THE
PHYSICAL REVIEW.

COLLOIDAL SOLUTIONS, AND THE REFRACTIVE
INDICES OF GOLD, PLATINUM AND SILVER.

BY B. J. SPENCE.

INTRODUCTION.

DURING the last few decades, there have appeared from time to time articles dealing with the question of the optical properties of turbid media.

It will be seen from the brief abstracts of these papers which form the introduction to the present article, that the theoretical conclusions at which the various writers arrive seem to indicate that the transmission of light by a turbid medium should be a simple function of the period of the light.

The theories have been tested in a number of instances in the somewhat narrow range of wave-lengths comprising the visible spectrum, with the result that while some investigators have found agreement between theory and experiment, others have reported disagreement.

The object of the present investigation has been to supplement the existing data obtained in the visible spectrum by extending the field of investigation as far as possible into the infra-red region of the spectrum.

The pioneer work of a theoretical character is due to Lord Rayleigh,¹ who deduced an expression for the light transmitted through an atmosphere containing small insulating particles in suspension. This was shown to depend on the number and size of

¹ Phil. Mag., XLI., 107, 1871; XII., 81, 1881.

the particles suspended in unit volume of the supporting medium. Lord Rayleigh¹ again took up the subject later, developing it more completely and obtained an expression for the energy transmitted as a function of the wave-length, index of refraction of the suspended particle, and the number of particles per unit volume, assuming that the particles were insulators and spherical in shape. The following formula is given by Lord Rayleigh

$$H = \frac{32\pi^3(\mu - 1)^2}{3N\lambda^4}$$

where H is given by the formula

$$E = E_0 e^{-Hd}.$$

In these expressions μ represents the refractive index of the suspended particle, N the number of particles per unit volume, d the thickness of the layer, E_0 and E are the incident and transmitted energies respectively. The first equation leads to the important deduction that the absorption varies as the λ^{-4} , and the correctness of the theory in this respect may be readily determined, after H has been experimentally found for the various wave-lengths for the given turbid medium.

Lord Rayleigh has also found that light scattered by these insulating particles, and produced by the incidence of plane polarized light, vanishes at all points in a plane normal to the magnetic induction, where the radius vector makes an angle of 90° with the direction of the incident light.

The theory to explain the transmission of light by solutions or atmospheres composed of conducting particles has been developed by J. J. Thomson,² who finds that the scattered light produced by the incidence of plane polarized light, vanishes in a plane through the center at right angles to the magnetic induction in the incident wave, along a line making an angle of 120° with the radius to the point at which the wave first strikes the sphere, and it does not vanish in any other direction than this. This is quite a different conclusion from that arrived at by Lord Rayleigh in his analysis for insulating particles.

¹ Phil. Mag., XXXXVII., 375, 1889.

² Recent Researches, p. 437.

Ehrenhaft¹ undertook an experimental test of Thomson's theory for media containing metallic particles in suspension, commonly known as colloidal solutions. For colloidal solutions of gold, silver, platinum and copper, he found the maximum of polarization to be at angles of 118° , 110° , 115° and 120° respectively with the incident energy. He also found that the amount of polarization varied directly as the amount of metal per unit volume of the supporting medium.

Ehrenhaft in his investigation found that the colloidal solutions which he examined possessed strong absorption bands in the visible spectrum. The absorption band of gold colloid occurred at a wave-length of 5.2×10^{-5} cm., that of platinum at 4.8×10^{-5} cm., and that of silver at a wave-length 3.8×10^{-5} cm. According to Thomson it is possible from the position of these bands, due to optical resonance, to compute the order of magnitude of the size of the suspended particles.

Let t represent the period of vibration of the particle, v the velocity of propagation of the disturbance, and a the radius of the metal sphere, then

$$t = \frac{4\pi a}{\sqrt{3}v}.$$

If n be the refractive index of the supporting medium, then $v = n/\lambda$ so that

$$a = \frac{\sqrt{3} \lambda}{4\pi n}.$$

From the values of the wave-lengths at which resonance takes place, Ehrenhaft computed the size of the particles to be of the order of magnitude of 40×10^{-7} cm., and this magnitude falls within the limits assigned to it by Thomson.

Another piece of experimental work, similar to that of Ehrenhaft, is that of Müller,² who found the azimuth of polarization for platinum, silver and gold colloids to be 112° , 97.5° , 125° , respectively, and that for a medium consisting of insulating particles, the azimuth of polarization was less than 90° . These values for colloidal solu-

¹ Sitz. ber. Akad., Wiss. Wien, 112, 11a., 1903.

² Ann. der Physik, 24, 1, 1907.

tions of platinum, silver and gold do not accord with the results of Ehrenhaft, who found a better agreement between the experimental and theoretical values. Müller's results afford no explanation of the optical properties of colloidal solutions based on the size of the particles.

More recently Mie¹ has published a paper which deals with the turbid media, based on the assumption that the particles may be regarded as spherical in shape, and that the turbidity is infinitely thin, in an optical sense. The light emitted by a particle may be calculated as a series of partial waves of which there are two groups, corresponding respectively to the electric and magnetic vibrations of the particles. In a colloidal solution consisting of very small particles the first harmonic is small, and corresponds to the formula of Lord Rayleigh, which was previously discussed. For coarser particles other electric and magnetic harmonics appear.

Mie also found from theoretical considerations that the unpolarized ray on passing through a medium should be linearly and partially polarized. The light diffused by gold particles up to a size of 1×10^{-5} cm. consists entirely of radiation corresponding to the Rayleigh formula, and the azimuth of polarization occurs at 90° . For particles from 1.6×10^{-5} cm. to 1.8×10^{-5} cm. in diameter the azimuth of polarization lies between 110° and 120° . These results, therefore, seem to account for the discrepancy between the results of Ehrenhaft and Müller, with regard to the azimuth of polarization, it being due merely to the different sizes of the particles which occur in colloidal solutions made under different conditions.

Mie's work also shows that the absorption of light by turbid media is proportional to the amount of metal per unit volume of the supporting medium, when the particles in suspension are small.

Garnett² has developed a theory, in which he has explained the optical properties of colloidal glasses, and since Garnett's work has been made the basis of the work contained in this paper, we shall give a brief resumé of his paper in so far as it will be necessary to make clear its bearing upon the present subject.

¹ Ann. der Physik, 25, 377, 1908.

² Phil. Trans., A., 204-205, 1905.

If light of a wave-length λ falls upon a metal sphere of radius a , of refractive index n , and extinction coefficient k , then the complex dielectric constant ϵ will be expressed by

$$N = n(1 - ik) = \sqrt{\epsilon}.$$

Lord Rayleigh¹ has shown that a metal sphere of radius a , index of refraction n , and extinction coefficient k , when excited by an electric force E_0 , emits the waves which would be emitted by a Hertzian doublet whose moment at a time t is

$$\frac{N^2 - 1}{N^2 + 2} a^3 E_0,$$

where N^2 is the complex dielectric constant of the metal and equals $n^2(1 - ik)^2$.

