ART. XXVI.—*On the Nature of Colloid Solutions*; by
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It seems to be the general opinion among scientists that the solutions of colloid substances, such as albumen, silicic acid, tungstic acid, etc., differ in their nature from solutions of crystalloid substances. The great difference in the velocity of diffusion of solutions of crystalloids on the one hand and of colloids on the other, together with the fact that certain animal membranes and parchment paper are impermeable for colloids, but allow crystalloids to pass freely through their pores, led Graham* to invent the names *crystalloid* and *colloid*, thus dividing substances into two great classes. Graham in his paper states distinctly the differences existing between crystalloids and colloids and ventures the question whether the basis of the colloid state may not be in the complex

* Liebig's Ann., cxxi, 1, 1862.

character of the molecule. However, the facts that the solutions of colloid substances do not have an appreciably higher boiling point than water nor a lower freezing point, and that, in dissolving a colloid, no change of temperature takes place, or, at least, but a very slight change, seems to indicate that a colloid solution is not a solution in the ordinary sense of the term, but rather a mechanical mixture, an emulsion, the colloid being held in a state of suspension in the water.

In the last few years, able investigators have occupied themselves with the subject, and their conclusion has pretty generally been that a colloid solution is really only an emulsion, i. e., a suspension of the finely-divided colloid in the solvent. Most of the experiments have been carried out with solutions of colloid silver. But silver has the property of assuming so many allotropic forms, as shown by the researches of Carey Lea, that it is hardly justifiable to apply the deductions drawn from the phenomena exhibited by it to other colloid substances. Muthmann* describes two experiments which to his mind are convincing proof that colloid silver forms a "suspension" or emulsion with water and not a true solution.

If a solution of colloid silver be mixed with a solution of gum arabic, by adding alcohol, both silver and gum arabic are precipitated, although alcohol does not precipitate a solution of colloid silver alone. According to Muthmann, the explanation of the phenomenon is that the finely-divided silver held in suspension is dragged down by the gum arabic when alcohol is added. But Carey Lea states that a solution of litmus in water, which every one admits to be a true solution, mixed with a solution of gum arabic is also precipitated by alcohol. Muthmann's experiment can then hardly be said to prove the existence of colloid solutions differing from crystalloid solutions in that particular.

In the second experiment, Muthmann let a solution of colloid silver freeze. After melting, the originally red color of the solution had changed to a black, and it was possible by means of a good microscope to distinguish small particles of silver so finely divided, however, that after standing for a week but a portion settled down. Yet this experiment does not prove that the colloid silver is held in suspension in the water. It only shows that, by freezing, the silver is made to pass into a state of greater molecular aggregation, so that the "tagmas"† formed are visible under the microscope. I have frozen solid a solution of colloid tungstic acid, without that the properties of the solution were in the least changed. At any rate, colloid

* Ber. der d. chem. Gesellschaft, xx, 983, 1887.

† By "tagma" is understood a combination of molecules, i. e., a molecule made up of several other molecules. See Pfeffer's "Osmotische Untersuchungen," p. 32.

silver is so anomalous in its behavior that the results of experiments carried out with it cannot be well applied to other colloid substances.

