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Colloidal Solution: The Intermediate State Between Solution and Suspension.

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I. SOLUTION AND SUSPENSION.

When water is poured upon finely divided gold the liquid wets the metal but no further effect is visible. In the absence of external disturbance the gold will remain at the bottom for an unlimited time. This behavior is commonly described by the statement that gold is *insoluble* in water. Modern chemistry has fairly well established the thesis that entire insolubility is an ideal limiting case not actually met with. Compounds like barium sulphate, calcium oxalate and the silver compounds of chlorine, bromine and iodine have solubilities in water which have not only been detected but measured. However, *practical* insolubility is frequent so that the old term is still useful and will be retained.

Now, if the water with the gold lying at the bottom is shaken up, a temporary distribution of the metal through the liquid—a *suspension*—is produced. The only difference is that the particles of gold are very much farther apart on the average than they were before. The liquid is turbid and the gold can be separated from it by a filter. Thus the most superficial inspection shows that there are two things present, a solid and a liquid. In the language of the Phase Rule there are three phases, water, which may have taken up an extremely minute quantity of gold; gold, which may have absorbed a still more minute quantity of water, and vapor, in which only water can be detected, but in which the presence of gold may be assumed for theoretical reasons.

But the Phase Rule, which has been of such supreme service in the treatment of heterogeneous systems in equilibrium, can give us no help in the present matter, for our suspension cannot be obtained in equilibrium. Left to itself, it instantly begins to separate—sedimentation goes on until each particle of gold has found a resting place. The suspension is dominated absolutely by gravitation. Other forms of energy play no role. The free energy which it contains is the same as that of a raised weight and can be calculated by multiplying the weight of the gold by the average fall, which would be approximately half the depth of the water.

When water is poured over copper sulphate the system conducts itself in an entirely different way. The blue color of the solid appears, first in the contiguous liquid and later in the remote. If the quantity of the sulphate is not too large, it disappears entirely; if it is in excess the liquid takes up a quantity which is always the same at the same temperature and pressure and which increases rapidly with the former and slowly with the latter. When equilibrium is reached, the distribution of the sulphate through the liquid is entirely uniform. The differences of concentration which arise during the dissolving are adjusted spontaneously by diffusion, without the intervention of any external agency. This final condition is absolutely permanent. Nothing analogous to sedimentation occurs, no matter how long a time is allowed, and so far as we know gravitation has no power whatever over the dissolved sulphate, for all attempts to establish a greater concentration in the lower portions when a long tube is filled with a solution and placed vertically, fail.

Just as the solution is the natural permanent state of the two substances—water and copper sulphate—when in contact, so the dissolving of the sulphate in the water is a self-acting, spontaneous process, which occurs without external energy being added to the system. On the contrary it reduces the free energy of the system and therefore can be made to do external work. In this work, which the dissolving process can be made to do, the driving force is the *osmotic pressure* of the copper sulphate. The sulphate tends, as we have seen, to distribute itself evenly through the liquid—it behaves like a gas which when liberated in an empty space proceeds to occupy evenly every portion of the space.

If a partition is interposed which is saturated throughout with the water but will not permit the sulphate to pass, the latter, in its effort to expand into the rest of the liquid, will exert osmotic pressure upon the partition and if it is adjusted to move against an external resistance, work will be done. The sulphate can be placed in the bottom of a vertical cylinder filled with water and a piston which allows the water, but not the sulphate to pass, inserted. Then as the sulphate dissolves and endeavors to expand into the water above the piston, it will exert a pressure and, if the latter be weighted, the weight will be raised and work will be done.

Conversely, if, after the copper sulphate has occupied the entire liquid, the piston is burdened with a weight which is kept in excess of the osmotic pressure it will be forced downward, the sulphate will be crowded into a smaller and smaller volume of liquid and will finally crystallize.

Thus by means of a "semi-permeable" membrane it can be shown that the dissolving of a solid can be made to do work and that when the same amount of work is done upon the system the dissolved substance is again separated from the solvent.

