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THE FOUNDATIONS OF COLLOID CHEMISTRY

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A SELECTION OF EARLY PAPERS BEARING ON THE SUBJECT

Edited, on behalf of the Colloids Committee of the British Association, by EMIL HATSCHEK
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PREFACE.

THE British Association Committee on Colloid Chemistry and its General and Industrial Applications—consisting at present of Prof. F. G. Donnan, F.R.S.; Prof. James W. McBain, F.R.S.; Prof. Wm. C. McC. Lewis; the writer; and Dr. Wm. Clayton, Secretary—which has been responsible for five reports on the subject, published by H.M. Stationery Office, resolved at a meeting in the spring of last year that it was desirable to reprint some of the early, and in part, inaccessible literature on colloids. Further discussion of the scope of the work resulted in the decision not to include papers by living authors, and in the writer being entrusted with the duties of editor. A tentative list submitted by him was supplemented by valuable suggestions from members of the committee, and the outcome is the selection offered in the present volume.

The development of colloid chemistry has been so rapid that much fundamental work has been done by authors who are still with us. Its exclusion has, however, afforded an opportunity of directing attention to the investigations of early pioneers who have hardly received the notice they deserve. The paper by Ascherson not only records the discovery of a very interesting and important absorption phenomenon, but expresses strikingly modern views regarding its mechanism. The remarkable work of Selmi is probably also unknown to the majority of students; Svedberg quotes extensively from the paper on colloidal sulphur in his *Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe*; while Selmi's biographer, Icilio Guareschi, drew the attention of colloid chemists to his studies on pseudo-solutions in an article published in the *Kolloid-Zeitschrift* in 1911. These papers are, as far as the writer is aware, translated or republished here for the first time. Faraday's work on gold and that of Carey Lea on silver of course receives mention in every textbook, but the latter's important papers on this subject and on the photo-haloids have never been republished in English, though a complete German edition is available. The papers by Faraday and by Carey Lea in the present volume, in conjunction with the little-known paper by

Muthmann, form what may be called the first chapter in the modern history of the metal sols, the intensive study of which, during the last thirty years, has been a powerful factor in the development of colloid chemistry.

Considerations of space have determined the inclusion of one of Graham's shorter papers instead of the fundamental "Liquid Diffusion Applied to Analysis," which, however, is fairly accessible in Angus Smith's edition. The papers by van Bemmelen, finally, develop for the first time the concept of the adsorption compound which has become indispensable to colloid chemistry, and his method of studying gels, in particular, has remained the foundation of all further work on these bodies.

With the object of avoiding foot-notes the authors' references have been placed in brackets in the text (with the omission of a few which have lost all interest), while the editor's notes are to be found at the end of each paper.

The writer gratefully acknowledges the loan of the *Nuovi Annali di Scienze Naturali di Bologna* from the Library of the Royal Society, and much valuable assistance from Mr. F. W. Clifford, Librarian of the Chemical Society.

EMIL HATSCHEK.

LONDON, *February*, 1925.

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THE FOUNDATIONS OF COLLOID CHEMISTRY

ON THE PHYSIOLOGICAL UTILITY OF THE FATS AND ON A NEW THEORY OF CELL FORMATION BASED ON THEIR CO-OPERATION AND SUPPORTED BY SEVERAL NEW FACTS.

By Dr. Ascherson.

ON THE PHYSIOLOGICAL UTILITY OF THE FATS AND ON A NEW THEORY OF CELL FORMATION BASED ON THEIR CO-OPERATION AND SUPPORTED BY SEVERAL NEW FACTS.

By Dr. Ascherson.

(Literal translation of a paper presented to the Paris Academy of Sciences on 12th November, 1838.)
(*Archiv. fuer Anatomie, Physiologie*, etc., 1840, p. 44.)

Ferdinand Moritz Ascherson, born 29th March, 1798, at Fürth. Educated privately, and later at Dessau. Took part in the campaign of 1815 as a volunteer. Studied medicine at Berlin; Dr.Med. in 1827; began practice as physician in 1828. Privatdocent at Berlin University, 1831. Retired as lecturer 1854. Died 19th February, 1879.

For biography and bibliography see *Biographisches Lexikon der hervorragendsten Aerzte aller Zeiten und Völker*, by August Hirsch, Wien und Leipzig (Urban & Schwarzenberg), 1884.

In presenting the present paper to the Academy I am well aware what prejudices the enunciation of a new theory by an unknown author is likely to rouse. I hope, however, that my choice of subject may neutralize them and may procure for me an unbiased examination. For a considerable time our general physiological knowledge concerning fat has progressed but little, and, by one of the familiar jests of fate, a body, which in the living organism is usually the faithful companion of inactivity, seems almost alone to have escaped the great activity which has brought modern physiology to so high a degree of perfection. In my opinion there is always some small merit in removing such stagnation, and if the following pages should contain essential errors I hope that even their refutation may lead to useful investigations.

The fats have for a long time attracted my attention by their constant presence in the ova of animals and plants. I could not help thinking that our physiological handbooks, which ascribe to them no use except that of serving as a food by their return into metabolism, give no satisfactory clue to the purpose for which the germs of probably all organisms are provided with a substance which, free from nitrogen and

incoagulable, appears incapable of entering into their structure without undergoing important alterations. Why, I asked myself, has not Nature, which prepares with such care the first nourishment for every nascent creature and always proceeds in the simplest fashion, preferred to have albuminous substances, etc., provided fully formed by the maternal organism, if the fats are intended only to be transformed into such substances ?

These and similar considerations induced me to examine in the first instance the manner in which fat behaves in the organism. By examining microscopically small, transparent animals, larger masses of animal fat, and vegetable seeds I found that fat occurs everywhere in the state of emulsion, i.e. in small droplets of $\frac{1}{40}$ to $\frac{1}{200}$ mm., and even smaller, which are suspended in a transparent aqueous fluid. The smallest of these droplets reach the dimensions of Brownian molecules. They also show molecular movement and allow so little light to pass that the masses formed by them, e.g. the fat of insects, appear almost opaque.

In the small microscopic crustaceans the fat, owing to the spherical form of the droplets and their often very vivid colouring, presents a very dainty picture. Thus in daphnis, cyclops, etc., it is frequently scarlet, and Swammerdam, who took these droplets for eggs, rightly ascribes to them the red colour of the animals, which, as is well known, has frequently given rise to the tale of a rain of blood. In the pale individuals, such as, e.g., Strauss appears to have observed (*Mem. du Musée*, tt. V and VI), the fat is almost colourless. In some individuals of *Cyclops quadricornis* I have found fat of three colours, viz., clear as water, deep orange approaching red, and dark Prussian blue. As the last two colours are complementary, I think it necessary to add that the appearance was certainly not due to an optical delusion. It is striking that these droplets of fat, although floating freely in a transparent liquid, change their positions but slightly during the most violent movements of the animal or its organs, which leads to the conjecture that they are further enclosed in transparent receptacles.

In the very transparent larva of a chironomus, which was kept under water and builds small cells from the root of lemna, I saw the fat below the skin enclosed in large, flat, irregular cells, which looked like the frontiers on a map. The drops were single and separated from one another by large, fairly equal interstices. Some cells could always be found in which they were arranged very regularly in groups of three to five droplets. As long as the animal is intact the fat droplets remain completely immovable; as soon, however, as the cell is torn by pressure on the animal, they immediately start moving (as in the crustaceans) and float away, while some of them always lose their spherical shape and become oblate. When I treated masses of fat from larger invertebrates or vertebrates with the compressorium I always obtained droplets of oil which appeared completely similar to those described. I think that I have also, like Leeuwenhoek and Raspail, observed them in the interior of the familiar fat cells of vertebrates, but I have not been able to arrive at certainty on this point.

In special conditions, which, however, I have not yet been able to define, the fat of vertebrates is often transformed by maceration into a crystalline mass in less than twenty-four hours, probably adipocere.

A short time ago I found that the sporidiola of fungi, small spherules which have long been known to occur in the spores of the Hellvellaceæ, and which I in common with several other observers have found in the spores of the majority of fungi, are nothing but oil droplets (see *Poggendorff's Ann.*, Bd. 44, p. 639). When the spores of a peziza, e.g. of *Peziza macropus*, are compressed between two glass plates, the sporidiola, subdivided into smaller spherules, can be seen to escape through a fissure without any residue, which obviously proves that they are drops of a liquid floating freely.

Having been engaged for several years in observing the development of a number of fungi, I have often noticed that the sporidiola as well as the spores themselves originate through the fusion of smaller droplets or spherules, with which the sporangia are filled at an earlier stage. I have even noticed

several times that the sporidiola or oil droplets already arrange themselves in regular groups before a trace of the spores themselves is to be seen. These observations and others, which I omit from lack of space, have convinced me that the oil or fat, without undergoing decomposition, must yet play an important part in the development of the fungi, a family of plants whose chemical composition, as is well known, closely approaches that of animals.

This result induced me to extend my investigations and to try whether I could claim for the fats a similar share in the first development of animals. A new and important discovery had just added, if possible, to the interest of this research. While the most famous physiologists appear to be agreed that the primitive tissue of animals consists of small granules or solid spherules, an opinion which, i.e., Valentin appears to have maintained in his prize essay (see his *Handbuch der Entwicklungsgesch.*), Schwann, one of our most excellent observers, had stated emphatically that muscles, nerves, vessels—in one word, all the tissues of the animal body—were nothing but transformed cells.

Starting from the assumption that it is never the facts which contradict one another, but that all disputes arise from their incomplete observation and varied interpretation, I endeavoured to find new facts fitted to elucidate the relations between the spherules observed by v. Baer, Carus, Valentin, and others, and the cells of Schwann. Valentin, in the book quoted above, mentions several kinds of spherules, without, however, giving a closer description, which would perhaps have been inadequate anyway without illustrations. To start, therefore, from a definite basis, I have examined the spherules of the egg, which are sufficiently exactly described by Valentin and appeared to me to present sufficient differences to decide the question. I thought that I could spare myself the difficult and troublesome investigation of the embryo if I should succeed in finding already in the unfertilized ovum cells as well as the structures or substances from which they originate.

In the ova of the principal classes of the animal

kingdom I was able to distinguish the following species of globules :

(1) Easily distinguished and frequently coloured oil drops, which are found in large numbers in the yolk of oviparous animals, singly in the liquid of Graaf's vesicle. A discovery to be referred to later in its proper place gave me the clue to the strange appearance which some of these drops present. They are by no means always spherical, but are found oval, pear-shaped, etc., e.g., in the yolk of the hens' egg, and their dull surface, which even shows small wrinkles, proves that they are surrounded by a skin. Sometimes pale, shaded circles may be noticed in their interior, which look like cavities, thus producing a striking resemblance to polygastric infusoria. In other cases they are so closely covered by very small globules that they are rendered almost opaque.

(2) Corpuscles covered with very minute granules and bearing the greatest resemblance to pus corpuscles. Like them they are of somewhat irregular shape, approaching the spherical. These corpuscles form, *inter alia*, the germ disc of the mammalian ovum, and appear to coat the internal surface of the folliculus. I have found them in man, cattle, and sheep. If the irregular masses of these corpuscles which float in the liquid of the follicle are compressed strongly, a considerable quantity of liquid fat is extruded. I cannot find that anyone has yet noticed that the ovaries of young birds and mammals contain so much of these corpuscles that they appear to consist almost entirely of them and that they behave in the compressorium like a sponge soaked in fat. These granular corpuscles are evidently cells, like the corpuscles of pus, of mucus, etc. (primitive cells according to Henle), and like them are mostly dissolved by dilute acetic acid, leaving one or more nuclei behind. Beyond doubt these are the cells found by Schwann in the strata of the germinal layer.

(3) The smallest globules in the ovum, as far as their shape can still be recognized by the microscope, are perfectly spherical. They show a sharp black edge and a transparent disc ; in one word, they resemble most completely the oil

drops of molecular size which are observed when a small spider or a small caterpillar or the like is compressed under the microscope. They always appear in the ovum sooner than the globules described previously. The ova of invertebrates and of birds at the beginning of their development are filled with them to such an extent as to be opaque. They are also found in the young ova (or follicles ?) of mammals, and I believe I have observed them in fully developed human and other mammalian ova. The yolk of hens' eggs consists in great part of these globules. (A fourth kind of corpuscles is found in ova, which are barely visible even at high magnification, and which are distinguished from the corpuscles just described by their pale outline. I shall refer to them again elsewhere.)

It is impossible to understand why physiologists almost unanimously ascribe to these molecular globules a nature quite different from that of the fat globules found in ova. Coste appears to have been the only one to suspect a certain similarity between the molecular globules in mammals and the fat droplets of yolk, and he has therefore been criticized by Valentin (*loc. cit.*, p. 4). Nevertheless, the simplest and most natural assumption seems to be that they are drops of oil. Their perfect sphericity, the natural shape of a drop surrounded by a heterogeneous liquid, their complete resemblance to the smallest fat droplets of animals and plants and to the sporidiola of fungi, the transitions in size and colour from unmistakable oil drops to these molecules, which are to be noticed particularly in the ova of invertebrates—all this tends to confirm the view expressed above, which, in my opinion, is proved correct by the following experiments. I have carried them out on the eggs of quite young chickens, so as to have the molecules more isolated :

(1) Alcohol coagulates the albumin of the eggs, but leaves the molecules quite liquid, so that they escape almost completely under strong pressure.

(2) The expressed globules disappear completely, or almost so, in ether.

(3) Alternate maceration and compression appears to

unite the globules into large ones, but this experiment is not quite reliable, since these larger drops may also arise from the substance of the ovary, which, as mentioned above, is permeated by fat.

These facts appear to me to prove conclusively that the molecules in the ovum are droplets of oil; and since their formation precedes that of the other corpuscles in the ovum, and particularly that of the cells, the assumption is not unreasonable that the oil is just as essential a factor in the formation of cells as, according to my observations, the oil drops hitherto called sporidiola are for the formation of the spores of fungi, which are also single cells.

While considering in what manner the liquid referred to could act, I found myself compelled to examine the theories of cell formation. I had to confine myself to the theory of plant cells, as the animal cells have been discovered only recently and a theory of their formation is lacking.

There are really only two theories designed to explain the formation of cells or vesicles from a liquid. The one assumes that solid globules become hollow and expand. This is conceivable, but the formation of those elementary globules still remains to be explained. The second theory assumes that the coagulable substance contained in the interior of a spherical drop coagulates on its surface, forming a vesicular membrane which encloses the other liquids. This theory would be entirely satisfactory if it could only explain how, without some *vis occulta*, a drop in the middle of a homogeneous liquid, or in contact with solids which have imbibed the same liquid, could isolate itself sufficiently to assume a spherical shape.

This theory inspired me with a third one, which appears to remove all difficulties. Imagine within a coagulable liquid, e.g. liquid albumin, a drop of oil, and assume that the albumin for some reason coagulates at the surface of contact: then a spherical vesicle will necessarily form round this nucleus, which, once formed, can easily alter its content by exosmosis or endosmosis. (All that is here essential is to explain the first formation of a cell; to explain its further metamorphoses

one may well call in those vital forces which no reasonable person will imagine can be dispensed with entirely in explaining organic processes.)

I was surprised at the simplicity of a theory which sufficiently explains the formation of cells by the aid of two substances to be found everywhere, in conformity with physical laws, and at the same time ascribes to the fats an indispensable function well calculated to make their constant presence in the germs of organic beings intelligible. To confirm this theory by experiment I endeavoured to find some means of actually producing the assumed coagulation of the albumin, and, with a pleasure which will be readily understood, I made the important discovery: *that coagulation in form of a membrane occurs inevitably and instantaneously when albumin comes into contact with a liquid fat*,[1] and that consequently an oil drop cannot be surrounded even for a moment by an albuminous liquid without a vesicular membrane or a cell forming round it. For the sake of brevity I shall call the property of forming membranes by contact *Hymenogony*, and the membranes thus formed *Haptogen* membranes.

The simplest way of producing this interesting phenomenon is to place a drop of fresh white of egg and a drop of olive oil close to each other on a glass plate and to unite their edges. According to hydrostatic laws the oil covers the white of egg in a thin layer, and the consequence is the almost instantaneous formation of a delicate and elastic membrane, which, by a kind of contraction, soon becomes wrinkled, sometimes in a very regular fashion. Or white of egg, diluted with an equal or double volume of distilled water, is covered with a layer of any animal or vegetable oil, and the oil, divided partly into small drops, is then forced some distance into the white of egg by blows of the palm on the rim of the vessel. The descending motion of the oil drops lasts a moment only, but this moment is already sufficient to cover them with a membrane and to form true cells. The existence of the membrane is proved by the often very strange shape of the artificial cells: it prevents the oil drops from resuming the spherical shape lost by their being forced violently into

a viscous liquid, and they are the more irregular the more consistent the liquid and the thicker the haptogen membrane. They have the shape of a sausage, a pear, spindle, or club, etc., and a strange fact, which I am unable to explain, is that the cells are often too large, so that their wrinkles can be seen with the unarmed eye, or at least by the aid of a low-power magnifier. I have already stated above that I have found cells filled with oil showing the same anomalies in the yolk of birds' eggs and Graaf's follicle.

For studying the properties of the haptogen membrane a few drops of oil are shaken with dilute white of egg or blood serum, and a small drop of this mixture is examined under the microscope, first uncovered and then between two glass plates. For greater contrast a coloured oil may be used, e.g. one digested with alcanna. The membrane formed by the contact of oil and albumin is surprisingly tough and elastic. It is often possible to compress the artificial cells so strongly that their circumference is increased fourfold, just as Fontana and Dellatorre have observed with blood corpuscles, which altogether show a striking resemblance to the artificial cells. It is also possible, by shifting the upper glass plate, to roll the large, flattened cells three or four times round their axes without tearing them, and the membrane does not prevent the fluid contained in it from adapting itself to all the obstacles it encounters nearly as easily as if it were quite free. It was frequently possible to divide a cell somewhat as a glass tube is parted in the blowpipe flame, and the membrane drawn out into a thin tube closed itself at the point of division in a point, without allowing the slightest quantity of fluid to escape. This manner of division must occur frequently when the cells are shaken with liquid, as a number of artificial cells are always found which terminate in a point.

It can hardly be doubted that hymenogony acts under the influence of life just as it does in the chemist's test-tube. The irregular cells which I have found in ova, and the dull surface and slight irregularities which a practised eye fairly easily discovers on the globules in milk or yolk larger than $\frac{1}{80}$ mm.,

prove the existence of a haptogen membrane formed in the living animal. This skin appears to be the only cause of the spherical shape and of the isolation exhibited by drops of fat in plants and animals according to my observations; likewise in milk, where Raspail had already conjectured the existence of a membrane on the globules, and in artificial milk. I have shaken oil with distilled water and have found that all drops which can conform to hydrostatic laws assume a lenticular shape with thin, very transparent edges, while they preserve their spherical shape and black margins even in the largest volume of water, provided they have previously had an opportunity of coating themselves with a haptogen membrane by the aid of a little mucus or albumin. This very decided difference can be perceived most easily when a few drops of oil are shaken with water containing only a little albumin. It is then still possible to distinguish among the droplets, the diameter of which does not exceed $\frac{1}{700}$ mm., those surrounded by a membrane, which increase in number with the albumin content of the liquid, from those which have remained free. The latter are best seen by focusing the microscope exactly on the surface of the liquid and illuminating from the side. The formation of a few globules which do not become flattened again is perhaps the most delicate reagent for discovering in distilled water the slightest trace of an organic substance, and I must add that up to now I have not found any which has passed this test completely. I even have reason to believe that the slightest organic admixture which water breathed out of the lungs may contain is already sufficient for the formation of a few oil globules.

The haptogen membrane, of course, forms equally on a drop of white of egg surrounded by oil, but the appearance is entirely different. The lower refraction of albumin causes the spaces occupied by it to appear void, and an oil drop containing smaller drops of albumin accordingly looks exactly like a polygastric infusorium, e.g. a vorticella. I have already mentioned that I have observed similar objects among the globules of yolk, whose genesis is easily explained by what has been said above, as are likewise the apparent voids in the

substance called by Dujardin "Glu animale" and found by him in the liver fluke and in several infusoria, while I have seen it in several microscopic crustaceans.

Hymenogony appears to occur to some extent between all heterogeneous liquids; but among those I have examined only albumin, oil, and Peru balsam are capable of forming, each with the two others, a distinct membrane covered with wrinkles.[2] There is a very easy means of testing the tenacity of the haptogen membrane. The two liquids to be examined have only to be brought into contact on a glass plate and the point of a needle drawn from one liquid into the other. When the two liquids possess the property of hymenogony in a high degree, the small drops which are in this way transported from one liquid into the other detach themselves hardly or not at all and assume an elongated or irregular shape; when, however, the hymenoplastic relation among them is weak, the droplets detach themselves easily and become perfectly spherical. This occurs, e.g., when mucilage and oil are used, and proves incidentally that the viscosity of the liquids is not the cause of the phenomenon. In general, a high degree of hymenogony is required for the formation of a distinct skin on the surface of two drops placed in contact, and there are several albuminous liquids which rapidly form even irregular cells and nevertheless produce only a very thin and almost imperceptible membrane, the formation of which takes a considerable time. This peculiarity, which is found, e.g., in the serum of human blood, has afforded me the welcome opportunity of following the genesis of the haptogen membrane under the microscope.

Having placed a drop of serum and a drop of almond oil in contact, I saw small, pale, and barely visible particles appear at the place of contact, such as are seen everywhere where infusoria are generated or organic substances are decomposed, and such as I have perceived in ova. These particles approached one another and at first formed small irregular accumulations, which, however, by the addition of further particles, soon assumed a spherical or discoid shape and showed some resemblance to pus corpuscles. These discs again united and

grew in circumference, at the same time losing their regular shape, and thus formed lobes of skin which were almost imperceptibly granulated on their surface. (These lobes very much resembled the so-called primitive ovary of the infusoria.) Finally, the haptogen membrane was formed by the coalescence of these lobes, but then the granulation just described disappeared gradually, and often gave place to a surface covered with small, irregular droplets, like a window pane covered with dew. Frequently every trace of texture disappeared ultimately, and the membrane could be recognized only by its slight wrinkles.

I omit several attempts to determine the chemical reactions of the haptogen membrane formed from albumin and oil, as I found later that reagents act quite differently on the membrane formed by the contact of two drops, and on those produced by shaking and consequently closed all round. Thus, to give an instance, dilute acetic acid instantly dissolves the first kind of membrane, whereas it even appears to penetrate into the interior of artificial cells without destroying them. This is one of the many reasons which induce me to regard hymenogony as a physical property, as a kind of capillary condensation which proceeds at the surface of heterogeneous liquids in contact,[3] but I must leave it to the physicists to decide this not unimportant question.

After all that has been set forth here, I believe it is no longer possible to doubt that cells are really formed in the animal organism from fat and albumin, as theory leads one to conjecture and as experiment shows. I propose to call these cells " elementary cells," since I believe that all the cells of the animal organism are only metamorphoses of the original, oil-filled cells, and there is no reason for assuming yet another, unknown, manner of formation. I even believe I have several times found transitional forms, especially in the ovaries, but I leave it to unbiased observers to confirm this fact. Cells have been known for some time which, although otherwise unlike the elementary cells, yet contain liquid fat and thus appear to betray their mode of origin. Henle has found them in the parenchyma of the liver, in Meibom's glands, and in

other places. There is no difficulty either in deducing the observed shapes of cells theoretically from elementary cells, and conversely observation actually reveals the modifications which theory predicts. The multiplication of the elementary cells is a matter of moments. As nearly all the fluids of the animal body contain albumin, an oil drop cannot remain in them for an instant without surrounding itself with a cell; nor can it divide into several, be they two or a hundred, without causing the formation of as many new cells.

I have expressed the surmise that the elementary cells may be able to alter their contents by endosmosis and exosmosis, and something of the kind may be observed with the artificial cells.[4] A quantity of them was prepared by shaking oil with albumin, and they were nearly all elongated and wrinkled. Then a drop of this emulsion was diluted with a dram of water. The cells became tense and assumed a more spherical form, just as blood corpuscles do in water. Although the wrinkles of the larger cells disappeared yet their envelope looked darker, and at high magnification it could be seen to be covered with an immense number of oil droplets. It is, of course, difficult to decide whether bodies so small are placed on the internal or external surface of a delicate membrane; yet I believe that these droplets were on the outside of the membrane and had been transported there by exosmosis, as in several cases I saw a few larger drops appear instead of many small ones, and these were distinctly on the outside of the membrane.

