Physics. — *"Experimental Inquiry into the Nature of the Surface-Layers in the Reflection by Mercury, and into the Difference in the Optical Behaviour of Liquid and Solid Mercury".* By Dr. J. J. HAAK and Prof. R. SISSINGH. (Communicated by Prof. H. A. LORENTZ).

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1. *Introduction.* Since in 1850 L. LORENZ [1]) advanced the supposition, that the elliptical polarisation on reflection by transparent bodies is the consequence of a gradual transition between the two adjoining media and elaborated this view theoretically, the influence of these surface layers has been more than once theoretically investigated, both in case of the reflection by transparent bodies and by metals [2]). There have, however, been made only few experimental investigations into the nature of these surface-layers and our knowledge of it is confined to more or less plausible suppositions. Great influence is always assigned to the grinding and polishing and also to the grinding and polishing material itself, with which these operations are made. An investigation by RAYLEIGH shows, however, that it is not yet possible to state in what way this influence arises [3]). Besides, an influence of the condensed gas layers has often been supposed and examined [4]). Up to now however, attempts to demonstrate the influence of a condensed gas layer have not yet succeeded.

2. *Purpose of the research.* In order to obtain the optical constants of a metal, quite independent of the grinding and polishing and the material used for this purpose, mercury was chosen for this investigation. Both the liquid mercury and a mirror of solid mercury can be examined. It becomes then also evident, whether at the transition from liquid to solid mercury the optical constants are subjected to a modification. In the investigation of liquid mercury the impression,

[1]) L. LORENZ, Pogg. Ann., **111**, 460, 1860; **114**, 238, 1861.

[2]) C. A. VAN RIJN VAN ALKEMADE, Thesis for the doctorate, Leiden, 1882; Wied. Ann., **20**, 22, 1883. P. DRUDE, Wied. Ann., **43**, 126, 1891; R. C. MAC LAURIN, Proc. Roy. Soc., (A), **76**, 49, 1905.

[3]) RAYLEIGH, Proc. Roy. Inst., **16**, 563, 1901.

[4]) J. J. SEEBECK, Pogg. Ann., **20**, 35, 1830; P. GLAN, Wied. Ann., 11, 464, 1880; R. SISSINGH, Thesis for the doctorate, Leiden, 1885; Arch. Néerl., 20, 171, 1886.

however, gained ground, that the layers of air, which are condensed on the surface, exert an appreciable influence on the elliptical polarisation at the reflection, so that in the first place this influence has been more closely examined.

3. *The used monochromator.* The determination of the optical constants took place in an entirely analogous way, as has been described by one of us [1]). For the investigation a goniometer has been used, the graduated circle of which can be placed vertical. Before the goniometer there is a monochromator of a very simple structure, which was constructed from material, present in the laboratory. The monochromator consists of a collimator with an aperture 1 : 6, a flint-glass prism of STEINHEIL with an angle of refraction of 60°, and a second collimator, which will be referred to in future as the collimator of the goniometer. The illumination takes place by means of an arc-lamp of 18 Ampères. A lens of 7 dioptrics forms an image of the crater on the slit of the collimator of the monochromator. Behind the prism a lens of 11 dioptrics forms a spectrum on the collimator of the goniometer. The axes of the two collimators are placed horizontal, the slits and the edge of the refracting angle of the prism vertical. Care has always been taken, that the image of the crater and the spectrum fall on the middle of the collimator slits. A silvered glass mirror is adjusted to the collimator of the goniometer; it can revolve round an horizontal axis and throws a monochromatic, cylindrical beam of light at the required angle of incidence on the mirror in the middle of the goniometer. The wave-length of the incident rays lies between 5790 and 5990 Ångström-units. During the observations the invariability of this colour-sifting of the incident beam of light is repeatedly examined. The fringes in the BABINET compensator are always uncoloured. Monochromator and goniometer are mounted on a firm foundation, erected free from the floor in the room, in which the observations have been made. The three levelling-screws of the legs of the goniometer stand each on two thick pieces of india-rubber, in order to prevent as much as possible the influence of vibrations on the liquid mercury surface.

4. *The goniometer.* For the adjustment and the centring of the parts of the goniometer we refer to the investigation of one of us [2]). Only a few points are briefly mentioned here.

[1]) R. SISSINGH, loc. cit.
[2]) R. SISSINGH, loc. cit.

