X. THE BAKERIAN LECTURE.—*Experimental Relations of Gold (and other Metals) to Light. By* MICHAEL FARADAY, *Esq., D.C.L., F.R.S., Fullerian Prof. Chem. Royal Institution, Foreign Associate of the Acad. Sciences, Paris, Ord. Boruss. pour le Mérite, Eq., Memb. Royal and Imp. Acadd. of Sciences, Petersburgh, Florence, Copenhagen, Berlin, Göttingen, Modena, Stockholm, Munich, Bruxelles, Vienna, Bologna, Commander of the Legion of Honour, &c. &c.*

THAT wonderful production of the human mind, the undulatory theory of light, with the phenomena for which it strives to account, seems to me, who am only an experimentalist, to stand midway between what we may conceive to be the coarser mechanical actions of matter, with their explanatory philosophy, and that other branch which includes, or should include, the physical idea of forces acting at a distance; and admitting for the time the existence of the ether, I have often struggled to perceive how far that medium might account for or mingle in with such actions, generally; and to what extent experimental trials might be devised which, with their results and consequences, might contradict, confirm, enlarge, or modify the idea we form of it, always with the hope that the corrected or instructed idea would approach more and more to the truth of nature, and in the fulness of time coincide with it.

The phenomena of light itself are, however, the best and closest tests at present of the undulatory theory; and if that theory is hereafter to extend to and include other actions, the most effectual means of enabling it to do so will be to render its application to its own special phenomena clear and sufficient. At present the most instructed persons are, I suppose, very far from perceiving the full and close coincidence between all the facts of light and the physical account of them which the theory supplies. If perfect, the theory would be able to give a reason for every physical affection of light; whilst it does not do so, the affections are in turn fitted to develope the theory, to extend and enlarge it if true, or if in error to correct it or replace it by a better. Hence my plea for the possible utility of experiments and considerations such as those I am about to advance.

Light has a relation to the matter which it meets with in its course, and is affected by it, being reflected, deflected, transmitted, refracted, absorbed, &c. by particles very minute in their dimensions. The theory supposes the light to consist of undulations, which, though they are in one sense continually progressive, are at the same time, as regards the particles of the ether, to and fro transversely. The number of progressive alternations or waves in an inch is considered as known, being from 37,600 to 59,880, and the number which passes to the eye in a second of time is known also, being from

458 to 727 billions; but the extent of the lateral excursion of the particles of the ether, either separately or conjointly, is not known, though both it and the velocity are probably very small compared to the extent of the wave and the velocity of its propagation. Colour is identified with the number of waves. Whether reflexion, refraction, &c. have any relation to the extent of the lateral vibration, or whether they are dependent in part upon some physical action of the medium unknown to and unsuspected by us, are points which I understand to be as yet undetermined.

Conceiving it very possible that some experimental evidence of value might result from the introduction into a ray of separate particles having great power of action on light, the particles being at the same time very small as compared to the wave-lengths, I sought amongst the metals for such. Gold seemed especially fitted for experiments of this nature, because of its comparative opacity amongst bodies, and yet possession of a real transparency; because of its development of colour both in the reflected and transmitted ray; because of the state of tenuity and division which it permitted with the preservation of its integrity as a metallic body; because of its supposed simplicity of character; and because known phenomena appeared to indicate that a mere variation in the size of its particles gave rise to a variety of resultant colours. Besides, the waves of light are so large compared to the dimensions of the particles of gold which in various conditions can be subjected to a ray, that it seemed probable the particles might come into effective relations to the much smaller vibrations of the ether particles; in which case, if reflexion, refraction, absorption, &c. depended upon such relations, there was reason to expect that these functions would change sensibly by the substitution of different-sized particles of this metal for each other. At one time I hoped that I had altered one coloured ray into another by means of gold, which would have been equivalent to a change in the number of undulations; and though I have not confirmed that result as yet, still those I have obtained seem to me to present a useful experimental entrance into certain physical investigations respecting the nature and action of a ray of light. I do not pretend that they are of great value in their present state, but they are very suggestive, and they may save much trouble to any experimentalists inclined to pursue and extend this line of investigation.

Gold-leaf—effect of heat, pressure, &c.

Beaten gold-leaf is known in films estimated at the $\frac{1}{282000}$th of an inch in thickness; they are translucent, transmitting green light, reflecting yellow, and absorbing a portion. These leaves consist of an alloy in the proportions of 12 silver and 6 copper to 462 of pure gold. 2000 leaves $3\frac{3}{8}$ths of an inch square are estimated to weigh 384 grains. Such gold-leaf is no doubt full of holes, but having, in conjunction with Mr. W. De la Rue, examined it in the microscope with very high powers (up to 700 linear), we are satisfied that it is truly transparent where the gold is continuous, and that the light transmitted is green. By the use of the balance Mr. De la Rue found that the leaf employed was on the average $\frac{1}{278000}$th of an inch thick. Employing polarized light

and an arrangement of sulphate of lime plates, it was found that other rays than the green could be transmitted by the gold-leaf. The yellow rays appeared to be those which were first stopped or thrown back. Latterly I have obtained some pure gold-leaf beaten by MARSHALL, of which 2000 leaves weighed 408 grains, or 0·2 of a grain per leaf: its reflected colour is orange-yellow, and its transmitted colour a warm green. Gold alloy containing 25 per cent. of silver produces pale gold-leaf, which transmits a blue purple light, and extinguishes much more than the ordinary gold-leaf.

So a leaf of beaten gold occupies in average thickness no more than from $\frac{1}{5}$th to $\frac{1}{8}$th part of a single wave of light. By chemical means, the film may be attenuated to such a degree as to transmit a ray so luminous as to approach to white, and that in parts which have every appearance of being continuous in the microscope, when viewed with a power of 700. For this purpose it may be laid upon a solution of chlorine, or, better still, of the cyanide of potassium *. If a clean plate of glass be breathed upon and then brought carefully upon a leaf of gold, the latter will adhere to it; if distilled water be immediately applied at the edge of the leaf, it will pass between the glass and gold, and the latter will be perfectly stretched; if the water be then drained out, the gold-leaf will be left well extended, smooth, and adhering to the glass. If, after the water is poured off, a weak solution of cyanide be introduced beneath the gold, the latter will gradually become thinner and thinner; but at any moment the process may be stopped, the cyanide washed away by water, and the attenuated gold film left on the glass. If towards the end a washing be made with alcohol, and then with alcohol containing a little varnish, the gold film will be left cemented to the glass †.

In this manner the leaf may be obtained so thin, that I think 50 or even 100 might be included in a single progressive undulation of light. But the character of the effect on light is not changed, the light transmitted is green, as before; and though that green tint is due to a condition of the gold induced by pressure, it as yet remains unchanged through all these varieties of thickness and of proportion to the progressive or the lateral undulation.

Gold-leaf, either fine or common, examined in the microscope, appears as a most irregular thing. It is everywhere closely mottled or striated, according as a part at the middle or the edge of a leaf is selected, minute portions which are close to other parts being four or five times as thick as the latter, if the proportion of light which passes through may be accepted as an indication. Yet this irregular plate does not cause any

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* The chlorine leaves a film of chloride of silver behind, the cyanide leaves only metal.

† Air-voltaic circles are formed in these cases, and the gold is dissolved almost exclusively under their influence. When one piece of gold-leaf was placed on the surface of a solution of cyanide of potassium, and another, moistened on both sides, was placed under the surface, both dissolved; but twelve minutes sufficed for the solution of the first, whilst above twelve hours were required for the submerged piece. In weaker solutions, and with silver also, the same results were obtained; from sixty to a hundredfold as much time being required for the disappearance of the submerged metal as for that which, floating, was in contact both with the air and the solvent. An action of this kind has probably much to do with the *formation* of the films to be described hereafter.

sensible distortion of an object seen through it, that object being the line of light reflected from a fine wire in the focus of a moderate microscope. Nor perhaps was any distortion due to consecutive convexities and concavities to be expected; for when the thicker parts of the leaf were examined they seemed to be accumulated plications of the gold, the leaf appearing as a most irregular and crumpled object, with dark veins running across both the thicker and thinner parts, and from one to the other. Yet in the best microscope, and with the highest power, the leaf seemed to be continuous, the occurrence of the smallest sensible hole making that continuity at other parts apparent, and every part possessing its proper green colour. How such a film can act as a plate on polarized light in the manner it does, is one of the queries suggested by the phenomena which requires solution.

When gold-leaf is laid upon glass and its temperature raised considerably without disturbance, either by the blowpipe or an ordinary Argand gas-burner, it seems to disappear, i. e. the lustre passes away, the light transmitted is abundant and nearly white, and the place appears of a pale brown colour. One would think that much of the metal was dissipated, but all is there, and if the heat has been very high (which is not necessary for the best results), the microscope shows it in minute globular portions. A comparatively low heat, however, and one unable to cause separation of the particles, is known to alter the molecular condition of gold, and the gold-beater finds important advantage in the annealing effect of a temperature that does not hurt the skins or leaves between which he beats the metal.

It might be supposed that the annealed metal, in contracting from the constrained and attenuated state produced by beating, drew up, leaving spaces through which white light could pass, and becoming itself almost insensible through the smallness of its quantity; and if gold-leaf unattached to glass be heated carefully with oil in a tube, it does shrink up considerably even before it loses its green colour, which finally happens. But if the gold-leaf laid upon glass plates by water only be carefully dried, then introduced into a bath of oil and raised to a temperature as high as the oil can bear for five or six hours, and then suffered to cool, the plates, when taken out and washed, first in camphine and then in alcohol, present specimens of gold which has lost its green colour, transmits far more light than before and reflects less, whilst yet the film remains in form and other conditions apparently quite unchanged. Being now examined in the microscope, it presents exactly the forms and appearance of the original leaf, except in colour; the same irregularities appear, the same continuity, and if the destruction of the green colour has not been complete, it will be seen that it is the thicker folds and parts of the mottled mass that retains the original state longest.

This change does not depend upon the substance in contact with which the gold is heated [*]. If the leaf be laid upon mica, rock-crystal, silver or platinum, the same result

* The disappearance of gold-leaf as metal, when mingled with lime, alumina and other bodies, and then heated, has been already observed; and referred to oxidation (J. A. BUCHNER). See GMELIN's 'Chemistry,' vi. p. 206, "Purple oxide of gold."

occurs; the surrounding medium also may change, and be air, oil or carbonic acid, without causing alteration. Nor has the gold disappeared; a piece of leaf, altered in one part and not in another, was divided into four equal parts, and the gold on each converted by chlorine gas into crystallized chloride of gold: the same amount was found in each division.

When the gold-leaf is laid by water on plates of rock-crystal, and then gradually heated in a muffle not higher than is necessary, an excellent result is obtained. The gold is then of a uniform pale brown colour by common observation, but when examined by a lens and an oblique light, all the mottle of the original leaf appears. It adheres but very slightly to the rock-crystal, and yet can bear the application of the pressure now to be described.

When gold rendered colourless by annealing is subjected to pressure, it again becomes of a green colour. I find a convex surface of agate or rock-crystal having a radius of from a quarter to half an inch very good for this purpose, the metal having very little tendency to adhere to this substance. The greening is necessarily very imperfect, and if examined by a lens it will be evident that the thinner parts of the film are rarely reached by the pressure, it being taken off by the thicker corrugations; but when reached they acquire a good green colour, and the effect is abundantly shown in the thicker parts. At the same time that the green colour is thus reproduced, the quantity of light transmitted is diminished and the quantity of light reflected is increased. When the gold-leaf has been heated on glass in a muffle, it generally adheres so well as to bear streaking with the convex rock-crystal, and then the production of the reflecting surface and the green transmission is very striking. In other forms of gold film, to be described hereafter, the greening effect of pressure (which is general to gold) is still more strikingly manifested, and can be produced with the touch of a card or a finger. In these cases, and even with gold-leaf, the green colour reproduced can be again taken away by heat, to appear again by renewed pressure.

