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Colours in Metal Glasses, in Metallic Films, and in Metallic Solutions. II

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VII. *Colours in Metal Glasses, in Metallic Films, and in Metallic Solutions.—II.*

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Contents.

1. *Introduction.*

This paper is an extension of a previous memoir on the "Colours in Metal Glasses and in Metallic Films"[*]; it is concerned with the application of mathematical analysis, akin to that already there developed, to the explanation and coordination of the colours which certain metals are, under a great variety of circumstances, capable of causing.

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[*] 'Phil. Trans.,' A, 1904, vol. 203, pp. 385–420.

From observations on gold and copper ruby glasses, it has been shown* that the first stage in the formation of a crystal of those metals is the small sphere; and from observations on the growth of sulphur crystals in CS_2, VOGELSANG† arrived at the conclusion that the small sphere is always the first stage in the formation of a crystal. He remarked, however, that it is by no means necessary that each of the small spheres, formed as crystallisation commences, should give rise to a separate crystal: the small spheres tend to coagulate, forming first rows and then groups of other and more complicated shapes, until the crystal is ultimately formed. To the intermediate bodies he gives the name of *crystallites*.

That the spherical form of the nascent crystal is governed by surface tension, was suggested in the former paper.‡ If this suggestion is correct, we should expect that when the conditions are not the same in all directions, the spherical form of the nascent crystal will be replaced by an ellipsoidal form. In particular, when a very thin film of amorphous metal is heated until the molecules are sufficiently free to allow crystallisation to commence, the nascent crystals may be expected to be spheroids of the planetary type, having their axes normal to the film. Mr. G. T. BEILBY§ has observed such spheroids in thin films of gold and silver.

Now it will appear below that metals are not only dichroic, exhibiting one colour by reflected light and, in thin films, another by transmitted light; but that one and the same metal may, as its physical condition is altered, show a great variety of colours by reflected light, and a corresponding other series of tints by transmitted light. The ultimate cause of all these colours is to be found in the structure of the molecule itself. Juxtaposition, however, causes one molecule to affect the vibrations of another. Thus consider a substance composed of molecules of a given metal separated from each other by the æther or by any other non-absorbing medium:‖ the "effective free period" of the molecule of such a substance is dependent on the geometrical arrangement and density of distribution of the molecules in question. The optical properties of the substance will therefore depend on its microstructure. The object of this paper is to obtain information concerning the ultramicroscopic structure of various metal glasses, colloidal solutions, and metallic films, by calculating optical properties corresponding to certain assumed microstructures, and by comparing the calculated properties with those observed.

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* *Loc. cit.* (pp. 388–392). When writing the former paper here cited I was unaware of VOGELSANG'S work.

† H. VOGELSANG, "Sur les Cristallites," 'Archives Néerlandaises,' V. (1870), p. 156; VI. (1871), p. 223; VII. (1872), pp. 38–385.

‡ *Loc. cit.*, p. 392. The further suggestion there made that in the colourless gold glass there are the molecules of gold present is, as will appear below, p. 251, erroneous. It is almost certain that in the colourless glass a gold salt is in solution, so that the heating has first to reduce the gold and then to allow the isolated molecules to run together into spheres.

§ 'Hurter Memorial Lecture,' Glasgow, 1903, p. 46.

‖ As, for example, glass in a metal glass, or water in a colloidal solution.

The microstructures to be assumed are suggested by the preceding remarks on crystallisation. Calculations will be made for three types of microstructure, namely, (1) amorphous—that in which the metal molecules are distributed at random; (2) granular—that in which the metal molecules are arranged in spherical groups; (3) spicular*—that in which these small spheres are replaced by oblate spheroids. It will subsequently appear that when the surrounding non-absorbing medium is of refractive index unity, an amorphous and a granular microstructure produce the same colours.

In order to calculate the optical constants—the refractive index and the coefficient of absorption—which correspond to any given microstructure, it is necessary to know the values of the constants for some standard amorphous state of the metal. Now BEILBY† has shown that the process of polishing a metal surface causes the surface layer to "flow" as a liquid, and thus the polished surface is that of the metal in the amorphous state. It follows that the optical constants which we are to use as data for our calculations should, so far as possible, be those which have been determined by means of reflection from the polished surface of the metal in its normal state according to DRUDE's‡ method, rather than those obtained by means of the light transmitted through thin prisms of the metal, after the method adopted by KUNDT.

2. *Expressions for Optical Constants of Media containing Metal in Amorphous or Granular Forms.*

The optical properties of a homogeneous isotropic medium are determined when the values of the refractive index n and the absorption coefficient κ, which correspond to light of every frequency, are known. We proceed to obtain the values of n and $n\kappa$ for a substance composed of molecules of metal embedded in an isotropic non-absorbing medium, the microstructure being amorphous.

Consider then a medium consisting of one substance A, in solution in another C, so that the molecules of each substance are distributed at random. Let the number of molecules present per unit volume in the standard amorphous forms of A and C be respectively $\mathfrak{N}_A$ and $\mathfrak{N}_C$, and let the number of molecules present per unit volume of the composite medium be $\mu_A\mathfrak{N}_A$ and $\mu_C\mathfrak{N}_C$ respectively. We shall assume μ_A and μ_C to be constant throughout the medium; or, more precisely, we assume that a length r_0, very small compared with a wave-length of light, can be found such that, for all values of r greater than r_0, the number of molecules of A contained by a spherical surface situated wholly within the medium having a radius r and its centre being

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* The calculations for a spicular microstructure are reserved for subsequent publication, see note p. 241.

† *Loc. cit.*, Lord RAYLEIGH (Royal Institution Lecture on Polish, March, 1901) also holds the view that the process of polishing is a molecular one.

‡ 'Ann. der Phys.,' XXXIX. (1889).

situated at any point, is independent of the position of that point; thus $\frac{4}{3}\pi\mu_A\mathfrak{N}_A r^3$ depends only on r: and similarly for C.

Suppose that when electromagnetic waves traverse this medium, the moments of the average molecule of A and C in the vicinity of the point (x, y, z) are

$$\mathbf{f}_A(t) \equiv (f_{A_1}, f_{A_2}, f_{A_3}) \quad \text{and} \quad \mathbf{f}_C(t) \equiv (f_{C_1}, f_{C_2}, f_{C_3}).$$

Then $\mathbf{f}_A$ and $\mathbf{f}_C$ are both proportional to $\mathbf{E}'$, the electric force exciting the average molecule*; thus

$$\mathbf{f}_A = \theta_A\mathbf{E}', \quad \mathbf{f}_C = \theta_C\mathbf{E}'.$$

The polarisation $\mathbf{f}'(t)$ of the compound medium is given by

$$\mathbf{f}'(t) = \mu_A\mathfrak{N}_A\mathbf{f}_A(t) + \mu_C\mathfrak{N}_C\mathbf{f}_C(t).$$

Writing now $\mathbf{E}$ for $\mathbf{E}_0$ in the general equation†

$$\mathbf{E}' = \mathbf{E}_0 + \tfrac{4}{3}\pi\mathbf{f}',$$

we obtain

$$\mathbf{E}' = \mathbf{E} + \tfrac{4}{3}\pi(\mu_A\mathfrak{N}_A\theta_A + \mu_C\mathfrak{N}_C\theta_C)\mathbf{E}',$$

so that

$$\mathbf{f}'(t) = \frac{\mu_A\mathfrak{N}_A\theta_A + \mu_C\mathfrak{N}_C\theta_C}{1 - \frac{4}{3}\pi(\mu_A\mathfrak{N}_A\theta_A + \mu_C\mathfrak{N}_C\theta_C)}\mathbf{E}.$$

But MAXWELL's equations for the composite medium are

$$4\pi\frac{d\mathbf{f}'(t)}{dt} + \frac{d\mathbf{E}}{dt} = c \operatorname{curl} \mathbf{H}, \quad \frac{d\mathbf{H}}{dt} = -c \operatorname{curl} \mathbf{E},$$

where c is the velocity of light *in vacuo*. These may be written

$$\mathrm{N}'^2\frac{d\mathbf{E}}{dt} = c \operatorname{curl} \mathbf{H}, \quad \frac{d\mathbf{H}}{dt} = -c \operatorname{curl} \mathbf{E},$$

when we put

$$\frac{\mathrm{N}'^2 - 1}{\mathrm{N}'^2 + 2} = \tfrac{4}{3}\pi(\mu_A\mathfrak{N}_A\theta_A + \mu_C\mathfrak{N}_C\theta_C) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

If now we write

$$\mathrm{N}' \equiv n'(1 - \iota\kappa') \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

then n' and κ' are the refractive index and absorption coefficient of the composite medium.

But the same analysis will show that if $\mathrm{N}_A \equiv n_A(1 - \iota\kappa_A)$ and $\mathrm{N}_C \equiv n_C(1 - \iota\kappa_C)$, where n_A, κ_A and n_C, κ_C are the optical constants of A and of C, then

$$\frac{\mathrm{N}_A{}^2 - 1}{\mathrm{N}_A{}^2 + 2} = \tfrac{4}{3}\pi\mathfrak{N}_A\theta_A \quad \text{and} \quad \frac{\mathrm{N}_C{}^2 - 1}{\mathrm{N}_C{}^2 + 2} = \tfrac{4}{3}\pi\mathfrak{N}_C\theta_C.$$

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* *Cf.* 'Phil. Trans.,' A, vol. 203, pp. 392, 393.

† *Loc. cit.*, equation (9), p. 393.

Substituting these expressions in equation (1) we obtain

$$\frac{N'^2-1}{N'^2+2} = \mu_A \frac{N_A^2-1}{N_A^2+2} + \mu_C \frac{N_C^2-1}{N_C^2+2}.$$

If, now, we suppose that C is a transparent isotropic substance of refractive index ν, and that A is a metal, we have, by omitting the suffix A and putting $\mu_C = 1-\mu$,

$$\frac{N'^2-1}{N'^2+2} = \mu \frac{N^2-1}{N^2+2} + (1-\mu)\frac{\nu^2-1}{\nu^2+2};$$

or,

$$\frac{N'^2-\nu^2}{N'^2+2} = \mu \frac{N^2-\nu^2}{N^2+2} \quad \ldots \ldots \ldots \quad (3).$$

When μ is very small this equation becomes

$$N'^2-\nu^2 = (\nu^2+2)\mu\frac{N^2-\nu^2}{N^2+2}. \quad \ldots \ldots \ldots \quad (4).$$

These equations give the optical constants of the metalliferous medium in the amorphous state. When the microstructure is granular, these equations (3) and (4) are, as has been already shown,* replaced by

$$\frac{N'^2-\nu^2}{N'^2+2\nu^2} = \mu \frac{N^2-\nu^2}{N^2+2\nu^2} \quad \ldots \ldots \ldots \quad (5),$$

so that when μ is small,

$$N'^2-\nu^2 = 3\nu^2\mu \frac{N^2-\nu^2}{N^2+2\nu^2} \quad \ldots \ldots \ldots \quad (6).$$

Comparison of equations (3) and (5) shows that the optical properties of a metalliferous medium, containing a given volume proportion μ of the metal, vary according as the metal is in small spheres or in a state of molecular subdivision, except when $\mu = 1$. Thus when metal is in solution in water or glass the colour of the compound medium will change as crystallisation commences. When, however, $\nu = 1$, the equations (3) and (5) both reduce to

$$\frac{N'^2-1}{N'^2+2} = \mu \frac{N^2-1}{N^2+2} \quad \ldots \ldots \ldots \quad (7).$$

It follows that the optical properties of a metal in a state in which its specific

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* *Loc. cit.*, equations (11) and (12), p. 394. The mathematical treatment of the optical properties of media containing minute metallic ellipsoids, instead of the spheres which give the granular microstructure, is under consideration, but, with the exception of the case wherein the volume proportion, μ, of metal is small, it is not yet complete.

[*Note added* 1st *August*, 1905.—The investigation of the general case (any value of μ) has now been completed. The results for the case when μ is small, which, when this memoir was communicated to the Royal Society, were given in § 12, have therefore been reserved for subsequent publication in a more complete form.]

gravity has any known value, are unaltered by a change in the microstructure from amorphous to granular.* Or, again, Professor R. W. WOOD'S clouds of sodium vapour,† for which $\nu = 1$ nearly, do not change colour as condensation commences.

3. *Formulæ Applicable only when the Volume Proportion of Metal is Small.*

The volume proportion of metal present in all the coloured glasses and colloidal solutions which we shall discuss below is small. We proceed to obtain, from equations (4) and (6) above, expressions for the optical constants of media, such as glass or water, holding in suspension metal in the amorphous and granular states.

Let $\mathrm{N}'' \equiv n''(1-\iota\kappa'')$ denote the optical constants of the compound medium when the metal is in the amorphous state—in true solution. Then, replacing N′ by N″ in equation (4), we have

$$\{n''(1-\iota\kappa')\}^2-\nu^2 = \mathrm{N}''-\nu^2 = (2+\nu^2)\,\mu\,\frac{\mathrm{N}^2-\nu^2}{\mathrm{N}^2+2} = (2+\nu^2)\,\mu\,(\alpha'-2\iota\beta'),\text{ say.}$$

Equating real and imaginary parts, we find that

$$\left.\begin{aligned} \alpha' &= \frac{n''^2(1-\kappa''^2)-\nu^2}{(2+\nu^2)\,\mu} = \frac{\{n^2(\kappa^2+1)\}^2+n^2(\kappa^2-1)(\nu^2-2)-2\nu^2}{\{n^2(\kappa^2-1)-2\}^2+4n^4\kappa^2} \\ \beta' &= \frac{n''^2\kappa''}{(2+\nu^2)\,\mu} \qquad\quad\;\; = \frac{n^2\kappa(\nu^2+2)}{\{n^2(\kappa^2-1)-2\}^2+4n^4\kappa^2} \end{aligned}\right\} \quad . \; . \; . \quad (8).$$

From (8) we have

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

so that, neglecting μ^2, we obtain

$$n''\kappa'' = (2+\nu^2)/\nu\,.\,\mu\beta', \quad n'' = \nu\,\{1+(2+\nu^2)/2\nu^2\,.\,\mu\alpha'\} \quad . \; . \; . \; . \; . \quad (9).$$

The corresponding values of $\mathrm{N}' \equiv n'(1-\iota\kappa')$, the optical constants when the metal is in the granular state, have already been obtained.‡ They are reproduced here for convenience of reference: thus

$$n'\kappa' = 3\mu\nu\beta, \quad n' = \nu\,(1+\tfrac{3}{2}\,.\,\mu\alpha) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (10),$$

where

$$\alpha = \frac{\{n^2(\kappa^2+1)\}^2-\{n^2(\kappa^2-1)\}\,\nu^2-2\nu^4}{\{n^2(\kappa^2-1)-2\nu^2\}^2+4n^4\kappa^2}, \quad \beta = \frac{3\nu^2n^2\kappa}{\{n^2(\kappa^2-1)-2\nu^2\}^2+4n^4\kappa^2} \quad . \quad (11).$$

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* For example, the tables given in the previous paper ('Phil. Trans.,' A, 1904, p. 406), and the curves shown (*loc. cit.*, pp. 411–414), as well as the tables and curves given in § 10 of the present communication, represent optical properties of the media as μ diminishes from unity to zero, whether that diminution is associated with the formation of small spheres or whether the metal retains its amorphous state throughout the change in μ.

† Brit. Assoc., Cambridge, 1904.

‡ *Loc. cit.*, § 5, pp. 394, 395.

Thus, when light of wave-length λ traverses a thickness d of a metalliferous medium, the intensity of the light is reduced in the proportion* $e^{-4\pi d\frac{n''\kappa''}{\lambda}}$ or $e^{-4\pi d\frac{n'\kappa'}{\lambda}}$ according as the metal is in true solution or in spherical aggregates.

Suppose now that two kinds of monochromatic light, of wave-lengths λ_1 and λ_2, are, by traversing a distance d in an absorbing medium, reduced in intensity by $e^{-K_1 d}$ and $e^{-K_2 d}$ respectively. Then the absorbing medium reduces the proportion of the intensities of the two kinds of light in the ratio $e^{-(K_1-K_2)d}$, which is a function of d. Thus the tint of a coloured medium, viewed by transmitted light, depends on its thickness.† We shall, however, speak of two absorbing media as possessing the same colour when, whatever be the values of λ_1 and λ_2, the ratio $K_1 : K_2$ is the same for either medium; for, if suitable thicknesses of such media be chosen, the light transmitted by them will be of precisely the same tint.

Since, therefore, it appears from equations (8) and (9) above that the ratio

$$(n''\kappa''/\lambda)_{\lambda=\lambda_1} : (n''\kappa''/\lambda)_{\lambda=\lambda_2}$$

is independent of ν, it follows that a molecularly subdivided metal produces the same coloration (by transmitted light) in all non-dispersive transparent isotropic "solvents," irrespective of their refractive indices.‡ Thus, neglecting the small dispersion, a borax bead and a glass bead, each containing a metal in solution, will be of the same colour; but so soon as crystallisation of the metal begins, so that part of the metal is in small spheres, the beads will cease to be of the same colour, since the ratio

$$(n'\kappa'/\lambda)_{\lambda=\lambda_1} : (n'\kappa'/\lambda)_{\lambda=\lambda_2}$$

is not independent of ν.

4. *Numerical Values of Optical Constants of Metal Glasses, &c.*

Consider any transparent isotropic non-dispersive medium of refractive index ν, containing either molecules or small spheres of a metal, the optical constants of which, for light of wave-length λ, are n and $n\kappa$, the particles of metal being so distributed that there are many of them to a wave-length of light. The "absorptions," $n'\kappa'/\lambda$ and $n''\kappa''/\lambda$, of the compound medium can be easily determined by means of equations (9) and (10), when the values of α, β, α', β', are known for light of wave-length λ. These values can be calculated by means of equations (11)

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* *Cf.* 'Phil. Trans.,' A, 1904, p. 395.

† Thus, for example, a thin sheet of gold ruby glass will appear *pink*, a considerable amount of blue light being transmitted, whereas a thick sheet of the same glass will appear deep *red*, almost like a copper ruby. Again, by increasing the depth of a silver stain on glass, we get all gradations in colour from *canary yellow* through *amber* to *red*.

‡ This, then, must be the colour of the vapour of the metal provided that the molecules are monatomic, or, at least, do not dissociate when the metal is vapourised. We shall term it the "vapour colour."

and (8), when the quantities n and $n\kappa$ have been determined for the light in question by direct experiment on the metal in the standard amorphous state. R. S. MINOR[*] has made such experimental determinations, for various kinds of monochromatic light, from the polished surfaces of silver and copper. His values of n and $n\kappa$ for silver and copper, together with the numerical values of α, β, α', β', and of certain other functions as calculated for various values of ν, are shown in Tables II. and III. The values of n and $n\kappa$, for $\lambda = \cdot 630$ and $\lambda = \cdot 589$ only, have also been determined by DRUDE[†] from the polished surface of gold; but values of n and $n\kappa$ for other values of λ have been obtained by HAGEN and RUBENS[‡] from gold prisms deposited on glass. Since however the state of the metal in the prisms is not known, these latter values cannot be depended upon for our purpose;[§] but as a rough estimate of the values of α, β, α', β', &c., may be formed by their means, the numerical values of these quantities have been calculated; the results are shown, together with all the observed values of n and $n\kappa$, in Table I. The wave-length λ of the light will throughout be measured in thousandths of a millimetre.

