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THE METALLIC REFLECTION OF SELENIUM.

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INTRODUCTION.

I. *Object.*

MUCH recent work has been done on the verification of modern dispersion formulæ as applied to substances having absorption bands in the visible or infra-red regions of the spectrum. Very little has been done on substances possessing absorption bands beginning in the visible region and extending out into the ultra-violet. Since selenium is a substance of this type the determination of its dispersion curve is of interest.

The dispersion curve for wave-lengths within the absorption band can not be directly determined and recourse must be had to the indirect method of metallic reflection for determining the indices of refraction and absorption in terms of the constants of elliptical polarization, assuming some formula of connection, several of which have been developed by various investigators. This has recently been done most successfully by Pflüger for cyanin, which has a strong absorption in the green. His work shows a very satisfactory verification of the Ketteler-Helmholtz formula for dispersion and Cauchy's formulæ for metallic reflection.

The metallic reflection of selenium is of interest because it is on the border line between transparent and true metallic media, and it is from media occupying such an intermediate position that much is

to be learned concerning the true nature of metallic reflection. "Vitreous selenium" reflects blue and violet light metallically and the longer wave-lengths vitreously. By passing it over into the allotropic form known as "metallic selenium," it behaves more like a true metal for all wave-lengths, at least in the visible spectrum.

It is the object of this paper, after briefly recounting the previous work on selenium, to determine just how the reflection from vitreous selenium assumes more and more of the characteristics of true metallic reflection as the wave-length of the incident light is decreased. The phase-condition and azimuth of restored polarization of the reflected light will be studied at various incidences for three different wave-lengths. The changes in these characteristics of the reflection will be noted as the selenium is transformed from the vitreous to the metallic form. The data thus secured will be interpreted analytically in order to secure values of the indices of refraction and absorption to compare with those determined directly by other workers.

The improvements in the methods of spectrophotometry in recent years have given a very satisfactory way of testing the formulæ for the reflecting power of media whose indices of refraction and absorption are known. Murphy¹ in 1897 verified Fresnel's reflection formulæ for glass as a type of transparent media, but so far as I know, no photometric verification in the case of an absorbing medium, for various angles of incidence and various wave-lengths, has been attempted. It becomes, then, the object of the second part of this paper to verify Cauchy's formulæ (page 203) for the intensity of the light reflected from metallic media, by means of observations with a Brace spectrophotometer.

2. *Forms of Selenium.*

The properties and transformations of the allotropic forms of selenium have been treated recently by Saunders.² Three forms are recognized: (1) Liquid (including vitreous, amorphous and

¹ Murphy, *Astro. Phys.*, Jan. 6, 1-10, 1897.

² A. P. Saunders, *Jour. Phys. Chem.*, IV., No. 2, June, 1900, pp. 423-513. A fairly complete bibliography on selenium is included. Some references given in this paper are omitted by Saunders.

soluble selenium); (2) crystalline red, (including perhaps two closely allied forms); (3) crystalline gray or metallic. The vitreous and metallic forms alone are of interest in the present research, and since previous workers have not been uniformly clear as to which form of selenium they employed, or as to the precise treatment of their mirror surfaces, I shall state briefly the general characteristics of these two forms.

The first form has the properties of an ordinary liquid above 220°C .; below this it becomes more and more viscous, remains soft down to about 60° , and at 30° – 40° gets quite hard and brittle, showing a red streak. In this form it is called vitreous selenium from its conchoidal and brilliant fracture. Amorphous selenium is the state in which the element separates from solutions of selenious acid on reduction, forming, when dry, an impalpable red powder with no trace of crystallinity. The amorphous form results whenever a deposit is secured from vaporized selenium, and the thin films of selenium secured by cathode deposit are also of the amorphous variety. Finely powdered vitreous selenium cannot be distinguished from the amorphous variety; and conversely, amorphous selenium when warmed to 40° – 50°C . darkens in color and coagulates to a soft mass which, on cooling, becomes hard and brittle, assuming somewhat the fracture of the vitreous form.

Gray crystalline or metallic selenium is obtained from any of the other forms at higher temperatures; in presence of certain liquids, the change takes place even at ordinary temperatures. This is the stable form of selenium at all temperatures from ordinary temperatures to the melting point. The other forms are unstable, the red crystalline representing an intermediate stage between "liquid" and metallic selenium. The reverse transformation from metallic into any other form is not possible below 217°C . With lapse of time the vitreous form passes gradually over into the gray crystalline or metallic form. The change in the optical properties accompanying this transition is illustrated by the observations on fresh and old mirrors.

While the preliminary and check observations in this research were made with mirrors of commercial selenium, which is the vitreous modification and contains considerable sulphur and some

tellurium as impurities, the mirrors for which the final values are given were made of chemically pure vitreous selenium. Some of the mirrors were converted into the metallic form in a manner described later.

3. *Optical Properties of Selenium. Emission and Absorption Spectra.*

Historical. — The previous work on the optical properties of selenium has comprised observations of the emission and absorption spectra of selenium vapor, the constants of elliptical polarization of light reflected from selenium mirrors, and the determination of its refractive index directly and indirectly. Recently, while this research was under way, Nutting has published values of the reflection coefficient for different wave-lengths.

In 1863 Werther¹ noted the similarity between the spectra of selenium and lead. Ditte² (1871) found well-marked yellowish-green lines in the selenium spectrum toward the *E* line, and also two brilliant blue bands near the *G* line. The work of Salet and of Plücker and Hittorf³ is summarized in the British Association Reports for 1884. The series spectra of selenium, showing principally triplets, was investigated by Runge and Paschen⁴ in 1897 and its analogy with the series spectra of oxygen and sulphur was noted.

The absorption spectrum of selenium vapor was studied by Salet (1871) and Gernez (1872), and it was found that white light passed through a porcelain tube containing selenium heated in an atmosphere of dry carbonic anhydride is gradually absorbed from the violet up to the red, without any appearance of black lines; on raising the temperature considerably the spectrum becomes brighter and dark bands appear furrowing the blue and violet.

HISTORICAL ACCOUNT OF THE WORK ON METALLIC REFLECTION OF SELENIUM.

The earliest work on the metallic reflection of selenium, as far as I have found, is that of Jamin⁵ (1850), who records the

¹ Werther, J. pr. Chem., 88, pp. 180-181, 1863.

² Ditte, Comp. Rend., 73, p. 622, 1871; Chem. Soc. Jour. (2), 9, p. 1146, 1871.

³ Brit. Assoc. Rep., 1884, pp. 440, 441.

⁴ Runge and Paschen, Wied. Ann. 61, p. 641-686, 1897; also Astro. Phys. Jour., 8, pp. 70-101, 1898.

⁵ Jamin, Ann. de Chim. d. Phys., 29, p. 303, 1850.

value of the principal incidence, the coefficient of ellipticity and the ratio of amplitudes of the principal incidence, for a single wave-length.

Quincke (1874) determined the principal incidence and principal azimuth for a number of metals, including selenium, by a modification of Brewster's double mirror method.¹ Though not so stated, his mirrors were in all probability of vitreous selenium. Just before observation they were polished with buckskin and a pinch of jeweler's rouge (p. 342, loc. cit.). Quincke's values of the principal azimuth are much higher than those of other observers, and the dispersion curve deduced from his results by Ketteler¹ gives a steadily *rising* refractive index (n) with increasing wave-length, which is contrary to all other observations, to be discussed presently. Some experiments looking toward a possible explanation of this discrepancy will be mentioned later on.

Glan² in 1879 studied the change in phase of monochromatic red light upon reflection from selenium surfaces by the method of Newton's rings for their films. He used vitreous selenium melted between glass plates. His angles of incidence ranged from 18° to 70° ; and his results show no great difference for red light between selenium and ordinary transparent substances. He also determined the variation in the difference of phase (Δ) with changing wave-length (λ) (for a given incidence of 30°); his results show only a small change in Δ with change in λ , but Δ increases with decreasing λ , as does the absorption of selenium.

Using a Babinet compensator in the ordinary way Glan measured the phase-difference for selenium in the neighborhood of the principal incidence (φ) and determined $\bar{\varphi}$ by interpolation for wave-lengths $631\mu\mu$ and $508\mu\mu$.

The latest work on the metallic reflection of selenium is that of Cornu³ (1889) who investigated a portion of the ultra-violet as well as the visible spectrum. In the visible region the phase condition of the reflected light was determined in the usual way with a Bravais compensator.

¹ This method is well described and its accuracy shown in a paper by Pflüger on the Metallic Reflection of Solid Cyanin, Wied. Ann., 65, pp. 214-224, 1898.

² Ketteler, "Theoretische Optik," Braunschweig, pp. 548-552, 1885.

³ Glan, Wied. Ann., 7, pp. 650-652, 1879.

⁴ Cornu, Comp. Rend., CXIII., 1889, pp. 917-923, 1211.

