exp\{\iota p(t - z/c)\}, \ 0, \ 0,$$

where $c/V = n(1 - \iota\kappa)$.

The boundary conditions at $z = d$ give

$$\left.\begin{aligned} A'e^{-2\pi n\kappa/\lambda} \exp\{-\iota . 2\pi dn/\lambda\} + B'e^{2\pi dn\kappa/\lambda} \exp\{\iota . 2\pi dn/\lambda\} &= C \exp\{-\iota 2\pi d/\lambda\} \\ n(1 - \iota\kappa)[A'e^{-2\pi dn\kappa/\lambda} \exp\{-\iota . 2\pi dn/\lambda\} - B'e^{2\pi dn\kappa/\lambda} \exp\{\iota 2\pi dn/\lambda\}] & \\ = C \exp\{\iota 2\pi d/\lambda\} & \end{aligned}\right\} (25).$$

It follows from these equations that B' is of the order of $A'e^{-4\pi dn\kappa/\lambda}$; if therefore $\pi dn\kappa/\lambda > 1$ we shall be correct within 2 per cent. (e^{-4}) when we neglect B'. Thus referring to the Table IV. it appears that if a piece of gold leaf before annealing be so thick that $d > \lambda/1{\cdot}5$ or $d > \frac{2}{3}\lambda$, then, so far as yellow and red light are concerned, $\pi dn\kappa/\lambda$ will be > 1 for all values of $\mu \geq {\cdot}5$, if we suppose d to vary inversely as μ, the number 1·5 being the smallest value of $\pi n\kappa/\mu$ for gold for values of μ from ·5 up to unity.

Eliminating $B'e^{2\pi dn\kappa/\lambda}$ from the last two equations above,

$$2A'e^{-2\pi dn\kappa/\lambda} = C\left\{\frac{1 + n(1 - \iota\kappa)}{n(1 - \iota\kappa)}\right\} \exp\{-\iota 2\pi d/\lambda(1 - n)\}.$$

From the boundary condition at $z = 0$ we obtain

$$A'\{1 + n(1 - \iota\kappa)\} = 2.$$

Eliminating A' from the last two equations

$$C \exp\{-\iota 2\pi d/\lambda(1 - n)\} = 4e^{-2\pi dn\kappa/\lambda}\left[\frac{n(1 - \iota\kappa)}{\{1 + n(1 - \iota\kappa)\}^2}\right].$$

Taking the moduli, the ratio $|C|^2$ of the intensity of the transmitted to that of the incident light is given by

$$|C|^2 = \frac{16n^2(1 + \kappa^2)}{\{(1 + n)^2 + n^2\kappa^2\}^2} e^{-4\pi dn\kappa/\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26).$$

It appears that when the thickness exceeds $\frac{2}{3}$ of the wave-length, the absorption is governed by $n\kappa$; but, to the same order of approximation, by $n^2\kappa$ when d is less than $\frac{1}{25}\lambda$.

The (comparatively) small effect of the coefficient

$$M_0 \equiv \frac{16n^2(1+\kappa^2)}{\{(1+n)^2+n^2\kappa^2\}^2}$$

on the colour by transmitted light will be considered later. For the present it is sufficient to observe that M_0 becomes small when $\mu = 1/\alpha$ for any colour, and hence that the variations of M_0 intensify the absorption bands, which will be shown to occur for gold and silver near $\mu\alpha = 1$.

§ 10. In order to illustrate the discussion of the colours exhibited by films of metal for various values of μ, graphs are given of $n\kappa$ and $n^2\kappa$ for gold, for silver, and for the amalgam, potassium-sodium, the constants of which for $\mu = 1$ were given by DRUDE (*loc. cit.*). The graphs of $n\kappa$ and $n^2\kappa$ for gold and for silver when the incident light is red or yellow are plotted from the values given in the accompanying table, with the help of the additional point corresponding to $\mu\alpha = 1$.

This last point is easy to plot, for we see from equations (18) and (19) that $n^2\kappa = \dfrac{3}{4\mu\beta} = \dfrac{3\alpha}{4\beta}$ and $n^2(\kappa^2 - 1) = 2$ when $\mu = 1/\alpha$.