All the calculated numbers given in Tables I., II., and III. have been carefully checked with a "Brunsviga" machine. I believe that in no case does an error amounting to 1 per cent. survive in these Tables, which must accordingly supersede those given in the former communication.[‖]

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[*] R. S. MINOR, 'Ann. der Phys.,' vol. X., 1903.

[†] 'P. DRUDE, 'Physik. Zeitschr.,' January, 1900.

[‡] RUBENS, 'Wied. Ann.,' vol. XXXVII., 1889.

[§] It will appear in the sequel that on this account the optical properties of silver glasses and of colloidal solutions of silver are much more accurately represented by our calculations than is the case with gold ruby glasses and colloidal solutions of gold.

[‖] *Loc. cit.*, p. 396.

TABLE I.—Gold.

λ		·6562 (C).	·6300	·5892 (D).	·5269 (E).	·4584 $\left(\frac{F+G}{2}\right)$.
$n\kappa$		2·91*	3·15†	2·82†	1·86*	1·52*
n		·38*	·31†	·37†	·53*	·79*
Glass $\nu = 1\cdot56$ . .	α	2·50	2·27	2·65	− ·83	− ·46
	β	·479	·251	·584	1·068	·552
	$\frac{\alpha^2+4\beta^2}{\lambda^4}$	38·63	34·44	69·57	68·13	32·42
	$\frac{n''\kappa''}{\mu\lambda} = \frac{(\nu^2+2)\beta'}{\nu\lambda}$	·47	·30	·58	4·47	5·63
	$\frac{n'\kappa'}{\mu\lambda} = \frac{3\nu\beta}{\lambda}$	3·42	1·86	4·64	9·49	5·63
Glass $\nu = 1\cdot5$ . . .	$\frac{n'\kappa'}{\mu\lambda} = \frac{3\nu\beta}{\lambda}$	2·33	1·30	3·12	8·97	5·17
Water at 19° C. $\nu = 1\cdot3333$.	$\frac{n'\kappa'}{\mu\lambda} = \frac{3\nu\beta}{\lambda}$	1·293	·766	1·687	9·906	6·034
Vacuum $\nu = 1\cdot0$ (Vapour colour) .	$\frac{n'\kappa'}{\mu\lambda} = \frac{3\beta}{\lambda}$	·338	·214	·417	3·191	4·019

* RUBENS. † DRUDE.

TABLE II.—Silver.

λ		·324	·346	·3611	·395	·450	·500	·550	·589	·630
$n\kappa$		·418	1·098	1·453	1·912	2·386	2·941	3·305	3·638	3·96*
n		·764	·219	·201	·155	·164	·169	·176	·177	·20*
Glass $\nu = 1{\cdot}6$	$\frac{n'\kappa'}{\mu\lambda}$	—	—	3·350	10·779	35·199	2·767	1·121	·601	·409
Glass $\nu = 1{\cdot}56$	α	—	—	−1·502	−3·804	5·664	2·817	2·161	1·855	1·663
	β	—	—	·261	1·152	2·284	·241	·112	·066	·049
	$\alpha^2+4\beta^2$	—	—	2·528	19·780	52·947	8·170	4·722	3·460	2·776
	$\alpha'^2+4\beta'^2$	—	—	432·78	12·323	4·712	2·748	2·216	1·936	1·746
	$\frac{n''\kappa''}{\mu\lambda}$	2·000	9·307	29·438	3·137	·780	·279	·165	·108	·084
	$\frac{n'\kappa'}{\mu\lambda}$	—	—	3·386	13·654	23·755	2·252	·957	·525	·362
Glass $\nu = 1{\cdot}5$	$\frac{n'\kappa'}{\mu\lambda}$	—	—	3·936	17·684	13·391	1·680	·759	·429	·302
Water at 19° C. $\nu = 1{\cdot}3333$	$\frac{n'\kappa'}{\mu\lambda}$	1·304	2·48	6·779	44·764	3·660	·796	·408	·246	·180
Water at 18·7° C. $\nu = 1{\cdot}3331$	α	—	—	—	—	—	—	—	1·571	—
	α'	—	—	—	—	—	—	—	1·333	—
Vapour colour $\nu = 1$	$\frac{n'\kappa'}{\mu\lambda}$	1·428	6·648	21·026	2·241	·557	·200	·115	·077	·060

* Determined by DRUDE—the other values of n and $n\kappa$ were given by MINOR.

Table III.—Copper.

λ . . .		·3467	·395	·450	·500	·535	·550	·575	·5892	·630
$n\kappa$ . . .		1·466	1·763	2·149	2·341	2·276	2·233	2·428	2·630	3·012
n . . .		1·190	1·173	1·131	1·098	1·004	·892	·651	·617	·562
Glass $\nu = 1·56$.	β	·435	·560	·683	·701	·781	·891	1·114	·890	·465
	$\frac{n''\kappa''}{\mu\lambda}$	4·602	3·838	2·677	2·050	2·102	2·208	1·571	1·115	·593
	$\frac{n'\kappa'}{\mu\lambda}$	5·875	6·661	7·107	6·559	6·829	7·579	9·279	7·065	3·453
Glass $\nu = 1·5$ . .	$\frac{n'\kappa'}{\mu\lambda}$	5·797	6·420	6·568	5·897	6·180	6·890	7·634	5·699	2·759
Vacuum $\nu = 1$ (Vapour colour)	$\frac{n'\kappa'}{\mu\lambda}$	1·104	·921	·642	·492	·504	·530	·404	·268	·142

We have now to compare the observed optical properties of various media coloured by gold, silver, and copper with those corresponding properties which, according to the Tables I., II., and III., would be exhibited by the media if the colouring agent were the metal itself, in either the molecularly subdivided or the granular state.

The simplest of the optical properties to observe and to measure is the absorption of light by the medium. Although the absorptions of colloidal solutions of various metals, and even of suspensions of metals in gelatine, have already been measured for several values of the wave-length, λ, of light, no such measurements of the absorption of glasses coloured by metals appear to have yet been made.* Owing, however, to their permanence, such media seemed likely to yield the surest information as to the chemical and physical nature of their colouring agents. The absorptions of a series of glasses coloured with gold, silver, and copper have therefore been measured for me at the National Physical Laboratory, under the supervision of Mr. F. J. Selby. The silver glasses consisted of a silver stain on one side of a colourless glass, the refractive index of which was, for sodium light, equal to $\nu = 1·579$. The gold ruby glasses were flashed on to colourless glass. Both the silver and gold glasses were, to ensure purity of materials, specially prepared at the Whitefriars Glass Works by

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* Except two gold glasses, the absorption curves for which are given by Zsigmondy ('Lieb. Ann.,' vol. 301, pp. 46–48).

Mr. H. J. Powell, to whom I am much indebted for the trouble he has taken on my account. The copper ruby glass used was the ordinary commercial flashed glass.

The absorptions of the various glasses are indicated by the curves marked Au (A) and Au (B) in fig. 2, Ag (B) in fig. 4, and Cu (X) in fig. 7; the ordinates representing the quantity K, where e^{-K} represents the proportion of light of wave-length λ, transmitted by the glass after allowance has been made for reflections, and the abscissæ representing the corresponding values of λ. The scales on which Au (A) and Au (B) are represented are such that K has the same value for both at the D line ($\lambda = \cdot 589$).

The following are the values of K measured at the National Physical Laboratory for the respective glasses:—

Table IV.

Glass . .	Au (A).	Au (B).	Ag (B).		Cu (X).	
λ.	K.	K.	λ.	K.	λ.	K.
·698	—	·080	·696	0	·698	·300
·696	·113	—	·664	0	·664	·378
·664	·154	·140	·606	·063	·634	·563
·606	·324	·406	·562	·112	·606	1·038
·562	·878	1·532	·528	·210	·584	2·496
·553	1·400	2·175	·500	·384	·573	3·309
·544	1·990	3·0065	·478	·809	·567	3·484
·537	2·487	3·7485	·458	1·363	·562	3·484
·528	2·551	4·050	·442	2·514	·544	3·091
·514	2·122	3·224	·436	2·894	·528	2·952
·500	1·495	2·344	·429	3·003	·514	2·985
·478	1·030	1·628	·422	2·225	·500	3·023
·458	·954	1·456	·406	1·520	·478	3·270
·442	·981	—	—	—	·458	3·484
—	—	—	—	—	·441	3·789
—	—	—	—	—	·436	3·807

5. *Diffusions of Gold. The Nature and Form of the Suspended Particles.*

The present section will be concerned with the colours produced by diffused particles of gold. The values of the expression $n'\kappa'/\mu\lambda$ for $\nu = 1\cdot5$, $\nu = 1\cdot3333$, and $\nu = 1$ given in Table I. are plotted in fig. 1. The curves shown in that figure have been drawn to pass through the plotted points, the coordinates of the maximum for each curve being determined by assuming n and $n\kappa$ to vary continuously for values of λ intermediate between the abscissæ of the plotted points on either side of those maxima. According to the remarks in the preceding section, these curves must not be regarded as accurately representing the absorption of gold spheres in glass, of gold spheres in water, and of gold vapour (or gold spheres *in vacuo*) respectively; they should, however, enable us to form a fair estimate of the absorption in question.*

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* See footnote §, p. 244.

Fig. 1. Gold—calculated values of $\frac{n'\kappa'}{\lambda}$.

(1) Spheres (or molecules) *in vacuo*, $\nu = 1 \cdot 0$: ....
(2) Spheres in water at 19° C., $\nu = 1 \cdot 3333$: ————
(3) Spheres in glass, $\nu = 1 \cdot 5$: - - - - - - -
Calculated values are shown thus: ⊙.

Fig. 2. Gold.

(1) K, observed for gold ruby glass Au(A): — . — . —
(2) K, observed for gold ruby glass Au(B): ————
Observed values: ⊙.
(3) $\frac{n'\kappa'}{\lambda}$, calculated for gold spheres in glass, $\nu = 1 \cdot 5$: - - - - - - -
Calculated values: ×.

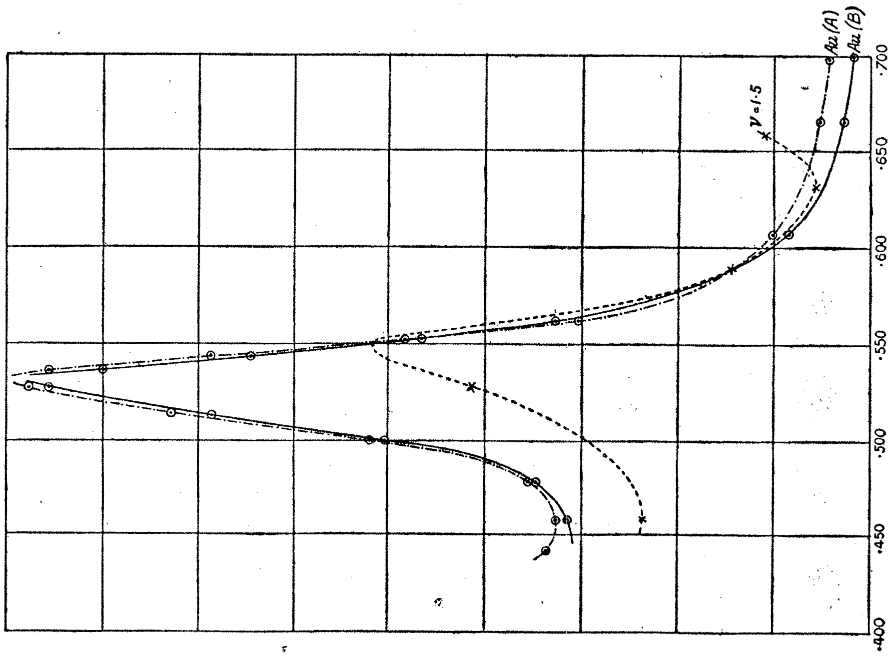

Fig. 2.

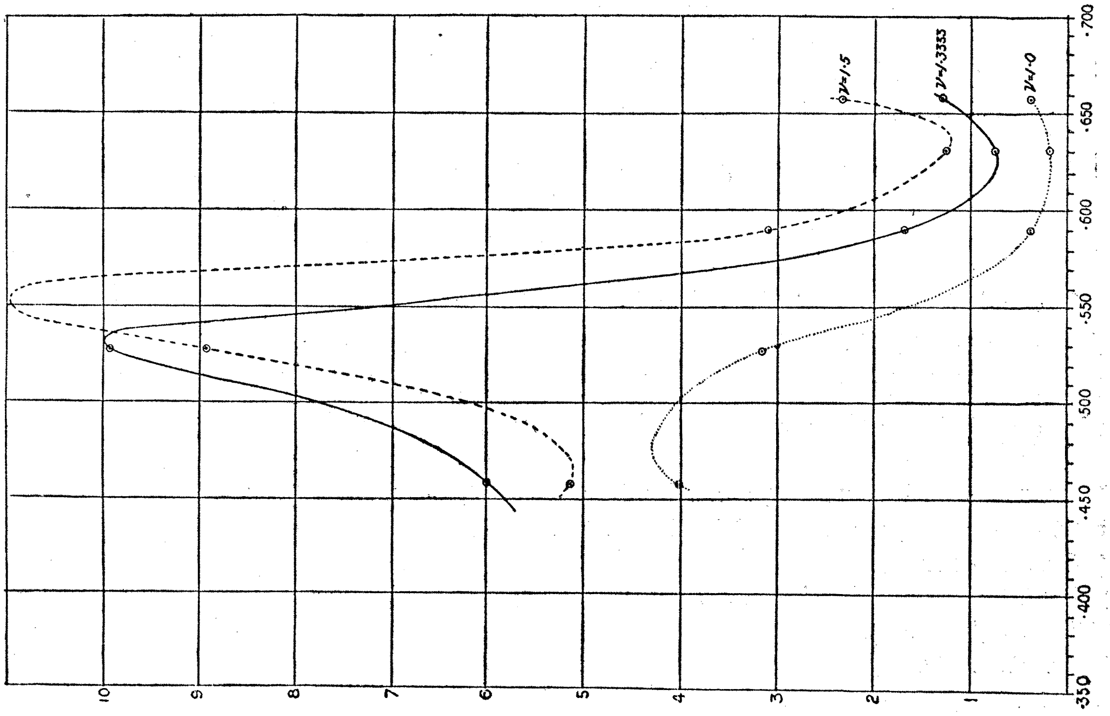

Fig. 1.

In fig. 2 the graph of $n'\kappa'/\lambda$ for glass ($\nu = 1{\cdot}5$), shown by a broken line in fig. 1, is again represented; but here on such a scale as to have the same ordinate at $\lambda = {\cdot}589$ as that of the graphs of the observed absorptions of Au (A) and Au (B). The calculated and observed curves resemble one another in having a minimum in the red and a maximum in the green, although the calculated maximum occurs at about $\lambda = {\cdot}550$, while the observed maximum falls at $\lambda = {\cdot}533$. Also both calculated and observed absorptions fall from green to blue, while the dotted curve in fig. 1 shows that the absorptions produced by molecularly divided gold will increase from green to blue, having a maximum at about $\lambda = {\cdot}475$. These results then, so far as they go, are in accordance with the suggestion, put forward in the former memoir, that the colouring agent of gold ruby glass consists primarily of diffused spheres of gold, although some discrete molecules may also be present. The following is the evidence which has accumulated to show that a gold ruby glass contains minute spheres of gold, many to a wave-length of light, and that it is to these small gold spheres that the pink colour of the glass is primarily due :—

(1) There are particles, presumably of gold, visible in all specimens of gold ruby glass in which the colour has been developed.*

(2) Whenever these particles are of diameter less than 10^{-5} centim. they are spherical in shape.†

(3) SIEDENTOPF and ZSIGMONDY state‡: "It is only in the case of *ruby* glasses that the particles are so dense that they cannot be fully separated under the microscope." In other words, whenever there are many small spheres to a wave-length of light, the glass is ruby.

(4) We have just seen that, within the limits of experimental error, this ruby colour is that which would be produced by small spheres (but not by molecules) of gold, many to a wave-length, embedded in the glass.

(5) The polarisation of the cone of light emitted by the particles in the path of a beam of white light traversing any of the three ruby glasses examined by SIEDENTOPF and ZSIGMONDY§ is that which would be possessed by the cone of light emitted by small spheres of metal embedded in the glass. Further, the colour of the cone of light in the case of these three glasses was *green*, while it has been shown in the former paper‖ that the intensity of light of wave-length λ emitted by small spheres of gold embedded in the glass is proportional to $(\alpha^2 + 4\beta^2)/\lambda^4$, and, according to Table I. above, this expression for gold spheres in a glass of refractive index $\nu = 1{\cdot}56$ has a maximum in the neighbourhood of $\lambda = {\cdot}560$, *i.e.*, in the yellowish-green.

We conclude then that the colouring agent of gold ruby glass is metallic gold,¶ the major portion of which is in the form of small spheres.

The irregular blue and purple which often appear, instead of the ruby at which the glass manufacturer aims, can be explained as indicated in the appendix to the former

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* SIEDENTOPF and ZSIGMONDY, 'Ann. der Phys.,' January, 1903.

† *Cf.* former paper, 'Phil. Trans.,' A, 1904, p. 391.

‡ *Loc. cit.*, p. 27.

§ See their table reproduced at p. 397 of the former paper and discussion following it on pp. 398–401 ('Phil. Trans.,' A, 1904).

‖ *Loc. cit.*, p. 400.

¶ Not *aurous oxide*, as stated in the text-books on glass making.

paper. We have already* seen that if gold glass when first made in the furnace be rapidly cooled, the glass remains colourless. In order to obtain ruby glass, the molten glass must be left in the annealing oven and maintained at a high temperature for about three days. If the glass is too violently heated or is kept too long at a high temperature, it becomes turbid, reflects brown light, and develops first an amethystine and then a blue tint by transmitted light. But it now appears that the gold cannot, as previously† suggested, be in solution in the colourless glass when first heated; for if metallic gold were in true solution in the glass it would have the vapour colour indicated by the dotted curve in fig. 1. The gold must therefore be gradually reduced during the annealing process. So long as the glass remains hot enough to admit of molecular movement, the molecules of gold go together to form spheres, and these small spheres tend to coagulate into crystallites.‡ If the glass cools before the coagulation of the small spheres, a gold ruby glass is obtained. If, however, some of the small spheres have coagulated into crystallites, the density of which exceeds ·6 of that of normal gold,§ these crystallites will reflect light which is predominantly yellow or red.‖ The glass will thus reflect brownish light; and since the more refrangible rays are less reflected than those of longer wave-length, the red end of the absorption curve will, owing to the crystallites, be raised relative to the blue. The glass will thus appear bluer than when no coagulation has occurred. Further, as these crystallites may be of dimensions comparable with a wave-length of light, they destroy the optical continuity of the medium and produce turbidity. Now the blue colour of a gold glass is always associated with turbidity and a brown appearance by reflected light, so that the formation of crystallites of gold in the glass accounts for the irregular blue and purple colours which gold glass sometimes exhibits.¶

Diffusions of gold particles in water—the so-called "colloidal solutions" of gold—have been prepared by FARADAY**, ZSIGMONDY,†† and STOEKL and VANINO‡‡, who

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* *Loc. cit.*, p. 392.

