PHASE CHANGE BY REFLECTION—PRIMARILY IN THE ULTRA-VIOLET.

BY OLIVER H. GISH.

THE first quantitative investigation of absolute phase change was made by Quincke[1] in 1872. This was followed by that of Wernicke,[2] Wiener,[3] Glan,[4] Hennig,[5] Drude,[6] Koenigsberger and Bender.[7] All these investigations were confined to the visible spectrum except that of Koenigsberger and Bender, who, in addition, measured for a few substances the phase change in the infra-red. So far no measurements of this phenomenon have been made in the ultra-violet.

Quincke used a total reflecting prism, a portion of whose reflecting surface was silvered. Light from a *point source, when reflected by this prism* showed interference bands due to the difference in phase of the waves reflected from the silver and those reflected from the glass. He observed variations in these bands with the angle of incidence, and also with the plane of polarization. From measurements of the width of these bands he arrived at values for the phase change from silver relative to that from glass. The complexity of this method made it unsatisfactory.

Wernicke devised a simpler method by which he measured the phase change of silver and several dyes. In this method a thin, plane parallel plate of glass was so mounted that white light reflected from it, entering a spectroscope produced a spectrum that showed vertical light and dark bands. The bands from the silvered portion of the plate showed a shift relative to those from the unsilvered part. From the relative shift the phase change was determined.

Wiener, later, by this method studied silver and obtained results that were in marked disagreement with those of Wernicke.

The work of these men was followed by a more exhaustive study, both theoretical and experimental, by Drude. In his measurements Drude

[1] G. Quincke, Pogg. Ann., 142, p. 192, 1871.
[2] W. Wernicke, Pogg. Ann., 155, p. 87, 1874.
[3] O. Wiener, Wied. Ann., 31, p. 629, 1887.
[4] P. Glan, Wied. Ann., 7, p. 640, 1879; 47, p. 252, 1892.
[5] R. Hennig, Gött. Nachr., 13, p. 365, 1887.
[6] P. Drude, Wied. Ann., 50, p. 595, 1893; 51, p. 77, 1894.
[7] J. Koenigsberger u. R. Bender, Ann. d. Phys., 26, p. 763, 1908.

used a wedge of glass so thin that it showed interference bands when illuminated by monochromatic light. The shift of the bands was then measured by a cathetometer. His measurements were in close agreement with those of Wiener and he suggested that the lack of agreement with Wernicke was due to the difference in the silver films.

It was known to Wernicke that the phase change varied with the thickness of the silver film, and he made use of this in an attempt to determine the direction of the shift of the interference bands, but Wiener was the first to make an extended study of the variation of the phase change with the thickness of the silver film. He found that with increasing thickness, the phase change increased until a full silver was obtained after which it remained constant, with a value approximately that for massive silver. In addition to the work on thick films Drude also investigated films of varying thickness and obtained results that were in close agreement with those of Wiener. To explain this phenomenon he assumed that over the reflecting surface of the silver was a very thin film (about one four-hundredths of a wave-length in thickness) having abnormal optical constants. Then when the silver film is sufficiently thick the light reflected from the normal silver back of this thin film is the more intense and consequently the effect of the latter is not observed.

Koenigsberger and Bender repeated the work of Drude with modifications designed to avoid surface films, and obtained results for gold and platinum, supposedly free of films, that were similar to those of Drude for silver with the assumed films. Hence they questioned the validity of Drude's explanation, suggesting rather, that instead of applying, as Drude did, a system of equations in which multiple reflections are neglected, more general forms such as the fundamental equations used for Hertzian waves should be applied in developing the theory.

METHODS.

The methods which may be employed for determining the phase change produced by reflection from the surfaces of metals and some other regularly reflecting substances are of two general classes:

1. *Polarimetric Methods.*—Methods of this class are not direct but require an application of the theory to determine the phase-change. The theory has not yet been sufficiently tested to accept its results as conclusive, and consequently more direct methods are desirable.