In the ultra-violet region flourspar lenses were used and approximate adjustments were made by means of a fluorescent eye-piece the final observations being secured photographically. The difficulty of effecting the double operation of compensator and analyzer was eliminated by using a Jamin-Babinet compensator and noting the displacement of the fringes instead of moving the quartz wedge. The reflected light was focused directly on the face of the compensator, which bore a ruled line for reference; an image of this, together with that of the displaced fringes, was focused by a second flourspar lens on a sensitive plate, between which and the compensator was placed the analyzing nicol. Since the position of the fringes is independent of the azimuth of the analyzer, a single exposure would suffice to determine the fringe-displacement, if

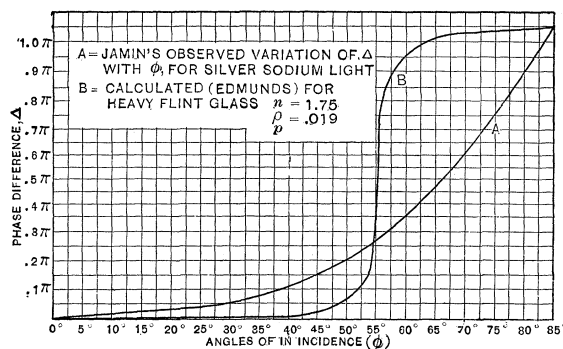


Fig. 1.

the analyzer is in position to give the bands at all. The exact azimuth of the reduced polarization was determined by a series of eight or ten exposures on the same plate, the analyzer being rotated each time through a small known angle; the azimuth for which there was maximum intensity of the fringes is the desired principal azimuth, when the angle of incidence corresponds to a fringe-displacement of $\pi/2$. This method is of course less precise than the measurements in the visible spectrum; but, so far as I know, this is the only recorded attempt to determine directly the phase relations in metallically reflected ultra-violet light.

Cornu's¹ mirrors were of vitreous selenium melted and pressed

¹Cornu, *Comp. Rend.*, LXXXVI., p. 649, 1878.

out between surfaces of polished quartz. He used two mirrors, one freshly made and the other seven years old. Age gave a more metallic character to the reflection, increasing the absorption very noticeably. Additional evidence along this line was secured in the present research.

The results of all previous workers are given in the accompanying table.¹ The wide variation in their observations exhibits the desirability of further work along this line. The work of Glan and of Cornu showed that selenium behaves as a true metal only for the shorter wave-lengths, acting more like a transparent substance for the longer wave-lengths. The difference between the forms of the curves in which the phase-difference (Δ) is plotted as a function of the incidence (ϕ) for vitreous and for metallic reflection was pointed out by Cornu in 1878, and is shown in the accompanying curves, Fig. 1, for glass and silver. The former shows an inflection at the point $\Delta = \pi/2$ (*i. e.* $\lambda/4$) so that the

TABLE I.

Previous Values of Constants of Elliptical Polarization of Light Reflected from Selenium Surfaces.

λ	$\bar{\phi}$	$\bar{\psi}$	Observer.	References.
280 $\mu\mu$	68°10'	10°10'	Cornu.	<i>Jamin</i> : 1850, Ann. d. Chim. et Phys., Vol. 29, p. 303.
431	(64 00) 70 10	(11 12) 15 30	Quincke.	
439	71 30	5 00	Cornu.	<i>Quincke</i> : 1874, Pogg. Ann., Jubel Bd., p. 336.
439	(68 15)	(7 58)		
486	71 00	13 14	Quincke.	<i>Glan</i> : 1879, Wied. Ann., Vol. 7, p. 640.
508	71 28	7 31	Glan.	
527	71 10	12 13	Quincke.	
589	71 23	11 32	Quincke.	
589	68 05	9 55	Jamin.	<i>Cornu</i> : 1889, Comptes Rendus, Vol. CVIII., p. 917, 1211.
631	69 49	4 8	Glan.	
656	71 26	8 24	Quincke.	
721	69 35	0 30	Cornu.	
721	(69 00)	(7 00)		

Cornu used two mirrors, one fresh, another seven years old. The figures in parentheses are for the old mirror.

¹ Plotted from the results given by Jamin, Ann. de Chim. et d. Phys., 19, p. 315, 1847.

rate of change of phase-difference with respect to the angle of incidence is very large in this region, whereas for metallically reflecting media, the phase-difference rises steadily with increasing incidence, and shows no such inflection. Such a curve showing the connection between the phase difference and the angle of incidence for any one wave-length can not be secured from the observations already cited, and so it was the object of the first part of the present investigation to secure such curves for several wave-lengths which will show just how the reflection from selenium surfaces acquires more or less of a true metallic character as the wave-length of the incident light varies. The general conclusion is that there is no sharp distinction between the two cases of vitreous and metallic reflection, and that selenium, like several other substances such as the aniline dyes, presents the transition from one to the other in a continuous manner as the wave-length of the incident light is changed.

PRESENT WORK ON THE REFLECTION OF LIGHT FROM SELENIUM.

Introduction.

The present experimental work on the reflection from selenium surfaces is divided into two main parts in the visible spectrum: (1) The determination of the phase condition and the azimuth of restored polarization of the reflected ray for different angles of incidence for red, yellow and blue light; (2) the direct observation of the reflecting power for various wave-lengths and at different angles of incidence by means of a spectrophotometer.

From a knowledge of the constants of the elliptical polarization of the reflected light as secured from part (1), the values of the refractive index (n) and the absorption coefficient (k') will be secured by an analytical interpretation of the phenomena, and then compared with the directly determined values of k' and n secured by other observers.

The directly observed values of the reflecting power R , secured from part (2) and those of previous workers will be compared with the values calculated from k' and n as given by part (1).

The foundations of the theory of metallic reflection are far from satisfactory physically, and accumulated experimentation under

proper and varied conditions is needed for an advance in this direction. The formulæ here used in the reduction of observed quantities to give the optical constants of the medium are not to be regarded as constituting a real theory of metallic reflection, but rather as convenient mathematical aids which, though founded on an unsatisfactory physical basis, have been found to give results which agree well with experiment. A theory of metallic reflection phenomena is yet to be developed in terms of the ionic theory of matter.

Metallic Reflection Formulæ.

Before recounting the present experimental work on the metallic reflection of selenium, attention is called to the formulæ which have been employed throughout the investigation in the reduction or interpretation of experimental results.

Notation.

$n_i \equiv$ index of refraction for incidence i .

$n_0 \equiv$ index of refraction for normal incidence; when written simply n , the variation with incidence is not considered.

$k \equiv$ absorption coefficient as defined by Drude.

$k' \equiv nk$, *i. e.*, absorption coefficient as defined by Walter; see p. 203.

$k'_i \equiv$ absorption coefficient for incidence i .

$k'_o \equiv$ absorption coefficient for incidence o° , when written simply k' , no account is taken of its variation with changing incidence.

$\Delta \equiv \delta_p - \delta_s \equiv$ difference in phase between the two components of the elliptically polarized reflected light, polarized in and normal to the plane of incidence.

$\phi \equiv$ azimuth of "restored" or "reduced" polarization of the reflected light with reference to the plane of incidence.

$\tan \phi = \rho \equiv \frac{A_p}{A_s} =$ ratio of the amplitudes of the two components of the reflected light.

$\varphi \equiv$ angle of incidence.

$\bar{\varphi} = \varphi$ and $\bar{\psi} = \psi$ when $\Delta = \pi/2$, *i. e.*, $\bar{\varphi}$ and $\bar{\psi}$ are the "principal incidence" and "principal azimuth."

$$R \equiv \text{reflecting power} \equiv \frac{\text{intensity of reflected light}}{\text{intensity of incident light}} \\ = \frac{A_R^2}{A\varphi^2}, \text{ for normal incidence.}$$

$R_i^p \equiv$ reflecting power at incidence i for light plane polarized in the plane of incidence.

$R_i^s \equiv$ same for light polarized normal to the plane of incidence.

Formulae.

*Approximate.*¹

$$(a) \quad \begin{cases} k = \sin \Delta \tan 2\psi \\ n = \sin \varphi \tan \varphi \cdot \frac{\cos 2\psi}{1 + \cos \Delta \sin 2\psi} \\ n^2(1 + k^2) = \sin^2 \varphi \tan^2 \varphi \cdot \frac{1 - \cos \Delta \sin 2\psi}{1 + \cos \Delta \sin 2\psi} \end{cases}$$

$$(a') \quad \begin{cases} k = \tan 2\bar{\psi}, & \text{At principal incidence or} \\ n = \sin \bar{\varphi} \tan \bar{\varphi} \cos 2\bar{\psi}, & \Delta = \pi/2. \end{cases}$$

*More rigorous.*¹

Putting

$$\sin \Delta \tan 2\psi = \tan Q, \quad \cos \Delta \sin 2\psi = \cos P, \\ \tan \frac{1}{2}P \sin \varphi \tan \varphi = S,$$

and neglecting $1/S^4$ in comparison with 1,

$$(b) \quad \begin{cases} n = S \cos Q \left(1 + \frac{1}{2} \frac{\sin^2 \varphi}{S^2} \right) = S \cos Q(1 + V) \\ nk \equiv k' = S \sin Q(1 - V), \quad V \equiv \frac{1}{2} \frac{\sin^2 \varphi}{S^2} \\ k = \tan Q \left(\frac{1 - V}{1 + V} \right) \text{ or } = \tan Q \left(1 - \frac{\sin^2 \varphi}{S^2} \right). \end{cases}$$

(If we further neglect $1/S^2$ in comparison with 1, we get from these last equations those under (a) above.)

At principal incidence:

$$\tan \varphi = \tan 2\bar{\psi}, \quad \cos P = 0, \quad S = \sin \bar{\varphi} \tan \bar{\varphi}.$$

¹ Drude: Theory of Optics, Amer. ed., pp. 274-295, 358-368; Wied. Ann., No. 36, p. 544, 1889; No. 39, p. 507, 1890; No. 64, pp. 161, 162, 1898. See also Winklemann, Handbuch d. Phys., p. 826.