† *Loc. cit.*, p. 392.

‡ In the case of copper ruby glasses the process continues until actual crystals of copper are formed, but I have not seen gold crystals in a glass, although it is probable that they are occasionally formed.

§ KIRCHNER and ZSIGMONDY ('Ann. der Phys.,' XIII., 1904, p. 591) estimate that a clump of gold particles in a blue gold-gelatine preparation contains at least 50 per cent. of gold. See below, p. 254.

‖ See fig. 12, below.

¶ The blue and violet [purple] colours of the glasses D and E in SIEDENTOPF and ZSIGMONDY'S table (see 'Phil. Trans.,' A, 1904, p. 397), as well as the red, yellow and brown colours of the cone of light emitted by them, are thus explained. STOKES (Royal Institution Lecture, 1864, 'Collected Works,' vol. IV., p. 244), without entering into the question why gold glass ordinarily transmits pink light, says that, it being the property of gold to transmit bluish light, the metallic gold in suspension causes the blue appearance.

** FARADAY, Bakerian Lecture for 1857, printed in 'Phil. Trans.' for 1857, and reprinted in his 'Researches in Chemistry and Physics.' References will be made to the pages of the reprint.

†† ZSIGMONDY, 'LIEB. Ann.,' vol. 301 (1898), p. 29, and 'Zeitschr. f. Electrochem.,' vol. IV., p. 546.

‡‡ STOEKL and VANINO, 'Zeitschr. f. Phys. Chem.,' XXX. (1899), p. 98.

precipitated the gold from its chloride by means of various reducing agents; and by BREDIG[*] and later by EHRENHAFT,[†] who used a gold terminal for an electric arc which was caused to spark under water.

All these preparations exhibited a gradual change in colour from red through purple to blue; this change was greatly accelerated by the introduction of a trace of salt into the water. ZSIGMONDY[‡] gives the absorption curves of a number of "solutions" of gold. STOEKL and VANINO[§] measured the absorptions of a red suspension containing a known volume proportion of gold. Lastly, EHRENHAFT[||] has made careful measurements of the absorptions of "colloidal" gold. The curves plotted from his measurements of the red "solutions" resemble the continuous curve shown in fig. 1. Again, EHRENHAFT states[¶] that the absorption band of a gold suspension which possessed a beautiful red colour began at $\lambda = \cdot 560$ and attained a maximum at $\lambda = \cdot 520$, while the solution was almost transparent in the ultra-violet. Now the maximum of the calculated absorption curve for spheres of gold in water ($\nu = 1 \cdot 3333$) occurs at $\lambda = \cdot 533$.[**] Again, the dotted curve in fig. 1, which will represent the absorption produced by a true solution of gold, does not sufficiently agree with the measured absorptions to admit of the gold being in true solution in the water. These results suggest that the coloration is due to diffused spheres[††] of gold, although some discrete gold molecules may also be present.

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[*] BREDIG, 'Zeitschr. f. Phys. Chem.,' XXXII., p. 127.

[†] F. EHRENHAFT, 'Ann. der Phys.,' XI. (1903), p. 489.

[‡] ZSIGMONDY, 'LIEB. Ann.,' vol. 301 (1898), pp. 46–48.

[§] *Loc. cit.*, p. 108. For a discussion of their results see below (footnote, p. 253).

[||] *Loc. cit.*, pp. 505, 506.

[¶] *Cf.*, table given, *loc. cit.*, p. 507.

[**] Thus the differences in wave-length between the observed maximum absorption of gold ruby glass and of the calculated maximum for gold spheres in glass ($\nu = 1 \cdot 5$), and between the observed maximum for colloidal gold and the calculated maximum for gold spheres in water, are respectively $\cdot 017$ and $\cdot 013$, and these differences are of the same size.

[††] EHRENHAFT also supposed that the gold was present in the form of small spheres; but he proceeded to define the average size of these spheres (and also of those of Ag, Pt, &c., in the "colloidal" solutions of these metals) by means of J. J. THOMSON'S equation connecting the radius of a conducting sphere with the wave-length corresponding to the free periods of its vibration, this wave-length being assumed to be that of the absorption maximum. KIRCHNER and ZSIGMONDY ('Ann. der Phys.,' 1904, p. 575), however, point out that there is no connection between size of particles and the absorption of light produced by them, and this we have seen to be the case, provided there are many particles to a wave-length; also the very small size (if spherical, their average diameters would be $7\mu\mu$) of the particles of gold, the gold content of which ZSIGMONDY measured would require the absorption maximum to be in the ultra-violet. KIRCHNER and ZSIGMONDY add that it would only be possible to get a large enough linear dimension to give a free period if the particles were not iso-dimensional, and they conclude therefore that the gold particles must be in the form of leaves or of rods; but they do not reconcile such a form with the polarisation and green colour of the cone of light emitted by the smaller particles. Since, however, we find that the small-sphere hypothesis accounts for the observed phenomena, we must agree with EHRENHAFT that the particles are spherical, although we cannot admit that the average diameter of the spheres is correlated to the wave-length of the light most absorbed.

This view enables us to explain the change of colour from red to blue, by the coagulation of the small spheres, just as in the case of the glasses coloured by gold; the simultaneous development of a brown reflection and a turbid appearance is at the same time explained. The following quotations must suffice to describe the phenomena in question.

FARADAY observes that

> "A gradual change goes on amongst the particles diffused through these fluids, especially in the cases where the gold is apparently abundant. *It appears to consist of an aggregation.* Fluids at first clear, or almost clear, to ordinary observation, *become turbid*; being left to stand for a few days, a deposit falls."*

When common salt, or any other substance which dissociates in water, was added to the fluid

> ". . . The salt diffused gradually through the whole, first turning the gold it came in contact with blue, and then causing its precipitation.†
>
> "Such results would seem to show that this blue gold is aggregated gold, *i.e.*, gold in larger particles than before."‡

Again

> "The supernatant fluid in specimens that had stood long and deposited was always ruby . . . there was every reason to believe that the gold was there in separate particles, and that such specimens afforded cases of extreme division."§

Observations made by subsequent physicists agree with those of FARADAY. Thus ZSIGMONDY writes

> "In every case the bright red colour [of suspensions of gold in water] changed to blue on the addition of salt; and decoloration of the upper part of the liquid showed that precipitation has then begun."‖

Again, STOEKL and VANINO, who examined a large number of suspensions of gold in water prepared by many different methods, state that

> "When the particles [of gold] are very small . . . the fluid appears red-yellow, ruby-red. When, however, the particles increase in size, the red and yellow rays are quite cut off and the transmitted light consists only of blue and violet rays, the fluid appearing blue-violet."¶

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[*] 'Researches in Physics and Chemistry,' p. 414.

[†] We may suppose that by friction against the water the gold spheres obtain that negative change which ZSIGMONDY ('LIEB. Ann.,' vol. 301, p. 36) found that they possess. The mutual repulsion of these like charges prevents the spheres from coagulating and thus keeps the gold in suspension in the water. But when an electrolyte is introduced into the fluid, the positive ions discharge the gold spheres, so that coagulation and precipitation result.

[‡] FARADAY, *loc. cit.*, p. 420.

[§] FARADAY, *loc. cit.*, p. 418.

[‖] ZSIGMONDY, 'LIEB. Ann.,' vol. 301 (1898), p. 34.

[¶] 'Zeitschr. f. Phys. Chem.,' XXX. (1899), p. 108.

As already stated, STOEKL and VANINO measured the absorption of light, for six different values of λ, by a suspension containing a known volume proportion of gold. Using their value of μ ($\cdot000003$) to determine the scale of the continuous curve in fig. 1, and comparing the values of $n'\kappa'/\lambda$ so obtained with

Finally, KIRCHNER and ZSIGMONDY record that in a gold suspension in water

> " . . . A given (generally large) number of particles which diffract green light [*i.e.*, small spheres] were brought together by the addition of an electrolyte into a single particle which diffracted yellow or red light with much greater intensity* than its components. With this uniting of particles occurs the change in the colour of the fluid from red to blue."†

We have already shown that, theoretically, the coagulation of the small spheres of gold should produce a colour change in the fluid, from red through purple to blue; and the above quotations have indicated that coagulation accompanies the change of colour. But that the coagulation takes place in the manner assumed for the purposes of the theory has been shown by KIRCHNER and ZSIGMONDY, who prepared suspensions of gold in gelatine, some of which preparations were red when wet, and changed to blue on being dried, at the same time developing a gold-bronze reflection.‡

Now these dry blue membranes contained a number of clumps, each composed of hundreds of ultra-microscopic resonators§ (small spheres); and these clumps were comparable in size with a wave-length of light, being directly visible when examined with a numerical aperture of 1·4: they would therefore be capable of reflecting light. Further, the change of colour to blue was most marked in those preparations in which the individual clumps were most dense,|| and it appears from fig. 12 below that the selective absorption of red and yellow light by a gold crystallite is greater the greater its density. The theoretical explanation of the change to blue requires the rays of lower refrangibility to be stopped by reflections from crystallites,¶ and this requirement is thus satisfied.

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the absorption curve obtained from STOEKL and VANINO'S observations, we find that the observed curve lies below the calculated curve, except for red light. But STOEKL and VANINO record that the observed fluid had a yellowish reflection, so that large particles (crystallites) must have been present in it; and the presence of these crystallites requires the volume μ' of gold, which per unit volume of the liquid is in the form of small spheres, to be less than the total volume proportion μ. This diminishes the absorptions throughout the spectrum. But the volume proportion $\mu - \mu'$ of crystallites produces absorption which is much greater for the red and yellow than for the green and blue rays. The superposition of the absorptions produced by μ' and by $\mu - \mu'$ would thus produce an absorption curve in accordance with that observed.

[*] The aggregate may be supposed to be comparable in size with a wave-length of light; the intensity of the light reflected from it would thus be proportional to the square of its diameter, while the intensity of the light diffracted by the small spheres is proportional only to the sixth power of their diameters.

[†] KIRCHNER and ZSIGMONDY, *loc. cit.*, p. 592.

[‡] *Loc. cit.*, p. 589.

[§] KIRCHNER and ZSIGMONDY, *loc. cit.*, p. 576.

[||] *Loc. cit.*, p. 577.

[¶] A similar explanation possibly applies to the fact that when light, transmitted through a stretched membrane containing gold in suspension, is polarised in the direction of stretching, the emergent light is red, but when the incident light is polarised in a perpendicular direction the colour is blue, the gold clumps being comparable with a wave-length in the direction of stretching, but not in a perpendicular direction. (*Cf.* AMBRONN, 'Ber. d. math.-phys. Kl. d. k. Sächs. Gesellsch. d. Wissensch.,' December 7, 1896, and AMBRONN and ZSIGMONDY, do., July 31, 1899).

In conclusion, we remark that most "colloidal solutions" of gold, even those which are of a ruby colour, contain crystallites in addition to the small spheres to which the colour is primarily due. Thus FARADAY could detect the green "cone of light," which indicates the absence of large aggregations, only in those liquids which had been cleared by prolonged precipitation and frequent decantation; and STOEKL and VANINO found that all the gold suspensions which they examined showed a yellowish reflection. A small number of the large aggregations may, however, cause the cone of light to appear yellow or red without appreciably altering the colour of the transmitted light. For, whereas the intensity of the (green) light emitted by a small sphere is proportional to the sixth power of the diameter, the intensity of the (brown) light reflected from a gold crystallite is proportional to the square of its linear dimensions. Gold solutions prepared chemically appear, however, to be freer from aggregated gold than are those prepared by BREDIG's method.*

6. *Diffusions of Silver. The Nature and Form of the Suspended Particles.*

We proceed to consider the absorption of light produced by diffused particles of silver. The values of $n'\kappa'/\mu\lambda$ for $\nu = 1\cdot6$, $\nu = 1\cdot5$, $\nu = 1\cdot3333$, and $\nu = 1\cdot0$ given in Table II. are plotted in fig. 3, the positions of the maximum of each curve being determined as in the case of gold. Since (*cf.* above, § 4) the values of n and $n\kappa$ for silver were all determined from the polished surface of the metal, these curves should represent the absorption produced by diffused spheres of silver in glass, in water, and *in vacuo*, with only a small error.† The dotted curve in fig. 1, which represents the absorptions of diffused molecules of silver *in vacuo* (and, on different scales, in other non-absorbing and non-dispersive media), shows that the silver molecule has a free period corresponding to $\lambda = \cdot360$, about. The existence of this free period is possibly responsible for the sensitiveness of silver salts to ultra-violet light.

In fig. 4 the graphs of $n'\kappa'/\lambda$ for glasses of refractive indices $\nu = 1\cdot60$ and $\nu = 1\cdot56$ are shown on such a scale as to have the same ordinate at the D line as the graph of K for the measured glass Ag (B), of which the measured refractive index at the D line was 1·579. The measured curve resembles those calculated, following them very closely from $\lambda = \cdot600$ to $\lambda = \cdot475$, and having a maximum for a value of λ intermediate between those values of λ which correspond to the maxima of the two calculated curves.‡ This close approximation of the observed absorptions to those

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* *Cf.* ZSIGMONDY, 'Zeitschr. f. Electrochem.,' p. 547. BREDIG's remark, that his gold solutions were *blue* red, points to the same conclusion.

† These curves show that in each case the absorption is less for red than for yellow. This is contrary to statements made in the previous paper (*loc. cit.*, pp. 399 and 420); the errors therein made were due to miscalculation for silver (red) (*loc. cit.*, Table I., p. 396).

‡ The cause of the depression of the observed maximum below those calculated is doubtless to be found in the fact, to which Lord RAYLEIGH has called attention in a recent lecture at the Royal Institution, that

Fig. 3. Silver—calculated values of $\frac{n'\kappa}{\lambda}$.

(1) Spheres (or molecules) *in vacuo*, $\nu = 1 \cdot 0$: ………
(2) Spheres in water, $\nu = 1 \cdot 3333$: ———
(3) Spheres in glass, $\nu = 1 \cdot 5$: – · – · –
(4) Spheres in glass, $\nu = 1 \cdot 6$: - - - - - -
Calculated values shown thus: ⊙.

Fig. 4. Silver.

(1) K, observed for glass Ag (B): ———
Observed values: ×.
(2) $\frac{n'\kappa'}{\lambda}$, calculated for silver spheres in glass, $\nu = 1 \cdot 56$: – · – · –
(3) $\frac{n'\kappa'}{\lambda}$, calculated for silver spheres in glass, $\nu = 1 \cdot 60$: - - - - -
Calculated values: ⊙.

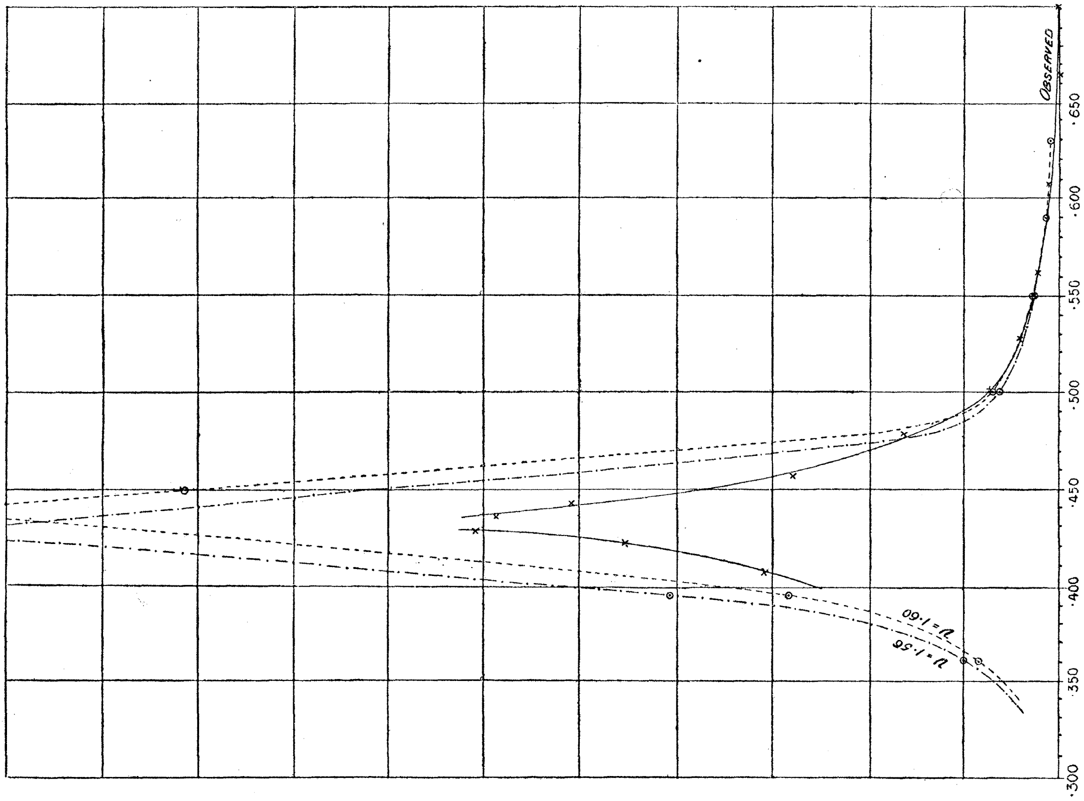

Fig. 4.

