of the sources of Fulcher's first band. We should, therefore, expect the intensity of each band to have a maximum at about $m = 1$, or $m = 2$. As a matter of fact, the strongest lines are found at $m = 4$ for 161 P, 162 R, 163 P and 164 R, and at $m = 5$ for 169 Q. Thus the intensity distribution indicates a higher moment of inertia than the value obtained from the term differences. I suggest as a possible explanation of this anomaly that in these combinations the rotational quantum jumps may be by more than one unit as from 1 to 3, 3 to 5, 5 to 7, and so on, or from 2 to 4, 4 to 6, 6 to 8, and so on. This would increase the moment of inertia computed from the term differences by a factor of 2, and would bring the values nearer to what is required for the observed intensity maximum.

The continuation of this paper will deal with about 200 further lines of this spectrum, which I have been able to arrange in series provisionally.

The Scattering of Light by Liquid Boundaries and its Relation to Surface-Tension.—Part I.

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(Received April 27, 1925.)

[Plate 24.]

1. *Introduction.*

The conception, introduced by Hardy and Langmuir, that a layer of orientated molecules forms the boundary of a liquid and determines its surface-tension, suggests some interesting questions for investigation regarding the optical properties of liquid surfaces. Should not the orientated molecular layer (assuming it to be real) be doubly refractive ? How is the configuration of the molecules at the boundary of a clean liquid surface influenced by the thermal agitation, and how is this related to the surface-energy of the fluid ? Is the surface-layer capable of producing (by reason of the thermal agitation or its optical anisotropy or other cause) the observed elliptic polarisation of the light reflected by liquid surfaces (clean or contaminated as the case may be) at the Brewsterian angle? The present paper is the first of a series describing the results of work undertaken to find answers to the questions here raised.

In various papers published previously, the internal scattering of light in transparent fluids has been discussed, and it has been shown that it is quantitatively connected with the spontaneous fluctuations in density arising from the thermal agitation of the molecules within the fluid. This internal scattering is a volume-effect and is quite distinct from another and very important type of light-scattering which may be expected, namely, that which occurs at the boundaries of reflecting and refracting media, and is a *surface-effect*, due to the agitation of the boundary. So far as we are aware, very little experimental work has been hitherto published on the subject of this surface-scattering by perfectly clean liquid surfaces.* That a substance in the special circumstances of the critical state when it has a vanishingly small surface-energy may exhibit an observable surface opalescence in addition to the familiar body opalescence, was suggested by Smoluchowski† in his paper of 1908, on the thermodynamics of the critical state. Nothing seems to have been done to follow up this suggestion till 1913, when Mandelstam‡ published some observations on the special case of the light incident on the boundary between the two layers of a mixture of carbon di-sulphide and methyl alcohol near the critical solution temperature, at which the liquid develops a milky opalescence. Mandelstam noticed that in directions not greatly removed from that of regular reflection from the interface there was also some scattered light, and conjectured from his somewhat meagre and qualitative observations, that the effect was analogous to that predicted by Smoluchowski for the critical state of a single liquid. Early in 1923, the present authors took up the general problem of the light-scattering from optical boundaries and succeeded in observing the bluish opalescence of the clean surfaces of transparent and metallic liquids and discovered the special polarisation effects exhibited for large angles

* Contaminated surfaces when illuminated, usually show a copious scattering of white light which, indeed, is why they are visible to the eye. This is a familiar observation; see, for instance, F. Jentsch ('Ann. der Phys.,' vol. 39, p. 997 (1912) who remarks that a surface of metallic mercury or fused alloy is easily seen in this way. As will appear later from our paper, this is far from being true when the surface has been rigorously cleansed. The residual scattering by a really clean mercury surface indeed requires very special arrangements to be perceived at all, and is of a beautiful *bluish white colour.*

† 'Annalen der Physik,' vol. 25, p. 228 (1908).