When I added acetic acid to the water I saw the cells swelling to such an extent that the majority of them burst; some appeared to save themselves by extruding a fairly large drop of oil. The oil-filled cells, on the contrary, are subject to perceptible shrinkage when immersed in the same liquid which they contain. Their wrinkles increase, the haptogen membrane appears to lose its elasticity, and this is even the best means of demonstrating conclusively its existence, for in these circumstances the cells may discharge their contents under moderate pressure without losing much of their previous size and shape. (I have found that blood corpuscles

also become wrinkled in oil, though it is difficult to free them sufficiently from serum to demonstrate this behaviour.)

[EDITOR'S NOTE.—The remaining pages of the paper are devoted to speculations on the structure of the ovum, the ovaries, the function of the blood corpuscles, etc., which are of purely physiological interest and outside the scope of this volume. The paper concludes with the following summary.]

Synopsis of the most Important Facts and Conclusions in the Present Disquisition.

(1) Contact between albumin and a liquid fat always leads to the formation of a tough and elastic membrane.

(2) This membrane is produced by the aggregation of an infinite number of small particles, as can be observed when the formation of the membrane is retarded by the procedure described in the paper.

(3) A drop of oil surrounded for an instant only by an albuminous liquid is immediately enclosed by a cell membrane, and it is thus possible to produce artificial cells at will.

(4) In the ova of mammals and of birds large cells filled with oil are found which in appearance and physical properties completely resemble the artificial cells.

(5) All drops of liquid fat occurring in plants and in animals are enclosed in cells which may be called elementary cells.

(6) The tissues of the animal organism consist of cells which may be regarded as metamorphoses of oil drops or elementary cells.

(7) The blood corpuscles are cells containing (besides pigment) liquid fat, and their principal function is to transport it to wherever formation of new cells is to take place.

(8) The primitive condition of the ovulum of animals is that of a drop of fat, and Wagner's "germ layer" is the remains of this drop.

(9) The cells of plants are likewise formed by the aid of a heterogeneous liquid, but it remains to be discovered whether the fatty oil alone, or yet other liquids, take part in the process.

[1] The adsorption of albumin has been studied chiefly by Ramsden, *Arch. f. Anat. u. Physiol., Physiol. Abt.*, 1894, p. 517; Proc. Royal Soc., **72**, 156 (1903); *Zeitschr. phys. Chem.*, **47**, 336 (1904). He also found that the albumin is denatured by adsorption.

[2] Many other organic liquids show the phenomenon with fresh albumin sols, e.g. carbon tetrachloride or chloroform.

[3] This remarkable anticipation of what is substantially the modern definition of adsorption appears to have been completely overlooked.

[4] Endosmosis can easily be shown by using chloroform as the "oil." Sufficient water diffuses into the chloroform droplets to burst the albumin membranes.

STUDIES ON THE DEMULSION OF SILVER CHLORIDE.

A STUDY OF THE PSEUDO-SOLUTIONS OF PRUSSIAN BLUE AND OF THE INFLUENCE OF SALTS IN DESTROYING THEM.

By Francesco Selmi.

STUDIES ON THE DEMULSION OF SILVER CHLORIDE.

By Prof. Francesco Selmi.

(*Nuovi Ann. d. Scienze Naturali di Bologna*, Serie II, t. IV, p. 146 (1845).)

Francesco Selmi, born 7th April, 1817, at Vignola near Modena. Licentiate of Pharmacy at about twenty. For three years Assistant and then Professor of Chemistry. Left Modena in 1848 for political reasons and entered Sobrero's Laboratory at Turin. Appointed Professor of Physics, Chemistry, and Mechanics at Collegio Nazionale in 1848. Implicated in revolutionary movement at Modena in 1859; returned there after the revolt and was elected Rector of the University. Called to Bologna as Professor of Chemistry in 1867. Discovery of ptomaines published 1870–71. Died 13th August, 1881, at Vignola.

For complete biography and bibliography see Icilio Guareschi: "Francesco Selmi e la sua opera scientifica" (*Mem. d. R. Accad. delle Scienze di Torino* (2), **62**, 121–272 (1911)). A portion of this paper dealing with Selmi's work on colloids was translated by Wo. Ostwald and published simultaneously (*Koll. Zeitschr*, **7**, 113 (1911)).

What Emulsions and Demulsions are.

The term emulsion, as every one knows, means an opaque and somewhat dense liquid, composed of a vehicle, generally water, and of one or more bodies in a state of extreme division which remain diffused, but not dissolved, therein. Berzelius considers that emulsions differ little from solutions and calls them similar to the latter, a view which in my own opinion is correct. The real difference between them consists in this: that in the former the diffused body penetrates the mass of liquid in the form of extremely fine particles which, like vapour bubbles, contain a certain number of molecules, while in the latter the dissolved substance pervades it in a state of molecular attenuation, or reduced to gas, and thereby rendered capable of allowing free passage to a portion of the rays of light or even the whole pencil of light.

In both cases two causes combine to keep the bodies thus subdivided: (1) The property inherent in them of resolving into minute particles, and of spreading and diffusing into the liquid immediately they are touched by it; (2) the adhesion

between the emulsified or dissolved particles and the films of vehicle in which they are imbedded.

Some emulsified substances, when the emulsion is viewed by the microscope, appear dispersed in the liquid in the shape of small globules, sometimes perfectly spherical, sometimes more or less squeezed out or elongated; others appear as shapeless fragments without any regularity.

Some remain associated with the vehicle for a long time, while others have a greater tendency to deposit; some derive from liquid or soft bodies, others from solid and hard ones.

The differences are sufficiently marked to make it advisable to distinguish the two conditions of emulsified substances by appropriate names which indicate whether they belong to the one or the other; for which reason I propose to retain the name of *emulsions* for the combination of a liquid with liquid or soft principles dispersed in the form of minute globules, and to call *demulsion* the association of a liquid with solid and hard principles reduced to exiguous, shapeless particles.

What is already known concerning the Demulsion of Silver Chloride.

The principal properties of this demulsion could not escape the watchful and attentive eye of the chemist, as he had frequently to deal with it in analyses for the determination of chlorine or of silver, and they are indeed to be found noted in the brilliant *Treatise of Chemistry* of Berzelius, in the article in which he speaks of silver chloride: (*a*) "In analysis [it reads] advantage is taken of the insolubility of silver chloride to determine the hydrochloric acid contained in a liquid. To accomplish this it is necessary to heat the liquid from which the chloride is to be precipitated, and, when there is no special reason to the contrary, it is advisable to acidify with nitric acid, as the precipitate then settles more easily and consolidates, and can be washed more successfully. When the liquid is perfectly neutral the precipitate remains suspended in it for a long time, makes it milky, and passes

with it through the filter. Hence it helps to begin washing the precipitate with water acidified with nitric acid ; without this precaution it sometimes happens that, when the saline solution has been removed by repeated washings, the last lot of pure water turns milky and runs through turbid. Many insoluble bodies possess similar properties." [1]

From the words quoted it appears clearly that the following are observed facts : (1) The property possessed by silver chloride of subdividing in, and rendering turbid, pure water ; (2) the power of nitric acid in small doses to accumulate the particles of demulsified silver chloride, whereby they become sufficiently large not to pass through the pores of the paper ; (3) that the same faculty belongs to saline substances ; (4) that the phenomena presented by the silver chloride are exhibited by many insoluble principles.

My studies of the emulsion of sulphur, and the demulsions of sulphur and biniodide of mercury, undertaken with the view of throwing light on the action of the vibrations of soluble and dissolved substances, have induced me to investigate specially the demulsion of silver chloride and its behaviour in presence of various soluble bodies ; having discovered some new things, I have recorded them in the present paper, which may be called related to the others composed by me on analogous subjects.

Preparation of the Demulsion of Silver Chloride.

Having tried which among the possible methods of preparation should be used in preference, so as to obtain the demulsion most sensitive to the action of precipitants, I have found that the most suitable method is to add, drop by drop, a neutral and extremely dilute solution of silver nitrate to distilled water containing a little sal-ammoniac or common salt. As the drops of silver nitrate fall into the salt solution a turbidity is formed, which should be mixed with the whole mass of liquid by rapid agitation with a glass rod, while the addition of silver salt is continued until nearly all the chlorine is reduced to silver chloride, care being taken to avoid

an excess of nitrate and rather to leave over some of the alkaline chloride.

The demulsion of silver chloride thus prepared is milky, very white, and stable for a certain time without depositing; yet after a few hours the demulsified substance begins to settle as flocculent aggregates which are difficult to demulsify afresh; beaten for a long time, it does not alter nor clear, because the silver chloride remains distributed in the menstruum without curdling.

Experiments on the Demulsion of Silver Chloride with various Reagents.

It would seem at first sight that nitric acid should strongly coagulate the demulsified silver chloride, because we have seen that it is sufficient in small quantity to aggregate the particles so as to make them larger than the pores of the filter paper. But the actual fact does not agree with this deduction: if a few drops of nitric acid be poured into the demulsion, it turns less milky, without, however, coagulating into large flakes as promptly as I have observed in other circumstances. It then appears that the effects produced by nitric acid are confined to associating together a few particles without continuing to assemble them in numbers sufficient for the formation of a coarser coagulum or fairly large flakes. More powerful than the action of nitric acid is that of potassium sulphate solution. If a volume of this liquid is added to one volume of the demulsion, care being taken to mix them without violent or long-continued agitation, the demulsion at first appears not to be destroyed; on being stirred rapidly and energetically, however, the whole of the silver chloride is observed to coagulate into large flakes, which are very compact, because they settle instantly and leave the liquid clear and almost brilliant.

With slight differences in their action the following behave like potassium sulphate: sodium sulphate, potassium chloride, sodium chloride, ammonium chloride, barium chloride and nitrate, potassium chlorate, lead acetate, zinc

chloride, and some other salts. The differences which can be observed consist in this—that some of the saline substances effect the precipitation of the silver chloride somewhat more quickly, with the production of aggregates of smaller or larger size, while others coagulate more slowly.

Silver nitrate and mercury bichloride deserve to be mentioned specially for their action on the silver chloride demulsion, and that for two reasons: their precipitating power and their influence in modifying the effects of light on the silver chloride.

If a little silver nitrate solution is added to a freshly prepared and neutral demulsion of silver chloride, the chloride, which until then remained diffused in the liquid, at once separates as voluminous, heavy curd, which falls rapidly to the bottom as if impelled by strong pressure;[2] the liquid becomes clear at once and brilliant after a short time, while the chloride remains at the bottom all collected together like the coagulum of soft sulphur precipitated from its emulsion. Agitation greatly assists the reaction, since stirring the liquid with a rod accelerates the formation of curds, and thus settlement.

Corrosive sublimate, on the other hand, seems hardly to destroy the demulsion of silver chloride; this body remains suspended for a long time in the mixed vehicle and separates little by little as a light, flocculent coagulum.

Silver nitrate exhibits a further peculiarity: it allows the precipitated silver chloride to blacken in diffuse light, more than the other acid and saline solutions permit it to do. Thus, when solutions of potassium sulphate, barium nitrate, sal-ammoniac, dilute nitric acid, and silver nitrate, each containing some silver chloride precipitated from the solution, were exposed in the same spot, in beakers of the same colourless glass, the following changes were observed after a couple of hours: the chloride in the first three had turned an ashy black, with some tendency to bluish black; the chloride in the fourth had assumed a brown colour tending to reddish, while the chloride in the fifth appeared a decided black. Similar phenomena were, moreover, noted by me in another

silver chloride steeped in lead acetate solution. Direct sunlight does not disturb the above diversity of colour, but, on the contrary, renders it more conspicuous.

The bichloride of mercury, on the other hand, has an action opposite to that of silver nitrate, inasmuch as it preserves the silver chloride unaltered by exposure to the sun's rays, and it exerts this influence so energetically as never to allow decomposition to take place, even when, through protracted exposure to direct sunlight, the whole of the vehicle has evaporated and the fixed portion has been left perfectly dry on the bottom of the vessel. Bichloride of mercury is not the only body capable of preventing the decomposition of silver chloride by light; Berzelius and Thénard state that sulphuric acid, ferric chloride, and cupric chloride prevent the slightest blackening.

Silver iodide is also protected from the decomposition which it undergoes in the presence of light by being bathed with a solution of corrosive sublimate; not, indeed, to the extent of remaining completely unaltered like silver chloride, as it sometimes loses its yellowish tint and becomes bleached, yet with sufficient energy to escape turning black or even a simple brown in the portions struck more immediately by the rays of light.

Reflections on the Observations described above.

I do not mean to attribute much importance to the things I have described concerning the demulsified silver chloride and its precipitation from acid and saline solutions; the very simplicity of the experiments carried out would not permit it, and the results obtained have no claim to extraordinary novelty. Nevertheless the connexion between them and other experiments and observations made by me, the evidence which they provide of the existence and influence of molecular vibrations in dissolved substances, induce me to discuss them at greater length, considering them from a point of view different from that from which others have regarded them.

In the first place, I must dwell on the precipitation of

the demulsified silver chloride. This body possesses the property of remaining permanently subdivided into extremely minute particles, being thus reduced to a state of diffusion in the water. These particles then show hardly any adhesion among one another and require an external impulse which brings their small masses together and drives them against one another with sufficient force, so that the intimate contact thus brought about leads to their association, and consequently to the formation of larger masses.

In our case the external impulse is derived immediately from the substances contained in those solutions which are capable of destroying the demulsion; these cannot operate by inducing changes in the nature of the menstruum since the silver chloride, not being truly dissolved, should not be affected by such small differences in the density as the addition of a little salt can produce; the increase in density should, on the contrary, assist in keeping the demulsified body longer in suspension.

Since then the precipitation of the silver chloride cannot be due to some small change in the density of the liquid, it becomes necessary to investigate to what cause it is due. If we consider that not all substances possess the same precipitating power and that rapid and continuous agitation promotes the formation of coagulum and its settling; if we remember, further, that certain of the precipitants have great, and others slight, energy, independently of their nature and quality, and in no proportion to their greater or lesser solubility or affinity; if we consider, lastly, that stirring cannot act except by producing vigorous agitation of the molecules dissolved in the liquid, we shall easily arrive at this conclusion: that the precipitation of the demulsified silver chloride is brought about by the force of the internal motion of the salts and acids added to the demulsion. In fact, if we admit that an external force is required to aggregate the particles of silver chloride into flakes and curds, that precipitation is not caused by the altered density of the medium; if we recognize that neither the affinity nor the variable solubility, nor the acid or saline character can have any influence, and if, finally, we note that

agitation powerfully assists the reaction, then there remains no way of rationally explaining the phenomenon except by the obvious existence of molecular motions and vibrations.

I consider it unnecessary to collect arguments calculated to prove that substances when dissolving in a menstruum move by diffusing and dilating through the mass of the same, and that shock and agitation set in motion the molecules already in solution, because the phenomena of lime water, studied by Bizio, and several others related by Liebig in his *Introduction to Organic Chemistry* seem to me more than sufficient, and because they speak very clearly and have the approbation of the learned. Unless this property of soluble solids, to be put in motion when placed in contact with a liquid, be recognized, it would be impossible to explain how gradually, in a perfectly quiet place, the solid disintegrates, resolves itself into molecules, and penetrates the liquid, thus entering into a peculiar association without losing any of its chemical properties.

If it cannot be denied that the molecules of a body are moved by the agitation which the solution undergoes, it seems to me repugnant to common sense to refuse to admit that these motions have some influence on the molecules and on the heterogeneous particles on which they impinge, communicating an impulse to them. They will collide with one another, and the effect will vary according to their nature, disposition, and tendency; they will decompose and crystallize, as Frémy has observed for the hydrates of metallic oxides boiled in alkaline or saline solution, or else they will agglomerate, as happens with soft sulphur, soap, soluble casein, and finally with mixtures of silver chloride and saline solutions. This likewise explains the curious difference in the precipitating power of various solutions, because each dissolved body will have its particular motion, and each emulsified or demulsified substance will be affected by the blows in the special manner proper to its nature. Silver nitrate, which precipitates the demulsified silver chloride so vigorously, will in its motion produce such vibrations as greatly affect the particles reduced to the demulsified state,

and they will collect and aggregate into large and massive curds. Corrosive sublimate, which destroys the demulsion very slowly, will excite vibrations of such a nature as not to cause a certain number of demulsified particles to join together ; hence curds of perceptible size will not be produced.

As regards the property of sublimate of preventing the blackening of silver chloride, I will add that this was recognized by Gay-Lussac, who noticed that a liquid containing both silver and mercury, when precipitated by common salt, gave a deposit which was unaffected by light. It is probable that in this case the bichloride of mercury acts similarly as the perchlorides of iron and copper, i.e. by reducing the black subchloride of silver to white chloride. I have, in fact, found that silver oxide, which gives off oxygen when exposed to the sun's rays, and blackens considerably through this reduction to suboxide, when immersed in sublimate solution and exposed to direct light, evolves oxygen and gradually becomes white.

It is to be noted in this connexion that the hydrated silver oxide, when mixed with sublimate solution, does not displace the mercury but, in the cold and in diffuse light, remains in contact without apparent reaction ; and that sublimate prevents the blackening of silver chloride not only in solution, but also when intimately mixed with it and dry.

[1] E.g. tellurium, boron, zirconium, arsenious sulphide : cf. Thé Svedberg, " Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe." Leipzig, 1920.

[2] Silver nitrate acts as an energetic coagulant through the complete removal of the stabilizing ion. For the conditions of stability of silver haloid sols generally cf. A. Lottermoser, *J. prakt. Chem.* (2), **72**, 39 (1905) ; **73**, 374 (1906).

A STUDY OF THE PSEUDO-SOLUTIONS OF PRUSSIAN BLUE AND OF THE INFLUENCE OF SALTS IN DESTROYING THEM.

By Francesco Selmi.

(*Nuovi Ann. d. Scienze Naturali di Bologna*, Serie II, t. VIII, 401 (1847).)

Having for some time devoted attention to the study of those curious compounds of a liquid or vehicle with soft or hard substances held suspended therein in the form of very minute particles, compounds called *emulsions* or *demulsions*, according to the mode in which the highly subdivided substance is associated with the liquid, I have lost no opportunity to resume and continue the work from time to time so as to test the evidence from all sides and to ascertain what are the most remarkable phenomena to which these singular associations of two substances owe their origin. Beginning with the demulsions of mercuric iodide I passed to the study of the sulphur emulsions and demulsions, then to the very transient emulsion of silver chloride, and I did not omit to carry out some experiments on that special mode of combination between casein and whey which cannot be called true solution, but is rather swelling or expansion. Here I shall give an account of some experiments carried out with the pseudo-solutions, or false solutions as they are called, of the Prussian blues in water, in alcohol, and in other media, relating the observed facts and showing at the same time how much they resemble those described in the previous papers.

What a Pseudo-solution is, and why the Prussian Blue incorporated with a Vehicle should not be called truly Dissolved.

Speaking of solution in another paper I have noted that it occurs whenever a body, hard, soft, or liquid, unites with a liquid substance without strictly combining with it, and diffuses in it uniformly subdivided to the same molecular fineness to which it is reduced when transformed into an elastic fluid; hence solution is the expansion of a body in

the form of gas within a liquid which takes the place of the atmosphere (Bizio). In the emulsions, on the other hand, I have shown that the body dispersed in the vehicle is less divided and comminuted than it is in solutions, since it exists there in the form of globules or fragments of sufficient size to be visible in a powerful microscope, sometimes quite opaque and sometimes pellucid, but always devoid of that brilliant transparence proper to the exiguous particles of gasified matter.

There is, however, a special type of association which stands midway between solution and emulsion, because the body dwelling in the vehicle by its complete transparency would induce one to believe that it is dissolved, whereas, on the contrary, it is dispersed therein in flakes, vesicles, or other shapes. Alumina and silica offer us remarkable examples of this, since they, when hydrated and of recent origin, or rather liberated at the time, remain expanded in the liquid in which the reaction took place which separated them from the other body with which they were chemically combined; meanwhile they do not deprive it of transparence nor render it viscous or mucilaginous, and they appear properly gasified. But after some time, not many days, they contract and separate gradually, with the appearance of insoluble precipitate or of gelatin—an effect which shows itself more rapidly on addition of a soluble alkali salt in certain quantities, or of other reagents. These, without entering into combination with the oxides, and without even the slightest tendency to do so, expel them from the vehicle as they do emulsified or swollen particles, e.g. sulphur in emulsion, or casein swollen in water. The spontaneous separation of alumina and silica from the medium, the precipitation induced by salts prove clearly that they exist therein in a condition which more closely approaches that of sulphur or of casein than a state of true solution. Furthermore, there is no instance of spontaneous deposition in true solutions, nor of easy segregation on addition of some foreign matter which does nothing beyond taking up room, and dissolving, in the medium. But how is it that alumina and silica, while

remaining incorporated with the liquid, do not render it opaque and turbid, or at least impart to it some slight degree of opalescence ? The reason lies in the peculiar qualities of finely divided alumina and of swollen and gelatinous silica, because, when they are at once examined in the light, it may be observed that they do not allow the entire pencil of rays to pass, without abstracting part or decomposing it, as do transparent bodies. This is certain that, as either becomes smaller and more attenuated, the transparence increases likewise ; therefore, while they remain diffused in a liquid and are reduced to the finest state of division, they will allow free passage to light and will not produce any appearance of turbidity or darkening.

I conclude that what happens with the bodies just mentioned should also occur with the Prussian blues soluble in water and in other menstrua ; for I had noticed in preparing the blue ink from iron ferro-cyanide and oxalic or tartaric acid that slight impurities were often sufficient to impede the formation, and I knew from various authors that the ferro-potassic blue, which easily dissolves in pure water, coagulates immediately on addition of some saline matter to the liquid. I assumed that the blues formed in the shape of slight and transparent flakes which refract the blue ray and that, swelling and subdividing, they could occupy the space offered to them by the medium, as happens generally with sulphur or mercury iodide when they form emulsions ; that, being also transparent, they would not deprive the liquid of its transparence ; that they would colour the water blue, being of that colour ; that they would not precipitate by themselves and would not be visible at the size to which they would be reduced, because they did not undergo any molecular change while remaining disseminated in the water ; and that they would shrink and separate from the medium on the addition of any substance.

Inasmuch as the combinations of Prussian blue with water and other analogous mixtures belong neither to the category of true solutions, nor to that of emulsions or demulsions, nor to the mucilages or jellies, I have thought it

expedient to call them by a special name, viz., that of *pseudo-solutions*, to indicate that they are not true solutions, although resembling them in appearance; wherefore they are easily confounded with the latter, unless they are observed and studied with great accuracy, and with due attention to the principal characteristics in which the true solutions differ from the false ones.

Pseudo-solution, or false solution, then, is that special mode of combination between a hard or soft body and any liquid, in which the former expands in the form of minute flakes without affecting the transparence, and can be easily separated by soluble foreign matter introduced into the liquid afterwards.

Blue prepared from a Ferric Salt and Yellow Prussiate of Potash used in excess.

It is generally known to chemists that, when a solution of a salt of peroxide of iron is added drop by drop to a solution of prussiate of potash, care being taken not to decompose the whole of the latter, a blue precipitate is formed, which, freed from the mother liquor, dissolves in water and remains so without precipitating, provided no salt is added, which, by contaminating the purity of the medium, renders it unsuitable for remaining united with the Prussian blue.

I have made such preparations and have observed carefully how they behaved during washing, and at what point they began to swell and go into pseudo-solution.

As long as the liquid passes through greenish-yellow, the blue shows no sign of altering or of tending to liquefy; but as soon as the water begins to become almost colourless, a sudden slowing of the filtration becomes noticeable, as well as a manifest tendency on the part of the blue to become intermingled with the liquid and to pass with it through the pores of the filter. Soon afterwards the first signs of solution show themselves, and after a time it becomes so complete that the last volume of distilled water which is poured on the filter takes with it the whole of the substance which has

remained undissolved on the paper, leaving the latter barely tinted an extremely faint blue. The pseudo-solution thus produced appeared transparent, of a beautiful but intense blue colour; hence it was necessary to dilute it with water to such a degree that the effects produced by various reagents could be observed clearly.

I have noticed that the blue did not wait to dissolve in the wash water until this was quite pure, but showed signs of still containing traces of prussiate in solution; hence the presence of foreign salts is not sufficient to prevent the formation of pseudo-solutions, provided there is not more than a certain quantity.

The pseudo-solution is completely miscible with alcohol, preserves its original transparence, and does not deposit the slightest trace of the dissolved substance.

On addition of ether the blue comes down, without, however, remaining precipitated, as it redissolves partly in the ethereal layer, which separates from the aqueous liquid.

The pseudo-solution was tested with various soluble salts, and the effects produced varied with the nature of each salt, the influence of the base being evident in some cases, and that of the acid in others.

