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LIV. *On the Scattering of Light by Metallic Particles.* By
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THE problem of the scattering of light by small conducting particles is treated by Prof. J. J. Thomson in his very welcome 'Recent Researches in Electricity and Magnetism.'

It would of course be absurd for me to offer any remarks on the formidable analysis by means of which Prof. Thomson reaches his conclusions; and therefore I shall limit myself to the consideration of §§ 367 and 378, in which similar conclusions are reached by different methods.

One of the most striking results is as follows ('Recent Researches,' p. 449):—"When non-polarized light falls upon a small non-conducting sphere, the scattered light will be completely polarized at any point in a plane through the centre of the sphere at right angles to the direction of the incident light. When the light is scattered by a conducting sphere, the points at which the light is completely polarized are on the surface of a cone whose axis is the direction of propagation of the incident light and whose semi-vertical angle is 120 degrees."

It may well be considered questionable whether small metallic particles can be regarded as the conducting particles to which the investigation refers, especially if we bear in mind the apparently excessive transparency of thin metallic films. However, there is no difficulty in observing the scattering from fine metallic particles; and what follows deals with some experiments I have made on the subject. To save time for any one who does not care to follow the detail of experimental work, I will state at once that I have observed no great difference in the effects produced by particles of gold, copper, iron, silver, and gum mastic. The position of the azimuth of maximum polarization with gold particles (which are most easily observed) does not differ from the corresponding position when mastic is employed by more than a degree or two, if at all. The observations with metals other than gold were nothing like so satisfactory; but so far as they go they confirm the results obtained with gold.

As long ago as 1888 I examined the properties of a gold "sky." In order that the gold particles might be suspended in a non-conducting medium, I shook up some terebene with a bit of solid phosphorus and added a very small quantity of a solution of gold chloride in ether; in the course of a few

* Communicated by the Author.

hours, or days, the gold was thrown down as usual in particles of extreme fineness. For the present purpose, however, there is no advantage in using terebene, since any solution which is transparent must be regarded as non-conducting for voltages reversed with the frequency of light-waves. Accordingly the gold deposits which I have examined have been formed in water. When a very dilute solution of the double chloride of gold and sodium—say, one centigram of the crystallized salt per litre—is reduced by the addition of a solution of phosphorus in some organic solvent, the solution is observed, after a time varying from a few hours to several days or even weeks, to become strongly coloured. The colour varies from a clear pink with dilute solutions to an opaque purple when the solutions are strong. A number of observations on these precipitates and on their removal from suspension (for they are too fine to subside of themselves) by moulds growing in the liquids have been published by Prof. Liversidge (Australian Association for the Advancement of Science, Report, 1890). I have to thank Prof. Liversidge for allowing me to examine these solutions.

There are certain preliminary questions which must be dealt with. In the first place the precipitate formed is really gold,

- (1) Because in rather strong solutions of the chloride the precipitate forms a film on the surface which possesses the lustre of gold ;
- (2) Because when the solutions are strong enough to give a precipitate coarse enough to sink, or when the fine precipitates are carried down by the growth of mould, the presence of metallic gold can be rendered evident by burnishing.

I have no formal proof that the precipitates consist of gold only ; but taking into consideration the number of experiments made by Prof. Liversidge and the great variety of reducing solutions used by him, together with the constancy of the phenomena observed, there can be no doubt that the precipitate is practically pure gold. Of course, when the precipitates are large enough to examine there is no doubt about their nature, and we have no chemical reason for supposing that the reaction will change in character by the mere influence of further dilution of the solutions.

The colour of the solutions is certainly to be attributed to the presence of the precipitate ; for when the precipitate is removed by moulds the colour disappears. The colour, therefore, must be due to the fine particles ; but without careful examination it is difficult to believe that the whole

effect is due to scattering. This, however, appears to be most probably the case, as the following experiments will show :—

Three typical samples prepared by Prof. Liversidge were examined. The first sample had been made up about two months before I examined it. The quantity of gold was so large that the precipitate had partly subsided ; and the solution was so dark that it was practically opaque in thicknesses of more than a few centimetres. The absorption spectrum was observed with the help of a wedge-shaped bottle. The absorption was chiefly in the green and greenish blue. At about the limit of transparency practically all the spectrum disappeared except the orange-red. The opacity was such that no satisfactory observations could be made on the scattered light.