‡ 'Annalen der Physik,' vol. 41, p. 609 (1913).

of scattering. A preliminary communication was published in 'Nature,' August 25, 1923. Since then, the subject has been extensively developed, no fewer than sixty liquids being studied, and quantitative observations made of the intensity and polarisation of the scattered light for the widest range of angles of incidence and observation and for different physical conditions of the fluid. The work has established a quantitative relationship between the surface-opalescence and the surface-tension of liquids. In Paper I of the series, the case of metallic liquids will be dealt with. In Paper II, transparent fluids will be considered. In Paper III, the effect of contamination on the surface-opalescence of water and the special phenomena of the critical state will be described. In Paper IV, the theory of the phenomena will be discussed. A recent (purely mathematical) paper, by Gans,* which appeared about a year after our preliminary announcement was published, may be mentioned in this connection.†

2. *Preparation of Clean Liquid Surfaces.*

If a pencil of sunlight be concentrated by a lens on the surface of mercury in an open vessel, the focal spot usually shows a film of some kind or other, covering the metallic surface, besides numerous dust particles floating upon it and strongly illuminated by the incident light. It is possible, however, to obtain a clean mercury surface *in vacuo* which does not exhibit these contaminations. For this purpose, the mercury, if not pure to start with, should first be chemically treated to remove dissolved impurities, then cleaned, washed and thoroughly dried. A suitable quantity of the mercury is then transferred into a distilling apparatus consisting of two fairly large bulbs, connected by a communicating tube which has itself been thoroughly cleaned, washed and dried. The apparatus with the mercury is then put under the pump, warmed, thoroughly exhausted and then sealed off. The mercury is transferred to one of the two bulbs which is then placed on a sand-bath, and slowly distilled over to the second bulb ; when sufficient mercury has distilled over it is then shaken back into the first bulb. Repeating this process half-a-dozen times, all the dust present in the apparatus may be concentrated in the first bulb, and mercury having a perfectly clean surface may be obtained in the second bulb. Sunlight is then concentrated by an achromatic lens upon the metallic surface, and such parts of the walls of the bulb are covered over outside by black paint

* R. Gans, 'Ann. der Physik,' vol. 74, p. 231 (1924).

† For some observations on the surface-scattering by clean *solid* surfaces, see L. A. Ramdas, 'Proc. Ind. Assn. Sc.,' vol. IX, Part II, p. 129 (1925).

as is necessary to secure a dark background for observation. The focal spot is then distinctly visible and exhibits a characteristic bluish-white opalescence. Examined under a microscope, this is seen to be perfectly structureless, uniform and continuous. The appearance under the microscope and the perfect reproducibility of the phenomenon are convincing evidence that we are here dealing with an effect which is truly characteristic of the metallic liquid surface. The method of repeated distillation described above is also used in the case of transparent liquids to obtain them dust-free and with a clean surface.

The phenomena of surface-scattering observed with metallic and transparent liquids differ notably in several respects. One obvious point is that the surface-effect which is observed at the boundary is always accompanied by the volume scattering in the interior in the case of transparent liquids, while in the case of metallic liquids, the penetration of the light into the fluid is so small that the volume effect does not exist, or at any rate is indistinguishable from the surface-effect. This difference is clearly indicated by the photographs reproduced in Plate 24, of which figs. 1 to 5 were obtained with dust-free hexane in an enclosed bulb, and fig. 6 with a clean mercury surface *in vacuo*.

3. *Surface-Scattering by Clean Mercury.*

Normal incidence of unpolarised light.—In this case the focal spot exhibits no striking variation of intrinsic brightness as the direction of observation is gradually altered from the vertical to a line inclined at, say, 15° to the horizontal. In directions more nearly grazing the surface, the apparent brightness seems to fall off, but whether this is a real effect or only due to the excessive foreshortening of the patch of light is an open question. Seen nearly vertically, the spot exhibits no polarisation, but as the line of observation is more and more inclined towards the horizontal, the two images of the spot seen through a double image prism suitably held become of unequal brightness, until finally one of them is of very small intensity in comparison with the other. The light scattered in a direction grazing the liquid surface is almost completely polarised, the principal component of the electric vector being then *perpendicular* to the surface. The notable feature is thus that the light scattered through 90° has its electric vector perpendicular to the wave-front of the incident light, instead of being parallel to it as in the Rayleigh scattering by small particles.