Exner* has made an examination of finely-divided bodies suspended in a liquid with a view to explaining the phenomena of the Brownian movements. He prepared emulsions of gamboge by adding water to a solution of gamboge in alcohol. In this way so fine an emulsion was obtained that under ordinary conditions it kept as such indefinitely. Exner found that, if a little of this "suspension" be put in a vessel and water carefully run down over it so as to form a distinct surface of separation between the two liquids, after some days this surface separating the liquids became obliterated, in other words, diffusion took place. Accordingly, finely-divided particles held in suspension in a liquid would seem to have the power of doing work against gravity; for it is only by the expenditure of energy that a particle would pass from a lower to a higher position in the liquid. But Exner found again that, if the experiment be conducted in a room of constant temperature, after three days not only no particles had passed from the lower liquid to the upper, but that, on the contrary, a portion of the gamboge had settled down as a deposit at the bottom of the vessel. The diffusion phenomena observed in the first experiment must then have been due to changes of temperature and jarring. According to the second experiment, emulsions do not possess the property of diffusion; they are only subject to the action of gravity. Muthmann's second experiment also affords additional proof for this conclusion. But solutions of colloids diffuse, as has been shown by Graham in the case of albumin, etc. Here is then a fundamental distinction between a true solution and an emulsion. Diffusion, as has been shown by Nernst,† is due to osmotic pressure. Therefore, we would expect that a solution that diffused, would have an osmotic pressure. Pfeffer, in the course of his researches on osmosis‡ has found the osmotic pressure of a 1 per cent solution of gum arabic to be 7.1^{cm} of mercury at 15°. This is the only determination of the osmotic pressure of a colloid that I know to have been made. Gum arabic, from a chemical standpoint of view, is hardly suited for an investigation of this character. Too little is known of the constitution of its molecule, and it is not always a chemical unity. What is wanted for an investigation of the osmotic pressure of colloids is a colloid as simple and stable as possible. The colloid modifications of tungstic and molybdic acids fulfill these conditions very well. A solution of colloid tungstic acid

* Wiener Ber.

† Zeitschr. f. phys. Ch., ii, 613, 1888.

‡ Osmotische Untersuchungen, Leipzig, 1877.

may be frozen or heated to 150° without alteration. I have therefore made some determinations of the osmotic pressure of solutions of colloid tungstic acid in the hope of obtaining results that may throw some light upon the nature of colloid substances in solution. As osmotic pressure affords a precious means, according to the theory of van't Hoff on dilute solutions, of determining molecular mass, the results should have some interest.

The apparatus used consisted simply of a tube about 8^{cm} long and 15^{mm} in diameter; one end was well-rounded off in the flame and the other drawn out so as to form a neck. The manometer was a capillary tube with a bore of about 0.5^{mm}, passing loosely into the neck of the osmometer. A bit of rubber tubing is used instead of a cork. The manometer should be so adjusted that it may be pushed to and fro in the osmometer. This is accomplished by greasing well the interior of the rubber tubing. By pushing the manometer into the osmometer or by drawing it out, the pressure may be increased or decreased at pleasure. The membrane used was thick parchment paper, which was bound over the wide end of the tube by means of silk thread, perfect contact between the paper and the glass being effected by the use of a solution of good sealing wax in alcohol. A hermetic joint may thus be obtained. Of course, a great degree of accuracy cannot be obtained with an apparatus of the above description, especially when it treats of measuring high pressures. Still with pressures not exceeding 30–40^{cm} of mercury quite good measurements can be made. I have modified the apparatus somewhat, so that it is capable of much greater precision. The results obtained with the second apparatus will be published in a succeeding paper.

The osmometer is filled with the solution, the osmotic pressure of which is to be determined and the manometer inserted in the neck, care being taken that no bubbles of air be present. The osmometer is then suspended vertically in a jar filled with pure water.

Two solutions of colloid tungstic acid were prepared, which I will designate by the Roman numerals I and II.

1 c. c. of sol. I contained .02467 grms. $(\text{H}_2\text{WO}_4)_n$

1 c. c. of sol. II contained .0100 grms. $(\text{H}_2\text{WO}_4)_n$

The solution of tungstic acid was prepared by adding to a 5 per cent solution of sodium tungstate just enough hydrochloric acid to take up the sodium. The whole was dialyzed until no trace of salt could be detected in the outer liquid.

I filled an osmometer with sol. I, adjusted the manometer so that the pressure was about 20^{cm} of the solution, as I did not employ mercury in the manometer in this experiment, and suspended the apparatus in pure water. The solution mounted