As to the essential cause of this change of colour, more investigation is required to decide what that may be. As already mentioned, it might be thought that the gold-leaf had run up into separate particles. If it were so, the change of colour by division is not the less remarkable, and the case would fall into those brought together under the head of gold fluids. On the whole, I incline to this opinion; but the appearance in the microscope, the occurrence of thin films of gold acting altogether like plates and yet not transmitting a green ray until they are pressed, and their action on a polarized ray of light, throw doubts in the way of such a conclusion.

It may be thought that the beating has conferred a uniform strained condition upon the gold, a difference in quality in one direction which annealing takes away; but when the gold is examined by polarized light, there is no evidence as yet of such a condition, for the green and the colourless gold present like results; and there is a little difficulty in admitting that such an irregular corrugated film as gold-leaf appears to be can possess any general compression in one direction only, especially when it is considered

that it is beaten amongst tissues softer than itself, and made up with it into considerable masses. The greening effect of pressure occurs with the deposited particles of electric discharges, and here it appears either amongst the larger particles near the line of the discharge, or amongst the far finer ones at a considerable distance. Such results do not suggest a dependence upon either the size of the particles or their quantity, but rather upon the relative dimensions of the particles in the direction of the ray and transverse to that direction. One may imagine that spherical or other particles, which, being disposed in a plane, transmit ruby rays or violet rays, acquire the power, when they are flattened, of transmitting green rays, and such a thought sends the mind at once from the wave of light to the direction and extent of the vibrations of the ether. For it does not seem likely that pressure can produce its peculiar result by affecting the relation of the dimension of the particle to the length-dimension of a progressive undulation of light, the latter being so very much greater than the former; but the relation to the dimension of the direct or lateral vibration of the particles of the ether may be greatly affected, that being probably very small and much nearer to, if not even less than, the size of the particles of gold.

Silver-leaf, as usually obtained by beating, is so opake, as perfectly to exclude the light of the sun. When this is laid by water on plates of rock-crystal and heated in a muffle, it begins to change, at a temperature lower than that required for gold, and becomes very translucent, losing at the same time its reflective power: it looks very like the film of chloride produced when a leaf of silver is placed in chlorine gas. When examined by a lens or an ordinary microscope, the leaf seems to be as continuous as in its original state; the finest hole, or the finest line drawn by a needle-point, appears only to prove the continuity of the metallic film up to the very edges of these real apertures. When pressure is applied to this translucent film, the compressed metal becomes either opake or of a very dark purple colour, and resumes its high reflective power. If a higher heat than that necessary for this first change be applied, then the leaf, viewed in the microscope, assumes a mottled appearance, as if a retraction into separate parts had occurred. At a still higher temperature this effect is increased; but the heat, whether applied in the muffle or by a blowpipe, which is necessary to fuse the metal and make it run together in globules, is very much higher than that which causes the first change of the silver: the latter is, in fact, below such a red heat as is just visible in the dark. Whatever the degree of heat applied, the metal remains as metallic silver during the whole time. When many silver leaves were laid loosely one upon another, rolled up into a loose coil, introduced into a glass tube, and the whole placed in a muffle and heated carefully for three or four hours to so low a degree that the glass tube had not been softened or deformed, it was found that the silver-leaf had sunk together a little and shaped itself in some degree upon the glass, touching by points here and there, but not adhering to it. But it was changed, so that the light of a candle could be seen through forty thicknesses: it had not run together, though it adhered where one part touched another. It did not look like metal, unless one thought of it as divided dead metal, and it even

appeared too unsubstantial and translucent for that; but when pressed together it clung and adhered like clean silver, and resumed all its metallic characters.

When the silver is much heated, there is no doubt that the leaf runs up into particles more or less separate. But the question still remains as to the first effect of heat, whether it merely causes a retraction of the particles, or really changes the optical and physical nature of the metal from the beaten or pressed state to another from which pressure can return it back again to its more splendid condition. It seems just possible that the leaf may consist of an infinity of parts resulting from replications, foldings and scales, all laid parallel by the beating which has produced them, and that the first action of heat is to cause these to open out from each other; but that supposition leaves many of the facts either imperfectly explained or untouched. The Arts do not seem to furnish any process which can instruct us as to this condition, for all the operations of polishing, burnishing, &c. applied to gold, silver and other metals, are just as much fitted to produce the required state under one view as under the other.

To return to gold: it is clear that that metal, reduced to small dimensions by mere mechanical means, can appear of two colours by transmitted light, whatever the cause of the difference may be. The occurrence of these two states may prepare one's mind for the other differences with respect to colour, and the action of the metallic particles on light, which have yet to be described.

Many leaves of gold, when examined by a lens and transmitted light, present the appearance of red parts; these parts are small, and often in curved lines, as if a fine hair had been there during the beating. At first I thought the gold was absolutely red in these parts, but am inclined to believe that in the greatest number of cases the tint is subjective, being the result of the contrast between the white light transmitted through bruised parts, and the green light of the neighbouring continuous parts. Nevertheless, some of these places, when seen in the microscope, appeared to have a red colour of their own, that is, to transmit a true red light. As I believe that gold in a certain state of division can transmit a ruby light, I am not prepared to say that gold-leaf may not, in some cases, where the effect of pressure in a particular direction has been removed, do the same.

Many of the prepared films of gold were so thin as to have their reflective power considerably reduced, and that in parts which, under the microscope and in other ways, appeared to be quite continuous: this agrees with the transmission of all the rays already mentioned, but it seems to imply that a certain thickness is necessary for full reflexion; therefore, that more than one particle in depth is concerned in the act, and that the division of gold into separate particles by processes to be described, may bring them within or under the degree necessary for ordinary reflexion.

As particles of pure gold will be found hereafter to adhere by contact, so the process of beating may be considered as one which tends to weld gold together in all directions, and especially in that transverse to the blow,—a point favourable to continuity in that direction, both as it tends to preserve and even reproduce it.

If a polarized ray be received on an analyser so that no light passes, and a plate of annealed glass, either thick or thin, be interposed vertically across the ray, no difference is observed on looking through the analyser, the image of the source of light does not appear; but if the plate be inclined until it makes an angle of from 30° to 45°, or thereabouts, with the ray, the light appears, provided the inclination of the glass is not in the plane of polarization or at right angles to it, the effect being a maximum if the inclination be in a plane making an angle of 45° with that of polarization. This effect, which is common to all uncrystallized transparent bodies, is also produced by leaf-gold, and is one of the best proofs of the true transparency of this metal according to the ordinary meaning of the term. In like manner, if a leaf of gold be held obliquely across an ordinary ray of light, it partly polarizes it, as Mr. DE LA RUE first pointed out to me. Here again the condition of true transparency is established, for it acts like a plate of glass or water or air. But the relations of gold and the metals in different conditions to polarized light shall be given altogether at the close of this paper.

Deflagrations of Gold (and other metals)—heat—pressure, &c.

Gold wire deflagrated by explosions of a Leyden battery produces a divided condition, very different to that presented by gold leaves. Here the metal is separated into particles, and no pressure in any direction, either regular or irregular, has been exerted upon them in the act of division. When the deflagrations have been made near surfaces of glass, rock-crystal, topaz, fluor-spar, card-board, &c., the particles as they are caught are kept separate from each other and in place, and generally those which remain in the line of the discharge have been heated by the passage of the electricity. The deposits consist of particles of various sizes, those at the outer parts of the result being too small to be recognized by the highest powers of the microscope. Beside making these deflagrations over different substances, as described above, I made them in different atmospheres, namely, in oxygen and hydrogen, to compare with air; but the general effects, the colours produced, and the order of the colours, were precisely the same in all the cases. These deposits were insoluble in nitric acid and in hydrochloric acid, but in the mixed acids or in chlorine solution were soluble, exactly in the manner of gold. There is no reason to doubt that they consisted of metallic gold in a state of extreme division.

Now as to the effects on light, i. e. as to the coloured rays reflected or transmitted by these deposited particles, and first, of those in the line of the discharge where the wire had been. Here the mica was found abraded much, the glass less, and the rock-crystal and topaz least. Where abraded, the gold adhered; in all the other parts it could be removed with the slightest touch. The gold deposited in this central place was metallic and golden by reflected light, and of a fine ruby colour by transmitted light. On each side of this line the deposit had a dark colour, but when particularly examined gave a strong golden metallic reflexion, and by transmission a fine violet colour, partaking of green and ruby in different parts, and sometimes passing altogether into green. Beyond this, on each side, where the tints became paler and where the particles appeared to be

finer, the transmitted tint became ruby or violet-ruby, and this tint was especially seen when the deposit was caught on a card. As to the reflected light, even at these faintest parts it is golden and metallic. This is easily observed by wiping off a sharp line across the deposit on glass in the very faintest part, and then causing the sun's rays collected in the focus of a small lens to travel to and fro across that edge; the presence of the metallic gold on the unwiped part is at once evident by the high illumination produced there. It is evident that all the colours described are produced by one and the same substance, namely gold, the only apparent difference being the state of division and different degrees of the application of heat. The thickest parts of these deposits are so discontinuous, that they cannot conduct the electricity of a battery of two or three pairs of plates, *i. e.* of a battery unable to produce a spark among the particles.

When any of these deposits of divided gold are heated to dull redness, a remarkable change occurs. The portions which before were violet, blue, or green by transmitted light, now change to a ruby, still preserving their metallic reflecting power, and this ruby is in character quite like that which is presented in the arts by glass tinged by gold. This change is often far better shown in the more distant and thinner parts of the deposit, than in those nearest to the line of discharge, for near the latter place, where the deposit is most abundant, the metal appears to run up into globules, as with gold-leaf, and so disappears as a film. I believe that the ruby character of the deposit *in* the line of discharge, is caused by the same action of heat produced at the moment by the electricity passing there. In the distant parts, the deposit, rubified by after heat, is not imbedded or fused into the glass, rock-crystal, topaz, &c., but is easily removed by a touch of the finger, though in parts of the glass plate which are made very hot, it will adhere.

If the agate pressure before spoken of, in respect of gold-leaf, be applied to ruby parts not too dense, places will easily be found where this pressure increases the reflect-ive power considerably, and where at the same time it converts the transmitted ray from ruby to green; making the gold, as I believe, then accord in condition with beaten gold-leaf. On the other hand, if parts of the *unheated* electric deposit, where they are purple-grey, and so thin as to be scarcely visible without care, be in like manner pressed, they will acquire the reflective power, and then transmit the green ray; and I think I am justified by my experiments in stating, that fine gold particles, so loosely deposited that they will wipe off by a light touch of the finger, and possessing one conjoint structure, can in one state transmit light of a *blue-grey* colour, or can by heat be made to transmit light of a *ruby* colour, or can by pressure from either of the former states be made to transmit light of a *green* colour; all these changes being due to modifications of the gold, as gold, and independent of the presence of the bodies upon which for the time the gold is supported; for I ought to have said, if I have not said so, that these changes happen with all the deposits upon glass, mica, rock-crystal, and topaz, and whatever the atmosphere in which they were formed.

When gold is deflagrated by the voltaic battery near glass (I have employed sovereigns

laid on glass for the terminals), a deposit of metallic gold in fine particles is produced. The densest parts have a dark slate-violet colour passing into violet and ruby-violet in the outer thinner portions; a ruby tint is presented occasionally where the heat of the discharge has acted on the deposit. The deposited gold was easily removed by wiping, except actually at the spot where the discharge had passed. When these deposits were heated to dull redness they changed and acquired a ruby tint, which was very fine at the outer and thinner parts. The portions nearer the place of discharge presented ruby-violet and then violet tints, suggesting that accumulation of that which presented a fine ruby tint would, by stopping more and more light, transmit a ruby-violet or violet ray only. Pressure with the agate surface had a like effect as before, both with the heated and the unheated portions, *i. e.* with the violet and the ruby particles; but the effect was not altogether so good, and the tint of the transmitted ray was rather a green violet than a pure green. Still the difference produced by the pressure was very remarkable. The unheated particles at the surface, away from the glass, presented by reflexion almost a black; being heated, they became much more golden and metallic in appearance.