(*b*) *Normal incidence of polarised light.*—In this case, the intensity as well as the state of polarisation varies greatly with the azimuth of observation, particularly when the focal spot is viewed in directions more or less nearly horizontal. Here again, contrary to the ordinary experience in the Rayleigh scattering by small particles, we find that the scattered light is of greatest intensity in the azimuth containing the electric vector of the incident waves and of minimum intensity perpendicular to it. In the latter case, it practically vanishes when viewed nearly parallel to the liquid surface. In the azimuth of greatest intensity the electric vectors lie in the plane containing the incident and scattered rays, while in the azimuth of minimum intensity they are perpendicular to it and are therefore horizontal. To make this clear and also to indicate the intensity and polarisation of the scattered rays in other azimuths, diagram 1 is drawn. Here the thick short double-headed arrows represent the electric vibrations in the scattered rays for the directions of observation corresponding to different points on the hemisphere.

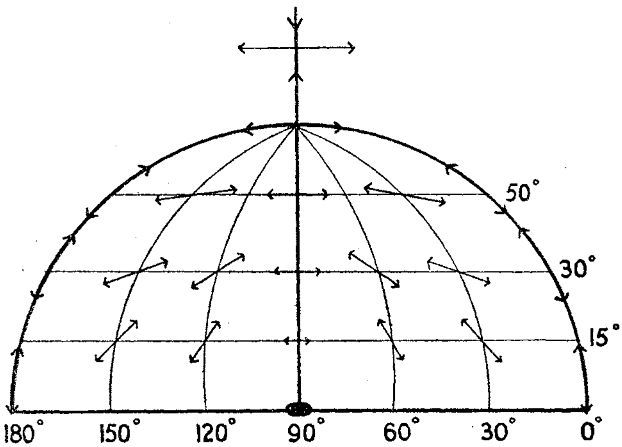


DIAGRAM 1.—Normal Incidence of Polarised Light.

The length of the arrow is in each case a rough indication of the relative intensity of scattering in the corresponding direction. The twisting round of the electric vector in any given azimuth from a nearly vertical to a horizontal position as the angle of observation is increased from 0° to 90° is a characteristic and interesting phenomenon.*

(c) *Nearly Grazing Incidence of Unpolarised Light.*—A very surprising effect observed in this case is that the light scattered forward (that is, in directions

* Thus, here again we have a reversal of the usual rule determining the polarisation in the scattering by small particles.

adjacent to the reflected rays) is actually much smaller in intensity than that scattered backwards (that is in azimuths adjacent to the incident rays). The vertically-scattered light is strongly but not completely polarised, with the electric vector of the stronger component in the plane of incidence. As we move down from the vertical to the horizontal direction in all azimuths from 0° (the plane of incidence) up to, say, 150° (30° away from the plane of incidence on the side of the reflected rays), the polarisation generally improves and the electric vector turns or twists round, so as ultimately to become perpendicular to the liquid surface. In the azimuth 0° the electric vector merely turns round from the horizontal to the vertical position, remaining throughout in the same plane. In other azimuths, 30°, 60°, 90°, and so on, there is also a rotation of its plane, which is one right angle, and a little less than two right angles for azimuth 150°. The nicol held in the hand of the observer has, in fact, to be rotated about its axis through almost two right angles to keep the spot quenched in this azimuth in passing from the vertical to the horizontal direction of observation. As we approach azimuth 180° (the one containing the regularly-reflected rays) this effect, however, becomes less distinct, owing to the scattered light becoming less and less perfectly polarised as the direction of regular reflection is approached; finally, in azimuth 180° the principal component of the electric vector lies always in the plane of incidence.

(*d*) *Nearly Grazing Incidence of Polarised Light.*—The remarkable effects described in the preceding paragraph become intelligible if we study the case in which the incident light is itself plane-polarised. It is noticed at once that both the intensity of the scattered light and its distribution in different directions depend very greatly on the primitive plane of polarisation. To casual observation, in fact, it seems as if the scattered light is practically quenched in all directions when this plane coincides with the plane of incidence; that is, when the electric vector is parallel to the liquid surface. A closer examination shows that this is not actually the case, and that when the light vector in the primary waves is horizontal, there is a small but quite definite scattering in the forward direction and very little backward, whereas when the light vector is in the plane of incidence—that is, nearly vertical—there is a weak scattering forward and a much more intense scattering backward. When the relative intensities of these two types of scattering and their states of polarisation in different azimuths are considered, their superposition is easily seen to lead to the effects described under (*c*) above, for the case of the unpolarised incident light.