Whence

$$(b') \quad \begin{cases} n = \sin \bar{\varphi} \tan \bar{\varphi} \cos 2\bar{\psi} \left(1 + \frac{\cot^2 \bar{\varphi}}{2} \right) \\ k' \equiv nk = \sin \bar{\varphi} \tan \bar{\varphi} \sin 2\bar{\psi} \left(1 - \frac{\cot^2 \bar{\varphi}}{2} \right) \\ k = \tan 2\bar{\psi} (1 - \cot^2 \bar{\varphi}). \end{cases}$$

Taking the variation of k' and n with φ into account, Ketteler¹ has deduced the equations of metallic reflection giving n and k' in terms of Δ , φ and $\bar{\varphi}$, which Walter² has put in the following form:

More Rigorous Formulæ in a Different Form.

Putting

$$\sin \bar{\varphi} \sin 2\bar{\psi} = \sin \chi,$$

$$\sin 2\bar{\varphi} \sin 2\bar{\psi} = \sin \theta,$$

$$k'_{\bar{\varphi}} = \tan \bar{\varphi} \sin \chi,$$

$$k' \equiv nk.$$

$$n_{\bar{\varphi}} = \tan \bar{\varphi} \cos \chi,$$

$$(c) \quad \begin{cases} k'_{\phi=0} \equiv k'_0 = \tan \bar{\varphi} \sqrt{\sin(\chi + \theta/2) \sin(\chi - \theta/2)}, \\ n_0 = \tan \bar{\varphi} \sqrt{\cos(\chi + \theta/2) \cos(\chi - \theta/2)}. \end{cases}$$

Formulæ for Reflecting Power. (Cauchy.)

For normal incidence, *i. e.*, $\varphi = 0$.

Light polarized in any azimuth:

$$(d) \quad R = \frac{n_0^2(1 + k_0'^2) + 1 - 2n_0}{n_0^2(1 + k_0'^2) + 1 + 2n_0} = \frac{(n_0 - 1)^2 + k_0'^2}{(n_0 + 1)^2 + k_0'^2},$$

at any angle of incidence $\varphi = i$. For light polarized *in* the plane of incidence,

$$(e) \quad R_i^p = \frac{\sin^2(i - r_i) + k_i'^2 \sin r_i}{\sin^2(i + r_i) + k_i'^2 \sin r_i};$$

and for light polarized *normal* to the plane of incidence,

$$(e) \quad R_i^s = \frac{\cos^2(i + r_i) \tan^2 i + k_i^2 \sin^2 r_i}{\cos^2(i - r_i) \tan^2 i + k_i^2 \sin^2 r_i} \cdot R_i^p;$$

¹ Ketteler, *Theoretische Optik*, Braunschweig, 1885.

² Walter, "Die Oberflächen oder Schiller-Farben," Braunschweig, 1895. See also Pflüger, *Wied. Ann.*, LXV., p. 220, 1898.

and $R = \frac{1}{2} (R_i^p + R_i^s)$, for ordinary light.

In these equations $\sin r_i = \frac{\sin i}{n_i}$.

$$n_i = \left[\frac{1}{2} \left\{ \sin^2 i + n_0^2 - k_0'^2 + \sqrt{(\sin^2 i - n_0^2 + k_0'^2) + 4n_0^2 k_0'^2} \right\} \right]^{\frac{1}{2}}$$

$$k_i' = \left[\frac{1}{2} \left\{ \sin^2 i - n_0^2 + k_0'^2 + \sqrt{(\sin^2 i - n_0^2 + k_0'^2) + 4n_0^2 k_0'^2} \right\} \right]^{\frac{1}{2}}$$

or

$$(f) \quad \begin{cases} n_i = \frac{1}{\sqrt{2}} (\sin^2 i + a + b)^{\frac{1}{2}}, \\ k_i' = \frac{1}{\sqrt{2}} (\sin^2 i - a + b)^{\frac{1}{2}}, \end{cases}$$

where $a = n_0^2 - k_0'^2$ and $b = \{(\sin^2 i - a)^2 - 4n_0^2 k_0'^2\}^{\frac{1}{2}}$.

A very essential difference in notation arises between these formulæ, the failure to notice which has led to errors in some recent papers on metallic reflection. Ketteler and Walter use k to represent the absorption coefficient of the medium in question for a given wave-length of light, regarding it as the damping factor per *wave-length measured in the ether*. On the other hand, Drude uses k to represent the damping factor per wave-length *measured in the medium itself*. The k of Walter is greater than the k of Drude in the ratio of the index of refraction n of the medium, or $k' = nk$, calling k of Walter $\equiv k'$, as is done throughout this paper.

THE CONSTANTS OF METALLIC REFLECTION.

(a) *Apparatus and Method of Observation.*

A Meyerstein spectrometer furnished with Nicol's prisms on collimator and telescope (lenses: 25 mm. diameter, 20 cm. focal length, Nicols: 22 mm. \times 16 mm. aperture) and with a Jamin-Babinet compensator, was used in the ordinary way to determine the phase difference (d) between the two components of the elliptically polarized reflected light in and normal to the plane of incidence, and the azimuth of restored polarization. The shift of the compensator bands was determined with reference to a pair of fixed parallel wires mounted directly on the face of the stationary wedge, and slightly farther apart than the width of a band. The linear scale on the compensator was graduated to .5 mm., and the divided head carried

by the screw operating the movable wedge was graduated in 100 parts so that .005 mm. could be measured directly. The distance between two consecutive bands for the shortest wave-length ($432\ \mu\mu$) used was 16.78, so that the instrument allowed a difference in phase of .0003 of a wave-length to be measured provided the sharpness of the bands permitted so close a setting. As a matter of fact the error in setting on the bands was such that the mean of ten readings is sure only to about .001 λ . Ten settings were made on each band with the screw always moving right-handedly. The variation from the mean is less than 1 per cent. and the variation in the determinations of the distances between consecutive bands is about 0.3 per cent. Settings were made on the bands with the analyzer in each of the conjugate positions, and from three to five bands were observed in each case in order to eliminate any variations in the figure of the wedges. A preliminary test of the wedge and a calibration of the screw proved the combination to be reliable to within the range of error of setting on a band.

In the azimuth determinations twenty settings of the analyzer were made for each of the conjugate positions, making forty settings in all for the full determination of an azimuth. Ten readings were taken in each quadrant in order to eliminate any eccentricity of the nicol in its mounting and also any local errors of graduation on the circular head, which could be read by a vernier to 1' of arc. Successive settings for maximum sharpness of the compensator bands varied by about three degrees, generally less, and the probable error in the azimuth determination, so far as the purely instrumental errors are concerned, is about 25'.²

The position of the central table carrying the mirror could be read directly to 1' and the position of this table when the mirror was normal to the collimator could be determined by successive trials to within 2'. The angle of incidence is then accurate to be about this amount. The telescope was brought into the proper position by means of a vertical hair in the eye-piece which was brought to the center of the reflected image of the collimator slit

¹ See Drude, *Theory of Optics*, pp. 255-258; or Preston, *Theory of Light*, pp. 404-409.

² The effect of a poor mirror surface on the value of the azimuth is noted later on.

for each new angle of incidence, and was then focused on the compensator. Since both the bands and the reference wires are outside the telescope, changing the focus back and forth from the collimator slit to the face of the compensator introduced no error.

The source of light for the red and blue was a Nernst filament (110 volts) the radiation from which was focused on the collimator slit after passing through appropriate screens to render it monochromatic. A plate of dense cobalt glass combined with a potassium bichromate screen gave a bright nearly monochromatic band of red light, and in the blue a double thickness of cobalt glass combined with a thin sheet of "signal green" gave a fairly monochromatic band. The wave-lengths transmitted by these screens were determined by locating the maximum intensity of the light transmitted by them when placed before the slit of an auxiliary prism-spectrometer, the horizontal surface of which had been previously calibrated in terms of known Fraunhofer lines. These wave-lengths were $.735 \mu\mu$ and $.432 \mu\mu$ respectively. For the yellow, a sodium flame was used. The correctness of the wave-length determinations is tested by their agreement with the distances between consecutive compensator bands for the three different colors.

	Red. Sc. Divs.	Yellow.	Blue.
Distance between bands.	28.56	22.86	16.78
Wave-lengths.	$735 \mu\mu$.	$589 \mu\mu$.	$432 \mu\mu$.
Ratio.	.03885	.03881	.03861

(b) *Method of Making Mirrors.*

(b₁) *Vitreous Selenium.*—To give accurate results the mirror surfaces must be free from scratches, free from films of any foreign substances, and must be perfectly plane; the latter is a rigorous requirement only in measurements of the absolute reflecting power.

In order to secure as clean mirrors as possible, the selenium was melted in a small porcelain crucible and a portion of the melted substance from beneath the surface was drawn up by suction into a hot glass tube; from this a bead of molten selenium about 5 mm. in diameter was blown upon a clean warm glass plate and after being pressed out into a circular film some 2 cm. in diameter between this

and a second warm glass plate, was allowed to cool under moderate pressure. When cold, one of the glass plates was knocked off. From a large number of mirrors thus made, the best were selected.

The glass covers were of the plane parallel "crystal" plate, selected for freedom from scratches. They were thoroughly cleaned, and just before being warmed to receive the bead of molten selenium, they were wiped with clean cotton wool dampened with alcohol and then wiped dry. With these precautions and using c. p. selenium, good mirror surfaces could be secured, without polishing, of about two to five square centimeters area. Any small regions which seemed defective were covered with black paper, as were also all exposed parts of the glass backing.¹ When not actually in use, the mirrors were wrapped in clean tissue paper. These details are given because the treatment and condition of the mirror surfaces are of prime importance on account of the rôle which the so-called "surface-layer" plays in metallic reflection.