For the case in which there are a great many spheres close together the electric force for each doublet would be the force E_0 together with that due to the neighboring doublets. Calling this E' then at any time t , the polarization is

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

which is regarded as the average moment. If m be the number of doublets present, then the polarization is expressed by

$$f'(t) = mf(t).$$

Lorentz and Larmor have shown that

$$E' = E_0 + \frac{4\pi f'}{3} = E_0 + \frac{4\pi}{3} ma^3 \frac{N^2 - 1}{N^2 + 2} E',$$

provided only that the doublets are scattered through a space large compared with the wave-length. Solving for E' and f , we obtain the expressions

$$E' = E_0 \left\{ \frac{1}{1 - \frac{4\pi}{3} ma^3 \left[\frac{N^2 - 1}{N^2 + 2} \right]} \right\}, \quad (1)$$

$$f = \frac{E_0 \left[\frac{N^2 - 1}{N^2 + 2} \right] a^3}{1 - \frac{4\pi}{3} ma^3 \frac{N^2 - 1}{N^2 + 2}}. \quad (1)$$

¹ Phil. Mag., XLIV., 28, 1897.

By the use of the Maxwell equations, the complex dielectric constant is expressed as

$$\epsilon \frac{\partial E}{\partial t} = c \operatorname{curl} (H) \text{ and } \frac{\partial H}{\partial t} = -c \operatorname{curl} (E),$$

it follows

$$\begin{aligned} \epsilon' &= \frac{E + 4\pi f'}{E}, \\ &= \frac{1 + 4\pi m a^3 \left[\frac{N^2 - 1}{N^2 + 2} \right]}{1 - \frac{4\pi m a^3}{3} \left[\frac{N^2 - 1}{N^2 + 2} \right]}. \end{aligned}$$

This shows that a medium consisting of small metallic spheres is optically equivalent to a medium of refractive index n' , and extinction coefficient k' , given by the expression

$$N' = n'(1 - ik') \equiv \sqrt{\epsilon'},$$

in which

$$\epsilon' = 1 + \frac{4\pi m a^3 \frac{N^2 - 1}{N^2 + 2}}{1 - \frac{4\pi m a^3}{3} \left[\frac{N^2 - 1}{N^2 + 2} \right]}.$$

This expression holds only for the case in which the metallic spheres are distributed in vacuo, many to the wave-length. If μ represent the relative volume, then

$$\mu = \frac{4}{3}\pi m a^3$$

and the above equation becomes

$$\epsilon = 1 + \frac{3\mu \frac{N^2 - 1}{N^2 + 2}}{1 + \mu \left[\frac{N^2 - 1}{N^2 + 2} \right]} = n'(1 - ik'). \quad (2)$$

This equation which is due to Garnett,¹ forms the point of departure for the mathematical analysis of the special problem with which the present paper deals.

EXTENSION OF THE THEORY.

A colloidal solution may be regarded as one consisting of small spherical particles, as Siedentopf² and Zsigmondy have shown by

¹ Loc. cit.

² Ann. der Physik, January, 1903.

means of the ultra microscope. Burton¹ in his work upon electrically prepared colloidal solution has shown that the diameter of the particles in such solutions is of the order of magnitude of 4×10^{-5} cm. to 6×10^{-5} cm. This value is in accord with the values which Bredig² found by theoretical considerations alone, Bredig shows that when these particles are viewed with a microscope of the highest power, the particles remain undetected, yet when a beam of light is passed through a solution containing them, the beam is scattered and polarized. The best microscopes can detect particles of the order of magnitude of 14×10^{-5} cm. and yet these particles since they diffuse light must be of the order of magnitude of a light wave, so that the lower limit to the size of the particle is 10^{-5} cm.

From the work which has been done by these investigators it seems that we are justified in assuming that the magnitude of this particle is 10^{-5} cm. as a lower limit, and so are at liberty to apply Garnett's analysis to the case of colloidal solution, for in them we are dealing with particles of approximately the same order of magnitude as those with which he had to deal in his work upon metal or colloidal glasses.

However, since it is impossible to prepare colloidal solutions in a medium which does not itself possess absorption in the infra-red spectrum, it has been found necessary for the purposes of the present investigation to extend Garnett's analysis to include the case of an absorbing medium whose complex dielectric constant is $v(1 - ig)$.

If now in equation (2) (which holds only for the case of spherical particles embedded in the æther) we replace the dielectric constant of the æther, unity, by the complex dielectric constant $\epsilon'' = v(1 - ig)$ of the supporting medium. We obtain the following equation

$$\epsilon' = \epsilon'' + \frac{3\epsilon''\mu \left[\frac{\epsilon - \epsilon''}{\epsilon + 2\epsilon''} \right]}{1 + \mu \left[\frac{\epsilon - \epsilon''}{\epsilon + 2\epsilon''} \right]}. \quad (2')^3$$

¹ Phil. Mag., II., 1906, p. 425.

² Drude's Ann., XI., 218, 1903.

³ The first term in the denominator of equation (2') is not a dielectric constant, but a pure number and hence is not replaced by ϵ'' .

In the above equation we may neglect

$$\mu \left[\frac{\epsilon - \epsilon''}{\epsilon + 2\epsilon''} \right]$$

with respect to unity since it is of the order of magnitude of 10^{-5} , and we thus obtain the equation

$$\epsilon' = 3\epsilon''\mu \left[\frac{\epsilon - \epsilon''}{\epsilon + 2\epsilon''} \right] + \epsilon'', \quad (3)$$

where

$$\begin{aligned} \epsilon &= n^2(1 - ik)^2, \\ \epsilon' &= n'^2(1 - ik')^2. \end{aligned}$$

Equation (3) may be written in the form

$$\epsilon' = \epsilon'' \left(1 + 3\mu \frac{\epsilon - \epsilon''}{\epsilon + 2\epsilon''} \right),$$

or it may be written

$$\frac{\epsilon'}{\epsilon''} - 1 = 3\mu \frac{\epsilon - \epsilon''}{\epsilon + 2\epsilon''} = \alpha + i\beta. \quad (4)$$

Replacing the values of ϵ , ϵ' and ϵ'' by their values in terms of refractive indices and extinction coefficients, we obtain for the second member of equation (4)

$$3\mu \left[\frac{n^2k^2 + v^2 + 2i(n^2k - v^2g)}{n^2k^2 - 2v^2 + 2i(n^2k - 2v^2g)} \right] = \alpha + i\beta.$$

Separating real and imaginary quantities we obtain for the value of β

$$\beta = 6\mu \left[\frac{(n^2k - v^2g)(n^2k^2 - 2v^2) - (n^2k + 2v^2g)(n^2k^2 + v^2)}{(n^2k^2 - 2v^2)^2 + (n^2k + 2v^2g)^2} \right]. \quad (5)$$

In the above equation g is of the order of magnitude of 10^{-5} , and hence terms containing g may be neglected with respect to terms containing n and k alone, and the equation for β becomes

$$\beta = \frac{-18n^2kv^2\mu}{(n^2k^2 - 2v^2)^2 + n^4k^2}. \quad (6)$$

The quantity k is an extinction coefficient and is not known, but

if we replace k by a/n , where a is the absorption coefficient of the metals and is quite accurately known from the work of Rubens¹ and Hagen, and n is the refractive index of the metals, we obtain an equation containing n and β as unknown quantities. Equation (6) then becomes

$$\beta = \frac{-18n\alpha v^2\mu}{(\alpha^2 - 2v^2)^2 + n^2\alpha^2}. \quad (7)$$

It is necessary to find a value of β in terms of quantities which may be experimentally determined. This we may do by replacing the values of ϵ' and ϵ'' by their values in terms of refractive indices and extinction coefficients in the first members of the equation (4) we obtain

$$\frac{\epsilon'}{\epsilon''} - 1 = \frac{\epsilon' - \epsilon''}{\epsilon''} = \frac{n'^2 - v^2 - 2i(n'^2k' - v^2g)}{v^2 - 2iv^2g} = \alpha + i\beta.$$