2. THE EFFECT OF DECREASING THE SIZE OF THE PARTICLES.

It is always easy to formulate distinctions which apply to the typical members of two different classes—it is the transitional intermediate ones that are difficult to classify. For instance, one would hardly expect any difficulty to arise in deciding whether to call a given system a solution or a suspension. The distinctions seem unmistakable—

Solution.	Suspension.
1 Homogeneous.	1 Heterogeneous.
2 Clear.	2 Turbid.
3 Permanent.	3 Temporary.
4 Formed by a spontaneous process or contact.	4 Formed by external action.
5 Non-separable by filtration or decantation.	5 Separable by these means.
6 Formation liberates energy and can produce work.	6 Formation absorbs energy.

Starting with matter in a state of coarse mechanical suspension in water let us imagine the size of the particles gradually to decrease. We shall find that the above criteria fail us and that it becomes almost impossible to decide whether we are to call the system a solution or a suspension.

By powdering in a mortar or similar mechanical means substances can be pulverized until the average diameter of the grain is $\frac{1}{4}$ of a micron.* Any substance, unless it happened to have the same refractive index as water, would produce a strong turbidity easily visible to the naked eye if the particles were as large as this. But we may anticipate that when the particles became very much smaller than the wave-length of light they might cease to reflect in such a way as to show their presence to the unaided vision. Now the wave-lengths of the visible frequencies of light are grouped between 1 micron and 0.1 micron. Therefore we might predict that somewhere about the diameter of 0.1 micron the particle would no longer render the liquid turbid to the unaided eye. This prediction is in full accord with experiment. Measurements of the size of the particles are difficult and few, but in the case of gold the limiting size of the particle-producing turbidity is about 0.1 micron—probably less. From the high density of gold and its behavior toward light we should expect it to produce turbidity with a smaller particle than other substances. So far as I am aware, exact measurements of the size of the particles in colloidal solutions of oxides, hydroxides, sulphides and organic colloids have not been made, but it is a safe statement that a much larger particle than 0.1 micron is required to make the solution turbid. Work is going on actively in this field and we may expect definite results in the near future.

Are we to call this clear liquid containing finely divided metallic gold a solution or a suspension? The most natural reply is that there has been no change in principle—the delicacy of the eye has failed us, that is all. Since the liquid still contains particles of gold distributed through water, it is a suspension.

It is true that the microscope will enable us to detect particles decidedly smaller than 0.1 micron floating in a liquid, but there is a far more powerful instrument for this purpose. Everyone has noticed that when a beam of light enters a dark room through a chink in the shutter the floating motes of the air spring into plain visibility. Tyndall was the first to call attention to the possibilities of the light-beam in detecting suspended matter. That the effect is really due to motes and not to the air itself can be demonstrated by a familiar lecture experiment. The inside of a glass box is smeared with glycerine and it is allowed to stand

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*A micron is .001 millimeter.

over night. The solid matter settles and then when the beam is sent through there is no trace of its passage—the box is "optically empty." The purest distilled water contains countless floating particles and it is difficult to eliminate them, so difficult that until recently it was an open question whether the water molecules themselves did not disperse the light, but Spring has shown that if a little zinc hydroxide is precipitated in it the suspended matter is all carried down and the water becomes optically empty.

Now if we focus an image of a powerful arc, or better, of the sun, in the liquid and examine it under the microscope, making provision for the prevention of any accidental light reaching the eye, we have the *ultra-microscope* of Siedentopf and Zsigmondy. This is an instrument of wonderful power in the investigation of the infinitesimal, and to it the recent great advance of our knowledge in this direction is largely due. With it particles as small as 5 millimicrons* can be *separately seen* and particles much smaller—how much smaller no one knows—can be detected by the visibility of the cone of light. By means of it all gold solutions down to and somewhat beyond 5 millimicrons can be shown to contain their gold in the solid form. This brings us in the midst of the domain of the infinitely little. The smallest particle which can be seen separately is only about $\frac{1}{100}$ of the dimensions of the smallest visible light wave and only 50 times the diameter assigned by van der Waals, Exner and others to the molecule of hydrogen (0.1 millimicron). The smaller particles which cannot be seen separately, but still reflect the light and polarize it, cannot contain more than a few molecules, but they must contain more than one, for there are other gold solutions still more finely divided which give no light cone at all—are optically empty—and yet are identical in their other properties.

