LIGHT SCATTERING IN GOLD SOLS IN RELATION TO PARTICLE SIZE AND SHAPE.

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1. Introduction.

The determination of the condition of the colloid particle and especially its size, shape and structure is one of the most important problems in the physics of the colloidal state. The study of the Tyndall effect is obviously one of the most fruitful methods that can be employed to resolve this problem. In an earlier paper by the author, the depolarisation of the Tyndall scattering in a number of typical colloids was reported on and the importance was emphasised of measuring the three values, namely, $\rho_u$, $\rho_v$ and $\rho_n$ of the depolarisation of the transversely scattered light referring respectively to the cases in which (a) the incident light is unpolarised, (b) it is polarised with its electric vector perpendicular to the direction of observation, (c) parallel to the direction of observation. The values of the three quantities, both absolutely and relating to each other, are very significant as indicators of the size, the shape and the structure of the particles. The value of $\rho_v$ by itself is an indicator of the anisotropy of shape or structure of the particles, while the value of $\rho_n$ is specially sensitive to the size of the particles. R. S. Krishnan has shown by an application of the theorem of reciprocity that the three quantities $\rho$ are connected by the relation

$$1 + \frac{1}{\rho_n} = \frac{1}{\rho_u} + \frac{1}{\rho_v}$$

which takes the special form

$$\rho_u = \frac{1 + \rho_u}{1 + \rho_v}$$

in the special case when the particles are exceedingly small, $\rho_n$ then becoming unity. It appeared of importance to investigate the relative values of $\rho_u$, $\rho_v$ and $\rho_n$ in the classical case of gold sols, the study of which, as is well known, played an important part in the history of the development of colloid science.

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2. Previous Work on Gold Sols.

Among the various investigators that have made a study of the phenomena exhibited by gold sols, mention must be made of Mie, Steubing, Lange, Diesselhörlst and Freundlich, and Bjornstål. Mie has developed formulae for the absorption and the scattering of light in colloids, assuming that the particles are spherical in shape. Steubing has shown experimentally that in gold sols, the transversely scattered light is not completely polarised, even when the incident light is plane polarised. From considerations based on Steubing's experimental results and his own theoretical calculations, Mie concludes that the particles in gold sols are not strictly spherical in shape though the other optical properties of these sols, such as the absorption of light, can be satisfactorily explained on the supposition that they are spherical. Subsequently, Lange has made detailed investigations of the absorption and the scattering of light in gold sols. The large depolarisations of the light scattered transversely by the sols indicate that the particles are in the form of rods or discs while the absorption measurements are strictly in accordance with Mie's theory indicating that the particles are spherical in shape. To solve this contradiction, Lange postulates that a large fraction of the particles in the sols are spherical in shape and these manifest themselves in absorption measurements and a small fraction of the particles are rods or discs and these cause the observed partial polarisation of the Tyndall light.

Diesselhörlst and Freundlich have considered the effects of the flow of colloids on the light absorption and the Tyndall scattering in them. According to them, colloids containing non-spherical particles bring about changes in these phenomena during their flow, but those containing spherical particles do not. The experiments showed that the particles in gold sols could be treated as spherical.

Bjornstål has made a study of the accidental double refraction in colloids. Gold colloids made by using nuclear sols and hydrogen peroxide as the reducing agent showed magnetic, electric and streaming double refraction. Those prepared by various other methods did not show any effect. A sample of gold colloid, made by using ferrous sulphate as the reducing agent, showed negative double refraction in a magnetic field. While this

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last result may be regarded as being due to the presence of small traces
of iron, it is difficult to understand why the sols made by using hydrogen
peroxide as the reducing agent should show accidental double refraction.
The results are surprising and the subject demands careful investigation.

In view of all this it was thought necessary to undertake a study of the
optical and the magnetic properties of colloids in order to find out their true
physical nature. A fresh investigation of the depolarisation of the Tyndall
scattering in gold sols, in the light of the new methods already indicated,
has been made. While Lange has confined his attention to the measurements
of $\rho_u$ alone, the measurements of $\rho_v$ and $\rho_u$ have also been made.
That the value of $\rho_u$ depends on wave-length has been shown experimentally
by Lange. The measurements reported in this paper have all been carried
out with incident white light. The dependence of $\rho_u$, $\rho_v$ and $\rho_u$ on wave-
length is being investigated and the results obtained will be published in
a separate communication.


In order to obtain clear, good and stable sols, the necessary precautions
were taken. All the vessels used were of resistance glass and they were
first cleaned thoroughly with hot chromic acid and then well steamed. The
necessary reagents and other solutions were prepared using double distilled
water. Six different sols were made. Two were prepared according to
the method employed by Faraday (I and II). Three were prepared according
to the nuclear method, using hydrogen peroxide as the reducing agent. This
was the method employed by Bjornstähl for the preparation of his sols which
showed accidental double-refraction. The nuclear sol used in all these
cases was Faraday's sol I. Another sol was made by the method given by
Zsigmondy (VI). All these sols are preserved in resistance glass bottles,
thoroughly cleaned and well steamed.

I. The method of Faraday for the production of colloidal gold consists
in the use of a solution of phosphorus in an organic liquid as the reducing
agent. A sol was made by adding 2.5 c.c. of a -6% chlorauric acid and
3 c.c. of -18 N potassium carbonate to 120 c.c. of pure double-distilled water
followed by the addition of 1 c.c. of a pure ether solution of phosphorus
prepared by diluting the saturated solution with five times its volume of ether.
In the cold the mixture changed to a brown colour, which gradually became
red, the reaction being complete in about 60 hours.

