A Theory of Colloidal Solution

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active air streaming against these metallic surfaces is transformed into ordinary air. Therefore this is simply a hypothesis relative to phenomena which require further study.

DISCUSSION.

The CHAIRMAN said he had observed the fact that metals were charged sometimes positively and sometimes negatively by active air.

Mr. WATSON asked if any experiments had been performed on the viscosity of gases rendered active by X-rays.

L. *A Theory of Colloidal Solution.* By F. G. DONNAN, M.A., Ph.D., Junior Fellow, Royal University of Ireland*.

THE main fact concerning "colloidal" solutions, a fact which has been established by experiment and thermodynamical reasoning, appears to be that such "solutions" are in reality complexes of *two* phases, of which one exists in a state of extremely fine division, interspersed throughout the other. It must be observed, however, that it is not a sufficient description to call such complexes mere "suspensions," for what we have here to deal with is not so much a certain sort of mixture or *pseudo-solution*, as rather a peculiar condition of matter, namely the "colloidal" state. This fundamental point was clearly emphasized by Graham, but seems to have been somewhat lost sight of by some modern writers. Thus Krafft† has proposed a theory of colloidal solutions in which it is supposed that the molecules of colloidally-dissolved substances rotate round each other in closed paths. Apart from the consideration that such a theory is invalid, inasmuch as it gives no explanation why these orbital systems should not possess translatory motion, it is evident that such a theory must, in any case, be highly unsatisfactory, for the really essential point would be the explanation of *how* such a state of affairs came about.

* Read March 8, 1901.

† *Ber. d. d. Chem. Ges.* vol. xxix. p. 1334 (1896).

What we have to account for, in fact, is the following. A solid substance C, when brought in contact with certain liquid media, breaks up or disintegrates into these media, but in such a manner that the disintegration process *does not proceed to the molecular limit*. The liquid medium appears then to be interspersed with minute aggregates of C, which are still so much larger than molecular magnitudes that they are subjected to a statistically almost uniform molecular bombardment, and hence possess only very small quasi-molecular motions. These complexes, moreover, are such that changes of temperature, or the addition of comparatively small quantities of other substances, frequently cause the sudden precipitation in mass of the substance C.

In what follows an attempt is made to show that all these phenomena can be explained by the application of a well-known hypothesis, namely by means of Laplace's theory of intermolecular attractive forces. In doing this it is necessary, and in the present case essential, to carefully distinguish between the *kinetic molecular equilibrium* and the *statical** (mechanical) *equilibrium* at the interface of solid and liquid.

Let us consider first the state of affairs between a crystalline solid and a liquid medium which dissolves it.

Here we have, at any given temperature, a definite concentration of the dissolved solid. This equilibrium is a *molecular-statistical* one, and consists in the balancing of two statistically equal and oppositely directed molecular fluxes. At the same time, owing to the fact that a *definite interface* exists between the solid and the liquid, it is clear that any small volume-element of the solid lying near the interface is in *statical* equilibrium. The resultant of all the intermolecular forces is, in fact, an inwardly-directed force urging this volume-element towards the inner part of the solid.

Thus a crystalline solid immersed in its saturated solution is

- (a) in statical equilibrium under a compressive stress ;
- (b) in kinetic-molecular equilibrium under equal and opposite molecular fluxes.

Hence, during the process of solution of a crystalline solid, although there is a net outward flux of molecules, we must

* In this connexion see Larmor, 'Ether and Matter' (1900), *passim*.
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suppose that the resultant mechanical force acting on any small volume-element of the solid in the immediate neighbourhood of the solid-liquid interface remains inwardly directed, so that the "molar" integrity of the mass is preserved, although "molecular" disintegration is taking place.

The theory which is here proposed for the pseudo-solution of colloidal matter regards this phenomenon as a process of *molar* or *mechanical* disintegration due to the non-existence of statical equilibrium in the thin surface-layers of the solid when the latter is in contact with certain liquid media.

Consider the solid, I, bounded by the planes AB, CD, and surrounded by the liquid medium O (it is sufficient to consider the problem in two dimensions). Let de be any small volume-element of I situated just at the bounding interface AB. Then de is acted on by two forces r and l , as indicated in the diagram, l being due to the attraction of I and r to that of O. For crystalline solids $l > r$; for "colloidal" matter in contact with certain liquids we assume that $r > l$.