[The author describes in great detail the effect of a number of salts on the pseudo-solution; as no concentrations are given, the results are merely summarized here. The following were tried:—

Ammonium chloride, nitrate, nitrite, sulphate, phosphate, oxalate, and tartrate. The last two hardly coagulate. Ammonia discolours the pseudo-solution.

Potassium sulphate, chlorate, arsenite, binoxalate.

Sodium sulphate, acetate, tribasic phosphate, borate, bicarbonate. The coagulum produced by the last named salt is brown, turns blue on addition of HCl and redisperses.

Calcium chloride and nitrate. These act more energetically than the alkali salts.

Magnesium chloride and nitrate act like the calcium salts.

Ferrous and ferric sulphate, manganous sulphate, and chloride.

Zinc and cadmium salts produce immediate precipitation.

Mercuric cyanide acts slowly.

The coagulation experiments are repeated with the pseudo-solution in alcohol of 34 Beaumé (about 83 per cent by volume) with similar results.]

The principal characteristic by which emulsion, demulsion, swelling, and other similar ways in which a solid substance becomes incorporated with a vehicle may be easily distinguished, consists in its inherent property of being separated from the medium and reduced to the solid state by the intervention of some foreign principle, which latter does nothing beyond dissolving in the liquid and exhibits no tendency to combine chemically with the precipitated matter. Indeed, if the emulsions of soft sulphur, the demulsions of hard sulphur, of silver chloride, of barium sulphate, and mercuric iodide are examined; if bodies swollen and expanded by imbibition, such as the soaps, albuminous substances, and also some mineral salts, are tested, it is found that these subdivided and suspended bodies separate from the vehicle in the presence of peculiar agents which have no affinity for them, but are simply more or less soluble in the medium; and that each emulsified or swollen substance appears to be affected in a special manner by a given agent, which may act slightly or not at all on the other emulsions. For example, the emulsified or demulsified sulphur precipitates rapidly and in large flakes more markedly with potassium sulphate than with other salts; silver chloride is acted upon promptly by the nitrate of that metal; soap is very rapidly coagulated by the alkaline chlorides; casein by rennet; and albumin by creosote. Therefore when a liquid presents itself which contains some substance not truly dissolved, but emulsified or swollen, but which nevertheless appears to the eye indistinguishable from a real solution, the characteristic mentioned must be appealed to, viz., the prompt precipitation of the substance associated with the medium by the addition of certain heterogeneous bodies, and its peculiar sensitiveness to a particular precipitant, which acts more vigorously and more perfectly.

As the supposed solution of basic Prussian blue shows the characteristics indicated, as appears from what is stated in the treatises of chemistry and as has been abundantly confirmed

by the experiments related, it can no longer be counted among the solutions, but belongs, on the contrary, to the family of the emulsions, and more especially to the class of pseudo-solutions.

But if we consider well in what manner a substance becomes emulsified and what kind of attenuation it must undergo in being incorporated with the medium, we shall conclude at once that in these instances extreme molecular subdivision or a comminution which goes as far as the separation of molecules from one another is not necessary, but that it is sufficient for the particles to distend, spread, subdivide, or swell with formation of thin membranes, flakes, or vesicles, more or less minute, either separated from one another or else in contact without really joining; all these membranes, etc., however small, still representing an accumulation or aggregation of many molecules and far removed from the extreme minuteness of the single and isolated molecule. The formation of emulsions will therefore not give rise to the phenomenon common to all true solutions, viz., the absorption of caloric or the production of cold by the dissolving substance, a phenomenon caused beyond doubt by its passing from the solid state of aggregation to that of extreme molecular division; for the dissolved molecules are as much separated as are the gasified molecules in space, and the act of solution implies that extreme loosening and separation of the molecular aggregates which occurs in evaporation (Gay-Lussac and Bizio). I have said above that the formation of an emulsion cannot be accompanied by cooling, because the body which is emulsified is not, properly speaking, rarefied, but only expanded, distended, or swollen. In order to make my conception better understood, I will illustrate it: let a dry bladder, doubled up and wrapped round itself, be immersed in water and left there for some time until it is penetrated and saturated. The bladder will gradually begin to soften and then to swell, and will appear to the eye to have acquired a larger volume; but in reality it will be neither more nor less voluminous than it was before. The apparent size will be caused rather by water introduced into the body

of the bladder than by a dilatation of the tissue composing the membrane. What happens with the turgid bladder in water, or with one inflated with air, occurs similarly with the emulsifiable substance, which on contact with the vehicle swell and expand therein, either preserving their vesicular form or else being reduced to flakes or to a network, etc. This is all the more certain as, in the majority of cases, they impart opacity, viscosity, or a gelatinous appearance to the liquid with which they become associated, even in small proportions: which quality proves the presence, not of free and separate molecules, but of an aggregate of particles more or less tenacious and dense, and therefore more or less active in reducing the transparence and fluidity of the medium. It may happen occasionally that the thin membranes or vesicles of the swollen material are transparent, detached rather than united, and fairly flexible; the liquid will then remain pellucid and fluid, as happens with the pseudo-solution of the basic blue, and it will differ from a true solution by the ease with which it is destroyed by foreign matter, and furthermore by this, that in the act of precipitation or formation of the emulsion there will be no liberation or loss of caloric. Emulsions will therefore not show the fall of temperature usually observed in solutions; nor will caloric be developed at the moment of coagulation of the emulsified body, contrary to what happens in crystallization and is clearly shown by all the salts, which remain dissolved up to their natural limit of saturation, and then crystallize out at once. I have, in fact, verified that in the coagulation of milk nothing but the slightest rise of temperature occurs, and that the thermometer does not fall when casein is liquefied in saline liquors, all of which agrees very well with the view expressed by me that the albuminoids are not dissolved in the medium, but only swollen.

If the basic blue does not combine with the liquid to true solution, but forms only an emulsion or, more correctly, a pseudo-solution, a thermometer placed in it should not, at the moment when it becomes incorporated with the water, show any rise or fall. It was important to carry out the

experiment with precision, which I did in the following manner :

Experiment designed to ascertain whether Caloric is developed when Basic Blue combines with Water.—For this purpose I prepared a fair quantity of blue, washed it on the filter until the washings began to show a bluish tint, collected if from the filter and placed it into a glass beaker. A second beaker contained distilled water, and I then took two comparable thermometers and immersed the bulbs, one in the blue and the other in the water. When I noted that the two instruments indicated the same point, I poured the water on the precipitate and mixed by stirring with a glass rod : the blue became associated with the water, forming a liquid of fine blue colour, transparent and not retained by a paper filter. But no perceptible rise or fall took place, and it is thus proved that false solution takes place without the usual phenomenon inseparable from true solution, viz., fall of temperature. The experiment was repeated in Venice, in the laboratory of theoretical chemistry, by the eminent Dr. Pisanello, assistant at the same, who fully confirms the result which I had foreseen and observed. It is therefore beyond doubt that the thermometer, since it does not fall when a pseudo-solution is formed, should not rise when the pseudo-dissolved substance is caused to precipitate. To assure myself of this fact I took a good quantity of the pseudo-solution of basic blue, took its temperature with the thermometer, added some sodium sulphate solution having the same temperature, and mixed. Observing the thermometer while the liquid became turbid and the blue began to deposit, I noticed neither a rise nor a fall of the mercury.[1]

It may therefore be concluded from this experimental result also that the basic Prussian blue is in pseudo-solution in water, and this statement may be extended to the case in which alcohol is employed as vehicle, since we have seen that the alcoholic pseudo-solution reacts with saline substances like the aqueous one.

Having come to this conclusion we are led to suspect that the supposed solution of the common Prussian blue, or ferro-

cyanide of iron, in tartaric or oxalic acid must also be considered a false or apparent solution. I have not taken the trouble to verify this conjecture by special experiments, which appeared to be superfluous, as we have sufficient confirmatory evidence in the known fact that slight causes destroy these combinations of blue and acid liquids, and that they do not form unless the blue is impure and contains substance capable of forming salts with a portion of the dissolving acid. I have rather tried to ascertain whether the blue, when collected in a state of finest division, can be made to distribute itself in water sufficiently to form a pseudo-solution.

Attempts to obtain Pseudo-Solutions of the ordinary Prussian Blue without the use of Solvents.

When the ferro-cyanide of iron is prepared by double decomposition, the substance produced is in a state of extreme division ; therefore whenever it is pseudo-soluble it ought to incorporate itself with the liquid, and to remain so in the semblance of a dissolved body. But the presence of the reacting salts and of the products of reaction certainly cannot allow this to happen, owing to their inherent virtue of collecting the minute particles of pseudo-soluble matter into curds or flakes, and of thereby separating them from the liquid ; when the common Prussian blue is separated from the saline liquid and washed with distilled water it does not in general pass into it, however protracted the washing : the blue therefore appears to be deprived of the property of forming pseudo-solutions.

Nevertheless, considering the great transparence of the coagulum which it forms in a medium, and its tendency to swell when imbibing a suitable liquid, and to shrink when drying, it appeared to me possible that it could in certain cases really form pseudo-solutions, if not permanently at least for a certain length of time, and exhibiting the proper characteristics of pseudo-solutions. Such cases ought to occur when the blue is in a high state of subdivision in water

and in presence of substances which have little or no precipitating power. There occurred to me the singular compound which is formed when sulphuric acid monohydrate is poured on the blue, which becomes colourless on contact with the acid (perhaps through dehydration), and recovers its colour suddenly on addition of water in sufficient quantity, and I determined to experiment with it, so as to present the blue in a state of fine division to the menstruum, to replace the lost water, molecule for molecule, and that in presence of a body (sulphuric acid) of slight coagulating power.

Preparation of the above-mentioned Compound and Experiments carried out with it.

I took Prussian blue of considerable purity and rubbed it down in the mortar with addition of sulphuric acid, until a thin white sludge was produced; the complete bleaching of the substance indicated the completion of the reaction. I then made several trials by allowing some drops of the sludge to fall into distilled water and mixing rapidly; the white substance soon assumed a blue tinge, but remained flocculent and failed to form a pseudo-solution. I repeated the experiment with greater accuracy on the same day, but always without success, so that I dispaired of confirming my surmise. On the following day I returned to the experiment, led by the conviction, which I had gathered in my chemical work, that there was no reason to be dispirited because the experiment had failed once, and that it was expedient to repeat it several times in order that I might succeed in the end; nevertheless, I did not obtain the pseudo-solution, although I noticed that the white substance took longer to turn blue than on the day before, and that in addition the blue flocculent mass seemed more finely divided and inclined to incorporate itself with the liquid.

After the lapse of two more days I tried again, and noticed with surprise that the white substance no longer turned blue at the first contact with water, as it had done before, but remained white for several seconds, and that it could be

dissolved in the liquid before becoming blue. In the act of dissolution the water turned whitish as the particles were diffused through it by stirring with a glass rod ; then all at once it assumed the blue colour and, while doing so, cleared and became transparent like a true solution. Observing it attentively I could not perceive more than the slightest trace of particles, so uniform and equally coloured did it appear.

When poured on a paper filter it first passed through deeply coloured ; after a time the colour became fainter, and finally the filtrate became quite colourless. The filtrate as well as the original coloured liquid, after about fifteen minutes, and sometimes sooner, began to lose their uniformity and to deposit large blue, translucent flakes, which collected on the bottom, on which they rested lightly.

Testing the blue liquid, before coagulation, with caustic ammonia, phosphate, and sulphate of ammonia, with zinc and cadmium salts and with other saline substances, I noticed effects similar to those observed with the pseudo-solution of basic blue ; thus I saw it turn violet immediately, and then rapidly yellow, with the alkalis ; turn violet also with the two ammonia salts ; deposit rapidly with the salts of zinc and cadmium and form voluminous coagula with the other saline substance.

To obtain clear and decisive results it is highly expedient to use freshly prepared liquids, because, if they are kept till on the point of precipitating spontaneously, they show themselves less sensitive to the precipitating power of saline substances.

Since the common Prussian blue can form pseudo-solutions in water when meeting it in a state of finest division and can remain incorporated with it for a certain time, I am of the opinion that the pseudo-solution could remain unaltered for a much longer time, or even indefinitely, provided the sulphuric acid, which served in the first instance to reduce the blue to minutest particles and thus to render it more easily dispersed in water, could be removed at once and without reacting chemically or forming salts.

For it seems to me to be beyond doubt that this acid remaining in the liquid with the pseudo-dissolved blue must tend perceptibly to separate the latter, owing to its inherent power of precipitating emulsified or pseudo-dissolved matter.

Characteristic Differences between Pseudo-Solutions, Emulsions, etc., and True Solutions.

I believe that in the minds of my readers, after they have read the description of the experiments carried out with the two Prussian blues, no doubt will remain regarding the appearance of a solubility which is not really one, in spite of external resemblances. The precipitation of the blues by saline substances and the original incorporation with water without perceptible development of caloric differentiate solutions from pseudo-solutions so decidedly and so clearly as to provide an affirmative answer to the question. The complete absence of any change in the total volume of the pseudo-solution when it is made to precipitate provides a third characteristic distinction.

Three clear, evident, and peculiar characteristics suffice admirably to distinguish the substance which is dissolved in a vehicle from that which remains in pseudo-solution :

(1) The easy, rapid, and complete precipitation of the pseudo-dissolved substance by means of soluble matter which neither decomposes the substance nor produces new compounds, and therefore acts merely by spreading in the medium of the pseudo-solution. This soluble matter need not be present in such quantity as to saturate the vehicle, but a small amount is generally sufficient; hence it cannot be objected that it expels the substance in pseudo-solution by completely impregnating the liquid and not allowing any other substances to remain incorporated. The sensitiveness of every substance in pseudo-solution, emulsion, or demulsion towards any one precipitant varies so that, while a given substance is capable of immediately and violently destroying one pseudo-solution or emulsion, it has little or no effect on other similar liquids. The emulsion of sulphur is particularly

sensitive to sulphate of potash; the Prussian blues are rapidly precipitated by zinc salts; casein is quickly curdled by the ferment of rennet; albumin is coagulated at once by creosote, etc.

The true solutions do not undergo precipitation by the presence of inert substances: if sometimes part of the dissolved matter is deposited from a solution this occurs when it is saturated with another soluble body which, attracting the solvent with greater avidity, displaces part of the first occupant.

(2) The constancy of temperature when the emulsifiable or pseudo-soluble substance becomes incorporated with the vehicle, or when it is forced to separate from it and to precipitate. Gay-Lussac observes that, whenever real solution of a solid in a liquid takes place, without the accompaniment of chemical combination between the two, the temperature of the mixture falls, because the solid body, when induced to break up its molecular piles and to diffuse in the manner of a gas throughout the liquid, requires caloric, as does every substance when it assumes the state of elastic vapour. In the emulsified or pseudo-dissolved substances there occurs rather an unfolding of thin membranes or of vesicles and particles which originally were wrinkled and folded on themselves; the dissolved body passes from the solid state to that of gas, or at least of liquid, while the pseudo-dissolved remains solid and only softens, swells, or distends itself owing to the interpenetration by the medium, which insinuates itself between the wrinkles and folds. Therefore, not actually changing its state or condition, it has no need of caloric which brings about this change, and thus no change of temperature should occur either in the act of formation or that of destruction of a pseudo-solution or emulsion.

(3) The constancy of the volume when two substances associate to form a pseudo-solution or emulsion, whence the total volume corresponds exactly to the sum of the volumes of the medium and of the pseudo-dissolved or emulsified substance.[2]

In order to make the importance of this third characteristic

difference clearer, I recall that Hosserfratz, investigating whether the specific weight of substances remained constant in the solid and in the dissolved state, found that it always differed more or less, which shows that in the act of dissolving the solids expand or contract, so that their specific gravity, and hence their volume, is altered (Thompson, *Système de chimie*, Tome troisième, pp. 109 *et seq.* Paris, 1818). The consequence of this change is the alteration of the aggregate volume of soluble substance and solvent; hence, if it were possible, as in coagulation, to separate the whole of the dissolved matter from the solvent, without concentrating or evaporating, and to keep them in presence of each other, an increase or decrease of the aggregate volume would be observed in the act of separation. In emulsions and pseudo-solutions and similar kinds of union between a solid and a liquid, no alteration of the respective volumes of the constituents occurs either in the act of combination or in that of separation. Albumin coagulates in water, in which it has become turgid, without decrease in volume in the whole mass, although at first sight it would appear that there ought to be contraction owing to the wrinkling of the albumin membranes. Casein is curdled in milk by rennet without a perceptible alteration in the aggregate volume of coagulum and supernatant whey. Therefore the swollen, pseudo-dissolved, or emulsified substances which form one category of special combinations between liquids and solids or plastics should certainly not produce contraction or dilatation when dispersing in the liquid.

Thus three characteristic differences have been stated which provide an easy test for distinguishing with certainty the true solutions from the false or apparent ones; I wish that my colleagues may keep them in mind when the opportunity occurs, so that they may be verified on a larger number of emulsions and pseudo-solutions than I have tested, and that their truth may be confirmed by evidence that they are reproduced constantly. As far as I know, nothing has been done up to now with the express intention of reducing the terms to that precision with which I have attempted to

describe them. Nor has anyone before me spoken of emulsions and pseudo-solutions of solid and plastic substances in liquids with the clearness with which I discussed them since 1845, when I published some considerations on certain curious phenomena observed by Frémy in the *Annali delle Scienze Naturali di Bologna*, in the March number of that year. I said there: "Starch, cholic acid, the albuminous principles should not be called truly dissolved in water, in the manner of salts, because they are present in it rather in a state of extreme swelling, their cells or globules being distended and penetrated by the menstruum, as Liebig also correctly surmises. They therefore resemble the emulsified bodies in some ways, and differ from them only in that they do not affect the transparency of the liquid, while the former impede the passage of the rays of light and render the liquid opaque. When salts precipitate the former from their dispersion in the liquid all they do is to produce molecular vibrations in the act of diffusing through the solvent, under the impact of which the distended membranes and cells contract and wrinkle and, no longer able to remain diffused, separate from the liquid and precipitate.

"The gelatinous basic didymium nitrate cannot be washed on the filter except with much trouble; when it begins to stop up the paper it is necessary only to wash it with ammonium nitrate, which compresses it and destroys the vesicular shape of its particles—and proves by its shrinkage that it is not unlike starch and the albuminoids."

In another paper entitled "Some Facts of Physiological Chemistry," published in the February number of 1846 in the same *Annali*, discussing the probable reason why blood coagulates when extracted from the veins, I stated that "the *fibrin is liquefied in the serum* and in coagulating it *shrinks and becomes wrinkled* in consequence of some ferment-like principle which tends to contract the vesicles of liquefied fibrin," and, extending my remarks to milk, I also added: "Rennet does nothing beyond causing the casein to shrink and transforming it from a swollen condition into more highly contracted cells."

Later, i.e. in April of the year afore-mentioned, I deposited with the Societa di Agricoltura di Reggio and transmitted to the R. Accademia Agraria di Torino a long theoretical and experimental paper on milk, in which I related several facts supporting my views regarding the state of apparent solution in which albumin, casein, and similar bodies exist in liquids. The same ideas are also to be found in various notes and papers, which it would be superfluous to quote one by one, the passages given above being sufficient. I have recalled those dates to the memory of chemists, not from vainglory, but lest it be forgotten that I anticipated by a year or more Baudrimont,[3] in some of the ideas which he sets forth in the last part of the *Treatise of Chemistry* (Baudrimont, *Traité de Chimie*, Paris, 1844–46, Vol. II); this treaty began to appear in 1844 and was not completed until the end of 1846 by the last part referred to above, nor did it get into my hands until the current year, i.e. two years after the publication of my *Considerations*. I shall not start a futile quarrel about priority, which in the end does not benefit science; I shall only advise chemists that, if they should have to adopt Baudrimont's opinions, they should not forget one who in Italy preceded, or at least travelled the same road with, the French chemist, in throwing some light on the singular ways in which substances which swell or are emulsified dissolve in liquids.

[1] This statement is not correct, but the heats of flocculation are, of course, much too small to be detected in this way. Kruyt and van der Spek (*Koll. Zeitschr.*, **24**, 145 (1919)) found 0·01 to 0·05 gm.-calories per gm. of As_2S_3 and 2 gm.-calories per gm. of Fe_2O_3 coagulated from the respective sols. Earlier attempts to determine heats of coagulation were made by Linder and Picton (*J. Chem. Soc.*, **61**, 144, 146, and 153 (1892)) and by Doerinkel (*Zeitschr. anorg. Chem.*, **66**, 20 (1910); **67**, 161 (1910)).

[2] This point has not been tested for suspensoid sols, but the statement is not correct of emulsoid sols, in which considerable contractions have been observed, e.g. various protein sols, H. Chick and C. J. Martin (*Koll. Zeitschr.*, **12**, 71 (1913)); Herlitzka (*Koll. Zeitschr.*, **7**, 250 (1910)).

[3] Cf. "Baudrimont as Colloid Chemist," by Wilder D. Bancroft (*J. Phys. Chem.*, **23**, 256 (1924)).

ON THE PRODUCTS OF DECOMPOSITION OF SULPHURETTED HYDROGEN AND SULPHUROUS ACID IN AQUEOUS SOLUTION.

By Ascanio Sobrero and Francesco Selmi.

ON THE PRODUCTS OF DECOMPOSITION OF SULPHURETTED HYDROGEN AND SULPHUROUS ACID IN AQUEOUS SOLUTION.[1]

By MM. Sobrero and Selmi.

(Abstract of a paper read before the Academy of Sciences at Turin, 11th June, 1849. (*Ann. Chim. et Phys.*, **28**, 210 (1850).)

Ascanio Sobrero, born 12th October, 1812, at Casale. Dr.Med. et Chir. 1832. Subsequently studied Chemistry at Turin, Paris, and Giessen. Member and Perpetual Secretary of Academy of Sciences of Turin 1844. Discovered nitroglycerine and nitromannite 1847. Professor of Technical Chemistry 1849; Professor of Pure Chemistry 1860. Died 26th May, 1888, at Turin.

When sulphurous acid and sulphuretted hydrogen are passed simultaneously into a flask filled with distilled water, the two gases dissolve and decompose each other with precipitation of sulphur. At the same time (and this is well known) the liquid assumes a very pronounced acid reaction and turns yellow while dissolving sulphur. It is generally known that M. Wackenroeder has found, as the product of this reaction, pentathionic acid. This chemist passed sulphuretted hydrogen into water previously saturated with sulphurous acid; he saturated the mixture with barium carbonate and then precipitated the salt with absolute alcohol. It appeared to us of interest to ascertain whether pentathionic acid was the only acid of the thionic series which could be formed by the above reaction. With this object in view we have modified M. Wackenroeder's procedure by passing the gases simultaneously and continuously for several days into a flask nearly filled with distilled water; in this way we were able to obtain highly concentrated acid liquids, in which we could recognize the various acids that might be formed; this would have been impossible with the very weak solutions which are produced by M. Wackenroeder's method. We therefore set up our apparatus and, after the operation had proceeded for several hours, a certain quantity of liquid was withdrawn from time to time and saturated with barium carbonate. The neutralized and filtered solution was poured into dilute alcohol so as to separate any barium hyposulphite which

might have formed and dissolved, and then into very strong alcohol. The precipitate formed in this liquid was then analysed. It is quite certain that by this means we ought always to have obtained the same analytical data, if the reaction between the two gases had produced nothing but pentathionic acid. But the experiment showed that the results were very variable. We have, in fact, very often obtained salts of a composition which proved them to be mixtures of pentathionate and tetrathionate. Sometimes we found the tetrathionate, the analysis of which gave the composition ascribed to this salt by MM. Fordos and Gelis. We found :

			Fordos and Gelis
Baryta	38·74 ..	38·65 ..	38·50
Sulphur	32·83 ..	32·68 ..	32·25
Oxygen (combined with sulphur)	19·31 ..	19·55 ..	20·16
Water	9·12 ..	9·12 ..	9·09

Several times, after neutralizing with barium cabonate and precipitating with strong alcohol, we allowed the clear liquid obtained by decantation to evaporate slowly in an imperfectly closed vessel, and obtained prismatic crystals which retained a little alcohol even after drying. In these crystals the ratio of baryta to sulphur was 1 equivalent of the former to 4·5 of the latter, corresponding to the composition of the barium tetrathionate of M. Ludwig. We have also found among the products of interaction of sulphuretted hydrogen and sulphurous acid pentathionic, hyposulphurous, and sulphuric acid ; we have never been able to find the acid of M. Langlois. It would be important to ascertain what circumstances favour the formation of one or the other of the acids mentioned ; the difference in the products must certainly depend on the ratio of the two gases, and, besides that, on the concentration of the liquid in which they react and on the temperature. We have no positive data on these points.