I prepared an apparatus by which many of the common metals could be deflagrated in hydrogen by the Leyden battery, and being caught upon glass plates could be examined as to reflexion, transmission, colour, &c. whilst in the hydrogen and in the metallic, yet divided state. The following are briefly the results; which should be considered in connexion with those obtained by employing polarized light. *Copper*: a fine deposit presenting by reflexion a purplish red metallic lustre, and by transmission a green colour, dark in the thicker parts, but always green; agate pressure increased the reflexion where it was not bright, and a little diminished the transmission, rendering the green deeper, but not changing its character as in the case of gold. *Tin* gave a beautiful bright white reflexion, and by transmission various shades of light and dark brown; agate pressure diminished the transmission and increased the reflexion in places before dull or dead; the effect appeared to be due simply to the lateral expansion of the separate particles filling up the space. *Iron* presented a fine steel grey, or slate metallic reflexion and a dark brown transmission; agate pressure gave the same effect as with tin, but no change of colour. *Lead*: a bright white reflexion, the transmission a dark smoky brown; agate pressure appeared to change this brown towards blue. *Zinc*: the reflexion bright white and metallic; the transmission a dark smoky colour with portions of blue-grey, brown-grey and pale brown; agate pressure tended to change the blue-grey to brown. *Palladium*: the reflexion fine metallic and dark grey; the transmitted light, where most abundant, sepia-brown; agate pressure converted the tint in the thinner places from brown towards blue-grey. *Platinum*: the reflexion white, bright and metallic; the transmission brown or warm grey with no other colours; agate pressure increased the reflexion and diminished the transmission as with tin. *Aluminium*: the reflexion metallic and white, very beautiful; the transmitted light was dark brown, bluish brown, and occasionally in the thinner parts orange; agate pressure caused but little change.

Films of Gold (and other metals) by Phosphorus, Hydrogen, &c.—effect of heat—pressure.

The reduction of gold from its solution by phosphorus is well known. If fifteen or twenty drops of a strong solution of gold, equal to about 1½ grain of metal, be added to two or three pints of water, contained in a large capsule or dish, if four or five minute particles of phosphorus be scattered over the surface, and the whole be covered and left in quietness for twenty-four or thirty-six hours, then the surface will be found covered with a pellicle of gold, thicker at the parts near the pieces of phosphorus, and possessing there the full metallic golden reflective power of the metal; but passing by gradation into parts, further from the phosphorus, where the film will be scarcely sensible except upon close inspection. If plates of glass be introduced into the fluid under the pellicle, and raised gradually, the pellicle will be raised on them; it may then be deposited on the surface of pure distilled water to wash it; may be raised again on the glass; the water allowed to drain away, and the whole suffered to dry. In this way the pellicle remains attached to the glass, and is in a very convenient condition for preservation and examination.

If phosphorus be dissolved in two or three times its bulk of sulphide of carbon, and a few drops of the fluid be placed on the bottom of a dry basin, vapour of the phosphorus will soon rise up and bring the atmosphere in the basin to a reducing state. If a plate of glass large enough to cover the basin have six or eight drops of a strong neutral solution of chloride of gold placed on it, and this be spread about by a glass stirrer, so as to form a flowing layer on the surface, the glass may then be inverted and placed over the dish. So arranged the gold solution will keep its place, but will have a film of metal reduced on its under surface. The plate being taken off after twenty, thirty, or forty minutes, and turned with the gold solution upwards, may then gradually be depressed in an inclined position into a large basin of pure water, one edge entering first, and the gold film will be left floating. After sufficient washing it may be taken up in portions on smaller plates of glass, dried, and kept for use. Mr. WARREN DE LA RUE taught me how to make and deal with these films: they may by attention be obtained very uniform, of very different degrees of thickness, from almost perfect transparency to complete opacity, and by successive application of the same collecting glass plate may be superposed with great facility.

These films may be examined either on the water or on the glass. When thick, their reflective power is as a gold plate, full and metallic; as they are thinner they lose reflective power, and they may be obtained so thin as to present no metallic appearance, all the coloured rays of light then passing freely through them. As to the transmitted light, the thinner films generally present one kind of colour; it appears as a feeble grey-violet, which increases in character as the film becomes thicker and sometimes approaches a violet; a greenish violet also appears; and the likeness of the grey-violet tint of these films to the stains produced by a solution of gold on the skin or other organic reducing substance, or the stain produced on common pottery, cannot be mistaken. Superposition

of several grey-violet films does not produce a green tint, but only a diminution of light without change of colour. In those specimens made by particles of phosphorus floating on the solution of gold, very fine green tints occur at the thicker and golden parts of the film. The colour of the gold here may depend in some degree on the *manner* in which these films are formed: the thicker parts are not produced altogether by the successive addition of reduced gold from the portion of fluid immediately beneath them. When a particle of phosphorus is placed on pure water, it immediately throws out a film which appears to cover the whole of the surface; in a little while the film thickens around the particle and is easily distinguished by its high reflective power. It is this film which reduces the gold in solution, being itself consumed in the action; the result is a continued extension from the phosphorus outwards, which, after it has covered the solution with a thin film of gold, continues to cause a compression of the parts around the phosphorus and an accumulation there, rendering the gold at a distance of half an inch from the phosphorus so thick, that it is brilliant by reflexion and nearly opake by transmission, whilst near to the phosphorus the forming film is so thin as to be observed only on careful examination, and is still travelling outwards and compressing the surrounding parts more and more. The phosphorus is very slowly consumed; a particle not weighing $\frac{1}{100}$th of a grain will remain for four or five days on the surface of water before it disappears.

Though the particles of these films adhere together strongly, as may be seen by their stiffness on water, still the films cannot be considered as continuous. If they were, those made by vapour of phosphorus could not thicken during their formation, neither could they dry on glass in the short time found sufficient for that purpose. Experimentally also, I find that vapours and gases can pass through them. Very thin films without folds did not sensibly conduct the electricity of a single pair of GROVE's plates; thicker films did conduct; yet with these proofs that these films could not be considered as continuous, they acted as thin plates upon light, producing the concentric rings of colours round the phosphorus at their first formation, though their thickness then could scarcely be the $\frac{1}{100}$th, perhaps not the $\frac{1}{500}$th of a wave undulation of light. Platinum, palladium, and rhodium produced films, showing these concentric rings very well.

Many of these films of gold, both thick and thin, which being of a grey colour originally, were laid on a solution of cyanide of potassium to dissolve slowly, changed colour as they dissolved and became green; if change occurred, it was always towards green. On the other hand, when laid on a solution of chlorine, the change during solution was towards an amethyst or ruby tint. The films were not acted upon by pure nitric, or hydrochloric, or sulphuric acids, or solutions of potassa or brine. They dissolved in damp chlorine gas, not changing in colour during the solution. I believe them to consist of pure gold.

When these gold films were heated to dull redness they changed. The reflexion, though not much altered, was a little more metallic and golden than before; more light was transmitted after the heating and the colour had altered from greenish to violet, or

from grey-green to ruby or amethyst; and now two or three films superposed often gave a very ruby colour. This action is like that of heat on the particles separated by electric explosions. If not overheated, the particles were not fused to the glass, but could be easily wiped off. Whenever these heated particles were pressed by the convex agate, they changed in character and transmitted green light. Heat took away this character of the gold, the heat of boiling oil, if continued, being sufficient; but on applying pressure at the same spot, the power of transmitting green light was restored to the particles. In many cases where the gold adhered sufficiently to the glass to bear a light drawing touch from the finger or a card, such touch altered the light transmitted from amethystine to green; so small is the pressure required when the particles are most favourably disposed.

Heating injured the conducting power for electricity of these films, no doubt by retraction of the particles, though there was no such evident appearance in these cases, as in the unattached gold-leaf of the particles running up into globules.

A given film, examined very carefully in the microscope by transmitted lamp-light, with an aperture of 90° and power of 700 linear, presented the following appearances. The unheated part was of a grey colour, and by careful observation was seen to be slightly granular. By very close observation this grey part was often resolvable into a mixture of green and amethystine striæ, it being the compound effect of these which in general produce the grey sensation in the eye. When a part of such a film was heated, the transmitted colour was changed from grey to purple, as before described, and the part thus heated was evidently more granular than before. This difference was confirmed in other cases. That the heated part should thus run up, seems to show that many of the particles must have been touching though they did not form a continuous film; and on the other hand, the difference between the effect here and with unattached gold-leaf, shows that the degree of continuity as a film must be very small. When these heated films were greened by agate pressure, or the drawing pressure of a card, the green parts remained granulated, apparently in the same degree as when purple. The green was not subjective or an effect of interference, but a positive colour belonging to the gold in that condition. Every touch of the agate was beautifully distinct as a written mark. The parts thus greened and the purple parts appeared to transmit about the same amount of light. Though the film appeared granulated, no impression was made upon the mind that the individual particles of which the film consisted were in any degree rendered sensible to the eye.

The unheated gold films when pressed by agate often indicated an improved reflective power, and the light transmitted was also modified; generally it was less, and occasionally tended towards a green tint; but the effect of pressure was by no means so evident as in particles which had been heated.

Films of some other metals were reduced by phosphorus in like manner, the results in all these cases being of course much affected by the strength of the solution and the time of action; they are briefly as follows. *Palladium*: a weak solution of the chloride

gave fine films, apparently very continuous and stiff; the reflexion was strong and metallic, of a dark grey colour; the transmission presented every shade of Indian ink. *Platinum* chloride gave traces of a film excessively thin, and very slow in formation. *Rhodium* chloride in three or four hours gave a beautiful film of metal in concentric rings, varying in reflecting and transmitting power over light and also in colour; those which reflected well, transmitted little light; and those which transmitted, reflected little light; one might have thought there was no metal in some of the rings between other rings that reflected brilliantly, but the metal was there of transmitting thickness; the transmitted colour of rhodium varied from brown to blue. *Silver*: a solution of the nitrate gave films showing the concentric rings; the light transmitted by the thinner parts was of a warm brown, or sepia tint; the film becomes very loose and mossy in the thicker parts and is wanting in adherence; pressure brings out the full metallic lustre in every part, and in the thin places converts the colour from brown to blue, being in that respect like the result with pale gold-leaf, in which the silver present dominates over the colour of the gold. I do not think there is phosphorus combined with this silver; I did not find any, and considering the surface action on metals which float as films between air and water, it seems improbable that it should be there.

Hydrogen was employed to reduce some of the metals, their solutions being placed in an atmosphere of the gas. The action differed considerably from that of phosphorus, as might be expected. *Gold* produced a very thin film, too thin to be washed; it had a faint metallic reflexion, and transmitted a slate-blue colour like the former films. *Platinum* chloride was acted on at once; minute spots appeared here and there on the surface; these enlarged, became rough and corrugated at the middle, though brilliant at the edges, and at last formed an irregular coat over the fluid; at the part where the film was flat and brilliant, it resembled that produced by the electric explosion, and by transmission gave a dark grey colour. *Iridium* required much time, and formed a crust from centres like the platinum. *Palladium* gave an instant action, but most of the reduced metal sunk in a finely divided state; a film may be obtained, but it has very little adhesion. *Rhodium* is reduced, but the film consists of floating particles, having so little adhesion that it cannot be gathered up. *Silver* is reduced, but the film is very thin and has no tenacity.

A copper film of very beautiful character may be obtained as follows in all varieties of thickness. Let a little oxide of copper be dissolved in olive-oil to form a bath, and having immersed some plates of glass, for which purpose microscope plates 3×1 inches are very convenient, let the whole be heated up to the decomposing temperature of the oil; being left to cool, and the plates then drained and washed successively in camphine and alcohol, they will be found covered with a film of copper, having the proper metallic lustre and colour by reflexion; and by transmission, presenting a green colour, which, though generally inclining to olive, is in the thinner films often more beautiful than the green presented by pressed gold.