Diagram (2) illustrates the relative intensity and polarisation of the scattering in different directions when the primary waves have their electric vector in the plane of incidence. The intensity diminishes steadily as we pass round from azimuth 0° to azimuth 180°. It is seen from the diagram (2) that

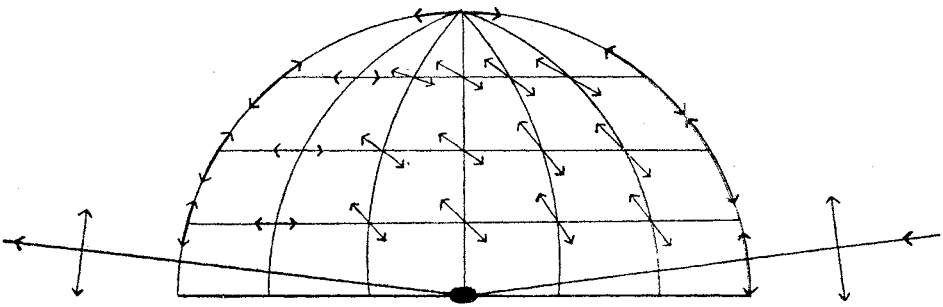


DIAGRAM 2.—Grazing incidence of plane polarised light.

[The incidence is in the plane of the paper. The azimuths of observations are referred to in the same way as marked in Diagram 1.]

the electric vector in the light scattered along the surface also turns round from the vertical to the horizontal position, first slowly and then more quickly. In the azimuth 180° it, however, again returns to the vertical position.

When we have the electric vector in the primary waves horizontal, we have results very different from those shown in diagram (2). The whole effect is very small and sensible only in azimuths between 180° and 120°. In the plane of incidence—that is, in azimuth 180°—the scattered waves have their electric vectors horizontal, and, as we move from azimuth 180° to 150°, the vector twists round and becomes vertical. Theoretically, in azimuth 0°, it should have become horizontal, though practically it is not possible to trace the scattered light in this case beyond azimuth 120°. Combining the effects noticed and described above, the results obtained for incidence of unpolarised light—that is, the partially polarised or unpolarised scattering in azimuth 180°—and the twisting round of the electric vector through nearly two right angles in azimuth 150° are both readily understood.

(*e*) *Incidence at* 45° *of Unpolarised Light.*—From a knowledge of the results for the cases of normal and grazing incidence, it is possible, at least in part, to foresee what we should expect for moderately oblique incidence of unpolarised light. The following are the principal features actually noticed in this case. For observation normal to the surface the focal spot appears distinctly brighter than for oblique observation, and is partially polarised, the stronger component of the electric vector being in the plane of incidence. For observation parallel to the surface the scattered light does not exhibit any striking variation of intensity with azimuth; in all azimuths it is strongly polarised with the electric vector vertical. In azimuths between 0° and, say, 145°, the degree of polarisation improves as we pass from the vertical to the horizontal direction of observation, while in azimuths from 145° to 180° this is not the case. In azimuth 180°, the polarisation actually becomes weaker and disappears in the vicinity of the regularly reflected rays, and then reappears, becoming strong again parallel to the liquid surface. The twisting round of the principal component of the electric vector from the horizontal to the vertical in other azimuths, which was remarked upon in para. (*c*), is also noticed in the present case, but is a less striking phenomenon here owing to the imperfection of the polarisation.

(*f*) *Incidence at* 45° *of Plane Polarised Light.*—The changes in intensity and polarisation of the scattered light observed in this case when the plane of primitive polarisation is rotated are very remarkable and interesting. We have to consider three cases: (1) when the incident light vector lies in the plane of incidence; (2) when it is perpendicular to it and therefore horizontal, and (3) intermediate positions.

Case 1.—Referring to diagrams 1 and 2, we notice that as we pass from normal to grazing incidence, the azimuth of minimum intensity shifts from 90° to 180°. We may expect, therefore, that for moderately oblique incidence an azimuth of minimum intensity would be found in an intermediate direction, and this is actually the case. The scattered light is most intense backwards, that is, in azimuth 0°, slowly diminishes in brightness and nearly disappears in azimuth 135°, and then increases again quickly to a second but feebler maximum in azimuth 180°. (From considerations of symmetry it is easily seen that 225° would also be a second azimuth of minimum intensity.) As in the case of normal and very oblique incidence, the azimuths of minimum intensity are planes in which the electric vector is horizontal, and as we move away from this plane on either side, the electric vector twists round from the horizontal to the perpendicular position, quickly if the observation is along the liquid surface and more slowly in directions inclined to it. In azimuths 0° and 180°, the electric vector is everywhere in the plane of incidence.