The liquid in which the reaction takes place gives a very

copious precipitate of sulphur; it also retains a good deal of sulphur, which separates from it whenever it is saturated with a carbonate or a strong base, potash, soda, etc. The sulphur which deposits during the reaction between the gases is always a beautiful yellow, but sometimes opaque and sometimes translucent or almost transparent. When separated from the liquid by decantation it shows a strong acid reaction; treated with water it suspends in it and forms an emulsion, from which it no longer separates, even on very prolonged standing (several months). When diluted with much water it gives a nearly transparent liquid. If a small quantity of an aqueous solution of a neutral potassium or sodium salt is added to this emulsion of sulphur, a precipitate of sulphur is immediately obtained, but (a singular matter) if a sodium salt has been used as precipitant, the sulphur has not lost its property of subdividing itself in the water. All that is necessary to establish this point is to decant the liquid containing the sodium salt and to wash the precipitate several times with distilled water; after the second or third washing the sulphur no longer settles but regenerates the emulsion. If, on the other hand, a potassium salt,[2] and especially the sulphate, has been used, the precipitated sulphur has completely lost the property of forming an emulsion in water; it has assumed a pasty consistence, has become sticky and elastic like india-rubber, and resists an indefinite number of washings without losing this very peculiar condition. Thus sulphur retains obstinately a certain quantity of the acids in which it has been precipitated; if acted upon by alkali carbonates or caustic alkalis, it immediately loses its elasticity. The emulsifiable sulphur loses this property when exposed to air for a long time; it becomes brittle, or, properly speaking, powdery. The elastic sulphur precipitated by potassium sulphate preserves its elasticity even after exposure to the air. We have some which was prepared several months ago and has lost nothing of this property. We have, furthermore, satisfied ourselves that, in spite of repeated washings, it always retains a little of the potassium sulphate used in precipitating it.

We have mentioned that the acid liquid produced by the

decomposition of the two gases retains much sulphur. To show this it is sufficient to add to it a little neutral sodium or potassium salt. We have had liquids showing 17 to 18 degrees on the areometer[3] which set to a coherent mass on addition of a small dose of the above salts. This enormous quantity of sulphur is, so to speak, dissolved, as it hardly affects the limpidity of the liquid. The precipitate obtained in this fashion exhibits the same differences and the same phenomena, as regards the properties of forming emulsions, or of being elastic and incapable of being emulsified, as we have described for the sulphur precipitated during the reaction. The state of the sulphur can therefore be modified, in a peculiar manner, by the presence of bodies in the medium in which it deposits, which bodies it retains obstinately, probably by simple adhesion; and the sulphur may thus acquire the property of forming emulsions, or a state of aggregation which prevents it from subdividing itself in water. It follows, in addition, that the emulsifiable sulphur presents phenomena analogous to those which can be observed in many other bodies having the property of dispersing or dividing themselves in a liquid without, however, absolutely dissolving in it, such as soap, starch, or Prussian blue, on which one of us, M. Selmi, has already made observations similar to those which we have here set forth. These phenomena belong to a class which M. Selmi has well characterized and has grouped together under the name of *pseudo-solutions*. It would appear that the number of *pseudo-soluble* bodies is fairly large. We have already undertaken some researches on this subject, and the organic bodies in particular appear to us to be of great interest from this point of view.

[1] For a complete bibliography of colloidal sulphur see Sven Odén's monograph "Der kolloide Schwefel" (*Nova Acta Reg. Soc. Scient. Upsaliensis*, Ser. IV., vol. III, No. 4). Cf. also Thé Svedberg "Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe" (*Zweite Auflage, Leipzig*, 1920, pp. 237–251). In this work Svedberg for the first time directed the attention of colloid chemists to the work of Selmi.

[2] For the effect of potassium salts see Sven Odén, *loc. cit.*, p. 157.

[3] "17 to 18 degrees on the areometer": presumably Beaumé, i.e. sp. gr. about 1·13 to 1·14, corresponding to about 25 per cent of sulphur.

ON THE EXPERIMENTAL RELATIONS OF GOLD (AND OTHER METALS) TO LIGHT.

By Michael Faraday.

ON THE EXPERIMENTAL RELATIONS OF GOLD (AND OTHER METALS) TO LIGHT.

By Michael Faraday.

(Only a part of the paper, that dealing with dispersions of gold in aqueous medium, is here reprinted.)

(*Phil. Trans.*, 1857, p. 145.)

Michael Faraday, born 22nd September, 1791, at Newington. From 1813 Assistant at the Chemical Laboratory of the Royal Institution, first to Sir Humphry Davy and then to W. Th. Brande, whom he succeeded as Professor in 1827. Elected F.R.S. in 1824. Discovered benzene 1825; induced currents 1831; Faraday's law 1833; magnetic rotation 1845. Died 25th August, 1867, at Hampton Court.

For biography, etc., see: *The Life and Letters of Faraday*, by Bence Jones, London, 1870; *Michael Faraday*, by B. J. H. Gladstone, London, 1878; also, *Faraday as Discoverer*, by John Tyndall, London, 1868.

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.[1]

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 reflection, 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 phosphorus 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[2] 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 opaque 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 preparation 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 to 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 show 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 opaque. 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 sides, 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 a 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, of 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 reflection, 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. Prévost[3] 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 increasing 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

become 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 resettled. 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 hundred-fold or even a thousand-fold, 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 blue the gold it came in contact with, 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, has any power to re-dissolve 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 alkalis, 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 grey-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 remain diffused ; and with their appearance when illuminated by the cone of the 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 the metallic mercury put into the same vessel.[4] 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 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 plates 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 rewetted 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. (See Gmelin's *Chemistry*, VI, p. 219, "Terchloride of Gold," for numerous references in relation to changes of these kinds.) If a drop of solution of protosulphate 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 reflection; 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. Hydrochloric 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 reflection 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 transmission. 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 precipitate 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.[5]

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 setting as on former occasions. A little glycerine with solution of gold reduces it at common temperatures, producing a fluid, brown by reflection, 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 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 caused 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, etc., 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, etc., 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, etc., equal to gold-leaf; but in the unpressed state, their transmitted colour is generally grey or violet-grey. The progression 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, etc., 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 adhere to the sides of the bottles or flasks in which the fluids had been preserved, and the process of boiling seemed to favour such results; 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 of 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 alkalis, 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 of 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.[6] 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.[7] 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 alkalis, 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 does 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 reflection 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.

[1] The method of reduction by phosphorus has been developed further by R. Zsigmondy, "Zur Erkenntnis der Kolloide," p. 100 (1905) (*Zeitschr. phys. Chem.* **56**, 65–76 (1906)), especially for the purpose of obtaining sols with amicroscopic particles to be used as nuclei for further reduction.

[2] This phenomenon has been noticed by many later observers, e.g. Bredig, *Anorganische Fermente* (Leipzig, 1901), p. 30; Liversidge, *Chem. News*, **62**, 277 (1890); v. Plotho, *Biochem. Zeitschr.*, **110**, 1 and 33 (1920).

[3] B. Prévost (*Ann. Chim. Phys.*, II, 4, 192, 436 (1817)) investigated the colour of light repeatedly reflected from metallic surfaces and found it a deep reddish orange with gold, yellow to orange with silver, and purple with copper.

[4] The absence of amalgamation even after prolonged contact with mercury has been confirmed by later observers; cf. R. Zsigmondy, *Kolloidchemie*, 3. *Auflage*, Leipzig, 1920, p. 151. Also W. Pauli, *Die Naturwissenschaften*, **12**, p. 548 (1924), where it is quoted as part of the evidence against the purely metallic nature of the particles.

[5] This view has been fully confirmed by R. Zsigmondy, who synthetized the purple from colloidal gold and colloidal stannic acid (*Liebig's Ann.*, **301**, 375 (1898)).

[6] This phenomenon has been reinvestigated by F. Kirchner and R. Zsigmondy (*Drude's Ann. d. Phys.* (4), **15**, 578 (1904)).

[7] W. Pauli (*loc. cit.* 4, p. 550) emphasizes the point that "the flocculated and washed gold gel, contains not inconsiderable quantities of *firmly held* water, which is retained in the desiccator as well as at 100 degrees, the weight remaining constant."

ON THE PROPERTIES OF SILICIC ACID AND OTHER ANALOGOUS COLLOIDAL SUBSTANCES.

By Thomas Graham

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Graham's fundamental paper "Liquid Diffusion Applied to Analysis" appeared in 1861 (*Phil. Trans.*, p. 183–224). "Chemical and Physical Researches of Thomas Graham" have been "collected and printed for presentation only" by R. Angus Smith, Edinburgh, 1876.

For biography see: *The Life and Works of Thomas Graham*, by R. Angus Smith. Glasgow, 1884.

The prevalent notions respecting solubility have been derived chiefly from observations on crystalline salts, and are very imperfectly applicable to the class of colloidal substances. Hydrated silicic acid, for instance, when in the soluble condition, is, properly speaking, a liquid body, like alcohol, miscible with water in all proportions. We have no degrees of solubility to speak of with respect to silicic acid, like the degrees of solubility of a salt, unless it be with reference to silicic acid in the gelatinous condition, in which it is usually looked upon as destitute of solubility. The jelly of silicic acid may be more or less rich in combined water, as it is first prepared, and it appears to be soluble in proportion to the extent of its hydration. A jelly containing 1 per cent of silicic acid gives with cold water a solution containing about 1 part of silicic acid in 5,000 water; a jelly containing 5 per cent of silicic acid gives a solution containing about 1 part of acid in 10,000 water. A less hydrated jelly than the last mentioned is still less soluble; and, finally, when the jelly is rendered anhydrous it forms gummy looking white masses, which appear to be absolutely insoluble, like the light, dusty silicic acid obtained by drying a jelly charged with salts, in the ordinary analysis of a silicate.

The liquidity of silicic acid is only affected by a change,

which is permanent (namely, coagulation or pectization), by which the acid is converted into the gelatinous or pectous forms, and loses its miscibility with water. This change may be brought about by time alone. The liquidity is permanent in proportion to the degree of dilution of silicic acid, and appears to be favoured by a low temperature. A liquid silicic acid of 10 or 12 per cent pectizes spontaneously in a few hours at the ordinary temperature, and immediately when heated. A liquid of 5 per cent may be preserved for five or six days, a liquid of 2 per cent for two or three months, and a liquid of 1 per cent has not pectized after two years. Dilute solutions of 0·1 per cent or less are, no doubt, practically unalterable by time, and hence the possibility of soluble silicic acid existing in nature. I may add, however, that no solution, weak or strong, of silicic acid in water has shown any disposition to deposit *crystals*, but always appears on drying as a colloidal glassy hyalite. The formation of quartz crystals at a low temperature, of so frequent occurrence in nature, remains still a mystery. I can only imagine that such crystals are formed at an inconceivably slow rate, and from solutions of silicic acid which are extremely dilute. Dilution, no doubt, weakens the colloidal character of substances, and may, therefore, allow their crystallizing tendency to gain ground and develop itself, particularly where the crystal once formed is completely insoluble, as with quartz.

The pectization of liquid silicic acid is expedited by contact with solid matter in the form of powder. By contact with pounded graphite, which is chemically inactive, the pectization of a 5 per cent silicic acid is brought about in an hour or two, and that of a 2 per cent silicic acid in two days. A rise in temperature of 1·1° C. was observed during the formation of the 5 per cent jelly.

The ultimate pectization of silicic acid is preceded by a gradual thickening in the liquid itself. The flow of liquid colloids through a capillary tube is always slow compared with the flow of crystalloid solutions, so that a liquid-transpiration tube may be employed as a colloidoscope. With a colloidal liquid alterable in viscosity, such as silicic acid, the increased

resistance to passage through the colloidoscope is obvious from day to day. Just before gelatinizing, silicic acid flows like an oil.

A dominating quality of colloids is the tendency of their particles to adhere, aggregate, and contract. This idio-attraction is obvious in the gradual thickening of the liquid, and when it advances leads to pectization. In the jelly itself the specific contraction in question, or *synæresis*, still proceeds, causing separation of water, with division into clot and serum, and ending in the production of a hard, stony mass of vitreous structure, which may be anhydrous, or nearly so, when the water is allowed to escape by evaporation. The intense synæresis of isinglass dried in a glass dish over sulphuric acid *in vacuo* enables the contracting gelatine to tear up the surface of the glass. Glass itself is a colloid, and the adhesion of colloid to colloid appears to be more powerful than that of colloid to crystalloid. The gelatine, when dried in the manner described upon plates of calespar and mica, did not adhere to the crystalline surface, but detached itself on drying. Polished plates of glass must not be left in contact, as is well known, owing to the risk of permanent adhesion between their surfaces. The adhesion of broken masses of glacial phosphoric acid to each other is an old illustration of colloidal synæresis.

Bearing in mind that the colloidal phasis of matter is the result of a peculiar attraction and aggregation of molecules, properties never entirely absent from matter, but greatly more developed in some substances than in others, it is not surprising that colloidal characters spread on both sides into the liquid and solid conditions. These characters appear in the viscidity of liquids, and in the softness and adhesiveness of certain crystalline substances. Metaphosphate of soda, after fusion by heat, is a true glass or colloid ; but when this glass is maintained for a few minutes at a temperature some degrees under its point of fusion, the glass assumes a crystalline structure without losing its transparency. Notwithstanding this change, the low diffusibility of the salt is preserved, with other characters of a colloid. Water in the form of ice has

already been represented as a similar intermediate form, both colloid and crystalline, and in the first character adhesive and capable of reunion or " regelation."

It is unnecessary to return here to the fact of the ready pectization of liquid silicic acid by alkaline salts, including some of very sparing solubility, such as carbonate of lime, beyond stating that the presence of carbonate of lime in water was observed to be incompatible with the co-existence of soluble silicic acid till the proportion of the latter was reduced to nearly 1 in 10,000 water.

Certain liquid substances differ from the salts in exercising little or no pectizing influence upon liquid silicic acid. But, on the other hand, none of the liquids referred to appear to conduce to the preservation of the fluidity of the colloid—at least not more than the addition of water would do. Among these inactive diluents of silicic acid are found hydrochloric, nitric, acetic, and tartaric acids, syrup of sugar, glycerine, and alcohol. But all the liquid substances named, and many others, appear to possess an important relation to silicic acid, of a very different nature from the pectizing action of salts. They are capable of displacing the combined water of the silicic acid hydrate, whether that hydrate is in the liquid or gelatinous condition, and give new substitution products.

A liquid compound of *alcohol* and silicic acid is obtained by adding alcohol to aqueous silicic acid, and then employing proper means to withdraw the water from the mixture. For that purpose the mixture contained in a cup may be placed over dry carbonate of potash, or quicklime, within the receiver of an air-pump. Or a dialysing bag of parchment paper containing the mixed alcohol and silicic acid may be suspended in a jar of alcohol; the water diffuses away, leaving in the bag a liquid composed of alcohol and silicic acid only. A point to be attended to is, that the silicic acid should never be allowed to form more than 1 per cent of the alcoholic solution, otherwise it may gelatinize during the experiment. If I may be allowed to distinguish the liquid and gelatinous hydrates of silicic acid by the irregularly formed terms of *hydrosol* and *hydrogel*, the two corresponding alcoholic bodies

now introduced may be named the alcosol and alcogel of silicic acid.

The *alcosol* of silicic acid, containing 1 per cent of the latter, is a colourless liquid, not precipitated by water or salts nor by contact with insoluble powders, probably from the small proportion of silicic acid present in solution. It may be boiled and evaporated without change, but is gelatinized by a slight concentration. The alcohol is retained less strongly in the alcosol of silicic acid than water is in the hydrosol, but with the same varying force, a small portion of the alcohol being held so strongly as to char when the resulting jelly is rapidly distilled at a high temperature. Not a trace of silicic ether is found in any compound of this class. The jelly burns readily in the air, leaving the whole silicic acid in the form of a white ash.

The *alcogel*, or solid compound, is readily prepared by placing masses of gelatinous silicic acid containing 8 or 10 per cent of the dry acid in absolute alcohol, and changing the latter repeatedly till the water of the hydrogel is fully replaced by alcohol. The alcogel is generally slightly opalescent, and is similar in aspect to the hydrogel, preserving very nearly its original bulk. The following is the composition of an alcogel carefully prepared from a hydrogel which contained 9·35 per cent of silicic acid :

Alcohol - - - -	88·13
Water - - - -	0·23
Silicic Acid - - -	11·64

Placed in water, the alcogel is gradually decomposed—alcohol diffusing out and water entering instead, so that a hydrogel is reproduced.

Further, the alcohol may be made the starting-point in the formation of a great variety of other substitution jellies of analogous constitution, the only condition required appearing to be that the new liquid and alcohol should be intermiscible, that is, interdiffusible bodies. Compounds of ether, benzole, and bisulphide of carbon have been produced. Again,

from *etherogel* another series of silicic acid jellies may be derived, containing fluids soluble in ether, such as the fixed oils.

The preparation of the *glycerine-compound* of silicic acid is facilitated by the comparative fixity of that liquid. When hydrated silicic acid is first steeped in glycerine, and then boiled in the same liquid, water distils over, without any change in the appearance of the jelly, except that when formerly opalescent it becomes now entirely colourless, and ceases to be visible when covered by the liquid. But a portion of the silicic acid is dissolved, and a *glycerosol* is produced at the same time as the glycerine jelly. A glycerogel prepared from a hydrate containing 9·35 per cent of silicic acid was found by a combustion analysis to be composed of :

Glycerine - - -	87·44
Water - - - -	3·78
Silicic Acid - - -	8·95
	100·17

The glycerogel has somewhat less bulk than the original hydrogel. When a glycerine jelly is dissolved by heat it does not fuse, but the whole of the glycerine comes over, with a slight amount of decomposition towards the end of the process.

The compound of sulphuric acid—*sulphagel*—is also interesting from the facility of its formation and the complete manner in which the water of the original hydrogel is removed. A mass of hydrated silicic acid may be preserved unbroken if it is first placed in sulphuric acid diluted with two or three volumes of water, and then transferred gradually to stronger acids, till at last it is placed in concentrated oil of vitriol. The sulphagel sinks in the latter fluid, and may be distilled with an excess of it for hours without losing its transparency or gelatinous character. It is always somewhat less in bulk than the primary hydrogel, but not more, to the eye, than one-fifth or one-sixth part of the original volume. The sulphagel

is transparent and colourless. When a sulphagel is heated strongly in an open vessel, the last portions of the monohydrated sulphuric acid in combination are found to require a higher temperature for their expulsion than the boiling point of the acid. The whole silicic acid remains behind, forming a white, opaque, porous mass, like pumice. A sulphagel placed in water is soon decomposed, and the original hydrogel reproduced. No permanent compound of sulphuric and silicic acids, in the nature of a salt, appears to be formed in any circumstances. A sulphagel placed in alcohol gives ultimately a pure alcogel. Similar jellies of silicic acid may readily be formed with the monohydrates of nitric, acetic, and formic acids, and all are perfectly transparent.

The production of the compounds of silicic acid now described indicates the possession of a wider range of affinity by a colloid than could well be anticipated. The organic colloids are, no doubt, invested with similar wide powers of combination, which may become of interest to the physiologist. The capacity of a mass of gelatinous silicic acid to assume alcohol, or even olein, in the place of water of combination, without disintegration or alteration of form, may perhaps afford a clue to the penetration of the albuminous matter of membrane by fatty and other insoluble bodies, which seems to occur in the digestion of food. Still more remarkable and suggestive are the fluid compounds of silicic acid. The fluid alcohol-compound favours the possibility of the existence of a compound of the colloid albumin with olein, soluble also and capable of circulating with the blood.

The feebleness of the force which holds together two substances belonging to different physical classes, one being a colloid and the other a crystalloid, is a subject deserving notice. When such a compound is placed in a fluid, the superior diffusive energy of the crystalloid may cause its separation from the colloid. Thus, of hydrated silicic acid, the combined water (a crystalloid) leaves the acid (a colloid) to diffuse into alcohol; and if the alcohol be repeatedly changed, the entire water is thus removed, alcohol (another

crystalloid) at the same time taking the place of water in combination with the silicic acid. The liquid in excess (here the alcohol) gains entire possession of the silicic acid. The process is reversed if an alcogel be placed in a considerable volume of water. Then alcohol separates from combination, in consequence of the opportunity it presents to diffuse into water, and water, which is now the liquid present in excess, recovers possession of the silicic acid. Such changes illustrate the predominating influence of mass.

Even the compounds of silicic acid with alkalis yield to the decomposing force of solution. The compound of silicic acid with 1 or 2 per cent of soda is a colloidal solution, and when placed in a dialyser over water *in vacuo*, to exclude carbonic acid, suffers gradual decomposition. The soda diffuses off slowly in the caustic state, and gives the usual brown oxide of silver when tested with the nitrate of that base.

The pectization of liquid silicic acid and many other liquid colloids is effected by contact with minute quantities of salts in a way which is not understood. On the other hand, the gelatinous acid may again be liquefied and have its energy restored by contact with a very moderate quantity of alkali. The latter change is gradual, 1 part of caustic soda dissolved in 10,000 water liquefying 200 parts of silicic acid (estimated dry) in 60 minutes at 100° C. Gelatinous stannic acid also is easily liquefied by a small proportion of alkali, even at the ordinary temperature. The alkali, too, after liquefying the gelatinous colloid, may be separated again from it by diffusion into water upon a dialyser. The solution of these colloids, in such circumstances, may be looked upon as analogous to the solution of insoluble organic colloids witnessed in animal digestion, with the difference that the solvent fluid here is not acid, but alkaline. Liquid silicic acid may be represented as the peptone of gelatinous silicic acid; and the liquefaction of the latter by a trace of alkali may be spoken of as the peptization of the jelly. The pure jellies of alumina, peroxide of iron, and titanic acid, prepared by dialysis, are assimilated more closely to albumin, being peptized by minute quantities of hydrochloric acid.

Liquid Stannic and Metastannic Acids.—Liquid stannic acid is prepared by dialysing the bichloride of tin with an addition of alkali, or by dialysing the stannate of soda with an addition of hydrochloric acid. In both cases a jelly is first formed on the dialyser, but, as the salts diffuse away, the jelly is again peptized by the small proportion of free alcohol remaining; the alkali itself may be removed by continued diffusion, a drop or two of the tincture of iodine facilitating the separation. The liquid stannic acid is converted, on heating it, into liquid metastannic acid. Both liquid acids are remarkable for the facility with which they are pectized by a minute addition of hydrochloric acid, as well as by salts.

Liquid Titanic Acid is prepared by dissolving gelatinous titanic acid in a small quantity of hydrochloric acid, without heat, and placing the liquid upon a dialyser for several days. The liquid must not contain more than 1 per cent of titanic acid, otherwise it gelatinizes spontaneously; but it appears more stable when dilute. Both titanic and the two stannic acids afford the same classes of compounds with alcohols, etc., as are obtained with silicic acid.

Liquid Tungstic Acid.—The obscurity which has so long hung over tungstic acid is removed by a dialytic examination. It is, in fact, a remarkable colloid, of which the pectous form alone has hitherto been known. Liquid tungstic acid is prepared by adding dilute hydrochloric acid carefully, and in slight excess, to a 5 per cent solution of tungstate of soda, and then placing the resulting liquid on a dialyser. At intervals of two days the addition of hydrochloric acid must be repeated two or three times, and the dialysis continued in order to remove the whole alkali. It is remarkable that the *purified* acid is not pectized by acids, salts, or alcohol at the ordinary temperature. Evaporated to dryness, it forms vitreous scales, like gum or gelatine, which sometimes adhere so strongly to the surface of the evaporating dish as to detach portions of it. It may be heated to 200° C. without losing

its solubility or passing into the pectous state; but, at a temperature near redness, it undergoes a molecular change, closing at the same time 2·42 per cent of water. When water is added to unchanged tungstic acid the acid becomes pasty and adhesive, like gum; and it forms a liquid with about one-fourth its weight in water, which is so dense as to float glass. The solution effervesces with carbonate of soda. The taste of tungstic acid dissolved in water is not metallic or acid, but rather bitter and astringent. Solutions of tungstic acid containing 5, 20, 50, 66·5, and 79·8 per cent of dry acid possess the following densities at 19°: 1·0475, 1·2168, 1·8001, 2·396, and 3·243. Evaporated *in vacuo* liquid tungstic acid is colourless, but becomes greenish in air, apparently from the deoxidizing action of organic matter. Liquid silicic acid is protected from pectizing when mixed with tungstic acid, a circumstance probably connected with the formation of the double compounds of these two acids which M. Marignac has lately indicated.