The following expedient proved very convenient in the mutual adjustment of the parts of the goniometer. The sledge on which the silver mirror stands, which served for these adjustments, was fastened to a socket, which fits over a conical pivot in the middle of the goniometer circle. This pivot can be levelled with three adjusting screws. The mirror with the socket can in this way easily be placed on the goniometer and can be removed from it [1]).

As polarizer a nicol is used with pretty large oblique end-planes, which only gives a small deviation to the rays of light, which pass through it. This amounts to 2′.5.

For the adjustment of the compensator we refer again to the investigation of one of us [2]).

The polarisation planes of *each* of the two compensator wedges are placed in the required position, i. e. parallel to the plane of incidence and normal to it [3]).

To bring the movable wedge in the required position, we make use of the images of the collimator slit, which are formed in the eye-piece behind the goniometer. There are formed three pairs of images. The images of each pair coincide, if the planes of the wedges are parallel. The principal positions of the nicols, in which their planes of polarisation are parallel to the plane of incidence or normal to it, have been determined both in the vertical and in the horizontal position of the goniometer circle. The azimuth of the polarizer is called 0, when the light, that the polarizer transmits, vibrates normal to the plane of incidence, that of the analyzer, when the direction of vibration of the transmitted light is pallallel to the plane of incidence. We obtained successively in the horizontal and vertical position of the goniometer circle:

				mean
Polarizer in azimuth	0°	81°57′,	81°43′;	81°50′
Analyzer „ „	0°	86°33′,	86°35′;	86°34′ [4]).

Considering the inevitable errors of observation, the agreement may be called satisfactory.

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1) For fuller details compare J. J. HAAK, Thesis for the doctorate, Amsterdam, 1918.

2) R. SISSINGH, loc. cit.

3) It is noteworthy, that it is *supposed* both in the investigation of R. HENNIG, Gött. Nachr, **13**, 365, 1887, as in that of P. DRUDE, Wien. Ann., **34**, 489, 1888; **36**, 532, 1889; **39**, 481, 1890, that the principal sections of the wedges are normal to each other and only the angle between the principal section of one of the wedges and the plane of incidence is determined and taken into account. Cf. SISSINGH in BOSSCHA's Textbook of physics, Light, II, p. 555, note 2.

4) All the experiments have been made by J. J. HAAK. Compare for further details Mr. HAAK's thesis for the doctorate, Amsterdam, 1918.

The positions of the movable compensator wedge, in which the difference of phase for the narrow beam of light, which passes between the threads before the fixed wedge, amounts successively to $-\frac{1}{2}, 0, +\frac{1}{2}$, are:

63.86; 49.52; 35.10.

As the displacements of the wedge are always reduced to those between 49.52 and 63.86, a displacement of 14.34 mm. corresponds with a phas-edifference of $\frac{1}{2}$ or π. [1])

The angle of incidence on the mercury surface is derived from the position, in which the line of sight of the telescope of the goniometer is horizontal. This position is found halfway between the positions, in which that line of sight runs successively parallel to that of an incident beam of light and of the corresponding beam of light, which is reflected by a liquid surface in the centre of the goniometer. These positions are 81°36′ and 104°24′, so that the axis of the telescope of the goniometer runs horizontal in the position 81°36′ + (104°24′—81°36′) : 2 = 93°0′. As reflecting surface is used that of thick machine oil, because this gives rise to a pure image of the slit, which is not the case with mercury. [2]) The goniometer circle is vertical, when the axis of the incident beam coincides with that of the tube in which later the polarizer is placed and after reflection with the axis of the telescope.

5. *Preliminary investigation of the optical influence of a condensed layer of air.* When, as was already communicated in § 2, it became evident from the observations, that the layer of air condensed on the mercury surface was optically active, the angles of principal incidence I and the principal azimuth H were determined on the mirror of pure mercury, immediately after the formation. This took place by the determination of the phase-difference and the restored azimuth for two angles on both sides of the angle of principal incidence from extensive series of observations. From these values those of I and H were obtained by interpolation. [3])

It was found that $I = 79°18'$, $H = 35°45'$.

This determination could be made within three hours.

On an earlier occasion we obtained $I = 78°23'$, H = 36°18′, in which the mercury surface was exposed to the air for some days,

[1]) The phase-differences are given as phase-retardations with respect to the light vector in the reflected light, perpendicular to the plane of incidence.