II. Another sample of a gold colloid was made exactly on the same
lines as I, but the reaction being rendered almost instantaneous by boiling
the mixture. A clear red sol resulted.
III. 2 c.c. of a 0.6% chlorauric acid were added to 100 c.c. of pure double-distilled water. 4 c.c. of the nuclear sol were added followed by the addition of a few drops of a very dilute solution of hydrogen peroxide. A clear red sol formed immediately.

IV. Another sample was made using the same method as that in III except that the mixture was kept boiling while the reducing agent was added. This was also a clear red sol.

V. Yet another sample was made. In this case the mixture was kept boiling and 6 c.c. of 0.18 N potassium carbonate solution were added and then the reducing agent. The sol obtained was clear and deep-red in colour.

VI. A blue sol was obtained as a result of employing a method of preparation suggested by Zsigmondy. 2 c.c. of 0.6% chlorauric acid were added to 100 c.c. of pure double-distilled water followed by 6 c.c. of 0.18 N potassium carbonate solution. The mixture was then heated to boiling and 4 c.c. of the nuclear sol were added followed by 5 c.c. of a 0.03% solution of formaldehyde drop by drop. The sol which resulted was boiled and it turned blue.

4. Experimental Results.

The experiments were made within a dark cabin into which sunlight was reflected by a single mirror Foucault Heliostat. A Dallmeyer photographic lens of adjustable aperture and focal length 1 foot fixed to the wall of the cabin served to bring the sunlight to a focus, at the centre of a rectangular glass cell containing water in which was immersed the bottle containing the sol. The rectangular glass cell itself was placed in a wooden box painted dull-black on the inside, having three openings, two for the entry and exit of the incident beam of light and the third for the observation of the scattered light exactly opposite the focus of the track in the disperse system. The wooden-box was mounted on a stand capable of being raised or lowered. The incident beam could be polarised in any plane by means of a nicol suitably mounted. The following measurements (expressed as percentages) were made:

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<th></th>
<th>Red Sols</th>
<th>Blue Sol</th>
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<tr>
<td></td>
<td>I    II   III   IV   V    VI</td>
<td></td>
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<tr>
<td>( \rho_f )</td>
<td>7.7   17.2  10.5  10.6  9.4  9.9</td>
<td></td>
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<tr>
<td>( \rho_s )</td>
<td>100  100   96.5  84   96.5 54.8</td>
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<tr>
<td>( \rho_f ) (observed)</td>
<td>14.5  29.5  19.8  21.7  16.9 23.3</td>
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<tr>
<td>( \rho_0 ) calculated from formula A</td>
<td>14.3  29.2  19.4  21  17.5 25.5</td>
<td></td>
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<tr>
<td>( \rho_v ) calculated from formula B</td>
<td>14.3  29.2  19.1  19  17.2 19.2</td>
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From the table we observe that in the blue sol, the value of $\rho_n$ is relatively small. Thus in this case, we are able to infer from depolarisation measurements alone, that we are dealing with particles which are relatively large. Amongst the red sols we find that $\rho_n$ has its maximum value unity in the case of I and II and differs from it to a small or large extent in the case of III, IV and V. Also it was observed that the intensities of scattering in I and II were far smaller as compared with those in III, IV and V. These indicate that the particles in I and II are much smaller in size than those in III, IV or V. Out of the last three, the value of $\rho_n$ in IV deviates more from unity than that in III or V, indicating that the gold particles in IV are relatively much larger in size as compared with those in III or V.

In order to confirm the conclusions drawn from the depolarisation values, observations were made by the "method of two double-image prisms". In this case we observe four images, $V_v, V_n, H_v, H_n$. In the case of the red sol IV and the blue sol VI, $H_n$ was definitely stronger than $H_v$ ($=V_n$). In the case of I, II, III and V, it was found that $H_n = H_v = V_n$. The small differences between the values of $\rho_v$ as calculated from $A$ and $B$ and observed, in the case of III and V, may be due to the unavoidable errors introduced by the glass bottles and the like. In the case of the blue sol the vertical component of the scattered light had a reddish tinge and the horizontal component had an yellowish tinge. This rendered the matching of the intensities of the two tracks very difficult.

The large values of $\rho_v$ in all cases indicate that we are dealing with particles whose shapes depart greatly from the condition of sphericity. That an increase in the rate of growth brought about by temperature results in an increase in the anisotropy is shown strikingly by the values of $\rho_v$ in I and II. By increasing the rate of growth the particles are also made larger as is shown by the values for III and IV. A comparison of III, IV and V indicates that the effect of potassium carbonate is to diminish the anisotropy and prevent the formation of very large particles.

In conclusion, it is my pleasant duty to express my heart-felt thanks to my professor, Sir C. V. Raman, for his kind encouragement and inspiring guidance.

Summary.

Previous work on gold sols with reference to the shape of the particle has been briefly recounted. Results of the measurements of the depolarisation of Tyndall scattering corresponding to the incident light being (a) unpolarised, (b) plane polarised with its electric vector perpendicular to the plane of

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8 R. S. Krishnan, Loc. cit.
observation, (c) plane polarised with its electric vector parallel to the plane of observation, have been reported. The values obtained and the observations made indicate that the particles in Faraday's sols are much smaller as compared with those in the other red sols prepared by using nuclear sols and hydrogen peroxide as the reducing agent; those in the blue sols are relatively the largest. In all the sols examined the shapes of the particles are far from being spherical. In general the size and the anisotropy of the particles appear to increase with the increase in the rate of growth brought about by enhancing the temperature during the preparation of the sol. The addition of potassium carbonate to the mixture before reduction seems to have the reverse effect.