If we equate real and imaginary quantities and collect imaginary quantities we obtain for β a value

$$\beta = 2 \left[\frac{g(n'^2 - v^2) - (n'^2k' - v^2g)}{v^2(1 + g^2)} \right].$$

If we make the approximation that in the range from a wavelength 5.8×10^{-5} cm. to 6.8×10^{-5} cm., the refractive index of the colloidal solutions differs only very slightly from the refractive index of the supporting medium we obtain by setting $n' = v$

$$\beta = -\frac{2v^2(k' - g)}{v^2} = 2(g - k').$$

This equation in terms of the extinction coefficients of the colloidal solution and the supporting medium may be transformed into one involving the absorption coefficients t and w by means of the relation $k'n' = t$ and $vg = w$. Since we have assumed that $n' = v$, we obtain

$$\beta = -\frac{2(t - w)}{v}. \quad (8)$$

¹ Phil. Mag., 7, 1904.

Equating equation (7) and equation (8), we obtain

$$t - w = \frac{9nav^3\mu}{(a^2 - 2v^2) + n^2a^2}. \quad (8')$$

Solving for n' , we obtain

$$n = \frac{av^3}{2a(t-w)} + \sqrt{\left(\frac{av^3}{2a(t-w)}\right)^2 - \frac{(a^2 - 2v^2)^2}{a^2}}. \quad (9)$$

If in equation (8) we neglect n^2a^2 with respect to $(a^2 - 2v^2)^2$, which can be done only when the value of n is considerably less than unity, we obtain a very simple equation for n

$$n = \frac{(t-w)(a^2 - 2v^2)^2}{9av^3\mu}. \quad (9')$$

Equation (9') may be used in computing the values of n for gold and silver for which the values of n known for the visible spectrum are much less than unity, but in computing the values of n for platinum equation (9) must be used owing to the fact that the values of n for platinum are much greater than unity in the visible spectrum.

We thus have arrived at an equation for the refractive indices of the metals, in terms of the absorption coefficients of the colloidal solution and of its supporting medium, the absorption coefficients of the metal forming the colloid, the refractive index of the supporting medium, and the relative volume of the metal present. The values of n for the three metals given by this method for the wave-length 5.89×10^{-5} cm. should agree fairly well with the values of n obtained by Drude¹ and Kundt,² for these metals at the wave-length 5.89×10^{-5} cm.

Several important deductions are immediately derived from equation (9'), first, if we neglect the absorption w due to the supporting medium, as Garnett did implicitly in his analysis, we obtain an equation

$$n = \frac{t(a^2 - 2v^2)^2}{9av^3\mu}$$

¹ Phys. Zeitschrift, January, 1900.

² Wied. Ann., 34, p. 469, 1888.

which shows that t , the absorption of the colloidal solution, is proportional to the concentration μ . Garnett arrived at an equation

$$\beta = \frac{n'k'}{3\mu v}$$

in which $k'n'$ measured the absorption and β is a function of the optical constants of the metals, that is, n and k . This equation also shows that the absorption $n'k'$ is proportional to the concentration.

If w be not neglected, we find from equation (g') that the difference between the absorption of the colloidal solution and the absorption of the supporting medium is directly proportional to the concentration.

Finally if n is to be an invariant for a given metal for a given wave-length, for any supporting medium, experimental determination of n should bring out the fact that n is independent of the supporting medium. The different supporting media in which small metallic particles will remain suspended long enough to admit of accurate observations are very few. However two supporting media were obtained which possessed widely different optical properties. The usual one, water, possesses very strong absorption bands in the range of wave-lengths from 5.89×10^{-5} cm. to 15×10^{-5} cm. and its general absorption is very large. The second supporting medium, ethyl malonate, is a complex organic compound, and possesses the usual bands due to the ethyl group. Its general absorption, however, is not so great as that of water, and it makes a much more desirable supporting medium owing to this fact.

The main results brought out of the above theoretical considerations are briefly these; first, the optical properties of colloidal solutions should be independent of the size of the particles, provided the diameter be small compared to the wave-length. We should thus expect to find the best argument between theory and experiment the longer the wave-length of light. Second, it should be possible to determine the optical constants of those metals, which may be brought into the colloidal state, by the determination of the difference between the absorption of the solution of known metal content and of the supporting medium; and the values so obtained should be independent of the nature of the supporting

medium. Third, the difference between the absorption of the colloidal solution and of the supporting medium should be directly proportional to the relative volume of the metal in the solution.

It will be seen further on that colloidal solutions of silver, gold and platinum exhibit optical properties which are in good agreement with these theoretical conclusions.

APPARATUS.

The investigation was carried on by means of a large spectrometer of special construction designed by A. Trowbridge. The bolometer strips forming the two arms of the Wheatstone's bridge were 0.5 mm. wide and 2.5 cm. long. Their thickness may be judged from the fact that each of them had a resistance of 3 ohms. The remaining two arms of the bridge consisted of balancing coils, small portions of which were shunted by mercury sliders so that the balancing of the bridge was made very simple.

The bolometer strips were enclosed in an air-tight chamber through which the energy to be measured was allowed to enter through a rock-salt window.

The bolometer and its accessories were surrounded by a water jacket in order to protect the bolometer coils and sliders from irregular temperature fluctuations.

By means of a low power microscope mounted axially in the bolometer case it was possible to make accurately all preliminary adjustments for collimation, and to check the adjustments from time to time during the course of experimentation.

The spectrometer was provided with a divided circle graduated to minutes, on which settings were made with a micrometer microscope. The head of the micrometer screw was divided into sixty parts of such size that one tenth of a division could be readily estimated, thus allowing the observer to read with considerable accuracy to one tenth of a second of arc. The arms of the spectrometer were about one meter in length, and allowed the use of very long focus mirrors of considerable aperture.

The rock-salt prism used in the investigation had an angle of $60^{\circ} 1' 37''$, was 12 cm. high, and had faces 7 cm. wide. It was mounted in a manner described by Wadsworth¹ in which the prism

¹ Phil. Mag., 38, 1894.

faces and a mirror are so arranged that a plane bisecting the angle of the prism passes through the axis of the spectrometer table, and is also at right angles to the plane of the mirror, which plane passes through the axis of the spectrometer table. Employing this arrangement Langley¹ has shown that if the arms of the spectrometer are so fixed that the undeviated beam passing through from the slit into the collimator, arrives at and is focused on the bolometer strip, and then the prism arrangement inserted in the manner described above, the spectrum will arrive at the bolometer in such a way that light of any wave-length falling on the bolometer strip will have passed through the prism under minimum deviation.

The prism and mirror were mounted on a large circular casting of iron, which in turn was held upon the spectrometer by means of a hole, slot and plane device. The whole was then enclosed within a sheet-iron case with diaphragms in it for the entrance and exit of the beam.

The galvanometer was similar to that designed by C. E. Mendenhall and described by L. R. Ingersoll.² It was a four-coil astatic needle instrument, magnetically shielded by a triple concentric shield of exceptionally soft iron, kindly furnished by Mr. Elihu Thompson. A similar shield has been used for the past three years by Mendenhall and Trowbridge, who found that it reduced the field of the earth to one four-thousandth of its value outside the shield.