Molybdic acid has hitherto been known (like tungstic acid) only in the insoluble form. Crystallized molybdate of soda dissolved in water is decomposed by the gradual addition of hydrochloric acid in excess, without any immediate precipitation. The acid liquid thrown upon a dialyser may gelatinize after a few hours, but again liquefies spontaneously when the salts diffuse away. After repeated additions of hydrochloric acid, and a diffusion of several days, about 60 per cent of liquid molybdic acid remains behind in a pure condition. In the dialysis of both tungstic and molybdic acids the osmose is very great, the acid solutions increasing to two or three times their original volume. The constant dilution causes the purification to be slow, as compared with that of silicic acid, where the osmose is inconsiderable. The solution of pure molybdic acid is yellow, astringent to the taste, acid to test paper, and possesses much stability. The acid may be dried at 100° without immediately losing its solubility. Dry molybdic acid has the same gummy aspect as tungstic acid. Heated short of the point at which it volatilizes pure molybdic

acid in powder will still dissolve in a solution of carbonate or bicarbonate of potash, with effervescence of carbonic acid gas. Both acids lose their colloidality when combined with soda and give a variety of crystallizable salts. The pure liquid acids also become insoluble when heated for some time with hydrochloric or other strong acids.

THE QUESTION OF THE SILVER SUBOXIDE COMPOUNDS.

By Wilhelm Muthmann.

THE QUESTION OF THE SILVER SUBOXIDE COMPOUNDS.

By Wilhelm Muthmann.

(*Ber.*, **20**, 983 (1887).)

Wilhelm Muthmann, born 8th February, 1861, at Elberfeld. Studied at Leipzig, Berlin, Heidelberg, and Munich. Ph.D. at Munich, 1886. Lecturer at Worcester, Mass., for about two years. "Ausserordentlicher Professor" at University of Munich, 1895; "Ordentlicher Professor" of Inorganic Chemistry at the Technische Hochschule of Munich, 1899. Died 3rd August, 1913.

It has recently been asserted by various authors that the so-called silver suboxide compounds do not exist, and that those bodies which Wöhler, von Bibra, and others took for Ag_4O were nothing but mixtures of oxide compounds and metal. Thus Pillitz (*Zeitschr. anal. Chem.*, **21**, 27 and 496) proved by a very careful investigation that nothing but such a mixture was produced when silver oxide compounds were treated with stannosates,[1] antimonites, and arsenites; Spencer B. Newbury (*Am. Chem. J.*, **8**, 196) likewise arrived at the same result when he tried to obtain silver suboxide compounds according to the methods indicated by Cavallier, Witzlar, and Wöhler. On the other hand, v. d. Pfordten (*Ber.*, **18**, 1407) claims that a lower stage of oxidation can be obtained by the reduction of alkaline silver solutions, but further details from this source must be awaited.

I have recently had the opportunity of making some observations which appear to contribute to a solution of this question, and which I propose to communicate here. As is well known, Wöhler was the first to pronounce the opinion that silver could form compounds of this kind, basing it on the fact that by a suitable reduction of the normal citrate a product could be obtained which dissolved in water with a red colour and gave a precipitate with hydrochloric acid the composition of which was intermediate between that of silver chloride and of silver. This view appeared to receive complete confirmation when Rautenberg (*Ann. Chem. Pharm.*, 114, 119) obtained from silver tungstate, molybdate, and chromate crystallized bodies the composition of which

agreed well with the formula $Ag_4Mo_2O_7$, etc. I happened to have a fairly large quantity of pure silver molybdate and tungstate at my disposal, and took this opportunity of studying the reduction of these bodies. The result was the proof that Rautenberg's bodies were mixtures of normal salts and metal, a conclusion at which I arrived by the following experiments and considerations.

Rautenberg's procedure was to dissolve silver molybdate in ammonia almost to saturation, heat the solution to 90°, and to pass hydrogen into it for several hours. He obtained in this way black, lustrous octahedra, the analysis of which led to the formula $Ag_4Mo_2O_7$. The substance was decomposed by ammonia into silver and the normal salt, which went into solution ; reduction would have to proceed according to the following equation :

$$2Ag_2MoO_4 + H_2 = Ag_4Mo_2O_7 + H_2O.$$

On reading Rautenberg's paper, I was immediately struck by his omission to keep the normal salt in solution by the occasional addition of ammonia.[2] Debray (*C. R.*, 66, 735) has shown that silver molybdate separates unchanged, in the form of lustrous transparent octahedra, when the ammonia is gradually withdrawn from its ammoniacal solution. I have verified the correctness of this statement : the crystals, whose analysis agreed exactly with the formula Ag_2MoO_4, were investigated in the laboratory of the mineralogical collection and found to be perfectly isotropic ; in addition to the faces of the octahedron they showed those of the obtuse ikositetrahedron 303.

It is obvious that such a separation had to occur in Rautenberg's experiments, if he did not replace the ammonia driven off by prolonged heating and by passing hydrogen through the liquid ; this could not occur to him, as Debray's observation, quoted above, was not published until seven years later. It thus appeared probable that Rautenberg's substance consisted mainly of unaltered normal salt which was coloured by finely divided metal ; the crystalline form also agreed with that of normal silver molybdate.

Further experiments have completely confirmed this surmise. In the first instance, 15 gm. of purest crystallized Ag_2MoO_4 was dissolved in ammonia, the liquid heated on the water bath to 90°, and hydrogen passed through for five hours. A black, crystalline powder was formed, in which octahedra could be distinctly recognized ; under the microscope a transparent substance, in which black particles were disseminated, could be seen. On the addition of a drop of ammonia it could be distinctly observed how the transparent substance went into solution and the black particles originally present in it remained behind. These particles consisted of pure metallic silver.

The experiment was twice repeated, with the modification, however, that a little ammonia was added every half hour, to prevent the separation of normal salt. In this way I succeeded in collecting about 0·2 gm. of the *real* product of reduction, which was analysed after careful washing and drying in the vacuum desiccator over sulphuric acid. It contained no trace of molybdenum and consisted of pure metallic silver ; found : 99·83 per cent Ag.

Experiments with the tungstate and chromate gave the same results, as could, indeed, be foreseen. In both cases metallic silver was formed when sufficient ammonia was present to keep the normal salt in solution, but a mixture of metal and normal salt resulted when all the ammonia had been driven off at the end of the operation.

It may appear surprising that Rautenberg's analyses agreed exactly with the formulæ $Ag_4Mo_2O_7$ and $Ag_4W_2O_7$ respectively. This agreement is, however, easily explicable : as regards percentage composition the normal molybdate Ag_2MoO_4 differs but slightly from the supposed $Ag_4Mo_2O_7$. The latter has a somewhat higher molybdenum and silver content ; as Rautenberg's body contained a small admixture of silver it is not astonishing that his analyses agreed tolerably with $Ag_4Mo_2O_7$. The figures are :

	Calculated for			Found by Rautenberg		
	Ag_2MoO_4	$Ag_4Mo_2O_7$				
Ag -	57·47	58·70	59·96	58·81	58·69	per cent
Mo -	25·53	26·09	24·50	25·78	25·96	„ „

The case of the tungstates is very similar, as appears from a comparison of the calculated value with Rautenberg's results:

	Calculated for		Found by Rautenberg	
	Ag_2WO_4	$Ag_4W_2O_7$		
Ag -	46·55	47·48	47·33	47·10 per cent
W -	39·66	40·35	38·94	39·73 „ „

It is evident that no conclusions regarding the existence of a suboxide salt can be drawn from these analyses, and therefore this objection to my statement would appear to be met.

In the second place, I propose to describe a few observations on the reduction of silver citrate. Wöhler and v. Bibra heated this salt in a current of hydrogen to 100°; Wöhler (*loc. cit.*) obtained Ag_2Cl; v. Bibra (*J. f. prakt. Chem.* **2**, 12, 39) Ag_4Cl_3 by treating the reaction product with hydrochloric acid; while Newbury tried in vain to arrive at a product of constant composition. This author suggested that the red colour of the aqueous solution of the reduction product was due to finely divided metallic silver. My experiments on the subject were as follow:

When pure, dry silver citrate is heated to 108° a violent reaction takes place, the salt being transformed, with considerable increase in volume, into a grey, porous mass, which assumes a metallic lustre when triturated in the agate mortar and does not give a red solution. When the salt is treated in this way, reduction to metal certainly occurs, with liberation of fumes smelling of formic and acetic acid. If the citrate is heated on the water bath in an inert gas no change takes place, even after six hours' heating.

If, however, hydrogen is passed over the citrate at 100°, it is gradually reduced, and the phenomena observed by me agree completely with the description given by Newbury. I may add that the products obtained by me occasionally aggregated into tough lumps when an attempt was made to powder them, i.e. that resinous products appear to be formed

by the reaction. It is therefore impossible that, as Wöhler and v. Bibra thought, the reaction should proceed according to the equation :

$$2C_6H_5Ag_3O_7 + H_3 = C_6H_5Ag_6O_7 + C_6H_8O_7 ;$$

but the citric acid takes a part in the reaction, which is not surprising as, according to Figuier, it reduces gold salts,[3] and as many oxy-acids react in the same manner ; the use of tartaric acids for producing silver mirrors is a well-known instance.

Since the red colour of the solution has been quoted again and again as proof that it contained compounds of silver suboxide, and as, apart from this property, nobody would probably have conceived the possibility of such compounds existing, my efforts were directed principally towards obtaining such a solution as concentrated and as free from impurities as possible, so as to ascertain what substance really produced the red colour. Somewhat to my surprise the best results were obtained when the product of reduction was treated with ammonia ; while all the supposed salts of silver suboxide are decomposed by ammonia into metal and normal salt, the citrate should, according to this observation, have just the opposite property. The liquid thus obtained was perfectly clear, had an intense red colour, fluoresced slightly, and showed the following interesting properties :

On addition of an acid or of any indifferent salt, such as potassium nitrate, sodium sulphate, or sodium acetate, the red colour instantaneously disappears and a black substance is precipitated, of which a few centigrammes could be collected and proved to be metallic silver. If the nitrate solution was added gradually the colour of the liquid changed : at first it became yellowish, then assumed a greenish tinge, and finally became colourless, while the metal settled out. Occasionally I did not obtain a red liquid at all, but at once a green solution ; this happened particularly when little ammonia was added to the substance and the mixture was rapidly diluted with water. This solution, exactly like the red one, became colourless on addition of salts and deposited metallic

silver; in transmitted light it appeared a beautiful grass green and was clear, in reflected light it looked violet and opaque. Whether this is a fluorescence phenomenon, or whether the green is the colour in transmitted light and the violet the surface colour of the body suspended in the liquid, is a question which must be left open; the latter assumption seems to me the more probable one.

The coloured substance is removed from both solutions by animal charcoal. Fifty c.c. of the red liquid, which was so concentrated that a layer 1 cm. thick was almost opaque, retained a feeble yellow tinge only after shaking for half a minute with animal charcoal which had been washed with hydrochloric acid and freshly ignited; after two minutes' further shaking it passed through the filter quite colourless. It has, of course, been shown several times that even crystallizing substances are abstracted from solutions by charcoal; thus G. A. Koenig (*Chem. News*, 45, 215) has demonstrated that the removal of gold chloride from solution by wood charcoal is not to be explained by reduction only, but that the salt is also absorbed as such; still, the experiments quoted appear to me to prove that the red colour is caused by metallic silver. Nevertheless, the phenomenon, which is of great interest in any case, was further investigated by submitting a quantity of the red solution to dialysis.[4]

As was to be expected, no trace of the red substance passed through the membrane, but fairly considerable quantities of normal salt and of ammonia. The experiment was continued for five days, the water in the outer vessel being renewed every twenty-four hours; after this time nothing more passed through the membrane. A small quantity of metallic silver had deposited in the dialyser, but the remaining red liquid after filtration still showed an intense red colour and the same properties as the original solution, except that a larger quantity of nitrate solution had to be used for precipitating the silver.

Altogether, the solution thus freed from foreign admixtures had become much more stable, if the expression is permissible; after standing for four months in a closed

vessel in a warm place it has not deposited any metallic silver.

That the colour is caused by a body suspended, and not dissolved, in the liquid is proved further by the following experiment:

The liquid was mixed with a solution of gum arabic and vigorously shaken; although the colour darkened somewhat, the liquid remained perfectly clear and transparent. If the gum was then precipitated by alcohol, it took down the silver and assumed a reddish grey colour; after the coagulum had settled, the supernatant liquid was perfectly colourless.[5] If the alcohol was then poured off and the gum arabic again dissolved in water, a transparent red solution of the original tint was again formed. Before carrying out the experiment I had, of course, satisfied myself that alcohol alone did not precipitate anything.

When the liquid is frozen the silver contained in it also separates as an extremely fine powder. About 350 c.c. of solution was kept for twelve hours at a temperature of $-12°$; the liquid obtained on melting the ice showed no trace of red colour, but was completely black and opaque. Under the microscope at high power the silver was seen to have separated in extremely small, irregularly shaped particles, which, however, were so fine that after standing for eight days a part only of the substance had settled. This, however, occurred at once on the addition of nitrate solution; microscopic examination of the precipitate showed that the silver particles had aggregated into much larger and perfectly spherical bodies; when the liquid was removed from the slide by blotting paper and was replaced by water they again broke up into the original small particles. This appears to me to explain the fact that precipitates during washing occasionally begin to pass through the filter when the greater part of the salts has been displaced, and that many precipitates, e.g. barium sulphate, are so difficult to wash out completely.

The weight of precipitate from the 350 c.c. of liquid after drying over phosphorus pentoxide amounted to 0·26 gm.; the solution had been so deeply coloured that a layer 1 cm.

thick did not allow any light to pass. The substance still contained a trace of potassium salt, as shown by the spectrum, although it had been washed until a portion passed through the filter. The precipitate was dissolved in nitric acid and the silver precipitated as chloride; the amount found was 98·89 per cent Ag on the quantity used.

These experiments prove conclusively that silver can be obtained in a state of apparent solution, and this fact agrees with the observations by O. Loew (*Ber.*, **16**, 2707) that silver is precipitated in a peculiar molecular condition from ammoniacal solutions of its salts when these are treated with proteins, and that in this form it gives a red or green colour to the liquid in which it is suspended. Dr. Loew was good enough to show me his preparations, and I have satisfied myself that his products give solutions which agree in their behaviour with those described by me.

Silver, however, is not the only body which exhibits this property. It has long been known to belong to amorphous bodies; I need refer to ferric hydroxide only. I myself have had the opportunity of observing a similar behaviour on the part of molybdenum hydroxide. When this substance is precipitated from the tetrachloride with ammonia and washed by decantation a period is reached when the whole substance dissolves to a clear solution; renewed addition of ammonium chloride again causes the hydroxide to separate. Selenium also, according to Schulze (*J. f. prakt. Chem.* **2**, 32, 390) forms a soluble modification; I have satisfied myself of the correctness of Schulze's observations and have found that the "selenium solutions" show the greatest similarity in their behaviour with the silver suspensions described above.

An attempt to explain adequately these peculiar phenomena would seem premature. W. Stein (*J. f. prakt. Chem.* **2**, 6, 172), who considers the so-called gold purple to be finely divided metal, ascribes the differences between these modifications and the so-called "dichroitic gold" to a smaller size of the molecules; and it is not impossible that the various modifications of silver observed by me correspond to

various molecular states. I am contemplating an exhaustive optical examination of the products described, and shall report later on the results.

As regards the silver suboxide compounds, there would appear to be no further reason for continuing to assert their existence. Isolated observations still to be found in the literature and tending to show the existence of bodies in which one atom of hydrogen is replaced by two atoms of silver are either easily explained in accordance with the deductions given above or they rest on an erroneous terminology, e.g. a notice in the annual reports (*Jahresbericht f.*, 1875, 223) stating that Isambert had produced silver suboxide by the action of uranium dioxide on silver nitrate.

The experimental investigations described in the present paper were carried out partly in the laboratory of the Royal Academy of Sciences and partly in the mineralogical collection here.

MUNICH, *March*, 1887.

[1] "Stannosates," i.e. stannites. Pillitz (*loc. cit.*) writes: "When a neutral solution of silver nitrate is added to an alkaline solution of stannous oxide. . . ."

[2] Crystallized silver chloride containing highly disperse silver has been obtained by W. Reinders (*Koll. Zeitschr.*, **9**, 10 (1911)) by an analogous method, i.e. slow evaporation of ammonia from ammoniacal solutions of AgCl exposed to light.

[3] Reduction by neutral sodium citrate is an excellent method of preparing red gold sols. Cf. K. Hiege, *Zeitschr. anorg. Chem.*, **91**, 145 (1915).

[4] This is the first record of the dialysis of a metal sol. Svedberg calls the investigation "of fundamental importance" ("Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe," Leipzig, 1920, p. 21). Compare M. Carey Lea's remarks on Muthmann's paper as illustrating the state of the subject at that period.

[5] An instance of the general rule that protected sols are coagulated by agents which precipitate the protective colloid. It holds equally for non-aqueous sols; thus nickel sols in toluene, protected by india-rubber (E. Hatschek and P. C. L. Thorne, *Proc. Royal Soc. A.*, Vol. CIII, p. 276 (1923)) are precipitated by acetone.

ON THE NATURE OF COLLOIDS AND THEIR WATER CONTENT.

By J. M. van Bemmelen.

ON THE NATURE OF COLLOIDS AND THEIR WATER CONTENT.

By J. M. van Bemmelen.

(*Rec. d. trav. chim. d. Pays-Bas*, **7**, 37 (1888).)

Jakob Maarten van Bemmelen, born 3rd November, 1830, at Almelo. Matriculated at Leyden 1847. Became assistant to van Kerckhoff at Gröningen in 1852; Doctor's degree at Leyden in 1854. From 1856 Teacher of Chemistry and Physics at Akademie Minerva. First work on soils published in 1863. Director of Secondary Schools at Gröningen and Arnhem during the following ten years; appointed Professor of Inorganic Chemistry at Leyden. From 1877 on, published important papers on soils and on inorganic colloids, a collected edition of which was published by Th. Steinkopff, Leipzig, 1910. Died 13th March, 1911.

For complete biography and bibliography see "Gedenkboek aangeboden an J. M. van Bemmelen" (C. de Boer, *Jr.* The Helder, 1910).

FIRST PAPER.

The article by MM. Carnelley and Walker in the *Journal of the Chemical Society*, **302**, p. 59–102 (January, 1888) on the dehydration of metallic hydroxides by heat induces me to publish, sooner than intended, my experiments and views on the colloidal hydroxides, chiefly because they differ from theirs in this point—that these gentlemen have in no way taken into account the state (colloidal or crystalline) in which the hydrates occur, nor the vapour tension of the water during dehydration.

It seems to me that one does not in general sufficiently distinguish the colloidal combinations of oxides or of salts with water from the true hydrates. The former are unstable bodies of indefinite composition, the latter true chemical compounds. In the textbooks of chemistry, and also in many recent researches, these compounds of indefinite composition appear with chemical formulæ, as if there were simple ratios between their constituent atoms or molecules, and as if they belonged to the class of ordinary chemical compounds.

This also applies to a large class of bodies which might be

called *absorption compounds*. They are met with particularly when colloidal substances are treated with solutions of an acid, a base, a salt, etc.

The concept of indefinite compounds has been abandoned since the views of Berthollet have given place to the atomic theory of Dalton, supported by the discoveries of Gay-Lussac, Berzelius, and others. Nothing but ordinary chemical compounds, composed of atoms or molecules in very simple ratios, has been investigated and accepted. Nevertheless, Gay-Lussac has broader views. In 1808, when he published his researches (*Mem. Soc. d'Arcueil*, II, p. 207), he came to the conclusion: "Gases always combine in the simplest ratios, according to M. Dalton's law; only in the gaseous state do substances follow regular laws," and added: "Berthollet thinks that compounds form in a continuous manner, e.g. the acid sulphates, the alloys, glass, mixtures of different liquids," and he believes that "the force which produces chemical combination is identical with that which produces solution."

Gay-Lussac is not inclined to reject this opinion altogether, for he says: "It is easy to reconcile the theories of Dalton and those of Berthollet," "one must admit that chemical action takes place indefinitely in a continuous manner between the molecules, whatever their number and their ratio; one can obtain compounds with very variable proportions."

When a compound with fixed proportions is formed, then "chemical action is exercised most powerfully." The substances interact with their masses and form very variable compounds, "at least unless the proportions are determined by special circumstances."

Avogadro, likewise, is not inclined to reject these indefinite compounds (*J. de Phys. par De la Methérie*, t. 73, 1811, p. 58–76): "As the molecules in solids and liquids approach each other the distances left between compound molecules are of the same order only as those between the elementary molecules, and this may give rise to more complicated ratios, and even to combination in all proportions; but these are of another kind, and this distinction may serve to

reconcile M. Berthollet's ideas with the theory of fixed proportions."

This conception of combination in variable proportions has been put aside. When compounds were encountered of which a great number, with different proportions, could be prepared, either very complicated formulæ were accepted, or else the percentage composition alone was given. I mention only the numerous hydrates of:

$$Fe_2O_3,\ Al_2O_3,\ Cr_2O_3,\ SiO_2,\ TiO_2,\ SnO_2,$$

many basic or acid salts, colloidal silicates—even relatively simple substances like the sulphides of phosphorus prepared at low temperature.

As regards compounds formed by absorption, no one has troubled about them so far.

I will confine myself for the moment to some hydrated oxides in the colloidal and crystalline state. Some preliminary remarks on the nature and the properties of colloids seem, however, desirable.

The colloidal state is a peculiar condition of matter. It is that of the majority of organic bodies in nature. Inorganic bodies too, elements as well as compounds, can generally assume this state. A number of compounds, when produced by wet process, are ordinarily obtained in the colloidal state only, e.g. the oxides of iron, aluminium, chromium, silicon, titanium, etc., and cannot always be transformed into crystalline hydrates, as is the case with those of aluminium or of zinc.

The colloids may be in solution in some liquids, or else separate from them as gelatinous substances. When dissolved, Graham considers them to be something like mixtures of one liquid with another (*Ann. Chim. et Phys.*, 1864, p. 321). He has shown that an aqueous solution of a colloid can be transformed into an alcoholic or glycerine solution—which he describes by the terms hydrosol, alcosol, glycerosol—through cautious substitution of one liquid for another by means of dialysis. Graham's view seems to me quite plausible, since the colloid can separate from the liquid as a nearly fluid

jelly which contains a very large quantity of this liquid, and can dissolve again.

Colloids are known which are soluble in water or other liquids in small quantities (like silicic acid), and others which are very soluble (like metatungstic acid). Since the researches of M. Alexejew (*Wied. Ann.*, 1886, 28, S. 385) have demonstrated that the mutual solubility of liquids depends on the temperature, and that a temperature exists above or below which two liquids are miscible in all proportions, it seems to me that the solution of a colloid (still semi-fluid) in any one liquid obeys an analogous law.

That colloids in solution form peculiarly aggregated complexes with the molecules or moles of the solvent also appears to follow from the fact that they do not pass through certain organic membranes.

The solution of a colloid in any liquid may be stable or unstable. Generally it is opalescent; when the colloid tends to separate from the liquid as a jelly, the solution becomes viscous, sometimes oily. It is not known in what conditions the solutions are stable to such a degree that they can be preserved indefinitely, or even heated and evaporated without coagulating (e.g. a glue solution heated for many hours, solutions of metatungstic and vanadic acid, etc.). Often unstable solutions are obtained, e.g. of silicic, ferric or aluminium oxide, arsenic, antimony and copper sulphide, which behave like supersaturated solutions. The slightest force then suffices to produce a more stable state, viz., the coagulation of the colloid with liberation of heat. One may apply to this change what R. Helmholtz says (*Wied. Ann.*, 1887, S. 401): "A chemical system is in equilibrium only when its free energy has assumed the minimum value possible at the prevailing temperature. As long as this is not the case, spontaneous changes may occur, though they may be retarded by small forces of which we are ignorant. When these small resistances are overcome, the labile state is terminated."

This is very probably the reason why coagulation often occurs spontaneously, or why it can be easily provoked or induced.

When a colloid deposits in a solution it can coagulate into a jelly or as a flocculent precipitate. The jelly is transparent and often encloses liquid; the precipitate likewise contains a large quantity of liquid. If the jelly of the flocculent mass is subjected to pressure, part only of the liquid is separated, for a certain quantity is strongly held by the colloid. Graham calls the colloids which set to jellies *gels*; he distinguishes the hydrogel, alcogel, glycerogel, etc., according to the liquid in which the gel has been formed or transformed. He has transformed the hydrogel (e.g. of silicic acid composed of about 9 parts of SiO_2 to 90 parts of water) into alcogel by placing it into absolute alcohol and renewing the alcohol from time to time. The volume of the gel remained almost unaltered, the 90 per cent of water being replaced by 90 per cent of alcohol. Similarly, a hydrogel placed in sulphuric acid of gradually increasing concentration changed to a perfectly transparent sulphogel and lost only a fifth or sixth part in volume. When this sulphogel is submitted to distillation, it becomes evident that, as acid is driven off, the remaining portion is held more strongly by the silicon dioxide (SiO_2); the temperature required to drive off acid has to be gradually raised and the last portion of monohydrate requires a temperature higher than the boiling point. Titanic acid also lends itself well to the preparation of various gels. To prepare a glycerogel it is sufficient to heat the hydrogel of TiO_2 with glycerine.