Consequently for

$$\mu = 1/\alpha,\ n^2(\kappa^2+1) = 2\sqrt{n^4\kappa^2+1},$$

so that

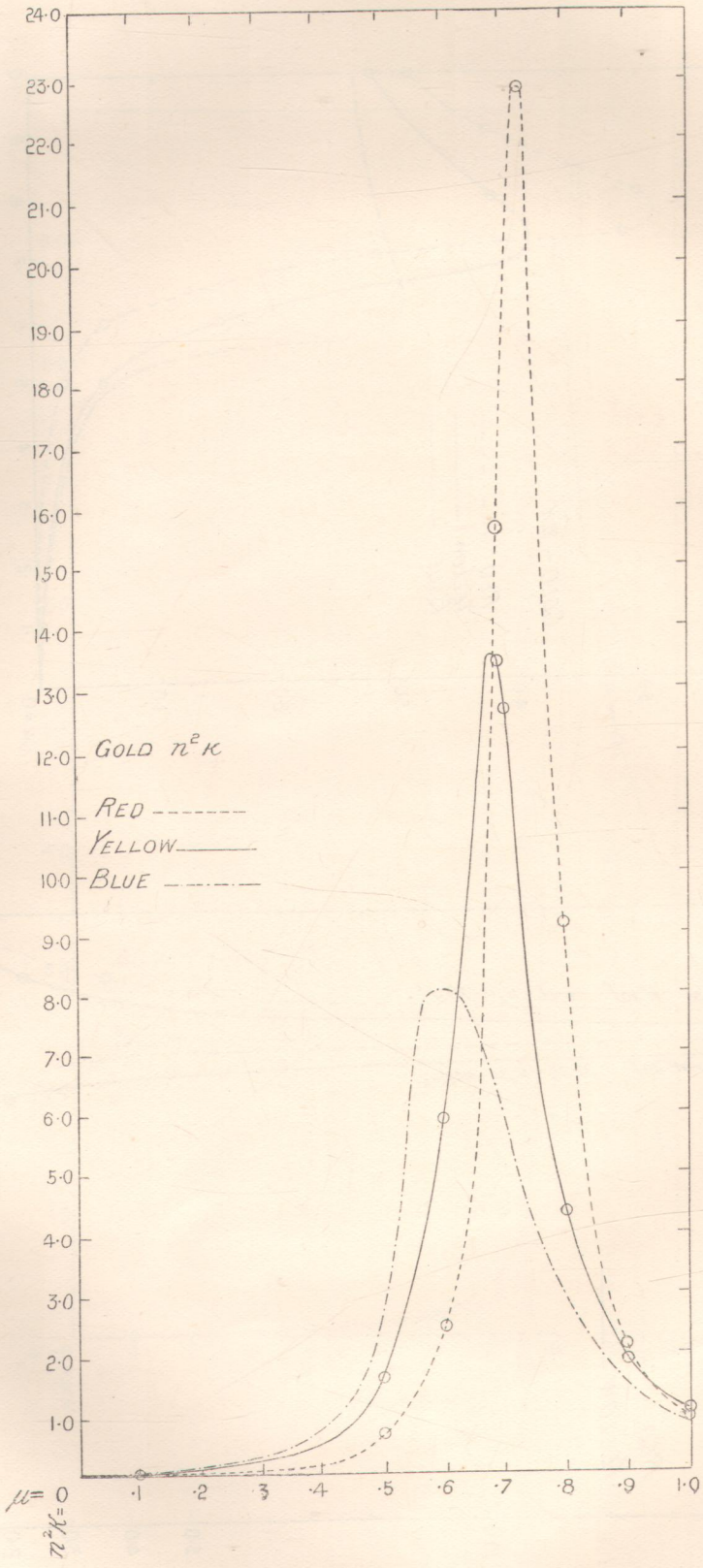
$$n^2\kappa^2 = \sqrt{n^4\kappa^2+1}+1 \quad \text{and} \quad n\kappa = \left\{\sqrt{\left(\frac{3\alpha}{4\beta}\right)+1}+1\right\}^{\frac{1}{2}}.$$

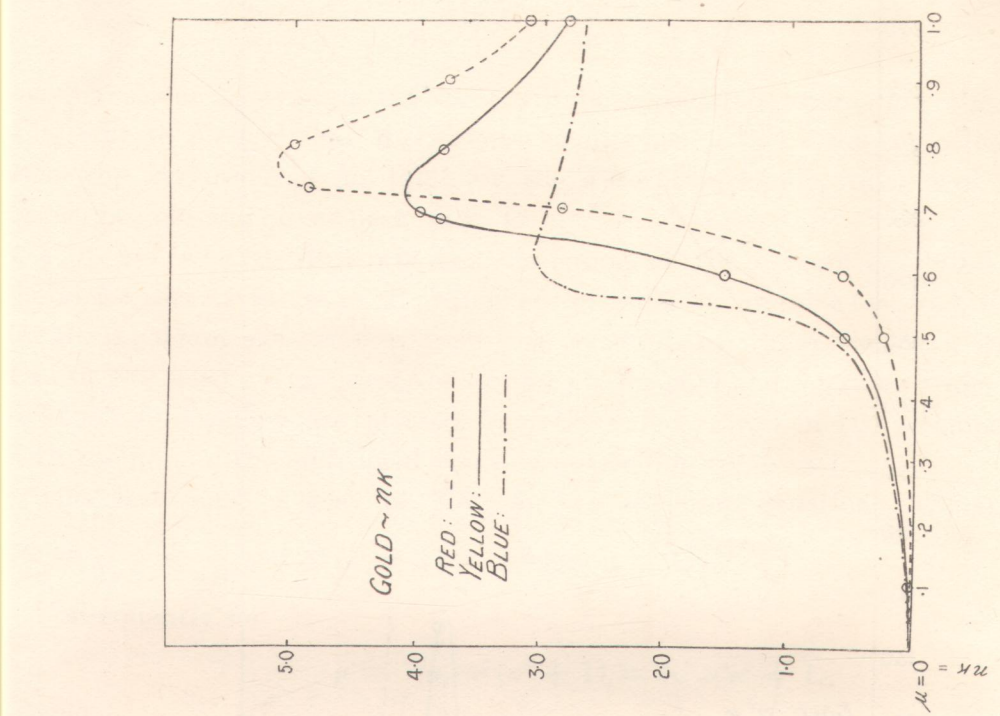
This point is also very near the maximum of $n^2\kappa$, owing to the smallness of β in comparison with α, and is also, in the graph of $n\kappa$, not far from the maximum, and in the graph of M_0 not far from the minimum. It will be shown that for each of these reasons there is in general an absorption band in the colour whose $\alpha = 1/\mu$.