The coils had each a resistance of twelve ohms, and were connected in multiple so that their combined resistance was three ohms. The needle system was made of tungsten steel elements mounted in two groups, the whole weighing about six milligrams. As ordinarily used, with a period of about ten seconds, the sensibility of its galvanometer-bolometer arrangement was such that a candle at a distance of one meter gave about fifteen hundred scale divisions.

As a source of current for the bolometer, storage batteries at first were used, but considerable difficulty was encountered in their use, due to their irregular behavior. There are periods in the discharge of a storage cell which are fairly constant, but these periods are not of long duration, and just when they occur is a matter of uncertainty, owing to inconsistent conditions of charging and of previous state.

¹ *Annals of Smithsonian Institution*, Vol. I.

² *Phil. Mag.*, 6, 61, p. 41, 1906.

In order to obviate this difficulty, four large standard cells were made of a type which Professor G. A. Hulett¹ had been using for potentiometer work. Large battery jars which allowed a mercury surface of 340 cm.² were used, and the wooden cover of each jar supported four anode cups, which contained the cadmium amalgam. These cups were 5 cm. in diameter. Since these cells were first constructed an improved form has been made, in which the anode cups were replaced by the rubber trays, supported by a glass frame resting upon the bottom of the jar. One and a half liters of acid cadmium sulphate solution, and 150 grams of mercurous sulphate were placed in each of these cells. The cells were then charged at a low current density. At first the charging was done without stirring, but later L-shaped stirrers were passed through the covers of the jars, and a much higher current density could be used without the danger of forming the basic salt. These cells were found to furnish a current of 0.2 ampere without the fluctuations experienced with the storage battery and with only a very slow drift. They are particularly well suited for bolometric work, for all the annoying features of the storage cell are removed.

The arrangement of the apparatus was as follows: A beam of light from a Nernst glower was allowed to fall upon a mirror, and was brought to focus upon the slit of the spectrometer. Before the slit was placed a sliding cell, containing the solution to be investigated. The energy from the slit was directed upon another mirror placed at such a distance from the slit, such that parallel light was reflected from it, and passed through the prism to another mirror of a meter focal length. This latter mirror brought to a focus upon the bolometer strip those rays which had passed through the prism under minimum deviation.

A simple and effective device was designed to carry the colloidal solution. Two quartz plates about 4 cm.² were separated by a hard rubber diaphragm, of known thickness. The rubber diaphragm was divided into two compartments. The plates and diaphragm were placed in a convenient cell and held in position by screws. The cell was made to slide on two brass ways so that either one of the compartments of the cell might be brought into the path of the rays

¹PHYS. REV., July, 1908.

of light to the slit or removed entirely. The liquid to be investigated was placed in one of these compartments, the deflection of the galvanometer noted when energy of a known wave-length was transmitted through the compartment containing it, then the deflection was noted when energy passed through the empty compartment. Thus the effect of the absorption of the quartz could be eliminated from the observation and only the transmission of the liquid was obtained.

In order to know in exactly what part of the spectrum the observations were being made, it was necessary to obtain a dispersion curve of the rock-salt prism. In order to do this the angle of the prism was accurately measured, and from the known values of the dispersion of rock salt, determined by Rubens¹ and Trowbridge, a dispersion curve in terms of wave-lengths and angles of minimum deviation was obtained. This gave a simple and rapid means of determining the wave-length at which one was working provided the reading of the spectrometer was known at which energy of a known wave-length passed through the prism under minimum deviation. The accuracy of the method was tested by first setting on the sodium lines and then determining the angular reading. The setting for the emission band of CO₂ at 44×10^{-5} cm. was computed. A Bunsen burner was placed before the slit and a maximum of emission sought. It was found and the reading taken. This angular reading agreed with the computed reading to within less than 1×10^{-5} cm. A device for roughly estimating the position of the infra-red spectrum at which observations were being made was obtained by placing a small concave mirror upon the case enclosing the prism, directly over the axis of the spectrometer table. A beam of light from a Nernst glower was focused upon a card-board fastened to the wall of the room. This was calibrated empirically for various wave-lengths.

EXPERIMENTAL.

The colloidal solutions employed were made according to the method of Burton.² Very stable colloids were obtained of gold,

¹ Wied. Ann., 60, 724, 1897.

² Phil. Mag., 11, 425, 1906.

platinum and silver. They remained in good condition almost indefinitely without coagulating or changing color.

Attempts were made to obtain colloids of the various metals in alcohol. In the cases of platinum, silver and gold the attempts were fruitless, owing to almost immediate precipitation. Lead, zinc and tin were tried and the resulting colloids appeared rough and granular. They began immediately to precipitate the metal, and in the course of a few days the entire metal content was precipitated. The constant change in the metal content made it impossible to obtain anything except a rough qualitative idea of the optical properties of these colloidal solutions.

The colloids of gold, platinum and silver which possessed a satisfactory stability were made in either water or ethyl malonate.

The amount of metal present per unit volume of supporting medium was readily and quite accurately determined by evaporating the colloidal solution to dryness, and weighing the residue. The weighings were made a number of times and the final error in the determination did not exceed three per cent. This method was also used by Burton.¹

To determine the absorption coefficients of the colloidal solution and its supporting medium for any given wave-length, it was necessary to make use of two thicknesses of the cell. For if λ is the wave-length in vacuo, d the difference in thickness between the two layers of solution used, and I_1 and I_2 the incident and transmitted energies respectively, then the absorption $k'n'$ is given by the expression

$$\frac{I_1}{I_2} = e^{-\frac{4\pi k'n'd}{\lambda}}.$$

Solving for $k'n'$, we obtain

$$k'n' = \frac{\lambda}{4\pi d} \log \frac{I_2}{I_1} \frac{1}{\log e}.$$

All these quantities in the right-hand member of this equation are known or capable of experimental determination. The ratio I_2/I_1 was determined by means of the bolometer, and d was measured by means of a micrometer caliper. The values of the absorption coef-

¹ Loc. cit.

ficients for the various wave-lengths were determined for the various colloidal solutions and their supporting media.

RESULTS.

Tables I., II. and III. contain the various quantities used in the determination of the values of the indices of refraction of the metal silver, for wave-lengths from 5.89×10^{-5} cm. to 15×10^{-5} cm. In the tables, columns 2 and 3 show the percentage of energy transmitted through the colloidal solution for two different thicknesses of the solution. The difference in thickness of the two layers was 0.214 cm. Columns 4 and 5 show the ratio of the energy transmitted through the colloidal solution to that transmitted through the supporting medium, which in the case of silver was water. Column 6 shows the values of the ratios from which the absorption coefficients of the colloidal solution were calculated. Column 7 shows the values of the absorption coefficients of the colloidal solution for the various wave-lengths. Column 8 gives the value of β , the difference between the absorption of the colloidal solution and the supporting medium, water. The last column contains the values of the refractive indices calculated from the fundamental equation.

Tables V., VI. and VII. contain the data for the platinum colloids reported in the same order as those for silver. The results in Table IV. were obtained with water as a supporting medium, and those in Tables V. and VI. with ethyl malonate as the supporting medium. The various concentrations μ are given at the bottom of each table.

Table IV. gives the results obtained in the case of colloidal gold in ethyl malonate, and Table IX. contains the absorption coefficients of water and of ethyl malonate, for the slit width and width of the bolometer strips employed throughout the research.