The second sample had a magnificent pink colour, very like a dilute solution of fluorescein, but of course without the fluorescence of that substance. The colour was exceedingly brilliant, and having only had experience of the colour produced by precipitates of gums in water, for a long time I imagined that some coloured substance had been formed. This specimen was described by Prof. Liversidge (*loc. cit.* p. 406). It was prepared in November 1889, and from the description of its colour cannot have changed appreciably since that date. The reducing substance was phosphorus in chloroform, and a smell of chloroform was still marked. The solution of gold chloride was of about the strength mentioned. The absorption spectrum was observed in a tube 69·3 centim. long. The absorption was not nearly so sharp as in the case of, say, chlorophyll, but was wonderfully sharp for a “sky” colour. The absorption extended from the yellow-green to the blue-green ; there also appeared to be a slight absorption in the blue ; but it was very slight. The scattered light was easily observed in this case, especially when a Nicol prism was used in conjunction with the spectroscope. It was thus discovered that the scattered light was practically green, and of about the proper apparent intensity. A line was drawn on a board so as to indicate a direction at right angles to the direction of the incident light ; and another line was drawn at 120 degrees to the same direction. By means of these lines the position for maximum polarization could be sufficiently closely observed. There can be no question as to the angle being much closer to 90°—even if it were not exactly 90°, as the observation seemed to show—than to 120°. I cannot say within what limits of angle the position was perpendicular to the direction of the incident light.

The third sample I examined had a full purple colour, and

was made at the same time as the one last described. The solution must have been of about the same strength, and the reducing agent was phosphorus dissolved in carbon bisulphide. The smell of that reagent had disappeared and been replaced by that of sulphuretted hydrogen. Observations similar to the last were made with the same general result, except that the absorption was stronger and that it extended rather further towards the red end of the spectrum. The scattered light was again seen to correspond with the part of the spectrum which was cut out in the last observation. The angle of maximum polarization occupied its former position.

A large number of similar experiments were made from time to time, but they all gave the same general results.

In order to avoid any risk of contaminating the gold with organic matter derived from the solvent used for the phosphorus, I shook up a bit of phosphorus with some distilled water, and found that I could obtain a sufficient reduction of the gold to enable me to be sure that the angle of maximum polarization occupied its former normal position.

I also set up solutions of different strengths, and observed them from day to day as the process of reduction went on ; but I never observed any change in the position of the maximum angle.

Most of the observations on the direction of the position of maximum polarization were made on about a litre of the solution contained in a vessel of glass with plane sides ; occasionally I used beakers, which did just as well.

The source of light was an arc lamp, and when the particles were only few and far between lenses were employed to condense the beam. Some experiments were also made with initially polarized light, but without any difference being in any case detected, whether a gold or a mastic sky was used.

Metals other than Gold.

1. *Copper*.—A solution of sulphate of copper was taken and diluted sufficiently with water that had been shaken up with phosphorus. Of course check experiments were made in this case, as in all others, to insure the absence of particles other than those desired. In many cases it was necessary to use platinum-distilled water, as ordinary once-distilled water contains too many motes. A very faint sky was obtained with the copper, and this behaved just as did the gold sky. I believe that the sky did actually consist of copper, for the solutions were both free from motes before mixing, or rather they gave a much stronger sky when mixed than when separate.

2. *Silver*.—The phosphorus-water was shaken with dilute

silver nitrate. In this case I did not succeed in satisfying myself that chlorides were sufficiently eliminated. The sky, whatever it was composed of, behaved just as before.