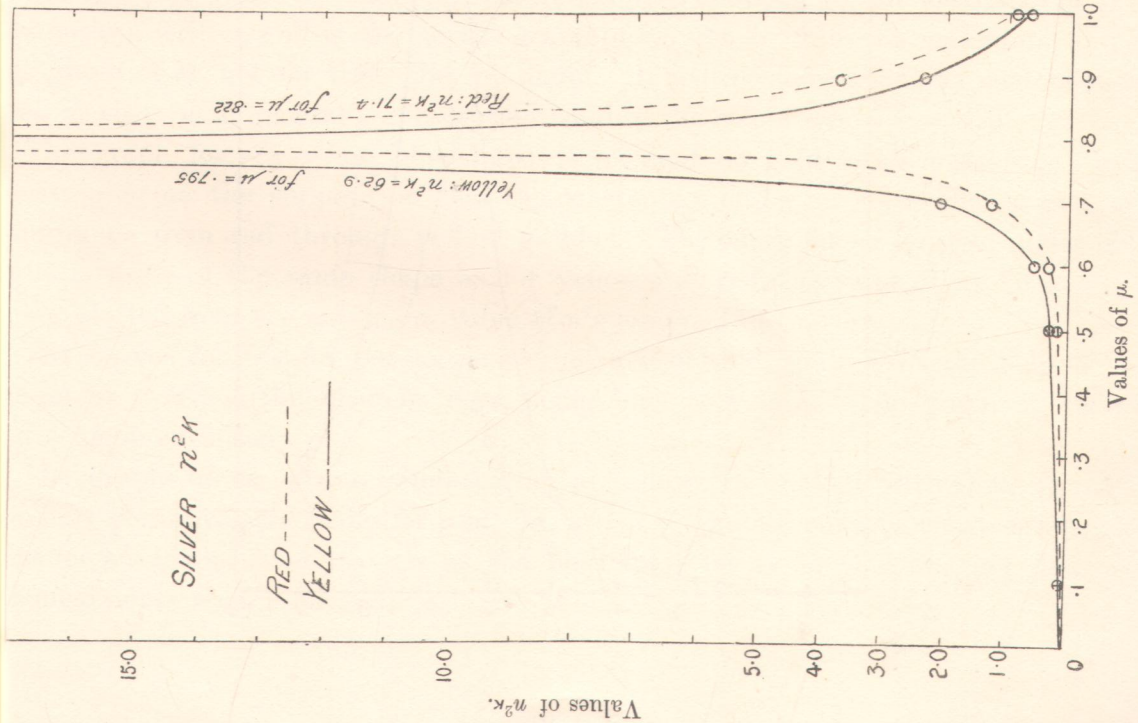
The graph for $n^2\kappa$ when blue light is incident on gold is surmised; *i.e.*, it is constructed on the supposition that the constants n and κ for gold, when $\mu = 1$, are continuous from red through yellow to blue. The curve for $n\kappa$ for gold under blue light is made of the same shape as for yellow and red, the value of $n\kappa$ for $\mu = \alpha^{-1}$ being plotted from the maximum value of $n^2\kappa$ assumed in that graph.

The curves for $n^2\kappa$ for potassium-sodium are plotted, again with the help of the points for $\mu = 1/\alpha$, the incident light being blue or yellow. The graph of $n^2\kappa$ for red is again surmised.

The graphs of $n\kappa$ for potassium-sodium are shown by analogy with those for gold, the only points plotted being for $\mu = 1/\alpha$, $\mu = 1$. The red curve is constructed from that for $n^2\kappa$ in the same manner as the blue curve for $n\kappa$ for gold was got from the assumed curve for $n^2\kappa$ for gold.