Table X. contains the values of the absorption coefficients of the metals gold, platinum and silver taken from the work of Rubens¹ and Hagen. Values which were not given by them and which were necessary for the present work were obtained by plotting the values given by them and drawing a smooth curve through those points. The necessary values were obtained from this curve and are given in the table.

¹ Loc. cit.

In Table VIII. are reported the data for the turbid medium made from gum mastic. The values of the absorption coefficients t are given for two concentrations, one being twice the other.

To obtain curves shown as Fig. 1, the absorption coefficients were plotted as ordinates and the wave-lengths as abscissæ. The

Fig. 1.

lowest of these curves represents the absorption curve of water, and the remaining three are the absorption curves of the three silver colloids used to obtain the data in Tables I., II. and III.

The uppermost of the four curves shown in Fig. 2, is the absorption curve of the gold colloid, obtained from the data of Table IV., the lowest is the curve of ethyl malonate, and the remaining two curves are those for the platinum colloids of Tables V. and VI.

In order to show graphically the manner in which the absorption due to the presence of the particles alone varied with the wave-length, the values in columns 4 and 5 for each table containing the data for the determination of the value of n , have been plotted as a function of the wave-length (Fig. 3). These curves show the ratio of the energy transmitted by the supporting medium, for a given thickness and for the various wave-lengths within the range of observation. They bring out clearly the effect of these minute particles upon the absorption of light, showing that they are less and less

effective as we proceed to the longer wave-lengths, the absorption of the colloidal solution being almost identical with the absorption of the supporting medium. The greatest effect is somewhere in the region of the visible spectrum, in all probability where Ehren-

Fig. 2.

haft¹ and Müller¹ concluded from their results that optical resonance occurred.

In view of these results, the question at once arises concerning the numerical relationship between the values of the absorption coefficients and the wave-lengths. Lord Rayleigh in his earlier work upon the subject of atmospheres containing suspended insulating particles has shown from theoretical considerations that for such an atmosphere containing these particles, whose sizes are small compared to a wave-length, the absorption varies inversely as the inverse fourth power of the wave-length. We have sufficient data given here to investigate the relationship for colloidal solutions. If for the short range of wave-lengths just beyond the wave-length 5.89×10^{-5} cm. we assume that the absorption due to the supporting medium is negligible, we can see from the character of the absorption curves of the colloids that no such λ^{-4} relationship seems to exist between the absorption coefficients and the wave-lengths. One cannot put this investigation to too rigorous a test owing to the fact that the range for determining a relationship

¹ Loc. cit.

of this nature is too limited. Furthermore, we cannot expect such a relationship to hold near a region of optical resonance, such as we know to exist in the case of these colloidal solutions, at a very short distance from the sodium lines of the spectrum. The data

Fig. 3.

Fig. 4.

obtained in this investigation give rise to no definite relationship between the absorption coefficient and the wave-length, with regard to colloidal solutions.

We may digress here for a moment to consider the case for which the relationship given by Lord Rayleigh, for insulating particles, should hold. In Table VIII. are given data for such a medium made of gum mastic, and the results are plotted in Fig. 4. Again assuming that the absorption of the supporting medium may be neglected where it is small, we can roughly determine the relationship between the absorption and the wave-length. A simple calculation shows that the absorption varies roughly as the inverse first power of the wave-length, which does not conform to the demands made by the

Rayleigh formula. In Table VIII. are also included the ratios of the difference between the absorption of the turbid medium and its supporting medium for the two concentrations used in obtaining the data. The ratios show that the absorption varies directly as the concentration.

TABLE I.

Silver Colloid No. 1 in Water.

1 Wave- length in cm.	2 I_1	3 I_2	4 $\frac{I_1^0}{I_1}$	5 $\frac{I_2^0}{I_2}$	6 $\frac{I_1}{I_2}$	7 t	8 $t-w$	9 $\frac{(a^2-2v^2)^2}{9av^2\mu}$	10 n
5.89×10^{-5}	86.0	66.2	86.0	66.2	1.30	$.5721 \times 10^{-5}$	$.5721 \times 10^{-5}$	.602	.35
6 "	87.3	74.8	86.3	73.8	1.165	.3400 "	.3400 "	1.061	.36
7 "	90.0	84.7	87.5	83.7	1.062	.1561 "	.1561 "	2.947	.46
8 "	81.3	87.3	89.5	85.4	1.046	.1220 "	.1220 "	4.215	.52
9 "	92.9	90.0	91.0	89.0	1.033	.1099 "	.0767 "	7.430	.57
10 "	92.3	85.8	92.3	92.3	1.076	.2740 "	.0595 "	10.246	.61
11 "	92.2	86.8	94.5	93.2	1.062	.2386 "	.0400 "	16.020	.64
12 "	82.3	63.9	95.8	95.5	1.287	1.1223 "	.0267 "	24.660	.66
13 "	68.2	37.4	96.0	93.5	1.823	2.8943 "	.0253 "	26.84	.68
14 "	19.4	2.42	97.5	97.0	8.010	10.786 "	.0203 "	34.45	.70
15 "	43.3	7.80	98.7	97.5	5.515	9.4831 "	.0177 "	40.70	.72

$$\mu = 2.12 \times 10^{-5}.$$

TABLE II.

Silver Colloid No. 2 in Water.

1 Wave- length in cm.	2 I_1	3 I_2	4 $\frac{I_1^0}{I_1}$	5 $\frac{I_2^0}{I_2}$	6 $\frac{I_1}{I_2}$	7 t	8 $t-w$	9 $\frac{(a^2-2v^2)^2}{9av^2\mu}$	10 n
5.89×10^{-5}	81.0	57.0	81.0	57.0	1.42	$.8844 \times 10^{-5}$	$.8844 \times 10^{-5}$	.444	.38
6 "	82.5	66.8	81.5	65.8	1.253	.5000 "	.5000 "	.780	.39
7 "	86.0	79.3	83.5	78.1	1.084	.2077 "	.2077 "	2.166	.45
8 "	87.1	81.8	85.5	79.9	1.065	.1845 "	.1710 "	3.099	.53
9 "	89.1	85.0	87.4	84.0	1.048	.1583 "	.1251 "	5.463	.56
10 "	89.6	82.6	89.6	88.8	1.084	.2981 "	.0831 "	7.460	.62
11 "	89.1	83.5	91.5	89.9	1.067	.2546 "	.0560 "	11.780	.66
12 "	80.2	62.1	93.4	92.8	1.291	1.1326 "	.0370 "	18.10	.67
13 "	67.3	36.8	95.0	92.0	1.830	2.903 "	.0340 "	19.71	.67
14 "	19.25	2.40	97.0	96.0	8.024	10.7935 "	.0275 "	25.30	.69
15 "	38.4	6.9	98.5	86.0	5.521	9.4891 "	.0237 "	29.90	.71

$$\mu = 2.76 \times 10^{-5}.$$

It was shown in the fundamental equation which was derived to fit the general case of colloidal solutions that the absorption due to the small metallic particles, small compared to a wave-length, was directly proportional to the concentration when the absorption of the supporting medium could be neglected. It was also shown

TABLE III.

Silver Colloid No. 3 in Water.