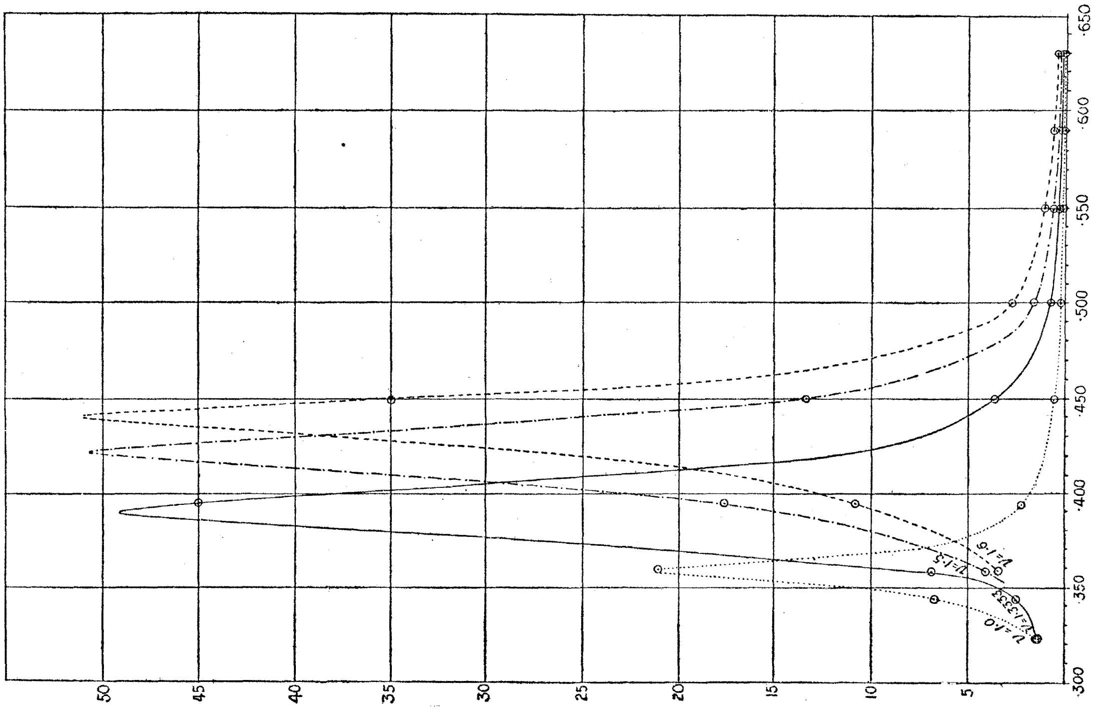

Fig. 3.

calculated suggests that the colouring agent of the yellow silver glass consists primarily of diffused spheres of silver. Since discrete silver molecules would produce an absorption maximum at $\lambda = \cdot 360$, not more than a comparatively small amount of silver can be present in the molecularly subdivided condition. The conclusion that silver glass owes its colour to diffused spheres of silver will be verified in the following section.

The absorption spectra of some colloidal solutions of silver, prepared by BREDIG'S method,[*] have been measured by EHRENHAFT. The continuous curve shown in fig. 3, representing the calculated absorptions of a diffusion of silver spheres in water, is of the same form as that which, according to EHRENHAFT'S measurements, represents the absorption of *visible* light by a colloidal solution of silver.[†] Using ultra-violet light, he further found that a brown colloidal solution of silver, examined before coagulation had seriously affected its colour, showed an absorption band which began at $\lambda = \cdot 503$ and attained a maximum at $\lambda = \cdot 380$, while the fluid was again quite transparent at $\lambda = \cdot 335$. Except for the fact that the maximum ordinate of the calculated curve for silver spheres in water is at $\lambda = \cdot 389$ instead of at $\lambda = \cdot 380$, the above observations admirably describe the continuous curve shown in fig. 3. Since the dotted curve given in that figure shows a maximum at $\lambda = \cdot 360$, and the absorption band does not begin until $\lambda = \cdot 450$, about, the colour of the "colloidal" solution is not that which would be exhibited by a suspension of discrete silver molecules, *i.e.*, by a true solution. We conclude, therefore, that the silver in a "colloidal" solution is present in the form of small spheres; discrete molecules may, however, also be present, and, as indicated above in the case of gold, prepared by BREDIG'S method, probably also crystallites, the number and size of which will increase with the age of the solution.

That the silver in a colloidal solution is in the form of small spheres is further shown by an experiment of BARUS and SCHNEIDER,[‡] who measured the refractive index of such a fluid. Their results are given in the following table,[§] in which n represents the measured refractive index :—

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the spectrum formed by the light which has traversed the glass is not quite pure, so that that image of the slit which should be illuminated only by light of wave-length, say, $\lambda = \cdot 433$, is also, owing to reflections from dust particles, &c., illuminated by light of other wave-lengths which has experienced a less absorption.

[*] BREDIG, 'Zeitschr. f. Electrochemie,' 4, pp. 514, 547.

[†] EHRENHAFT, *loc. cit.*, p. 506.

[‡] BARUS and SCHNEIDER on "The Nature of Colloidal Solutions," 'Zeitschr. f. Phys. Chem.,' VIII., p. 278.

[§] Tabelle 5, *loc. cit.*, p. 296.

TABLE V.—Index of Refraction of Colloidal Solution of Silver for Sodium Light (λ = ·589).

Solution.	Percentage of silver.	Percentage of foreign salts.	Temperature, ° C.	n.
Water	0	0	18·0	1·3306
	0	0	18·2	1·3315
Silver Solution* . . .	1·16	0·18	18·6	1·3369
	1·16	0·18	18·6	1·3363
	1·16	0·18	18·6	1·3369
	1·16	0·18	17·0	1·3363
Water	0	0	18·7	1·3331
	0	0	19·0	1·3333

* The solutions were prepared by CAREY LEA'S method of precipitating silver nitrate with ferrous citrate—they were subsequently dialysed for 60 hours.

Thus the mean refractive index of silver in water at 18°·6 was $n = 1{\cdot}3367$, while the refractive index of water at 18°·7 was $\nu = 1{\cdot}3331$. Taking the specific gravity of silver as 10, the volume proportion silver was $\mu = {\cdot}00116$.

The values of the functions α and α' for sodium light and water at $\nu = 1{\cdot}3331$ are, according to Table II., $\alpha = 1{\cdot}571$ and $\alpha' = 1{\cdot}333$. Substituting these values of ν, μ, and α in equation (10), namely

$$n' = \nu\left(1 + \tfrac{3}{2}\mu\alpha\right),$$

we obtain

$$n' = \nu(1{\cdot}00273) = 1{\cdot}33674.$$

Similarly, from equation (9),

$$n'' = \nu\left\{1 + \frac{2+\nu^2}{2\nu^2}\mu\alpha'\right\},$$

we have

$$n'' = \nu(1{\cdot}002078) = 1{\cdot}33587.$$

Comparison of these values of n' and n'' with the observed value, namely $n = 1{\cdot}3367$, requires that practically the whole of the silver must have been in suspension in the form of small spheres.*

Once more, CAREY LEA† prepared suspensions of silver in water by precipitating the silver from the nitrate by means of a mixture of ferrous sulphate and sodic citrate. He describes how, after careful washing, the silver frequently "dissolved," forming a liquid which varied from red to yellow‡ and was generally blood red; he adds:—

> "On one occasion the substance was obtained in a crystalline form. Some crude red solution had been set aside in a corked vial. Some weeks after the solution had become decoloured with crystalline deposit on the bottom. The bottle was carefully broken; the deposit, examined by a lens, consisted of short black needles and thin prisms."

If, then, the diffused particles of silver when aggregated and precipitated had become crystalline, they must before have been in the form of nascent crystals, and for gold and for all the substances examined by VOGELSANG,§ such nascent crystals were spherical.

7. *Blue Reflection from the Stained Face of Silver Glass.*

When clear glass is flashed with silver glass, or when a clear glass is so stained on one face with silver that the volume proportion μ of silver does not gradually diminish to zero as we proceed inwards from the stained face, but that the stained region ends abruptly, a blue reflection from the interface can be observed if the glass is held with the stained face away from the eye. No blue reflection can be seen from the air-glass interface when the stain is held towards the eye. STOKES observed this blue reflection, and stated that the interface presented the appearance of being coated with a fine blue powder.‖

We proceed to examine whether the presence of small spheres of silver, which has been shown to account for the colour of the light transmitted by silver glass, will also account for this blue reflection. Consider, then, plane polarised light travelling in a medium of refractive index ν' and directly incident on the surface, $z = 0$, of an absorbing medium whose optical constants are n' and κ', where $N' \equiv n'(1 - \iota\kappa')$. Then we may take as the electric and magnetic vectors for

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* BARUS and SCHNEIDER (*loc. cit.*, p. 297) make the following comment on their experiment:—

"KUNDT has found for normal metallic silver a refractive index of about 0·27. It would, therefore, be expected that the presence of the silver would diminish the refractive index of the water. It is by no means denied that it might be possible to explain the normal refractive indices of the above table in accordance with MAXWELL's Theory of Light."

The investigation in the text attempts to give such an explanation.

† CAREY LEA, 'Amer. Journal of Science,' 1889, and 'Phil. Mag.,' 1891.

‡ *Cf.* above, p. 243, especially second footnote.

§ *Cf.* above, § 1.

‖ STOKES, 'Collected Works,' vol. III., p. 316.

Incident light :—

$$X = \exp\{\iota p(t-\nu' z/c)\}, \qquad Y = 0, \qquad Z = 0,$$
$$\alpha = 0, \qquad \beta = \nu' \exp\{\iota p(t-\nu' z/c)\}, \qquad \gamma = 0.$$

Reflected light :—

$$X = B\exp\{\iota p(t+\nu' z/c)\}, \qquad Y = 0, \qquad Z = 0,$$
$$\alpha = 0, \qquad \beta = -\nu' B\exp\{\iota p(t+\nu' z/c)\}, \qquad \gamma = 0.$$

Light inside absorbing medium :—

$$X = C\exp\{\iota p(t-N' z/c)\}, \qquad Y = 0, \qquad Z = 0,$$
$$\alpha = 0, \qquad \beta = N'C\exp\{\iota p(t-N' z/c)\}, \qquad \gamma = 0.$$

Making X and β continuous at Z = 0, we have

$$C = 1+B, \quad N'C = \nu'(1-B).$$

Hence

$$B = \frac{\nu'-N'}{\nu'+N'} = \frac{\nu'-n'+\iota n'\kappa'}{\nu'+n'-\iota n'\kappa'}.$$

Taking the square of the modulus, we have, for the value R of the ratio of the intensity of the reflected light to that of the incident light,

$$R \equiv (B)^2 = \frac{(\nu'-n')^2+n'^2\kappa'^2}{(\nu'+n')^2+n'^2\kappa'^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12).$$

If, now, the absorbing medium consist of minute spheres of metal embedded in a transparent medium of refractive index ν, we have equations (10), namely,

$$n'\kappa' = 3\mu\nu\beta, \quad n' = \nu(1+\tfrac{3}{2}\mu\alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10).$$

Substituting these values of $n'\kappa'$ and of n' in (12) we obtain

$$R = \left(\frac{\nu-\nu'}{\nu+\nu'}\right)^2\left[1+\frac{6\mu\nu\nu'}{\nu^2-\nu'^2}\alpha+\frac{9\mu^2\nu^2}{\nu^2-\nu'^2}\left\{\frac{\nu\nu'}{\nu^2-\nu'^2}(\alpha^2+4\beta^2)-\alpha^2\right\}+\ldots\right] \quad . \quad . \qquad (13),$$

in which powers of μ higher than the second have been neglected.

Suppose first that $\nu' = 1$, so that we consider the reflection at the front face of the stained glass. Omitting powers of μ except the lowest which occur, we then have from (13)

$$R_1 = \left(\frac{\nu-1}{\nu+1}\right)^2\left\{1+\frac{6\mu\nu}{\nu^2-1}\alpha\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14).$$

It appears from equation (14) that light is reflected from the stained glass almost as if the stain did not exist, the effect of the stain being slightly to increase the reflection of those colours (in the blue) for which, according to Table II., α is greatest.

Now, however, suppose that $\nu' = \nu$, so that the light is reflected at the interface between colourless glass and the same glass containing small spheres of metal. Neglecting μ^3, equation (13) then reduces to

$$R = \tfrac{9}{16}\mu^2(\alpha^2+4\beta^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (15).$$

Since this expression for R contains no large constant term, the light from the interface will in this case be highly coloured in the case of those metals for which $\alpha^2+4\beta^2$ varies greatly for different values of λ.

If, however, the absorbing medium contain molecularly divided metal, equations (10) are replaced by

$$n''\kappa'' = (2+\nu^2)/\nu\,.\,\mu\beta', \quad n'' = \nu\left(1+\frac{2+\nu^2}{2\nu^2}\mu\alpha'\right) \quad . \quad . \quad . \quad . \quad . \qquad (11).$$

Replacing $3\mu\beta$ and $3\mu\alpha$ in equations (14) and (15) by $(2+\nu^2)/\nu^2\,.\,\beta'$ and $(2+\nu^2)/\nu^2\,.\,\alpha'$ respectively, we obtain, as the intensities of the light reflect from the front face of the stain and from the interface respectively,

$$R_1' = \left(\frac{\nu-1}{\nu+1}\right)^2\left\{1+\frac{2(\nu^2+2)}{(\nu^2-1)\nu}\alpha'\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16),$$

$$R' = \frac{\mu^2}{16}\left(\frac{2+\nu^2}{\nu^2}\right)^2(\alpha'^2+4\beta'^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (17).$$

As before, it appears that when the stain is held towards the eye the reflection R_1' is almost as if the stain were not there; while when the stained face is away from the eye, the reflection is highly coloured.

Sir William Abney has kindly measured for me the intensities R_0 of light reflected from the interface between the unstained and stained regions of one of Stokes' specimens of silver glass. The values of R_0 are given in the following table:—

Table VI.—Blue Reflection from Silver Glass. Measured Value of ν at D Lines = 1·532.

λ.	R_0.	λ.	R_0.	λ.	R_0.
·4200	·25	·5000	·067	·5800	·014
·4300	·285	·5100	·050	·5900	·016
·4400	·290	·5200	·042	·6000	·018
·4500	·267	·5300	·032	·6100	·020
·4600	·237	·5400	·025	·6200	·021
·4700	·195	·5500	·020	·6300	·022
·4800	·146	·5600	·018	—	—
·4900	·095	·5700	·016	·6800	·022

Fig. 5. Blue reflection from silver glass.

Calculated values : ⊙.

(1) R ∽ spheres in glass, $\nu = 1 \cdot 56$: _ . _ . _

(2) R′ ∽ molecules in glass, $\nu = 1 \cdot 56$: ....

Observed values : ×.

(3) R_0 ∽ observed : ———

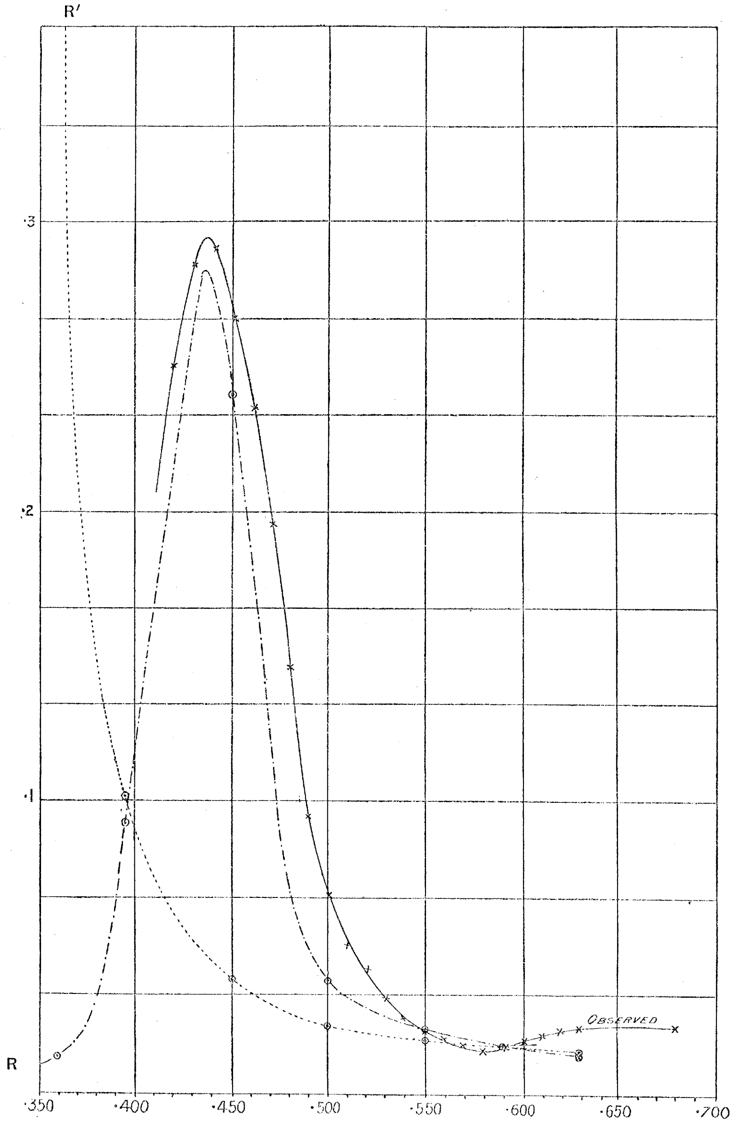

Fig. 5.

The continuous curve shown in fig. 5 has been fitted to the plots of these values of R_0. In the same figure are also shown the calculated values of R and of R′, obtained from equations (15) and (17) by means of the values of $\alpha^2+4\beta^2$ and of $\alpha'^2+4\beta'^2$ given for silver and glass of refractive index $\nu = 1{\cdot}56$ in Table II. The scales on which R and R′ are represented are so chosen that the ordinates corresponding to $\lambda = {\cdot}589$ shall be the same as that for the continuous curve.

It appears that while the graphs of R′ and R_0 widely differ, the positions of the respective maxima falling near $\lambda = \cdot 360$ and $\lambda = \cdot 436$ respectively, the graph of R closely resembles that of R_0,* the maxima of R and of R′ occurring at almost the same value of λ. We conclude that the presence of small spheres of silver throughout the stained region of the glass will account for the blue reflection; and we thus confirm the view, to which absorption phenomena led us, that silver glass consists of a suspension of small spheres of silver in a colourless glass.

Before leaving the consideration of the blue reflection from silver glass, it may be noticed that the light is not reflected as from a plane interface between glass and silver glass. Thus when the source of light is an electric arc, the blue colour is clearly discernible by an observer whose eye is not in the straight line determined by the ordinary law of reflection. This effect is due to the irregularity of the interface, the silver not having penetrated the glass to a uniform depth. An alternative explanation, however, suggests itself,—the blue colour might be due to independent radiation from discrete spheres (or molecules) of silver so far apart as not to form an optically homogeneous medium. The intensity of the emitted light would then be proportional to $(\alpha^2+4\beta^2)/\lambda^4$ (in the case of spheres, or $(\alpha'^2+4\beta'^2)/\lambda^4$ in the case of molecules). Further, the blue colour would be equally visible if the light illuminating the discrete spheres (or molecules) entered the silver glass from the air side or the clear glass side; and this is not the case.

It is of interest to notice that while each individual sphere in glass radiates out light of an intensity proportional to $(\alpha^2+4\beta^2)/\lambda^4$, a surface separating a glass, containing many of the spheres to a wave-length of light, from a region of the same glass in which no spheres are present, reflects light with an intensity proportional to $\alpha^2+4\beta^2$. This is due to the fact that the number of spheres (on the reflecting surface), the phase of the forced vibrations of which lies at any instant between given limits, is proportional to λ^2; so that the intensity of the reflected light is proportional to λ^4 times the intensity of the light emitted by a single sphere.