[2]) For the mercury surface the compensator fringes remain however straight, only slightly less sharply defined. The accuracy of the adjustment of this fringe is somewhat less than with a solid surface, viz. 0.03 instead of 0.02

[3]) R. Sissingh, loc. cit.

but protected against contact with dust, before the observations took place. In both cases the mercury had been distilled in vacuum.

With mercury that had been purified by being shaken with potassium hydroxide and nitric acid and had then been dried, we found in the same way some days after the formation of the mercury surface:

$$I = 78°14' \quad , \quad H = 36°12',$$

which is in satisfactory agreement with the second determination. The sign of the difference between the values of I and H in the two first determinations is the same as is to be derived from the theoretical research by DRUDE. A surface layer greatly diminishes the angle of principal incidence and enlarges the principal azimuth but little [1]).

The following observations show the influence of the layer of air very clearly. The pure mercury is in a well cleaned receptacle of LEYBOLD with plane parallel side walls, as is very often used for light-filters. The observations have been made at an angle of incidence of 78°, with the analyzer at an azimuth of 45° [2]).

	Adjustment of the Compensator	Adjustment of the Polarizer
	56.46 [3])	43°33′

Two days later, during which time the mercury was protected from dust,

	56.71	43°47′

After the mercury in the receptacle had been shaken and a new surface had been formed:

	56.44	43°33′
After one day	56.64	43°44′
After shaking	56.42	43°34′

In a following set of observations, in which a pure surface was obtained by means of the method of overflowing of RÖNTGEN [4]), which has also been used by RAYLEIGH, the observations yielded:

	Adjustment of the Compensator	Adjustment of the Polarizer
	56.43	43°44′
After two days	56.74	43°41′

[1]) P. DRUDE, Wied. Ann., **36**, 532, 865, 1889; **43**, 126, 1891.

[2]) At this azimuth the error in the determination of the phase-difference introduced by the metallic reflexion and of the azimuth of the restored plane polarisation, which henceforth will be referred to as restored azimuth, is a minimum. Cf. R. SISSINGH, Thesis for the doctorate, p. 57; Arch. Néerl., **20**, p. 188.

[3]) These and all the further values are every time the mean of four readings.

[4]) RÖNTGEN, Wied. Ann., **46**, 152, 1892; RAYLEIGH, Phil. Mag., (5), **30**, 398, 1890.

After overflowing	56.45	43°37′
After one day	56.68	43°44′
After overflowing	56.45	43°50′

The polarizing action of the side walls of the glass receptacles not having been examined, these values have no absolute value, but they represent the change by the adsorbed air layer no doubt very accurately.

6. *Change of the thickness and the influence of the layer with the time.*

There is no doubt but the thickness of the adsorbed layer of air and so also its optical influence increases with the time. In order to examine this influence the adjustments must be effected in a short time. Those of the polarizer have been omitted, because it appears from § 5, that the influence of the layer of air on the restored azimuth is very small and about of the order of magnitude of the errors of observation. In order to be able to execute the observations in a short time, only observations at one angle of incidence, viz. the angle 79°46′, which is very near the angle of principal incidence, were made, the analyzer also always being set in the same quadrant. The determination of the phase-difference, that arises at metallic reflection between the components vibrating perpendicular to and in the plane of incidence, took place only by annulling this phase difference [1]).

The shifting of the movable compensator wedge was therefore exclusively from 49.52 → 63.86 (see § 4). In this way the errors in consequence of the deviation of the light in the polarizer and the inaccurate position of the planes of polarization of the compensator wedges continue to exist, but their influence on the slight change in the phase-difference, that is to be determined, may be considered as of the second order of magnitude. Care should, however, be particularly taken, that the incident beam of light consists always of the same part of the spectrum and keeps the same direction, i. e. always falls on the middle of the slit of the collimator of the goniometer. A slight shifting of the spectrum, which was not even so much as the height of the spectrum, already modified the compensator-reading by 0.06. This is to be ascribed to the change in the angle of incidence. In the observations the mercury was placed in a shallow iron dish, attached to the bottom of a bronze cylinder. Two side-tubes, closed by plane parallel glass plates, the axes of which lie in a same meridian plane

[1]) SISSINGH, Thèsis for the doctorate, p. 79: Arch. Néerl., **20**, 196, 1886.

of the cylinder, enable us to make the light strike the mercury at the required angle of incidence. The mercury is conveyed into the dish by a tube in the upper surface of the cylinder. This bronze cylinder is attached to the middle of the goniometer circle. A vertical sledge makes it possible to place the mercury surface so, that the axis of the goniometer lies in it. By means of an horizontal sledge the dish may be placed so, that the axes of the incident and the reflected beam of light pass through the middle of the glass windows. The cylinder can be exhausted and filled with air, that has been dried with calcium-chloride, sulphuric acid, potassium-hydroxide and phosphor-pentoxide.