1 Wave-length in cm.	2 I_1	3 I_2	4 $\frac{I_1^0}{I_1}$	5 $\frac{I_2^0}{I_2}$	6 $\frac{I_1}{I_2}$	7 t	8 $t - w$	9 $\frac{(a^2 - v^2)^2}{9av^3\mu}$	10 n
5.89×10^{-5}	89.0	76.0	89.0	76.0	1.17	$.5224 \times 10^{-5}$	$.5224 \times 10^{-5}$	.879	.28
6 "	90.5	82.7	89.5	81.7	1.094	.2105 "	.2105 "	1.14	.34
7 "	94.1	90.6	91.5	89.6	1.038	.0963 "	.0963 "	4.30	.42
8 "	94.3	92.1	92.5	90.3	1.024	.09426 "	.08126 "	6.153	.50
9 "	95.5	91.5	93.5	90.5	1.044	.08330 "	.0500 "	10.84	.54
10 "	94.3	87.9	94.3	94.3	1.072	.2550 "	.0403 "	14.95	.60
11 "	92.6	87.1	95.0	93.6	1.062	.2358 "	.03721 "	17.49	.65
12 "	82.2	63.9	95.7	95.5	1.285	1.1130 "	.0184 "	36.0	.66
13 "	68.8	38.6	97.0	96.5	1.783	2.7863 "	.0173 "	39.2	.68
14 "	19.5	2.46	98.0	97.9	7.926	10.7199 "	.0139 "	50.3	.70
15 "	43.6	8.1	99.0	98.5	5.382	9.4777 "	.0123 "	59.4	.73

$$\mu = 1.45 \times 10^{-5}.$$

that in general, when the absorption of the supporting medium could not be neglected, that the difference between the absorption of the colloidal solution and the supporting medium was proportional to the concentration. If we take the ratio of $(t - w)$ for any two concentrations for a given wave-length, the result should be equal to the ratio of the concentrations. Table XI. contains the results of such computations for the colloids of platinum and silver. At the bottom of each column is given the ratio of the concentrations. The results contained therein show conclusively that the relationship deduced from the theory is correct. The range over which these values extend is about three times the length of the visible spectrum and yet there are no evidences of marked regular deviation from proportionality. In this connection it must be borne in mind that an error of a fraction of one per cent. in the experimental determination of I_1 and I_2 introduces a very large error in the value of the

absorption coefficient, owing to the fact that the expression for the absorption contains a logarithmic function, and hence any regular deviation from the prediction by the analysis would make itself evident when the absorption coefficient had been determined.

TABLE IV.
Gold Colloid in Ethyl Malonate.

1 Wave-length in cm.	2 I_1	3 I_2	4 $\frac{I_1^0}{I_1}$	5 $\frac{I_2^0}{I_2}$	6 $\frac{I_1}{I_2}$	7 t	8 $t-w$	9 $\frac{(a^2-2v^2)^2}{9av^2\mu}$	10 n
5.89×10^{-5}	75.2	45.0	75.1	45.0	1.672	1.008×10^{-5}	1.008×10^{-5}	.4088	.45
6 "	77.81	49.31	76.2	48.3	1.578	.9626 "	.0626 "	.4988	.48
7 "	84.90	77.61	80.1	73.9	1.093	.2290 "	.2290 "	2.640	.60
8 "	90.23	86.75	84.3	80.9	1.040	.1151 "	.1153 "	6.250	.71
9 "	93.50	91.13	86.1	85.1	1.026	.0860 "	.0740 "	10.403	.77
10 "	92.87	90.69	87.2	83.0	1.024	.0850 "	.0490 "	16.67	.82
11 "	96.50	93.68	91.0	87.5	1.030	.1147 "	.0341 "	24.93	.85
12 "	94.72	87.30	92.0	91.9	1.085	.3642 "	.02324 "	37.42	.87
13 "	96.10	78.64	94.2	90.2	1.222	.5624 "	.01772 "	50.20	.89
14 "	96.81	88.17	94.9	97.0	1.098	.4856 "	.01280 "	64.39	.90
15 "	95.50	77.39	96.5	94.5	1.234	1.1701 "	.01126 "	80.80	.91
16 "	81.25	50.94	98.0	97.5	1.595	2.8872 "	.00928 "	99.93	.93
17 "	74.90	55.40	98.6	99.0	13.57	2.8963 "	.00762 "	123.3	.94
18 "	88.00	59.37	99.0	99.0	14.77	2.6183 "	.00652 "	146.52	.95

$$\mu = .759 \times 10^{-5}.$$

It has thus been shown that for the colloidal solutions investigated, the absorption is directly proportional to the concentration, and that furthermore, the conditions for the application of the analysis for the determination of the refractive indices of the metals is warranted; namely, that there are many particles to the wave-length. This confirms the results obtained by Mie,¹ from purely theoretical considerations, and also agrees with the direct experimental results obtained by Zsigmondy¹ and Siedentopf, who by ultra-microscopic means found that these colloidal particles are small compared to a wave-length and are spherical in shape.

If in the application of the analysis we find that the values for the refractive indices remain constant for a given wave-length, for any metal, no matter what the supporting medium is, we are further assured of the correctness of the deductions. The values of n ob-

¹ Loc. cit.

TABLE V.

Platinum Colloid No. 3 in Water.

1 Wave- length in cm.	2 I_1	3 I_2	4 $\frac{I_1^0}{I_1}$	5 $\frac{I_2^0}{I_2}$	6 $\frac{I_1}{I_2}$	7 t	8 $t-w$	9 $\frac{(a^2-2v^2)^2}{a^2}$	10 n
5.89×10^{-5}	69.20	34.77	68.2	34.7	1.990	1.500×10^{-5}	1.500×10^{-5}	10.32	1.75
6 "	73.41	35.79	72.5	34.9	2.051	1.596 "	1.596 "	10.93	2.40
7 "	81.23	51.70	79.0	50.2	1.571	1.177 "	1.177 "	16.63	3.45
8 "	84.10	62.15	82.5	61.0	1.353	.907 "	.907 "	22.14	4.1
9 "	85.98	69.11	84.0	68.6	1.244	.726 "	.726 "	27.56	4.3
10 "	87.07	70.90	87.0	76.2	1.228	.7918 "	.5768 "	35.08	4.4
11 "	88.16	76.79	90.0	82.2	1.184	.6860 "	.4870 "	42.00	4.5
12 "	78.92	56.18	91.0	84.3	1.387	1.4532 "	.3576 "	54.77	4.62
13 "	64.75	33.81	91.2	77.0	1.915	3.1281 "	.3591 "	55.05	4.75
14 "	18.51	21.79	93.3	87.0	8.492	11.0887 "	.3127 "	62.32	4.82
15 "	41.25	71.57	93.9	89.5	5.762	9.7281 "	.2627 "	71.79	4.85
16 "	51.47	12.44	95.1	92.4	4.134	8.4085 "	.2085 "	81.39	4.89
17 "	46.42	14.86	96.0	91.1	3.122	7.1656 "	.2156 "	88.09	4.92

$$\mu = 2.18 \times 10^{-5}.$$

TABLE VI.

Platinum Colloid No. 2 in Ethyl Malonate.

