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EQUILIBRIA IN DISPERSED SYSTEMS AND THE THERMODYNAMIC THEORY OF COLLOIDS.

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The purpose of this article is to consider the conditions necessary for thermodynamic equilibrium in *dispersed systems*, with the hope of providing a partially new point of view for some of the phenomena of *colloids*.

Part I. Equilibria in Dispersed Systems.

Dispersed systems including the colloids may be treated as a special case of *divided systems*, and in their consideration incidental use will be made of the principles of equilibria in divided systems which have already been developed by the author.[1] The particular characteristic distinguishing dispersed systems from other divided systems is that the degree of division of at least one of the phases, the dispersoid, has become so high that the properties of the system depend appreciably on the size or number of the dispersoid particles present. Hence in a thermodynamic consideration of dispersed systems, as has already been pointed out by Pavlov,[2] the degree of dispersion and the concentration of dispersed particles will be among the variables upon which the free energy of dispersoid or dispersing medium can depend. We shall first consider somewhat in detail the free energy of the dispersoid and of the dispersing medium.

The Free Energy of the Dispersoid.—Owing to surface tension at the boundary between dispersoid and dispersing medium it is evident that the free energy of the material inside of a particle of dispersoid will depend appreciably on the size of the particle, that is, on the degree of dispersion.

If we consider dispersoid regions which have the volume v and the surface s, we may call the ratio $\rho = \partial s/\partial v$ the degree of dispersion.[3] If now we introduce into such a region an infinitesimal quantity of a component which has the partial specific volume $\bar{v}$, the increase in surface per gram of material introduced will evidently be $\bar{v}\ \partial s/\partial v = \bar{v}\rho$, and hence if σ is the surface tension the work that has to be done per gram of material introduced will be $\bar{v}\rho\sigma$. A better understanding of the nature of the quantity $\bar{v}\rho\sigma$ may be obtained by dividing it into the two factors $(\bar{v})$ and $(\rho\sigma)$. The latter of these is the work per unit increase in volume

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[1] "The General Principles of Equilibria in Divided Systems." THIS JOURNAL, preceding article.

[2] Z. physik. Chem., 75, 48 (1910).

[3] The ratio s/v is a common measure of degree of dispersion; see W. Ostwald, "Grundriss der Kolloidchemie," third edition, 1912, p. 29. We have adopted $\partial s/\partial v$ as our measure of degree of dispersion, because of its mathematical convenience. For a sphere $s/v = 3/r$, $\partial s/\partial v = 2/r$.

of the region, hence it has the dimensions of pressure and indeed may be considered as the pressure which the surface tension produces on the material in the interior of the region.

We may now write for the partial free energy[1] of the component under consideration

$$\bar{F} = \bar{F}_c + \bar{v}\rho\sigma \qquad (1)$$

where $\bar{F}_c$ is the partial free energy which the component would have in a large quantity of undivided phase having the same composition as the particle in question.

Let us now consider the various quantities on the right-hand side of equation (1), upon which the partial free energy of any one of the n components in the dispersoid particle depends. $\bar{F}_c$ is evidently determined by the $(n - 1)$ concentrations $(c_1, c_2, c_3, \ldots c_{n-1})$ which fix the composition of the dispersoid particle. $\bar{v}$, the partial specific volume, is very nearly a constant, but will depend to some extent on the composition of the dispersoid and the size of the particle. ρ, the degree of dispersion, is an independent variable. And, finally, σ, the surface tension, depends greatly on the $(n - 1)$ concentrations $(c_1, c_2, c_3, \ldots\ldots c_{n-1})$ which determin the composition of the dispersoid, and equally on the further $(n - 1)$ concentrations $(c_1', c_2', c_3', \ldots\ldots c'_{n-1})$ which determin the composition of the surrounding dispersing medium, small concentrations of the electrolytes often having a particularly large effect on surface tension. We shall also find that the surface tension is dependent to some extent on the size of the particle, that is, on the degree of dispersion ρ, and we must admit the possibility that it may be affected by the presence of neighboring dispersoid particles when their concentration per cubic centimeter, C_D, becomes high. In general, then, we may write the partial free energy of any component in the dispersoid particle as a function of the independent variables considered above.

$$\bar{F} = f(c_1, c_2, c_3, \ldots\ldots c_{1\,n-1}, c_2', c_3', \ldots\ldots c'_{n-1}, \rho, C_D, p, T). \qquad (2)$$

Of these variables C_D is certainly very often negligible.[2]

The Free Energy of the Dispersing Medium.—The free energy, $\bar{F}$, of any component of the dispersing medium will obviously depend in the first instance on the composition of the dispersing medium, that is, on the variables $(c_1', c_2', c_3', \ldots\ldots c'_{n-1})$. Moreover, since it has been shown experimentally that a dispersed phase may exert a measurable osmotic pressure[3] depending on the concentration, it is evident from the

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[1] Throughout the article by free energy we shall understand in general the partial free energy per unit mass of the component under consideration.