8. *Diffusions of Copper. The Nature and Form of the Suspended Particles.*

We proceed to discuss the colours produced by diffused particles of copper in order to discover the cause of colour of copper ruby glass. The values of the expression $n'\kappa'/\mu\lambda$ for $\nu = 1{\cdot}56$, $\nu = 1{\cdot}5$, and $\nu = 1{\cdot}0$ given in Table III., are plotted in fig. 6, the maxima being determined as in the case of fig. 1 (*cf.* § 5 above). As in the case of silver, these curves should fairly accurately represent the absorptions produced by copper spheres in glass $\nu = 1{\cdot}56$, in glass $\nu = 1{\cdot}5$, and by copper spheres or molecules

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* The fact that R_0 increases from yellow to red, while R diminishes in the same range, would be accounted for if the black paper with which Sir WILLIAM ABNEY backed the stained face of the glass reflected 2 per cent. of the light incident on it. Further experiments are to be made on this.

Fig. 6. COPPER—calculated values of $\frac{n'\kappa'}{\lambda}$.

(1) Spheres (or molecules) *in vacuo*, $\nu = 1 \cdot 0$: ....

(2) Spheres in glass, $\nu = 1 \cdot 5$: — · — · —

(3) Spheres in glass, $\nu = 1 \cdot 56$: - - - - - - -

Calculated values shown thus: ⊙.

Fig. 7. COPPER.

(1) K, observed for copper ruby glass Cu (X): ———

Observed values: ×.

(2) $\frac{n'\kappa'}{\lambda}$, calculated for copper spheres in glass, $\nu = 1 \cdot 5$: - - - - - - -

(3) $\frac{n'\kappa'}{\lambda}$, calculated for copper molecules in glass: ....

Calculated values: ⊙.

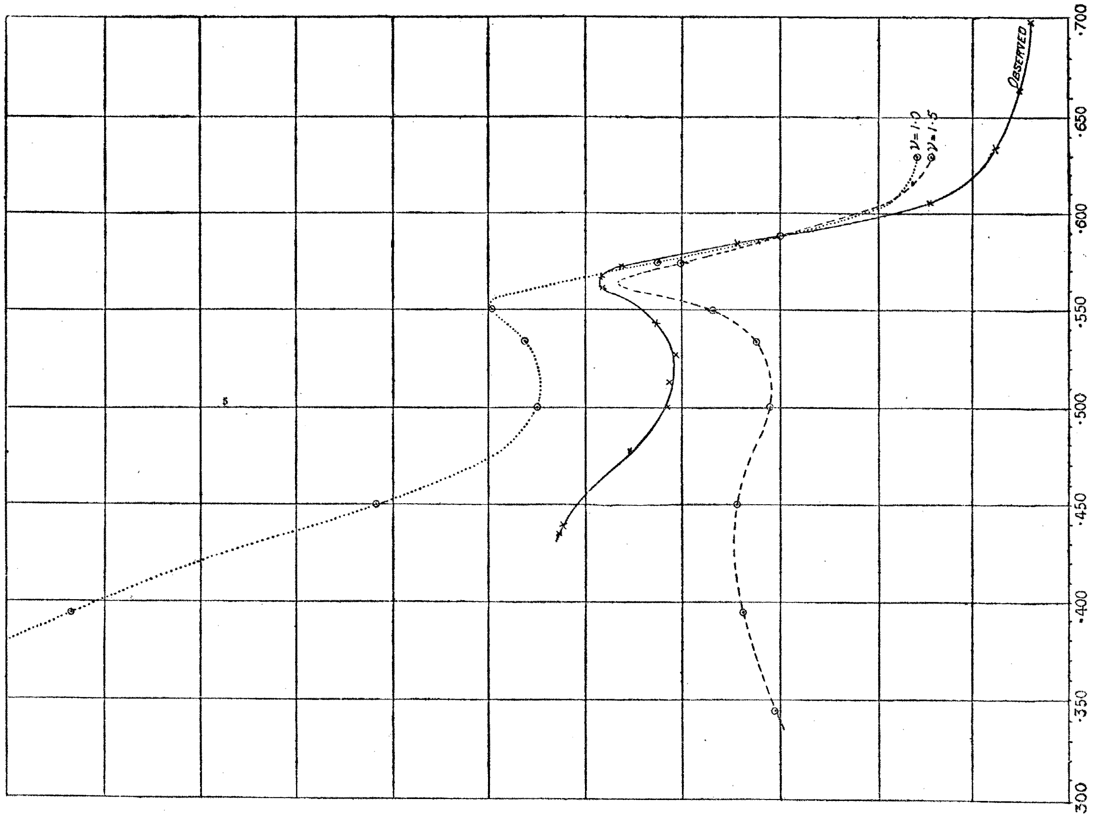

Fig. 7.

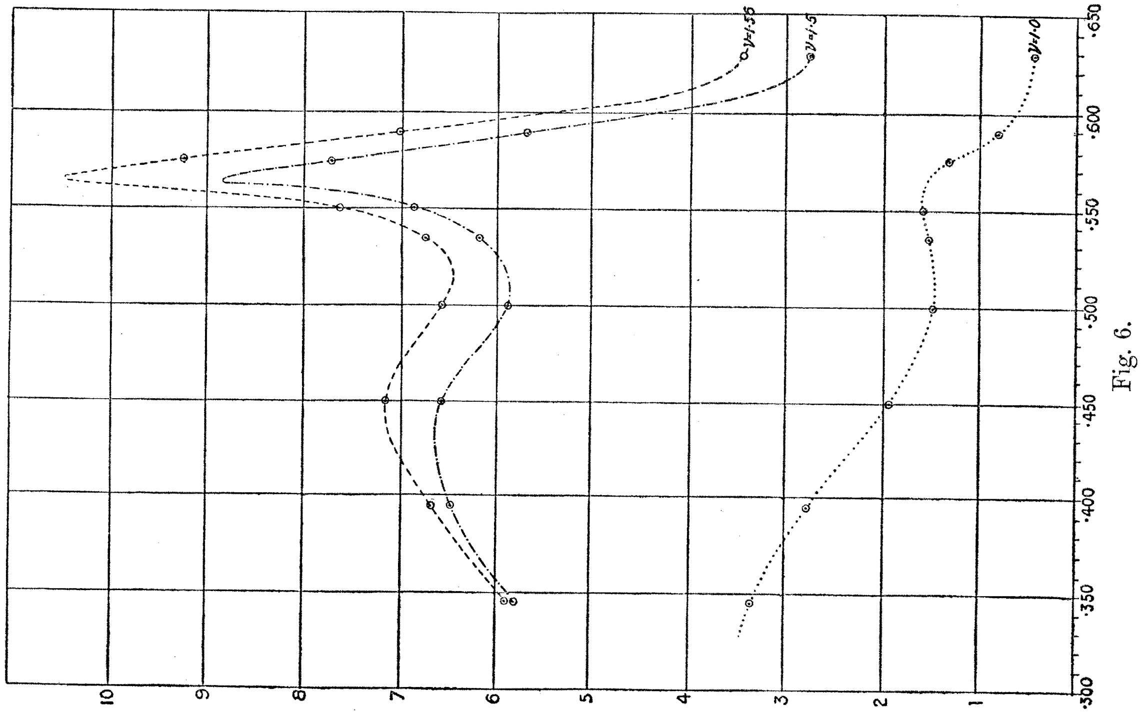

Fig. 6.

(copper vapour) *in vacuo* respectively. The absorption band in the yellow green shown by the top two curves in fig. 6 was observed by STOKES in the spectrum of a copper ruby glass.

In fig. 7 the graphs of $n'\kappa'/\lambda$ for glass ($\nu = 1{\cdot}5$) and of $n''\kappa''/\lambda$* are reproduced from fig. 6 on such a scale as to have the same ordinate at the D line as that possessed by the continuous curve which has been fitted to the plots of the measured absorption K of the glass Cu (X). The curves in fig. 7 all have a minimum in the red or infra red and a maximum in the yellow-green; but while that ($n'\kappa'/\lambda$) which represents the absorptions of spheres in glass has a secondary maximum near $\lambda = {\cdot}480$, the dotted curve shows that the absorption of copper molecules in glass continues to increase till $\lambda < {\cdot}350$. Also the maximum in the yellow green for the "sphere" curve occurs for approximately the same value of λ as corresponds to the maximum observed absorption; while the value of λ at the maximum of the dotted ("molecule") curve is about $10\mu\mu$ less, and the latter maximum is much less marked than are the former two. Finally, the last readings obtained for K in the violet indicate that the continuous (observed) curve rapidly approaches a maximum near $\lambda = {\cdot}480$.

We conclude that copper ruby glass is coloured by metallic copper,† and that the greater part of the copper is present in the form of small spheres, although some probably remains in the form of discrete molecules.‡

The manufacture of copper ruby glass closely resembles that of gold ruby.§ Like gold ruby, the copper ruby glass becomes turbid if kept too long at a high temperature. This turbidity is also probably due to the formation of crystallites by the coagulation of small spheres, since, when the conditions necessary for the development of turbidity are long maintained, actual crystals, apparently of copper, are formed in the glass.‖

9. *Colouring Effects of the Radiation from Radium, Cathode Rays, &c.*

It has long been well known that cathode rays produce a blue-violet coloration in soda glass. Soda glass tubes, after containing the emanation from radium, show the

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* The graph of $n'\kappa'/\lambda$ for $\nu = 1$ can, by increasing all the ordinates in the proper constant proportion, be changed into the graph of $n''\kappa''/\lambda$ for any value of λ. *Cf.* § 3 above.

† STOKES ('Math. and Phys. Papers,' vol. IV., p. 242) supposed that the colouring agent was suboxide of copper. The blue colour exhibited by overheated specimens of the glass (*loc. cit.*, p. 243) is probably caused by the coagulation of the small spheres into crystallites and crystals which reflect out the red light.

‡ Measurements will have to be made with ultra-violet light in order to determine how much copper remains in the molecularly subdivided condition.

§ *Cf.* above, § 5, p. 251.

‖ *Cf.* 'Phil. Trans.,' A (1904), p. 392. Some of the crystalline glazes made by Mr. BURTON at PILKINGTON'S tile works exhibit the same effect. I have seen a pot with a copper glaze in parts of which the copper was apparently reduced, for in passing from the colourless glaze (where the copper was not reduced) into regions where the reduction had been effected, a deep red (copper ruby) was first reached; that colour increased in intensity until, in the central portions of the region, crystals, apparently of copper, could be seen.

same colour, and crystals of each salt acquire under cathode rays a beautiful violet tint.[*] Experiment has also shown that exposure to the emanation from radium gives to gold glass a ruby colour, to silver glass a yellow colour, and to potash glass a brown colour.

Now we have seen[†] that a molecularly subdivided metal possesses the same colour by transmitted light whatever be the nature of the surrounding transparent medium, supposed non-dispersive and isotropic. This colour may be called the vapour-colour of the metal. It has further appeared that although the transmitted colour of a metal subdivided into small spheres, many to a wave-length of light, does depend on the refractive index ν of the medium in which the small spheres are "embedded," yet this colour approaches to the vapour-colour as ν approximates to unity. As is shown by the dotted curve in fig. 1, the vapour-colour of gold must be red.[‡] The colour of glass containing molecularly distributed gold is thus red,[‡] although when the gold is collected into spheres the glass is pink. Similarly, reference to the relative values of β'/λ in Table II. shows that the vapour-colour of silver is yellow. Glass coloured by small spheres of silver is also yellow. Again, Professor R. W. WOOD showed to the British Association[§] in Cambridge that the vapour-colour of sodium is violet, this colour being due to the absorption at the D lines. This violet colour is also produced at the cathode in the electrolysis of sodium chloride,[||] the molecules of sodium formed at the cathode being distributed throughout the water in its neighbourhood and giving rise to the vapour-colour.[¶] Analogy with the cases of gold and of silver indicates that small spheres of sodium would produce in glass a colour not greatly different from the vapour-colour produced by the molecularly subdivided metal.

Thus the colours developed in gold, silver, or soda glass by the radiation from the emanation from radium are approximately the same as the colours which would be given to the glass by the presence of the reduced metal, either molecularly divided or in small spheres (nascent crystals).

It is therefore very probable that the metal in the glass is reduced by the action of the radiation. This view finds considerable support in the discovery of VILLARD,[**] that cathode rays exert a reducing action, as well as from the fact, already cited,[††] that ELSTER and GEITEL found the salts of the alkali metals, which had been coloured by exposure to cathode rays, to exhibit photo-electric effects as if they contained traces of the free metal.

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[*] GOLDSTEIN, 'WIED. Ann.,' liv., p. 371, 1898.

[†] *Vide ante*, p. 243.

[‡] Or *yellow*; see the second footnote, p. 243.

[§] August, 1904.

[||] *Cf.* J. J. THOMSON, 'Conduction of Electricity through Gases,' pp. 495, 496.

[¶] BUNSEN found that common salt, after heating to about 900° C., exhibited a violet colour, due apparently to the reduced metal, although BUNSEN suggested a subchloride.

[**] 'Journal de Phys.,' 3me Séries, VIII., p. 140, 1899.

[††] See 'Phil. Trans.,' A, 1904, p. 400.

Sir WILLIAM RAMSAY, when I first called his attention to the explanation of the coloration of glass by radium which is afforded by supposing the radiation to reduce metal in the glass, suggested that the reduction might be effected by the discharge of free ions of the metal. Since that time the further evidence that has accumulated seems to favour the truth of this theory. Thus, as all the colour-changes from pink to blue exhibited by gold glass can be imitated with suspensions of gold in water, the glass appears to behave as a liquid, although a very viscous one; and it seems, therefore, reasonable to suppose that the salt of a metal which will dissociate in water will dissociate also in glass. As an alternative hypothesis, we might suppose the compound molecules broken up by the rays. But, were this the case, the α-rays would be far more efficient than the β in producing the colour. And this is not true; for the coloration produced in the splinters of gold and silver glass, as well as in soda and potash glasses, are not, apparently, stronger on the sides of the glass, but seem to be of uniform strength throughout. From this it appears that the β-rays are alone capable of producing the colour. This is in accord with the former hypothesis. For the ions of the metal in the glass would be positively charged, and their discharge by the negatively-charged β particles (or cathode rays) would change them into molecules—just as the sodium ions in the electrolysis of common salt are discharged at the cathode, and thus are transformed into molecules of sodium, imparting a violet colour to the water and capable of forming caustic soda.

It appears, therefore, possible that all glasses contain free ions of metal, and that it is by the discharge of these ions, and consequent reduction of the metal, that cathode and Becquerel rays are able to produce coloration in them.

10. *Numerical Values of the Optical Constants of Media containing Large Volume Proportions of Certain Metals.*

The preceding sections of this paper have treated only of the optical properties of those media for which the volume proportion, μ, of metal is very small. The consideration of media in which μ may have any value up to unity will now, however, be resumed, in order to discover what may be the physical explanation of those colours and changes of colour which FARADAY,* BEILBY,† and others have found to be exhibited by thin metallic films. In § 11 of the former communication‡ the question whether films built up of small spheres of silver or of gold would, for any given volume proportion of metal, transmit red or yellow light more easily, was discussed, and the conclusions reached were compared with the results of Mr. BEILBY'S experiments† on the effect of heat on thin films of metal. The present section extends the scope of that enquiry.

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[*] Bakerian Lecture for 1857, 'Phil. Trans.,' A, 1857. Reprinted in FARADAY'S 'Researches in Chemistry and Physics,' pp. 391 *et seq.* (Reference will be made to the pages of the reprint.)

[†] 'Roy. Soc. Proc.,' vol. 72, 1903, p. 226.

[‡] 'Phil. Trans.,' A, 1904, p. 415.

It has been shown that the optical properties of a metal, so diffused *in vacuo* ($\nu = 1$) that μ has some definite value, are the same whether the microstructure be amorphous (molecularly sub-divided) or consist of small spheres, these optical properties being in either case deducible from equation (7), p. 241.* If then, in accordance with the notation adopted in the former communication (pp. 403 *et seq.*), the accents hitherto used to denote the optical constants, n and $n\kappa$, when μ differs from unity, be now omitted, and the values of those constants corresponding to any particular value μ' of μ be denoted by a suffix (*e.g.*, $n\kappa_{(\mu=\mu')}$), the values of n and $n\kappa$ are given by equation (17), p. 404,† namely,

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

where, as in equation (13′), p. 403,†

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

By these equations the values of n and $n\kappa$, determining optical properties of amorphous or "small-sphere" metallic media of any density, may be calculated for light of wave-length λ, in terms of the values of $n_{\mu=1}$ and of $n\kappa_{\mu=1}$ for the same monochromatic light. The values of n and of $n\kappa$ for gold and for silver have already been calculated for all values of μ in the case of red light ($\lambda = {\cdot}630$) and in that of yellow light ($\lambda = {\cdot}589$). The results are given in Table IV. of the former communication.‡ But in order to obtain a true conception of the colours of such media, corresponding calculations must be effected for other colours also.

Now, in the case of silver, the numerical values of all those functions of $n\kappa_{\mu=1}$ and $n_{\mu=1}$ which have hitherto been calculated for the case of $\nu = 1$—those functions, in fact, which relate to molecules or small spheres of silver *in vacuo*—vary continuously from red ($\lambda = {\cdot}630$) to blue ($\lambda = {\cdot}450$). If, therefore, the values of n and $n\kappa$ corresponding to $\lambda = {\cdot}450$ and $\lambda = {\cdot}500$ be now calculated for all values of μ, the values of n and $n\kappa$ for other colours may be obtained approximately by interpolation between $\lambda = {\cdot}630$ and $\lambda = {\cdot}450$.

The values of n and $n\kappa$ corresponding to $\lambda = {\cdot}450$ and $\lambda = {\cdot}500$ have therefore been calculated for certain values of μ, by means of equations (18) and (19). The values of $n\kappa_{\mu=1}$ and $n_{\mu=1}$ used for the calculations were carefully determined by R. S. MINOR.§ The results are tabulated below (Table VIII.).

In the case of gold it is not so easy to apply this method of interpolation. The values of n and $n\kappa$ corresponding both to blue ($\lambda = {\cdot}458$) and to green ($\lambda = {\cdot}527$)

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* 'Phil. Trans.,' A, 1904, equation (16), p. 403.

† 'Phil. Trans.,' A, 1904.

‡ 'Phil. Trans.,' A, 1904, p. 406.

§ *Loc. cit.* (*vide ante*, Table II.).

TABLE VII.