Liquids containing solids in this condition of excessive subdivision have received the name of *colloidal solutions*. The facts just discussed have led some chemists† to regard them simply as suspensions of great fineness. But the matter is not so simple as this and before settling it in this off-hand way we ought to inquire how true solutions behave toward the cone of light.

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*A millicron is .001 micron = .000001 millimeter.

†Stöckl & Vanino. Zeitschr. Pysikal. Chem. 30, p. 98 (1899).

Spring† and Lobry de Bruyn‡ have done some interesting work upon this point which has not attracted as much attention as it deserves. The results briefly are as follows: Solutions of salts of K, Na, Ca, Sr, Ba, Zn, Mn, Co, Ni, Cd are optically empty, but water solutions of chlorides, nitrates or sulphates of Al, Cr, Fe^{III}Cu and Pb show the passage of the beam strongly. Spring has attributed this to hydrolysis producing a colloidal solution of the hydroxide and his explanation is supported by the facts that the solutions in question redden litmus and that hydrochloric acid weakens the cone and, in sufficient quantity, causes it to disappear. However, true solutions of high molecular weight, for instance, ordinary sugar, raffinose, phosphomolybdic acid and the benzoyl esters of mannite and dulcite, show the effect strongly.

Starting with the molecular theory, it is clear that the homogeneity of any solution is only apparent and detecting solid matter in it is a question of delicacy of method. Van Calcar and Lobry de Bruyn placed solutions—e. g. of KI, KCNS, Na_2SO_4—in a centrifugal machine making 2400 turns per minute. The experiment was arranged so that at the end of the centrifugation the liquid was contained in four different compartments. The dissolved substance was contained chiefly in the solution from the outer compartment. From a 9% solution of Na_2SO_4 about one-third crystallized in the outer compartment.

It seems, therefore, that using the utmost refinement of experimental method we can prove that colloidal solutions are heterogeneous and therefore turbid, but it also appears that if we called them mere suspensions on this account we should have to treat most true solutions in the same way—the conception solution would disappear from science.

We may also note the fact that a colloidal solution is permanent so long as the fineness of subdivision persists. Sedimentation takes place in many cases, but it is always preceded by the union of many of the smaller particles to larger ones—a kind of coagulation. There are various ways of preventing this, and so long as it is prevented, the distribution remains uniform. Gravitation does not determine the sequence of events. It has retired

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†Bulletin Acad. Royale Belg., 1899, p. 300.

‡Rec. Travaux Chimiques des Pays Bas, 23, p. 155 (1904).

into the background, as we shall see later, in favor of kinetic energy, surface energy and electrical phenomena. It follows, of course, that the solid cannot be separated from the liquid by decantation. Ordinary filtration is completely without effect.

We have now seen the justification for collecting these substances in a class by themselves. Naturally it is not easy to define the exact boundaries which separate them from true solutions on the one side and suspensions on the other. Probably there is no exact line of separation, the classes merging into each other. We shall take up this point later.

3. THE COLLOIDAL SOLUTION OF GOLD.

Preparation. The first necessity is doubly-distilled water of special purity. For the second distillation a silver condenser must be used. Access of air or contact with a ground glass stopper will charge it with solid particles and make it useless. It is kept in bottles stoppered with corks wrapped in tinfoil. When the electric arc is allowed to burn between two gold wires under this water the metal is obtained in very fine division on account of the sudden cooling of the vapor, and a colloidal solution is produced. This method is due to Bredig and it applies also to Pt, Pd, Ag and many other metals.*

The other general method is by the reduction of an extremely dilute solution of gold chloride with formaldehyde at a boiling temperature or with an etherial solution of phosphorus in the cold. If the experiment succeeds the liquid is bright red and entirely clear. In some cases the gold particles are so small that even the ultra-microscope fails to detect them. Sedimentation does not occur so long as coagulation is prevented. Under favorable circumstances if the water used was pure and freezing is not allowed, the solutions are practically permanent. In those prepared by the arc the subdivision is not so fine. They are purple-red or violet, and somewhat less stable.

