chloride as mentioned in (6), a sol is formed stable on standing but forming a powdery sediment on dialysis and completely settling out.

9. In all examples of peptization by salts as mentioned in (6), (7) and (8) the action is due to acid hydrolysis, as shown by the fact that hydrochloric or nitric acid may be used as peptizing agents with equally good results. The sols formed by acids give excellent gels on dialysis but lighter in color than those formed from ferric chloride solution. If sulfuric acid is used the results are those observed in the use of any sulfate as the peptizing agent. There are at least two kinds of peptization of these arsenates and phosphates, that by acids and that by bases.

10. The formation of the sol and gel in the case of the acid peptizations is due to the disturbance of the equilibrium by dialysis. This is shown by the fact that good gels may be formed by dialyzing dilute mixtures of ferric chloride solution and arsenic or phosphoric acid, the phosphoric acid giving a gel excellent in clearness as well as in texture.

11. The metaphosphate, pyrophosphate and hypophosphite of ferric iron behave like the orthophosphate in peptization by acids and ferric chloride. Ferric pyrophosphate in ferric chloride solution formed a splendid deep red gel on dialysis.

OBERLIN, OHIO.

THEORY OF COLLOIDS.

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The object of the present paper is the promulgation of further reasoning in favor of the "complex" theory of colloid formation and the elucidation of the very interesting and important conclusions which follow. The fundamental assumption of this theory is that the colloidal state in sols owes its stability to the formation of a complex between the particles of the disperse phase and certain substances present or formed in the dispersion medium during the preparation of the colloid. The sols of the noble metals have been cited as an argument against this theory, but Beans and Eastlack[1] have shown that the presence of chloride, bromide, iodide, or hydroxide ions in concentrations from 0.00005 N to 0.005 N has a marked stabilizing effect on gold sols and that the colloid particles become negatively charged. In concluding, these authors consider that the electrical synthesis of colloids consists of a thermo-mechanical dispersion of the metal, followed by the formation of a colloidal complex between the dispersed metal and certain ions present in the medium.

The assumption of the formation of such a complex between any colloid particles and electrolytes present in the dispersion medium is not unreasonable. Carbon is a typical *adsorbing* agent and happily one, the stability of whose compounds has been extensively investigated. The

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[1] THIS JOURNAL, 37, 2667–83 (1915).

data leading to the formulation of Baeyer's Strain Theory indicates that the four valencies of the carbon atom are directed toward the vertices of a regular tetrahedron, of which the carbon atom is the center. This being true, any atom *within* a given particle of carbon will attract and be attracted by the atoms immediately surrounding it, but one at the surface is attracted only towards atoms of the particle and consequently has one or more of its valencies directed away from the particle, and therefore unsatisfied. In a lump of carbon this free or residual valency might be relatively insignificant but would increase to huge proportions as the carbon became more and more highly dispersed. It is probable that every substance possesses a certain amount of residual valency at its surface, which tends to cause it to combine with substances approaching its surface. As in chemical combination in general, such combination is probably selective. Indeed, Beans and Eastlack (*Loc. cit.*) have shown that the presence of fluoride ions does not stabilize gold sols, while Lenher[1] has shown that gold fluoride is incapable of existence, not only in the presence of water, but under ordinary laboratory conditions.

Apparently the colloid particle takes its electrical charge from the ions with which it combines, or in some cases, acquires a charge by ionizing itself. Such a charge seems to be necessary to the stability of the colloid state in sols, which is explained to some extent by the fact that particles with like charges tend to repel each other, thus preventing coalescence.

Associated with any charged particle there will be a number of ions of opposite charge, which cannot be separated from the surface of the particle, excepting by very small distances, or by being replaced by other ions of the same sign, which means that the distribution of ions in the layer of solution surrounding the particle will be different from that in the bulk of the dispersion medium, a condition to which Donnan's[2] work on membrane equilibria can be applied. Donnan considers an aqueous solution of a salt, NaR, such as Congo red, in contact with a membrane which is impermeable to the anion R' and the nonionized salt, but will allow Na^+ or any other ion to pass freely through it. On the other side is an aqueous solution of sodium chloride, which will diffuse from its Solution II into the Solution I of NaR. When equilibrium is established, if a small virtual change is made reversibly at constant temperature and volume, the free energy will remain unchanged, *i. e.*, no work will be done. The change here considered is the transfer of δn moles of Na^+ and Cl' from II to I. The work which equals zero is

$$\delta n \, RT \log \frac{[Na^+]_{II}}{[Na^+]_{I}} + \delta n \, RT \log \frac{[Cl^-]_{II}}{[Cl^-]_{I}} = 0$$

or

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[1] This Journal, 25, 1136 (1903).