2. *Interferential Methods.*—Of these, the method of O. Wiener[1] and that of G. Sagnac[2] are the only direct ones. All other interferential

[1] O. Wiener, Wied. Ann., 40, p. 203, 1890.

[2] G. Sagnac, C. R., t. 154, pp. 1346–1349, May, 1912.

methods are indirect, yet because of their greater convenience, they have been the more generally used.

The indirect methods: If a sufficiently thin wedge-shaped piece of glass is illuminated with monochromatic light a series of interference bands, due to the interference of waves reflected from its front and back surfaces, may be observed over the plate. If now the back of the plate be coated with some substance, for example, silver, the effect is to shift the interference bands from their original position toward the thinner or thicker portion of the wedge, according to whether the phase change is a retardation or an *acceleration*. By stripping off then, a portion of the coating in a direction at right angles to the bands, two sets of bands are obtained. Their relative displacement serves as a measure of the relative phase change. The phase change by reflection from transparent substances has been thoroughly studied, and theoretically the light (electric vector) suffers no change of phase upon the reflection from air into glass. Accepting this, measurements with the above wedge should give absolute phase change in the transparent region for glass.

A glass plate having parallel faces, should show no interference bands when illuminated with monochromatic light from a broad source; but when white light reflected from it is dispersed by a spectroscope a series of vertical bands extending throughout the spectrum, in ordinary working conditions, may be observed. These bands arise from the fact that waves, of such length that their effective path in the plate is an odd number of half wave-lengths, produce destructive interference in the reflected light. A set of bands from the coated part of the plate and a set from an adjacent uncoated part will be shifted relative to each other. The magnitude of the phase change may be determined from this shift.

The latter method is essentially that of Wernicke; the former that used by Drude, and by Koenigsberger and Bender. Both have been used in the present work.

Because of the convenience of obtaining thin parallel plates mica was used in part of the work, but other advantages led finally to the use of thin wedge-shaped plates of glass. The substances investigated for phase change were silver, fuchsin, doppel-grun, crystal-violet, cyanin, eosin and aniline-orange.

First Method.

In the observations with mica the following plan was followed. A mica plate coated, except for a central strip, with the substance to be tested, was so mounted (Fig. 1), that a source (s) was focused by means of a quartz lens (a) upon the mica (p) at a small angle of incidence (about 2.5 degrees). Then, by means of another quartz lens (b) an image of this

plate by the reflected light was cast on the slit of a four foot Rowland grating spectroscope. This method requires a source giving a continuous spectrum. Sources fulfilling this requirement and also giving sufficiently intense radiation in the ultra-violet were not available. With a Nernst glower and with exposures eight hours in duration it was found that the

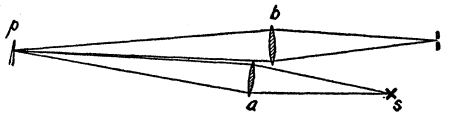

Fig. 1.

limit into the ultra-violet to which observations could be extended was 340 $\mu\mu$.

Second Method.

For most of the measurements the following method was used, which, since it made possible the application of a discontinuous spectrum, permitted measurements to be extended farther into the ultra-violet region.

Thin glass wedges were selected from several boxes of cover slips and from a small supply of thin glass plates that were at hand. All being discarded that failed to show straight bands of sufficient breadth when illuminated by monochromatic light. The breadth of band which gave the best photograph in the shorter wave-lengths was found from a few trials. These were then coated on the back with the substances whose phase change was to be investigated. Then a strip of the coating was removed in a direction at right angles to that of the bands. At first the glass wedge was simply substituted in place of the mica plate, of the method described above, and the slit of the spectroscope opened to a width of about 4 mm. With the copper arc as a source, images of the