It thus follows that the gelatinous hydrates, and the gels in general are peculiar compounds of bodies with liquids such as water, alcohol, glycerine, sulphuric, and acetic acid, which can replace each other osmotically.

MM. E. Wiedemann and Luedeking have proved that the coagulation of a colloid develops heat. They neutralized a potassium silicate solution with dilute hydrochloric acid, and then induced instantaneous coagulation by adding a drop of ammonia; 11 or 12 calories were produced (*Wied. Ann.*, 25, S. 145).

M. Graham has also observed this heat (p. 122).

When the gel dries gradually and slowly, it finally becomes

vitreous; it appears to me that this state resembles that of the glasses obtained by fusion.

The colloidal substances which separate, not as gels but as flocculent precipitates, probably differ from the gels in that their agglomeration is already more advanced. I quote as examples copper sulphide precipitated in ammoniacal solution, antimony, or arsenic sulphide; selenium (*J. prakt. Chem.*, 1885, 32, S. 390) and the colloidal precipitates of oxalates, phosphates, and various oxides. All these colloids enclose a good deal of water, but not as much as the gels. There are still other forms in which amorphous bodies can separate from a solution, such as the spherulitic form, which I have observed with stannic acid precipitated from its alkaline solution by carbonic acid.

M. Muthmann (*Ber.*, 1887, p. 983) mentions a water-soluble silver which was precipitated in the form of globules by a little saltpetre.[1]

What place, among the different amorphous states in which the elements and their chemical compounds may exist, is to be assigned to the colloidal state? This is a problem of great interest; but it seems to me that we have not yet advanced sufficiently to attack it.

Various circumstances can produce coagulation:

(*a*) *Time.*—If it occurs with time, without external agencies, the causes may be very various. When a solution of $SnCl_4$ or of Al_2Cl_6 or Fe_2Cl_6 coagulates after hours, days, or an even longer time, it is certain that a slow separation between the oxide and the hydrochloric acid has taken place. In other cases small quantities of alkali dissolved gradually out of the glass by water may coagulate solutions of oxides (prepared by dialysis) or colloidal sulphides. There remains the further possibility that the colloidal matter itself, in supersaturated solution, undergoes very slow molecular modifications through changes in temperature, etc.

(*b*) *Heating.*—It is often sufficient to raise the temperature, whereby an acid or a base which keeps the colloid dissolved may separate from it, or the colloid itself may undergo a change. A silicic acid solution prepared from an alkaline

silicate coagulates sooner by heating than a solution prepared from methyl silicate. The latter, however, also coagulates gradually in the end.

(*c*) *Influence of certain indifferent Bodies.*—Graphite accelerates the coagulation of silicic hydrogel. A solution containing from 5 to 2 per cent, which coagulates spontaneously only after a time varying from five days to two or three months, in the presence of graphite coagulates in one to two hours. This phenomenon, observed by Graham, suggests that a change takes place in the liquid by the play of molecular forces. Colloidal arsenic sulphide is precipitated from its solution by charcoal (Schultze).

(*d*) *Influence of Crystallizable Substances such as Acids, Bases, Salts.*—It has long been known that the coagulation of colloidal substances is produced by these agents. While the phenomenon has often been observed it has not been assumed to be general. The various acids, bases, and salts do not all possess this faculty, and in addition the quantities required, generally very small, are different. A little hydrochloric acid coagulates the sols of Al_2O_3, As_2S_3, and Sb_2S_3, but not that of SiO_2. Alcohol, tartaric and acetic acid do not coagulate silicic acid.

It appears to me that the action of acids, bases, and salts in producing or accelerating coagulation belongs to the domain of capillary phenomena. It is conceivable that changes in the concentration of the solution produce variations of its capillary constant; for this reason the phenomenon is reversible, *provided the gel does not undergo further changes in molecular aggregation.* Examples are very numerous; I quote one only: when a dialysed ammoniacal solution of copper oxide is coagulated by a small quantity of ammonium chloride it redissolves at once when the chloride is removed by washing.

When, however, a colloid can form a gel with a liquid, it seems to me such a liquid has no effect on the coagulation of that colloid in aqueous solution. The hydrogel of silicic acid can be transformed into alcogel, sulphogel, acetogel; alcohol, sulphuric, and acetic also do not coagulate silicic acid in

aqueous solution. These liquids can enter into the liquid molecular complexes which exist in the aqueous solution. The hydrogel can be transformed into glycerogel, and at the same time glycerine dissolves a little silicic acid. Glycerine can keep several colloids in solution, e.g. ferric oxide in presence of an alkali (Grimaux, *C. R.*, 98, p. 1485). It has also been observed with several other colloids that acetic acid does not coagulate them.

It is to be noted that, while a small quantity of acid or salt, etc., is sufficient to coagulate a colloid, on the other hand a small quantity of a substance which can form a liquid molecular complex or else a gel with the colloid is sufficient to make it pass into labile solution again. A small quantity of HCl, for example, can redissolve the hydrogel of SiO_2; Graham redissolved 200 parts of SiO_2 as hydrogel with 1 part only of potash in 10,000 parts of water by heating together for an hour at 100°. I have been able to redissolve up to 20 molecules of metastannic acid by 1 molecule of K_2O in very dilute solution, at ordinary temperature, by agitating them together for a very short time.[1] Graham has obtained an aqueous solution of stannic acid by dialysing the hydrogel which forms when the hydrochloric solution is saturated with alkali, or the alkaline solution w th hydrochloric acid. When the salts have been removed by diffus on, a moment arrives when the very small quantity of free alkali (which is retained by the gel more energetically than the acid and salts) can redissolve the whole of the hydrogel. This alkali can still be removed by prolonged dialysis, especially if a few drops of iodine solution are added. Similarly, a very small quantity of hydrochloric acid is sufficient to redissolve the stannic hydrogel.

In my opinion it is not possible to speak of the solubility of colloids in acids and alkalis, in the ordinary sense of the term. The phenomenon must be regarded as a peptization (Graham's term). Each portion of the colloid in turn forms a soluble molecular complex with the alkali or with the acid, and is then separated from it by the action of the water, which is slower than that of the acid or alkali. The more

perfect the hydrogel state of the colloid (in other words, the nearer the liquid state) and the less it has been modified by further aggregation, the more easily redissolution takes place. When this is complete, the peptizing agent may be removed from the solution and the colloid remains dissolved.

The same reasoning is applicable also to the peptization of albuminoid substances.

In certain cases a larger quantity of alkali or acid can produce a change in the liquid which causes separation of the colloid, especially if the colloid forms an adsorption compound with the alkali or acid. This occurs with metastannic acid.

A very small quantity of HCl produces a change in an aqueous solution of alumina sufficient to cause coagulation, but on the addition of a little more acid the alumina dissolves. Some time afterwards the decomposition of the soluble molecular complexes of alumina and hydrochloric acid has progressed so far that the colloidal alumina slowly deposits while undergoing gradual changes of aggregation.

That the coagulation of colloidal solutions depends chiefly on a change in the capillary constant of the liquid is also made probable by the agglomeration of the portions already coagulated on further addition of the coagulating substances. When the very small quantity of acid, base, or salt has been added to the more or less opalescent solution of the colloid, a stronger opalescence is first observed as the gel forms. During this period the particles perhaps have dimensions of the order of wave lengths of light and may reflect the light which illuminates them in a peculiar manner. When the colloid does not set to a transparent gel, but flocculates or forms microscopic spherites, it remains suspended in the liquid. This also occurs when the gel is squeezed out and again suspended in water, or when a pure insoluble colloid like clay is treated with pure water.

These fine particles in suspension can be changed into coarser aggregates which deposit rapidly, by increasing the concentration of acid or salt—generally speaking, of the coagulant. It is therefore sufficient to alter the capillary constant a little more. When the colloid undergoes no gradual

change after this agglomeration the action is reversible; on dilution the precipitate subdivides and goes into solution once more.

Generally speaking, a colloid, when separating from a liquid as gel or as amorphous precipitate, can partly absorb the crystallizable substances which were in solution. I hope in a later paper to treat of these compounds, which I propose to call "absorption compounds."

It appears to me possible to assume that the aggregation into flocculent precipitate is the consequence of a change in the surface tension of liquid membranes between the approaching colloidal particles—in such fashion that these membranes between the particles are torn at some point and the particles can attract one another and aggregate. The explanation of the mechanism of this phenomenon remains still to be found.[3]

It is easy to explain why the flocculent aggregates deposit more rapidly than the minute particles from which they have been formed, if the laws governing the fall of a solid in water are taken into account. As soon as the ratio volume/surface of the aggregates has become large enough, they can assume a uniform velocity which overcomes the currents that are never absent in the liquid; while the fine particles before their agglomeration always remain their plaything and therefore keep in suspension.

Modifications of Colloids.

One and the same colloid may have a very varying constitution according to the circumstances of its formation. The black colloidal MnO_2, e.g. which is precipitated from a solution of a manganous salt by hypochlorites, differs considerably from the red colloidal MnO_2 prepared by M. Frémy's method, as regards the combined water or, in other words, its power of absorbing water. (Van Bemmelen, *Arch. Neerl.*, XV, p. 321 (1880) and *J. prakt. Chem.*, XXIII, p. 324 (1881).) Stannic acid deposits from a fresh solution of stannic chloride when the hydrochloric acid is neutralized with potash; but when the solution is old and

dilute, neutralization produces a coagulum consisting chiefly of metastannic acid. It is frequently to be observed that the concentration and the temperature at which coagulation takes place affect the constitution and composition of the colloid. (See alumina in the third paper.)

The molecular modifications which colloids can undergo are various, and in this point they differ a good deal, not only among one another, but even one and the same colloid is more or less liable to become modified after preparation. It is for this reason that colloids, and any one colloid, show such great variations in their composition (water content) and that analysis does not lead to the formula of a hydrate of simple and constant composition. The hydrogel of stannic acid, when kept under water for a long time, gradually changes until it is transformed into metastannic acid; the change is greatly accelerated by heating. I have even observed that a hydrogel of stannic acid, dried at ordinary temperature and kept in a well-stoppered flask, had become partly modified without having lost water. Many colloids cannot be heated without losing their capacity for retaining water or for absorbing crystalloid substances from solution, or the property of redissolving under the influence of certain substances. (See stannic acid, etc., in the following papers.) All these changes are gradual.

Other colloids, on the contrary, do not change much in similar conditions. When silicic acid gel has been dried at ordinary temperature until it has become dry to the touch, it still contains a good deal of water (over 4 molecules). It loses the greater part of this water in a dry atmosphere or at 100°, but takes it up again completely at ordinary temperature in an atmosphere saturated with water vapour; its absorptive power for salts, etc., has not altered sensibly, nor its solubility in potash.

Other colloids in solution can be heated without losing their solubility in potash.

The changes in molecular aggregation proceed with evolution of heat. M. Berthelot has proved this for the hydrogel of Fe_2O_3 and several others. When silver iodide is pre-

cipitated in the colloidal state (by mixing a solution of KI with one of $AgNO_3$) less than 21 calories are developed at first, corresponding to a heat of combination of about 7·7 calories for the silver iodide. Afterwards this body becomes more condensed, and this aggregation develops a further 6·6 calories. M. Berthelot (*C.R.*, **103**, pp. 911 and 966; **104**, p. 1666) and M. Joly (*C.R.*, **104**, p. 905) have also found that the colloidal phosphates of the alkaline earths develop a considerable number of calories when their colloidal state changes to the crystalline.

If these observations are taken into consideration, it seems to me that one may picture the formation and composition of a hydrogel, or generally of a colloid, in the following manner: at first a complex of molecules, which is not far from the liquid state, separates from the liquid, with the evolution of little heat. The larger the quantity of water with which the colloid separates, the more easily does it dissolve again when the salt or the acid, or generally the coagulating substance, has been removed or deprived of its activity by dilution; and when the hydrogel has not become modified too far. This water is very feebly combined with the oxide or salt, and it often remains uncertain whether a true hydrate or rather the anhydrous oxide has separated in the colloidal state. With silicic acid the latter case seems to me plausible; with magnesia the former is possible.

When the colloid loses water and the coagulum becomes less gelatinous, the molecular aggregation changes continuously and the water is held more strongly. This water can nevertheless be replaced almost completely by another liquid, which proves that there is no question yet of a chemical hydrate. As the hydrogel keeps losing water at constant temperature the loss proceeds with decreasing velocity, which agrees with the assumption that the strength of the bond increases.

Up to now the hydrogels have been analysed after setting and drying over sulphuric acid at ordinary temperature—or after heating to temperatures between 15° and 100° or over —and the results have been calculated as if the bodies thus

obtained were true hydrates. An unlimited number had to be accepted.

The results to which my researches on the colloidal oxides BeO, SiO_2, SnO_2, Al_2O_3, Fe_2O_3, MnO_2 (see the following papers) have led, combined with the observations of various chemists, prove that the water remaining in the colloid when it has become dry to the touch is still wholly or in part colloid water (i.e. colloidally combined), so that there can be no question of a chemical hydrate of definite composition—always with this reservation, that the colloid itself may be a definite hydrate which in addition occludes colloidal water in indefinite ratio.

In the following papers the results obtained are briefly summarized.

When the colloid has lost water to such an extent that it is dry to the touch, it still contains a good deal: thus silicic acid contains over 4 moles, alumina and ferric oxide about 6 moles, stannic oxide over 3 moles, chromic oxide about 13 moles, etc. As they dry further, aggregation changes continually and with it the composition. When the colloid, *at a certain temperature*, has lost so much water that its vapour tension has become equal to that of water at the same temperature, further loss of water can be arrested by placing the colloid in a closed space over water and maintaining the temperature constant. When the dry colloid, placed in a dry atmosphere (e.g. over sulphuric acid), has lost so much water that its vapour tension has become practically zero, it can take it up again wholly or partially in an atmosphere saturated with water vapour.

Let us assume that the colloid placed in atmosphere saturated with water vapour contains at t° a number *a* of molecules of water per molecule of anhydrous substance, and that it loses *b* molecules in a dry atmosphere, still at t°, it will take up the *b* molecules again in the event only that the change of molecular aggregation it has undergone in losing *b* molecules is completely reversible. I have observed this with silicic acid. The stannic and ferric colloids, on the other hand, do not entirely take up the water again at constant

temperature. When the colloid is kept in an atmosphere partially saturated with water vapour, it loses water until its vapour tension has become equal to that of the medium.

The dry hydrogel of chromic oxide, which contains much water and changes very little between 15° and 100°, affords a good illustration of these laws, as shown by the following table:

Molecules of H_2O *per* 1 *molecule of* Cr_2O_3.

(Initial composition $Cr_2O_3.11H_2O$.)

Temperature	In Atmosphere Saturated with Water Vapour	In ordinary Atmosphere	Over Sulphuric Acid
±15° - - -	12–13	7·8–8·0	7·05
±45° - - -	—	5·9	—
±65° - - -	7·9	5·77	5·0
±100° - - -	—	—	—
After heating to 50°			
At 15° - -	—	7·9	—
After heating to 100°			
At 15° - -	±12·5	7·0	5·2
Silicic acid gave:			
At ±15° - -	4·3	1·45	0·26
48° - -	1·57	0·33	0·23
100° - -	0·37	0·2	0·14

This dehydration is not a chemical dissociation. When a hydrated salt or oxide of definite composition dissociates at a certain temperature, because its vapour tension is greater than that of the surrounding medium, a certain number of molecules are decomposed, either completely or into a definite lower hydrate and steam. Dissociation ceases as soon as the number of molecules decomposed had provided sufficient steam to saturate the surrounding atmosphere at the prevailing temperature. When the hydrate is exposed in a dry atmosphere the velocity of dehydration is uniform. When the body can form several hydrates the velocity is uniform as long as molecules of the hydrate undergoing decomposition still exist. At the moment when all the molecules are decomposed, and when a still lower hydrate or an anhydride begins to form, the velocity decreases suddenly, and then becomes uniform again. The vapour tension at constant temperature is constant for a definite hydrate, independently of the number of molecules decomposed.

When a colloid is placed in a dry atmosphere at constant temperature, the velocity of dehydration is always observed to decrease continuously, until it reaches a minimum.

The following is an example :

At 15° in a current of dry air.

Stannic colloid. Initial composition 3·3 to 2·9 H_2O; final 1·04. Velocity of decomposition per day :

During 7 days, decreasing from 1·2 mol. H_2O to $<0·3$ mol.
„ the next 9 days, decreasing to $<0·003$ mol. H_2O.
„ „ „ 30 „ „ to $<0·002$ mol. H_2P.

At 15° in a current of dry air.

Metastannic colloid. Initial composition 2·25 H_2O; final 0·79. Velocity of decomposition per day :

1st day - -	about	0·55	mol. H_2O per day.
2nd day - -	„	0·25	„ „ „ „
3rd day - -	„	0·2	„ „ „ „
4th to 7th day	„	0·04	„ „ „ „
8th to 10th day	„	$0·02_6$–0·02	„ „ „ „
11th to 13th day	„	0·017–0·01	„ „ „ „

The progress of the phenomenon with colloids is therefore different from that with hydrates.

It seems to me probable that the molecules or moles of the colloid all decompose at the same time; they all lose a certain quantity of water if their vapour tension exceeds that of the surrounding atmosphere. The force with which the water is retained depends also on the mass of the combined water; the molecular aggregation of the complex changes continually with the loss of water and with it the vapour tension.

The course of the dehydration and rehydration of colloids resembles the attraction of water by a solution, or its evaporation from it, more closely than the corresponding phenomenon in the true hydrates.

A soluble chemical hydrate, when placed at a certain temperature in an atmosphere constantly saturated with water vapour, attracts all the water, because its solution has a lower tension than water at that temperature; in a dry atmosphere it loses water until completely transformed into a lower hydrate, the tension of which at that temperature is zero. If all possible hydrates still have a vapour pressure at that temperature, the anhydride is formed. In an atmosphere partially saturated with vapour it takes up or loses water until that hydrate is formed which has a tension lower than that of the atmosphere.

As long as the dehydration or rehydration of a hydrate continues (between two possible hydrates, or between a hydrate and an anhydride), the velocity of the process is constant at constant temperature. As regards a solution of an oxide, a salt, etc., it attracts all the water, at any temperature, with decreasing velocity, as long as its vapour tension is lower than that of water at the same temperature. In a dry atmosphere it loses water with decreasing velocity, until it becomes dry. In a partially saturated atmosphere it takes up or loses water until the vapour pressures of the atmosphere and the solution are equal.

Colloids in general take up and lose water like solutions, inasmuch as the course of the phenomenon is a function of the concentration at each temperature. (By concentration I

understand the percentage of water held colloidally.) Beyond that the phenomenon depends on the particular state of aggregation of the specimen of colloid. For this reason the exposure of colloids to the ordinary air gives fortuitous and useless figures. The atmosphere is an unlimited reservoir in which the vapour tension is variable.

The colloid takes up or loses water with decreasing velocity until its vapour pressure is equal to that of water. In general, no definite hydrates are formed when the colloid loses water, as is the case with solutions of substances which can form definite hydrates. The final composition of the colloid is different for each temperature, both in a saturated and in a dry atmosphere ; in this respect colloids differ from solutions as well as from true hydrates.

The irreversible transformations, which the majority of colloids undergo when drying or when heated (already between 0° and 100°) singularly complicate the course of dehydration or rehydration. In general, as I have remarked above, the irreversible modifications reduce the power of absorbing water but strengthen the bond between the colloid and the remaining colloidal water. The vapour tension in this case is more or less reduced.

If the temperature is raised, a true hydrate decomposes with increased velocity ; but in a dry atmosphere, between certain limits of temperature, decomposition stops at the same final product as at a lower temperature, i.e. at a lower hydrate or the anhydride—unless the body loses its crystalline constitution and becomes amorphous. This probably occurs with several chemical hydrates in which, above certain temperatures, decomposition takes a course resembling that of colloids.

With colloids the progress of decomposition, when the temperature is raised, is gradual. At first the vapour tension of the colloid increases, and with it the velocity of decomposition ; afterwards it keeps decreasing and reaches a minimum. The water content of the colloid, either in a saturated or in a dry atmosphere, will be lower than that obtained at the lower temperature, and that the more the greater the molecular

change which the colloid has undergone through the action of heat. The following is an example:

Stannic Colloid.

At 55° in an atmosphere saturated with vapour	Initial composition 2·9 H_2O — final 1·82 H_2O Velocity of decomposition *per hour*: Decreasing in 10 hours from 0·33 to < 9·93
At 55° in a dry atmosphere	Initial composition 1·82 H_2O — final 0·89₅ H_2O Velocity of decomposition *per hour*: Decreasing in 7 hours from > 0·31 to 0·01 H_2O Decreasing in 4 hours following to < 0·004 H_2O
At 100° in a dry atmosphere	Initial composition ± 3·0 H_2O — final 0·74 H_2O Velocity of decomposition *per hour*: First hour about 2 mol. H_2O Decreasing in the 9 hours following from 0·1 to < 0·003

Colloidal alumina.

At 220°–225°	Initial composition 1·8 H_2O — final 0·8₇ H_2O Velocity of decomposition: Decreasing in 40 hours from 0·17 mol. H_2O to < 0·01

When the colloids are heated to higher temperatures they are modified still further and gradually lose the rest of their water. It is known that stannic acid, alumina, and several others have to be heated to several hundred degrees before the last traces of water are given off.

At each temperature a limit composition is reached after prolonged heating; the higher the temperature the shorter the time in which it is reached. Thus, for colloidal

stannic acid with ± 3 mol. H_2O initial water the following water contents are reached :

$$1{\cdot}0\ H_2O \begin{cases} \text{At } 15^\circ \text{ in several days} \\ \text{,, } 103^\circ \text{ ,, 1 hour} \end{cases}$$

$$0{\cdot}9\ H_2O \begin{cases} \text{At } 55^\circ \text{ in about 15 hours} \\ \text{,, } 100^\circ \text{ ,, 2 hours} \\ \text{,, } 105^\circ \text{ ,, 1 hour} \end{cases}$$

$$0{\cdot}7\ H_2O \begin{cases} \text{At } 100^\circ \text{ in 10 hours} \\ \text{,, } 150^\circ \text{ ,, a few hours} \end{cases}$$

When the same specimen of colloid is successively exposed to higher and higher temperatures, care being taken that the decomposition at each temperature has reached a minimum, increases or decreases in the velocity of decomposition are frequently observed. For alumina I have observed acceleration at about 200° ; for glucinia at 215°. Messrs. Carnelly and Walker have observed several instances. These accelerations indicate more profound changes in the state of aggregation. They often manifest themselves in changes of colour and changes in the solubility in acids. (M. R. Wagner has seen the colour of colloidal titanic acid change from white to green, brown, dark brown : *Ber.*, 1888, p. 961.) M. Chatelier (*C. R.*, 104, p. 1517) has observed that, when colloidal aluminium silicates are heated to high temperatures, dehydration is discontinuous at certain temperatures, which shows itself in retardation in the rise in temperature, or else by liberation of heat accompanied by a molecular transformation (increase in density, etc.).

At the moment of complete dehydration, or at least at some temperature near it, the phenomenon of incandescence has been observed with several colloids, indicating a very profound change, e.g. with the oxides of iron, chromium, titanium, and particularly with copper antimoniate. It appears to me very remarkable that the incandescence is stronger when the colloid has been prepared as a hydrogel rich in water, i.e. at a

low temperature in dilute solution; this is the case with the reddish brown ferric colloid and the bluish chromic colloid. On the other hand, the yellow ferric colloid, which is denser from the beginning, does not exhibit the phenomenon of incandescence. This phenomenon, as far as I know, has not been observed with crystallized hydrates.

Colloids, therefore, preserve up to a high temperature a portion of the potential energy which they have received at the moment of their formation.

Since colloids can be changed by suitable treatment into true hydrates of definite composition (see the next paragraph), it is possible that some of them undergo this change when heated to a certain temperature. For the moment I know one colloid only to which this hypothesis applies—that of glucinium oxide. Its composition became $BeO.1{\cdot}00H_2O$ a little below 150°, and remained such up to about 215°. I recall what I have said above regarding colloidal magnesia, which behaves like a colloid of the hydrate $MgOH_2O$ itself.

Transformation of Colloids into Crystallized Substances.