(*b*₂) *Metallic Selenium*. — Some of the films of vitreous selenium thus formed were converted before the glass plate was removed into the metallic or gray crystalline variety by being heated in an oven at about 180° C. for 4–6 hours, and then allowed to cool gradually. When cold they no longer adhered to the glass covers and were very brittle; their surfaces were far from mirror-like, showing a dull gray luster. To secure a mirror such a film was cemented to a glass plate and the exposed surface thoroughly polished with soft chamois skin and jeweler's rouge, and just before observation they were rubbed slightly with clean chamois. An attempt was made to get a better surface before polishing with the rouge by rubbing the metallic film with fine "crocus" cloth, but the selenium scratched too readily. The mirrors of metallic selenium were not so perfect as the vitreous ones, and the numerical values given for them later on are to be regarded merely as indicating the direction of the modification in the reflected light, not the exact magnitude of the change.

The effect of polishing a mirror of vitreous selenium was also tried in order to correlate, if possible, Quincke's values for polished mirrors with Cornu's and my own for unpolished vitreous mirrors.

¹ Cf. Drude, Wied. Ann., 39, p. 497, 1890.

TABLE II.
Kind of Mirror: Vitreous Selenium, Unpolished.

Wave-Length: 735μμ. Distance Between Bands: 2 <i>a</i> = 28.56 Sc. Div.					589μμ 22.86.				432μμ 16.78.			
φ	Shift δ <i>x</i>	Phase Δ in π	ψ	Ratio of Amplitudes <i>A_p</i> / <i>A_s</i>	δ <i>x</i>	Δ	ψ	<i>A_p</i> / <i>A_s</i>	δ <i>x</i>	Δ	ψ	<i>A_p</i> / <i>A_s</i>
20°	0.32	.0224	41°21′	.880	0.60	.0525	42°08′	.905	0.38	.0453	42°03′	.902
30							40 36	.857				
40			32 14	.630	1.60	.1400	34 09	.678	0.61	.0727	32 19	.633
50	0.87	.0610					27 15	.515				
60			16 51	.303	2.30	.2012	18 25	.333	1.18	.1405	23 53	.443
65			10 24	.184	2.98	.2607	13 30	.240	1.88	.2241	13 36	.242
67	3.72	.2609	8 50	.155								
68			7 45	.136	3.40	.2974	11 42	.207	2.42	.2884	11 33	.204
69												
70	6.88	.4825	6 17	.110	4.52	.3954	9 03	.159	3.14	.3742	10 09	.179
71												
72												
73	10.91	.7651	8 14	.145	7.64	.6684	9 34	.168	4.76	.5673	10 55	
75	12.54	.8794	11 33	.204	8.66	.7576	10 35	.187	5.31	.6329	12 00	.213
78	13.11	.9194	16 55	.304								
80	13.48	.9453	22 35	.416	10.46	.9151	19 43	.358	6.90	.8224	17 43	.320

Notation: δ*x* ≡ mean shift of bands with reference to their position for direct transmission. Δ ≡ δ_{*p*} − δ_{*s*} = $\frac{\delta x}{a} \pi$ where *a* = half distance between consecutive bands. $\psi = \frac{\psi'' - \psi'}{2}$ where ψ'' and ψ' are the mean settings of the analyzer for the two sets of bands.

$\frac{A_p}{A_s}$ = amplitude // to incidence-plane
 amplitude ⊥ to incidence-plane = tan ψ.

(e) Results.

(c₁) *General Transition from Vitreous to Metallic Reflection with Decreasing Wave-length.* — The observed values of the phase-difference (Δ) and the azimuth (ψ) for various angles of incidence for different wave-lengths and for the several kinds of mirrors are given in the following tables (II.-IV.) and are also represented graphically in the accompanying curves.

The quantities observed for each incidence are : (1) The settings of the analyzer for maximum sharpness of the two sets of compensator bands, from which the azimuth is secured by the relation $\psi = \frac{1}{2}(\psi'' - \psi')$; (2) the position of the bands in each case, from which, by reference to their positions for direct transmission, δx

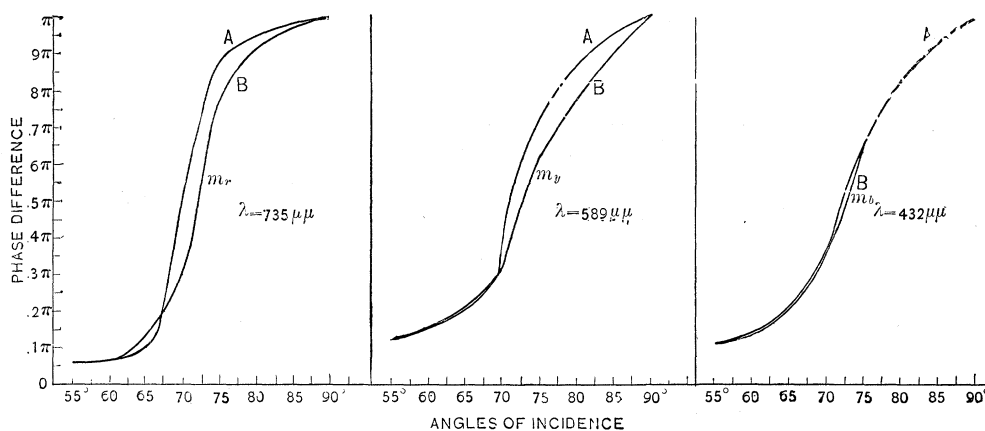


Fig. 2. Difference in the phase conditions of light reflected from mirrors of vitreous and metallic selenium. Curves *A* are for vitreous selenium. Curves *B* are for metallic selenium.

can be determined, and so Δ by the relation $\Delta = \pi \delta x / a$, where a is the half-distance between consecutive bands. The ratio of amplitudes A_p/A_s is given by the relation $A_p/A_s = \tan \psi$.

Table II. is for an unpolished mirror of vitreous selenium. The variation of phase-difference and of amplitude-ratio with change of incidence is shown by the curves in Figs. 2, 3 and 5, from which it is seen by comparison with those of Fig. 1 for glass and for silver, that selenium behaves in the matter of elliptical polarization by reflection more like a transparent substance for the longer wave-

lengths, and more metallicly for the shorter wave-lengths. The gradual disappearance of the region of inflection near $\lambda = \pi/2$ as we pass from red to blue is well brought out in the phase curves,

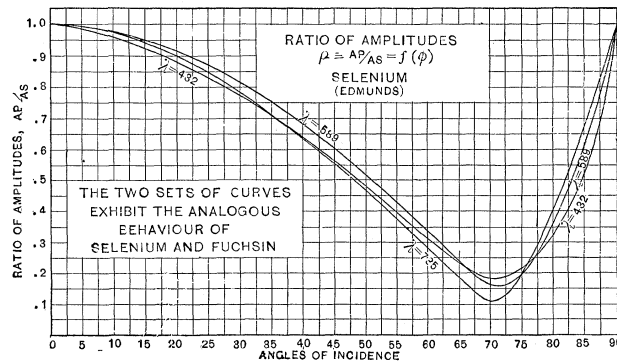


Fig. 3.

as is also the disappearance of the sharpness of the minimum in A_p/A_s in the amplitude curves.

Similar curves secured by Merkel for fuchsin, Figs. 4 and 6, are presented for comparison with those of selenium. The change in the character of the phase curves and of the amplitude curves, as

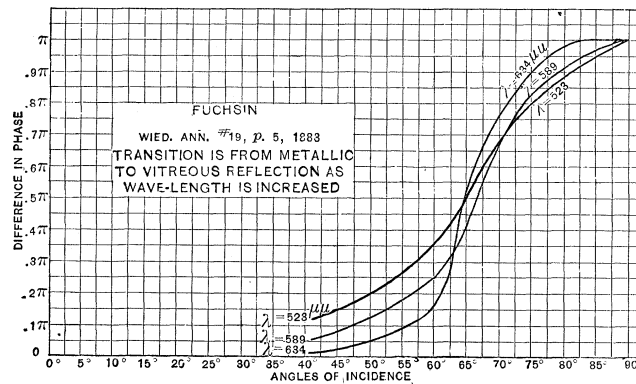


Fig. 4.

we pass from longer to shorter wave-lengths, is perfectly analogous in the two cases, though, of course, for fuchsin the amount or rapidity of the transition is much more marked than for selenium.

This gradual disappearance of the region of inflection in the phase curves and the broadening or rounding off of the minimum in the amplitude curves is characteristic of substances possessing surface color, and the magnitude of the transition as different wave-lengths

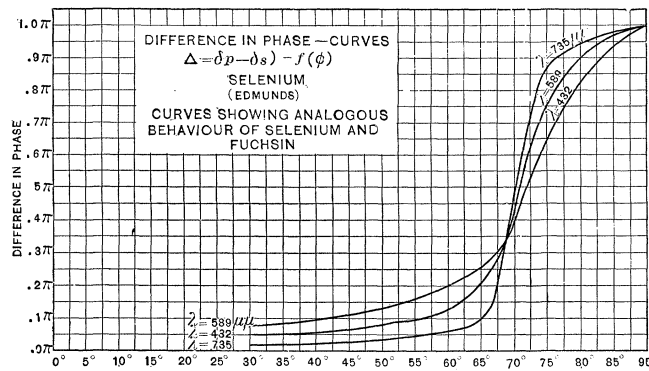


Fig. 5.

are used determines the prominence or intensity of the surface color. I shall discuss the surface color of selenium in more detail later in the paper.