3. *Iron*.—A properly reduced solution of ferrous ammonium sulphate was obtained and mixed with phosphorus-water as before. The solution was more or less preserved from oxidation by covering it with a layer of "albolene" oil. I am not sure that an appreciable increase of the sky took place on this occasion by the action of the phosphorus : what sky there was behaved as before.

The above experiments were repeated, a piece of phosphorus being left in the liquid ; but though the skies became rather stronger, no differences could be detected. These experiments suffer from the uncertainty that the skies might have been formed by particles separated direct from the phosphorus.

Assuming that Prof. Thomson's views are correct, these experiments must, I think, be taken as showing that at all events gold in particles fine enough to scatter light behaves as an insulator. At all events, the phenomena are consistent with the great transparency of gold-leaf.

No difference was observed between the scattering of plane waves, and the scattering from a pencil of rays converging from the condenser of the lantern.

Returning to the gold solutions, I have no hesitation in saying that they afford the simplest and most beautiful illustration of the colours produced by fine particles. It is worthy of note that the colours are so brilliant, even if we allow for the manner in which the colour of the scattered light depends on the size of the particles.

The apparent perfect transparency of the more dilute solutions, when considered in connexion with the comparative sharpness of the absorption spectrum, must indicate a uniformity in the dimensions of the particles which is, so far as I know, unique.

Judging from the appearance of the spectrum only, especially in the case of the stronger solutions—*i. e.*, those that just do not settle by themselves—I think that perhaps an excellent light for photographic purposes might be obtained by using these skies as light-filters.

Supplementary Note.

After concluding the above experiments it appeared to me that the only metal for which the evidence I had to offer was satisfactory was gold. I therefore made the following experiments with the object of observing the action of a "sky "

of platinum particles. Platinum is certainly one of the most opaque, if not the most opaque metal ordinarily dealt with ; and it seemed possible that very fine particles of platinum might act as conductors even to electric disturbances reversed with the frequency of blue light.

A sky of platinum particles was easily produced as follows:—A litre bottle with a wide neck was three quarters filled with boiling distilled water, the water having boiled for an hour before being poured into the bottle. The rubber bung used to close the bottle was pierced by three holes—one allowing the introduction of a thick glass tube carrying a sealed-in electrode and passing into the water ; another carried a second electrode of platinum reaching down to within about half an inch of the water surface ; the third carried a tube permitting communication to be made between the inside of the bottle and the water-pump. On placing the bung in position and working the pump, most of the air was rapidly sucked from the bottle, the water began to boil, and after a time the connexion was sealed-off. The bung and tubes were well waxed, and the bottle was left to cool down. Next day it was found that the water “hammered” in a satisfactory manner when the bottle was shaken. The electrode, owing to several causes, was now about $1\frac{1}{2}$ centim. from the surface of the water. An induction-coil worked by a transformer was then caused to pass a current between the water surface and the free electrode, the current being regulated so that at a frequency of about 60 ~ it just failed to produce sufficient electrolysis to free gas. The electrode was white hot. The bottle was placed before an arc-lamp and studied by a Nicol prism, as previously described, while the coil was actually at work. It was noted that before the discharge began the water was nearly optically clean, and looked exactly like a check-sample of the boiled distilled water which had been preserved for the purpose of comparison. After about half an hour’s discharge no appreciable increase in the scattered light could be detected ; but on shaking the bottle, small brightly-reflecting metallic scales became apparent. The discharge produces considerable motion of the water-surface, and it had been erroneously assumed that this would prevent the formation of a platinum film on the water surface. The hint was taken, however, and the bottle was shaken by hand for about two hours while the discharge was taking place, during the whole of which time the scattering of light by the water particles continually increased, and was finally fairly brilliant. At no time did the direction of maximum polarization appear to vary from the perpendicular to the direction of propagation

of the light. The platinum sky behaved, in fact, in a quite normal manner. The more carefully the directions of the incident and observed light were adjusted to perpendicularity, the more complete the extinction produced by rotating the Nicol appeared to be. The fine particles remaining well suspended for a considerable time (at least a week), several friends were good enough to examine the polarization phenomena for me, and all the observations agreed perfectly.