When the position of the movable prism of the compensator, immediately after the formation of the mercury surface is called c_0, that t seconds later c, and the final position c_∞, a very plausible supposition on the increase of the thickness of the layer of air and its optical influence leads to the differential equation:

$$\frac{d(c-c_0)}{dt} = k(c_\infty - c)$$

So that

$$c - c_0 = (c_\infty - c_0)(1 - e^{-kt}).$$

In this k will be proportional to the pressure of the air. This supposition is confirmed by series of observations, made at a pressure of one and of half an atmosphere, which are graphically represented in fig. 1. There have been traced six curves for different values of k. It appears clearly from the traced lines within what limits the value of k lies for the two series of observations. As value of $c_\infty - c_0$ has been taken 0.25, viz. the change of the readings in dry air after 24 hours. When the cylinder is exhausted, no change in the compensator-readings can be demonstrated even after 8 hours. Compare the line . . ., which indicates the observations in the exhausted cylinder. Here follow the means of three series of observations in dry air for a pressure of an atmosphere.

Time	Angle of Incidence 79°46′	
0	$C_0 = 56.84$	$C-C_0$
½ hour	$C = 56.863$	0,023
1 ,,	56.89	0.05
1½ hours	56.92	0.08
2 ,,	56.918	0.078
2½ ,,	56.94	0.10
3 ,,	56.965	0.125
3½ ,,	56.975	0.135
4 ,,	56.972	0.132

$4\frac{1}{2}$ hours	56.97	0.13
5 „	56.992	0.152
$5\frac{1}{2}$ „	56.99	0.15
6 „	57.00	0.16
$6\frac{1}{2}$ „	57.01	0.17
7 „	57.013	0.173
$7\frac{1}{2}$ „	57.03	0.19
8 „	57.03	0.19

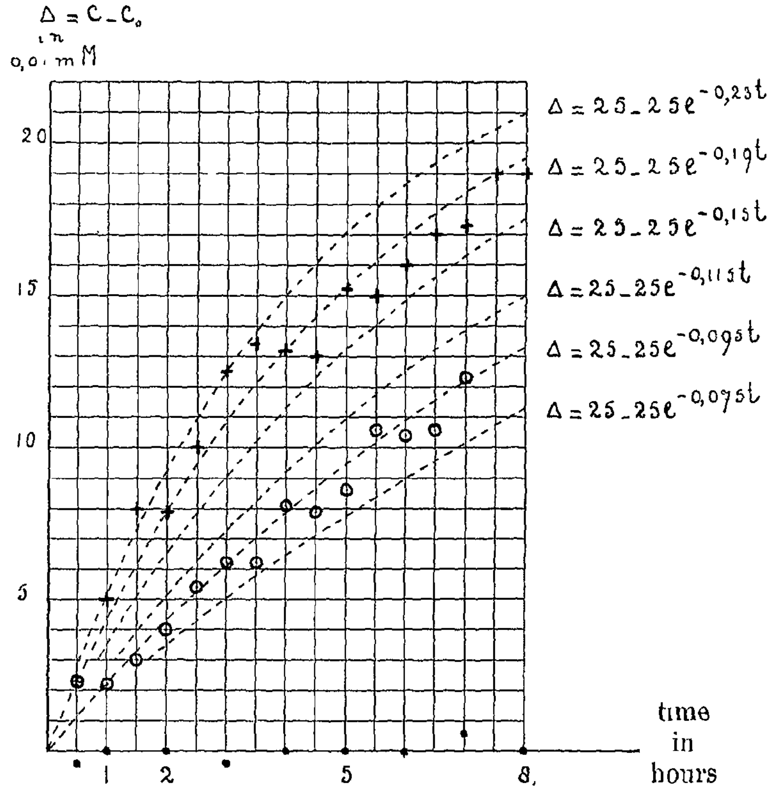

Fig. 1.