24·0
23·0
22·0
21·0
20·0
19·0
18·0
17·0
16·0
15·0
14·0
13·0
12·0
11·0
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
GOLD $n^2\kappa$
RED
YELLOW
BLUE
$\mu = 0$
$n^2\kappa = 0$
·1
·2
·3
·4
·5
·6
·7
·8
·9
1·0


GOLD ~ $n\kappa$
RED: - - - - - -
YELLOW: ———
BLUE: —·—·—·—
$n\kappa = 0$
$\mu = 0$
5·0
4·0
3·0
2·0
1·0
·1
·2
·3
·4
·5
·6
·7
·8
·9
1·0


SILVER $n^2\kappa$
RED - - - - - -
YELLOW ———
Red: $n^2\kappa = 71{\cdot}4$ for $\mu = {\cdot}822$
Yellow: $n^2\kappa = 62{\cdot}9$ for $\mu = {\cdot}795$
Values of $n^2\kappa$.
Values of μ.
15·0
10·0
5·0
4·0
3·0
2·0
1·0
0
·1
·2
·3
·4
·5
·6
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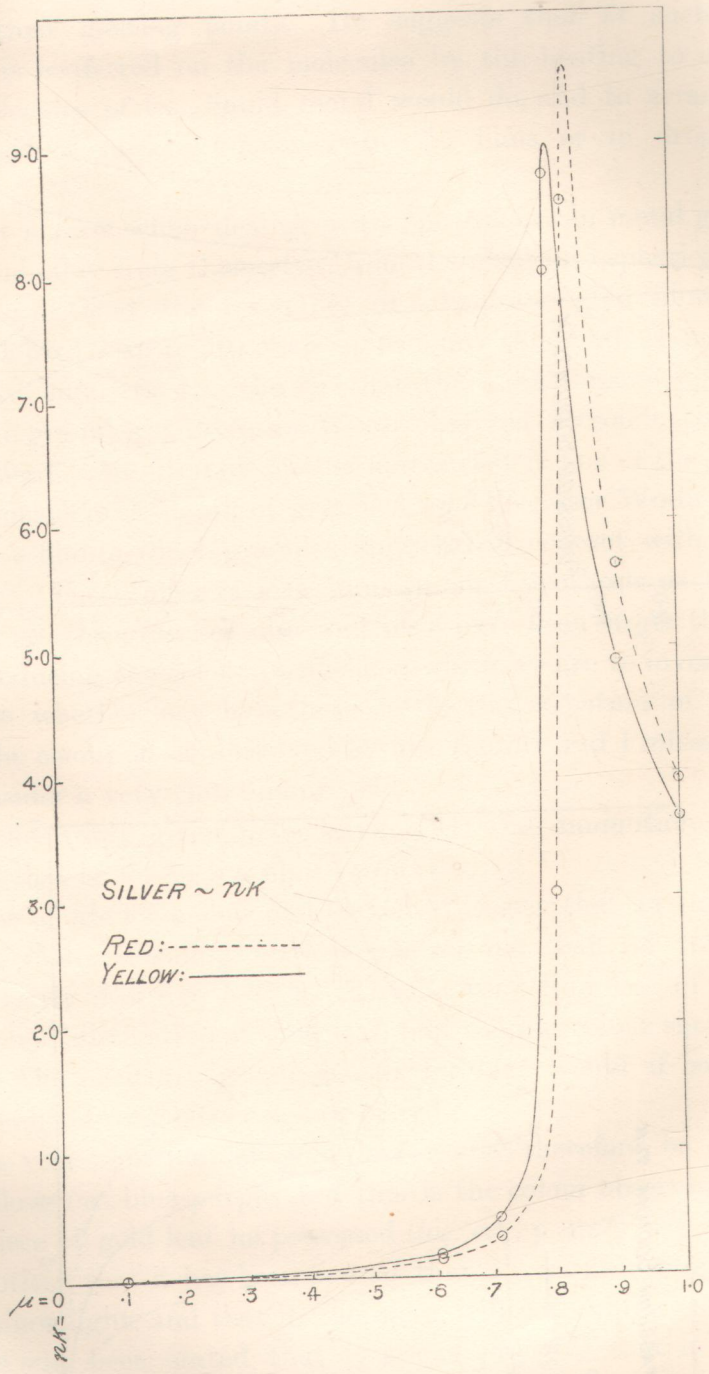
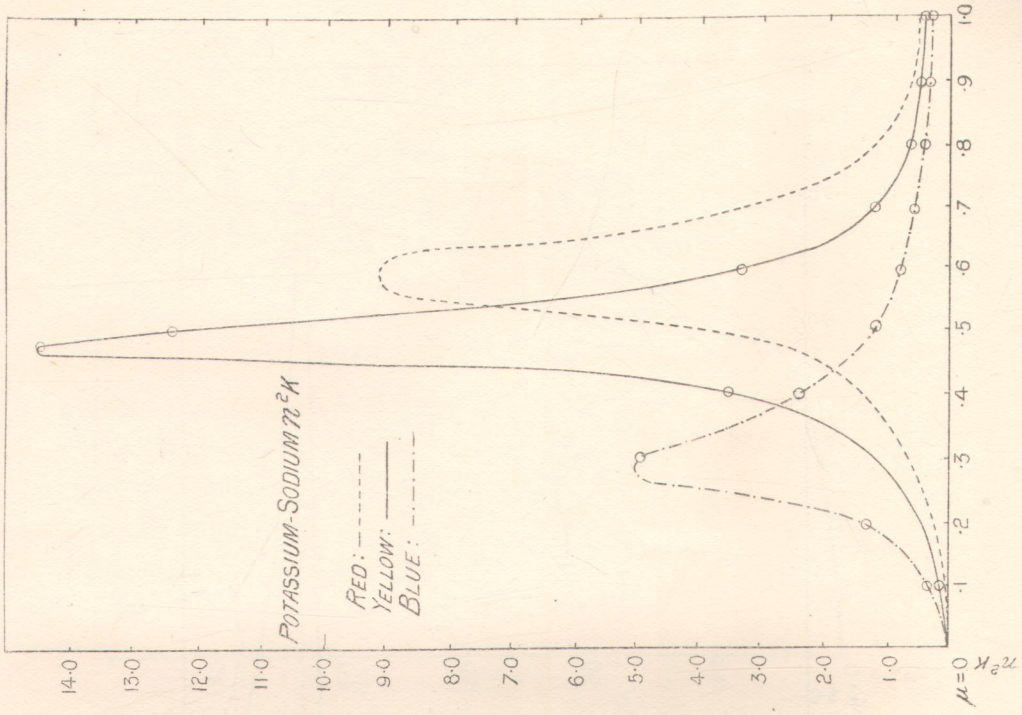
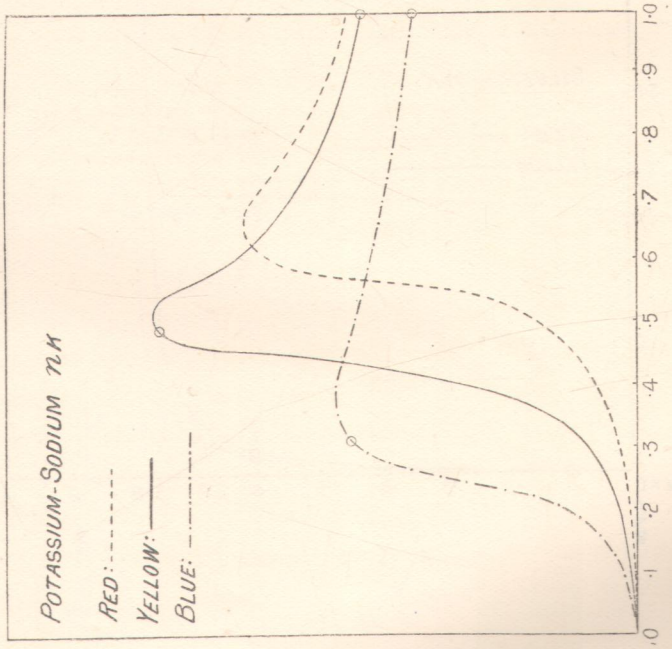
1·0