[2] *Z. Electrochemie,* 17, 572 (1911).

$$[\mathrm{Na}^+]_{\mathrm{II}} \times [\mathrm{Cl}^-]_{\mathrm{II}} = [\mathrm{Na}^+]_{\mathrm{I}} \times [\mathrm{Cl}^-]_{\mathrm{I}}.$$

By a continuation of this reasoning it can be shown that whatever diffusible binary electrolytes be added to Solution II, when equilibrium is established, the *products* of concentrations of any pair of diffusible and oppositely-charged ions will be equal in the two solutions.

If a substance is dispersed to the colloid state in a solution of the electrolyte MN and combines with a portion of M^+ (not necessarily in equivalent quantity from a chemical standpoint), then at the surface of the colloid particles there will be a certain concentration of N' bound by electrochemical attractions to the colloid. This surface layer of solution will also contain M^+ and N^- and will thus bear the same relation to the bulk of solution as did Solution I to Solution II in Donnan's work just quoted, and consequently the product $[M^+] \times [N^-]$ will be equal in the surface layer and bulk of solution, and since the concentrations of M^+ and N^- are *unequal* in the surface layer and *equal* in the bulk of solution, *the total concentration of ions will be greater in the former than in the latter.*

In the bulk of solution let x = concentration of positive or negative ions.

In the surface layer surrounding particle let y = concentration of ions of same sign as charge on the colloid particle.

z = concentration of ions bound to the colloid by electrochemical attractions.

Therefore $y + z$ = concentration of ions of opposite sign to that on the colloid particle.

Let e = excess of concentration of diffusible ions of the surface layer over that of the bulk of solution.

In order to keep the reasoning as simple as possible only binary electrolytes will be considered, although it will be obvious that the reasoning can be extended to include ions of any valency. From the law of "equality of products" just discussed

$$x^2 = y(y + z)$$

and since

$$2x + e = 2y + z$$

$$z = \sqrt{4ex + e^2}.$$

If unit quantity of colloid and unit volume are considered, *z represents the quantity of electrolyte combined with the colloid.* But the generally accepted *empirical* formula for *adsorption* (using the same system of notation) is

$$z = kx^{1/p}$$

where p represents a constant, usually *about* 2, so that generally

$$z = k\sqrt{x}.$$

The similarity of the equations is striking and in certain cases, and within limits, they would give similar curves, but they are not identical, and here it should be noted that the latter formula is at best only empirical, while the former follows from well-founded assumptions.

The different distribution of ions in the surface layer and bulk of solution will result in a difference of potential, the formula for which is given by Donnan[1] as follows:

$$E = \frac{RT}{F} \log \frac{1}{\lambda}$$

Or, in the notation adopted in this paper,

$$E = \frac{RT}{F} \log \frac{x}{y} = \frac{RT}{F} \log \frac{2x}{-z + \sqrt{4x^2 + z^2}}.$$

But z has a limiting maximum value, since the amount of electrolyte which can combine with a colloid of definite degree of dispersion is limited by the amount of residual valency at the surface, or, in the case of an ionizing colloid, the portion ionized cannot exceed the whole. Hence,

$$\overset{\text{limit}}{x = \infty} E = \frac{RT}{F} \log \frac{2x}{\sqrt{4x^2}} = 0,$$

proving that the difference of potential existing between the surface layer surrounding the colloid particle and the bulk of solution will diminish as the concentration of electrolyte is increased, after the combination of colloid and electrolyte has reached *or neared* its maximum. When this difference of potential has become sufficiently small a condition is established which is favorable to the coalescence of the particles. Assuming that a given potential difference is required for the maintenance of the colloid state in sols, the amount of electrolyte required for precipitation of the colloid will depend upon the maximum value for z. In the case of suspensoids this is probably very small, while for many emulsoids it is known to be comparatively high.

Where a charged particle combines directly with an ion of opposite sign, precipitation must follow. The cause of the co-precipitation of oppositely-charged colloids is equally obvious, but it might be well to point out in passing that the rate of this precipitation might be controlled by suitable regulation of the concentration of electrolytes in the dispersion medium. Similar lines of reasoning explaining the swelling and contracting action of electrolytes upon colloid jellies have been worked out by H. R. Procter and the author and appear elsewhere.[2] Whatever herein expressed may seem opposed to the generally-accepted views on colloids can be tested as the formulas derived are quantitative in character. The author expresses the hope that they may lead a step nearer to the goal of colloid chemists.

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[1] *Loc. cit.*

[2] *J. Chem. Soc.*, 109, 307 (1916); *J. Am. Leather Chem. Assoc.*, 11, 8 (1916).