When it is borne in mind, that the error in the readings of the compensator amounts to 0.03, the agreement of the observations with the curves traced may be considered as very satisfactory. As according to § 4 a displacement of 14.34 of the movable compensator wedge corresponds to a difference of phase of π in circular measure, $c_\infty - c_0$ denotes a difference of phase of $0.25 : 28.68 = 0.0087$. In the following way the change in the angle of principal incidence I, corresponding with this, could be obtained.

The measurements on pure mercury, immediately after the formation of the mirror, gave·

Angle of Incidence	Compensator	Angle of Principal Incidence
78°38′	56.24	79°18′.

Observations made at the same angle of incidence on the mirror with an adsorbed layer of air yielded:

78°38′	56.90	78°19′.

It follows from this, that if the compensator-reading in the neighbourhood of the angle of principal incidence diminishes by 0.66, the angle of principal incidence increases by 59′, so that it follows from the observed value $c_\infty - c_0 = 0.25$, that the adsorbed layer of air decreases the angle of principal incidence by 22′.5. It is to be doubted very much whether the change, which has been observed for crystals on natural cleavage surfaces, shortly after the splitting, in the phase difference between the components of the reflected light, which vibrate normal to and in the plane of incidence, should be attributed to layers of air. DRUDE found this change for fresh cleavages surfaces of antimony glance, calcspar, and rock-salt. [1]) For rock-salt the cause is not to be looked for in a layer of water on the hygroscopical crystal. The observed change in the phase difference is greatest for antimony glance at the angle of principal incidence. According as the optical axis of the crystal is parallel to the angle of incidence or normal to it, this change amounts successively to 0.01 and 0.06. This value is many times greater than has been observed for mercury. Besides the greater part of the change has already taken place in 2 hours and the retardation in the increment of the ellipticity on standing is much more considerable than for mercury. DRUDE considers fresh cleavage-planes as unsaturate and thinks that also a greater condensation of the gas layers would have to result from this. Experiment should decide, however, whether gas layers play a part also here. Fresh cleavage-planes of lead glance do not exhibit a change in the elliptical polarisation with the time.

7. *On the changes in the phase-difference obtained in a previous investigation.*

It appears from the observations mentioned in § 5, that changes of nearly 1° in the angle of principal incidence caused by surface-layers were observed. Hence the question is, what gives rise to these greater changes? Very probably these occur in consequence of liquid layers, which are enveloped by the dust falling on the mercury. When

[1]) DRUDE, Wied. Ann., **34**, 489, 1888; **36**, 532, 1889.

some dust is swept up from the floor and some of it is strewn over the mercury, the displacement of the compensator fringe can immediately be observed without any adjustment. No liquid is, however, to be observed on the mercury either with the naked eye or with a telescope. When the dust is taken from a place, where oil has been spilt, the compensator-fringe assumes a tortuous form and liquid streaks are to be observed on the surface by means of the telescope. The sinuous compensator-fringe indicates, that not everywhere an equal quantity of liquid is spread over the mercury.

That in this case really a liquid is spread over the mercury surface, is also in agreement with the fact, that the mercury surface is smoother, so that an image may be observed in the telescope of the thread, stretched across the centre of the slit of the collimator of the goniometer. This does not succeed with a clean mercury surface in consequence of the vibrations caused by the traffic in the streets.

8. *On the values of I and H for mercury without surface layer.* It follows from § 6 that for a pressure of air of one atmosphere, the curve for $k = 0.79$ best represents the observations, so that the compensator reading successively increases by 0.045, 0.08, and 0.11 in 1, 2, and 3 hours or on an average by 0.04 an hour. As the determinations of I and H, mentioned in § 5, took up three hours, I has been diminished by 6′ on an average in this time, the principal azimuth H has, however, remained unchanged. The change in H lies namely within the errors of observation. From this follows, that for mercury without adsorbed layer of air:

$$I = 79°24' \qquad H = 35°45'$$

We subjoin the values obtained by other investigators:

BREWSTER [1])	78°27′	34°46′
QUINCKE [2])	77° 3′	33°47′
DES COUDRES [3])	79° 3′	33°30′
DRUDE [4])	79°34′	35°43′
MEYER [5])	78°23′	35°17′
MEESE [6])	79°22′	36° 7′