steadily in the manometric tube and in four days had reached the height of about three yards. Having thus got an idea of what osmotic pressure the solution would exert, I repeated the experiment, using mercury* in the manometer. I pushed in the manometer so that the mercury stood at about 40^{cm}. In twenty-four hours, it had fallen to 25.3^{cm}, and remained at this height for about four days. It then fell slowly and in three weeks had fallen nearly 6^{cm}. In another experiment I "set" the osmometer at about 15^{cm}, and in a day or so found that the mercury had risen to 25.1^{cm}. Taking the mean, a solution of colloid tungstic acid containing 24.67 grms. to the liter, exerts an osmotic pressure of 25.2^{cm} of mercury. The temperature at the time of the readings was 17°. Applying the formula for dilute solutions, $p v = RT$, I have $T = 290^\circ$. $R = 84500$, and, if the molecular mass of colloid tungstic acid be 250, i. e., H_2WO_4 , $v = 10377$, $p = 2317.6^{\text{grm}}$ per cm^3 or 170.5^{cm} of mercury. But the experiment gave only an osmotic pressure of 25.2^{cm} of mercury, which is 6.77 times less than the theoretical. Hence, as molecular mass varies inversely as the osmotic pressure, the molecular mass of $(H_2WO_4)_n$ must be about 1693 and n nearly equal to 7.

With sol. II, I obtained as a mean of several determinations an osmotic pressure of 14.1^{grm} per cm^3 . As the pressure with this solution was so feeble I used the solution itself in the manometer, reckoning it as water. This pressure corresponds to a molecular mass of 1718, which corresponds closely with that obtained with sol. I.

In round numbers then the molecular mass of colloidal tungstic acid is about 1700 or nearly seven times 250, and the colloidal molecule consists of seven simple molecules.

All of the phenomena exhibited by colloids may be easily explained on the assumption that the colloid molecule is very large. A solution of a colloid does not seem to lower the freezing point nor raise the boiling point because the molecular mass is so great that it has but little influence. The raising of the boiling point and lowering of the freezing point is a function of molecular mass; the larger the molecule, the less marked these properties of solutions. Colloid solutions do not differ essentially from crystalloid solutions in this particular; and the apparent difference is but one of degree. Colloid solutions lower the freezing point and raise the boiling point only a very little. A 5 per cent solution of colloidal tungstic acid, for instance, would not depress the freezing point more than 0.05°, a depression which could not be accurately measured. I determined the freezing point of sol. I, finding

* Tungstic acid attacks mercury so that at the surface of contact a blue zone forms, which gradually spreads. Yet, I do not think that it had any influence upon the osmotic pressure.

it to be 0.1° , which corresponds to a molecular mass of 456, a number upon which no weight can be laid, as doubtless most of the depression was due to the salt present in the solution.* The presence of a small amount of salt would have no effect, however, upon the osmotic pressure, since the salt could pass freely through the membrane. Osmotic pressure is then due to the colloid alone. The delicacy of the osmotic pressure method is very great. Using the solution itself to measure the pressure, a molecule 2000 times heavier than hydrogen in 1 per cent solution would support a column more than a yard high.

A colloid solution might be regarded as a step between a true solution and a true emulsion. The colloid molecule is so much larger than the water molecule that it stands to reason that the properties of colloid solutions must differ markedly from solutions of substances which possess a molecule but several times heavier than water. Hence diffusion of colloids takes place slowly; the osmotic pressure is small; and but a slight lowering of the freezing point and raising of the boiling point occurs.

As to the nature of this large molecule and how the simple molecules are combined to form the complex molecules, it is hard to give an opinion. The ease with which colloidal substances are coagulated, i. e., pass into the solid state, indicates that there exist in the solution molecular groupings similar to those existing in a solid. It is generally admitted that in solids the simple molecules unite to form more complex molecules or "tagmas." Similar "tagmas" might exist as such in the solution.

The facts are that solutions of colloids have a definite rate of diffusion and exert a definite osmotic pressure. As osmotic pressure, diffusion, lowering of the freezing point and raising of the boiling point are intimately related, we can say that colloid solutions also have freezing and boiling points differing from those of the solvent. We conclude then that a colloid solution is a solution in the ordinary acceptance of the term and not a "suspension."

I am occupied in making determinations of the osmotic pressure of colloid substances, especially of the albuminoids. Certain albuminoids, as is well known, are insoluble in pure water, but quite soluble in a solution containing a little of some salt. As this salt does not affect the osmotic pressure in the least, its presence does no harm. Thus I hope to get more of an insight into the nature of the complex substances of animal origin.

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*I might have determined the amount of salt present and thus easily found what depression was due to the acid alone; but as the depression was so small and the solution so dilute, the results would have been worthless.