Fig. 1.

It follows then that the solid I will begin to disintegrate into the liquid medium O. It is difficult to form an accurate mental picture of what exactly happens in this case. Probably the solid "mixes" into O in the form of excessively thin sheets or extremely fine and branching filaments. It must be observed that the colloidal solid is not in an "explosive" state, for the disintegration only affects at any moment

the excessively thin surface-layers. The question now arises as to how far this process will continue : for if it be supposed to go on until the limit of molecular intermixture be arrived at, it is evident that a true solution must result. But as we understand by colloidal matter that condition of matter which gives "colloidal solutions" (defined by certain peculiar properties), it is clear that there exists something which arrests the disintegration-process before the molecular limit is arrived at, and yet at a point where the resulting "grain" is exceedingly fine. The essence of the theory here proposed lies in the nature of the assumptions whereby this stoppage of the process of disintegration or intermixture is accounted for.

Let the attraction of the matter contained in the semicircle PQR be a very large percentage of the attraction due to the infinite (or practically infinite) mass of O lying to the right of *de*. Let similarly the attraction due to LMN be the same very large percentage of the total attractive force exerted on *de* by the practically infinite mass of I. These circles correspond in fact to the so-called "spheres of molecular action." We assume that not only is $r > l$, but that also semicircle PQR > semicircle LMN.

The physical significance of these assumptions may be stated as follows:—It is assumed that the molecular "adhesion" between I and O is greater than the molecular "cohesion" of the colloid I, and that the intermolecular attractive forces fall off more rapidly with increasing distance in the case of the molecular cohesion of I than in the case of the adhesion between I and O. It is easy to express these conditions in a precise mathematical form by choosing a suitable law of force with two constants, but considering our present want of knowledge such a formulation could only serve the purposes of illustration.

With the assumptions made, it now becomes possible to explain why the process of intermixture is arrested before the molecular limit. Suppose that the sheets, filaments, or particles have become so thin that the plane CD occupies a position (CD' within the semicircle PVR (see fig. 1). Then it is evident that the value of r will be diminished since there now exists an effective component due to O acting on the left

of de . In fact, the resultant attraction due to O bears a ratio to its former value equal to the ratio of PRST to semicircle PQR. At the same time, so long as the plane $C'D'$ lies within the semicircle PVR but *outside* LMN the value of the force l will not be sensibly altered.

Accordingly there exists a *critical* thickness of I such that the forces l and r just balance. When this state of division is reached the process of disintegration ceases, and there results a *two-phase* medium consisting of the medium I distributed throughout the medium O in some state of extremely fine division. Such a medium corresponds on the present theory to a colloidal solution.

Fig. 2, which requires no further explanation, applies to the case of *spherical* particles of I immersed in O.

If the medium O be continuously removed by evaporation or otherwise, or if sufficient of I be colloiddally dissolved,

Fig. 2.

there results an interlacing network of I distributed through O, and a more or less *elastic jelly* is produced (*cf.* the views of van Bemmelen).

For thicknesses of I greater than the critical, the medium I has a tendency to *increase* its common surface with O, *i.e.*, it possesses an effectively *negative* surface-tension. For thicknesses less than the critical, however, there will be a *positive* surface-tension. Hence if the substance I be produced in the

medium O by chemical means, its aggregates will grow to this critical size and stop there, *i. e.*, will remain in colloidal solution.

If a colloid be defined as a substance which forms those pseudo-solutions termed colloidal, it follows from the above that this description is not sufficient unless the other medium, *i. e.* the *pseudo-solvent*, be specified. This point is well illustrated by the result obtained by Krafft* with the soaps; these substances give true solutions with alcohol, and colloidal solutions with water.