[2] For a discussion of what is meant by negligible variables, see the author's previous article, *Loc. cit.*, p. 309.

[3] Freundlich, "Kapillarchemie" 1909, p. 335, p. 402, *et seq.*; W. Ostwald, *Loc. cit.*, p. 296, *et seq.*

well-known relations connecting free energy and osmotic pressure, that the partial free energy of the components of the dispersing medium will also depend upon the concentration of dispersoid particles C_D.

It was shown by the work of Perrin[1] that the osmotic pressure exerted by a dispersoid in some cases follows very closely the law of van't Hoff $PV = nRT$. Expressing R in suitable units, n may be taken as the number of dispersoid particles in the volume V, and we see that the osmotic pressure would be directly proportional to C_D, the concentration of dispersoid particles per cubic centimeter and would be *independent* of the nature of the dispersoid particles. Hence, in case the osmotic pressure produced by the dispersoid does follow the law of van't Hoff or any other law which makes it independent of the nature of the dispersoid particles, we may write

$$\overline{F}' = f'(c_1', c_2', c_3', \ldots . c'_{n-1}, C_D, p, T_1). \qquad (3)$$

If the nature of the particles should have an important specific effect on the osmotic pressure, we may include among our variables the concentrations $(c_1, c_2, c_3, \ldots \ldots c_{n-1})$ of the various components in the dispersoid particles and the degree of dispersion ρ, and since these would in general completely specify[2] the specific nature of the dispersoid particles, we should then be justified in writing as a complete formulation

$$\overline{F}' = f'(c_1, c_2, c_3, \ldots c_{n-1}, c_1', c_2', c_3' \ldots c'_{n-1}, \rho, C_D, p, T). \qquad (4)$$

We may notice in this equation that the free energy of the dispersing medium depends on the same variables as have already been used for the dispersoid.

We are now in a position to discuss the equilibrium relations in dispersed systems.

Equilibrium between Different Particles of Dispersoid.—If we consider the different variables upon which the free energy of any component of a dispersoid particle depends, as shown in equation (2), we see that two dispersoid particles can differ from each other only in composition and in the value of ρ, the degree of dispersion. This is true because for all ordinary systems the other variables—pressure, temperature, composition of the dispersing medium, and concentration of dispersoid particles—are obviously uniform throughout. Now it has been shown[3] that different regions, containing the same phase, can exist at equilibrium only when their properties are either identical or differ in the value of at least two variables other than those specifying the composition. Since different dispersoid particles can differ from each other only in composition and in

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[1] Perrin, *Ann. chim. phys.*, 18, 5 (1909).

[2] It is obvious that two particles having the same ratio $\partial s/\partial v = \rho$ might nevertheless differ in shape. We are tacitly neglecting cases in which shape or other variables than those given in equation (4) have to be considered.

[3] Tolman, *Loc. cit.*, p. 312.

the one other variable ρ, it is evident that *for equilibrium all the particles of dispersoid have to be thermodynamically identical, that is, of the same size.* The truth of the principle is corroborated by the microscopic examination of dispersed systems which have come to equilibrium.

This important principle justifies the somewhat loose manner in which we have used the variable ρ both for the ratio $\partial s/\partial v$ for some particular particle of dispersoid and for the degree of dispersion of the whole dispersoid.

The necessity for the principle which we have just derived is indeed quite obvious in the simple case of one-component systems. For, with a positive value of surface tension, this substance would have the greatest free energy per gram in the smallest particles. Hence the small particles would have a higher vapor pressure than the large ones and the latter would grow at the expense of the former. With a negative value of surface tension, the small particles would tend to grow at the expense of the large. In either case equilibrium could not exist unless all the particles were the same size.

In the case of systems formed from more than one component, the special reasons making such a principle necessary are not so immediately obvious. A somewhat further analysis is valuable, showing that we might have been led to this consideration even without the help of the equilibrium rule. Considering equation (1), which gives the partial free energy of any dispersoid component, we may differentiate with respect to ρ and obtain

$$\frac{d\bar{\mathrm{F}}}{d\rho} = \frac{d\bar{\mathrm{F}}_c}{d\rho} + \bar{v}\sigma + \bar{v}\rho\frac{d\sigma}{d\rho} + \rho\sigma\frac{d\bar{v}}{d\rho}. \qquad (5)$$