Curves *A* and *B* in Fig. 1 represent the two limiting cases of

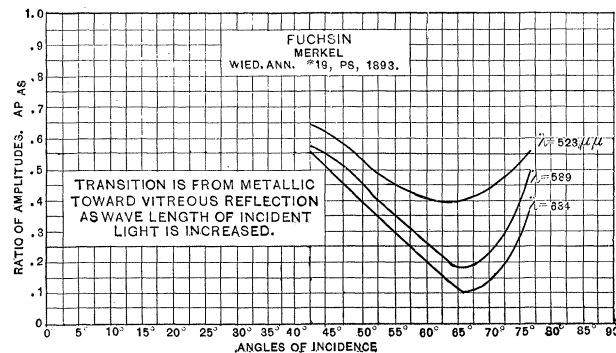


Fig. 6.

elliptical polarization by reflection; the first is characteristic for very heavily absorbing media, and the latter for perfectly transparent media. The equations which can be deduced on the electromagnetic theory for a relation between the difference in phase

and the angle of incidence in terms of the optical constants of the medium apply perfectly well to these limiting cases. But in the case of a medium which is neither transparent nor very heavily absorbing, such as selenium or fuchsin for certain wave-lengths, notably the red, some ambiguity may arise as to which set of equations to apply, *i. e.*, under which method of interpretation shall the experimental results be treated, for the experimental curves themselves lie between the two characteristic curves *A* and *B*. An examination of the analytical development by which the final relations between φ , Δ , ψ , k' and n are obtained in the case of true metallic reflection seems to show that there is no objection to applying them to any case where k' has a value, no matter if small; and this has been done by Pflüger¹ and others in deducing k' and n from observed values of the principal incidence $\bar{\varphi}$ and the principal azimuth $\bar{\psi}$ in the case of fuchsin and cyanin, the phase curves of which are intermediate between *A* and *B* (Fig. 1) as are the curves for selenium. Ketteler, in giving an analytical interpretation of Quincke's observations on selenium, applied the equations of metallic reflection, but in the case of fuchsin he applied those of vitreous reflection also and presented the comparison of the two methods of interpretation as applied to this latter substance.

This comparison in the case of selenium is presented in the following :

(a) Using the experimental curves giving Δ as a function of φ and determining that incidence $\varphi = \bar{\varphi}$ for which $\Delta = \pi/2$, by means of Lagrange's interpolation formula, we get

For $\lambda =$	735 $\mu\mu$	589 $\mu\mu$	432 $\mu\mu$
$\varphi_{\Delta=\pi/2} =$	70° 08'	71° 06'	71° 34'
A_p/A_s	.112	.156	.182
$\bar{\psi} = \tan_{\Delta=\pi/2}^{-1}(A_p/A_s)$	6° 23'	8° 55'	10° 20'

These values show an increase in both principal incidence and principal azimuth with decreasing wave-lengths; which is in agreement with the results of Cornu and Glan, but contrary to those of Quincke. The value of $\bar{\varphi}$ determined directly with a quarter-wave plate for sodium light was $\varphi_D = 71^\circ 32'$, and $\bar{\psi}_D = 9^\circ 15'$. Quincke found by the method of double reflection $\varphi_D = 71^\circ 23'$, but his

¹ Pflüger, Wied. Ann., 5, 1898, pp. 192-224.

value of $\bar{\psi}_D$ is high. I adopt as the final value of φ for $\lambda = 589\mu\mu$, the mean of my two determinations, viz: $\bar{\psi} = 71^\circ 19'$.

(b) Interpreting the experimental curves of vitreous selenium as those of a transparent substance as opposed to a metallically reflecting surface, we can by interpolation determine the angle of maximum polarization, the tangent of which is the index of refraction. We get:

$\lambda = 735 \mu\mu$	$589 \mu\mu$	$432 \mu\mu$
ρ_p .1095	.1509	.1785
φ_p $70^\circ 20'$	$71^\circ 15'$	$70^\circ 20'$
$n = \tan \varphi_p$ 2.798	2.946	2.798

Where $\rho_p \equiv$ minimum value of amplitude-ratio and $\varphi_p \equiv$ corresponding incidence, *i. e.*, the polarizing angle.

This verifies in a general way the turn in the dispersion curve in the green obtained by Professor Wood¹ and Mr. Pfund by means of thin-film interferometer measurements.

(c) In the following Table III. values of the phase difference are given for red light, (1) as observed, (2) as calculated on the assumption that selenium acts as a transparent medium, and (3) as calculated on the assumption of true metallic behavior of the selenium for red light. Judging from this table there is hardly any choice as to which set of formulæ to apply to the observations, for the observed values differ as much from one set of calculated values as from the other, and curiously enough in the same direction from both.

A comparison of the values of the refractive index secured by treating selenium as a vitreously reflecting substance with those secured by application of the equations of metallic reflection is presented in accompanying tabulation, which shows that in general the tangent of the polarizing angle gives a higher value of the refractive index than that calculated from the principal incidence and principal azimuth. The difference is greater in the case of fuchsin than for selenium.

A substance for which this transition from vitreous to metallic reflection as different wave-lengths are considered is even more

¹ Wood, Phil. Mag., June, 1902, p. 607; and also Proc. Phys. Soc. Lond., Vol. XVIII., pp. 607-622, 1902.

TABLE III.

Vitreous Selenium. $\lambda = 735 \mu\mu$.

Angle of Incidence ϕ .	Phase Difference. Δ in π .		
	Observed.	Cal. ¹	Cal. ²
30°	.0224	.0142	.0131
60	.0610	.1097	.0932
65	.0926	.1937	.1593
68	.2609	.3192	.2587
70	.4825	.4716	.3964
73	.7651	.7147	.6829
75	.8794	.8100	.8018
78	.9194	.8870	.8886
80	.9453	.9177	.9206

¹ $\Delta\pi$ calculated on assumption that the selenium acts as a transparent medium for the red, $\phi_p = 70^\circ 19'$, $\rho_p = .1095$; using the formula of Drude given on page 202.

² $\Delta\pi$ calculated on assumption of true metallic behavior by means of Drude's formulæ (Optics, Eng. ed., p. 346; see p. 202, this paper), using $\bar{\phi} = 70^\circ 8'$, $\bar{\psi} = 6^\circ 23'$, whence $k = .1988$, $n = 2.704$.

C: Comparison of Fuchsin and Selenium.

Fuchsin.			
λ	455 $\mu\mu$	589 $\mu\mu$	634 $\mu\mu$
Principal incidence, $\bar{\phi}$	48° 00'	67° 00'	64° 00'
Polarizing angle, ϕ_p	44 48	67 15	66 50
Refractive index, n (as cal. from $\bar{\phi}$ and $\bar{\psi}$)	0.687	2.2307	2.0275
$\tan \phi_p$	1.010	2.385	2.337
Principal azimuth, $\bar{\psi}$	26° 50'	9° 40'	5° 15'
Absorption coeff't, k (as cal. from $\bar{\phi}$ and $\bar{\psi}$).	.575	.293	.146
$k' = nk$.3950	.6534	.2959

Selenium.			
λ	432 $\mu\mu$	589 $\mu\mu$	735 $\mu\mu$
$\bar{\phi}$	71° 34'	71° 06'	70° 08'
ϕ_p	70 20	71 15	70 20
n	2.811	2.8198	2.704
$\tan \phi_p$	2.798	2.946	2.798
$\bar{\psi}$	10° 20'	8° 55'	6° 23'
k	.3375	.2863	.1988
$k' = nk$.9487	.8073	.5375

marked than for selenium or fuchsin, is nitroso-dimethylaniline. Professor Wood has shown that it is transparent to the ultra-violet while having a heavy absorption band in the blue region of the

spectrum and another in the extreme ultra-violet, being very transparent for yellow. He locates the center of the first band at $431\mu\mu$. Inasmuch as the refractive index cannot for this region be determined by direct prism measurements, I have studied its metallic reflection in a liquid form for $\lambda = 432\mu\mu$ in order from a knowledge of the principal incidence and principal azimuth to calculate the indices of absorption and refraction. Suffice it to point out here that for $\lambda = 432\mu\mu$ a phase-curve was secured very closely analogous to curve *A* in Fig. 1, while for yellow light, $\lambda = 589\mu\mu$, the nitrosodimethylaniline acted very nearly as a neutral liquid giving almost entirely plane polarized light for an incidence of $60^\circ \pm$; the region

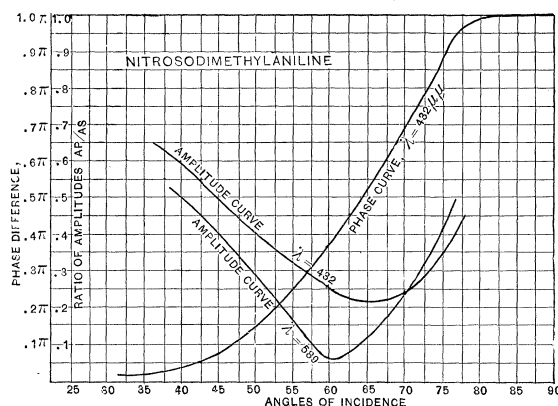


Fig. 7.

of the minimum on the amplitudes-curve being quite narrow. The results are shown in Fig. 7.