Metal.	Colour.	α.	β.	$\frac{1}{\alpha}$.		$\mu = \cdot 1$.	$\mu = \cdot 2$.	$\mu = \cdot 4$.	$\mu = \cdot 5$.	$\mu = \cdot 6$.	$\mu = \cdot 7$.	$\mu = \cdot 8$.	$\mu = \cdot 9$.	$\mu = 1 \cdot 0$.	Given value for solid metal.	$\mu = \frac{1}{\alpha}$.
Silver .	Blue ($\lambda = \cdot 450$)	1·7818	·08354	·561	$n\kappa$	·029	—	·406	1·57	4·57	3·52	2·92	2·59	2·387	2·386	4·126
					n	1·28	—	2·84	4·22	2·22	·667	·345	·225	·164	·164	3·877
					$n^2\kappa$	·037	—	1·15	6·62	10·15	2·34	1·01	·580	·391	—	16·00
	Green ($\lambda = \cdot 500$)	1·4431	·03326	·693	$n\kappa$	·011	·026	·099	·216	·701	6·278	4·501	3·425	2·941	2·941	11·585
					n	1·227	1·489	2·253	2·944	4·363	4·896	·672	·282	·169	·169	5·617
					$n^2\kappa$	·014	·039	·222	·635	3·058	30·737	2·990	·967	·497	—	32·537
Gold .	Blue ($\lambda = \cdot 458$)	·83957	·61410	—	$n\kappa$	·196	·403	·845	1·044	1·208	1·332	1·419	1·480	1·520	1·520	—
					n	1·120	1·216	1·278	1·236	1·160	1·065	·967	·874	·790	·790	—
					$n^2\kappa$	·216	·489	1·080	1·291	1·400	1·418	1·373	1·294	1·201	1·201	—
	Green ($\lambda = \cdot 527$)	1·67017	·56048	·599	$n\kappa$	·190	·454	1·282	1·659	1·858	1·921	1·919	1·893	1·860	1·860	1·857
					n	1·254	1·501	1·686	1·484	1·200	·971	·764	·629	·530	·530	1·203
					$n^2\kappa$	·238	·681	2·161	2·463	2·230	1·827	1·467	1·191	·9858	·9858	—

have been calculated; but the values of $n\kappa_{\mu=1}$ and $n_{\mu=1}$ used for the purpose are those given by HAGEN and RUBENS,* and are not by any means so accurate as those which MINOR has determined for silver.† The results are included in Table VII.

We return to the consideration of the transmission and reflection of light by a metallic film. We confine our present attention to films the microstructure of which is either amorphous or consists of small spheres of metal; the films in question are thus optically isotropic. Suppose that, as explained in the preceding section, the optical constants of the film are n and κ when its specific gravity is μ times that of the metal of which it is composed.

When light of wave-length λ *in vacuo* is directly incident on such a film, ot thickness d, let R_0 and T_0 denote the ratios of the intensities of the reflected and of the transmitted light to that of the incident beam. Adopting the analysis already given in the previous paper, p. 409, we suppose the film to be bounded by $z = 0$ and $z = d$, and that

Incident wave is

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

Reflected wave is

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

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

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

Transmitted wave is

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

where $c/\mathrm{V} = n\,(1-\iota\kappa)$.

We shall suppose‡ that $\pi dn\kappa/\lambda > 1$, so that we shall be correct within 2 per cent. when we neglect B′ in comparison with A′. The boundary conditions at $z = 0$, namely the continuity of the components of $\mathbf{E}$ and $\mathbf{H}$ which are parallel to the interface, then give

$$1+\mathrm{B} = \mathrm{A}'\,;\quad (1-\mathrm{B}) = c/\mathrm{V}\,.\,\mathrm{A}' = n\,(1-\iota\kappa)\,\mathrm{A}'.$$

Eliminating A′ we obtain, by taking the squares of moduli,

$$\mathrm{R}_0 \equiv |\mathrm{B}|^2 = \frac{(1-n)^2+n^2\kappa^2}{(1+n)^2+n^2\kappa^2}\quad \ldots\ldots\ldots \quad (20).$$

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* *Loc. cit.*

† *Cf.* above, § 4.

‡ *Cf.* 'Phil. Trans.,' A, 1904, p. 409.

In equation (26), on p. 409,* we have already proved that

$$T_0 \equiv |C|^2 = \frac{16n^2(1+\kappa^2)}{\{(1+n)^2+n^2\kappa^2\}^2} e^{-\frac{1}{2}\pi d n\kappa/\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (21)$$

If we write

$$M_0 = \frac{16n^2(1+\kappa^2)}{\{(1+n)^2+n^2\kappa^2\}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (22),$$

equation (21) may be written

$$T_0 = M_0\, e^{-4\pi\, d n\kappa/\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (23).$$

Equations (20) and (21) are thus correct within 2 per cent. for directly incident visible light, and for $\mu = 1$ in the case of gold if $d \geq 91\mu\mu$, or in the case of silver if $d \geq 60\mu\mu$, where $1\mu\mu \equiv 10^{-6}$ millim.

For convenience of reference the corresponding results for obliquely incident light are given below. Let θ be the angle of incidence. When the incident light is polarised in the plane of incidence, the ratios R, T of the intensities of the reflected and of the transmitted beams to that of the incident light are given by

$$R = \frac{(1-u)^2+v^2}{(1+u)^2+v^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (24),$$

$$T = \frac{16(u^2+v^2)}{\{(1+u)^2+v^2\}^2} e^{-4\pi d\frac{v\cos\theta}{\lambda}} = M e^{-4\pi d\frac{v\cos\theta}{\lambda}}, \text{ say} \quad . \quad . \quad . \quad . \quad . \qquad (25),$$

where u and v are defined by the equation

$$(u, v)\cos\theta = \frac{1}{\sqrt{2}}\left[\{(n^2\overline{\kappa^2-1}+\sin^2\theta)^2+4n^4\kappa^2\}^{\frac{1}{2}} \mp (n^2\overline{\kappa^2-1}+\sin^2\theta)\right]^{\frac{1}{2}} . \quad . \qquad (26).$$

When, however the incident light is polarised perpendicular to the plane of incidence, the corresponding ratios are given by

$$R' = \frac{(1-u')^2+v'^2}{(1+u')^2+v'^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (27),$$

$$T' = \frac{16(u'^2+v'^2)}{\{(1+u')^2+v'^2\}^2} e^{-4\pi d\frac{v\cos\theta}{\lambda}} = M' e^{-4\pi d\frac{v\cos\theta}{\lambda}} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (28),$$

where

$$u' - \iota v' = \{n(1-\iota\kappa)\}^2/(u-\iota v) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (29).$$

Putting $\theta = 0$, we obtain

$$R = R' = R_0, \quad T = T' = T_0,$$
$$u = u' = n, \quad v = v' = n\kappa.$$

It appears from equation (23) that the colour of the light transmitted by a metallic film, although principally dependent on the values of $n\kappa/\lambda$ for different values of λ, is also affected by the corresponding values of M_0. The thicker the film, however, the less important is M_0 in determining the colour.

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* 'Phil. Trans.,' A, 1904.

The values of $n\kappa/\lambda$, calculated from Table IV. of the former paper,* using however new and more accurate values in the case of silver with red light, and from Table VII. above, are shown in Table VIII. The corresponding values of M_0 are given in Table IX., in which table the values of the reflecting power R_0 have also been included.

In order to facilitate the consideration of the colours which should, according to the above analysis and calculations, be exhibited by gold and silver films when their specific gravities vary but their microstructures remain amorphous or granular (small spheres), graphs of $n\kappa/\lambda$, of M_0, and of R_0 are given in the accompanying figures (figs. 8, 9, 10, 11, 12, and 13). In these figures the abscissæ represent the volume proportion, μ, of metal, and the ordinates the value of the function. The curves have been fitted to the plots of the numerical values shown in Tables VIII. and IX. In each case the positions of the plots of calculated values have been indicated by small circles.

TABLE VIII.—Value of $n\kappa/\lambda$.

Metal.	Colour.	λ.	$\mu = \cdot 1$.	$\mu = \cdot 2$.	$\mu = \cdot 4$.	$\mu = \cdot 5$.	$\mu = \cdot 6$.	$\mu = \cdot 7$.	$\mu = \cdot 8$.	$\mu = \cdot 9$.	$\mu = 1\cdot 0$.	$\mu = \frac{1}{\alpha}$.	$\frac{1}{\alpha}$.
Gold	Blue .	·458	·420	·879	1·845	2·279	2·637	2·908	3·099	3·240	3·319	—	—
	Green .	·527	·360	·861	2·432	3·149	3·526	3·646	3·642	3·592	3·529	3·524	·599
	Yellow	·589	·046	—	—	·896	2·555	6·90	6·45	5·42	4·79	6·47	·685
	Red .	·630	·022	—	—	·381	·960	4·56	7·95	5·96	5·00	7·76	·734
Silver	Blue .	·450	·064	—	·902	3·50	10·16	7·81	6·49	5·76	5·30	9·17	·561
	Green .	·500	·022	·053	·197	·431	1·401	12·557	8·901	6·850	5·882	11·585	·693
	Yellow	·589	·008	—	—	·112	·238	·762	14·84	8·33	6·23	13·52	·791
	Red .	·630	·006	—	·046	·082	·163	·444	4·885	9·005	6·286	13·599	·822

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* 'Phil. Trans.,' A, 1904, p. 406.

TABLE IX.

$$M_0 = \frac{16n^2(1+\kappa^2)}{\{(n+1)^2+n^2\kappa^2\}^2}; \quad R_0 = \frac{(1-n)^2+n^2\kappa^2}{(1+n)^2+n^2\kappa^2}.$$

	Colour.	$\frac{1}{\alpha}$.		$\mu = \cdot 1$.	$\mu = \cdot 4$.	$\mu = \cdot 5$.	$\mu = \cdot 6$.	$\mu = \cdot 7$.	$\mu = \cdot 8$.	$\mu = \cdot 9$.	$\mu = 1\cdot 0$.	$\mu = \frac{1}{\alpha}$.
Silver	Red λ·630	·822	M_0	·985	·801	·695	·560	·380	·123	·430	·858	·087
			R_0	·007	·105	·167	·252	·385	·669	·928	·953	·792
	Yellow λ·589	·791	M_0	·984	—	·675	·529	·331	·105	·563	·972	·100
			R_0	·008	—	·179	·274	·419	·800	·930	·951	·778
	Green λ·500	·693	M_0	·979	·725	·573	·365	·184	·634	1·056	1·384	·174
			R_0	·010	·149	·245	·403	·736	·881	·916	·932	·709
	Blue λ·450	·561	M_0	·969	·592	·367	·423	·894	1·29	1·60	1·79	·308
			R_0	·016	·238	·432	·716	·824	·867	·891	·907	·620
Gold	Red λ·630	·734	M_0	·982	—	·622	·449	·247	·436	·848	1·190	·231
			R_0	·009	—	·215	·338	·576	·798	·863	·895	·666
	Yellow λ·589	·685	M_0	·979	—	·578	·406	·374	·695	1·048	1·344	·354
			R_0	·011	—	·252	·405	·626	·759	·820	·850	·595
	Green λ·527	·599	M_0	·983	·915	·996	1·138	1·308	1·478	1·637	1·779	—
			R_0	·0197	·239	·335	·421	·493	·550	·597	·634	·420
	Blue λ·458	1·191	M_0	1·006	1·078	1·129	1·196	1·276	1·363	1·454	1·544	—
			R_0	·0114	·134	·188	·242	·294	·343	·387	·427	—

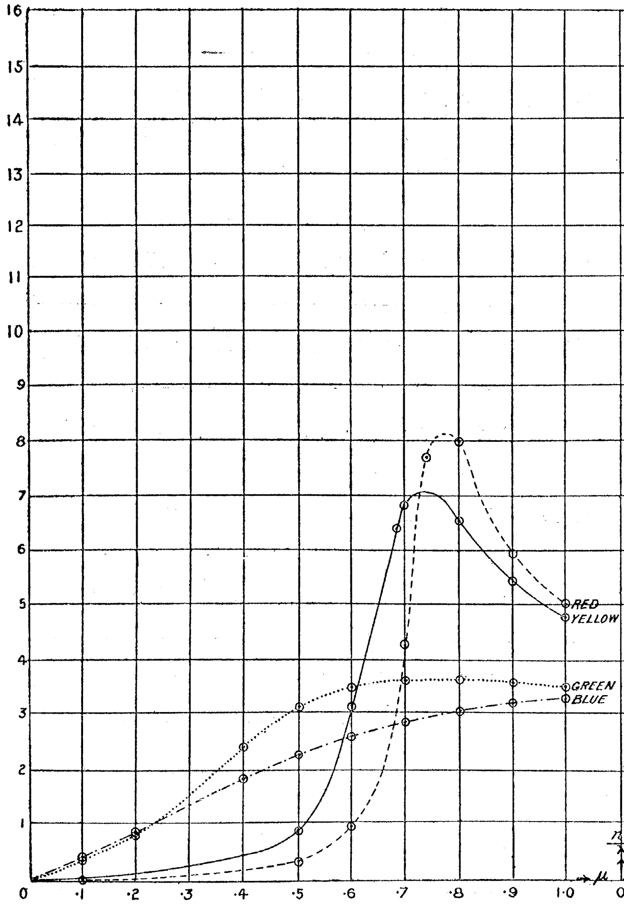

Fig. 8. Gold—$\frac{n\kappa}{\lambda}$.

Red ($\lambda = \cdot 630$): - - - - - - -

Yellow ($\lambda = \cdot 589$): ————

Green ($\lambda = \cdot 527$): . . . .

Blue ($\lambda = \cdot 458$): _ . _ . _

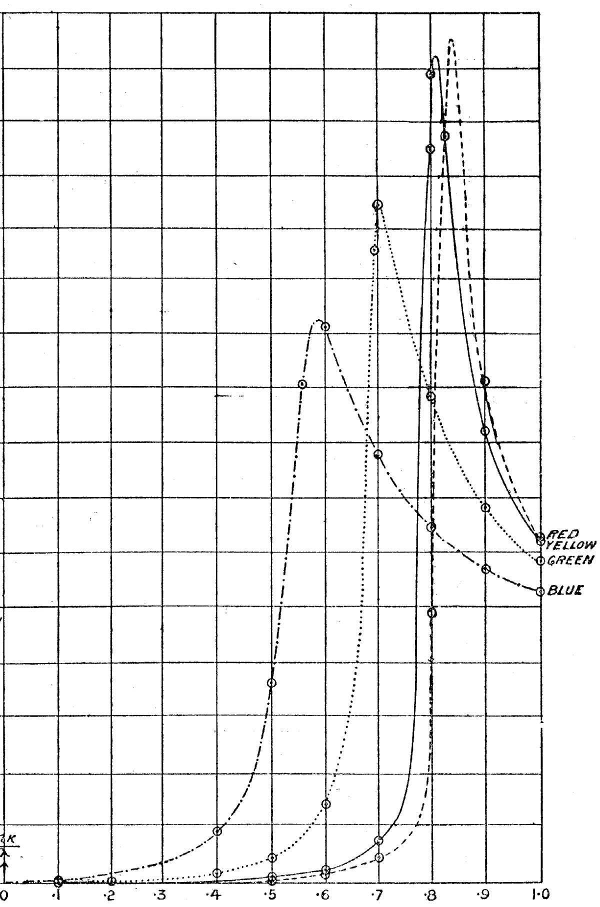

Fig. 9. Silver—$\frac{n\kappa}{\lambda}$.

Red ($\lambda = \cdot 630$): - - - - - - -

Yellow ($\lambda = \cdot 589$): ————

Green ($\lambda = \cdot 500$): . . . .

Blue ($\lambda = \cdot 450$): _ . _ . _

Fig. 10. Gold—M_0.

Red ($\lambda = \cdot 630$): -------
Yellow ($\lambda = \cdot 589$): ———
Green ($\lambda = \cdot 527$): ....
Blue ($\lambda = \cdot 458$): _._._

Fig. 11. Silver—M_0.

Red ($\lambda = \cdot 630$): -------
Yellow ($\lambda = \cdot 589$): ———
Green ($\lambda = \cdot 500$): ....
Blue ($\lambda = \cdot 450$): _._._

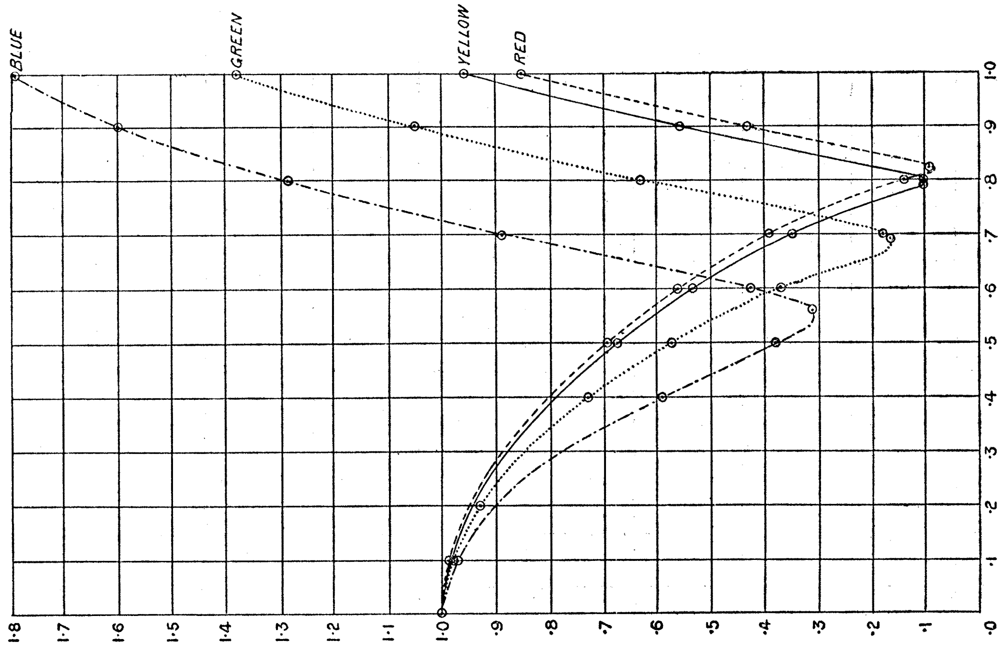

Fig. 11.