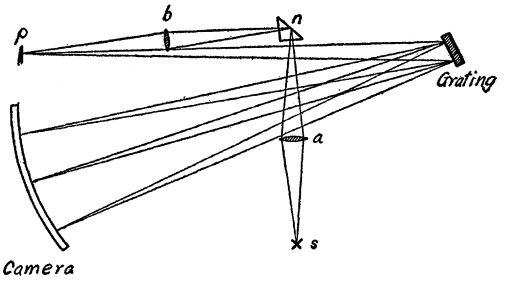

Fig. 2.

slit were distributed throughout the spectrum each showing a set of from three to six bands depending on the wave-length. Due to the achromatism of the quartz lens only a limited portion of the spectrum was in

focus at a time, so to avoid this, the glass plate itself was diaphragmed down to an aperture of 4 by 10 mm. and mounted in place of the slit of the spectroscope (Fig. 2). By means of two quartz lenses (*a* and *b*) and a total reflecting quartz prism (*n*) an image of the arc was formed on this, the light being incident as before at an angle of about 2.5 degrees. When properly adjusted all the images of the set of bands were found well defined. Photographic records were obtained upon heavy films of such length as to include the first order spectrum and a large portion of the ultra-violet region in the second order. The displacement of the bands was measured with a micrometer microscope.

Method of Measurement.

The difficulty of finding glass plates giving perfect bands was one source of error. To eliminate as much as possible that arising from the curvature of the bands, the cross line of the microscope was first adjusted tangent to some band of one set, and measurements of the shift of all the bands in the set then made. It was then adjusted tangent to a band of the opposite set and the series of readings again taken. Each of these series of readings was repeated, the respective adjustments being on another band of each of the two sets. The mean of these four sets of readings should be practically free from the error arising from curvature, provided that curvature is not abrupt and the points on the bands on which the settings are made are not too far from the line of division of the two sets. The first condition depends on the selection of the glass plates; the second on the care observed in making the settings. A small region between the two sets of bands, owing to the astigmatism of the grating, was not well defined. This necessitated setting on points that were somewhat removed from the real line of division. However this should in no case have caused a greater error than one per cent. The accuracy with which a setting on the center of a band could be repeated depended largely upon the intensity of the photograph.

Method of Depositing Films.

The silver films used were deposited by Brashear's method and were of such density that only a trace of light could be seen on looking through at the bright sky.

In obtaining films of the dyes, these were first dissolved in absolute alcohol and as concentrated a solution was used as could be dried on the plate without the substance crystallizing. The plates were coated by dipping them in the solution and quickly drying over a Bunsen flame. Considerable difficulty was met in obtaining coatings of heavy and uni-

form thickness. This lack of uniformity in the coatings is the cause of some irregularities observed in the measurements. In the region of the spectrum where the substance is most transparent distortions of the bands probably arising from this cause could usually be observed.

Thickness of Films.

Some measurements of the thickness of the films used were made as follows: Interference bands formed by laying another glass plate on the coated side of the plate holding the film to be measured, in general, showed a shift between the bands over the coated portion and those over the cleared portion of the plate. This shift was measured for two wave-lengths far enough apart so that a measurable difference in path in wave-length could be observed. The shift of the bands due to the thickness of the coating was measured in the direction in which their gain over those from the coating surface took place, as light of shorter wave-length was used. By varying the wave-lengths of the light illuminating the plate it was readily seen that the thickness was, in all measurements, less than a wave-length provided the phase change be neglected. Since fuchsin is very transparent in the red its phase change there should be the same approximately as that of glass, provided its refractive index is greater than one. Under this assumption, that the phase change from glass in air and from fuchsin in air are the same for the red, the relative shift of the bands is a direct measure of the thickness of the film. Values obtained by this method from adjacent parts of one film were 275 and 333 $\mu\mu$. The films of eosin and aniline-orange were so thin as to show Newton's colors.

Observations.