1 Wave- length in cm.	2 I_1	3 I_2	4 $\frac{I_1^0}{I_1}$	5 $\frac{I_2^0}{I_2}$	6 $\frac{I_1}{I_2}$	7 t	8 $t-w$	9 $\frac{(a^2-2v^2)^2}{a^2}$	10 n
5.89×10^{-5}	80.21	48.00	78.9	47.5	1.671	$.6458 \times 10^{-5}$	$.6458 \times 10^{-5}$	10.32	1.40
6 "	81.40	56.53	80.5	56.0	1.440	.8114 "	.8114 "	10.93	2.55
7 "	85.64	65.71	87.2	64.0	1.288	.5918 "	.5918 "	16.63	3.59
8 "	89.30	76.65	82.7	71.5	1.165	.4549 "	.4549 "	22.14	4.05
9 "	93.31	81.01	86.5	75.9	1.153	.4753 "	.3633 "	27.56	4.30
10 "	95.52	87.55	90.0	83.3	1.091	.3261 "	.2911 "	35.08	4.49
11 "	97.81	91.84	93.0	87.1	1.065	.2540 "	.2454 "	42.00	4.59
12 "	96.80	86.57	94.0	91.2	1.117	.4939 "	.1799 "	54.77	4.67
13 "	96.02	82.61	94.1	93.0	1.163	.7252 "	.1805 "	55.05	4.81
14 "	96.91	86.29	95.0	94.5	1.123	.6299 "	.1571 "	62.32	4.86
15 "	94.60	76.85	95.5	93.2	1.231	1.1901 "	.1326 "	71.79	4.89
16 "	79.59	49.01	96.0	93.3	1.624	2.8732 "	.1148 "	81.39	4.93
17 "	73.32	53.40	96.7	95.5	1.373	1.9947 "	.1060 "	88.09	5.15

$$\mu = 1.091 \times 10^{-5}.$$

tained for gold, platinum and silver show that they are independent of the supporting medium. The values of the refractive indices for silver range from 0.34 for the wave-length 5.89×10^{-5} to 0.72 for the wave-length 15×10^{-5} cm. The values for platinum begin with 1.48 at the wave-length 5.89×10^{-5} cm. and rise steadily to 5.02 at a wave-length 17×10^{-5} cm., while for gold the values extend from 0.45 to 0.95 for the wave-lengths, 5.89×10^{-5} cm. to 18×10^{-5} cm. respectively.

TABLE VII.

Platinum Colloid No. 1 in Ethyl Malonate.

1 Wave-length in cm.	2 I_1	3 I_2	4 $\frac{I_1^0}{I_1}$	5 $\frac{I_2^0}{I_2}$	6 $\frac{I_1}{I_2}$	7 t	8 $t-v$	9 $\frac{(a^2-2v^2)^2}{a^2}$	10 n
5.89×10^{-5}	87.0	74.89	87.0	74.9	1.163	$.3282 \times 10^{-5}$	$.3282 \times 10^{-5}$	10.32	1.30
6 "	88.4	72.40	87.5	71.5	1.221	.4262 "	.4262 "	10.93	2.40
7 "	95.2	84.86	89.0	80.8	1.123	.3129 "	.3129 "	16.63	3.50
8 "	96.03	88.50	89.9	82.8	1.085	.2429 "	.2429 "	22.14	4.0
9 "	97.5	91.89	90.5	85.7	1.061	.1985 "	.1835 "	27.56	4.2
10 "	98.49	94.43	93.1	80.0	1.043	.1563 "	.1527 "	35.08	4.5
11 "	99.83	96.64	94.2	92.7	1.033	.1401 "	.1315 "	42.00	4.6
12 "	97.61	89.00	94.8	93.7	1.096	.4100 "	.0960 "	54.77	4.65
13 "	97.10	85.03	95.2	97.5	1.142	.6412 "	.0965 "	55.05	4.80
14 "	97.89	87.95	96.0	96.5	1.113	.5556 "	.0828 "	62.32	4.85
15 "	95.81	78.09	96.8	95.1	1.227	1.7277 "	.0702 "	71.97	4.90
16 "	80.59	51.43	97.1	98.0	1.567	2.8186 "	.0602 "	81.39	4.95
17 "	74.40	54.58	98.0	97.5	1.363	1.9475 "	.0588 "	88.09	.05

$$\mu = .584 \times 10^{-5}.$$

It was quite surprising to learn that the values of the refractive indices increased with increasing wave-length, yet after having found this to be the case, it was at once apparent that the behavior of the metals as regards their reflection would lead one to expect that there should be found a region of anomalous dispersion, extending into the infra-red, and having its origin in the region of the visible spectrum.

Drude¹ and Kundt² have obtained values of the refractive indices for the metals, gold, platinum and silver, at a wave length 5.89×10^{-5} cm., the values for the above metals are 0.38, 2.1 and

¹ Theory of Optics, p. 366.

² Phil. Mag., 26, p. 5.

0.18 respectively. The values obtained in this paper do not agree very closely with those obtained by these observers. The values reported by Drude were obtained by a katoptric method, which is open to the objection that it is indirect and that large experimental error may be introduced both in observation and by the existence of surface films on the metallic surfaces.

TABLE VIII.

Absorption Coefficients.

Of Gum Mastic No. 1.								
Wave-length in cm.	I_1	I_2	$\frac{I_1^0}{I_1}$	$\frac{I_2^0}{I_2}$	$\frac{I_1}{I_2}$	t'	$t'-w$	
5.89×10 ⁻⁵								
6 "								
7 "	38.0	4.9	7.75	4.85	7.75	5.51 ×10 ⁻⁵	5.51 ×10 ⁻⁵	
8 "	47.5	10.5	46.5	10.3	4.50	4.448 "	4.448 "	
9 "	57.0	16.5	56.0	16.2	3.45	4.118 "	4.118 "	
10 "	65.0	22	65.0	23.5	2.95	4.000 "	3.78 "	
11 "	68.0	28	70.0	30.2	2.43	3.619 "	3.42 "	
12 "	65.0	26	76.0	39.0	2.50	4.080 "	3.00 "	
13 "	56.0	16	79.0	40.0	3.50	6.032 "	4.27 "	
14 "	29.5	2.0	67.8	79.0	14.74	13.96 "	3.20 "	
15 "	39.1	5.7	89.0	71.0	6.8	10.65 "	1.19 "	

Of Gum Mastic No. 2.								
Wave-length in cm.	I_1	I_2	$\frac{I_1^0}{I_1}$	$\frac{I_2^0}{I_2}$	$\frac{I_1}{I_2}$	t	$t-w$	$\frac{t'-w}{t-w}$
5.89×10 ⁻⁵								
6 "	62.0	19.1	3.26	61.5	18.8	2.522×10 ⁻⁵	2.522×10 ⁻⁵	
7 "	68.5	25.9	2.64	66.5	25.7	2.513 "	2.513 "	2.2
8 "	75.0	34.0	2.21	73.5	33.2	2.344 "	2.344 "	1.9
9 "	80.0	41.0	1.95	78.0	40.5	2.223 "	2.223 "	1.86
10 "	86.0	47.1	1.83	86.0	50.5	2.230 "	2.00 "	1.68
11 "	88.0	52.3	1.69	90.5	56.0	2.134 "	1.94 "	1.70
12 "	78.1	43.0	1.82	91.0	64.1	2.664 "	1.57 "	1.54
13 "	65.0	28.0	2.32	91.5	70.0	4.043 "	2.28 "	1.94
14 "	21.1	1.9	11.1	93.2	76.0	12.474 "	1.70 "	1.90
15 "	40.9	68.2	5.77	93.0	85.0	10.06 "	6.0 "	2.0

Kundt's method was a very direct one. He succeeded in obtaining very acute-angled prisms, to which he applied the ordinary

method for determining the value of n . This method is open to the objection that it is highly probable that such metallic prisms are not homogeneous in structure, and it is a very difficult task to obtain a measurement, by means of such small angled prisms.