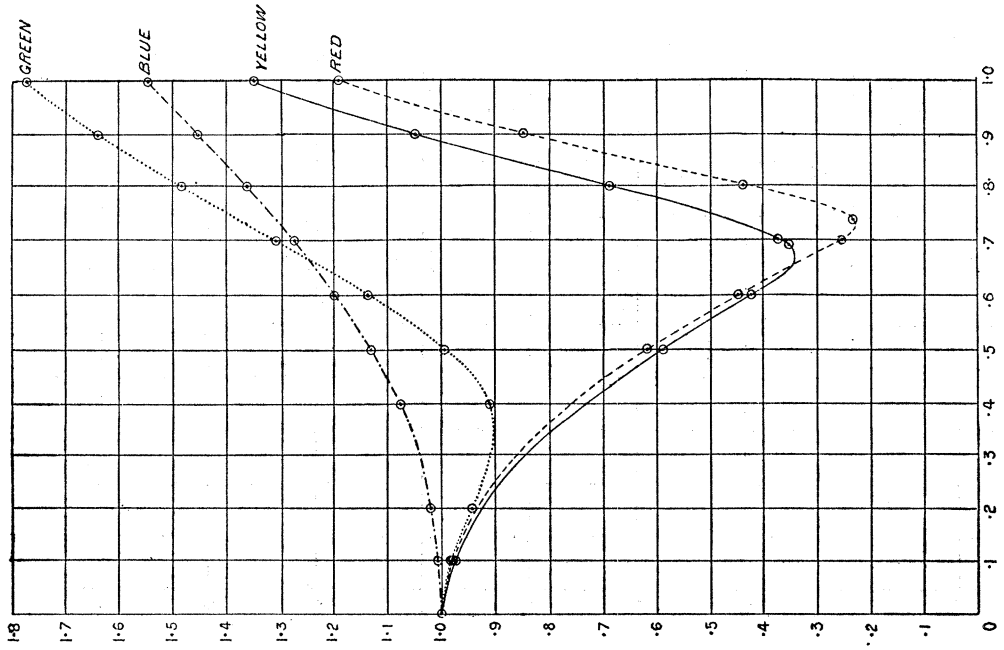

Fig. 10.

Fig. 12. Gold—R_0.

Red ($\lambda = \cdot 630$): - - - - - - -

Yellow ($\lambda = \cdot 589$): ———

Green ($\lambda = \cdot 527$): ....

Blue ($\lambda = \cdot 458$): _ . _ . _

Fig. 13. Silver—R_0.

Red ($\lambda = \cdot 630$): - - - - - - -

Yellow ($\lambda = \cdot 589$): ———

Green ($\lambda = \cdot 500$): ....

Blue ($\lambda = \cdot 450$): _ . _ . _

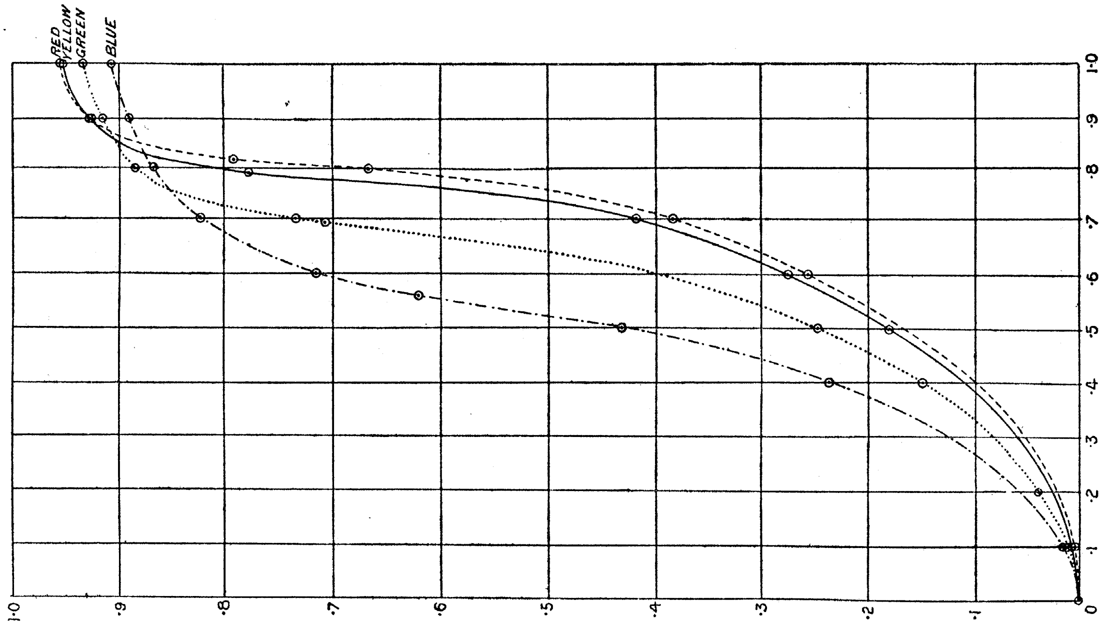

Fig. 13.

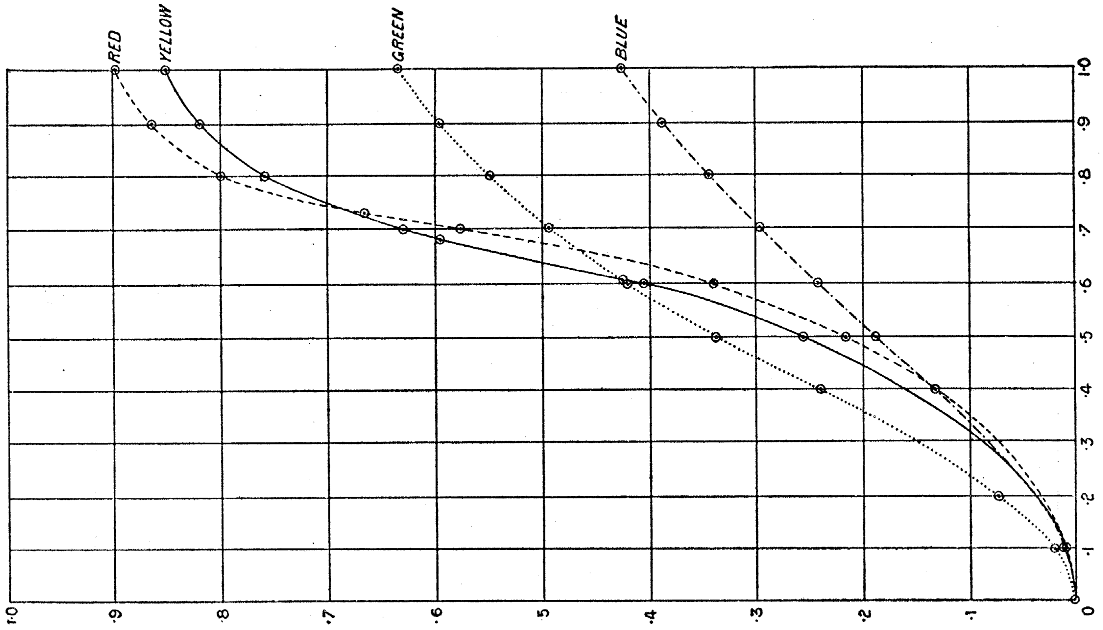

Fig. 12.

11. *Colour Changes Caused by Heating Metal Films.*

In the Bakerian Lecture* for 1857, FARADAY described a number of experiments concerning the colours which gold and other metals were, in various conditions, capable of exhibiting.

Mr. G. T. BEILBY's investigations on the colour and structure of films of metal are described in his paper on "The Surface Structure of Solids."†

The average thickness of the gold leaf which FARADAY used in his earlier experiments was about 90 $\mu\mu$.‡ Reference to p. 271 above will show that, with a probable error of 2 per cent., the optical properties of such a leaf will be subject to the analysis given in § 10 above.

Thus, for example, if we assume that, in a gold leaf as it leaves the beater, the gold is in an amorphous state, its colour by directly transmitted light is that for which T_0, as given by equation (23), namely

$$T_0 = M_0 \exp \{-4\pi d . n\kappa/\lambda\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23),$$

is a maximum. If, further, the metal has its normal specific gravity, so that $\mu = 1$, the values of $n\kappa/\lambda$ and of M_0 in this equation are those given for $\mu = 1$ in Tables VIII. and IX., or figs. 8 and 10.

Now, when $\mu = 1$, the value of $n\kappa/\lambda$ is much smaller for blue and green than for yellow and red, and is slightly smaller for blue than for green; while the value of M_0 is greater for green and blue than for yellow and red, and is considerably greater for green than for blue. Thus both the factors of T_0 in equation (23) are greater for blue and green than for yellow and red. The former colours therefore predominate in the transmitted light. Further, in very thick films, for which $n\kappa/\lambda$ is of supreme importance, blue should, in the transmitted beam, predominate over green; while in thinner films, on account of the greater value of M_0 for green than for blue, green light should be more intense.

FARADAY found that all his gold leaf appeared olive-green by transmitted light.

Again, Table IX., or fig. 12, shows that the reflecting power, R_0, is, when $\mu = 1$, much greater for red and yellow than for green and blue; and this result is again in accordance with the observed colour of gold leaf by reflected light.

FARADAY,§ however, states that gold leaf still appeared green by transmitted light when its thickness was reduced to only 10 $\mu\mu$ or 5 $\mu\mu$. Now equation (24) of the former communication,|| namely,

$$T_0 = 1 - 4\pi d . n^2\kappa/\lambda,$$

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* Reprinted from the 'Phil. Trans.' in his 'Researches in Chemistry and Physics,' p. 391. References will be made to the pages of this reprint.

† Glasgow, 1903.

‡ *Loc. cit.*, p. 394.

§ *Loc. cit.*, p. 395.

|| 'Phil. Trans.,' A, 1904, p. 408.

shows that, for a film of such thinness, the intensity T_0 of the transmitted light is greatest for red light.* This red colour has been seen both by FARADAY† and by BEILBY‡ in parts of their green films. FARADAY says the red colour was extremely faint but appeared to have an objective reality, while BEILBY describes the effect as that of "an irregular film of pink jelly."

It appears that extremely thin films of gold are, by surface tension, drawn up into green patches, leaving larger areas covered by an almost transparent, but faintly red, film. The effect on the unaided eye is that of a transparent green.

The silver leaf used by BEILBY was over 300 $\mu\mu$ thick. It therefore comes well inside the range for which the analysis of § 10 applies. Now Table VIII., or fig. 9, shows that, for amorphous silver of normal specific gravity ($\mu = 1$), $n\kappa/\lambda$ is least for the more refrangible rays. Again, Table IX., or fig. 11, shows that, for $\mu = 1$, M_0 is greatest for the same rays. It follows therefore, from equation (23) above, that, on both these accounts, the light transmitted by silver leaf should be *blue;* and, in fact, silver leaf transmits a deep blue light. The approximately equal values of the reflecting power, R_0, shown in Table IX., or fig. 13, for $\mu = 1$, correspond to the almost colourless reflection from polished normal silver.

Consider now the colour changes which, according to figs. 8 to 13, deduced from the calculations of § 10, should accompany a diminution in the density of gold and silver films from its normal value ($\mu = 1$) to zero ($\mu = 0$). This diminution of density may be conceived either as an increase of the distance between adjacent molecules or as due to the aggregation of groups of neighbouring molecules into small spheres. For geometrical considerations show that so soon as two spheres form adjacent to one another in an otherwise amorphous mass of metal, the density of the mass must begin to diminish. And it has been shown that the calculations in question are applicable whether the metal is in small spheres or in an amorphous state, and thus when it is partly in the one condition and partly in the other.

Taking first the case of gold, it appears from figs. 8 and 10, in conjunction with equation (23), that, as μ begins to diminish from unity, the absorptions of red and yellow light increase rapidly, owing both to the increase of $n\kappa/\lambda$ and to the decrease in M_0. Meanwhile, owing to the decrease of the ratio of M_0 (green) to M_0 (blue) and to the increase of $(n\kappa/\lambda)$ (green)$-(n\kappa/\lambda)$ (blue), the relative intensity of green to blue in the transmitted beam diminishes. Thus the first effect is to make the transmitted light bluer, and this effect continues until $\mu =$ about ·75. As μ continues to diminish below this value, the absorption of red rapidly decreases until, at $\mu =$ ·68, in a very thick film,§ the absorption of red has become as small as that of blue. The film is

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* *Cf.* Table IV., p. 406 of former paper, and Table VIII. above.

† *Loc. cit.*, p. 400.

‡ *Loc. cit.*, p. 40.

§ When $\exp(-4\pi d \,.\, n\kappa/\lambda)$ is the dominating factor in T_0. The corresponding value of μ is less in thinner films for which M_0 is very important.

then purple. As μ still further diminishes, the relative absorption of red continues to become small, so that the film becomes pink. Finally, at $\mu = 0$, the absorption of green is less than that of blue, and the colour has changed from pink to red.* It is further seen, from fig. 12, that the reflecting power R_0 has, as μ began to diminish, become more yellow. At $\mu = {\cdot}60$, when the colour of T_0 is still purple or pink, the colour of R_0 has become green; and thenceforward R_0 remains green as μ diminishes from ·6 to zero.

Similar consideration of figs. 9 and 11 shows that in the case of silver, as μ begins to diminish from unity, the colour by transmitted light becomes at first bluer, then changes to purple in the neighbourhood of $\mu = {\cdot}8$, and thence, through pink, to red or "amber" as μ further diminishes to $\mu = 0$. In fact, it appears from the four colours for which calculations have been made, that there is, for any value of μ, a well-defined absorption band at some position in the (visible or invisible) spectrum, and that, as μ diminishes, the position of this absorption band moves from the infra-red through the visible spectrum towards the shorter wave-lengths, being at $\lambda = {\cdot}630$ for $\mu =$ about ·83, at $\lambda = {\cdot}589$ for $\mu =$ about ·80, at $\lambda = {\cdot}500$ for $\mu =$ about ·69, and at $\lambda = {\cdot}450$ for $\mu =$ about ·55. Fig. 13 shows that the colour of the reflected light becomes distinctly blue at about $\mu = {\cdot}75$, and remains blue down to $\mu = 0$.

With a view to determining what may be the explanation of the colours and changes of colour exhibited by gold and silver films, we have now to compare the latter colours with those which we have found above to be consequent upon a mere isotropic change in density.

Beilby† has prepared gold films by using paints in which "the metal had been brought into solution in an essential oil." Having smoothly coated a plate of glass or mica with the paint, he heated it to a temperature of about 400°, thereby driving off the oil and other volatile constituents. A film of pure gold with full metallic reflection, and transmitting green light, is left adhering to the glass.

When these films are kept at a high temperature for some time, they change colour. By transmitted light, the original olive-green colour becomes at first bluer, then changes to purple, in which, as the annealing process is still continued, the red predominates more and more over the blue, until finally the purple has given place to pink. The reflecting power of the film has, meanwhile, diminished. But the colour of the light reflected from the blue films remains yellow, while the pink films reflect a green colour. I have before me a gold film prepared in this way and subjected to lengthy annealing. By transmitted light it appears striated with pink and blue bands. By reflected light the blue striæ become golden, but the pink striæ green. Under the microscope the film appears continuous, and is quite thick.

These colour changes, both with transmitted and with reflected light, are just

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* Or *yellow*, if the colour is faint. See the second footnote on p. 243 above.

† *Loc. cit.*, p. 40.

those which have been shown above to be consequent upon a continuous diminution in the density of a gold film, which throughout remains either amorphous or "granular" (*i.e.*, possessing a microstructure of small spheres). The view that the film is initially amorphous or granular, and that heating diminishes its density, is supported, as has already been pointed out,[*] by the fact that the curves in figs. 8 and 10 show that the absorption of light increases rapidly as μ begins to diminish from unity, while BEILBY'S films exhibited just such an increase of absorptive power when first heated. This view is also in accordance with the loosening of structure which is suggested by the great decrease in electric conductivity which accompanies heating. But direct evidence of the correctness of the view that heating produces decrease in density is not wanting, for BEILBY[†] has estimated the thickness of a film which had been annealed to the purple stage. He found, by weighing the gold from a given area, that, had the density of the gold been then normal ($\mu = 1$), the film would have been $160\mu\mu$ thick, whereas, under the microscope, the thickness seemed to be much greater than this. The density of the gold in the purple film thus appeared to be less than in the normal green films.

We conclude, therefore, that (*a*) *the films, as first prepared, are amorphous or granular* in structure; and (*b*) *heating diminishes the density of the film, while pressure is able to increase the density again.*[‡]

Further, BEILBY found[†] that, when the heating of a film was continued after it had reached the purple stage, "the film assumes a frosted appearance by reflected light and becomes paler by transmitted light." The frosted surface appeared, under the microscope, to consist of granules at least $100\mu\mu$ in diameter. This phenomenon suggests that in the earlier stages of annealing, smaller granules were formed, which, as annealing proceeded, ran together to form larger granules: and the formation of such minute granules, while, according to our analysis, it does not affect the optical continuity of the film, will explain the diminution in density which occurs on heating. It is, therefore, most probable that (*c*) *the diminution in density produced by heating is effected by the passage of metal from the amorphous to the granular phase and the growth of the larger granules at the expense of the smaller; and the increase in density produced by pressure may be accompanied by the passage of metal from the granular to the amorphous phase.*[§]

The optical properties of the films of gold which FARADAY produced by reducing that metal from its solution by means of phosphorus, tend to show that these films are composed of amorphous or granular gold of density less than the normal. The films appeared to consist of pure gold;[||] when first prepared the films appeared of a grey

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[*] 'Phil. Trans.,' A, 1904, p. 415.

[†] *Loc. cit.*, p. 41.

[‡] *Cf.* the effect of pressure on FARADAY'S "phosphorous" films after heating—see next page.

[§] [*Note added* 31*st August*, 1905.—Subsequent analysis has, however, shown that a sufficient flattening of the granules would cause the colours of the standard metal ($\mu = 1$) to be exhibited.]

[||] FARADAY, *loc. cit.*, p. 408.

colour, which was frequently resolvable into a mixture of green and amethystine striæ. These colours would be shown by an amorphous or granular film for which the density was in parts as low as $\mu = \cdot 7$. Moreover, such a structure agrees with the fact that "the films did not sensibly conduct electricity" and that "the films cannot be regarded as continuous."[*] FARADAY further states[†] that, though they are certainly porous to gas and to water-vapour, the films have evident optical continuity.

Heating diminished the conducting power and changed the colour to amethyst or ruby, just as with BEILBY'S films, pressure, which we should expect to increase the density of the film, changed the transmitted colour to green and increased the reflecting power; and these are precisely the changes which would, according to calculation, accompany an increase in μ to the neighbourhood of unity in the case of an amorphous or granular film.

Closely allied to these phosphorous films are the deposits of gold on glass which FARADAY[‡] obtained "by deflagrating a gold wire by explosions of a Leyden battery." "There is no reason to doubt that these deposits consisted of metallic gold in a state of extreme division." This method of preparing these deposits is similar to BREDIG'S[§] method of obtaining suspensions of gold in water; it is, therefore, to be expected that the deposits consist of small spheres of gold together with some large crystallites. The films were so discontinuous as to be unable to conduct electricity;[||] but they were such as to present an optical continuity.[¶] FARADAY sums up their colour changes as follows:—

> "Fine gold particles, loosely deposited, can in one state transmit light of a *blue-grey* colour [μ = about $\cdot 8$], or can by heat be made to transmit light of a *ruby* colour [$\mu < \cdot 7$], or can by pressure from either of the former states be made to transmit light of a *green* colour,[**] all these changes being due to modifications of gold as gold and independent of the presence of the bodies on which for the time the gold is supported."