Silver.—The photographs taken for silver on mica showed a relative shift of about three-tenths of a band at 580 $\mu\mu$, decreasing slowly with decreasing wave-length to about 442 $\mu\mu$ where the two sets of bands seem to coincide. The shift with silver on glass was practically the same as for mica except that the position at which the bands coincide seemed to be shifted farther toward the ultra-violet (to about 390 $\mu\mu$). They continued to coincide throughout the transmission region for silver and as far as the photograph showed distinct bands (296 $\mu\mu$). Because of the high reflection coefficient of silver the silvered portion did not give well defined bands in the greater part of the spectrum. The accuracy with which these could be measured did not justify more than qualitative observations.

Drude's formula[1] for the absolute phase change (Δ) at the boundary

[1] P. Drude, Wied. Ann., 51, p. 86, 1894.

between a transparent medium of refractive index n_1, and an absorbing medium having an index of absorption k and an index of refraction n is:

$$tg\,\Delta = -\frac{2nn_1k}{n^2 - n^2k^2 - n_1^2}.$$

From this formula, values for the relative phase change were calculated from values for n and k obtained by Minor.[1] These were in close agreement with the observed values for the red, but, being practically constant down to about 320 $\mu\mu$, they are in very poor agreement with the observed values at the shorter wave-lengths. In the region where the bands coincide the calculated values ranged from .38 for 326 $\mu\mu$ to .32 for 275 $\mu\mu$. Minor's observations however were made on massive silver, mine on partially transparent films. The experiments on the variation of phase change with thickness of the film would hence lead one to expect poor agreement in the region of the spectrum where the substance is transparent.

Fuchsin.—The measurements on fuchsin (Table I., Fig. 3) show a decreasing phase change for decreasing wave-length until between 420

TABLE I.

Fuchsin.

Wave-Length.	Phase Change.	Wave-Length.	Refractive Index of Fuschine.
577.8	0.39	589	2.64 to 2.70
568.5	.38	527	1.85 to 1.91
521.8	.33	486	1.05 to 1.07
510.6	.33	461	0.83
465.1	.26	431	0.95
424.0	.00		
406.3	.60	425	1.00
402.3	.57	413	1.15
382.7	.51	405	1.18
353.0	.39	399	1.24
333.8	.43	397	1.32
296.1	.31	360	1.52
282.3	.27	344	1.60

and 440 $\mu\mu$ where coincidence, or at least, a minimum phase-change, is observed. Beyond this point the phase change suddenly mounts to its highest value, after which a gradual decrease is observed to 280 $\mu\mu$ where its value is .27 wave-length. The transmission region for this fuchsin film was determined by mounting it before the slit of the spectroscope so that a portion of the light falling on the slit went through the film and

[1] Minor, Ann. d. Phys., 10, p. 617, 1903.