The favorable effect of great dilution of the $AuCl_3$ in chemical reduction is easily understood. In a strong solution the minute particles first formed find abundant dissolved gold in the liquid and grow at the expense of it until glittering flakes of gold

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*Colloidal solutions of K, Na, Li, Rb and Cs in anhydrous ether have been made by a similar method.

are produced and sedimentation occurs. But when the quantity of gold in each c.c. is very small the production of the first submicroscopic particle exhausts it and growth is impossible.

Properties. As already stated, the subdivision is so extreme in some solutions that the light cone is scarcely visible in the ultra-microscope. Particles slightly larger produce a cone which cannot be separated into individuals. That these liquids really contain colloidal gold and not some red compound of the metal can be proved by adding a solution of almost any soluble acid, base or salt—any electrolyte—when the color of the liquid changes to blue and the particles in the cone at once become visible. From about 5 millimicrons upward the particles are separately visible. They are brightly colored—green, red or yellow. Some solutions contain only green particles, some only red, some only yellow and in still others all three are present. Naturally, the color of the liquid by transmitted light is complementary to that of the particles it contains. The red solutions contain chiefly green particles, the violet yellow ones. It is impossible to predict the size of a particle from the color. All three occur in widely different dimensions, but on the whole the green are the finest and the yellow the coarsest.

The particles are in continual motion, the smaller ones moving most rapidly. Zsigmondy* compares the appearance of the light-cone to a swarm of gnats in the sunlight. The motion of the smallest particles can be resolved into two components. There is a direct progression in which the particle covers from 1,000 to 10,000 times its own length in a second and an oscillation of very short period. The progressive movement is zig-zag and variable, so that a particle after describing a zig-zag, each line of which is 100 to 1,000 times its own diameter and taking perhaps $\frac{1}{8}$ of a second for each, will rush quite off the field of view in a straight line. This motion shows no decrease with time. Solutions more than a year old exhibit it just as actively as at first, unless coagulation has begun.

It is natural to expect some connection between the heat and light which are projected into the liquid and the motion of the particles. On this point Zsigmondy calls attention to the facts:

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*Zur Erkenntnis der Kolloide, p. 107. This book is an excellent monograph on the colloidal gold solutions.

1. That when a water chamber is interposed the motion is unaffected. 2. That there is no relation between the direction of motion and the direction of light. 3. That the motion is independent of the length of time the beam has acted. When the beam is suddenly shifted to a new part of the liquid which has been in darkness the motion is found to be quite as active. 4. That the motion is independent of the intensity of the light, being just as active in the wider parts of the cone as at the focus and just as active when electric light is employed as by sunlight.

The cause of this most interesting phenomenon is obscure. It may be electrical in nature—all the particles are negatively charged. But it must be recalled that these masses can contain only a few molecules. The fact that the motion greatly increases with decreasing size of the particle may indicate that we are here observing the kinetic energy of the molecule which we call heat.

The method by which the size of the particles is ascertained is interesting. Of course direct measurement is absolutely out of the question. The quantity of gold in each c.c. of the liquid is known from the weight of gold chloride used in making it. Dividing this by the density of gold which may be taken as 20 we obtain the volume of the gold in the unit of volume of the liquid. The ultra-microscope has an attachment—an ocular micrometer—by means of which the volume of the illuminated portion of the liquid can be determined. Thus the total volume of gold in the light cone becomes known. If the liquid is so diluted that the number of particles is not too great, they can be counted and by division the volume of each particle is obtained. The cube root of this gives the diameter on the assumption that the particle is a cube. Putting this into a formula we have

$$D = \sqrt[3]{\frac{M}{20\ N}} \cdot$$

where D is the diameter sought
M the weight of gold in the light cone
N the number of particles.

There is no reason to think that the particles are cubical, but some shape must be assumed and the effect on the result would be small. It is clear that the figure obtained is an average simply. The error does not exceed 20%.

When a solution of any electrolyte—common salt answers well—is added to a red colloidal gold solution, the color changes to blue and the gold collects in larger particles. Thus a bright-red solution so finely divided as scarcely to show the track of the beam was placed in the ultra-microscope and sodium nitrate solution added.* The light-cone became visible, moving spherical yellow cloudy masses appeared in the liquid. The clouds condensed to numberless minute particles in violent motion. These particles in turn coalesced to larger ones which moved, but more slowly than before.