Diffused particles of gold—production—proportionate size—colour—aggregation and other changes.

Agents competent to reduce gold from its solution are very numerous, and may be applied in many different ways, leaving it either in films, or in an excessively subdivided condition. Phosphorus is a very favourable agent when the latter object is in view. If a piece of this substance be placed under the surface of a moderately strong solution of chloride of gold, the reduced metal adheres to the phosphorus as a granular crystalline crust. If the solution be weak and the phosphorus clean, part of the gold is reduced in exceedingly fine particles, which becoming diffused, produce a beautiful ruby fluid.

This ruby fluid is well obtained by pouring a weak solution of gold over the phosphorus which has been employed to produce films, and allowing it to stand for twenty-four or forty-eight hours; but in that case all floating particles of phosphorus should be removed. If a stronger solution of gold be employed, the ruby fluid is formed, but it soon becomes turbid and tends to produce a deposit. When the gold is in such proportion that it remains in considerable excess, still the ruby formation is not prevented, and being formed it mingles unchanged with the excess of gold in solution. If an exceedingly weak solution of gold be employed, the production of ruby appears to be imperfect and retarded. The nearer the solution is to neutrality at the commencement the better; when a little hydrochloric acid was added the effect was not so good, and the colour of the fluid was more violet than ruby.

If a pint or two of the weak solution of gold before described be put into a *very clean* glass bottle, a drop of the solution of phosphorus in sulphide of carbon added, and the whole well shaken together, it immediately changes in appearance, becomes red, and being left for six or twelve hours, forms the ruby fluid required; too much sulphide and phosphorus should not be added, for the reduced gold then tends to clot about the portions which sink to the bottom.

Though the sulphide of carbon is present in such processes and very useful in giving division to the phosphorus, still it is not essential. A piece of clean phosphorus in a bottle of the gold solution gradually produces the ruby fluid at the bottom, but the action is very slow. If the phosphorus be attached to the side of the bottle, but always beneath the surface of the solution, the streams of ruby fluid may be seen moving both upwards and downwards against the side of the glass, and forming films in the vicinity of the phosphorus perfect in their golden reflexion, and yet transmitting light of ruby, violet, and other tints, thus giving, first a proof that the particles are gold, and then connecting the present condition of the gold with that of the films already described. On the other hand, the phosphorus may be excluded and the sulphide of carbon employed alone; for when it and the solution of gold are shaken together, the gold is reduced and the ruby fluid formed; but it soon changes to purple or violet.

A quick and ready mode of producing the ruby fluid, is to put a quart of the weak solution of gold (containing about 0·6 of a grain of metal) into a clean bottle, to add a little solution of phosphorus in ether, and then to shake it well for a few moments: a

beautiful ruby or amethystine fluid is immediately produced, which will increase in depth of tint by a little time. Generally, however, the preparations made with phosphorus dissolved in sulphide of carbon, are more ruby than those where ether is the phosphorous solvent. The process of reduction appears to consist in a transfer of the chlorine from the gold to the phosphorus, and the formation of phosphoric or phosphorous acids and hydrochloric acid, by the further action of the water.

The fluids produced may easily be tested for any gold yet remaining unreduced, by trial of a portion with solution of protochloride of tin. If any be found, it is easily reduced by the addition of a little more of the phosphorus in solution. After all the gold is separated as solid particles, the fluid may be considered in its perfected state. Occasionally it may smell of phosphorus in excess, even after it has been poured off from the deposited particles of it and the sulphide. In that case it is easy to deprive it of this excess by agitation in a bottle with air. When kept in closed vessels mouldiness often occurs. If this be in groups it is collected with facility at the end of a splinter of wood and removed, or the whole fluid may be poured through a wet plug of cotton in the neck of a funnel, the reduced gold passing freely. All the vessels used in these operations must be very clean; though of glass they should not be supposed in proper condition after wiping, but should be soaked in water, and after that rinsed with distilled water. A glass supposed to be clean, and even a new bottle, is quite able to change the character of a given gold fluid.

Fluids thus prepared may differ much in appearance. Those from the basins, or from the stronger solutions of gold, are often evidently turbid, looking brown or violet in different lights. Those prepared with weaker solutions and in bottles, are frequently more amethystine or ruby in colour and apparently clear. The latter, when in their finest state, often remain unchanged for many months, and have all the appearance of solutions. But they never are such, containing in fact no dissolved, but only diffused gold. The particles are easily rendered evident, by gathering the rays of the sun (or a lamp) into a cone by a lens, and sending the part of the cone near the focus into the fluid; the cone becomes visible, and though the illuminated particles cannot be distinguished because of their minuteness, yet the light they reflect is golden in character, and seen to be abundant in proportion to the quantity of solid gold present. Portions of fluid so dilute as to show no trace of gold, by colour or appearance, can have the presence of the diffused solid particles rendered evident by the sun in this way. When the preparation is deep in tint, then common observation by reflected light shows the suspended particles, for they produce a turbidness and degree of opacity which is sufficiently evident. Such a preparation contained in a pint bottle will seem of a dull pale-brown colour, and nearly opake by reflexion, and yet by transmission appear to be a fine ruby, either clear or only slightly opalescent.

That the ruby and amethystine fluids hold the particles in suspension only, is also shown by the deposit which occurs when they are left at rest. If the gold be comparatively abundant, a part will soon settle, *i. e.* in twenty-four or forty-eight hours; but if the pre-

paration be left for six or eight months, a part will still remain suspended. Even in these portions, however, the diffused state of the gold is evident; for where, as in some cases, the top to the depth of half an inch or more has become clear, it is seen that the ruby portion below is as a cloud sinking from it; and in the part which has apparently been cleared from colour by the settling of the particles, the lens and cone of light still shows the few, or rather the fine diffused particles yet in suspension, though the protochloride of tin can show no gold in solution. The mould or mucus before spoken of, often collects the larger, heavier particles, and becomes of a dark blue colour; it may then be taken out by a splinter of wood, and being shaken in water, disengages the particles, which issue from it in clouds like the sporules from a ripe puff-ball.

A gradual change goes on amongst the particles diffused through these fluids, especially in the cases where the gold is comparatively abundant. It appears to consist of an aggregation. Fluids, at first clear or almost clear to ordinary observation, become turbid; being left to stand for a few days, a deposit falls. If the supernatant fluid be separated and left to stand, another deposit may be obtained. This process may be repeated, and whilst the deposition goes on, the particles in the fluid still seem to aggregate; it is only when the fluid is deprived of much gold that the process appears to stop. Even after the fluid has attained a fine marked ruby tint, if allowed to stand for months in a place of equable temperature, the colouring particles will appear in floating clouds, and probably the aggregation is then still going on. That the particles of gold when they touch each other do in many cases adhere together with facility, is shown in many experiments. In order to test this matter mechanically, I gave much agitation to a dense ruby fluid, but did not find it cause any sensible change in the character. When gold particles of a much larger size were agitated in water, they did cohere together, and the fluid, which required a certain time for settling at the beginning of the experiment, settled in a much shorter time at the termination.

If these fluids be examined generally their appearances differ, not merely under different circumstances, but also under the same circumstances, though they always consist of a colourless liquid and diffused particles of gold. A certain fluid in a bottle or glass, looked at from the front, i. e. the illuminated side by general daylight, may appear hazy and amethystine, whilst in bright sunlight it will appear light brown and almost opake. From behind, the same fluid may appear of a pure blue in both lights, whilst from the side it may appear amethystine or ruby. These differences result from the mixture of reflected and transmitted lights, both derived from the particles, the former appearing in greatest abundance from the front or side, and the latter from behind. The former is seen by common observation in a purer state if a black background be placed behind the fluid; when a white background is there, much of the transmitted light from that source comes to the eye, and the appearance is greatly altered. A mode of observing the former by a strong ray of light and a lens has been already described; but even in that case some effects of transmitted light are observed if the focus is thrown deep into the fluid; and it is only the particles near the surface, whether illuminated by the base

or the apex of the cone, which give the nearly pure effect of reflexion. In order to observe the transmitted ray in an unmingled state, a glass tube closed at one end was surrounded with a tube of black paper longer than itself, and with the black surface inwards. When a fluid (or the particles in it) was to be examined, it was put into this tube, and a surface of white paper illuminated by daylight or the sun, regarded through it, other light being excluded from the eye; or the tube was sometimes interposed between the eye and the sky, and sometimes the rays of the sun itself were reflected up to the eye through it. In speaking hereafter of the tints of the light transmitted by the particles (which will of course vary with the proportion of different rays in the original beam of light), a pure white original light is to be understood, but occasionally differently-tinted papers were employed with this tube as sources of different coloured lights.

The very oblique angle at which reflected light comes to the eye from the diffused particles, is well seen when the lens cone, or a direct ray of the sun, is passed into the fluid and observed from different positions; it is only when the eye is behind and nearly in the line of the ray, that the unmixed transmitted ray is observed. In the dark tube I think that no reflected light arrives at the eye: for if half an inch in depth of water be introduced, white light passes; if a drop of the washed deposit, to be hereafter described, be introduced, the light transmitted is either blue or ruby, or of other intermediate tint, according to the character of the deposit; but if water be then added until the column is six inches or more in length, the quantity of light transmitted does not sensibly alter, nor its tint; a fact which I think excludes the idea of any light being reflected from particle to particle, and finally to the eye.

If a given ruby-tinted fluid, containing no gold in solution, be allowed to stand for a few days, a deposit will fall from which the fluid may be removed by a siphon; being now allowed to stand for a week, a second deposit will be produced; if the fluid be again removed and allowed to stand for some months, another deposit will be obtained, and the fluid will probably be of a bright ruby; if it be now allowed to stand for several months, it will still yield a deposit, looking however more like a ruby fluid than a collection of fine particles at the bottom of the fluid, whilst traces of yet finer particles of gold in suspension may be obtained by the lens. All these deposits may be washed with water and will settle again; the coarser are not much affected, but the finer are, and tend to aggregate; nevertheless specimens often occur, especially after boiling, which tend to preserve their fine character after washing, if the water be very clean and pure.

The colour of these particles whilst under, or diffused through water, is by common reflected light brown, paler and richer, sometimes tending to yellow, and sometimes to red. The same difference is shown when illuminated by sunlight. Everything tends to show that the light reflected is very bright considering the size of the particles, and therefore of the reflecting surfaces; yet comparing by the cone of light a ruby fluid when first prepared and before it has become very sensibly turbid, with the same fluid after the evident turbidity is produced, in both of which cases I believe the gold to

be in solid metallic particles, though of different sizes, it would seem that more light is transmitted and absorbed and less reflected by the finer particles than by the coarser set, the same quantity of gold being in the same space. I believe that there may be particles so fine as to reflect very little light indeed, that function being almost gone. Occasionally some of the fluids containing the very finest particles in suspension, when illuminated by the sun's rays and a lens, appeared to give a fine green reflexion, but whether this is a true colour as compared to white light, or only the effect of contrast with the bright ruby in the other parts of the fluid, I am not prepared to say.

When the deposits were examined in the dark tube by transmitted light, being first diffused in more or less water to give them the form of fluid, those first deposited, and therefore presumed to be the heavier and larger, transmitted a pure blue light. The second and the third had the same character, perhaps the fourth, if the subdivision into portions had been numerous; then came some which transmitted an amethystine ray from the white of paper; and others followed progressing to the finest, which transmitted a rich ruby tint. It is probable that many of these deposits were mixtures of particles having different characters, and this is perhaps the reason that in some cases, when the fluids were contained in round-bottomed flasks, the lens-like deposit was ruby at the edges, though deep violet in the middle, the former having settled last; but as a pure blue deposit could be obtained, and also one transmitting a pure ruby ray, and as a comparatively pure intermediate preparation transmitting a ruby violet, or amethystine ray was obtained, it is probable that all gradations from blue to ruby exist; for the production of which I can see no reason to imagine any other variation than the existence of particles of intermediate sizes or proportions.