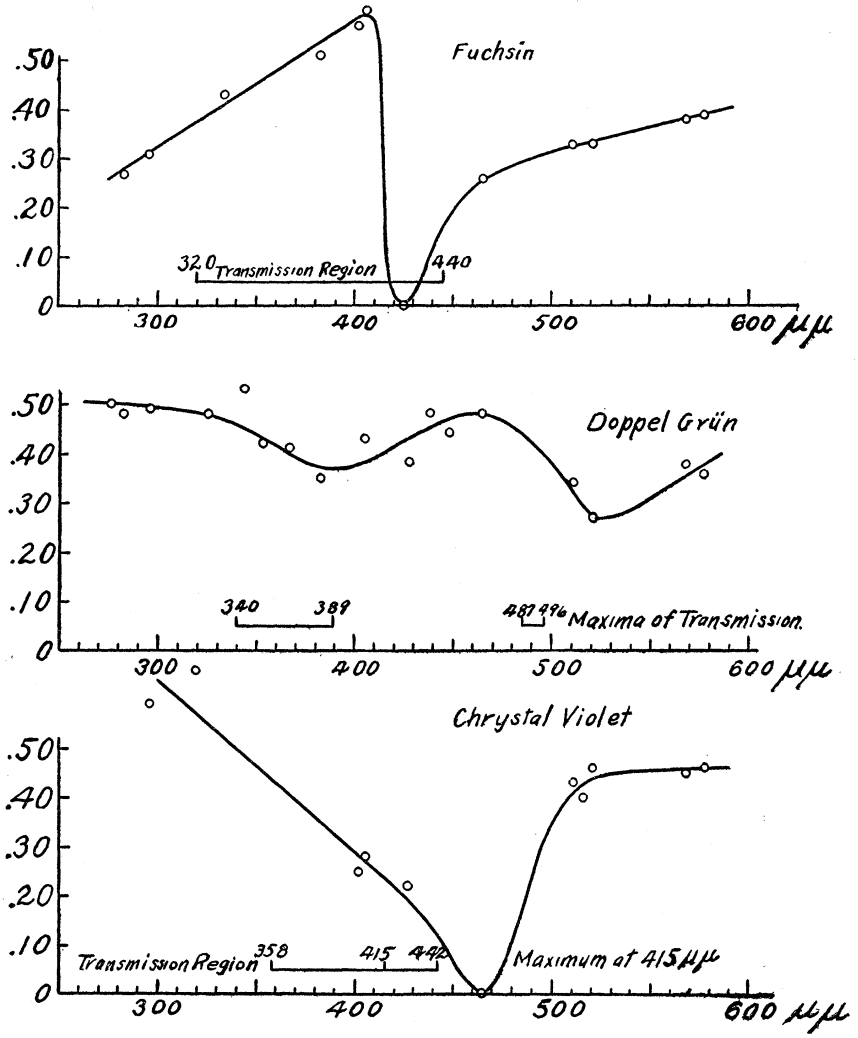

Fig. 3.

the glass plate, while the other passed through the glass plate only. By comparing these two portions in the photograph, it was observed that, between 440 and 320 $\mu\mu$ fuchsin was practically as transparent as glass. The abrupt change in phase difference at 420 $\mu\mu$ from zero to one-half wave-length probably arises from the refractive index of the fuchsin, which is less than glass at 425 $\mu\mu$, rising above it between 425 and 410 $\mu\mu$.

Doppel-Grün.—The values for the phase change at the surface of this substance goes through two minima in the portion of the spectrum here

TABLE II.

Doppel-grün.

Copper Arc.		Nernst Glower.	
Wave-Length.	Phase Change.	Wave-Length.	Phase Change.
577.8	.36	580	.34
568.5	.38	570	.25
521.8	.27	560	.25
510.6	.34	550	.28
465.1	.48	540	.23
448.0	.44	530	.21
437.8	.48	520	.21
427.5	.38	510	.20
406.3	.43	500	.18
382.4	.35	490	.18
367.1	.41	480	.30
353.2	.42	470	.39
344.2	.53	460	.45
326.0	.48	450	.47
		440	.41
296.1	.49	430	.35
283.0	.48	420	.35
276.7	.50	410	.39

investigated (Table II., Fig. 3). The transmission of this film was determined in the same way as for fuchsin, and it was found that between 496 and 487 $\mu\mu$, and between 389 and 340 were maxima of transmission. The magnitude of the transmission was considerably less than that for glass.

Crystal-Violet.—For this substance the phase change (Table III., Fig.

TABLE III.

Phase Change.

Wave-Length.	Crystal Violet.	Cyanin.	Eosin.	Aniline Orange.
577.8	0.46	0.23	0.52	0.00
568.2	.45	—	—	—
521.8	.46	.00	—	.33
515.3	.40	—	—	—
510.6	.43	—	.32	—
465.1	.00	.36	.31	.59
456.4	—	.34	—	—
427.5	.22	—	.36	.58
406.2	.28	.48	—	—
402.3	.25	.48	.42	.61
368.7	—	.42	—	—
353.2	—	.48	.32	.61
333.4	—	.46	—	—
330.8	—	.52	—	.60
319.3	.66	.43	.48	—
296.1	.59	.42	.32	.56