It appears, therefore, that the conclusions (*a*), (*b*), (*c*), arrived at on p. 280 for BEILBY'S films, are also applicable to FARADAY'S "phosphorous" films and to FARADAY'S "deflagration" films.

One more experiment of FARADAY'S[††] on coloured gold deposits remains to be noticed. When a drop of solution of chloride of gold is evaporated in a watch-glass until the gold is reduced, a portion of the gold is generally found to have been carried by the vapour on to the neighbouring part of the glass. This part has the ruby tint; and we have seen that a ruby tint is characteristic of the light transmitted by

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[*] *Loc. cit.*, p. 407.

[†] *Loc. cit.*, p. 439.

[‡] *Loc. cit.*, p. 401.

[§] *Cf.* above, p. 252, and footnote, p. 255.

[||] *Loc. cit.*, p. 402.

[¶] *Loc. cit.*, p. 439.

[**] Probably $\mu = 1$ nearly; but see fourth footnote on p. 280, above.

[††] *Loc. cit.*, p. 428.

amorphous or granular gold, the density of which is in the neighbourhood of ·6 of that of normal gold.

The similarity of this method of preparing a metallic film with $\mu < 1$ to that by which Professor R. W. Wood prepared the sodium and potassium films, described in § 12 of the former communication,* is deserving of notice, and, from a different standpoint, tends to confirm the view there expressed as to the physical nature and structure of Professor Wood's films.

The conclusions (*a*), (*b*), (*c*) arrived at above (p. 280) as to the effect of heat and pressure on metallic films do not apply only to gold, as the following observations on silver films show. Faraday† obtained silver films by reducing silver from a solution of the nitrate. The thinner parts of these films transmitted light of a "warm brown or sepia tint [$\mu < \cdot 8$]. Pressure brought out the full metallic lustre and converts the colour from brown [$\mu < \cdot 8$] to blue [$\mu > \cdot 8$]." The behaviour of these films corresponds to that of the gold films obtained with phosphorus. Again, R. W. Wood‡ prepared films by chemically depositing silver on glass. These films, as originally prepared, show the same reddish-brown colour by transmitted light, and have a good blue-green reflection. It has been shown above that both these colours are characteristic of amorphous or granular silver, for which μ is appreciably less than ·8. These films showed no electrical conductivity; § so that, as in the case of Beilby's gold films,‖ the evidence of a loose structure afforded by the colours exhibited is confirmed by the evidence from conductivity.

12. *The Exceptional Case of Beaten Metal Leaf.*

There is one class of metallic film which, when heated, does not exhibit the colour changes that, according to our calculations, correspond to a *gradual* diminution in the density of the film. To such films the conclusions (*a*), (*b*), (*c*) of p. 280 do not directly apply. Instead of being obtained from finely divided metal by chemical deposition, deflagration, &c., the films in question are prepared by beating sheets of the solid metal into thin leaves.

Faraday¶ observed that heat caused gold leaf to lose its olive-green colour and silver leaf to lose its deep blue colour, the films at the same time becoming more

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* *Loc. cit.*, p. 412.

† *Loc. cit.*, p. 409.

‡ 'Phil. Mag.,' August, 1903. The silver was prepared by the method of Carey Lea ('Amer. Journ. of Sc.,' 1889). A further memoir on Wood's silver films is now in course of preparation.

§ *Cf.* Barus and Schneider, 'Zeitschr. f. Phys. Chem.,' VIII., p. 285, 1891, who attempted to measure the conductivity of a silver film prepared by Carey Lea's method, and found that, so soon as a drop of the silver suspension dried, so that the charged particles of silver could no longer move about, the conductivity of the drop vanished.

‖ See above, p. 280.

¶ *Loc. cit.*, p. 395 *et seq.*

transparent and tending to shrink during the process.* Thus a silver leaf which before heating was opaque, or only able to transmit deep blue light, and that very feebly, was so altered by heating that the light of a candle could be seen through forty thicknesses.† But in every case the original colour of the leaf, whether of gold or of silver, returns when the leaf is subjected to pressure.

The differences between the effect of heat on chemically prepared films and on beaten leaf correspond to differences between the laminated† structure of the leaf and "the closer and more horn-like texture of the films deposited by chemical agents."‡

The optical properties of a laminated metal leaf may be estimated and compared with the corresponding properties of an amorphous or granular film of the same metal, if the optical constants of a plate built up of a number of flat spheroids§ with their polar axes normal to the plate can be calculated. The general problem of the transmission of electromagnetic waves by a medium composed of a number of minute similar and similarly situated ellipsoids, distributed at random many to a wave-length, has now been solved, and it is hoped that the discussion of the optical properties of gold and silver leaf, of the change in those properties which is produced by heat, and of the relations of metal films (spheroidal, granular, and amorphous) to polarised light, may form the subject of a future memoir.

With these exceptions, namely, the properties peculiar to beaten leaf and the relations of metal films to polarised light, all the experimental relations of gold (and other metals) to light, which FARADAY described in his Bakerian Lecture have now been discussed, and we are led to the conclusion that the phenomena exhibited—whether by chemically or electrically deposited films, or by particles of gold diffused in glass, jelly, or water—are due to different groupings of the metal molecules and to variations in the mean distance between adjacent molecules, and in no case are they due to allotropic modifications of the molecules themselves.

13. CAREY LEA'S "*Allotropic*" *Silver.*

In the former communication‖ it was suggested that CAREY LEA'S "allotropic" silver was in reality only finely divided silver, the division being sufficiently fine to admit of the films being optically continuous.¶ He advances** two principal arguments

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* *Loc. cit.*, p. 396.

† FARADAY, *loc. cit.*, p. 399.

‡ BEILBY, *loc. cit.*, p. 43. The difference in structure is shown by the fact that while mercury will diffuse slowly and uniformly in the compact film, in the leaf thin streams of mercury may be seen shooting rapidly in all directions.

§ BEILBY (*loc. cit.*, pp. 48 *et seq.*) has shown that a layer of exceedingly flat spheroids is generally found on the surface of a metal.

‖ 'Phil. Trans.,' A, 1904, p. 419.

¶ It is not necessary to suppose the microstructure of the finely divided silver to be granular, as was done in the former paper. It may be in part granular and in part amorphous.

** *Vide* 'Amer. Journal of Science,' 1889, and 'British Journal of Photography,' March, 1901. Also 'Phil. Mag.,' vols. 31, 32 (1891).

for the allotropy of silver in the form in which he prepared the metal. We proceed to examine these arguments.

In the first place, then, all CAREY LEA's silver films were prepared from silver suspensions. He claims that these suspensions were "true solutions," and that the ability of the silver to remain in solution in water was evidence that the molecules of the silver in question differed from those of normal silver, or, in other words, the silver was in an allotropic form. We are now, however, familiar with the fact that particles of normal silver, as of many other metals, are able, in consequence of mutual electrostatic repulsions,* to keep themselves in suspension in quite pure water. Again, we have seen that, when a silver solution is prepared by BREDIG's method, its refractive index is that which is possessed by a suspension of small spheres, but not of molecules, of silver in water,† and in the same case there is a strong absorption band at exactly that point of the spectrum at which small spheres, but not molecules, of silver in water would produce a maximum;‡ so that in this case the greater part of the silver is certainly present in the form of small spheres. Further, if, when prepared by deflagration, silver in suspension in water takes the small sphere form, it is *primâ facie* probable that it does the same when obtained by CAREY LEA's method,§ and this probability is increased by the fact that CAREY LEA's silver suspensions exhibited the same red, yellowish-red, and yellow colours which are shown by BREDIG's suspensions of different densities.

We conclude that CAREY LEA's "solutions of allotropic silver" consisted of small spheres of normal silver in suspension.||

We should therefore expect that the films obtained by CAREY LEA would be similar in constitution and behaviour to BEILBY's "gold paint" films¶ and to FARADAY's phosphorous films.** This leads us to CAREY LEA's second argument for the allotropy of his silver; he states:—

> "The brittleness of the substances B and C [blue and gold coloured respectively, by reflected light], the facility with which they can be reduced to the finest powder makes a striking point of difference between allotropic and normal silver. It is probable that normal silver, precipitated in fine powder and set aside moist to dry gradually may cohere into brittle lumps, but there would be mere aggregations of discontinuous material. With allotropic silver the case is very different, the particles dry in optical contact with each other, the surfaces are brilliant, and the material evidently continuous. That this should be brittle indicates a totally different state of molecular constitution from that of normal silver."††

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[*] See footnote p. 253 above.

[†] See above, p. 258.

[‡] See above, p. 257.

[§] Above p. 259.
Cf. also the fact that the silver in a silver-stained glass is in the form of small spheres.

[||] *Cf.* also evidence given on p. 259 above.

[¶] See above, p. 279.

[**] See above, p. 281. This expectation is verified by a further examination of WOOD's films. See note above p. 282.

[††] 'Brit. Jour. Phot.,' March 1901, p. 21.

All these properties are shared by FARADAY'S "phosphorous" gold,[*] so that our expectation is, so far, fulfilled. We are, in fact, perfectly familiar with "mere aggregations of discontinuous material" which are optically continuous—for example, gold ruby glass.

Many of the observations which CAREY LEA has recorded on the colours of his silver films are in accordance with the expectation that these films, like BEILBY'S gold films and FARADAY'S "phosphorous" gold, should behave according to the laws (*a*), (*b*), and (*c*) stated above. But two difficulties arise in the way of this accordance, for, in the first place CAREY LEA'S recorded observations do not sufficiently distinguish between transmitted and reflected light. For example he records[†] that his freely precipitated silver dissolves to a blood-red colour, and proceeds

> "When the substance is brushed over paper and dried rapidly it exhibits a beautiful succession of colours. At the moment of applying it it appears blood red[‡]; when half dry it has a splendid blue colour and lustrous metallic reflection;[§] when quite dry this metallic effect disappears and the colour is matt blue."[||]

Lastly, in the case of the films discussed in § 11 above, the colour depended on the fact that the density of the film was less than that of the metal composing the film when in its normal state; but pressure increased the density to its normal value, at the same time bringing out the normal colour, both by reflected and by transmitted light, of the metal. And CAREY LEA'S silvers "show a lower specific gravity than that of normal silver;"[¶] and pressure "instantly converted gold-coloured allotropic silver into normal silver."[**]

We conclude from the above evidence that this silver was not "allotropic," but consisted of normal silver in a finely divided state.

14. HERMANN VOGEL'S *Silver*.

Before leaving the consideration of these discontinuous forms of silver, reference must be made to a paper by HERMANN VOGEL,[††] in which the author describes how

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[*] "The least touch of the finger removed the film of gold. . . . These films, though they are certainly porous to gas . . . . have evident optical continuity" (FARADAY, *loc. cit.*, p. 439). *Cf.* also the facts that films analogous to CAREY LEA'S did not conduct (BARUS and SCHNEIDER, *loc. cit.*, p. 285), and that the phosphorous films did not sensibly conduct electricity (FARADAY, *loc. cit.*, p. 407).

[†] 'Brit. Journ. Phot.,' March, 1901, p. 19.

[‡] This is the colour by transmitted light when μ is fairly small. *Cf.* figs. 9 and 11.

[§] This is the reflected colour for values of μ from zero to nearly $\cdot 8$. *Cf.* fig. 13.

[||] Professor R. W. WOOD repeated this experiment, using glass instead of paper to support the silver film. The metallic effect, then, does not disappear, but remains after the film has become quite dry. *Cf.* above, p. 282.

[¶] 'Brit. Journ. Phot.,' March, 1901, p. 21.

[**] 'Phil. Mag.,' vol. 31, p. 244, 1891.

[††] 'Pogg. Ann.,' CXVII., p. 316, 1861.

he prepared silver of less specific gravity than that of normal silver, by depositing that metal on the platinum electrode of a platinum-zinc battery. He also prepared silver in suspension in water by chemical means, observing the characteristic amber colour and noticing that precipitation could be accelerated by the addition of salt to the water.

VOGEL concludes (*loc. cit.*, p. 337) that there are three forms of silver, (1) regular dendritic silver [crystalline]; (2) granular powdery silver [small spheres]; (3) mirror silver [amorphous]. He found that the second type "tended to the formation of a coloured powder," but could be changed into the third type by pressure. He adds (*loc. cit.*, p. 441) that the silver precipitated by photography is of the second type, and this is the view suggested in the preceding memoir (p. 417), because of the red-brown transmitted colour and the green colour of the reflection from fogged photographic films, which, according to the analysis given above, § 10, are the colours exhibited by films of amorphous or granular silver,* of less than standard density.

15. *Allotropic Forms of Metal.*

In the course of the preceding investigations we have been led to recognise that variation of the relative position of the molecules of a metal will cause the metal to change colour, whether it be examined by reflected or by transmitted light. It has been shown, for example, that mere variation in density causes gold in one state to transmit green light, in another blue, in another purple, and, in another again, ruby. Further, this discovery has led us to the conclusion† that, in order to account for the properties of CAREY LEA's anomalous silvers, it is not necessary to assume the existence of an "allotropic" molecule of silver. The question thus arises: Are there any other cases in which an allotropic molecule has been unnecessarily postulated?

ROBERTS-AUSTEN‡ has collected particulars of a large number of supposed cases of allotropic§ states of metals. We proceed to the examination of these particulars in order to determine whether the effects, for the explanation of which the allotropic molecule was postulated, are not merely those which, according to the analysis of § 10 above, would be due to a decrease in the density of the metal in a granular or amorphous state.

In the first place, then, the discovery that metals in different states, corresponding to different methods of preparation, possessed different densities and had widely different properties, although chemical analysis could detect no change in the

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* *Cf.* figs. 9, 11 and 13, and also p. 282 above, where the same colours, exhibited by one of R. W. WOOD's silver films, are discussed.

† Above, p. 285.

‡ 'Metallurgy,' pp. 87 *et seq.*

§ ROBERTS-AUSTEN defines "allotropy" as follows (*loc. cit.*, p. 89): "The occurrence of elements in . . . . allotropic states means that . . . . the atoms are differently arranged in the molecules."

composition,[*] does not require those different states to have been allotropic. Again, it is unnecessary to suppose that BOLLEY'S lead,[†] prepared by electrolysis, and similar in composition to sheet-lead, is allotropic because it oxidises rapidly in air while sheet-lead does not: for the electrolysis gives the essential fine division, and the consequent large amount of surface exposed to the air greatly accelerates oxidation.

Lastly, SCHÜTZENBERGER[‡] supposed that the copper deposited on the platinum electrode of a copper-platinum cell was allotropic because it was very fragile, its density was only about ·9 of that of normal copper, it oxidised rapidly in air, and it could be converted into normal copper by prolonged contact with dilute sulphuric acid. Here, too, the supposition of allotropy is not required to account for the facts. For the low density, the fragility and the rapid oxidation are all accounted for by the loose structure which we should expect in such a deposit of copper, while CAREY LEA found that his silvers, which, if our conclusion at p. 285 is correct, were only finely divided silver, could be transformed to normal silver by contact with sulphuric acid. Similar remarks apply to SCHÜTZENBERGER'S silver.[‡]

Consider now MATTHIESSEN'S important generalisation,[§] that metals may sustain change in their molecular condition by union with each other in a fused state. ROBERTS-AUSTEN points out[||] that the evidence that metals ever assume allotropic states, when they enter into union with each other, is difficult to obtain. When obtained, the evidence is generally composed of the facts that the specific gravity of the normal metal is greater than that of the metal in the state alleged to be allotropic; that the chemical activity is less in amount, although the same in kind, for the former than for the latter state; and that the appearance of the metal is different in the two states. Reference is also sometimes made to a difference in physical properties which is accounted for by lack of continuity, and consequently of electric conductivity, in the supposed allotropic state.[¶] Occasional reference is also made to a readiness to form hydrates which the metal in the latter state exhibits. Setting this last property aside, as not yet established, the remaining evidence is not conclusive, for all the facts in question are also characteristic of optically continuous granular (or amorphous) pieces of metal. Increase of chemical activity, for example, is a consequence of the enormous effective surface in a medium built up of independent granules.

Further, when one metal is united with another in a fused state, a chemical compound is not, in general, formed, but the molecules of the two metals freely mix. Thus one metal is in solution in the other. So long, therefore, as the temperature remains sufficiently high to permit the molecules to move about freely, the molecules of each metal tend to segregate, and to group themselves into separate crystals as the

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[*] JOULE and LYON PLAYFAIR, 'Memoirs of the Chem. Soc.,' vol. iii., p. 57 (1846).

[†] ROBERTS-AUSTEN, *loc. cit.*, p. 90.

[‡] 'Bull. Soc. Chim.,' XXX., p. 3 (1878).

[§] ROBERTS AUSTEN, *loc. cit.*, p. 87.

[||] *Loc. cit.*, p. 91.

[¶] *Cf.* PETERSEN on "Allotropic Forms of Metals" ('Zeitschr. f. Phys. Chem.,' 8, pp. 601, 1891).

temperature is slowly lowered. It is, however, probable that, as in the case of gold and copper ruby glasses, the molecules of each metal first group themselves into small spheres. If the temperature were rapidly lowered at this stage, this granular structure would be fixed in the alloy. If, then, one metal—that, suppose, of which the larger volume is present—were suddenly annihilated, the other metal would remain in a granular form, possessing a colour* quite different from that exhibited by the normal form of that metal.

Now when an alloy of potassium and gold containing about 10 per cent. of the precious metal is thrown on to water, the potassium is, in effect, annihilated,† and the gold is released as a black or dark brown powder. It will be seen from fig. 12 that granular gold, with a density slightly over ·6 of that of normal gold, would reflect light of a brown colour, while the reflecting power would not exceed ·5. A granular structure is thus in accordance with the dull appearance and with the colour of the powder. Similarly when a silver-gold alloy containing two parts of silver to one of gold is treated with nitric acid the silver is removed, the gold remaining in the form of a dull brown powder, which can be converted into bright metallic gold by slight pressure or by heating to redness. It appears, therefore, that this brown powder is probably granular gold, the component particles being small compared with a wave-length of light; so that, once more, the evidence‡ does not require us to suppose this form of gold to be allotropic.

Finally, it seems unnecessary to assert that iron released from its amalgam by distilling away the mercury is in an allotropic form because it takes fire on exposure to the air. For this burning of the iron would be the consequence of the large surface exposed to the air by an extremely finely divided form of the metal.

We conclude, therefore, that in none of the cases of supposed allotropy, which we have examined in this section, has the existence of an allotropic form of metal been established.

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* See § 10 above.

† *Cf.* ROBERTS-AUSTEN, *loc. cit.*, p. 91. The potassium does not catch fire, but combines with the water to form KHO (which immediately passes into solution and is thus removed) and H which catches fire.

‡ We must except that of the alleged formation of auric hydrate, but I have been unable to obtain any confirmation of the existence of such a compound.