When light other than white was passed through the fluids, then of course other tints were produced, yet some of these were unexpected. A fluid of a pure blue colour, whilst in the dark tube, would in an open glass and by reflected light appear of a strong ruby-violet tint. Dropping some of the wet deposit into pure water, the striæ which it formed would in one part be ruby in colour and in another violet: these effects were referable to the light reflected from the solid particles back through the fluid to the eye, but it seemed redder than any which light reflected from gold was likely to produce. However, upon regarding the surface of dull gold-leaf, or the thick wet deposit of gold, or the hand, it was found that the red rays easily passed through the blue fluid and formed a ruby-violet tint. PREVOST showed in old times, how much the red and warm rays are reflected by gold, in preference to the others contained in white light.

The supernatant fluid in specimens that had stood long and deposited, was always ruby; yet because it showed no dissolved gold, because it showed the illuminated cone by the lens, and because by standing ruby clouds settled in it, there was every reason to believe that the gold was there in separated particles, and that such specimens afforded cases of extreme division, which by long standing would form deposits of the finest kind.

Those fluids which on standing gave abundance of deposits, transmitting blue light, consisted in the first instance of particles transmitting a ruby light, and in these cases

it would seem that the particles at their first separation were always competent to transmit this ruby light; and if the preparation were not too rich in gold the ruby condition appeared to be retained, the division being then most extreme. But purple or amethystine fluids could be procured, which, containing no colouring particles other than suspended gold, still retained them in suspension for many months together, so that they must have been as light or as finely divided as those in the ruby fluids. When the phosphorous ether was employed for the reduction of the gold such fluids occurred; also when the solution of the phosphorus in sulphide of carbon was used, provided the solution of gold had a very little chloride of sodium contained in it. They appear to show that the mere degree of division is not the only circumstance which determines the aptitude to transmit in preference this or that ray of light.

Considering the fluids as owing their properties to diffused particles, it may be observed, that many of them which in small quantities in the dark tube transmit an amethystine light, send forward a ruby light when the quantity is increased; and this appears to be the general progression. I have not found any which by increase in quantity tended to transmit the blue rays in preference to the red.

Elevation of temperature had an effect upon these fluids which is advantageous in their preparation. On boiling an apparently clear ruby fluid for some time, its colour passed a little towards amethystine, and on boiling a like amethystine fluid, its tint passed towards blue. The separation of the gold particles was also facilitated, for now they would settle in three or four days from a fluid which, prior to this operation, would not have deposited them in an equal degree for weeks. In the case of the ruby fluids the colour often became more rosy and luminous, and by reflected light the fluid seemed to have became more turbid, as if the particles had gained in reflective power; in fact the boiling often appeared to confer a sort of permanency on the particles in their new state. When settled, they formed collections looking like little lenses of a deep ruby or violet colour, at the bottom of the flasks containing the fluid; when all was shaken up the original fluid was reproduced, and then, by rest, the gold re-settled. This effect could be obtained repeatedly. The particles could fall together within a certain limit, but many weeks did not bring them nearer or into contact; for they remained free to be diffused by agitation. The space they occupied in this lens-like form must have been a hundredfold, or even a thousandfold, more than that, which they would have filled as solid gold. Whether the particles be considered as mutually repulsive, or else as molecules of gold with associated envelopes of water, they evidently differ in their physical condition, for the time, from those particles which by the application of salt or other substances are rendered mutually adhesive, and so fall and clot together.

In preparing some of these fluids, I made the solution of gold hot and boiling before adding the solution of phosphorus. The phenomena were the same in kind as before: but when the phosphorus was dissolved in sulphide of carbon, the gold soon fell as a dark flocculent deposit; when it was dissolved in ether a more permanent turbid ruby fluid was obtained, which, if it does not go on changing in aggregation, may give a good ruby deposit.

The particles in these fluids are remarkable for a set of physical alterations occasioned by bodies in small quantities, which do not act chemically on the gold, or change its intrinsic nature; for through all of them it seems to remain gold in a fine state of division. They occur most readily where the particles are finest, i. e. in the ruby fluids, and so readily that it is difficult to avoid them; they are often occasioned by the contact of vessels which are supposed to be perfectly clean. An idea of their nature may be obtained in the following manner. Place a layer of ruby fluid in a clean white plate, dip the tip of a glass rod in a solution of common salt and touch the ruby fluid; in a few moments the fluid will become blue or violet-blue, and sometimes almost colourless: by mingling up the neighbouring parts of the fluid, it will be seen how large a portion of it can be affected by a small quantity of the salt. By leaving the whole quiet, it will be found that the changed gold tends to deposit far more readily than when in the ruby state. If the experiment be made with a body of fluid in a glass, twelve or twenty-four hours will suffice to separate gold which in the ruby state has remained suspended for six months.

The fluid changed by common salt or otherwise, when most altered, is of a violet-blue, or deep blue. Any tint, however, between this and the ruby may be obtained, and, as it appears to me, in either of two ways; for the intermediate fluid may be a mixture of ruby and violet fluids, or, as is often the case, all the gold in the fluid may be in the state producing the intermediate colour; but as the fluid may in all cases be carried on to the final violet-blue state, I will, for brevity sake, describe that only in a particular manner. The violet or blue fluid, when examined by the sun's rays and a lens, always gives evidence showing that the gold has not been redissolved, but is still in solid separate particles; and this is confirmed by the non-action of protochloride of tin, which, in properly prepared fluids, gives no indication of dissolved gold. When a ruby solution is rendered blue by common salt, the separation of the gold as a precipitate is greatly hastened; thus when a glass jar containing about half a pint of the ruby fluid had a few drops of brine added and stirred into the lower part, the lower half of the fluid became blue whilst the upper remained ruby; in that state the cone of sun's rays was beautifully developed in both parts. On standing for four hours the lower part became paler, a dark deposit of gold fell, and then the cone was feebly luminous there, though as bright as ever in the ruby above. In three days no cone was visible in the lower fluid; a fine cone appeared in the upper. After many days the salt diffused gradually through the whole, first turning the gold it came in contact with blue, and then causing its precipitation.

Such results would seem to show that this blue gold is aggregated gold, i. e. gold in larger particles than before, since they precipitate through the fluid in a time which is as nothing to that required by the particles of the ruby fluid from which they are obtained. But that the blue particles are always merely larger particles does not seem admissible for a moment, inasmuch as violet or blue fluids may be obtained in which the particles will remain in suspension as long as in the ruby fluids; there is probably some physical

change in the condition of the particles, caused by the presence of the salt and such affecting media, which is not a change of the gold as gold, but rather a change of the relation of the surface of the particles to the surrounding medium.

When salt is added in such quantity as to produce its effect in a short time, it is seen that the gold reflexion of the particles is quickly diminished, so that either as a general turbidness or by the cone of rays it becomes less visible; at last the metal contracts into masses, which are comparatively so few and separate, that when shaken up in the fluid, they confer little or no colour or character, either by reflected or transmitted light. In these cases no re-solution of the metal is effected, for neither the salt nor hydrochloric acid, when used in like manner, have any power to redissolve the gold. The same aggregating effect is shown with all the fluids whatever their colour, and also with the deposits that settle down from them. When salt is added to the solution of gold *before* the phosphorus, and therefore before the reduction of the gold, the fluid first produced is always ruby, but it becomes violet, purple, or blue, with a facility in proportion to the quantity of salt present. If that be but small, the ruby will remain for many days unchanged in colour, and the violet-ruby for many weeks, before the gold will be deposited, the degree of dilution or concentration always having its own particular effect, as before described; the more finely divided preparations, *i. e.* the ruby and amethystine, appear to be more permanent than when the salt is added after the separation of the gold.

Many other bodies besides salt have like action on the particles of gold. A ruby fluid is changed to or towards blue by solutions of chlorides of calcium, strontium, manganese; sulphates of magnesia, manganese, lime; nitrates of potassa, soda, baryta, magnesia, manganese; acetates of potassa, soda, and lime; these effect the change freely: the sulphate of soda, phosphates of soda and potassa, chlorate of potassa, and acetate of ammonia acted feebly. Sulphuric and hydrochloric acids produce the change, but show no tendency to dissolve the gold. Nitric acid acts in the same manner, but not so strongly: it often causes re-solution of the gold after some time, because of the hydrochloric acid which remains in the fluid.

Amongst the alkalies, potash produces a similar action in a weak degree. So also does soda. Lime-water produces a change in the same direction, but the gold quickly precipitates associated with the lime.

Ammonia causes the ruby fluid to assume a violet tint; the deposit is slow of formation and often ruby in colour; the alkali apparently retards the action of common salt.

Chlorine or nitromuriatic acid turns the ruby fluid blue or violet-blue before they dissolve the gold.

Solution of sulphuretted hydrogen changes the ruby slowly to purple, and finally to deep blue. Ether, alcohol, camphine, sulphide of carbon, gum, sugar and glycerine cause little or no change in the fluids; but glycerine added to the dense deposits causes serious condensation and alteration of them, so that it could not be employed as a medium for the suspension of particles in the microscope.

All endeavours to convert the violet gold back into ruby were either failures, or very imperfect in their results. A violet fluid will, upon long standing, yield a deposit and a supernatant ruby fluid, but this I believe to be a partial separation of a mixture of violet and ruby gold, by the settlement of the blue or violet gold from ruby gold, which remains longer in suspension. Mucus, which often forms in portions of these fluids that have been exposed to the air, appears sometimes to render a fluid more ruby, but this it does by gathering up the larger violet particles; it often becomes dark blue or even black by the particles of gold adhering to it, many of which may be shaken out by agitation in water; but I never saw it become ruby-coloured as a filter can, and I think that in these cases it is the gathering out of the blue or violet particles which makes the fluid left appear more ruby in tint. I have treated blue or violet fluid with phosphorus in various ways, but saw no appearance of a return in any degree towards ruby. Sometimes the fluids possess a tendency to re-solution of the gold, a condition which may often be given by addition of a very little nitric acid, but in these cases the gold does not become ruby before solution. It would rather appear that the finer ruby particles dissolve first, for the tint of the fluid, if ruby-violet at the commencement, changes towards blue. One effect only seemed to show the possibility of a reversion. Filtering-paper rendered ruby by a ruby fluid was washed and dried; being wetted by solution of caustic potash, it did not change; but being heated in a tube with the alkali, it became of a gray-blue tint; pouring off the alkali, washing the paper, and then adding dilute sulphuric or nitric acid to it, there was no change; but on boiling the paper in the mixed acids there was a return, and when the paper was washed and dried it approached considerably to the original ruby state. Again, potash added to it rendered it blue, which by washing with water, and especially with a little nitric acid, was much restored towards ruby. These changes may be due to an affection of the surface, or that which may be considered the surface of the particles.

The state of division of these particles must be extreme; they have not as yet been seen by any power of the microscope. Whether those that are ruby have their colour dependent upon a particular degree of division, or generally upon their being under a certain size, or whether it is consequent in part upon some other condition of the particles, is doubtful; for judging of their magnitude by the time occupied in their descent through the fluid, it would appear that violet and blue fluids occur giving violet deposits, which still consist of particles so small as to require a time equally long with the ruby particles for their deposition, and indeed in some specimens to remain undeposited in any time which has yet occurred since their formation. These deposits, when they occur, look like clear solutions in the fluid, even under the highest power of the microscope.