9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
SILVER ~ nk
RED:----------
YELLOW:——————
μ = 0
nk =
·1
·2
·3
·4
·5
·6
·7
·8
·9
1·0


POTASSIUM-SODIUM n²K
RED: - - - - - - -
YELLOW: ———
BLUE: -·-·-·-
14·0
13·0
12·0
11·0
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
·1
·2
·3
·4
·5
·6
·7
·8
·9
1·0
μ=0 H₂L


POTASSIUM-SODIUM nK
RED: - - - - - - -
YELLOW: ———
BLUE: -·-·-·-
·1
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·7
·8
·9
1·0

§ 11. In a paper on "The Effects of Heat and of Solvents on Thin Films of Metal," 'Roy. Soc. Proc.,' vol. 72, 1903, p. 226, Mr. G. T. Beilby gives an account of some experiments on the behaviour of gold and silver films when heated to temperatures far below their melting points. He suggests that at such temperatures sufficient freedom is conferred on the molecules by the heating to enable them to have as the molecules of the liquid metal would do, and to arrange themselves under the influence of surface tension either in films or in drop-like granular forms.

We have already shown, when dealing with the colours in metal glasses, how the small particles of metal excrete themselves from the glass into spherical forms.

Mr. Beilby records that the resistance of silver and gold films increased, on annealing, from a few (0·2 up to 50) ohms up to many thousands of megohms. This, of course, strongly supports the theory that the metal breaks up under surface tension into minute granules. Professor Wood observed no conductivity in his films as originally deposited. Mr. Beilby further states that in one of the gold films there appeared to be a considerable depth of granules, and Professor Wood records absence of conductivity in a film in which granules appeared in contact with and piled upon top of one another. These observations support our hypothesis as to the structure of the films, although the granules observed may have been larger than those which are effective in producing the colour phenomena which we are to investigate.