In this the following points are noteworthy. BREWSTER gives 26°0′ as restored azimuth after two reflections under the angle of principal incidence. From this the above given value of the principal azimuth

1) BREWSTER, Phil. Trans., 287, 1830.
2) QUINCKE, Pogg. Ann., **142**, 202, 1871
3) DES COUDRES, Thesis for the doctorate, Berlin, 1887.
4) DRUDE, Wied. Ann., **39**, 511, 1890.
5) MEYER, Ann. d. Phys., **31**, 1017, 1913.
6) MEESE, Gött. Nachr., 530, 1913.

has been calculated. It cannot be inferred from BREWSTER's records, whether his observations have been made on a free mercury surface or on mercury against glass. In the latter case scratches in the glass may be responsible for the too low value of the principal azimuth. Also the too low value of the principal azimuth determined by QUINCKE should be attributed to scratches[1]). DES COUDRES' observations have been made on a free surface. The deviations seem to be owing to inaccuracies in the observations. DRUDE obtains a clean mercury surface by the aid of two funnels. No further particulars are given about this. The method is probably similar to RONTGEN's method of overflowing. The observations were made within two hours after the formation of the mercury mirror. QUINCKE and MEYER used a mercury surface against glass. A surface layer between mercury and glass has undoubtedly caused the too low value of the angle of principal incidence. MEESE also made observations on mercury against glass and demonstrates the existence of surface layers, that are then present. The values of I and H given here, have been calculated from his observations. In how far a condensed layer of air has also exerted an influence cannot be ascertained. From the values determined by us and those of DRUDE, MEESE, and MEYER, whose value for I, which is certainly too low, has not been taken into account, the following values of the optical constants for mercury may be assumed as the most probable:

$$I = 79°27' \qquad H = 35°43'.$$

§ 9. *The thickness of the adsorbed layer of air.* Both VAN RIJN VAN ALKEMADE (see § 1) and DRUDE have given equations, from which the thickness of the surface layer may be derived. According to DRUDE[2]) the change in the phase-difference between the components of the reflected light, parallel to and normal to the plane of incidence, brought about by the surface layer is:

$$\Delta' - \Delta = \frac{4\pi}{\lambda} \frac{Cos\varphi Sin^2\varphi\,(a - Cos^2\varphi)}{(a - Cos^2\varphi)^2 + a_1^2} \int_0^L \left(1 - \frac{1}{n^2}\right) dl$$

In this φ is the angle of incidence, L the thickness of the surface layer, n the index of refraction in this layer at the distance l of the reflecting metal surface:

$$a = \frac{Cos\,4\,H}{Sin^2 I tg^2\, I} \quad , \quad a_1 = \frac{Sin\,4\,H}{Sin^2 I tg^2\, I.}$$

[1]) J. J. HAAK, Thesis for the doctorate, Amsterdam, 1918, p. 47.

[2]) DRUDE, Wied. Ann., **39**. 481, 1890.

The index of refraction n of the surface layer will increase on approaching the reflecting metal surface. When for n a mean value is taken, viz. that between n_{air} and the value for the greatly condensed air, immediately adjoining the metal and when with QUINCKE[1]) it is supposed, that the density of this is equal to that of the mercury, $n = 4.048$ is found for this by the aid of the relation: $(n-1):d =$ constant[2]). Hence the mean value of n is $(4.048 + 1.003):2 = 2.52$. As $\Delta'-\Delta$, the phase difference for the absorbed layer of air, amounts to 0.0087 (see § 6) and $\varphi = 79°46'$ (see § 6), we find with the values of l and H mentioned in § 8:

$$L = 1.6 \ \mu\mu.$$

This value is in agreement with that for the transition layer liquid-vapour, for which BAKKER[3]) gives 1—2 $\mu\mu$.

When in the same way the thickness of a layer of oil ($n = 1.5$, $d = 0.9$) is calculated, which according to § 5 can modify the angle of principal incidence by 1°, the compensator-reading by 0.50 and more, we find, introducing the value 0.50, $L = 3$ $\mu\mu$. This is in accordance with RAYLEIGH's and FISCHER's[4]) determinations. RAYLEIGH found, namely, for the thickness of the thinnest layer of oil, that stops the movements of the camphor particles on water, $2\mu\mu$. FISCHER found for liquid layers, which spread over mercury, thicknesses smaller than $5\mu\mu$.