Case 2.—In this case, again, the intensity varies greatly with the azimuth of observation, the effects, however, being approximately the reverse of those noticed in Case 1. There is practically no scattering backwards, that is, in azimuth 0° and in nearly horizontal directions. As we pass from azimuth 0° to azimuth 180° there is first a steady increase in intensity which reaches a maximum somewhere about 135°, and then a distinct fall as we approach azimuth 180°. The scattering in azimuth 180° is, however, quite appreciable in magnitude. In the plane of incidence, that is, in azimuths 0° and 180°, the electric vector is everywhere perpendicular to it, and is therefore horizontal. As we move parallel to the liquid surface from azimuth 0° to 180°, the electric vector which is horizontal in azimuth 0°, twists up and becomes nearly vertical in the range from 45° to 135°. It then twists further again into the horizontal position as we pass from azimuth 135° to 180°; this time much more quickly.

Case 3.—When the electric vector in the infalling waves is neither parallel nor perpendicular to the plane of incidence but is inclined to it, say, at 45°, the curious feature noticed is that the scattering is not symmetrical with respect to the plane of incidence, but is much more intense on one side of it than on the other. There may be little or no scattering to be observed in azimuths from 45° to 135°, and quite strong scattering in azimuths from 225° to 315°, or *vice versa*; and when the polarising nicol is rotated about its axis, the azimuths of minimum intensity swing round in a remarkable way. Further details of these effects may be reserved for later consideration.

4. *Measurement of the Intensity of the Light Scattered by Mercury Surface.*

The intensity of light scattered by the mercury surface when a beam of sunlight is focused on it is an exceedingly small fraction of the intensity of the incident beam. To enable the ratio to be determined, one or more intermediate standards have to be used for purposes of comparison. A smooth white surface of plaster of Paris scatters practically the whole of the light falling on it. As an intermediate standard, it was found convenient to use a small quantity of black varnish which, when poured on a piece of black paper, presents a surface of very small scattering power. The brightness of the illuminated mercury surface was compared with that of the black varnish and the latter with the plaster of Paris. The photometric comparisons were made visually, a suitable colour filter being held in front of the eye to neutralise the differences in tint of the surfaces observed.

The experimental method used may be indicated as follows. Two discs of plaster of Paris were set side by side, and two pencils of sunlight were focused upon them by means of suitable mirrors and lenses. The apertures of the lenses used could be varied in such a way that the focal spots on the discs appeared of equal brightness. One of the discs was then replaced by a fresh surface of the black varnish, and by altering the apertures of the lenses and by interposing a rotating sector in the path of the pencil focused upon the other disc, the surfaces of the varnish and the plaster of Paris were equalised in brightness. The apertures used determined the ratio of the scattering powers. The mercury surface and the black varnish were then compared in the same way. A clean mercury surface illuminated normally with unpolarised light in the green part of the solar spectrum and viewed at 45° is found to have only $5 \cdot 7 \times 10^{-7}$ times the brightness of a plaster of Paris surface viewed under the same conditions. The colour of the opalescent spot is bluish, but not perhaps such an intense blue as the internal scattering in liquids.

Summary.

(*a*) Perfectly clean liquid surfaces when illuminated strongly are found to scatter light appreciably in all directions, the effect being attributable to the irregularities of the surface resulting from thermal agitation as controlled by the surface tension of the fluid. Photographs of the phenomenon are published.

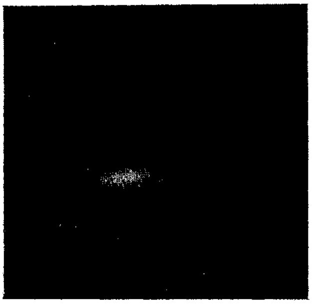
(*b*) The bluish-white opalescence shown by an illuminated metallic mercury surface has been very fully studied and measurements made of its intensity. Some very remarkable effects have been observed in respect of the polarisation and distribution of intensity of the scattered light in different directions, and these are described in detail.