I endeavoured to obtain an idea of the quantity of gold in a given ruby fluid, and for this purpose selected a plate of gold ruby glass, of good full colour, to serve as a standard, and compared different fluids with it, varying their depth, until the light from white paper, transmitted through them, was apparently equal to that transmitted by the standard glass. Then known quantities of these ruby fluids were evaporated to dryness,

the gold converted into chloride, and compared by reduction on glass and otherwise with solutions of gold of known strengths. A portion of chloride of gold, containing 0·7 of a grain of metal, was made up to 70 cubic inches by the addition of distilled water and converted into ruby fluid: on the sixth day it was compared with the ruby glass standard, and with a depth of 1·4 inch was found equal to it; there was just one hundredth of a grain of gold diffused through a cubic inch of fluid. In another comparison, some gold leaves were dissolved and converted into ruby fluid, and compared; the result was a fluid, of which 1·5 inch in depth equalled the standard, a leaf of gold being contained in 27 cubic inches of the fluid. Hence looking through a depth of 2·7 inches, the quantity of gold interposed between the light and the eye would equal that contained in the thickness of a leaf of gold. Though the leaf is green and the fluid ruby, yet it is easy to perceive that more light is transmitted by the latter than the former; but inasmuch as it appears that ruby fluids may exist containing particles of very different sizes (or that settle at least with very different degrees of rapidity), so it is probable that the degree of colour, and the quantity of gold present, may not be always in the same proportion. I need hardly say that mere dilution does not alter the tint sensibly, *i. e.* if a deep ruby fluid be put into a cylindrical vessel, and the eye look through it along the axis of the vessel, dilution of the fluid to eight or ten times its volume does not sensibly alter the light transmitted. From these considerations, it would appear that one volume of gold is present in the ruby fluid in about 750,600 volumes of water; and that whatever the state of division to which the gold may be reduced, still the proportion of the solid particles to the amount of space through which they are dispersed must be of that extreme proportion. This accords perfectly with their invisibility in the microscope; with the manner of their separation from the dissolved state; with the length of time during which they can remain diffused; and with their appearance when illuminated by the cone of sun's rays.

The deposits, when not fixed upon glass or paper, are much changed by drying; they cannot be again wetted to the same degree as before, or be again diffused; and the light reflected or refracted is as to colour much altered, as might be expected. Whilst diffused through water, they seem to be physical associations of metallic centres with enveloping films of water, and as they sink together will lie for months at the bottom of the fluid without uniting or coming nearer to each other, or without being taken up by metallic mercury put into the same vessel. This is consistent with what we know of the manner in which gold and platinum can be thoroughly wetted if cleaned in water, and of the difference which occurs when they are dried and become invested with air. I endeavoured to transfer the gold particles unchanged into other media, for the purpose of noting any alteration in the action on light. By decanting the water very closely, and then carefully adding alcohol with agitation, I could diffuse them through that fluid; they still possessed a blue colour when looked through in the dark tube, but seemed much condensed or aggregated, for the fluid was obscure, not clear, and the particles soon subsided. I could not transfer them from alcohol to camphine; they

refused association with the latter fluid, retaining a film of alcohol or water, and adhering by it to the glass of the vessel; but when the camphine was removed, a partial diffusion of them in fresh alcohol could be effected, and gave the colour as before. All these transfers, however, injured the particles as to their condition of division. In one case I obtained a ruby film on a white plate; on pouring off the water and allowing parts to become dry, these became violet, seen by the light going through them to the plate and back again to the eye. I could not wet these places with water, a thin feebly reflecting surface remained between it and them. Using alcohol, the parts already dry remained violet, when wetted by it; but wetting other parts with alcohol before they were dry from water they remained rosy, became bluish when dry from the alcohol, and became rosy again when re-wetted by it.

It will be necessary to speak briefly of the reduction of gold into a divided state by some other chemical agents than those already described*. If a drop of solution of proto-sulphate of iron be introduced to, and instantly agitated with, a weak neutral solution of chloride of gold in such proportion that the latter shall be in excess, the fluid becomes of a blue-grey colour by transmission and brown by reflexion; and a deposit is formed of a green colour by transmitted light, greatly resembling the colour of beaten or pressed metal. It is not however pure gold, but an association of it and oxide of iron. Hydro-chloric or other acids remove the iron and reduce the gold to a dark, dense, insoluble set of particles, in very small quantity apparently, yet containing all that was present in the bulky green deposit. If the solution of gold be made slightly acid beforehand, then the change and precipitation is to appearance much less; the reflexion by the particles is feeble but of a pale brown colour, the general transmitted light is amethystine; in the dark tube the tint is blue; the particles are much condensed and settle quickly, but occasionally leave a good ruby film on the side of the glass, which has all the characters of the ruby films and particles before described. The loose gold particles quickly adhere together. Hence it appears that the green precipitate often obtained by protosulphate of iron is not pure gold in a divided state; and that when care is taken to produce such pure divided gold, it presents the appearances of divided gold obtained by other means, the gold being competent to produce the ruby, amethystine, and blue colours by trans-mission. Usually the gold rapidly contracts and becomes almost insensible, and yet the test of protochloride of tin will show *that* all has been separated from solution; it then forms a *striking* contrast to the depth of colour presented by the same solution of gold precipitated by phosphorus, and most impressively directs attention to the molecular condition of the metal in the latter state.

A very small quantity of *protochloride of tin*, added to a dilute solution of gold, gave, first the ruby fluid, showing diffused particles by the cone of rays; this gradually became purple, and if the gold were in sufficient quantity a precipitate soon began to fall, being the purple of CASSIUS. If the chloride of tin were in larger quantity, a more bulky pre-

* See GMELIN's 'Chemistry,' vi. p. 219, "Terchloride of gold," for numerous references in relation to changes of these kinds.

cipitate fell and more quickly. Acid very much reduced this in quantity, dissolving out oxide of tin, and leaving little else than finely-divided gold, which, when diffused and examined in the dark tube, transmitted a blue colour. I believe the purple of CASSIUS to be essentially finely-divided gold, associated with more or less of oxide of tin.

Tartaric acid being added to a weak solution of gold gradually reduced it. The amethystine tint produced by diffused particles first appeared, and then a blue deposit of larger particles, whilst the side and bottom of the glass became covered by an adhering film of finer particles, presenting the perfect ruby tint of gold.

Ether added to a weak solution of gold gradually reduced it; the fluid was brown by reflected light, fine blue by transmitted light, and gave a good cone by the sun's rays and lens. The blue colour was not deep, though all the gold had been separated from solution; the preparation closely resembled that made with protosulphate of iron and a little acid.

A weak solution of gold, mingled with a little sugar, being heated, yielded a very characteristic decomposition. The gold was reduced into diffused particles, which rendered the fluid of a ruby-amethystine colour, and which, upon standing for twenty-four hours, gave signs of separation by settling as on former occasions. A little glycerine with solution of gold reduces it at common temperatures, producing a fluid, brown by reflexion, blue by transmission, giving a fine cone of rays by its suspended particles. Heat quickens the action, and causes a blue deposit.

Organic tissues often reduce solutions of gold, light if present assisting the action; and they afford valuable evidence in aid of the solution of the question relative to the condition of the metal in the divided state. If the skin be touched with a solution of gold, it soon becomes stained of a dull purple colour. If a piece of the large gut of an ox be soaked first in water, then in a solution of gold, and be afterwards taken out and allowed to dry, either exposed to light or not, the inner membrane will become so stained, that though of a dull purple colour by common observation, a transmitted ray will show it to be generally a very fine ruby, equal to that of ruby-coloured glass, or the gold fluids already described, though perhaps in places of a beautiful violet hue. The character of the particles which are here located and not allowed to diffuse and aggregate, as in the fluids, will be resumed when dealing with the whole question of the metallic nature of the particles of the variously divided gold.

Chloride of gold is reducible by heat alone. If a drop of solution of chloride of gold be evaporated in a watch-glass, or on a plate of rock-crystal, and then heated over a spirit-lamp until the gold is reduced, it will generally be found that the vapour has carried a portion of gold on to the neighbouring part of the glass, and that this part, when placed over a sheet of white paper, has the ruby tint. With the rock-crystal both ruby and blue parts are produced; and when the ruby parts are subjected to rock-crystal pressure, they become beautifully green. In the arts also glass is oftentimes coloured ruby by gold; I think that glass in this state derives its colour from diffused divided gold; and if either the ruby glass or the watch-glass be examined by a lens and

the cone of rays, it will be seen that the colours are not due to any gold dissolved, but to solid and diffused particles. .There is nothing in any of the appearances or characters, or in the processes resorted to to obtain the several effects, that point at any physical difference in the nature of the results; and without saying that gold cannot produce a ruby colour whilst in combination or solution, I think that in all these cases the ruby tint is due simply to the presence of diffused finely-divided gold.

Metallic character of the divided gold.

Hitherto it may seem that I have assumed the various preparations of gold, whether ruby, green, violet, or blue in colour, to consist of that substance in a metallic divided state. I will now put together the reasons which cause me to draw that conclusion. With regard to *gold-leaf* no question respecting its metallic nature can arise, but it offers evidence reaching to the other preparations. The green colour conferred by pressure, and the removal of this colour by heat, evidently belong to it as a metal; these effects are very striking and important as regards the action on light, and where they recur with other forms of gold, may be accepted as proof that the gold is in the metallic state. Although I do not attach equal importance to the fact already described, that gold-leaf frequently presents fine parts that appear to be ruby in colour, I am not as yet satisfied that they are not in themselves ruby; and if they should be so, it will be another proof by analogy of the metallic nature of other kinds of preparations eminently ruby. ·

The *deflagrations* of gold wire by the Leyden discharge can be nothing but divided gold. They are the same whatever the atmosphere surrounding them at the time, or whatever the substance on which they are deposited. They have all the chemical reactions of gold, being, though so finely divided, insoluble in the fluids that refuse to act on the massive metal, and soluble in those that dissolve it, producing the same result. Heat makes these divided particles assume a ruby tint, yet such heat is not likely to take away their metallic character, and when heated they still act with chemical agents as gold. Pressure then confers the green colour, which heat takes away, and pressure reconfers. All these changes occur with particles attached to the substances which support them by the slightest possible mechanical force, just enough indeed to prevent their coalescence and to keep them apart and in place, and yet offering no resistance to any chemical action of test agents, as the acids, &c., not allowing any supposition of chemical action between them and the body supporting them. Still this gold, unexceptionable as to metallic state, presents different colours when viewed by transmitted light. Ruby, green, violet, blue, &c. occur, and the mere degree of division appears to be the determining cause of many of these colours. The deflagrations by the voltaic battery lead to the same conclusion.

The *gold films* produced by phosphorus have every character belonging to the metallic state. When thick, they are in colour, lustre, weight, &c. equal to gold-leaf, but in the unpressed state, their transmitted colour is generally grey, or violet-grey. The progres-

sion of their lustre and colour is gradual from the thickest to the thinnest, and the same is generally true, if thick films are gradually thinned and dissolved whilst floating on solvents; the thick and the thin films must both be accepted as having the same amount of evidence for their metallic nature. When subjected to chemical agents, both the thick and the thin films have the same relations as pure metallic gold. These relations are not changed by the action of heat, yet heat shows the same peculiar effect that it had with preparations of gold obtained by beating, or by electric deflagrations. The remarkable and characteristic effect of pressure is here reproduced, and sometimes with extraordinary results; since from the favourable manner in which the particles are occasionally divided and then held in place on the glass, the mere touch of a finger or card is enough to produce the result. Yet with gold thus proved to be metallic, colours including grey, grey-violet, green, purple, ruby, especially by heat, and green again by pressure, and by thinning of grey films, may be obtained by transmitted light, almost all of them at pleasure.