Where the gold solution is pure this change is irreversible—the gold once coagulated cannot be restored to solution except by converting it into gold chloride and repeating the reduction. All colloidal metals and most oxides and sulphides act in the same way and are called *irreversible* colloids. On the other hand, dextrim, gum arabic, gelatine and most kinds of albumin when separated from water can again be dissolved in it and the separation and re-solution repeated an unlimited number of times. Such substances are called *reversible* colloids. It is an interesting fact that in presence of a reversible colloid, like gelatine, the coagulation of gold becomes reversible. Thus, if gelatine is added to a colloidal gold solution and the mixture allowed to evaporate on a glass plate, it coagulates to a blue or violet mass. This is composed of larger units, but the gold particles have not coalesced. Compound particles containing from a hundred to a thousand gold particles imbedded in gelatine have been formed. They seem to contain equal volumes of gold and gelatine and of course are very much richer in gold by weight. When heated with water the gold particles are again disseminated and the colloidal solution is reproduced. The addition of a small quantity of gelatine or some other reversible colloid to a gold solution will entirely prevent the coagulation by electrolytes and the consequent change in color from red to blue. Different colloids exhibit great differences in the quantity required to produce this protective action. Thus gelatine is, weight for weight, about 20 times as effective as egg-albumin and about 100 times as efficient as gum arabic.

4. We may now return for a moment to the distinction between colloidal solutions and true solutions on the one side and

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*Zsigmondy, p. 115.

true suspensions on the other. This is a most interesting and important question, but investigation has not gone far enough to return a complete answer to it.

The greatest difference between true crystalloidal solutions and colloidal solutions is the lack of the osmotic energy of volume which practically determines the behavior of the latter. Hence a colloid exerts little or no osmotic pressure and no external work is afforded by the process of dissolving it. For the same reason the freezing and boiling points are sensibly identical with those of the pure solvent. Another aspect of the same fact is that the force which holds solvent and colloid together is far weaker than in the case of an ordinary solution. Their separation is easier.

Another important difference is the behavior toward the electric current. A crystalloidal solution is either a non-conductor—like sugar—or else it is dissociated into ions which transport equivalent amounts of electricity to both poles. But a colloid all migrates either to one pole or the other—usually to the anode—although some, like the hydroxides of iron, aluminum, chromium, thorium, zinconium and cerium pass to the cathode. Accordingly the particles in most colloidal solutions must be negatively charged and this is in agreement with experiments which show that when two substances are brought into contact the one with the highest dielectric constant is charged positively and the other negatively. Owing to the very high dielectric constant of water (80) most substances would be charged negatively on contact with it.

Lack of optical homogeneity is another distinction, but we have seen that many true solutions show the same phenomenon.

There is nothing in crystalloidal solutions corresponding to the *coagulation* of colloids. This distinction holds good whether we consider the turning of the red gold solutions to blue with simultaneous coalescence of the particles or the setting of other colloids to a jelly, as in the case of gelatin, alumina and silicic acid.

When a solution of a positively charged colloid like stannic acid is mixed with one in which the particles have a negative charge, like gold, then, if the proportions are correct, electrical neutralization occurs and both precipitate in an extremely intimate mixture. In this particular case the precipitate is "purple of Cassius," which is mixed colloid of stannic acid and gold.

Among the distinctions between colloidal solutions and suspensions we have in the first place the immensely fine division of the solid.*

Then the settling of a suspension is a reversible process. One can always shake it up and distribute the solid again in the liquid. The irreversible coagulation of some colloids and the setting of some to jellies are without good analogies among the suspensions; though these are suggestive phenomena in the coalescence of fine particles in suspension which sometimes precedes settling.

The coagulation of a colloid may liberate considerable quantities of energy. Thus when a gram atom of colloidal silver coagulates something like 27,000 cal. are set free, and when the precipitated jelly turns to ordinary silver there is a further liberation of about 6,500 cal. This is a most important distinction between colloidal solutions and suspensions and is of itself a complete justification for making them a separate class, for the trifling amount of gravitational energy which is set free in the settling of a suspension could not be measured in any colorimeter.