Let us now see whether our hypothesis as to the structure of the films is in agreement with the colour effects observed by Mr. Beilby and Professor Wood.

First, then, consider a very thin film of gold.

According to the result given in equation (24) the diminution in intensity of light of wave-length λ is, for such a film, $4\pi d/\lambda \,.\, n^2\kappa$.

From the graphs of $n^2\kappa$ for yellow and for red, it is seen that for the solid metal for which $\mu = 1$, *i.e.*, before annealing, $n^2\kappa/\lambda$ is less for red than for yellow, and this is true from $\mu = 1$ nearly down to $\mu = \cdot 9$. Thus, a very thin leaf of gold should *not* show the green colour distinctive of gold leaf, but the red colour should predominate over the yellow. The arbitrary graph for $n^2\kappa$ for blue would, if correct, show that blue should predominate over either yellow or red.

The colour of a very thin film of gold leaf would, therefore, be chiefly blue, less red, and least yellow, *i.e.*, blue-purple, and this is the colour observed by Mr. Beilby in the thinnest piece of gold leaf he possessed (*loc. cit.*, p. 227).

It should be noticed that it has been *proved* that a very thin film will let through more red than yellow light, and that it, therefore, will not exhibit the green colour of gold leaf. It has only been stated that it seems *probable* that it will let through more blue than either.

We now suppose that when the film is being annealed, surface tension acts and causes the gold to form into spherical drops, many to a wave-length, but of quite varying sizes. Thus μ, the volume of metal in a unit volume of the film,

continuously diminishes from unity downwards so long as the metal is kept at a temperature of about 400°.

Just before μ has reached ·9 the yellow begins to get through better than the red, but the absorption of both increases rapidly. The value of $n^2\kappa$ for red becomes equal to 24 when $\mu = ·734$ about. It almost immediately starts to diminish, being only 15·88 when $\mu = ·7$. There is thus a strong and quite narrow absorption band in the red for $\mu = ·734$.

Similarly, $n^2\kappa$, when the incident light is yellow, rises to a high value near $\mu = ·686$, and when μ has that value, $n^2\kappa = 15$ nearly.

Between $\mu = ·7$ and $\mu = ·734$, red and yellow are absorbed to the same large extent. It seems probable that blue will not be absorbed so greatly for this value of μ. The film should therefore probably be blue. Mr. BEILBY finds (*loc. cit.*, p. 228) that a gold film turns blue or purple (absorption chiefly of yellow) in the earlier stage of annealing, though, presumably, the films for which this effect was observed fall into our class of thick films. The turning blue will therefore be again referred to when we come to consider thick films of gold.

When $\mu = ·6$, the red light is much less diminished in intensity than the yellow, and probably less than the blue. The film is therefore pink, and remains pink down to the dimensions of coloured glass for which μ is of the order of 10^{-5}. The thin film observed by Mr. BEILBY was rose pink after annealing (p. 227).

The high transparency observed by FARADAY and by Mr. BEILBY corresponds to the very small values of $n^2\kappa$ for values of $\mu < ·5$.

Consider next a thick film of gold.

The absorption being now, according to the result given on p. 409, dependent principally upon the value of $n\kappa/\lambda$, we see from the table for $n\kappa$ or from the graph that, for the solid metal, yellow light is less absorbed than red. The colour of thick gold leaf is, in fact, olive-green by transmitted light. As μ diminishes the absorption of both yellow and red increases, the latter more rapidly. Now when $\mu = ·734$, there is a great absorption of red, according to the values of $n\kappa$, which is intensified, since M_0 is for this value of n reduced to ·177. The colour should then be more yellow than red, and probably more blue than either. When μ is $< ·7$, the colour is much more red than yellow. If our assumed curve for $n\kappa$ for blue is correct, the colour of the film should be blue between $\mu = ·85$ and ·7, purple at ·7, and principally red from $\mu = ·65$ through all the range of values of μ from gold glass down to $\mu = 0$. (If our curve for blue is correct, the figure shows that the film is red when the blue curve crosses the yellow.)

According to Mr. BEILBY, a gold film, originally green, turned blue-purple after annealing. Gold leaf turned, by annealing, pink with brown-green patches, the latter, presumably, corresponding to large and the former to small values of μ.

The rise in the absorption as μ begins to diminish from unity was noticed by Mr. BEILBY (*loc. cit.*, p. 232).

It has therefore been shown that all the observed colour changes in gold films are in accordance with the theory and numerical results set forth in this paper.

The points corresponding to $\mu\alpha = 1$, referred to on p. 410, which were plotted in for red and yellow, were

$$n\kappa = 4{\cdot}89 \text{ for } \mu = {\cdot}734 \text{ for red,}$$
$$n\kappa = 3{\cdot}80 \text{ ,, } \mu = {\cdot}685 \text{ ,, yellow.}$$

Let us now consider silver films.