In favourable circumstances colloids can be transformed into chemical hydrates of definite composition.

I have proved this for glucinium oxide (*J. f. pr. Ch.*, 26, p. 227 (1882)). When the colloid (obtained by precipitating a salt with ammonia) is dissolved in an excess of alkali, diluted and heated to boiling, a crystalline hydrate gradually deposits.

	In Moist Air	In Dry Air
While the colloid has the composition at 15° - -	$\pm 4{\cdot}0\ H_2O$	$1{\cdot}47\ H_2O$
The crystallized hydrate has the composition at 15° -	$\pm 1{\cdot}2\ H_2O$	$1{\cdot}00\ H_2O$

The crystallized hydrate is therefore very slightly hygroscopic; it has a definite composition and keeps it up to about 200°. From 204° to 215° a very slight decomposition be-

comes noticeable : 0·99 H_2O at 204° and 0·95 at 212° ; but from 215° to 220° the decomposition is relatively rapid, so that the composition after 12 hours is 0·18 H_2O.

Crystallized alumina, of the definite composition $Al_2O_3 3H_2O$, is obtained by the action of carbonic acid on the solution in potash. It is hardly hygroscopic and preserves its composition up to about 170°. It begins to decompose at 180° ; decomposition becomes more rapid at about 225°.

These two definite hydrates, which absorb so little water in an atmosphere saturated with water vapour, do not absorb salts, etc., from their solutions either, as do colloidal glucinia and alumina.

M. Ville (*C. R.*, 101, p. 375) has obtained a crystallized zinc hydrate $ZnO.H_2O$ by dissolving 1 equivalent of carbonate in 2 equivalents of dilute potash (1 in 10). After half an hour the whole of the zinc was deposited as crystals in the solution of bicarbonate of potash. Similarly, M. Schulten (*C. R.*, 101, pp. 72, 195, 1265) has prepared crystallized hydrates of definite composition :

$$Mg.H_2O,\quad Cd.H_2O,\quad MnO.H_2O,$$

by heating respectively at 180°, 185°, and 160° a mixture of the chloride or iodide with a large excess of potash and a limited volume of water. At these temperatures and pressures the oxide dissolves in the potash, and on cooling the hydrate deposits as a chemical compound of the oxide and water.

It is remarkable that the oxides of the fourth series of Mendelejeff-Lothar Meyer form true hydrates with such difficulty. None are known of silicon or tin dioxide. By the action of carbonic acid on a potash solution of stannic acid I have obtained a spherulitic body only, which after some time in a dry atmosphere, or after short heating to about 100°, assumes the composition $SnO_2.H_2O$, but is still unstable.

A stable hydrate can perhaps be formed under other temperature conditions. The action of carbonic acid on a

potash solution of germanium oxide gave me a colloid which retained potash (*This Rec.*, 1887, 6, p. 205). The bodies which have been described as hydrates of titanium dioxide (Rose, Demoly, Merz, Tuettschew) are certainly mostly unstable colloids, which become modified by drying and by heating; possibly the body prepared by Tuettschew, by placing the compound $PCl_5.TiCl_4$ in a closed vessel near milk of lime, is a true hydrate, stable up to 110°.

As regards lead oxide, a true crystallized hydrate only, of the composition $3(PbO).H_2O$, stable up to 130°, has been obtained (Payen, 1837, *Ann. Ch. Phys.*, 66, p. 49).

M. Ditte has recently described hydrates of vanadic acid soluble in water, and proposes the formulæ:

$$V_2O_5H_2O,\ V_2O_52H_2O,\ \text{and}\ V_2O_58H_2O.$$

I have prepared this body according to M. Ditte's method.[4] (*Ann. Ch. et Phys.*, 1888, 13, p. 190: "Ammonium vanadate is heated in a covered crucible, to convert V_2O_5 into V_2O_4 and V_2O_3, and then oxidized by nitric acid, which is driven off by heating. I have observed that the preparation is facilitated by passing a current of ammonia through the crucible during heating.") I have satisfied myself that the body is a colloid: the purplish red aqueous solution is opalescent and is precipitated by salts. The dry colloid attracts water with decreasing velocity; it assumes an equilibrium with the vapour tension of the medium—as, indeed, M. Ditte himself remarks—the figures $1\,H_2O$, $2\,H_2O$, and $8\,H_2O$ are accidental only and do not represent hydrates of definite composition.

The compounds of colloidal stannic acid and of colloidal metastannic acid with sulphuric acid and with potash are likewise absorption compounds of indefinite composition. But by heating and by evaporating these colloids with the potash and the concentrated sulphuric acid, these compounds are transformed into true and crystallized chemical compounds:

$SnO_2.K_2O.3H_2O$ (Marignac, Moberg)

$SnO_2.2SO_3.2H_2O$ (Ditte, *C. R.*, 104, p. 172).

The red colloid of MnO_2 absorbs potash or soda from

aqueous solution, as I have described elsewhere (*J. pr. Ch.*, 1881, pp. 247 and 379). This compound is indefinite, but Rousseau (*C. R.*, 103, p. 261) and Gorgeu (*C. R.*, 104, p. 1796) have obtained crystallized and definite compounds with MnO_2 with Na_2O by fusing the chloride at red heat with sodium nitrate and caustic soda.

The colloidal phosphates obtained by saturating phosphoric acid with alkaline earths, or by precipitating alkaline phosphates with salts of the alkaline earths or of metals, have an uncertain composition; at least, they retain an excess of base, or soluble salts; but when they are, more or less rapidly, transformed into crystallized bodies, they have a normal composition, particularly as regards the number of molecules of water; and they no longer retain a portion of the substances in solution.

These instances could be multiplied. One fact appears to emerge from all these observations. The colloid, in order to be transformed into hydrate or generally into a compound of definite composition, must, at a suitable temperature, undergo such a modification that it is no longer soluble in a solution of the agent which kept it dissolved (or rather peptized) while it was still colloidal.

To sum up: I consider the compounds of elements, oxides, sulphides, salts, etc., with water, in the colloidal state, not as chemical and definite compounds, but as indefinite compounds in a peculiar state of aggregation. This state still approximates to the liquid state, when the colloid separates from a liquid as gel. The water in hydrogels can be replaced by other liquids. At no temperature, in either a dry or a saturated atmosphere, does the colloid possess a definite composition, unless it has been transformed into a chemical hydrate. In general, the vapour tension of a colloid varies continuously with its water content. At constant temperature, in an atmosphere saturated with vapour, the colloid takes up or loses water so that its vapour pressure equals that of the atmosphere; in a dry atmosphere it retains so much that the pressure becomes approximately zero. The vapour

tension varies, not only with the temperature, but also with the irreversible modifications which colloids ordinarily undergo through the influence of drying or heating, or by other agencies. The course of dehydration and rehydration of a colloid differs entirely from that of a true hydrate.

I therefore doubt that the hypothesis of several chemists (Geuther, Henry, Carnelly) is satisfactory, while admitting that in the dehydration of a colloid there are formed successively definite chemical compounds between an increasing (but definite) number of oxide molecules (a polymerization) and a decreasing (but also definite) number of water molecules. Although molecular condensation must be admitted, the course of dehydration is contrary to that hypothesis.

SECOND PAPER.

THE HYDROGEL OF SILICIC ACID.[5]

I HAVE treated the subject of the composition of this hydrogel already in 1879. The gel was prepared by the action of an acid on the alkaline solution, and will be referred to as *a*. (*Arch. Neerl.*, 15, p. 321.)

Since then M. Grimaux (*C. R.*, 98, p. 1437) has published his researches on silicic acid obtained by the decomposition of methyl silicate by water. He heated a mixture of 8 gm. of $(CH_3)_4SiO_4$ with 200 c.c. of water under a reflux condenser, and drove off the methyl alcohol by evaporating to three-fourths of the volume. The hydrogel formed spontaneously after some weeks.

This solution, which contains 2·26 per cent of SiO_2 before gelatinizing, will stand heating to boiling temperature. A relatively large proportion of an alkaline salt is necessary to make it gelatinize when hot. It thus differs in this point from the hydrogel *a*.

M. Grimaux has compared the formation of this hydrogel, which I have called *b*, with the etherification of alcohol by time, which is accelerated by heat. He assumes that the

Successive Operations (to constant weight)

Hydrogel of SiO_2	Dried by Rapid Squeezing	Exposed to Free Atmosphere at 15°	Exposed to Air Saturated with Vapour at 15°	Exposed to Dry Air at 15°	At 100°		After Heating to 100°		After Gentle Ignition.		After intense Ignition in Air Saturated with Water Vapour
					In ordinary Air	In current of Dry Air	Exposed to Air Saturated with Water Vapour	Exposed to Free Air	In Air Saturated with Water Vapour	In Free Air	
a from sodium silicate ..	mol. H_2O	mol. H_2O	mol. H_2O	mol. H_2O	mol. H_2O	mol. H_2O	mol. H_2O	mol. H_2O	mol. H_2O	mol. H_2O	
	4·3	1·4 to 1·5	4·0	0·26	0·2	0·17	4·0	1·45	3·0	0·45 to 0·52	0·03
bα } from methyl silicate {	4·4	2·08	4·2	0·36	0·36(0·35)	0·28	—	—	0·7	0·6	0·003
bβ } from methyl silicate {	4·0	1·8	—	—	0·32(0·31)	—	1·7	1·6	—	—	—
c from silicon chloride ..	—	1·57(1·54)	1·8	0·3	0·28	0·19	—	—	0·25	Traces	0·000
d from silicon fluoride (very voluminous) ..	—	0·53	2·25	0·36	0·37	0·24	—	—	0·5	Traces	0·2

To illustrate the influence of the vapour tension on the composition of the colloid I add the following table :

To constant weight

	Temperature	In Atmosphere Saturated with Vapour	In ordinary Atmosphere	In current of Air dried by Sulphuric Acid
		mol. H_2O	mol. H_2O	mol. H_2O
Dry hydrogel *a* from sodium silicate	15°	4·3 (after several days)	1·4 to 1·5	0·26 (after several days)
	48°	1·57 (after 11 hours)	0·33 (after 8 hours)	0·229 (after 7 hours
	100°	0·36 (after 5 hours)	0·20	0·14 (after 3 hours)

[*To face page* 145

silicic acid separates from methyl silicate as $Si(OH)_4$, and that two molecules combine afterwards with loss of one molecule of water; these new molecules are supposed to combine again with loss of one molecule of water, and the condensation to proceed in this fashion, until it reaches a final state.

The hypothesis that this hydrogel is originally the normal hydrate is not founded on analysis, and appears to be in contradiction with the nature of colloidal substances.

The hydrogel *a*, according to my analyses, still contains 4 molecules of water at the moment when it becomes dry to the touch; loses $3\frac{3}{4}$ thereof in a dry enclosure at ordinary temperature, but takes it up again in an atmosphere saturated with water vapour. I have prepared the hydrogel *b* according to M. Grimaux's prescription. The methyl silicate was prepared in my laboratory according to the method of M. Friedel; its boiling point was from 120° to 124°.

The gel possessed all the properties described by this author. I also collected the transparent particles which deposited when the solution was evaporated to drive off methyl alcohol (*b*α); after some weeks the whole liquid set to a jelly (*b*β). The gels *b*α and *b*β were freed from liquid water by being pressed rapidly between blotting paper, and immediately transferred to a closed flask, before losing any water by exposure to the atmosphere.

I afterwards compared their composition in different circumstances with that of hydrogel *a*, and again with those of the gels prepared by the action of water on silicon chloride (*c*) and silicon fluoride (*d*). The quantities analysed varied between 1 and 2 gm., so that a loss in weight of one milligramme corresponds to less than 0·01 molecule of H_2O.

In all these cases repeated weighings (every hour or every two hours) showed that decomposition proceeded with decreasing velocity.

All these determinations prove sufficiently that the hydrogels obtained in different ways differ in their states of aggregation. These differences manifest themselves by a different power of retaining water at different temperatures. All of them attain equilibrium with the humidity of the atmosphere

at every temperature. It is for this reason that hydrogel *a* can retain at 50°, or even at 100°, more water in an atmosphere saturated with water vapour than it can at 15° in a dry atmosphere.

The hydrogels *a* and *b* have the same vapour tension as water, at ordinary temperature, when they have absorbed about 4 molecules of H_2O; the hydrogels *c* and *d* show this tension when they have absorbed about 1·8 and 2·2 molecules; the tension decreases as this water is driven off and approaches zero when the following compositions have been reached:

For *a*	0·26 H_2O	For *b*	0·36 H_2O
„ *c*	0·3 H_2O	„ *d*	0·3 H_2O

since they assume this composition over sulphuric acid.

Messrs. Carnelly and Walker have found 0·33 H_2O at a temperature approaching 100°, but they heated the colloid *a* in air and not in dry air, and did not continue the heating for more than two hours.

Hydrogel *a* absorbs and loses water most readily. It is least modified by heating to 100°—and even by heating to red heat for a short time—in so far as its power of absorbing water is not reduced by treatment at 100°, and much less than that of the others by ignition.

Hydrogel *b*, which is the most stable in a solution, retains water more energetically than the three others in a dry atmosphere and at 100°, but its absorptive capacity is greatly reduced by heating to 100°.

The dry hydrogel *d* is the most voluminous of all and retains the smallest quantity of water in air at ordinary temperature.

When the hydrogels are heated in a dry atmosphere at temperatures above 100°, they continue to lose water gradually and at the same time become modified. The figures which have been obtained up to now are of little value, because they differ according to the length of time during which heating to constant weight has been continued, and also according to the moisture of the surrounding atmosphere, etc.

Messrs. Carnelly and Walker have heated the colloid *a* at higher temperatures (two hours heating in air at thirty-five different temperatures between 15° and 815°). They have obtained the same composition at 159° which I have obtained at 15° already, in a dry atmosphere, viz., $SiO_2\frac{1}{4}H_2O$.

Although their figures have a relative value only, it follows clearly from them that decomposition between 50° and 800° is gradual, without perceptible jumps.

When the colloids *a*, *b*, and *c* are strongly calcined they lose the power of absorbing water completely. The voluminous colloid *d* still takes up a small quantity at 15° in a saturated atmosphere.

It remains possible that a true hydrate is present, or forms, in the colloid when it becomes dry (e.g. $(SiO_2)_4H_2O$ or $(SiO_2)_5H_2O$), and that this hydrate is in the colloidal state. There is, however, no means of deciding whether it exists. For, at what temperature and in what circumstances can it be assumed that absorption by the amorphous substance ceases and that the combined water belongs exclusively to the chemical hydrate ?

What is certain is that the molecules of water which these dry hydrogels retain between 15° and 100° in a moist atmosphere are held, not after the fashion of true chemical compounds, but after that of absorption compounds. These compounds are indefinite and their composition depends on (1) the state of molecular aggregation of the hydrogel, (2) the vapour pressure of the water in the surrounding atmosphere, and (3) the temperature.

[1] See this volume, p. 109.

[2] For the complete theory of the modifications of stannic acid see W. Mecklenburg, *Zeitschr. f. anorg. Chem.*, **64**, 368 (1909); **74**, 207 (1912).

[3] This statement still holds good. Cf. M. V. Smoluchowski, *Physik. Zeitschr.*, **17**, 587 (1916); *Zeitschr. phys. Chem.*, **92**, 129 (1917).

[4] The vanadium pentoxide sol is now exclusively made by W. Biltz's method: ammonium vanadate is decomposed with hydrochloric and the resulting gel washed until it passes through the filter. It has acquired considerable importance by its optical properties (accidental double refraction of aged sols, Freundlich and Diesselhorst, *Physik. Zeitschr.*, **16**, 419 (1915)).

[5] For summaries of more recent work on silicic acid gel see Zsigmondy, *Kolloidchemie* (Leipzig, 1920), pp. 217–237.

The paper on silicic acid is followed by four papers, describing similar investigations on alumina and aluminium hydroxide, stannic and metastannic acids, ferric oxide and chromic oxide. All of these exhibit the behaviour defined in the concluding paragraph of the paper on silicic acid.

ON ALLOTROPIC FORMS OF SILVER.

By M. Carey Lea.

ON ALLOTROPIC FORMS OF SILVER

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(*Amer. Journal of Science*, 87, 476 (1889).)

Mathew Carey Lea, born 16th August, 1823, at Philadelphia. Educated privately. Studied Law and was admitted to the Bar in 1847, but never practised. Entered the laboratory of Prof. Jas. C. Booth. Published *Manual of Photography* in 1868, and important papers on the subject from 1870 to 1878. Papers on the photo-haloids in 1887. Elected member of National Academy of Sciences 1892. Died 15th March, 1897.

(The collected papers on allotropic forms of silver and on the photo-haloids have been translated and edited by Lüppo-Cramer, Dresden, 1908.)

Silver is capable of existing in allotropic forms possessing qualities differing greatly from those of normal silver. There are three such forms, or rather three modifications of one form, differing from each other in many respects, but all more nearly related to each other than any one of them to normal silver. One of these forms is soluble in water, passing readily to an insoluble form, and this last may, by the simple presence of a neutral substance exercising no chemical action upon it, recover its solubility. Another form closely resembles gold in colour and lustre.

Whether metallic silver shall be reduced from its compounds in its normal or in an allotropic form depends upon the reducting agent applied, so that it cannot be said with any certainty whether it exists in its compounds, in its ordinary normal form, or in an allotropic condition : the latter alternative seems at least equally probable.

These allotropic forms of silver are broadly distinguished from normal silver by colour, by properties, and by chemical reactions. They not improbably represent a more active condition of silver, of which common or normal silver may be a polymerized form. Something analogous has already been observed with other metals, lead, and copper.

Much having been written, especially within the last few years, on the products of the reduction of silver compounds, a brief summary of what has appeared may be desirable

before proceeding further. The study of this subject has led to remarkable divergencies of opinion on the part of the chemists engaged in it. Almost all the views advanced have been successively disproved by each subsequent publication. It follows that what has obtained a place in the textbooks is almost wholly incorrect.

The earliest experimental work was Faraday's, but his product has been proved to be a mixture. (G. H. Bailey and G. J. Foster, *Chem. Soc.*, 1887, 416. *Bericht D. Ch. G.*, XX, Ref. 360.) The next was the well-known paper of Wöhler, published in 1839. It is not my purpose here to enter upon a criticism of this memoir. If this illustrious chemist succeeded in obtaining by the means employed a true citrate of silver hemioxide—as would appear from his analyses—no chemist since his time seems to have done so. The next publication to Wöhler's was that of von Bibra, who used Wöhler's method and, whilst affirming that he obtained a similar citrate, found an entirely different constitution for the corresponding chloride. For instead of obtaining a hemichloride Ag_2Cl, he gives, as the result of fifteen concordant analyses, the constitution of his product as Ag_4Cl_3. (Erdmann, *J. prakt. Chim.*, 1875, 120, 39. Von Bibra precedes his paper with a brief summary of the conclusions reached by previous chemists on the subject of the action of light and chemical reducing agents on silver compounds.) The collection is interesting as showing to what inconsistent and even contrary opinions careful observers have come on these reactions. A citrate, to yield such a chloride (if such a chloride exists) by the simple action of hydrochloric acid, could scarcely have the constitution assigned to it by both Wöhler and von Bibra.

In 1882, Pillitz published two papers. (*Zeitschr. f. ann. Chem.*, XXI, pp 27 and 496.) He commences by disputing the probability of the existence of Ag_4O on grounds of valency, namely, as implying that oxygen may be quadrivalent. Although it is very doubtful that anyone has up to the present time obtained Ag_4O, the argument seems futile, as are many arguments deduced from supposed laws of valency. Similar

reasoning would make Ag_2Cl impossible, which substance undoubtedly exists and it would also deny the existence of K_2Cl, which stands upon such authority as that of Rose, Kirchhoff, and Bunsen. (*Gmelin Kraut*, II, 1, 72.) Pillitz carefully examined the so-called hemioxide precipitated by alkaline solutions of antimony and tin, and could find no trace of Ag_4O in any of them. He did not examine Wöhler's products.

The first person to deny categorically the existence of Wöhler's series of hemi-compounds of silver appears to have been Dr. Spencer Newbury. In two interesting papers (*Am. Chem. Jour.*, VI, 407; VIII, 196) he describes a repetition of Wöhler's methods, and declares it to be impossible to obtain products of constant composition. The red solution taken by Wöhler to be argentous citrate, Dr. Newbury concludes to be a suspension of finely divided silver. Muthmann (*Ber. D. Ch. Ges.*, XX, 983), after a careful examination of Rautenberg's products, concludes that that chemist was wholly in error in asserting the formation of compounds of chromic, molybdic, and tungstic acids with silver hemioxide. He next studies the red liquid obtained by Wöhler's process, and comes to the same conclusion as Newbury—that it consists of finely divided silver suspended in water.

I shall not dispute the correctness of this opinion in the case of the liquid examined by these two chemists. At the same time I cannot accept the tests of solution employed by Muthmann—that a substance will not pass through a dialyser shows that it is colloidal, and is no proof whatever that it is not in solution. Animal charcoal takes up many substances from true solutions. Decolorization by animal charcoal is no proof whatever that the colour removed was not in true solution. By freezing, the molecular condition of a substance may be changed. Muthmann found that when the red liquid was mixed with gum water and precipitated by alcohol, the precipitated gum carried down with it the red substance, thence deducing that it was only in suspense. This conclusion is scarcely justified. A solution of litmus was mixed with gum water and precipitated with alcohol: the mass of the litmus

went down with the gum ; a trace only appeared in the filtrate. With Hoffmann's violet, the same result. Yet no one, I think, will assert that these two substances do not make true solutions in water. Even, however, if these arguments could be admitted they would not apply to the solutions presently to be described, which can be proved by optical means to be true solutions. I propose presently to show that silver may exist in a perfectly soluble form, dissolving easily and abundantly in water. Starting from this, it may show all degrees of solubility down to absolute insolubility, still, however, existing in an allotropic form and quite distinct from normal or ordinary silver. The solutions formed are as perfect as those of any other soluble substance.

Wöhler's process was next repeated by G. H. Bailey and G. J. Foster, who came to the conclusion that no citrate of hemioxide was formed, and that Wöhler's results must be rejected.

Von der Pfordten (*Ber. D. Ch. Ges.*, XX, 1458), endeavoured to obtain hemi-compounds of silver by acting on the nitrate with an alkaline solution of sodium tartrate, and also with phosphorous acid. His determinations were made volumetrically, based on an opinion that a permanganate solution acidified with sulphuric acid would dissolve silver hemioxide but not metallic silver. Previously to receiving his paper I had found that sulphuric acid, even diluted with ten times its bulk of water, was capable of acting on finely divided normal silver and of dissolving an easily recognized quantity. Von der Pfordten's conclusions were thus vitiated entirely. It should, however, be remarked that the difficulties of the subject are extremely great. In his last paper (*Ber. D. Ch. Ges.*, XX, 2288) this chemist abandons his views as to the existence of silver hemioxide ; so that at the present time the formation of Ag_4O by Wöhler's method, or by any other known method, is admitted by no one. That such an oxide may exist appears by no means improbable. The existence of Ag_2Cl and K_2Cl seems almost to involve that of Ag_4O and K_4O. This latter product Davy believed that he had obtained. The black substance which von der Pfordten

formerly regarded as Ag_4O he now takes to be silver hydrate, Ag_4H_2O.

The reduction products described by von der Pfordten are strongly distinguished from those which I shall presently describe by two decisive reactions :

1. None of his products could be amalgamated with mercury (*loc. cit.*, 2296). All of mine readily amalgamate.[1]

2. None of my products give off the slightest trace of gas when treated with dilute sulphuric acid. All of his do so (*loc. cit.*, 2291.)

Moreover, the difference of appearances is extremely great.

Early in the year 1886 I took up the study of the reduction products of silver in connexion with that of the photosalts. I commenced with Wöhler's process, giving it up after a few trials as affording no satisfactory results, and sought for a more reliable means. This I found, in March, 1886, in a reaction which I still use, namely, the reduction of silver citrate by ferrous citrate. At first, however, the results obtained were most enigmatical, the products very unstable, and impossible to purify. Much time was lost and the matter was given up more than once as impracticable. Eventually, by great modifications in the proportions, stable products, and capable of a fair amount of purification were got. Even the earlier and less pure forms were exceedingly beautiful; the purer are hardly surpassed by any known chemical products.

The forms of allotropic silver which I have obtained may be classified as follow :

(*a*) Soluble, deep red in solution, mat lilac, blue, or green whilst moist, brilliant bluish green metallic when dry.

(*b*) Insoluble, derived from (*a*), dark reddish brown while moist, when dry somewhat resembling (*a*).