5. GENERALITIES.

In the main, the chemist in the enormous development of his science during the 19th century proceeded from crystal to crystal. The analytical chemist has been forced—much to his discomfort—to occupy himself somewhat with colloidal matter—for instance, in the case of silica and some sulphides—while the organic chemist has started with materials purified by re-crystallization, has purified his products in the same way and has thrown everything which could not be induced to crystallize under the head of tarry side products, "Schmieren." The chemist has devoted himself essentially to the crystalloids and this was a necessary specialization. The vast advance which has been made is an effective answer to anyone who would criticize the point of view. But as we have seen, the problem of colloidal matter has now been attacked and much more than a beginning has been made. The new science is not only born but is in sound, vigorous and wonderfully rapid growth. In it the simple and

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*Zsigmondy. Zur Erkenntnis der Kolloide, p. 11.

beautiful laws which have guided so surely the development of the classical chemistry must be set aside. Possibly the stochiometric laws themselves are merely the result of the limitations upon possibility which are set up by the enforcement of a definite arrangement of the molecules in the crystal. This bold suggestion is due to Lottermoser. An obvious objection is that the stochiometric laws apply to liquids and gases in which there is no definite molecular arrangement. But they certainly do not apply to colloidal compounds. If I have a salt solution and am certain that it contains no other compound of sodium or of chlorine I can determine the chlorine and calculate the sodium with the utmost exactness. The analogous calculation is impossible with a colloidal compound. In a sample of purple of Cassius both the gold and the stannic acid must be determined, for their percentage may vary within wide limits and with the variation occurs a continuous alteration in properties. Much interesting work has been done by Sabanajeff and others upon the molecular weights of dissolved colloids. The figures obtained are enormous—50,000 for silicic acid. But it is doubtful how much reliance to place upon them, for the fundamental assumption that the van't Hoff-Raoult laws apply to colloidal solutions is extremely questionable. It is very uncertain that the slight observed depressions of the freezing point were really due to the dissolved colloid. When "silicic acid" is made from sodium silicate and hydrochloric acid the jelly obstinately retains sodium chloride Even when washed with hot water until most of the jelly has dissolved and the chlorine reaction has long been absent in the washings, appreciable quantities of salt are still present. This obstinate retention of traces of other substances is an undesirable colloid characteristic which has long been familiar to the analyst. Thus the trifling observed depressions and indications of osmotic pressure may be accounted for and the basis for the calculation of the molecular weight disappears.

This same fact, the formation of a compound undecomposable by water, accounts for the astounding poisonous action of infinitestimal quantities of silver, mercury and notably copper on plant cells. The albumin absorbs the copper, forming an irreversible colloidal compound, and so it happens that copper in a dilution of 1 : 1,000,000,000 will damage and finally kill organisms upon which HCN 1 : 1000 (a million times as concentrated) has no appreciable effect.

I have already trespassed far too long upon your attention. It would be interesting to discuss in detail the applications, both scientific and industrial, of our subject, but this alone would furnish material for many lectures. Physiology is concerned chiefly with colloids. Enzymes are in colloidal solution, and their peculiar activity is the result of the enormous surface exposed owing to the fine division. In the dyeing industry the fibres are typical colloids and many of the dye-stuffs are in colloidal solution. In photography the gelatin and albumin of plates, films and paper are colloids and the silver haloids are at first in colloidal solution and separate in crystalloidal state during the ripening. The modern industry of high explosives works with colloidal matter. Colloidal metals are employed in the preparation of filaments for the incandescent lamp. The decomposable matters of sewage are mainly in colloidal solution, negatively charged like most colloids and the use of iron compounds in coagulation is an instance of the electrical neutralization and mutual precipitation of two oppositely charged colloids, the positive colloid being ferric hydroxide. The colloids now have a journal devoted entirely to their interests. It is not extravagant to express the hope that the expansion of this subject may in time produce an organized body of knowledge which will equal in scientific interest and practical importance the chemistry of crystalline matter.

Book Notices.

PUBLICATIONS RECEIVED.

The Submarine *versus* the Submersible, by Simon Lake. 13 pages, plates, 8vo. Reprinted from Journal of the American Society of Naval Engineers, May, 1906.

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