ART. LXII. *Remarks on Colloidal Silver*; by C. BARUS.

1. IN the absence of Dr. E. A. Schneider I wish to say that there does not seem to be any real issue between the recent note of Mr. Carey Lea* and our own work.† It was our endeavor to arrive at new data relative to colloids in general, and colloidal silver was chosen merely as a promising subject for attack. We showed at length that colloidal silver possesses properties which can be explained with reference to the analogous behavior of suspended sediments. Differences neces-

* Carey Lea: this Journal: October, 1894.

† Barus u. Schneider: Ostwald's Zeitschrift: viii, p. 278, 1891; Wied. Annalen, xlviii, p. 327, 1893. Full references to the above and other allied physical questions are there given.

sarily remained as a result of differences in the size of particles in the two cases, the silver being much more finely comminuted. For this reason we can not admit that Mr. Lea's recent experiment is decisive. A similar test had already been made by Prange* and it was repeated by us with the remark that the Tyndall experiment is no valid criterion unless precise statements are made as to the size of particles which just appreciably interfere with optical clearness. In other words the dimensions below which Tyndall's experiment practically fails are here vitally in question, and data for these have not been forthcoming.

Suppose a solid is dropped into an excess of its solvent. In order that the system may become a solution, the disaggregation must at least reach the molecule. In electrolytes it may even go further as is evidenced by Arrhenius's celebrated factor 2. But, under other circumstances, may not the separation stop short *before* the molecule is reached; or conversely, when a precipitate is being formed out of individual molecules, may not the process of growth be arrested in virtue of an equilibrium of forces when the particles formed consist of 2, 10, 100 or even 1000 molecules? To answer affirmatively is to find a home for the family of colloids, and they will more nearly resemble solutions in proportion as the particles are smaller. Certainly the beam of light is no longer an available criterion, for the whole phenomenon is mapped out on a scale which is small even in comparison with the wave length of light.

2. About a year and a half ago I incidentally made an experiment in connection with certain meteorological questions, which has a precise bearing on the point here at issue. In the endeavor to pass compressed air through a wet porous porcelain septum into water, I was struck by the magnitude of the pressures necessary. Supposing I waited long enough to insure the transpiration of liquid, no flow of gas through the septum occurred for pressure excesses of even above 100 lbs., excepting at isolated points which were obviously the seat of fissures. Now let T be the surface tension of water in dynes per linear centimeter, α the angle of capillarity, r the mean radius of the pores of the septum, and x the pressure of the gas in atmospheres. Then (very nearly) $10^6 x \pi r^2 = 2 \pi r T \cos \alpha$, or

$$r = 2 T \cos \alpha / 10^6 x$$

If therefore in the above experiment, $x = 8$ atm., $T = 71$ (Everett's tables, p. 50), $\cos \alpha = 1$ (say, for the superior limit is in question),

$$r = 18 \times 10^{-6} \text{ cm,}$$

* Prange: Rec. des Trav. chim. des Pays. Bas, ix, p. 125.

nearly, making the diameter ($2r$) of the pores smaller than the wave length of violet light. Schneider showed however that colloidal silver passes readily through such a septum whereas the alcoholic precipitate fails to do so. The particles are therefore respectively smaller and larger than the diameter* given. If 10^{-8} cm be taken as the order of molecular dimensions, the size in question is at least 1000 times as large, showing the aggregates to consist of the enormous number of 10^9 molecules, at least. There is thus an abundance of room for particles containing (say) 100 molecules to the aggregate, and forming suspensions in water (colloids) in their general aspects hardly distinguishable from true solutions.

It is interesting to ask how great a pressure would force the water out of a septum just large enough to let the particles of the size in question (5×10^{-8} cm) pass. It would take several thousand atmospheres, and it is therefore quite impossible to test finer septa like animal membrane to the extent in question. Nevertheless if the attempt be made to *grade* porous clay septa, prepared by successive vitrifications, by the method given, I dare say that a range of mean diameters of pores could be obtained, sufficient to answer many outstanding dimensional questions† in relation to the colloidal state; but one should be prepared to exert pressures as high as 100 atmospheres.

2. There is another point of view from which colloidal silver invites treatment, this time in the solid state. Dr. Schneider and I interpreted the high degree of insulation which we detected in Carey Lea's metallic mirrors as an instance of the allied behavior of non-coherent metallic matter, in general. Wöhler (quoted by Wernicke) showed this some 50 years ago; but our references were chiefly directed to the recent work of Auerbach‡ and of Ed. Branly§ the latter of whom in particular proved that non-conduction ceased when an electric spark was passed through the column of powder. One therefore readily calls to mind the startling results recently obtained by Oliver Lodge|| with his "coherer," and the question is pertinently asked whether solid colloidal silver, swept by a train of electric surges will begin to show increased electric conduction, as it does for instance under the influence of heat.

* By the hydrodynamic method particles smaller than 2×10^{-6} were measured, supposing the method vouched for. Ostwald's Zts., l. c.

† I may here call to mind the allied geological fact that hot water will pass through porous rock in virtue of capillarity, in the face of enormous withstanding steam pressures.

‡ Auerbach: Wied. Ann., xxviii, p. 604, 1886.

§ Branly: Phil. Mag., (5), xxxiv, p. 530, 1892.

|| Lodge: Nature, vol. 1, p. 136, 1894.

Oberbeck's* electric work, undertaken in a different direction with a view of showing the occurrence of an allotropic state in Carey Lea's silver has quite failed to convince us. We see no reason for withdrawing the views which we originally expressed (l. c.)

3. At the close of our experiments† we suggested that a field of great promise would be found in the metallic optics of colloidal silver. Work of this kind has since been taken up with success by Wernicke.‡ The change of phase observed on the reflection of light from thin metallic laminæ enclosed between clear media, with the front plate of greater refractive index, is either an acceleration or a retardation, according as the metal is intrinsically coherent or non-coherent. The method is remarkably sensitive and applicable to metallic films so thin as to be quite invisible to the eye. Tested in this way colloidal silver according to Wernicke§ takes rank with bodies which in their ultimate nature are an aggregate of individual particles, however small they may be, or however perfect the mirroring surface which an even distribution may produce. It is this method which is to be looked to for decisive results, not only for silver but for other colloids.

4. Of the two interpretations which may be given of Carey Lea's brilliant discovery, the one originally advocated by Dr. Schneider and myself is to me intensely the more interesting. As an aggregate of excessively fine suspended particles, colloidal silver introduces a whole series of fascinating physical problems, subject to forces which as to their nature are almost tangible. Even in an ordinary case of sedimentation if I write

Muddy water + acid = acidulated water + mud,

the latter body being precipitated, I have a chemical equation in embryo,—an equation|| which so far as can now be discerned lacks stoichiometric precision, but which in its general character is undoubtedly a double decomposition. If the actuating forces be traced, they must lead by slow gradations up to affinity.

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* Oberbeck: *Wied. Ann.*, xli, p. 265, 1892; xlvii, p. 353, 1892;

† Barus u. Schneider: *Wied. Ann.*, xlviii, p. 336, 1893.

‡ Wernicke: *Wied. Ann.*, li, p. 448, 1894; lii, p. 515, 1894.

§ Wernicke: l. c. p. 523.

|| In the same way I picture to myself the remarkable physical effects produced by traces of foreign admixtures in metallurgy.