Platinum particles therefore scatter light like ordinary non-conducting particles within the limits of accuracy of the observations.

I was anxious to try the effect of a sky of iron particles, and made the following experiments and observations on this matter.

The apparatus used was similar to that described in the case of platinum, except that "pure" iron electrodes were formed by binding the iron wire sold as "pure for chemical analysis" round the sealed-in ends of the platinum wires. Five or six layers of fine iron wire were bound round the platinum wire, and connected then to the actual electrodes—two short lengths of Swedish charcoal-iron carefully cleaned. Sparks were taken between the two electrodes, and were practically confined in their effects to the charcoal-iron. As a medium for catching and supporting the fine iron-dust, I first tried a nearly dry sample of glycerine, prepared by heating the strongest commercial glycerine in the presence of strong sulphuric acid under reduced pressure. After sparking for some hours a sky was formed, but the heat of the discharge had been sufficient to obviously decompose some glycerine vapour, and consequently the sky might have been due to iron, oxide of iron, or carbon, or any mixture thereof. I therefore tried to find some more suitable substance than glycerine. I wished to exclude oxygen, if possible, from the medium employed, and yet have a substance which should have only a small vapour-tension. After a good many trials I settled on a vaseline oil (?) known as "albocarbene oil." The vapour-tension of this substance was at least 2 centim. at 24°C . even after heating and exposing in a vacuum several times. Under the circumstances it hardly appeared worth while to attempt to take up the oxygen it might hold by the action of sodium, especially as I was not sure of the complete action of the sodium; while the certainty of its making the oil dirty opened up the probability of other disadvantages. The atmosphere employed was hydrogen disengaged from zinc and hydrochloric acid in presence of chromous chloride; it was washed by solution of sodium hydrate, and finally dried

over phosphorus pentoxide. The pressure was about two inches of mercury. The sparking &c. was carried out as before, and after about four hours' of sparking a fairly good sky was visible in spite of the strong fluorescence of the oil. On opening the bottle a decided smell of hydrocyanic acid was noted (nitrogen was known to be present in small quantities), and there were traces of decomposition on the sides of the bottle. An attempt was made to concentrate the particles by standing the bottles on the poles of a Jamin magnet, but no concentration could be observed after twenty-four hours. Considering the viscosity of the oil, this was not regarded as of much weight. The oil was then poured through a filter made from Schleicher and Schull's special quality paper for stopping fine particles. The paper was washed with kerosene, gasolene, alcohol, and water, and was finally digested in dilute hydrochloric acid. The resultant liquid, on evaporation, showed the presence of traces of iron in an unmistakable manner. The filtered oil was not examined as to its scattering properties, owing to an accident.

The light scattered from the supposed iron sky behaved in a perfectly normal manner, *i. e.* like all substances hitherto examined. In this case it was found more convenient to use a beam of sunlight than the light from the arc-lamp; observations are rendered difficult by the blue fluorescence of the oil. The question turns entirely on the point as to whether the scattering was produced by metallic iron or by its oxide. That the scattering was produced by one or the other I have no doubt; for after filtering the oil I could discern a faint darkening of the filter-paper which disappeared by treatment with hydrochloric acid, and so disposes of the supposition that the particles were carbon. The iron afterwards found was from the deposit and not originally in the acid or reagents, or in the filter-paper (for check-experiments were made). Some dust on the electrode appeared to be magnetic when tested by a magnetized sewing-needle, but the quantity that I could collect was too small to make the observation conclusive. Of course if I had been in a position to secure a sample of a definite hydrocarbon of small vapour-tension, the matter could easily have been determined; but such a thing does not exist, to my knowledge, in Australia.