The results for *thin* films are not of much interest, as probably none of the films observed came into this class. We may, however, notice that, according to the graphs of $n^2\kappa$, the thin film should start by being more yellow than red. There is an absorption band in the red about $\mu = {\cdot}822$, for which value of μ, $n^2\kappa = 71{\cdot}4$ for red. There is great absorption in the yellow for $\mu = {\cdot}795$ when $n^2\kappa = 62{\cdot}9$. The nearness of these values of μ for the maxima of the absorption of yellow and red suggests that thin films of silver should be blue or else very opaque when μ is about ·8. The thin film should turn more red than yellow for μ slightly $> {\cdot}8$ and remain red down to small values of μ, at least as far as $\mu = {\cdot}1$.

Passing to thick films, for which the absorption is measured by $n\kappa/\lambda$, we observe from the graphs that as μ diminishes from unity the absorption at first increases rapidly. This may be correlated with the increased conductivity manifested by a silver film in the early stages of annealing. Shortly before $\mu = {\cdot}8$ the film becomes more red than yellow, and although by the time $\mu = {\cdot}6$ the absorption has already become extremely small, the film remains more red than yellow until μ vanishes.

Putting $\mu = 1/\alpha$, we find the additional points on the graphs of $n\kappa$

$$\text{for red . . . . } n\kappa = 8{\cdot}51 \text{ when } \mu = {\cdot}822,$$
$$\text{,, yellow . . . } n\kappa = 7{\cdot}99 \text{ ,, } \mu = {\cdot}795.$$

The red colour of silver films for low values of μ is observed in those obtained by depositing silver on glass in the manner described by Professor Wood ('Phil. Mag.,' August 1903). It is also often seen in fogged photographic plates.

§ 12. We proceed to consider the potassium and sodium films discussed by Professor R. W. Wood, in the 'Phil. Mag.,' 1902, p. 396, *et seq.* Owing, however, to the inavailability of the numerical values of the constants for potassium or sodium for more than one colour when $\mu = 1$, the numbers used are those given by Drude (*loc. cit.*) for "potassium-sodium," for blue and yellow light. Consequently the same degree of numerical accuracy as for gold and silver has not been aimed at.

The yellow and blue curves for $n^2\kappa$ are plotted from the numbers tabulated in Table IV., p. 406.

The graph of $n\kappa$ has been constructed to pass through the untabulated points

$$\text{Yellow . . . } n\kappa = 3{\cdot}811 \text{ for } \mu = 1/\alpha = {\cdot}484, \; n\kappa = 2{\cdot}18 \text{ for } \mu = 1.$$
$$\text{Blue . . . . } n\kappa = 2{\cdot}225 \text{ ,, } \mu = 1/\alpha = {\cdot}306, \; n\kappa = 1{\cdot}78 \text{ ,, } \mu = 1.$$

The films made by Professor Wood were obtained by the condensation of the vapour of the evaporated metal on the insides of exhausted glass bulbs. We should therefore expect the film in its original form to be in drops, which, in accordance with Part I., § 3, when very small, approximate to the spherical form.

The absence of conductivity in these films supports this view of their structure. The effect of heating up to and beyond the melting point would be to fuse these drops into continuous metal, and although surface tension tends to a re-formation into spheres, it is probable that μ will generally be considerably increased by the fusion.

It appears, from our graphs of $n^2\kappa$ and $n\kappa$, that thin or thick "potassium-sodium" films should transmit more blue than yellow light, provided that $\mu \geqq \cdot 4$, there being a very strong absorption of yellow for $\mu = \cdot 49$ (about) in both cases. It is interesting to note that Professor Wood always refers to the yellow absorption bands as particularly strong. As μ increases, the absorption of yellow relative to blue increases in both thick and thin films.

If now we introduce our hypothetical curves for $n^2\kappa$ and for $n\kappa$ for red light, we find that for $\mu \leqq \cdot 4$ the film should be red. Near the greatest absorption of yellow ($\mu = \cdot 49$), red and blue should be equally absorbed and the film be purple. As μ increases further, red should be most absorbed, and blue least, so the film should be blue. Thus, in general, the film should turn from purple to blue when heated, as was the case with most of the films observed. Professor Wood (*loc. cit.*, p. 407) further states that the particles which he observed were distinctly closer in the blue than in the pinkish-purple part, thus again suggesting that a change from purple to blue accompanies an increase in μ.

So far, then, as they go, our results are in good accordance with observation. When, however, numbers can be obtained for n and $n\kappa$ for potassium and for sodium for blue, yellow, and red light, it may be possible to state with more certainty that our explanation of the colours of the films and of the changes in colour due to heating is the true one.