This comparison of the methods of interpreting the experimental results suggests that in all probability a result nearer the truth will be secured by applying the formulæ of metallic reflection to the observed values of azimuth and phase difference found for selenium for various incidences. These formulæ are given on page 201, and the result of applying them to the present observations to secure values of absorption coefficient and refractive index are given from here on.

(d) Effects of polish and scratches on phase difference (Δ) and azimuth (ψ).

The effect of polishing a mirror of vitreous selenium with chamois skin and rouge is shown in Table IV. There are also recorded for comparison the values of Δ and ψ for $\lambda = 432 \mu\mu$ for a mirror which was badly scratched when the glass cover was knocked off in its preparation. The scratches were quite deep and slightly curved. They had a marked effect upon both the azimuth and the difference in phase, giving larger values of the azimuth and smaller values of the phase-difference than for the unpolished mirror. Those parts of the mirror which were not scratched had a much better mirror-surface than many of the other mirrors made. The

TABLE IV.

Effects of polish and of scratches on values of Δ and ψ .

Vitreous Selenium.							
Kind of Mirror Vitreous Selenium.	$\lambda\mu\mu$	ϕ	ψ	δx	a^1	Δ	Diff. in Δ
Polished.	589	68	—	3.46	11.37	0.3027^π	.0315
Unpolished.	589	68	—	3.10	11.43	0.2712^π	
Polished.	735	65	13 05	1.87	14.35	0.1303^π	.0377
Unpolished.	735	65	10 24	1.32	14.26	0.0926^π	

Diff. in ψ , 241. $\lambda = 432 \mu\mu$.

ϕ	ψ					Δ in π				
	Pol.	Diff.	Unpol.	Diff.	Scrat.	Pol.	Diff.	Unpol.	Diff.	Scrat.
65	17° 13'	3° 37'	13° 36'	1° 05'	14° 42'	0.2598^π	.036	.2241	.002	.226
70	12 09	2 00	10 09	3 27	13 36	.4148	.020	.395		
75	13 13	1 13	12 00	3 45	15 45	.6555	.021	.634	.101	.533
80	19 49	2 06	17 43	3 23	21 06	.8700	.046	.824	.016	.808
Approx. Mean dif. 2°+			3°+			+.03 π		— .04 π		

effect on the phase is in agreement with the results of Drude² who showed that scratches on the mirror (made by rubbing it in a single direction with emery cloth No. 0000) in a direction parallel to the plane of incidence had little or no effect on the value of Δ , while scratches perpendicular to the plane of incidence

¹ The variations in a are due to the fact that the compensator was removed between these different observations and when replaced did not make the same angle with the light falling on it. But since δx as well as a is affected by the cosine of the angle which the face of compensator makes with the direction of the beam incident on it, the ratio $\delta x/a$, which alone enters the value of Δ , is unaffected.

² Drude, Wied. Ann., 39, 1890, pp. 481–554, especially in this connection pp. 497, 498.

gave Δ a little less than the normal value (*i. e.*, the value observed for as perfect mirrors as he could obtain). The difference, however, is small for the metals Drude investigated, amounting only to about $.003\lambda$ – $.005\lambda$, while in the present case for vitreous selenium deeply scratched (some of the scratches were also wide), the decrease in phase-difference is $\pi.04$ or $.02\lambda$.

The effect of polishing with rouge and chamois was to increase Δ for all three wave-lengths, the change being slightly greater for the longer wave-lengths, *i. e.*, for those to which the unpolished selenium would be more transparent. This is in accord with previous work of Drude and others on the rôle played by the surface or transition layer, the condition of which is of capital importance in determining the metallic character of the reflection. The surface molecules are altered, perhaps in their manner of aggregation in such a way as to increase the apparent absorption coefficient, and naturally the effect of polishing a pseudo-metal like selenium by increasing the thickness of the transition layer, is more marked for those wave-lengths which before polishing were just on the border line between absorption and transparency.

The effect of polish on the values of the azimuth, ϕ , as given by the observations recorded in Table IV., is, in general accord with Drude's results, which showed a larger value of ϕ for the better mirror surfaces. The effect of the deep wide scratches in the selenium mirror was to increase ϕ some 2° or 3° , and this is in general agreement with Drude's observation that a silver mirror rubbed in a direction normal to the plane of incidence with emery cloth No. 0000 gave ϕ somewhat *greater* than for a perfectly good surface. On the other hand, he found that a silver mirror rubbed in all directions with emery cloth gave ϕ some 16° *less* than the normal value. The scratches on the selenium mirror were, in general, normal to the plane of incidence, though being slightly curved they were in part somewhat parallel to the plane of incidence.

Scratches parallel to the plane of incidence would naturally be expected to increase the azimuth of the reflected light, since a scratch would reflect a vibration along its length but would have a destroying effect on a vibration at right angles to its length by absorbing it on account of multiple reflections from side to side.

Hence in the light reflected from a scratched mirror there would be a larger relative amount of light whose vibrations were parallel to the orientation of the scratches, and hence the resultant vibration would be turned toward the direction of the scratches and $\tan \phi = A_p/A_s$ would be increased and so ϕ , the azimuth, would be increased when the scratches are parallel to the plane of incidence.

The opposite would be expected for scratches normal to the plane of incidence.

The true azimuth for an unscratched surface could be secured then, from observations on a scratched mirror by taking the mean of two determinations of ϕ made with the mirror in two positions with reference to a horizontal axis (in case the mirror is vertical) which differ by 90.

The values of Δ given in this paper are probably affected by scratches, etc., only within the error of observation, while the values of the azimuth may be a little too small on this account.

(c_{III}) *Metallic Selenium Mirrors*. — Table V. represents the observed values of ϕ and Δ for different angles of incidence for a mirror of metallic selenium, made in the manner already described, for red, yellow and blue light. For red, Δ is considerably less for metallic selenium than for a vitreous mirror for all incidences greater than 65°, the same is true for yellow for $\phi > 68^\circ$ and for blue when $\phi > 73^\circ$. The effect on the blue is less marked than for yellow and red, and this is what we should expect, inasmuch as the blue is more heavily absorbed by the vitreous form than is either yellow or red, and so the change in Δ made by transforming the mirror from the vitreous to the metallic variety is greater for those wave-lengths for which the vitreous mirror was the more transparent or, rather, less absorbing than the metallic. In general the azimuth of the reflected light is greater for the metallic selenium than for the vitreous, except in the case of red light for $\phi > 73^\circ$.

The effect *in toto* of the transition from the vitreous to the metallic form is to make the selenium behave more like a true metal for all three wave-lengths investigated, the change being more marked for the longer wave-lengths. This is illustrated in the curves *B*, *B*, *B* in Fig. 2. For blue the change is very slight, indeed, and for red and yellow it is much less than was anticipated by reason of the

apparently large difference in the absorption coefficient for red; a film of amorphous selenium 0.1 mm. thick allowing a good deal of red light to pass, while a much thinner film of the metallic variety is entirely opaque.

TABLE V.

Polished Mirror of Metallic Selenium.

ϕ	Wave-Length: $735\mu\mu$				$589\mu\mu$				$432\mu\mu$			
	Dist. bet. Bands: 16.80 Sc. Divs.				22.76.				28.60.			
	δx	$\Delta\pi$	ψ	A_p/A_s	δx	$\Delta\pi$	ψ	A_p/A_s	δx	$\Delta\pi$	ψ	A_p/A_s
65°	1.84	π .129	$12^\circ 15'$.217	2.38	π .209	$13^\circ 52'$.247	1.86	π .221	$17^\circ 06'$.307
68	3.43	.240	8 15	.145	3.72	.327	11 08	.197	2.43	.290	14 38	.261
70	4.54	.318	7 11	.126	4.10	.360	10 30	.185	3.27	.390	13 22	.237
73	8.62	.603	6 35	.115	6.64	.583	10 45	.190	4.22	.500	13 52	.247
75	11.12	.777	9 57	.175	7.48	.655	12 20	.219	5.42	.645	15 19	.274

REDUCTION OF OBSERVATIONS TO DETERMINE OPTICAL INDICES.

The values of the absorption coefficient (k and k') and the index of refraction (n) secured from the values of the principal incidence ($\bar{\varphi}$) and the principal azimuth ($\bar{\psi}$) observed by previous investigators together with those presented in this paper are given in the following Table VI. Columns 1, 1' and 1'' have been calculated by the approximate formulæ; 2, 2' and 2'' by the more rigorous formulæ; 3, 3' and 3'' by the second form of the more rigorous formulæ. The results show how closely the last two agree, and also how approximate the first really is, giving considerably smaller values of n and larger values of k than the more rigorous formulæ, and of the two latter, the third set of formulæ gives consistently higher values for the absorption while giving identical values of the refractive index in comparison with the second set of formulæ; unless we apply, as I think we should, the formulæ given on page 203 to reduce n_ϕ and k_ϕ' to n_0 and k_0' , in which case, as the columns 4 and 3 show, the third set of formulæ gives higher values of the refractive index also.

To secure values of the optical constants which shall agree well with those obtained by direct experiment, the observations of the phase difference and the azimuth must be confined to the immediate neighborhood of the principal incidence, and the second set of

TABLE VI.