It may be thought that the *fluid preparations* present more difficulty to the admission, that they are simply cases of pure gold in a divided state; yet I have come to that conclusion, and believe that the differently-coloured fluids and particles are quite analogous to those that occur in the deflagrations and the films. In the first place they are produced as the films are, except that the particles are separated under the surface and out of the contact of the air; still, when produced in sufficient quantity against the side of the containing vessel to form an adhering film, that film has every character of lustre, colour, &c. in the parts differing in thickness, that a film formed at the surface has. Whilst the particles are diffused through the fluid it is difficult to deal with them by tests and reagents; for their absolute quantity is very small and their physical characters are very changeable, chiefly as I believe by aggregation; still there are some expedients which enable one to submit even the finest of them to proof. In several cases particles from ruby and amethystine fluids adhered to the sides of the bottles or flasks in which the fluids had been preserved, and the process of boiling seemed to favour such a result; the adhesion was so strong, that when the fluid contents were removed and the bottles well washed, the glass remained tinged of a ruby or a violet colour. These films, in which the fine particles were fixed mechanically apart and in place, were then submitted to the action of various chemical agents. Drying and access of air did not cause any marked alterations in them. Strong nitric acid produced no change, nor hydrochloric acid, nor sulphuric acid. Neither did a solution of chloride of sodium, even up to brine, cause any alteration in the colour or any other character of the deposit. A little solution of chlorine or of nitromuriatic acid dissolved them at once, producing the ordinary solutions of gold. I can see no other mode of accounting for these effects (which are in strong contrast with what happens when ruby fluid is acted on by these agents), than to suppose that the gold particles, being in a high state of division, were retained in that state for the time by their adhesion to the glass. Of course chemical change was free to occur, but not a change dependent upon their mutual aggregation; yet they were not

held by any special chemical attraction to, or combination with, the glass; for a touch with a card, a feather, or the finger, was sufficient to remove them at once, and if rubbed off with a point of wood, they coated it with brilliant metallic gold.

Again, though these particles are so finely divided that they pass easily through ordinary filters, still a close filter catches some; and if a ruby fluid be passed through again and again, the paper at last becomes of a rosy hue, because of the gold which adheres to it; being then well washed, and, if needful, dried, the gold is again ready for experiment. Such gold paper, placed across the middle of the dark tube and examined by transmitted light, was of the same ruby tint as when looked through in the open air. It was unaffected by salt or brine, though these, added to the rosy fluid which had passed the filter, instantly changed it to violet-blue. Portions of the paper were put into separate glasses with brine, solutions of hydrochloric, nitric and sulphuric acids, ammonia, potassa, soda and sulphuretted hydrogen, but no change occurred with any of them in two days. On the other hand, a very dilute solution of chlorine immediately turned the ruby to blue, and then gradually dissolved the gold. A piece of the ruby paper immersed in a strong solution of cyanide of potassium suffered a very slow action, if any, and remained unaltered in colour; being brought out into the air, the gold very gradually dissolved, becoming first blue. A portion of the ruby paper was dried and heated in oil until the oil and the paper began to change their hue; the gold had not altered in its colour or character. Another portion was heated in the vapour of alcohol and also of ether until the paper began to alter; the gold remained unaltered. A blue fluid being passed oftentimes through a filter gave a blue paper, which, being washed and tried in the same manner, was found to contain particles unchanged by the simple acids or alkalies, or by heat or vapours, but dissolving, as gold would do, in chlorine or nitromuriatic acid. These tests are, I think, sufficient to prove the metallic nature and permanence of the gold as it exists in the ruby, amethystine, violet, and other coloured fluids.

The production by such different agents as phosphorus, sulphide of carbon, ether, sugar, glycerine, gelatine, tartaric acid, protosulphate of iron and protochloride of tin, of gold fluids all more or less red or ruby at the commencement, and all passing through the same order of changes, is again a proof that only gold was separated; no single one or common compound of gold, as an oxide or a phosphide, could be expected in all these cases. Many of the processes, very different as to the substances employed to reduce the gold, left good ruby films adhering to the glass vessels used, presenting all the characters of the gold described already; this was the case with phosphorus, sugar, tartaric acid, protosulphate of iron, and some other bodies.

Again, the high reflective power of these particles (unalterable by acids and salts), when illuminated by the sun's rays and a lens, and the colour of the light reflected, is in favour of their metallic character. So also is their aggregation, and their refusal to return from blue, violet or amethystine to ruby; for the cohesive and adhering force of the gold particles and their metallic nature and perfect cleanliness is against such a

reverse change. Particles transmitting blue light could be obtained in such quantity as to admit of their being washed and dried in a tube, and being so prepared they presented every character of gold: when heated, no oxygen, water, phosphorus, acid of phosphorus, nor any other substance was evolved from them: they changed a little, as the film when heated changed, becoming more reflective and of a pale brown colour, and contracted into aggregated porous masses of pure ordinary gold.

Gold is reduced from its solution by organic tissues; and *stained gut* has been quoted as a case. I have a very fine specimen which by transmitted light is as pure a ruby as gold-stained glass, and I believe that the gold has been simply reduced and diffused through the tissue. The preparation stood all the trials that had been applied to the ruby films on glass or the gold deposit on filtering-paper. Portions of it remained soaking in water, solution of chloride of sodium and dilute sulphuric acid for weeks, but these caused no change from ruby to blue, such as could be effected on loose ruby particles. Strong hydrochloric acid caused no change as long as the tissue held together; but as that became loose the gold flowed out into the acid in ruby-amethystine streams, finally changing to blue. Caustic potassa caused no change for days whilst the tissue kept together, but on mixing all up by pressure the loosened gold became at last blue. Strong nitric acid caused no change of colour until, by altering the tissue, the gold particles first flowed out in ruby and amethystine streams, and then were gradually changed to the condition of common aggregated gold. All these effects, and the actions on light, accord with the idea that the stain was simply due to diffused particles of finely-divided gold; and I am satisfied that all such stains upon the skin, or other organic matter, are of exactly the same nature.

As to the gold in ruby glass, I think a little consideration is sufficient to satisfy one that it is in the metallic condition. The action of heat tends to separate gold from its state of combination, and when so separated from the chloride, either upon the surface of glass, rock-crystal, topaz, or other inactive bodies, a ruby film of particles is frequently obtained. The sunlight and lens show that in ruby glass the gold is in separated and diffused particles. The parity of the gold glass, with the ruby-gold deflagrations and fluids described, is very great. These considerations, with the sufficiency of the assigned cause to produce the ruby tint, are strong reasons, in the absence of any to the contrary, to induce the belief that finely-divided metallic gold is the source of the ruby colour.

When a pure, clean, stiff jelly is prepared, and mixed, whilst warm and fluid, with a little dilute chloride of gold, as if to prepare a ruby fluid, it gelatinizes when cold, and if left for two or three days may become a ruby jelly; sometimes, however, the gold in the jelly changes but little or changes to blue, or it may happen that it is reduced on the surface as a film, brilliant and metallic by reflected light, and blue-grey by transmitted light. I have not yet ascertained the circumstances determining one or the other state. If a trace of phosphorus in sulphide of carbon be added to the solution of gold in a dilute state, and some salt be added to the warm jelly, and the latter be then mixed gradually and with agitation with the gold solution, a ruby jelly is generally produced.

In such ruby jelly the reduced particles of gold preserve their state and relative place, and the tint does not pass to blue, even though a considerable proportion of salt be present. Such jelly will remain in the air for weeks before it decays, and has every character, in colour and appearance, of gold ruby glass. It is hardly possible to examine the series of ruby glass, ruby membrane, ruby jelly cold and gelatinous, ruby jelly warm and fluid, and the ruby fluids, to consider their production, and then to conclude that the cause of their common ruby colour is not the same in all.

When the warm ruby jelly is poured into a capsule or on to a plate, allowed to gelatinize and then left in the air, it gradually becomes dry. When dry, some of these jellies remain ruby; others will probably be of an amethystine violet colour, or perhaps almost blue. When one of the latter is moistened with water, and has absorbed that fluid, it becomes gelatinous, and whilst in that state resumes its first ruby colour; but on being suffered to dry again it returns to its amethystine or blue colour. This change will occur for any number of times, as often as the jelly is wetted and dried. Here the gold remains in the same metallic state through this great change of colour, the association or the absence of water being the cause: and the effect strengthens in my mind the thought before expressed, that in the ruby fluids the deposited particles are frequently associates of water and gold. It is a striking case of the joint effect of the media and the gold in their action on the rays of light, and the most striking case amongst those where the medium may be changed to and fro.

When a ruby jelly is prepared with salt, and being warm is poured out in thin layers on to glass or porcelain, it first gelatinizes and then dries up; in which case the salt is excluded and crystallizes. When the dry jelly is put into cold water, the salt dissolves and can be removed. The jelly then swells to a certain amount, after which it can be left soaking in water for a week or longer, until everything soluble is separated. No change takes place in the ruby tint, no gold is removed. When the last water is poured off and the remaining jelly warmed, it melts, forming a fine ruby fluid, which can either be dissolved in more water, or regelatinized, or be dried and preserved for any length of time. It is perfectly neutral; gives no signs of dissolved gold by any of the tests of the metal; is not changed by sulphuretted hydrogen, gallic acid, pyrogallic acid, dilute caustic alkalies, or carbonated alkalies or lime-water; or by dilute sulphuric, hydrochloric or nitric acids, the actions being continued for fourteen days:—being boiled with zinc filings it does not change; and even when dilute sulphuric or hydrochloric acid is added to evolve nascent hydrogen, still the ruby character undergoes no alteration. Strong sulphuric, or nitric, or hydrochloric acid do not alter it whilst cold; but when warmed, the first causes the gold to separate as dark aggregated metallic particles, and the two latter gradually cause the change to amethyst and blue formerly described. Chlorine, or a mixture of hydrochloric and nitric acids, dissolves the gold, the ruby colour disappears, and the ordinary solution of gold is produced. In all these cases the ruby gold behaves exactly as metallic gold would do with the same agents, and quite unlike what would be expected from any possible combination of oxygen and gold.

In some of these jellies the ruby particles are so determinate as to give the brown reflexion by common observation; in others they are so fine as to look like ruby solutions, unless a strong sunlight and a lens be employed; and the impression again arises, that gold may exist in particles so minute as to have little or no power of reflecting light. Ruby particles of extreme fineness, when present in small amount in water, appear to remain equally diffused for any length of time; if in larger amount, that which settles to the bottom will remain for weeks and months as a dense ruby fluid, but without coming together: both circumstances seem to imply an association of the particles of gold with envelopes of water. Many circumstances about the ruby jellies imply a like association with that animal substance, and many of the stains of gold upon organic substances probably include an affinity of the metal of the like kind.

### Relations of Gold (and other metals) to polarized Light.

It has been already stated, that when a ray of common light passes through a piece of gold-leaf inclined to the ray, the light is polarized. When the angle between the leaf and the ray is small, about 15°, nearly all the light that passes is polarized; but as the leaf is really very irregular in thickness, and ill-stretched as a film, parts inclined at different angles are always present at once. The light transmitted is polarized in the same direction as that transmitted by a bundle of thin plates of glass, inclined in the same direction. The proportion of light transmitted is small, as might be expected from the high reflective power of the metal. The polarization does not seem due to any constrained condition of the beaten gold, for it is produced, as will be shortly seen, by the annealed colourless leaf-gold, and also by deposits of gold particles; but is common to it with other uncrystallized transparent substances. It would seem that a very small proportion of the gold-leaf can be occupied by apertures, since the light which passes is nearly all polarized. On subjecting thin gold-leaf, or heated gold-leaf, or films of gold, or any preparations which required the support of glass, results of polarization were obtained, but the observations were imperfect because of the interfering effect of the glass.

Proceeding to employ a polarized ray of light, it was found that a leaf of gold produced generally the same depolarizing effect as other transparent bodies. Thus, if a plate of glass be held perpendicular to the ray, or inclined to it either in the plane of polarization or at right angles to it, there is no depolarization; but if inclined in the intermediate positions, the ray is more or less depolarized. So it is with gold-leaf; the same effects are produced by it. Further, the depolarization is accompanied by a rotation of the ray, and in this respect the quadrants alternate, the rotation being to the right-hand in two opposite quadrants, and to the left in the intervening quadrants. So it is with gold-leaf; the same effects are produced by it, and the rotation is in the same direction with that produced by glass, when inclined in the same quadrant.