§ 11. By considering the oblique incidence of plane-polarised light on thick films of metal by the method adopted in § 9 in the case of thin films, it can be shown that equation (26) is replaced by :—

(1.) When the incident light is polarised in the plane of incidence

$$|C|^2 = \frac{16\,(u^2 + v^2)}{\{(1+u)^2 + v^2\}^2}\, e^{-4\pi dv/\lambda \,.\, \cos\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27).$$

(2.) When the incident light is polarised perpendicular to the plane of incidence

$$|C|^2 = \frac{16\,(u'^2 + v'^2)}{\{(1+u')^2 + v'^2\}^2}\, e^{-4\pi dv/\lambda \,.\, \cos\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28),$$

where u, v and u', v' are certain functions of n, κ, θ such that when the angle of incidence, θ, is zero,

$$u = u' = n \quad \text{and} \quad v = v' = n\kappa.$$

It can further be proved that the variations with μ of the coefficients

$$M_\theta \equiv \frac{16(u^2+v^2)}{\{(1+u)^2+v^2\}^2} \quad \text{and} \quad M'_\theta \equiv \frac{16(u'^2+v'^2)}{\{(1+u')^2+v'^2\}^2}$$

are such that a change in (27) from M_θ to M_θ' would strengthen the absorption bands. The complete analysis is somewhat lengthy; I have therefore refrained from reproducing it here.

This result, however, shows that in general the absorption band should be weaker when the incident light is polarised in the plane of incidence than when it is polarised perpendicular to that plane. And this effect Professor Wood observed in almost every film.

PART III.

§ 14. Metallic media composed of small spheres of metal, many to a wave-length, have many interesting properties in addition to those already referred to. The very vivid colour effects which are exhibited according to the graphs given above for $n\kappa$ for gold, silver and "potassium-sodium" when light traverses such media, in consequence of the different absorptions of different colours, suggest enquiry whether metals in bulk have ever been obtained giving brilliant colours by transmitted and reflected light, such metals being ordinary metals with μ less than unity. For instance, have any of the metals we have discussed been obtained in states in which the specific gravity was not the normal value for that metal and in which the colour changed with the specific gravity?

I hope in the near future to examine Carey Lea's work in detail with a view to finding out whether his allotropic silver is a medium of the type we have considered—silver with μ less than unity. But the first glance at his papers ('American Journal of Science,' 1889) shows the following remarkable correspondence between the properties he observed and the properties which should, according to our calculations for yellow and red light, be possessed by silver with $\mu < 1$:—

(i.) Carey Lea's silvers were obtained from solution; and we have shown that gold, and therefore, presumably, silver, crystallises out of solutions into particles which are spherical if they are very small. Our silver ($\mu < 1$) is composed of minute spheres.

(ii.) Carey Lea's silver can be changed by pressure or heating into normal silver. We should expect μ to be increased by pressure.

(iii.) The specific gravities of the two principal forms of allotropic silver were appreciably less than that of normal silver.

(iv.) From our graph of $n\kappa$ for silver we see that red and yellow light are about equally, and very powerfully, absorbed when $\mu = \cdot 81$. The ratio of the

specific gravities of CAREY LEA's gold-coloured silver, C, and normal silver is given by him to be 8·51/10·62 = ·81. This strongly supports the theory that allotropic silver is of the nature of the media we have discussed.

(v.) CAREY LEA's silvers were very brittle, but could be toughened by heating. Further, his gold-coloured silver could be transformed into normal silver by shaking; and this transformation could be greatly impeded by packing the gold-coloured silver in cotton wool. These properties suggest a discontinuous structure for allotropic silver.

(vi.) If we might assume an absorption graph of $n\kappa$ for blue light, the fact that if light is obliquely reflected from a film of "B" silver, then the yellow light is polarised in the plane of incidence and the blue perpendicular to that plane can, I think, be explained by our theory: but the proof is not yet complete.

(vii.) The red colour exhibited by all the more dilute forms of the allotropic silver is in accordance with the fact, exhibited by the graph, that $n\kappa$ is smaller for red than for yellow light for small values of μ.

[APPENDIX, *added 28th July*, 1904.—Using the values of the refractive index and absorption coefficient of gold for red (C), green (E), and blue light, as given by RUBENS ('Wied. Ann.,' 1889), the following values of the quantity β/λ, which governs the absorption of the gold glass, have been calculated:—

		Red (C).	Red (·630).	Yellow (D).	Green (E).	Blue $\frac{1}{2}$(F+G).
Gold	n. . . .	·38	·31	·37	·53	·79
	$n\kappa$ . . .	2·91	3·15	2·82	1·86	1·52
	β . . .	·48	·25	·59	1·07	·46
	β/λ . . .	·73	·40	·99	2·03	1·01

The refractive index of the glass has been taken to be 1·56, as in Table II., from which the values of β for red and for yellow have been copied.

The colours, in the order of the degree in which they are transmitted by gold glass, therefore are

Red, Yellow, Blue, Green.

The corresponding order for silver as obtained by calculation is

Yellow, Red, Green, Blue.

The orders accord with observations on gold-ruby glasses and silver glasses respectively.

It will be seen that large particles of gold (diameter $> 0{\cdot}1\ \mu$) in a gold glass would, by reflecting out the red and yellow light, give the glass a blue colour by transmitted light, and a brown turbidity by reflected light—as in glasses D of Table I.]