As I desired further evidence I repeated the whole investigation up to the sparking, but this time introduced a small plate of glass between the oil and the electrodes. After sparking as before for three hours (using the coil-contact and three gallon leyden jars with an air-gap) I could see no mirror, though obviously a good deal of oil-vapour had been

decomposed. (Professor Wright, of Yale, warned me in 1889 that iron mirrors are not easily made.) The experiment was perforce interrupted for three days, and on turning on the coil on the fourth day a smart explosion resulted, bringing the observations to a conclusion by scattering every part of the apparatus, the writer having a rather lucky escape. The electrodes were picked up and found to be perfectly clean and bright. After consideration I decided not to pursue the matter further, first because I am not quite sure of the importance of an investigation of iron in the present state of electromagnetic theory, and secondly because the investigation can be easily made by anyone who has a suitable hydrocarbon, whereas I can only hope to obtain inconclusive results with the oils at my disposal.

I will add a note on producing oxygen-free atmospheres. If hydrogen is employed the difficulty is to get rid of oxygen from the water and acid used to act upon the zinc. Several ways of absorbing small quantities of oxygen are known and dealt with in a paper by me, "On the Preparation of Pure Nitrogen and Attempts to Condense it," *Phil. Mag.* January 1893.

The most convenient way of obtaining large quantities of hydrogen free from oxygen is to half fill a very large flask with granulated zinc and keep this covered with a solution of chromous chloride—the "liquide brute" of Recoura. Hydrochloric acid can be added fearlessly by means of an ordinary safety funnel; for any air carried down is instantly deprived of its oxygen by the blue liquid. If the flask be permanently sealed to a potash wash-bottle and drying-tubes, a means of procuring dry hydrogen with traces of nitrogen is instantly and continually available. The blue liquid does not last for ever, however, though if a little acid be added from time to time its life is sufficiently prolonged. Following Recoura in the paper quoted, I recommended that the potassium dichromate should be finely ground in the chromous chloride preparation. I now find that if it is dissolved in the hydrochloric acid before the latter is added to the zinc, it does just as well and saves a good deal of trouble.

To sum up :—

1. The scattered light from gold and platinum particles behaves like light scattered from particles of gum mastic or milk so far as the polarization phenomena are concerned.
2. The same remark applies to iron, or iron oxide, or carbide, whichever it was that I examined. I rather think, on the whole, that the sky was iron simply.

Note on the preceding Paper by Prof. J. J. THOMSON.

I made, about two years ago, some rough experiments on the polarization of light scattered by small particles of gold, the results of which were in agreement with those of Professor Threlfall. I regarded these experiments as confirming the results of Maxwell and Wien, that the resistance of metals to the very rapidly alternating currents which constitute light is much greater than to steady currents.

It is, moreover, difficult to make these experiments so as to be a fair test of the theory, as it is only when the size of the particles is within narrow limits that the theory would be applicable, even supposing the resistance to be as low as for steady currents. To scatter the light the diameters of the particles must be small compared with the wave-length of light, while the theory given in my 'Researches on Electricity and Magnetism' requires that the depth to which the currents produced by the light penetrate the particle should be a small fraction of the radius of the particle. Now at a depth d below the surface of the sphere the intensity of the induced current varies as e^{-kd} , where $k = \{2\pi\mu p/\sigma\}^{\frac{1}{2}}$, where μ is the magnetic permeability, σ the specific resistance of the metal, and $2\pi/p$ the time of oscillation of the incident electrical vibration. Thus the currents at a depth $1/k$ below the surface will only be $1/e$ of their value at the surface; we may therefore take $1/k$ as the measure of the thickness of the film filled by the currents. For gold $\sigma = 2100$ for steady currents, $\mu = 1$, and for the D line $p = 2\pi \times 5.097 \times 10^{14}$; thus $1/k = 3.2 \times 10^{-7}$. The wave-length of the D line is 5.89×10^{-5} , about 170 times $1/k$. Thus, for the theory to be applicable, the diameter of the particles must be small compared with λ and large compared with $1/k$. As λ is only 170 times $1/k$ this makes the range for the diameter very small. A more satisfactory test of the theory could be made with longer wave-lengths and larger particles; for the thickness to which the currents descend varies as the square root of the wave-length, so that the ratio of the wave-length to the thickness of the current-film increases as the wave-length increases.