Observer.	Observed.			Calculated.				Calculated.				Calculated.			
	λ	ϕ	ψ	1	2	3	4	1'	2'	3'		1''	2''	3''	4''
Cornu.	280 $\mu\mu$	68 10'	10 10'	2.172	2.350	2.343	2.333	.3706	.3146	.3186		.8049	.7393	.7465	.6841
" (old).	280	64 00	11 12	1.704	1.906	1.901		.4122	.3246	.3312		.7024	.6187	.6295	
Quincke.	431	70 10	15 30	2.235	2.381	2.381	2.339	.6009	.5275	.5297		1.3430	1.2560	1.2613	1.1757
* Edmunds.	432	71 34	10 20		2.811		2.794		.3375				.9487		.8984
Cornu.	439	71 30	5 00	2.791	2.947	2.944	2.943	.1763	.1576	.1586		.4921	.4644	.4669	.4403
" (old).	439	68 15	7 58	2.239	2.417	2.412		.2855	.2434	.2458		.6392	.5883	.5928	
Quincke.	486	71 00	13 14	2.458	2.604	2.603	2.5956	.4978	.4421	.4439		1.2236	1.1512	1.1554	1.0955
Glan.	508	71 28	7 31	2.731	2.885	2.884	2.863	.2686	.2400	.2439		.7335	.6924	.7033	
Quincke.	527	71 10	12 13	2.526	2.673	2.672	2.649	.4543	.4044	.4062		1.1476	1.0810	1.0855	1.0202
Quincke.	589	71 23	11 32	2.588	2.735	2.733	2.714	.4358	.3801	.3820		1.1279	1.0400	1.0440	.9832
* Edmunds.	589	71 19	8 54		2.8198		2.8076		.2863				.8073		.7637
Glan.	631	69 49	4 8	2.527	2.697	2.692	2.694	.1453	.1269	.1279		.3672	.3422	.3443	.3212
Quincke.	656	71 26	8 24	2.702	2.854	2.851	2.843	.3019	.2697	.2711		.8157	.7697	.7729	.7287
Cornu.	721	69 35	0 30	2.517	2.692	2.686	2.692	.0174	.0152	.0153		.0438	.0409	.0412	.0387
" (old).	721	69 00	7 00	2.360	2.534	2.529		.2493	.2151	.2171		.5883	.5451	.5490	
* Edmunds.	735	70 08	6 23		2.704		2.698		.1988				.5375		.5052

VITREOUS SELENIUM.

Indices of refraction (n_0), absorption coefficients (k_0'), and reflecting power (R) calculated from observed values of phase difference (Δ) and azimuth (ψ) in neighborhood of principal incidence ($\bar{\phi}$).

	$\lambda = 432 \mu\mu$				$589 \mu\mu$			$735 \mu\mu$		
ϕ	69° 40'	70° 40'	71° 40'	72° 40'	70°	71°	72°	69° 10'	70° 10'	71° 10'
ψ	14° 47'	14° 25'	14° 46'	15° 47'	13° 28'	13° 35'	13° 19'	6° 41'	7° 01'	7° 55'
Δ	.4592 π	.5371 π	.5849 π	.6244 π	.4747 π	.5444 π	.5927 π	.4300 π	.5333 π	.61695 π
$\log S$.39991	.40540	.40031	.39776	.39625	.41114	.41018	.36850	.40545	.40073
$\log \tan Q$	1.75377	1.73781	1.73759	1.75438	1.70455	1.70603	1.68158	1.36529	1.39546	1.42272
n_i	2.3366	2.3852	2.3632	2.3314	2.3796	2.4522	2.4762	2.4579	2.6372	2.6044
k_i	.49332	.47636	.47376	.49080	.4391	.4441	.4189	.1975	.2168	.2297
$n_i k_i = k_i'$	1.1527	1.1365	1.1197	1.1445	1.045	1.089	1.0372	.4855	.5716	.5982
n_0	2.2985	2.3495	2.3271	2.2921	2.3487	2.4214	2.4483	2.4511	2.6296	2.5958
$k_0' (= n_0 k_0)$	1.0733	1.0597	1.0413	1.0621	.9727	1.0176	.9686	.4503	.5356	.5391
Means (1) $n_0 = 2.3168$ $k_0' = 1.059$					Means (1) $n_0 = 2.406$ $k_0' = .9863$			Means (1) $n_0 = 2.559$ $k_0' = .5150$		
By interpolation using LaGrange's formulæ, $\bar{\phi} = 69^\circ 46'$, $\bar{\psi} = 14^\circ 43'$					$\bar{\phi} = 70^\circ 22'$, $\bar{\psi} = 13^\circ 31'$			$\bar{\phi} = 69^\circ 50'$, $\bar{\psi} = 6^\circ 54'$		
Whence by Walter's formulæ: (2) $n_0 = 2.3674$ $k_0' = 1.171$					(2) $n_0 = 2.500$ $k_0' = 1.129$			(2) $n_0 = 2.645$ $k_0' = .5716$		
Reflecting power, $R = 25.50\%$ from (2)					$R = 26.06\%$ from (2)			$R = 22.28\%$ from (2)		
23.53 “ (1)					24.09 “ (1)			20.78 “ (1)		

formulae applied. The observations already cited having given for the latter the following values :

$$\begin{array}{lll} \lambda = 432 \mu\mu & 589 \mu\mu & 735 \mu\mu, \\ \bar{\varphi} = 71^\circ 34' & 71^\circ 19' & 10^\circ 08', \end{array}$$

observations of phase difference (Δ) and azimuth (ψ) were made on the same mirror (now five months old) as shown by the following summary.

The index of refraction is found to increase with increasing wave-length for an old mirror, and this agrees with Quincke's observations and tends to confirm the view that his mirrors of selenium were not used till some time after making.

Effect of Time on the Principal Incidence and Principal Azimuth.

— In order to show the effect of time on the values of the principal incidence ($\bar{\varphi}$) and principal azimuth ($\bar{\psi}$), I shall apply the same method to both mine and Cornu's observations of these constants of elliptical polarization for a fresh and an old mirror. The results are presented in Table VII. Walter's formulae were used in calculating the index of refraction n_0 , the absorption coefficient k_0' , and the reflecting power R , from the principal incidence and azimuth.

Lapse of time decreases the principal incidence some $18'$ to $1^\circ 48'$ after five months interval, the decrease being greater for the shorter wave-lengths. An interval of seven years gave a much larger decrease of from $0^\circ 35'$ to $4^\circ 10'$ in $\bar{\varphi}$, the greatest change being for the ultra-violet. Interpreted in terms of phase-difference, this means that the surface has changed in such a way as to increase the phase-difference (Δ) for any given incidence and to make the value $\Delta = \pi/2$ occur at a smaller incidence.

The effect of time is to increase the principal azimuth by several degrees in general; no simple variation of this change with wave-length appears and the change after five months is only $31'$ for the red. Since, roughly speaking, the absorption is directly proportional to the $\tan \bar{\psi}$, the observations show an increase in absorption for all wave-lengths as time elapses.

The effect of these variations in the values of the principal incidence and principal azimuth with time is to decrease the index of refraction and to increase the absorption coefficient, as calculated

TABLE VII.
Effect of Time on Vitreous Selenium.

Observer: Cornu. Time Interval: 7 Years.														
Mirror.	$\lambda = 280\mu\mu$					$\lambda = 439\mu\mu$					$\lambda = 721\mu\mu$			
	ϕ	ψ	n_0	k_0	R	ϕ	ψ	n_0	k_0	R	ϕ	ψ	n_0	R
New.	$68^\circ 10'$	$10^\circ 10'$	2.343	.746	20.08°	$71^\circ 30'$	$5^\circ 00'$	2.944	.467	25.34°	$69^\circ 35'$	$0^\circ 30'$	2.686	21.01°
Old.	$64^\circ 00'$	$11^\circ 12'$	1.901	.630	13.71°	$68^\circ 15'$	$7^\circ 58'$	2.412	.593	19.55°	$69^\circ 00'$	$7^\circ 00'$	2.529	19.91°
Diffs.	$-4^\circ 10'$	$+1^\circ 02'$	-0.442	-.116	-6.37°	$-3^\circ 15'$	$+2^\circ 58'$	-0.532	$+1.26^\circ$	-5.79°	$-0^\circ 35'$	$+6^\circ 30'$	-1.157	-1.10°

Observer: Edmunds. Time Interval: 5 Months.														
Mirror.	$\lambda = 432\mu\mu$					$\lambda = 589\mu\mu$					$\lambda = 735\mu\mu$			
	ϕ	ψ	n_0	k_0	R	ϕ	ψ	n_0	k_0	R	ϕ	ψ	n_0	R
New.	$71^\circ 34'$	$10^\circ 20'$	2.811	.949	27.10°	$71^\circ 06'$	$8^\circ 55'$	2.820	.807	26.00°	$70^\circ 08'$	$6^\circ 23'$	2.704	22.79°
Old.	$69^\circ 46'$	$14^\circ 43'$	2.367	1.171	25.50°	$70^\circ 22'$	$13^\circ 31'$	2.500	1.129	26.06°	$69^\circ 50'$	$6^\circ 54'$	2.645	22.28°
Diffs.	$-1^\circ 48'$	$+4^\circ 17'$	-.444	$+2.32^\circ$	-1.60°	$-0^\circ 44'$	$+4^\circ 36'$	-.320	$+3.22^\circ$	$+0.06^\circ$	$-0^\circ 18'$	$+0^\circ 31'$	-.069	$+0.51^\circ$

from these constants of metallic reflection. Both Cornu's observations and mine show the change in the refractive index to be considerable and to be nearly as great after five months as at the end of seven years.