(*c*) Gold silver, dark bronze whilst wet ; when dry exactly resembling metallic gold in burnished lumps. Of this form there is a variety which is copper-coloured. Insoluble in water, appears to have no corresponding soluble form.

Properties possessed by all the Varieties in common and distinguishing them all from Normal Silver.

All these forms have several remarkable properties in common.

1. *That of Drying with their Particles in Optical Contact, and consequently forming a Continuous Film.*—If either is taken in a pasty condition and is spread evenly over paper with a fine brush, it takes on spontaneously in drying a lustre as high as that of metallic leaf. (*c*) when so treated would be taken for gold leaf. But this property is much better seen by brushing the pasty substance over glass. When dry, an absolutely perfect mirror is obtained. The particles next the glass, seen through the glass, are as perfectly continuous as those of a mercurial amalgam, and the mirror is as good. (*a*) and (*b*) form bluish-green mirrors, (*c*) gold or copper-coloured mirrors.

2. *The Halogen Reaction.*—When any of these allotropic forms of silver are brushed over paper and the resulting metallic films are exposed to the action of any haloid in solution, very beautiful colourations are obtained. The experiment succeeds best with substances that easily give up the halogen, such as sodium hypochlorite, ferric chloride, iodine dissolved in potassium iodide, etc. But indications are also obtained with alkaline salts, such as ammonium chloride, etc., though more slowly and less brilliantly. With sodium hypochlorite the colours are often magnificent—intense shades with metallic reflections, reminding one of the colours of a peacock's tail. Blue is the predominating tint. These are interference colours, caused by thin films, but whether of a normal silver haloid or a hemi-salt cannot be said. When silver leaf (normal silver) is fastened to paper and a comparative trial is made, the contrast is very striking. This matter will be more particularly examined in the second part of this paper, and is mentioned here as one of the reactions distinguishing allotropic from ordinary silver.

3. *The Action of Acids.*—The stronger acids, even when much diluted, instantly convert the allotropic forms of silver into normal grey silver; even acetic acid, not too much

diluted, does this. It is important to remark that this change takes place absolutely without the separation of gas. I have more than once watched the whole operation with a lens and have never seen the minutest bubble escape.

4. *Physical Condition.*—All these allotropic forms of silver are easily reduced to an impalpable powder. One is surprised to see what is apparently solid burnished metal break easily to pieces and by moderate trituration yield a fine powder.

A. *Soluble Allotropic Silver.*

A solution of ferrous citrate added to one of a silver salt produces instantly a deep red liquid. (Ferrous tartrate gives the same reaction but is less advantageous.) These red solutions may either exhibit tolerable permanency or may decolorize, letting fall a black precipitate. It is not necessary to prepare the ferrous salt in an isolated form : a mixture of ferrous sulphate and sodic citrate answers perfectly.

When, however, concentrated solutions are used with a large excess of ferrous sulphate and a still larger one of alkaline citrate, the liquid turns almost completely black. It should be stirred very thoroughly for several minutes, to make sure that the whole of the precipitated silver citrate is acted upon by the iron. After standing for ten or fifteen minutes, the liquid may be decanted and will leave a large quantity of a heavy precipitate of a fine lilac-blue colour. It is best to adhere closely to certain proportions. Of a 10 per cent solution of silver nitrate, 200 c.c. may be placed in a precipitating jar. In another vessel are mixed 200 c.c. of a 30 per cent solution of pure ferrous sulphate and 280 c.c. of 40 per cent solution of sodic citrate. (The same quantity of ferrous sulphate or of sodic citrate in a larger quantity of water will occasion much loss of the silver product.) I think some advantage is gained by neutralizing the ferrous solution, which has a strong acid reaction, with solution of sodium hydroxide : as much may be added as will not cause a permanent precipitate. To the quantities already given, about 50 c.c. of 10 per cent soda solution. The reaction takes place equally well without the

soda, but I think the product is a little more stable with it. The mixed solution is to be added at once to the silver solution.

The beautiful lilac shade of the precipitate is rather ephemeral. It remains for some time if the precipitate is left under the mother water, but when thrown upon a filter it is scarcely uncovered before the lilac shade disappears and the precipitate takes a deep blue colour, without losing its solubility. It may be washed, either on a filter or by decantation, with any saline solution in which it is insoluble and which does not affect it too much. On the whole, ammonic nitrate does best, but sodic nitrate, citrate, or sulphate may be used, or the corresponding ammonia salts. Although in pure water the precipitate instantly dissolves with an intense blood-red colour, the presence of 5 or 10 per cent of any of these salts renders it perfectly insoluble. I have usually proceeded by adding to the precipitate (after decanting the mother water as completely as may be and removing as much more as possible with a pipette), a moderate amount of water; for the above quantities about 150 c.c. Much less would dissolve the precipitate but for the salts present: this much will dissolve the greater part but not the whole, which is not necessary. A little of a saturated solution of ammonic nitrate is to be added —just enough to effect complete precipitation.

As the material appears continually to change, the amount of washing needed must depend upon the object in view. If wanted for analysis, the washing must be repeated many times until ferric salt ceases to come away, but no amount of washing will entirely eliminate it. After seven or eight solutions in pure water and as many precipitations, the material is to be thrown on a filter, the liquid forced out as completely as possible with a pump, and then the ammonic nitrate washed out with 95 per cent alcohol until the filtrate leaves nothing on evaporation. The substance at this point is still soluble in water, though much less so than at first. During the washing the solubility slowly but steadily diminishes—a fact rendered noticeable by less and less ammonic nitrate being needed to precipitate it from its solution.

Analysis.—The product, after thorough washing as above

described with alcohol, was dried at ordinary temperatures or a little above, and was then reduced to very fine powder and washed again with water as long as anything dissolved. It was then dried at 100° C. in water bath. Three silver determinations were made :

A1	-	-	-	97·31	per cent silver.
A2	-	-	-	97·18	„ „
B	-	-	-	97·21	„ „

A1 and A2 were made with different portions of the same material ; B with different material prepared in exactly the same way.

The substance therefore contained on an average 97·27 per cent of silver. The nature of the residue would decide whether the material was silver with a certain amount of impurity firmly attached to it, or whether we had to do with silver in chemical combination with other elements.

The filtrate from the silver chloride in analysis A2 was evaporated to dryness and was found to contain chiefly iron and citric acid. The iron was thrown down as sulphide, redissolved in nitric acid, precipitated hot, washed with boiling water, and gave 0·8947. The residue, therefore, consisted of ferric oxide and citric acid, probably in the form of ferric citrate and attached so strongly that even the very careful and prolonged washing given failed to remove them. Stronger means would be required than could be used without altering the condition of the substance. The conclusion, therefore, seemed to be justified that the material consisted of uncombined silver simply mixed with impurity.

To verify this conclusion by additional evidence the substance was examined as to its behaviour when heated. For if any other element were chemically combined with the silver it would only be (in view of the high percentage of silver) hydrogen or oxygen. We might have to do with a hydride, analogous to Wurtz's hydride of copper, or possibly an oxide, but not probably as Ag_4O would contain only 96·43 per cent of silver.

The presence of either hydrogen or oxygen in combination

with silver seems to be pretty certainly negatived by the action of dilute sulphuric acid on this (and the two other substances, B and C, to be described further on). They are all converted into grey metallic silver without the slightest escape of gas. This seems tolerably conclusive in itself; and the result of exposing a great number of specimens of all the forms A, B, and C to the action of heat was equally so. As the object was to expose the fresh and moist material to a gradually increasing heat from that of boiling water to a low red heat without interrupting the process, the following arrangement was found convenient:

A piece of Bohemian glass tube about six inches long was sealed in the lamp at one end, the other closed with a rubber cork, through which passed a small gas delivery tube and another tube passing into a small test tube partly filled with water and having another tube through the cork passing under the surface of the water, thus preventing regurgitation. The material was thus first exposed for some hours to a heat of about 150° C. in a chloride of calcium bath; this was next removed and the heat continued to low redness. Only traces of gas were evolved, and this was found to be, in all of the many trials made, carbonic acid, derived from the citric acid adhering. This treatment was repeated many times with all the different varieties of the substance and with the same result. The temperature was always raised sufficiently high to ensure the complete conversion of the material into normal grey silver, but in no case was oxygen or hydrogen set free.

It could not be overlooked that in all these trials the material had passed into an insoluble form before the silver determination was made. There remained therefore this possibility: that the silver, so long as soluble, might be in combination with citric acid, and that its change to the insoluble condition was caused by its separating from the citric acid. It seemed desirable that this view should be tested. As the object was to determine the condition of the silver in the substance as originally formed, avoiding as far as possible to change that form by attempts at purification, the only course available was

to determine the ratio between the silver on the one hand and the citric acid on the other, either excluding from the determination, or else removing, that portion of the citric acid which was combined with sodium (sodic citrate being used in excess) or with iron. The first attempt was to exclude without removing it, by using Wolcott Gibb's ingenious method of precipitating the base by hydrogen sulphide, and determining the acid thus set free in a solution originally neutral. It was ascertained by careful experiment on weighed quantities of pure anhydrous citric acid that exact titration could be made with the aid of phenolphthalein. The silver was next redissolved, and estimated as chloride. A large number of determinations were made, but the method proved unsatisfactory. It was found that portions of the same material operated upon separately gave different (even widely different) results. In fact, this very discordance was in itself a proof that no stœchiometrical combination existed between the silver and the citric acid.

The importance of the matter led me to take it up again with different means, estimating the citric acid by Creuse's method. In this method the solution, after being reduced to a small bulk, is exactly neutralized (with ammonia or acetic acid), is treated with a slight excess of barium acetate and then mixed with twice its bulk of 95 per cent alcohol, let stand a day and filtered and washed with 65 per cent alcohol. In igniting, a few drops of sulphuric acid convert the barium salt into sulphate in which form the estimation is made. A preliminary trial with a weighed quantity of citric acid showed that this method gave fairly good results. I was obliged to vary the method somewhat: the precipitate of barium citrate carried down with it enough iron to render it ochry in appearance. It was therefore, after thorough washing with 65 per cent alcohol till every trace of barium acetate was removed, dissolved on the filter with dilute hydrochloric acid (acid 1, water 10) in which barium citrate is extremely soluble and washed through. This was followed by still weaker acid and finally with water. From the filtrate, sulphuric acid precipitated snow-white barium sulphate.

But this method requires that both the sulphates and the excess of sodic and ferric citrate shall first have been perfectly removed. The blue precipitate was therefore washed with dilute solution of ammonic nitrate until this was effected. The necessity for this purification was regrettable, as introducing a possibility of a change during the treatment. It was, however, indispensable that the ferrous, ferric, and sodic citrates present should be got rid of. The material after this treatment was still freely soluble in water, to a dark-red solution. An examination of its absorption spectrum showed it to be still a true solution. From this solution the silver was first removed by H_2S, and then the citric acid was determined in the above-described way. (If the silver were thrown down by hydrochloric acid, the reliability of the citric determination would be impaired.) Next, the silver sulphide was converted into chloride and weighed. The result gave the ratio

1 gm. silver to ·03195 gm. citric acid.

In this case washing out the sulphates, etc., was an affair of several days. The work was repeated, reducing the time as much as possible. The material was precipitated, decanted as soon as settled, thrown upon a filter pump, and the funnel kept constantly full of ammonic nitrate in dilute solution by a wash bottle. By using very thick paper and a powerful pressure the entire washing was rapidly finished, so that in about six hours from the first precipitation the material was thoroughly washed, redissolved, and again filtered and placed under the action of H_2S. The result was :

1 gm. silver to ·0130 citric acid.

When these relations are reduced from weights to equivalents, they become :

No. 1, 1 equiv. citric acid to 55·63 equivs. silver.
No. 2, 1 „ „ 193·7 „

indicating both that the proportion of citric acid present is variable and that it is certainly not in stœchiometrical combination with the silver in the substance examined.

It has been already said that these solutions before being acted upon by H_2S were examined optically and found to be true solutions.[2] The inference, therefore, seems to be very strong that there exists an allotropic form of silver freely soluble in water. This is a property so exceptional in a metal that I have admitted it with much hesitation. The principal arguments are as follow:

The content of silver in the various products was very carefully, and I believe I may say quite accurately, determined: it was extremely high, always above 97 per cent. As already remarked, this virtually excludes the presence of all elements except hydrogen and possibly oxygen. These elements were carefully searched for, but their presence could not be detected. To suppose that we had to do with a mixture in which some compound of silver was mixed with metallic silver was not possible, for as the whole was soluble we should still have to admit the solubility of silver.

We have consequently to deal with a substance containing over 97 per cent of silver, and neither hydrogen nor oxygen in combination with it, the remaining 2 or 3 per cent fully accounted for by ferric oxide and citric acid determined as present as accidental impurity; the substance itself readily amalgamating with mercury by simple friction, nevertheless abundantly soluble in water. If I had been able to find any other explanation for these facts without admitting the solubility of silver, I should have adopted it. But none presented itself.

Whether in solution it exists as a hydrate, that is, in more intimate combination with one or more equivalents of water, cannot be said with entire certainty; but the easy amalgamation with mercury seems hardly to favour that view. No means could be found for settling the question absolutely. Certainly at 100° C. all water is expelled, but this is, of course, not an argument. All the water is not expelled by indefinite exposure to a vacuum over sulphuric acid. But the proportion left is very small.

The material examined was in all cases as nearly as possible the same as that originally precipitated, but absolute identity

could not be obtained. The purification absolutely necessary effects some change. This is shown by the colour. The freshly precipitated material dissolves to a blood-red liquid, by great dilution yellowish-red. The purified substance gives a darker red solution, which with dilution remains still red. Of the nature of the substances in the condition in which they were analysed, I can speak with some positiveness, and these include a substance soluble in water and nevertheless appearing to be nearly pure silver.

The constitution of the lilac-blue substance at the moment of formation and whilst still under its mother water is a matter of more difficulty : it could not be said with certainty that it was not in some way altered in the purification. Much time and labour were spent in endeavouring to settle this point, without entirely satisfactory results, and I am at present engaged in the search for a better method.

When this blue soluble substance, purified either by washing very moderately by ammonium nitrate, or by washing with pure water, using those portions which remain undissolved after most has been carried through the filter, is brushed over paper and dries rapidly, it exhibits a very beautiful succession of colours. At the moment of applying it appears blood-red ; when half-dry it has a splendid blue colour with a lustrous metallic reflection ; when quite dry this metallic effect disappears and the colour is mat blue. Examined with a polarizer it shows the same characters as to two reflected beams of light polarized in planes perpendicular to each other that are described further on under B.

When the blue substance prepared in either way dries more slowly in lumps the result is very variable ; sometimes it is bright bluish metallic ; sometimes dull lead colour, with a metallic reflection only where it has dried against a smooth surface.

B. *Insoluble Form of the Foregoing.*

The solution of the blue product just described is influenced in a remarkable way by the addition of almost any neutral substance. So far I have not found any that does not

precipitate it. Not only saline solutions do this, but even a solution of gum arabic.

Neutral salts may precipitate the silver in either a soluble or an insoluble form. Alkaline sulphates, nitrates, and citrates throw down the soluble form; magnesium sulphate, cupric sulphate, ferrous sulphate, nickel sulphate, potassium bichromate, and ferro-cyanide, barium nitrate, even silver nitrate, and other salts throw down a perfectly insoluble form. The soluble form constitutes a blue or bluish-black precipitate; the insoluble, a purple-brown, which by repeated washing by decantation or otherwise, continually darkens.

What is very curious is that the insoluble form may be made to return to the soluble condition. Many substances are capable of effecting this change. Sodium borate does so, producing a brown solution, potassium and sodium sulphate produce a yellowish-red solution and ammonium sulphate a red one. None of these solutions has the same blood-red colour as the original solution; the form of silver seems to change with the slightest change of condition.

The solutions used must be extremely dilute, otherwise the silver, though rendered soluble in pure water by them, will not dissolve in the solution itself, a singular complication of effects. So that if a moderately strong solution of one of the above substances is poured over the insoluble silver substance it does not dissolve, but by pouring off the saline solution and replacing it with pure water, the substance now dissolves readily. The insoluble substance is also readily soluble in ammonia. The solution has a fine red colour, and not the yellowish-red of the sodium sulphate solution.

Most neutral salts act in one or other of the ways just described, precipitating the solution of the blue substance A in either the soluble or the insoluble form, the latter soluble in ammonia, but sodium nitrate is an exception: its solution effects an entire change and renders the substance wholly insoluble, probably reconverting it to normal silver.

Sometimes the substance will spontaneously pass into a soluble form. A specimen, rendered insoluble by precipitation with ferrous sulphate, after much washing began to run

through, not only as a suspension, which often happens, but as a solution, clearing itself, after a day or two, of insoluble portions and furnishing a rose-red solution. I have kept this solution in a corked vial for eight months, during which time it has remained unchanged.

The general properties of this substance can be much better observed in the thin films obtained by brushing the moist substance over paper than in the lumps. The films thus obtained are bright greenish metallic, and this green evidently results from a mixture of blue and yellow, as in some lights the blue, in others the yellow, is most evident. When these films are examined by light reflected from them at a large incidence with the normal and a Nicol's prism or an achromatized prism of calc-spar is interposed between the film and the eye, it becomes at once apparent that the blue and yellow light are oppositely polarized. The yellow light is polarized in the plane of incidence, the blue light perpendicularly to that plane. All specimens show the yellow light, but the quantity of blue light is very variable and is directly connected with the amount of washing applied to the precipitate. The more it is washed the more the yellow predominates. To see the blue form in its full beauty, a little of the red solution may be precipitated with a very little magnesium or aluminium sulphate and be thrown on a filter. As soon as the liquid has drained off and without any washing, the deep bronze-coloured substance is to be brushed over paper. On drying, it has all the appearance of a bright blue metal with a remarkable lustre. The mirrors obtained by brushing the substance over glass are so beautiful and so perfect that it seems as if this property might have useful applications, especially for silvering irregular surfaces. Much care, however, would be necessary in the preparation to obtain a permanent product.

Crystallization.—On one occasion this substance was obtained in a crystalline form. Some crude red solution had been set aside in a corked vial. Some weeks after, it was noticed that the solution had become decolorized, with a crystalline deposit at bottom. The bottle was carefully broken; the deposit, examined by a lens, consisted of short

black needles and thin prisms. Evidently the saline matters present had balanced the silver in solution so nearly as not to cause an immediate precipitation, but a very gradual one only. The mother water was drained off and a few drops of pure water were added. No solution took place, the crystals were therefore of the material B, the insoluble form. The contact of pure water instantly destroyed the crystallization and the substance dried with a bright green metallic lustre. Contact with pure water evidently tends always to bring this form of silver into the colloidal state, sometimes soluble and sometimes not; whilst the contact with certain neutral salts renders it crystalline.

The extraordinary sensitiveness which allotropic silver shows to external influences contrasts strongly with the inertness of normal (probably polymeric) metallic silver. When we place this fact alongside of the well-known sensitiveness of many silver compounds to light, heat, and (as I have elsewhere shown) to mechanical force, we are led to ask whether silver may not exist in this form in these very sensitive compounds.

To obtain the substance in a pure condition suitable for analysis it is necessary to choose a precipitant not giving an insoluble product with either citric or sulphuric acid. Magnesium sulphate or nickel sulphate answers well; I have generally used the first named. A very dilute solution is made of it and the red solution of A is to be filtered into it. The precipitate soon subsides. A large quantity of water is to be poured on, and then washing by decantation can be continued to three decantations, after which the substance remains suspended. It can be made to subside by adding a very small quantity of magnesium sulphate; $\frac{1}{4000}$ part (0·25 gm. to one litre) is sufficient. The substance may then be thrown on a filter and washed with pure water.

Analysis.—A specimen dried *in vacuo* over sulphuric acid gave

No. 1	-	-	97·17 per cent silver.
No. 2	-	-	97·1 „ „

A specimen dried first *in vacuo* and then at 100° C. lost in the second drying ·88 per cent water.

So that the substance dried at 100° contained 97·96 per cent of silver. The remaining 2·04 per cent consisted of ferric oxide and citric acid.

C. *Gold-Yellow and Copper-coloured Silver.*

It has been long known that golden-yellow specks would occasionally show themselves in silver solutions,[3] but could not be obtained at will and the quantity thus appearing was infinitesimal. Probably this phenomenon has often led to a supposition that silver might be transmuted into gold. (I have a little volume published in Paris in 1857 by a chemist named Tiffereau who was firmly convinced that in many reactions, minute portions of silver are converted into gold, especially with the aid of powerful sunlight. In Mexico, he affirmed, he had artificially produced several grammes of gold, a portion of which he presented to the French Academy with one of his papers. To his great disappointment he did not succeed in repeating these experiments in Paris, with more than an infinitesimal result. All gold in his opinion had been originally silver, and this belief, he affirms, is universal amongst Mexican miners. The book has for title "*Les Métaux sont des corps composés.*") This yellow product, however, is only an allotropic form of silver, but it has all the colour and brilliancy of gold, a fact which was apparent even in the minute specks hitherto obtained.

By the means presently to be described silver can be converted wholly into this form. It is a little curious that its permanency seems to depend entirely on details in the mode of formation. I found many ways of obtaining it, but in a few months the specimens preserved changed spontaneously to normal silver. This happened even in well-closed tubes. The normal silver produced in this way is exquisitely beautiful. It has a pure and perfect white colour like the finest frosted jewellers' silver, almost, in fact, exceeding the jewellers' best products. I found, however, one process by which a quite

permanent result could be obtained. Specimens made by it in November, 1886, are now, at the end of thirty months, unchanged.

In forming the blue product which I have called A, very concentrated solutions were necessary. C, on the contrary, is best obtained from very dilute ones. The following proportions give good results:

Two mixtures are to be prepared: No. 1, containing 200 c.c. of a 10 per cent solution of silver nitrate, 200 c.c. of 20 per cent solution of Rochelle salt and 800 c.c. of distilled water. No. 2, containing 107 c.c. of a 30 per cent solution of ferrous sulphate, 200 of a 20 per cent solution of Rochelle salt and 800 of distilled water. The second solution (which must be mixed immediately before using only) is poured into the first with constant stirring. A powder, at first glittering red, then changing to black, falls, which on the filter has a beautiful bronze appearance. After washing, it should be removed whilst in a pasty condition and spread over watch glasses or flat basins and allowed to dry spontaneously. It will be seen that this is a reduction of silver tartrate by ferrous tartrate. The metallic silver formed by reduction with ferrous citrate and ferrous tartrate is in an allotropic condition; with ferrous oxalate this result does not seem to be produced.

Although the gold-coloured silver (into which the nitrate used is wholly converted) is very permanent when dry, it is less so when wet. In washing, the filter must be kept always full of water: this is essential. It dries into lumps, exactly resembling highly polished gold, especially the surfaces that have dried in contact with glass or porcelain. For this substance has in a high degree of the property already described in forms A and B—that of drying with the particles in optical contact. When the thick, pasty substance is extended over glazed paper, it dries with the splendid lustre of gold leaf, with this essential difference, that these allotropic forms of silver B and C assume spontaneously in drying the high degree of brilliancy which other metallic surfaces acquire by elaborate polishing and burnishing. By brushing a thick paste of this substance evenly over clean glass, beautiful gold-coloured

mirrors are obtained ; the film seems to be entirely continuous and the mirror is very perfect.

By continued washing the precipitate changes somewhat, so that in drying it takes on a coppery rather than a golden colour, and is rather less lustrous, though still bright and permanent.

Two silver determinations by conversion into chloride made in November, 1886, gave :

No. 1 - - 97·81 per cent silver.
No. 2 - - 97·86 „ „

Recently these experiments have been repeated and the washing was more successful. Ferric tartrate adheres very obstinately, and after a time washing with water ceases to remove it. Stronger means cannot be employed without affecting the substance itself. These last determinations gave :

No. 1 - - 98·750 per cent of silver.
No. 2 - - 98·749 „ „

The residue of No. 2 was examined and consisted almost wholly of ferric citrate.

CHESTNUT HILL, PHILA., *April*, 1889.

NOTE.—The editors have received from the author of the above paper samples of the three allotropic forms of silver which he describes, and also strips of glass and paper coated with them. Mr. Lea is to be congratulated on his very important results. The coated strips, including the gold-coloured mirror made with the " gold-silver," answer fully to his description. The mirror is remarkable for its perfection and brilliancy.

[1] In this respect they differ markedly from all gold sols. Cf. Note (4) to Faraday's paper, p. 92.

[2] The optical examination presumably was microscopic. Carey Lea does not appear to have used Faraday's method, as he would without doubt have noticed the marked Tyndall cone which many sols prepared by his method show, especially on dilution.

[3] E.g., according to Lüppo-Cramer, in physical developers for collodion plates, in which silver is slowly deposited from a mixture of silver salts and reducing agent.

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