The method of this paper is a direct one from an experimental point of view, and the measurements are capable of considerable accuracy, if carefully taken and with accurate apparatus. The fundamental assumptions make the method of finding an equation for n an indirect one, but it is no more indirect than Drude's method of obtaining n , in terms of the azimuth of restored polarization and the principal angle of incidence.

TABLE IX.

Absorption Coefficients.

Wave-length in cm.	Ethyl Malonate.				Wave-length in cm.	Water.			
	I_1^0	I_2^0	$\frac{I_1^0}{I_2^0}$	w		I_1^0	I_2^0	$\frac{I_1^0}{I_2^0}$	w
5.89×10^{-5}	100	100	1.00	0	5.89×10^{-5}	101	101	1.00	0
6 "	101	101	1.00	0	6 "	101	101	1.00	0
7 "	105	105	1.00	0	7 "	103	103	1.00	0
8 "	107	107	1.00	0	8 "	102	102	1.00	0
9 "	108.5	107	1.01	$.0120 \times 10^{-5}$	9 "	102	101	1.01	$.0033 \times 10^{-5}$
10 "	106.1	105.2	1.01	.036 "	10 "	100	93.0	1.06	.2150 "
11 "	106.0	104.0	1.02	.0806 "	11 "	97.5	93.0	1.05	.1986 "
12 "	103.0	95.0	1.08	.3140 "	12 "	86.0	67.1	1.28	1.0956 "
13 "	102.0	87.0	1.12	.5447 "	13 "	71.1	40	1.78	2.769 "
14 "	102.0	91.0	1.094	.4728 "	14 "	19.95	2.5	7.98	10.766 "
15 "	99.1	82.1	1.21	1.0575 "	15 "	44.0	8.0	5.50	9.465 "
16 "	83.0	52.5	1.592	2.7584 "	16 "	54.0	13.5	4.0	8.700 "
17 "	76.1	56.0	1.35	1.8887 "	17 "	49.0	16.27	3.013	6.950 "
18 "	89.0	60.0	1.48	2.6118 "	18 "				

The final and most striking test of the correctness of the values of n obtained by the method of this paper is by means of an equation deduced by Drude¹ for the reflection coefficient in terms of the absorption coefficients a , and the refractive indices n . The equation is

$$R = \frac{(n^2 - 1)^2 + a^2}{(n^2 + 1)^2 + a^2}.$$

¹ Physik des Aethers, p. 457.

The values of the absorption coefficients are known from the work of Rubens¹ and Hagen, and the same investigators have obtained accurate measurements of the reflection coefficients. Substituting the values of n given in this paper and the values of a , the values of R , thus computed, should agree with the observed values of R . Table XII. contains the results of such computations. The computed and observed values of R show a remarkable agreement in the case of silver, and the agreement in the case of platinum and gold is very good. It will be noticed that an error in n , would, on account of the fact that it enters as the second power in the above equation, produce a correspondingly greater error in the calculated value of the reflecting power of the solid metal. In view of the good agreement between calculated and observed values of R , it seems that the correctness of the values of n reported in this paper is placed beyond question.

TABLE X.

*Absorption Coefficients.*¹

Wave-length in cm.	Platinum.		Gold.		Silver.	
	a	a^2	a	a^2	a	a^2
5.89×10^{-5}	4.08	16.65	2.82	7.95	3.67	13.47
6 "	4.16	17.30	2.91	8.49	4.20	17.64
7 "	4.81	23.13	4.13	17.06	5.52	30.47
8 "	5.36	28.83	5.19	26.94	6.21	37.70
9 "	5.94	34.28	6.00	36.00	7.25	52.56
10 "	6.47	41.86	6.90	47.61	8.00	64.00
11 "	6.85	46.92	7.80	60.84	9.15	83.40
12 "	7.85	61.65	8.85	78.33	10.3	110.0
13 "	7.87	61.93	9.70	94.04	10.9	118.8
14 "	8.32	69.22	10.5	110.25	11.8	138.2
15 "	8.93	79.27	11.3	127.69	12.4	153.96
16 "	9.38	88.34	12.1	146.41		
17 "	9.80	95.04	13.0	169.10		
18 "			13.7	187.67		

CONCLUSION.

In the endeavor to supplement the existing data obtained for colloidal solutions and turbid media in the visible spectrum by extending the field of investigation into the infra-red region of the spectrum

¹ Phil. Mag., 7, p. 157, 1904.

TABLE XI.

Wave-length in cm.	<i>Silver.</i>			<i>Platinum.</i>		
	(<i>t-w</i>) for No. 1 (<i>t-w</i>) for No. 2	(<i>t-w</i>) for No. 1 (<i>t-w</i>) for No. 3	(<i>t-w</i>) for No. 2 (<i>t-w</i>) for No. 3	(<i>t-w</i>) for No. 1 (<i>t-w</i>) for No. 2	(<i>t-w</i>) for No. 1 (<i>t-w</i>) for No. 3	(<i>t-w</i>) for No. 2 (<i>t-w</i>) for No. 3
5.89 10 ⁻⁵	.65	1.10	1.69	.50	.21	.427
6 "	.68	1.62	2.40	.517	.265	.51
7 "	.75	1.66	2.04	.517	.265	.50
8 "	.70	1.50	2.01	.53	.26	.52
9 "	.61	1.52	2.50	.50	.25	.50
10 "	.71	1.49	2.07	.52	.26	.50
11 "	.715	1.08	1.51	.54	.27	.50
12 "	.73	1.45	2.05	.50	.265	.49
13 "	.735	1.46	2.01	.50	.27	.50
14 "	.736	1.46	2.01	.51	.257	.49
15 "	.747	1.44	2.02	.54	.27	.50
16 "				.52	.28	.53
17 "				.55	.24	.38
Mean	.706	1.43	2.03	.52	.26	.50
Ratios of Concentrations.	No. 1 No. 2 = .76	No. 1 No. 3 = 1.46	No. 2 No. 3 = 1.94	No. 1 No. 2 = .537	No. 1 No. 3 = .27	No. 2 No. 3 = .50

as far as present means will permit, the writer, by the help of the analysis developed in the course of the research, has arrived at the following conclusions :

1. That the difference between the absorption of the colloidal solution and the absorption of the supporting medium is directly proportional to the concentration. For turbid media this cannot be said to be the case, generally, owing to the variation of the size of the particles for different media.

2. That the Rayleigh formula,

$$H = \frac{32\pi(n^2 - 1)}{3n\lambda^4},$$

where H is the absorption, n the refractive index of the particle, and λ the wave-length, holds neither for the case of turbid media, for which it was developed, nor for colloidal solutions. The law of absorption cannot be stated definitely from this work.

3. That the values of the refractive indices n , for the metals, determined by this method are independent of the supporting medium and are strictly inherent in properties of the metals themselves.

4. That the final test as to the correctness of the analysis, by means of the equation of Drude,

$$R = \frac{(n^2 - 1)^2 + a^2}{(n^2 + 1)^2 + a^2},$$

where R is the reflection coefficient and a the absorption coefficient, places the values of the refractive indices obtained for the metals gold, silver and platinum beyond question.

The writer wishes to express his gratitude to Professor A. Trowbridge at whose suggestion and under whose direction and advice, the work was finally brought to its present state. The writer also expresses his indebtedness to Professor G. A. Hulett for valuable suggestions and aid in the construction of the standard batteries.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY.