

A STUDY OF THE REFLECTING POWER OF METALS  
AS DEPENDENT ON THE REFRACTIVE INDEX  
OF THE SURROUNDING MEDIUM.

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INTRODUCTION.

THE object of this paper is an experimental study of the reflecting power of metals in media (*i. e.*, *liquids*) of various optical densities.

As is well known, the Fresnel reflection laws for surfaces of transparent substances apply equally well to such surfaces when overlaid or surrounded with a liquid (say) if the index of refraction of the substance is taken as relative to that of the liquid. In metals we have a more complicated case, for the formula for reflecting power at normal incidence as stated by Drude<sup>1</sup>

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

involves two constants,  $n$  the refractive index and  $k$  the absorption index of the metal. For the case of a metallic surface in contact with a transparent medium of index other than unity, the above formula is customarily extended by the assumption that the refractive index is then to be taken as relative to that of the medium, the absorption index remaining practically constant. From a somewhat different standpoint Maclaurin<sup>2</sup> arrives at similar conclusions.

While the above assumptions are quite reasonable, this formula as applied to metal surfaces overlaid with transparent substances has never been subjected to experimental proof. The few scattering observations which are recorded, such as that of Hagen and Rubens<sup>3</sup> on the reflection of glass backed by silver, and of Conroy<sup>4</sup> for a

<sup>1</sup> Lehrbuch der Optik, 1906.

<sup>2</sup> R. C. Maclaurin, Theory of Light, Part I., Camb., 1908, pp. 249 and 261.

<sup>3</sup> Hagen and Rubens, Ann. d. Phys., I., p. 352, 1900.

<sup>4</sup> J. Conroy, Proc. Roy. Soc., 35, p. 26, 1883; 28, p. 242, 1879; 31, p. 486, 1881.

particular case of steel under water, are not in sufficiently good agreement with the theory to give it any support.

On the other hand Conroy, Des Coudres,<sup>1</sup> and a number of other investigators<sup>2</sup> have studied the related problem of the influence of an overlying medium on the measured optical constants of a metal. The results<sup>3</sup> in the case of Conroy have been discussed by Voigt<sup>4</sup> and Drude<sup>5</sup> and are in fair agreement with the theory, but somewhat low. The presence of a transition layer has been assumed to explain the remaining discrepancy, but the two additional constants<sup>6</sup> which are introduced to take account of a transition layer, and which are determined from the results themselves, necessarily bring about a better apparent agreement between theory and facts; hence this assumption is to be avoided if possible.

In the present work an attempt is made to show that the reflecting power of perfect metal surfaces in various liquids is in good agreement with the simple theory outlined above. Surfaces imperfect because of scratches and other defects have also been studied, and while they do not by any means afford results identical with those of perfect surfaces, an empirical law is deduced which expresses the relation between their reflecting powers in air and in another medium.

#### METHOD AND APPARATUS.

The method of measuring reflecting power was that of comparison with a known standard, *e. g.*, a silver surface. For this purpose a spectrophotometer of the Martens-Koenig type was used and the optical train arranged as in Fig. 1. One half the field of view in the spectrophotometer was illuminated by light from the Nernst glower *G*, reflected from the concave mirror  $M_1$  and the small prism: the other half by light reflected in succession at  $M_2$ ; at *S*, which was either the comparison mirror or the surface to be tested, each

<sup>1</sup> Des Coudres, Inaugural Dissertation, Berlin, 1887.

<sup>2</sup> G. Quincke, Pogg. Ann., 128, p. 541, 1866. Also P. Drude, Wied. Ann., 39, p. 481, 1890.

<sup>3</sup> The angle of principal incidence was decreased on surrounding a metallic surface with a liquid. The principal azimuth was only slightly affected, if at all; in some cases it showed a very small increase.

<sup>4</sup> W. Voigt, Wied. Ann., 23, p. 137, 1884.

<sup>5</sup> P. Drude, Wied. Ann., 39, p. 481, 1890.

<sup>6</sup> R. C. Maclaurin, Theory of Light, p. 251.

being in the form of a small plane mirror ; at  $M_3$  ; and from  $D$  into the instrument.

The focal lengths of the mirrors (between 30 and 40 cm.) were so chosen that sharp images of the glower were formed on each slit of the spectrophotometer, as well as on the surface  $S$ . The advantage of working with the surface to be tested in the focus of the beam are obvious, when it is considered that in this way a minimum of surface is required, and moreover any small departure of the surface from planeness is of least effect under such circumstances. The departure from strictly normal incidence — about  $5^\circ$  — was not enough to affect the reflecting power to an appreciable extent.

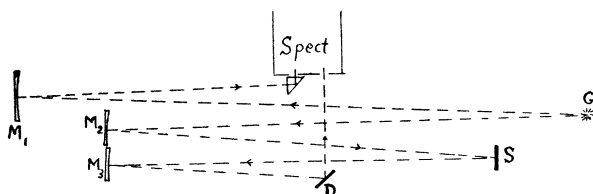


Fig. 1.

*Comparison Mirrors.* — For such, a large number of plate glass surfaces were silvered by the Brashear process and polished with rouge and chamois skin. Of perhaps twenty which were tested, the reflecting power of the best was, for a variety of reasons, assumed at 94.5 per cent., for the wave-length of sodium light, this being the wave-length used exclusively in this investigation. The average reflecting power of the surfaces tested was, on the assumption of the best being 94.5 per cent., about 93 per cent., which was that found by Hagen and Rubens<sup>1</sup> for a surface of much larger area than these. The theoretical reflecting power of silver computed from its optical constants is somewhat larger than either of these values, viz., 95.1 per cent. for sodium light.

But while the probable error of this assumption of reflecting power is not thought to exceed one half per cent., such a surface would be very difficult to use as a working standard, as it would be subject to continual change ; hence it was immediately compared with three other surfaces, viz., a plate of polished steel, one of pol-

<sup>1</sup> Ann. d. Phys., I., p. 352, 1900 ; 8, p. 1, 1902.

ished silicon, and an iron cathode surface. The last two apparently suffered no loss of reflecting power with age, while the steel surface changed only slightly and was frequently compared with the other two to eliminate any error from this source.

*Observations.*— In any series of observations a considerable number of settings of the spectrophotometer were first made with the comparison mirror in the position *S*. The surface to be tested was then introduced and a like number of settings taken, from which the relative reflecting power of the surface could be readily computed. The absolute reflecting power would, of course, follow on multiplication by that of the comparison mirror.

In measuring the reflecting power under liquids, small drops were placed on the surface and it was then covered with a slip of microscope cover glass of tested planeness, which spread the fluid out in a thin layer. To facilitate this part of the work it was found desirable to have the surface under test held horizontally. This was the arrangement used in the latter part of the work and was accomplished with the aid of an additional plane mirror (not shown in the diagram).

*Correction.*— The presence of the cover glass necessitated a small correction which was obtained as follows :

Let  $I$  be the intensity of the incident light, and  $I'$  the observed intensity of the reflected light. Let  $r$  be the fraction of light directly reflected at the air-glass and glass-liquid surfaces, the latter part being almost negligible. Then if  $R'$  is the fraction reflected at the liquid-metal surface, or in other words the reflecting power we desire to measure, we may write

$$I' = Ir + I(1 - r)^2 R' + I(1 - r)^2 R' r + \dots$$

The third term is so small that its value,  $Ic$ , may be computed with sufficient accuracy by assigning an approximate value to  $R'$ . Then

$$R' = \frac{(I'/I - r - c)}{(1 - r)^2},$$

where  $r$  is approximately .040.

This gives at once the desired reflecting power  $R'$  from the measured apparent reflecting power  $I'/I$ .

*Errors.*—As a considerable number of settings of the spectrophotometer—usually twenty—were made for each measurement of reflecting power, the probable error arising from this source did not exceed one half per cent.

Inaccuracy of adjustment might easily cause an error several times as large as this and had to be carefully guarded against. A fruitful source of trouble of this sort was a tendency of the small cover slip to assume a tilted position when used with viscous liquids.

Contamination of the cover glass or surface under test might introduce considerable error. Great care was used in cleaning all surfaces with alcohol but in some cases a variation of the results is supposed to be due to this cause. Contamination of the comparison mirror or a wrong assumption as to its reflecting power would introduce errors in the determinations of the absolute reflecting powers, but would not affect our determination of the relative change of reflecting power when under the fluid, and, as will be noted later, this is of greater interest than the absolute reflecting powers.

*Probable Error.*—The general effect of the above sources of error is not enough, in our estimation, to cause a probable error in the determination of reflecting power in excess of one per cent. This is about the magnitude of the casual variations which are noted in the results.

#### RESULTS.

*Metals.*—The metal surfaces experimented upon were the following:

1. Silver on glass deposited chemically. Also glass-backed-by-silver mirrors on microscope cover glass.
2. A very perfectly polished steel mirror, as well as several steel surfaces ground with No. 0000 emery paper but not polished.
3. Several good silicon surfaces.
4. A rather imperfect gold surface obtained by buffing with rouge and machine oil.
5. Two cobalt surfaces ground with No. 0000 emery paper and polished with dry rouge.
6. Several cathode surfaces of platinum and iron.

With the exception of gold all the above surfaces were prepared

in this laboratory. The process in the case of steel consisted in rough grinding with graded emery or carborundum on an iron plate; then fine grinding with the finest precipitated powders on a lead disk, after which it was polished in the usual way with rouge and water, using a pitch and beeswax tool. Silicon was prepared in much the same way.

*Liquids.*—For determining the reflecting power in media other than air, the liquids monobromnaphtalin, Canada balsam, glycerine and water were tried. It was soon found, however, that satisfactory results could not be obtained with water or Canada balsam, as the former evaporated too quickly and the latter was too viscous. The results recorded are for glycerine ( $N_D = 1.466$ ) and monobromnaphtalin ( $N_D = 1.658$ ).

No attempt will be made at a detailed presentation of the results which embody in all several thousand observations, but the general conclusions may be readily drawn from the table and curves which follow. It will be convenient to consider the results under two general heads, viz., those for perfect and for imperfect surfaces, the word "perfect" applying to the state of polish, rather than of planeness.

*Perfect Surfaces.*—As practically perfect surfaces were considered those free from casual defects and which gave reflecting powers within one or two per cent. of the theoretical, computed from the optical constants of the metal. As may be realized, such surfaces are extremely hard to prepare and only three of those used in the present investigation—silver, steel and silicon—were of this class. Fortunately, however, these metals may be regarded as typical, since they represent, as regards their optical properties, the two extremes and the mean. Thus silver has a low index of refraction, high absorption, and high reflecting power, while silicon has a high index, low absorption and low reflecting power. The optical properties of steel are more nearly like those of the majority of metals.

In Table I. the results are given for these metals. The optical constants used for steel and silver are those of Drude. For silicon they had not been previously determined and were measured by Mr. J. T. Littleton, Jr., of this laboratory, to whom acknowledgment is also due for the preparation of the silicon surfaces. The figures are all for the wave-length of sodium light,  $\lambda = 5893 \text{ \AA.U}$

TABLE I.

Meta	Medium.	R		$\frac{R(\text{liquid})}{R(\text{air})}$		$\frac{1-R(\text{liq.})}{1-R(\text{air})}$	
		Theor.	Obs.	Theor.	Obs.	Theor.	Obs.
Silver $n = 0.18$ $k = 20.39$	air	.951	.941	}.976	.969	1.462	1.490
	monobrom	.929	.912				
	air	.951	.926	}.981	.964		
	glycerine	.934	.892				
glass ( $n_D = 1.49$ )	.933	.912	.980	.978			
Steel $n = 2.41$ $k = 1.41$	air	.585	.570	}.738	.730	1.368	1.358
	monobrom	.432	.416				
	air	.585	.566	}.800	.785		
	glycerine	.468	.444				
Silicon $n = 4.10$ $k = 0.20$	air	.385	.377	}.507	.497	1.310	1.305
	monobrom	.195	.187				
	air	.385	.381	}.624	.609		
	glycerine	.240	.232				

The results for a glass-silver surface, included in the table, are of interest, as they show a somewhat better agreement with theory than those of Hagen and Rubens<sup>1</sup> for a similar case, in which they found a reflecting power of only 82–88 per cent. It is quite probable that the better agreement of the present results with theory is due to the very small area of surface used (about 1 mm.  $\times$  4 mm.), thus enabling one to select a very perfect part of the surface of such small area.

*Conclusion for Perfect Surfaces.*—An inspection of the above table shows that the experimental and theoretical results agree within what are probably the limits of experimental error. It is true that the observed values of  $R(\text{liquid})/R(\text{air})$  are uniformly a trifle low, and this might be explained by assuming a transition layer; but on the other hand, the small outstanding discrepancy could be readily accounted for by the fact that the mirrors tested only approximated perfect surfaces, as will be noted by the difference between the theoretical and observed values of  $R$  in air. In the ratio  $[1 - R(\text{liquid})]/[1 - R(\text{air})]$ , the particular significance of which will be discussed later, the disagreement is large in the case of silver; but it will be noted that this is the ratio of two very

<sup>1</sup> Ann. d. Phys., I, p. 352, 1900.

small values and would be largely affected by a small experimental error.

We may then conclude for perfect metallic surfaces that the simple extension of the theory which is customarily made is experimentally justified. That is, the reflecting power when overlaid with a transparent substance of refractive index  $m$ , may be obtained by replacing in the formula for metallic reflection the index  $n$  of the metal by  $n/m$ ,  $k$  remaining unchanged.