As the adsorbed layer of air of a thickness of 1.6 $\mu\mu$ changes the compensator-reading by 0.25 and the mean error in the reading amounts to 0.02, a layer of a thickness of 0.13 $\mu\mu$ can still be demonstrated in this way by this optical method. Such a layer is of the thickness of a molecule. It is not possible to prove the existence of such thin layers by the aid of the capillary phenomena.

It is not possible to remove the once adsorbed layer of air by means of a very far exhausted vacuum, as the mercury airpump of GAEDE can bring about. After eight hours' pumping no displacement of the compensator reading could be demonstrated[5]).

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1) QUINCKE, Pogg. Ann., **108**, 326, 1859.

2) L LORENZ—H. A. LORENTZ's formula cannot be applied here, as n^2 would become negative. Let $\frac{n_1^2+2}{n_1^2-1}d_1$ be $= \frac{n^2+2}{n^2-1}d$, then $\frac{n^2+2}{n^2-1}\frac{d}{d_1}$ must be > 1, if n_1^2 is to be positive. In the case considered here $\frac{d_1}{d} = 10^4$, $\frac{n^2+2}{n^2-1} = 5.10^3$, so that the condition is not fulfilled.

3) G. BAKKER, Z. f. Phys. Chem., **91**, 571, 1916.

4) RAYLEIGH, Phil. Mag., (5), **30**, 396, 1890; FISCHER, Wied. Ann., **68**, 436, 1899.

5) This result is in agreement with other experiments, which show with how

10. *Testing of the obtained results by means of a mercury mirror got by distillation of pure mercury.* According to § 6 the phase-difference was measured with the compensator by annulling this phase-difference, in order to determine the influence exerted by the adsorbed layer of air. From the values given in § 4 it appears, that the lowest compensator-reading corresponds with the smallest phase-difference. As according to DRUDE every surface layer diminishes the angle of principal incidence, hence increases the phase-difference for every angle of incidence, the mercury surface is the better, i.e. less contaminated by surface layers, as the compensator-reading is smaller. For an angle, somewhat greater than *I*, this smallest reading was 56.84 [1]). Mercury, distilled in vacuum, which was conveyed into a dish after being filtered through a paper funnel, yields the reading 56.84. This dish had been placed free in the air and was not surrounded by a case (see § 6), so that the rays of light need not pass through glass windows. Mercury purified by being shaken with potassium hydroxide and nitric acid, but not distilled in vacuum, yields the reading 56.85. The difference with the preceding value falls within the errors of observation. Mercury, conveyed into the dish through a drawn-out glass tube, yields 57.00, if the tube has not been very well cleaned. For a thorough cleaning heating to a dull red glow is generally sufficient. Touched by a piece of cloth, which is not clean, the mercury gives the adjustment 57.20. When breathed upon, the mercury yields a reading increased by 0.04 or 0.05.

In order to prove by another way, that 56.84 is the reading for pure mercury without surface layer, pure mercury was distilled in vacuum into the iron dish, which is situated in the bronze cylinder. It was previously ascertained, that the glass windows — carefully cooled glass plates of a thickness of 3 mm. — did not modify the compensator-reading, even though the cylinder was exhausted of air. For this purpose an iron mirror was placed in the dish and the compensator-reading was observed before and after the exhaustion. The pure mercury was heated in a glass globe. The vapour was condensed in the spiral windings of a glass cooler and received in a glass bottle, from which it flows out into the iron vessel through a glass tube with drawn-out point. All the junctions of this apparatus consist of sealed glass. The air-tight connection of the glass tube with

great a force these adsorbed layers of air are attached to the surfaces. Cf. among others VOIGT, Wied. Ann., **19**, 39, 1884. Likewise it is in agreement with the fact, that the layer of air cannot be removed by means of carbon powder, which has been heated just before to a red glow. Cf. among others SISSINGH, Thesis for the doctorate, p. 162; Arch. Néerl. **20**, 228, 1886.

[1]) The values recorded here are again the means of four readings.

drawn-out point, which passes through the short tube in the upper wall of the bronze cylinder, with this short tube was effected by means of an airpump tube and a little collodion. A GAEDE mercury airpump exhausts the space. The compensator-adjustment was 56.84, hence exactly the same as that which prevails for mercury without adhering layer of air, according to the observations communicated in this §.