(*c*) At the suggestion of the senior author, some observations were made at the Norman Bridge Laboratory of Physics (Pasadeña), by Mr. B. C. Burt, with clean surfaces of molten sodium obtained *in vacuo* by electrolysis through glass, and these exhibited phenomena similar to those described by mercury, but somewhat more conspicuously.

(*d*) The case of transparent liquids has also been studied and will be treated in the succeeding instalment of the paper.

DESCRIPTION OF PLATE 24.

FIG. 1.—The bright patch at the centre of the feeble cross is the opalescent spot at the surface of the liquid (dust-free hexane) viewed from below in an azimuth perpendicular to the plane of incidence in a direction making 30° with the surface. The lower arms of the cross are due to the tracks of the incident and reflected beams, while the upper arms are their images seen by reflection at the surface. The light is incident at the critical angle.



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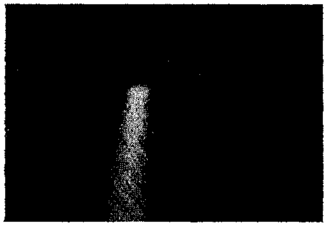

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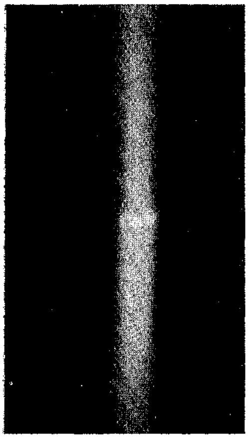

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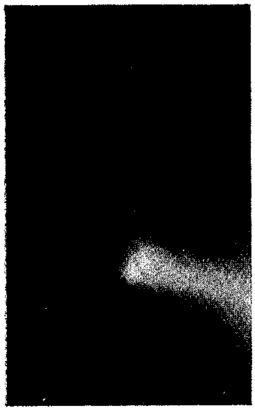

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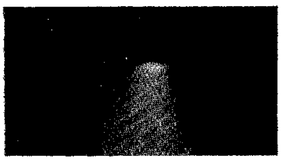

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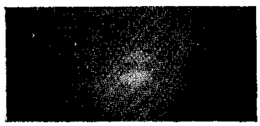

6.

[*Facing p.* 570.

Fig. 2.—The opalescent spot at the surface is seen here as a bright cap at the top of the normally incident beam. The photograph is taken from above and the incidence also is from above.

Fig. 3.—The conditions are the same as in fig. 2, but the photograph is taken from below. The opalescent spot is seen at the centre of the vertical track, the upper half of which is the reflection of the lower half at the liquid surface.

Fig. 4.—In this figure the elliptical, intense patch is the surface scattering viewed nearly in the direction of the totally-reflected beam when light is incident at the critical angle. The more intense of the two tracks is that of the reflected beam.

Fig. 5.—Is similar to fig. 2, but the incidence is from below.

Fig. 6.—Shows the scattering by the pure mercury surface as observed through a double-image prism. The brighter of the two elliptic patches has the electric vector vertical. The light is incident normally and the direction of observation is nearly parallel to the surface.

On the Series Spectrum of Gold.

By J. C. McLennan, F.R.S., Professor of Physics, and A. B. McLay, M.A., University of Toronto.

(Received May 11, 1925.)

1. *Introduction.*

In Bohr's scheme of electronic orbits for the atoms of the elements, the stable atoms of gold, silver and copper are supposed to have an outermost system consisting of one electron. This electron is represented as describing an elliptical orbit, in the case of gold of the 6_1 type, in the case of silver of the 5_1 type, and in the case of copper of the 4_1 type. Following the analogy afforded by the series spectra of the alkali elements, this would mean that the arc spectra of gold, silver and copper should consist, in part at least, of doublet systems. Such doublet series have been partially identified in the case of silver and copper, and the results are recorded by Fowler* and by Paschen and Götze.† These writers, however, do not record any series for the arc spectrum of gold.

Hicks, in his work on 'The Analysis of Spectra,' has grouped many of the wave-lengths in the arc spectrum of gold into a number of doublet series, but it would appear from a consideration of experimental data recently obtained that some of his conclusions will require to be modified. The key to further progress in the disentanglement of the series arc spectrum of gold appears to be given

* Fowler, 'Series Spectra.'

† Paschen and Götze, 'Seriengesetze der Linienspektren.'