There is nothing to prevent a substance being partly colloiddally distributed throughout a given medium and partly in true molecular solution†. Hence all gradations may occur. The foregoing considerations render intelligible many of the peculiarities exhibited by colloidal solutions, namely, their small diffusibility and small osmotic pressure, their frequent want of optical transparency, their "solidification" to jellies, their precipitation by changes of temperature or by the addition of comparatively small quantities of certain substances, &c., &c. It is necessary, however, to remark that only *reversible* changes admit of explanation on the above theory. The *irreversible* phenomena so frequently exhibited by organic colloids can only be explained by intra-molecular changes. As regards the nature of the "colloidal" state, as distinct from a colloidal solution, the present theory lends support to the view that in matter in the colloidal state the intermolecular forces are in general smaller than in the case of crystalline matter, and fall off comparatively rapidly with increasing distance. This view is in harmony with the fact that substances which tend to assume the colloidal condition are in general those which possess feeble powers of crystallization. A solid colloid is in fact an amorphous body possessing only an exceedingly minute velocity of crystallization. Whether, however, a colloid body is quite analogous to a highly supercooled viscous liquid with excessively small velocity of crystallization, such as "solid" glass, is not a

* *Ber d. d. chem. Ges.* xxvii. p. 1747; xxviii. p. 2556; xxix. p. 1328.

† So far as I am aware, this possibility was first mentioned by Mr. W. B. Hardy.

question which I shall attempt to consider here. Some colour, is, however, given to this view by the recent work of Barus, who considers he has obtained colloidal solutions of glass in water.

The whole question is intimately connected with the hitherto unsolved problem as to the real nature of the solid state.

Chemical Laboratory,
University College, London, W.,
Christmas, 1900.

DISCUSSION.

Dr. GLADSTONE said that the study of colloids was one which had been too much neglected. It involves both a knowledge of physics and of chemistry. A colloid is an unstable body, and is always altering its composition. Water of combination may be given off at the ordinary temperature, even if the surrounding atmosphere is saturated, and the colloid cannot take up the water again. It is impossible to make a sharp distinction between colloids and crystalloids—they merge into one another. Transition forms are not uncommon.

Dr. LEHFELDT asked if it had been proved that colloids have osmotic pressure.

Prof. THRELFALL said that in colloidal solutions some of the substance was not in suspension. Dr. Martin had filled a filter with silicic acid under pressure, and found that it allowed sugar solution to pass through, but stopped colloidal solutions. The author had used opacity as a test for colloids, but silicic acid could be got transparent. There are two kinds of opalescence. One cannot be removed, and exists because the substance is a two-phase system. The other can be removed with difficulty by filtering, and leaves a transparent substance. The want of transparency should be used cautiously as an argument.

Dr. DONNAN, in reply to Dr. Gladstone's remarks on the transition from crystalloids to colloids, said that a substance might be a crystalloid with one medium and a colloid with another. In reply to Dr. Lehfeldt, he said that the only

indisputable evidence in favour of osmotic pressure of colloids is that colloidal solutions diffuse. He agreed with Prof. Threlfall that opacity should be used carefully as an argument, but stated that his theory referred to a two-phase system.

LI. *A Direct-reading Conductivity-Bridge.*

By ROLLO APPELEYARD*.

WHEN it is required to check the conductivity of several tons of copper wire, of the same nominal diameter, the method employed generally resolves itself into making a careful test of the conductivity of the wire of a selected hank, and afterwards balancing a length of this on a slide-bridge against successive equal lengths of the remaining hanks of wire of that diameter. If an ordinary slide-bridge is employed, the scale-readings corresponding to the balance-position of the sliding contact are not directly proportional to the successive conductivities. To arrive at the conductivity a certain amount of arithmetic is necessary. If, however, the slide-bridge is arranged somewhat differently, the readings of the slider can be made to be directly proportional to conductivities.

Let a be the resistance of the selected wire of known conductivity k_a , and let b be the resistance of any of the remaining wires whose conductivity k_b is to be determined. The third arm of the bridge is a fixed resistance d , and the fourth arm is the slide-wire c , the resistance of which can be adjusted to balance d by moving the slider.

We have therefore,

$$\frac{d}{b} = \frac{c}{a}.$$

Or, replacing the reciprocals of b and a by their conductivities

$$dk_b = ck_a,$$

$$k_b = \frac{k_a}{d} c.$$

* Read March 8, 1901.