11. *Inquiry into a difference in the optical constants of liquid and solid mercury.* At first the air in the bronze cylinder was very carefully dried. The cooling of the cylinder and the dish with mercury in it took place by putting a mixture of solid carbonic acid and ether on a tin plate screwed on to the bottom of the cylindrical case. By means of ebonite as heat-insulator the conduction of heat from the metallic parts of the goniometer to the cylinder is prevented. In order to prevent the cooling of the glass windows in the side tubes, because no water vapour from the air may settle on them, these windows are cemented to ebonite tubes, which are screwed on to the side tubes of the bronze cylinder. The air-tight closure was effected by means of very tough Ramsay-grease. As it appeared that in spite of this precaution some water-vapour deposits on the glasses, a current of dry air was blown along them by means of a GAEDE box pump, which quite remedied this evil.

During the cooling the following phenomena are observed. When during the cooling the compensator is adjusted for the dark compensator-fringe, this winds, while the mercury is still liquid and becomes less dark, after which it disappears altogether. At last the fringe, which has then become black again, jumps back to its original position. When the telescope, which is placed behind the analyzer, is then adjusted on the mercury, ice crystals appear to float on the mercury. From this it is evident, that the explanation of the observed phenomenon is the following. In spite of the careful drying the air contains traces of water vapour, which are deposited on the mercury surface during the cooling and spread over it as a liquid [1]). The compensator-fringe is probably sinuous, when the water layer consists of incoherent patches and is very thin. When the water forms a coherent layer and this layer has become so thick, that the reflection takes place on water, the fringe disappears, as at the chosen angle of incidence of 79° 46′ water does not perceptibly polarize the light elliptically on reflection. As soon as the tempera-

[1]) These phenomena are not observed on an iron mirror during the cooling, so that the condensed water vapour does not seem to spread over this mirror.

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ture falls below 0°, the water freezes and contracts to a few ice crystals, which lie spread with large interstices on the mercury. Then we have again a mercury surface and the normal adjustment of the compensator-fringe. In the meantime the mercury is still liquid.

Attempts to prevent this deposition of the water vapour by careful drying of the air proved unsuccessful. This was done thoroughly however by exhausting the bronze cylinder. When an iron mirror is placed in the cylinder, it appears, that the glasses on the side-tubes do not become bi-refringent when the case is exhausted, but that they do so through the one-sided cooling during the fall of the temperature of the bronze cylinder by solid carbonic acid and ether. Then the adjustment of the compensator-fringe changes by the constant amount 0.08. During the cooling of the mercury in vacuum no sudden change in the position of the compensator-fringe is observed at the moment of the freezing. The reading of the compensator-fringe diminishes gradually, till this change reaches an amount of 0.08. It appears from this that only the slight double refraction of the glasses plays a part here and that neither during the freezing of the mercury, nor during the further cooling down to —80° the phase-difference, hence also the angle of principal incidence of the mercury changes perceptibly.

At first the position of the polarizer presented a change during the freezing, which could amount to as much as 3°. This, however, must be attributed to the influence of wrinkles, which make their appearance with the freezing in consequence of inevitable vibrations caused by the traffic in the streets or by tram cars. This is in agreement with the observations of FIZEAU, DRUDE, and HAAK [1]) on the diminution of the restored azimuth through grooves or scratches in various directions on the reflecting surface. In order to prevent these wrinkles as much as possible, the iron dish is filled brimful with mercury and then the temperature is slowly lowered. When the traffic in the streets is not too great, it is then sometimes possible to get such a smooth mercury mirror, that a pure image of the collimator slit can be observed. In this case the adjustment of the polarizer does not change. It appears from this, that on freezing and cooling of the solid mercury to — 80° neither the angle of principal incidence nor the principal azimuth are subjected to any change. Optically liquid and solid mercury behave in the same way [2]),

[1]) FIZEAU, Ann. de Chim. et de Phys., 3, 373, 1861; DRUDE, Wied. Ann., **39**, 497, 1890; J. J. HAAK, Thesis for the doctorate, Amsterdam, 1918.

[2]) Besides it follows from this that LUMMER and SORGE's supposition (Ann. der Phys., **31**, 325, 1910), according to which internal tensions would give rise to the elliptical polarisation, cannot be valid for solid mercury.