My observations show the absorption coefficient to increase considerably, though less in the red than for yellow and blue; while Cornu's values give a decrease for the ultra-violet and a large increase in the blue and red.

The dispersion and absorption curves obtained by plotting values given in columns 1, 2 and 3 of Table VI. are shown in the accompanying diagram (Fig. 8) together with those directly observed by Sirks and by Wood¹ and Pfund.

The general discrepancy between the results of the several observers is very marked, especially for the absorption coefficient. The difference between the observed values of the principal incidence and principal azimuth of various observers are shown graphically in Fig. 9 and are probably to be accounted for in great part by the influence of scratches, polish, age, etc., as already demonstrated in this paper. The values of the absorption coefficient calculated from these metallic reflection experiments differ as much among themselves as they do from the directly observed values.

COMPARISON OF RESULTS.

In the metallic reflection experiments we are really studying surface conditions only, whereas in the experiments in which direct observations are made for absorption and refraction we are studying phenomena, having their seat inside the medium. In the metallic reflection experiments no doubt the surface conditions have varied widely and in an unknown manner. In the direct measures of absorption, the selenium was in a form entirely different from that employed in the metallic reflection experiments. Wood and Pfund used their films of amorphous selenium secured by cathode deposit, and close examination of these films shows that they are not perfectly continuous but are rather of a spongy structure which accounts in part for the much lower values of absorption secured by these observers, although their neglect to take into account the loss by reflection at the first surface would certainly tend to balance this. Their direct measures of the refractive index, n , were in the red and yellow region of the spectrum made with small-angle prisms of melted vitreous selenium, and as might be expected, there is a

¹R. W. Wood, *Phil. Mag.*, June, 1902, p. 607.

closer agreement in that region with the values of n calculated from the metallic reflection experiments. In the green-violet re-

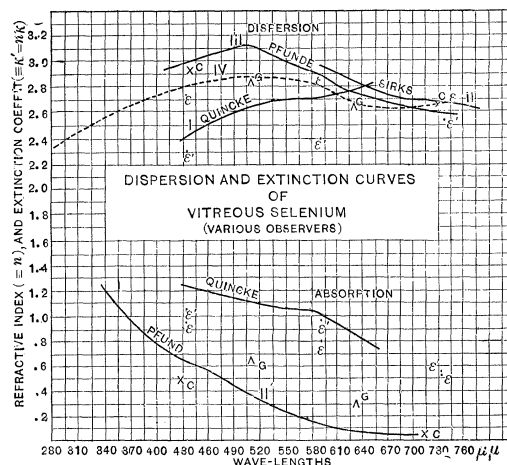


Fig. 8.

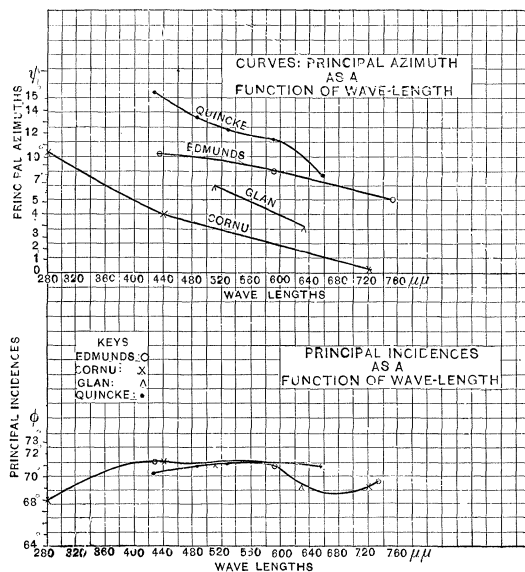


Fig. 9.

gion the direct measures of n were made by interferometer measurements on very thin films of amorphous selenium, and there is some doubt as to the validity of these results.

TABLE VIII.

Index of refraction and absorption coefficient of vitreous selenium.

Column:	1	2	3	4	5	6
Wave- Length	n Direct.	Cal. n by Reflec.	kn Direct.	kn Cal. Metal. Reflec.	kn Cal. Reflec.	kn Cal. Reflec.
214 $\mu\mu$						
280		2.333		.6841		
334						.9767
395						.9614
400	2.93		.785			
410	2.957					1.0275
415	2.910		.736			
425	2.98		.677			
430						1.1437
431		2.381		1.2613		
432	3.00	2.811		.9487	1.1776	
439		2.947		.4669		
442	3.025		.598		.8205	
454						
466	3.065		.571			
475	3.075					
486		2.604		1.1554		
490	3.120		.478		.4544	
503	3.130					
508		2.885		.7033		
510						1.1354
515			.358			
520	3.085					
524						
527		2.673		1.0855	.7232	
550	3.020		.254			1.0020
580	2.95	2.735		1.0440		
589	2.925	2.8076	.155	0.7637	.7813	.8827
605	2.90					.8415
620					1.1916	1.0728
631		2.697		.3443		
640	2.765		.0879			
656		2.854		.7729	1.1046	
660						
710	2.655		.0456			
721		2.692		.0412		
735		2.704				
748				.5376	.3478	
760	2.61		.0234			

Observers : Cols. 1 and 3, Pfund and Wood.

Cols. 2 and 4, Cornu, Quincke, Glan, Edmunds.

Col. 5, Edmunds.

Col. 6, Nutting (cal. by Edmunds).

From the data at hand, it is extremely uncertain just what form to assign to the dispersion curve of selenium. Quincke's observations, though covering a good portion of the visible spectrum, give, no matter from what point of view we consider them, results which are contrary to those of all other observers. His values of refractive index increase with increase of wave-length, and his values of the absorption coefficient are very much higher than any other determinations. I am at a loss to explain his results except that they may possibly be due, as the high absorption would suggest, to the fact that his mirrors were made some time before he actually observed with them, and so had a chance to pass over into the gray crystalline or metallic form, the apparent absorption of which he further increased by polishing just before observing.

The present work on the metallic reflection of selenium was undertaken to secure merely check values of refractive index and absorption coefficient for two or three wave-lengths in the visible spectrum. It would seem, however, desirable to make a more extended study so as to be able actually to plot a full dispersion curve from a single set of experiments.

Neglecting Quincke's observations, the values of refractive index secured by other determinations of the principal incidence and principal azimuth lie on a smooth dispersion curve which agrees in general "march" with that observed directly. The discrepancy in the values of the absorption coefficient is, however, very great, and further experiments are required to determine the extinction curve of selenium. All that the present observations enable us to say definitely is that the absorption increases from the red toward the blue end of the spectrum. Some experiments attempting to secure "Reststrahlen" in the ultra-violet by multiple reflections from selenium surfaces showed no great increase in reflecting power in that region; if anything, there was a falling off.

Lack of time and a desire to measure the reflecting power of selenium directly by photometric methods have as yet prevented the determination of more accurate dispersion and extinction curves.

The values secured from the present experiments with the fresh mirror for the wave-length 589μ will be used as a basis in calculating the reflecting power for different angles of incidence for com-

parison with the directly observed values of R . And in determining the absorption curve from the experimentally determined reflection curve for normal incidence, the dispersion curve resulting from all the experiments on metallic reflection, excepting those of Quincke, will be adopted. In this way all the quantities used and compared will result from experiments in which the chief rôle is played by the surface, and so there will be a common ground for the comparison.

SUMMARY OF EXPERIMENTS ON METALLIC REFLECTION.

The present experimental work on the metallic reflection of selenium has shown that the elliptical polarization of plane-polarized light by reflection from vitreous selenium is such as is characteristic of a transparent substance for wave-lengths in the red, and that the reflected light assumes more and more the characteristics of light reflected from true metal surfaces as the wave-length of the incident light is decreased, till in the blue selenium acts quite like a metal. In this respect selenium is somewhat analogous to fuchsin.

The variation of the principal incidence and the principal azimuth with changing wave-length was noted. The principal azimuth increases as the wave-length is decreased, while the principal incidence passes through a minimum at about $680\mu\mu$ and then remains fairly constant as the wave-length is decreased.

The effect of transforming the vitreous selenium into the gray crystalline or metallic form is to increase the absorption for all wave-lengths in the visible spectrum and to render the condition of the elliptically polarized reflected light more like that from a true metal, the change being more marked for yellow light than for blue or red.

Scratches on the surface of the mirror increase the value of the azimuth and decrease the difference in phase of the two components of the reflected light, for any given angle of incidence.

Polishing the mirror with rouge and chamois increases the phase-difference, the change being greater for the wave-lengths to which the unpolished selenium is more transparent. Polishing increases the value of the azimuth for all wave-lengths.

Lapse of time makes the vitreous selenium behave more like a metal, decreasing the principal incidence and increasing the princi-

pal azimuth. This is doubtless due to the formation of a surface layer in which the conditions are very different from those of interior portions of the selenium.

The analytical interpretation of the elliptical polarization phenomena by means of formulæ developed chiefly by Drude showed discordant values of the refractive index and absorption coefficient when the observations of different observers are compared. In general, however, the dispersion curve rises as the wave-length is decreased and has a turning point in the green at about 505μ . The absorption rises gradually as the wave-length is decreased, and all the experiments as well as the application of the dispersion formulæ seem to indicate a number of overlapping absorption bands in the blue-violet region of the spectrum.

The experiments indicate that the closer and more extended study of the absorption and dispersion of selenium will doubtless present a very interesting case to which as a test the various formulæ of metallic reflection and of the dispersion of metals may be applied.

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PHYSICAL LABORATORY, May, 1903.