*Imperfectly Polished Surfaces.*— Because of the extreme difficulty, if not impossibility, of obtaining metallic surfaces with perfect polish, it becomes of interest to study these relations of optical properties under different media, for the case of imperfect surfaces. General planeness being assumed, the several causes for the departure of a surface from its “normal state,” that is, a state of perfect polish, may be grouped under three heads :

(a) Opaque absorbing spots or masses covering some fraction of the area of the surface.

(b) A transparent surface layer of variable or constant index of refraction.

(c) Surface indentations or irregularities. This includes all such casual defects as corrugations, scratches, and “pit marks,” of any size whatever.

The last class of defects is much the most common of the three, as the first two may be guarded against to a great extent by a suitable choice of abrasives for the final polishing and care in cleaning. To study briefly their effects on the reflecting power under different circumstances, it will be noted that opaque spots would result in a reduction of the reflecting power by a certain fraction which would be the same whatever the surrounding medium. This means that the ratio  $R(\text{liquid})/R(\text{air})$  would be constant. In other words, if points are plotted with  $R(\text{liquid})$  as ordinates and  $R(\text{air})$  as abscissæ they should all fall on straight lines passing through the origin. This, in general, has not been found to be the case.

The effect of a surface layer might be accounted for by introducing its hypothetical refractive index  $m'$  and calculating what this would have to be to give the observed diminished reflecting power. When such a calculation is extended to cover the case of an added



overlying medium the curves of  $R(\text{liquid})$  and  $R(\text{air})$  are found to be lines curving with the convex side downwards. The results of the present investigation do not fit such curves any better than the straight lines mentioned above, so we may safely conclude that neither of these classes of defect was prominent in the surfaces used.

We may then study the results with the view of determining if

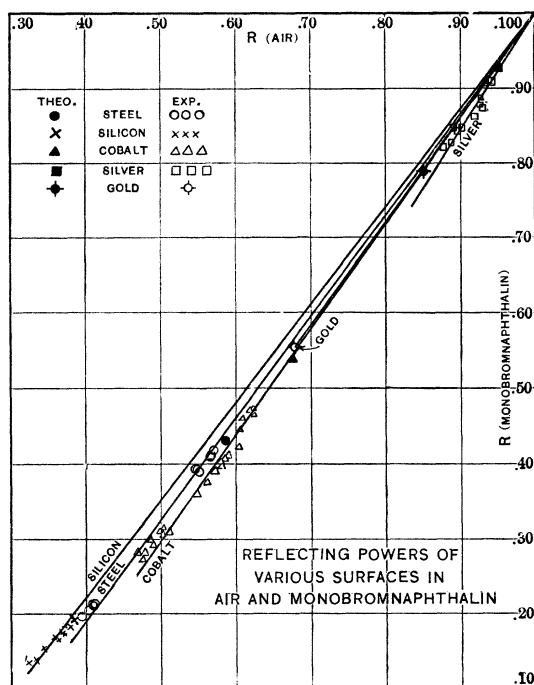


Fig. 2.

possible the effect of the more common class of defects, such as scratches and corrugations, on the optical properties here studied. Drude<sup>1</sup> found that sharp scratches had, in all cases save that of steel, a very decided effect in reducing the angles of principal incidence and hence the apparent refractive indices. But when these sharp scratches are removed by rouge polishing, although the metal may then give nearly its normal optical constants, its reflecting power may

<sup>1</sup>Wied. Ann., 39, p. 481, 1890.

still be considerably below the theoretical. Examination with a glass shows that the scratches have been merely rounded off into a myriad of minute corrugations with many small holes, and this, in the writers' experience, is the type of metal surface produced by the customary grinding and polishing process — buffing being excluded as it destroys the figure of the surface. In special metals, as already noted, these defects may be minimized so that a practically perfect surface results.

The results of a large number of observations on many different surfaces of this sort are given in the curves of Fig. 2. The abscissa of each point is the reflecting power of the corresponding surface in air, and the ordinate that in monobromnaphthalin — that liquid proving the most satisfactory to use. Points showing the lowest reflecting power correspond to surfaces having the most scratches or corrugations. Theoretical points for perfect surfaces, which are shown as small black circles, squares, etc., are derived from the optical constants of each metal tested.