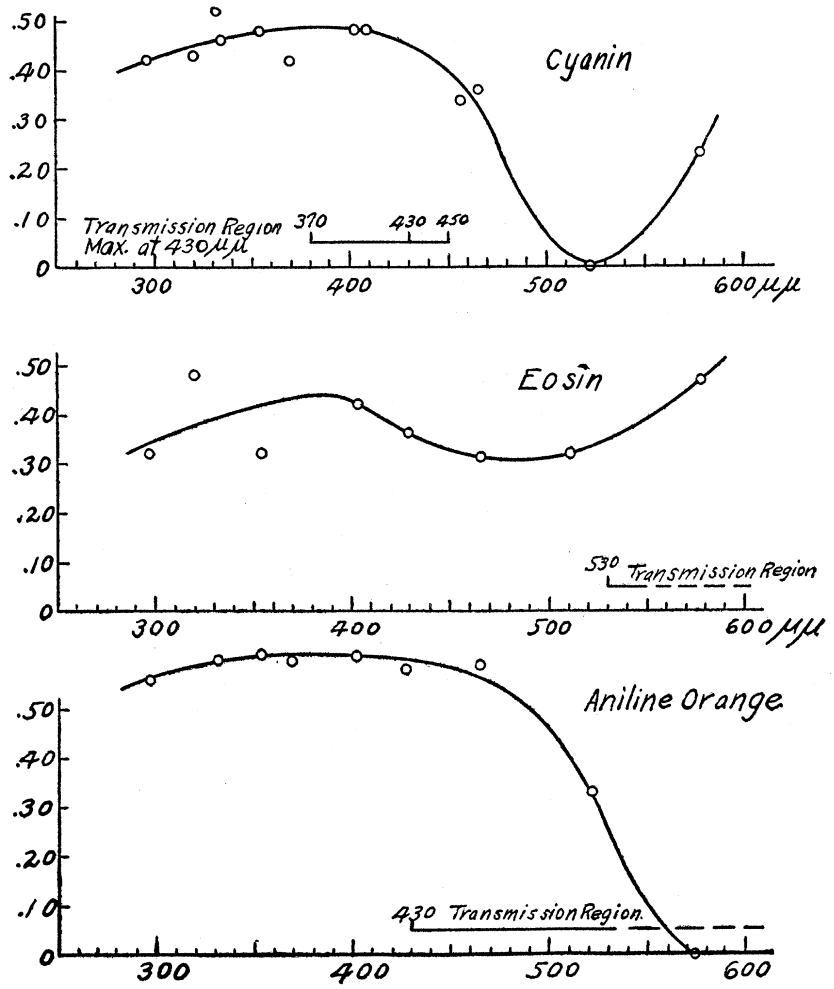

Fig. 4.

3) decreases gradually from about .5 of a wave at 580 to a minimum, approximately zero, at about 460 $\mu\mu$ then from this point on gradually increases to a value of about .6. Its transmission region extends from 442 to 358 $\mu\mu$ with a maximum at about 415 $\mu\mu$. The degree of transmission was between that of Doppel-grün and glass. Here the minimum phase change falls near the upper end of the transmission region.

Cyanin.—The transmission for cyanin extended from 450 to 370 $\mu\mu$ with a maximum at about 430 $\mu\mu$ where it appeared to be as transparent as the glass. The minimum phase change (Table IV., Fig. 4) is not so near the maximum of transmission as in the case of the other substances tested. Considerable difficulty in obtaining a coating of cyanin was

had and the film here used was more granular in appearance than was the case with the other substances.

Eosin.—The film of eosin used showed but little transmission for the portion of the spectrum recorded photographically except very slightly in the red above 530 $\mu\mu$.

Aniline Orange.—Absorption for this substance becomes evident at about 430 $\mu\mu$ when it increases rather abruptly being nearly complete below 415 $\mu\mu$. The region above 430 $\mu\mu$ as far as recorded is nearly as transparent as the glass plate. The films of both cyanin and aniline orange gave Newton's colors in reflected light.

In general the results obtained leave much to be desired in accuracy of measurements; however, in all cases the form of the curves is fairly well established.

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