As further observation in this direction was stopped by the necessity of employing glass supports for the leaves, films, &c., I sought for a medium so near glass in its cha-

racter, as should either reduce its effect to nothing, or render it so small as to cause its easy elimination. Either camphine or sulphide of carbon was found to answer the purpose with crown-glass; but the latter, as it possesses no sensible power of rotation under ordinary circumstances, is to be preferred. Should a medium of higher optic force be required, it would probably be supplied by the use of that dangerous fluid, phosphorus dissolved in sulphide of carbon. A rectangular glass cell being provided, which did not itself affect the polarized ray, was placed in its course and filled to a certain height with sulphide of carbon. A plate of crown-glass was then introduced perpendicularly to the ray; it did not affect it; being inclined as before described, the effect on the ray was still insensible, the glass appearing to be, for all ordinary observations such as mine, quite as the medium about it. I could now introduce gold-leaf attached to glass into the course of the polarized ray, its condition as a flat film or plane being far finer than when stretched on a wire ring as before. It proved to be so far above the sulphide of carbon, as to have powers of depolarization apparently as great as those it had in air, and being inclined, brought in the image at the analyser exceedingly well. It was indeed very striking to see, when the plate was moved parallel to itself, the darkness when mere glass intervened, and the light which sprung up when the gold-leaf came into its place; the opake metal and the transparent glass having apparently changed characters with each other. By care I was able to introduce a stretched piece of gold-leaf (without glass) into the sulphide of carbon; its effects were the same with those just described.

In all the experiments to be described, the plane of polarization and the plane of inclination had the same relation to each other: the figure shows the position of the polarizing NICOL prism, as the eye looks through it at the light, and a, b represents the vertical axis, about which the plates were inclined. Whether they were inclined in one direction or the other, or had the glass face or the metal face towards the eye, made no difference. In all cases with gold-leaf, it was found that the ray had been rotated; that it required a little direct rotation of the analyser to regain the minimum light; that short of that red tints appeared, and beyond it blue or cold, these being necessarily affected in some degree by the green colour of the gold-leaf. Thinned gold-leaf produced the same results; but as holes appeared in those that were thinnest, the results were interfered with, because the light passing through them was affected by the analyser in a different manner, and yet mingled its result with that of the light which had passed through the gold.
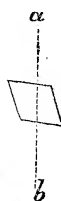
The gold-leaf plates, deprived of green colour by heating in oil, were found with the glass in such good annealed condition, as not to affect the ray; but when they were moved, until the oblique colourless gold came into the course of the ray, it was depolarized; a red image appeared; direct rotation of the analyser reduced this a little in intensity and then changed the colour to blue. The reduction was not much, and both in that and the first appearance of the red image, there is a difference between the heated and the unheated gold: probably the green tint of the latter, which would tend to extinguish the red and produce a minimum, may be sufficient to account for the effect. Gold

which had been re-greened by agate pressure acted in like manner on the polarized ray, but the experiments were imperfect.

A glass plate having gold-leaf on one part of it, had a second glass plate put over it and gummed at the edges. In the sulphide of carbon, therefore, it represented in one part a plate of air, and in another a compound plate of air and gold; both acted in the same direction, but the air and gold much more than the air. Gold on glass in this medium, or gold in air, or glass in air, all gave results in the same direction, i. e. required direct rotation of the analyser to compensate for them.

I proceeded to examine the other forms of gold; and first, the deposits on glass obtained by *electric deflagration.* These affected the ray of polarized light exactly in the manner of gold-leaf, and that even at the distant parts of the deposit. It was most striking to contrast the thinnest and faintest portion of such a film with the neighbouring parts of the glass from which it had been wiped off. It must be remembered that such a preparation is a layer of separate particles; that these particles are not like those of starch or of crystals, for they have no action whilst in a plane perpendicular to the polarized ray; nor have they a better action for being in a thick layer, as in the central parts of the deposit. The particles seem to form the equivalent of a continuous plate of transparent substance; and as in such a plate it is the two surfaces which act, so there appears to be the equivalent of these two surfaces here; which would seem to imply that the particles are so small and so near, that two or more can act at once upon the individual atoms of the vibrating ether. Their association is such as to present as it were an optical continuity.

The gold films by phosphorus were then submitted to experiment, and gave exactly the same result. All of them depolarized, and required direct rotation of the analyser to arrive at a minimum, or to pass from the red to the blue tints. Graduated films, of which I should judge from the depth of tint that one place was at least twenty times as thick as another, gave the effect as well in the thinnest as the thicker or any intermediate part; indicating that thickness of the plate, and therefore any quality equivalent to crystalline force of the particles, had nothing to do with the matter. A glass beaker, which had been employed to contain ruby fluid, had a film of gold deposited on its inner surface so thin, as to be scarcely perceptible either by reflexion or otherwise, except by a ruby tint which appeared upon it in certain positions; but being examined by a polarized ray, it gave an effect as strong and as perfect as gold-leaf, showing how thin a film of gold was sufficient for the purpose. This thin film appeared to be almost perfect in its continuity, for when the red image was brought in, direct rotation of the analyser reduced it to a minimum which was quite dark; after which, further rotation brought in a good blue image. The least touch of the finger removed the film of gold and all these effects with it. These films, though they are certainly porous to gas, and to water in some form, for it can evaporate from beneath them through its body, have evidently optical continuity.

In order to submit the gold fluids to experiments, cells were made of two glass plates,

separated by the thickness of a card, and fastened at the edges by varnish internally and gum externally. These being filled with dense ruby or blue fluid, gave no indication of action on the ray, showing that the diffused particles were inoperative. The same fluids, dried on plates of glass so as to leave films, did act just as the gold deflagrations had done; for though the particles were very irregularly spread, parts of the general deposit, and these not the thickest, could be selected, which produced the effect excellently well.

When the coloured jellies are laid upon glass plates and allowed to dry, the plates introduced obliquely into the sulphide of carbon affect the ray, but not as gold films; the light image becomes visible, but the plane of polarization is not changed; the light is coloured by the ruby or blue tint of the gold present, but a film of jelly without gold makes it visible to the same extent. In this case the gold is not in one plane, but diffused through the dry jelly, and the effect is the same as if it were diffused through water, being negative.

Such are the effects with the various preparations of divided gold. I will hastily notice what occurs with some other metals. *Platinum deflagrated* in hydrogen: it depolarized the ray, required direct rotation of the analyser to attain a minimum, therefore rotated the plane of polarization; but did not present sensible colour on either side of the minimum of light. *Palladium deflagrated* in hydrogen: it depolarized, producing a red image; direct rotation of the analyser lessened the light to a minimum, and then brought in a blue image. The films of palladium obtained by phosphorus acted well in the same manner. These films appear to be exceedingly continuous, and it could be observed in them, that though the thickest were not the best, yet films could be obtained so thin as to be distinctly inferior to other parts a little thicker; also that where the brilliancy of reflexion which indicates perfect smoothness passed in any degree into dulness, the action of the film was injured: the perfect condition of the surfaces of the films seems to be essential to their good action. *Rhodium films* by phosphorus gave good actions, like those produced by gold. *Silver deflagrations*, either in air or hydrogen, gave depolarizing results like those with gold. Silver films also gave excellent results of the like kind. A thin pale brown film was much better than a thicker one. *Copper* deflagrated in hydrogen: depolarized, bringing in a red image, which by direct rotation of the analyser was lowered a little and then converted to blue. The copper films obtained from oil acted in the same manner; the red and blue images appeared in their order; but very little direct rotation of the analyser was required to produce the minimum of light. *Tin* deflagrated in hydrogen: depolarized and rotated the ray, as with gold; the images were only feeble in colour. *Lead* deflagrated in hydrogen: acted as tin. *Iron* deflagrated in hydrogen: acted as tin. *Zinc* deflagrated in hydrogen: acted as tin. *Aluminium* deflagrated in hydrogen: had like action with the rest; the image brought in by it was red, which direct revolution of the analyser reduced at a little distance to a minimum and then converted to blue. A film of *mercury* produced by sublimation, a film of *arsenic* produced in like manner, and a film of *smoke* from a candle, though all of them sufficiently pervious to light, did not produce any result of depolariza-

tion. Films of the smoke of burning *zinc*, of *antimony*, or of *oxide of iron* produced no effect.

I placed some metallic solutions in a weak atmosphere of sulphuretted hydrogen. Gold and platinum gave no films; silver so poor a film as to be of no use; and lead one so brittle as to be unserviceable. That obtained with palladium I believe to be the metal itself. The films of sulphuret of mercury, sulphuret of antimony which was orange, and sulphuret of copper which was pale brown, all acted on the light and depolarized it. The sulphuret of copper presented a difference from the metals generally, worth recording; it depolarized the light, producing an image which, if not blue at once, was rendered blue by a little direct rotation of the analyser; after which the same motion brought in a minimum and then produced an orange or red tint, *i. e.* with the sulphuret of copper the warm and cold tints appear on opposite sides of the minimum to those where they occur when films of the metals are employed, though the minimum in both cases is in the same direction.

Many of the results obtained in the sulphide of carbon were produced also in camphine, the analyser being in each case adjusted to the minimum of light before the metallic plate or film was introduced. I pass, however, to a very brief account of some polarizations effected by the metals themselves in the sulphide of carbon, in which case the polarizing NICOL prism was dispensed with. The results show that all the dry forms of gold accord in giving the same manifestation of action on light, whatever the state of their division, provided they be disposed in a thin regular layer, equivalent to a continuous film. It was first ascertained that a plate of crown-glass in an inclined position in sulphide of carbon gave no signs of polarity to a ray of light passing through it. When fine gold-leaf was on the glass and inclined to the ray, it polarized the light, and exactly in the same manner and direction as a bundle of glass plates in the same position in the air. More light passed than when the gold-leaf was in air, but it could not be so completely polarized; the minimum light was of a pale bluish colour. A thinned gold-leaf produced the same effect, but let more common light through. I think the difference between gold-leaf and sulphide of carbon is sensibly less than that between the metal and air. The depositions of deflagrated gold, the films of gold obtained by phosphorus, and even the heated deflagrated gold, produced polarizing effects, which, though not large, were easily recognized and distinguished from the non-action of the glass. Gold-leaf and gold films on glass produced a like effect in a camphine-bath, the results being easily distinguished from those of the glass and camphine only, in places where the glass had been cleared from gold.

Films of palladium, rhodium, silver, a plate with deposited gold particles, and a layer of deflagrated silver particles gave a like result, the effect varying in degree. The sulphuret of copper before spoken of as in contrast with the metals, gave only a doubtful result, if any.

Before concluding, I may briefly describe the following negative results with the preparations of gold. I prepared a powerful electro-magnet, sent a polarized ray across

the magnetic field, parallel to the magnetic axis, and then placed portions of the ruby and violet fluids, also of their deposits wet and dry, also portions of the gold films, of gold-leaf, the results of deflagrations, &c., in the course of the ray; but on exciting the magnet could not obtain any effect beyond that due to the water or glass, which in any case accompanied the substance into the magnetic field. In some cases very dense preparations of the ruby and blue deposits were employed, the intense electric lamplight being required to penetrate them.

I passed the coloured rays of the solar beam through the various gold fluids and films that have been described. For this purpose a beam of sunlight entering a dark room through an aperture $\frac{1}{6}$th of an inch in width, was sent through two of BONTEMPS's flint-glass prisms, and its rays either separated, or at once thrown on to a pure white screen; the different objects were then interposed in the course of the ray, but I could not perceive when any portion of a ray passed (and that was generally the case) that it differed sensibly in colour or quality from the ray passing into the preparation. In like manner, the objects were put into the differently coloured rays and observed by the reflected light, a lens being sometimes employed to concentrate the light; but I could not find any marked difference between the colour or character of the ray reflected and the impinging ray, except in quantity.