*Empirical Law.*—It will be noted that for each metal the points for the different surfaces all fall fairly well on a straight line passing through the point (1, 1) and therefore having the equation  $[1 - R(\text{liquid})]/[1 - R(\text{air})] = \text{a constant}$ . Moreover, the lines for the different metals have very nearly the same slope. The small deviations of points from these lines are readily explained by the presence, in small measure, of defects of the first two classes above discussed, which could not be entirely eliminated. Not only do the points for surfaces of various qualities fall on these lines, but also those for theoretically perfect surfaces, as well as for the nearly perfect surfaces actually studied.

This then, the writers believe, is the law which expresses the relation between reflecting powers in air and in some other medium for metal surfaces of all degrees of polish, presupposing that surface layers — for example oil films — and spots such as oxidation and dirt are guarded against.

The theoretical basis of the law is not apparent. The action of scratches and corrugations on the incident light is undoubtedly two-fold,— viz., to introduce in some cases more than one reflection and hence greater absorption; and to scatter in various directions a

fraction of the incident light. As the present method of investigation utilized a conical beam of small solid angle, rather than strictly parallel light, it is possible that the poorer sort of surfaces might show a somewhat higher reflecting power than if measured by a method using only parallel light; for in the present case some of scattered light might still fall within the limits of the cone which reaches the measuring instrument. However, as reflecting power under these circumstances is somewhat a matter of definition, neither method has an obvious advantage.

These considerations enable us to suggest a possible explanation of one result of experiment. It will be noted in the case of the poorer sort of surfaces of any one metal, that the fractional reduction of reflecting power on overlaying with monobromnaphtalin is much greater than for the better surfaces. We may suppose that for such a surface the portion of the incident light reflected is scattered into a cone of solid angle  $\omega'$ , of which only  $\omega$  can reach the instrument. When covered with liquid the fraction reflected—less, of course, than if the liquid were not present—is scattered into the same cone  $\omega'$  which on emerging from the plane surface of the liquid becomes, following the ordinary laws of refraction, a cone of wider angle  $\omega''$ .

Consequently a still smaller fraction of the returned light reaches the spectrophotometer than in the first case and this would account for the observed result. But this does not by any means explain the fairly exact relations which experiment shows to exist and which cannot reasonably be ascribed to any particular instrumental arrangement.

*Cathode Surfaces.*—The few cathode surfaces of iron and platinum which were tested were deposited with a rather high current density, and while they showed perfect mirror surfaces, their reflecting powers were considerably less than the normal for these metals. When experimented on with various liquids their results did not agree with those for polished surfaces, but the discrepancy was greatly reduced when the actual optical constants for these surfaces were measured and introduced into the formula. When plotted as in Fig. 2 the points for these surfaces fell on lines somewhat intermediate between those on the diagram and one through the origin. This might mean the presence of metal in a finely divided state,

*e. g.*, platinum black, and some color is lent to this view by finding that the reflecting power of these surfaces could be improved by polishing with rouge and chamois.

However, as noted by all who have worked with cathode surfaces, including Skinner and Tool,<sup>1</sup> and one of the writers,<sup>2</sup> they may be produced in a variety of forms according to the conditions of deposit, varying from a state resembling that of the fused metal to states widely different from this. Accordingly, without special and more or less exhaustive study of these optical properties for this kind of surface, it is impossible to draw definite conclusions. But it may be noted in this connection that one of the writers,<sup>3</sup> in studying the effect on the magnetic rotation (Kerr effect) produced by overlaying iron surfaces with various liquids, found that cathode surfaces obey the theoretical law (rotation proportional to the index of the liquid) better than polished surfaces.

#### SUMMARY.

1. The extension of the formula for the reflecting power of a metal in terms of its optical constants, to include the case where the metal is covered by a transparent substance of any optical density, is experimentally justified for the case of perfect or practically perfect surfaces. This extension is made by replacing in the formula the actual refractive index  $n$  of the metal by the relative index  $n/m$ , where  $m$  is the index of the covering medium, the absorption index  $k$  of the metal remaining unchanged.

2. When a surface has a reflecting power lower than its normal value for that metal this condition is due in most cases to the presence of minute scratches, corrugations or indentations. While it is difficult to treat this case theoretically, the experimental results indicate that for all this class of surfaces as well as for those theoretically perfect, the relation  $[1 - R(\text{liquid})] / [1 - R(\text{air})] = \text{a constant}$ , exists for any particular metal.

PHYSICAL LABORATORY,  
UNIVERSITY OF WISCONSIN,  
June 8, 1909.

<sup>1</sup> C. A. Skinner and A. G. Tool, *Phil. Mag.*, December, 1908.

<sup>2</sup> L. R. Ingersoll, *Phil. Mag.*, July, 1909.

<sup>3</sup> *Ibid.*