Of the terms on the right-hand side of the equation it is evident that the second one, $\bar{v}\sigma$, is the most important. The first term is small since it depends on the change in concentration of the dispersoid components with change in size. In most dispersoid systems the dispersoid, for all sizes of particles, contains one of the components nearly pure (gelatin, ferric oxide, etc.). The third term is small because it contains the change of surface tension with the size of the particle, and although we shall see that such changes are probable, they are presumably small. The fourth term is negligible since the partial specific volume of a substance is nearly a constant. Neglecting the smaller terms we may write

$$\frac{d\bar{\mathrm{F}}}{d\rho} = \bar{v}\sigma. \qquad (6)$$

Examining this equation we see that with a positive value of surface tension all the components have the greatest free energy in the smallest dispersoid particles since they have largest value of ρ, while with a negative value of surface tension they have the greatest free energy in the largest particles.[1] Hence, also, in a system made from more than one component the large particles will tend to grow at the expense of the small, if the surface tension is positive, and the small particles will tend to grow at the expense of the large, if the surface tension is negative; and we again see the truth of our principle that for equilibrium all the particles must have the same size.

Metastability of the Equilibrium.—For equilibrium not only must the dispersoid particles all be of the same size and composition, but it is very important to notice that with a positive or negative value of surface tension even such an equilibrium is metastable. With a positive value of surface tension this is obvious, since equation (6) shows us that the dispersoid components all have the smallest free energy in the largest particles, and hence any particles accidentally larger than the others tend to grow at the expense of the rest with the final result of a complete loss of dispersion. With a negative value of surface tension, since the accidentally *smaller* particles would tend to grow at the expense of the large, we should at first sight expect permanent stability if it were not for the fact that with negative surface tension each individual particle will tend to increase its own surface by automatic deformation until complete dispersion is reached or the surface tension becomes zero.

Application of the Equilibrium Rule.—We can now apply to dispersed systems the equilibrium rule derived for divided systems in general

$$f = c - r + v$$

where f is the number of degrees of freedom, c the number of components, r the number of regions, and v the number of variables, which, *together with the necessary concentrations*, are just sufficient to determin completely the free energy of each component in each region. For the particular case that the only division of any phase is into identical regions, it has been shown that the equation reduces to the form

$$f = c - p + v$$

where p is the number of phases. Since we have already shown that for equilibrium all the dispersoid particles must be of the same size and composition, it is evident that the equation in this form may be applied to simple dispersoid systems.[2]

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[1] We are assuming a positive value of partial specific volume for the components. In general this is obviously justifiable.

[2] For a derivation of the equations in this paragraph, see the previous article, *Loc. cit* Without presenting a satisfactory derivation, the equation $f = c - p + v$ was taken by Pavlov (*Loc. cit.*) for the classification of dispersed systems. Our application of the equation to colloidal solutions will differ from that of Pavlov, however, and in particular we shall find that permanent colloidal solutions have the same number of degrees of freedom as "true" solutions instead of one more as found by him.

For colloidal systems containing both sol and gel we shall have to apply the equilibrium rule in its more general form, $f = c - r + v$.

One-Component Systems with Positive Surface Tension.—In nature and in the laboratory we find numerous examples of one-component dispersed systems, and the surface tension between the phases is usually positive. Finely divided drops of water or other liquid in contact with their vapor, finely divided solids in contact with their melts, are familiar examples of two-phase one-component dispersed systems. Applying to such systems the equilibrium rule, we have one component c, two phases p, and three variables v, pressure, temperature and degree of dispersion if, as is usual, the concentration of dispersoid is small enough to be negligible as a variable.[1] We shall thus expect two degrees of freedom, and indeed in the case of droplets or small particles in contact with their vapor it is well known that by specifying the temperature and size of the droplets the pressure (*i. e.*, vapor pressure) is thereby determined.[2] In the case of a dispersed solid in contact with its melt, with a fixed value of the pressure (*i. e.*, atmospheric pressure) we shall expect the melting point to be determined by the size of the solid particles, and this has been shown by the experiments of Pavlov.[3]

As has already been pointed out for all dispersed systems with positive surface tension, those just described must be metastable, and indeed the gradual growth of the larger particles and disappearance of the smaller is a well-known phenomenon.

Two-Component Systems with Positive Surface Tension.—As an important example of two-component dispersed systems we may consider finely divided salts in contact with their saturated solution. Here, again, if the surface tension between the phases is positive, we shall expect the system to be metastable, and in fact we find in such systems that the larger particles grow at the expense of the smaller. Applying our equilibrium rule we have two components c, two phases p, and at constant pressure we shall have two variables v, the temperature and degree of dispersion. We shall expect two degrees of freedom, and in fact if we specify the temperature and degree of dispersion, it is well known that the concentration of the salt in the solution is thereby determined, as shown by the experiments of Ostwald[4] and of Hulett.[5]

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[1] For a discussion of negligible variables, see the author's previous article, *Loc. cit.*, p. 309.

[2] For sulfur this relation has been shown experimentally by W. Ostwald, "Grundlinien der anorganischen Chemie," 1904, p. 269.

For *m*- and *p*-dichlorobenzene the relation has been shown by Küster, "Lehrbuch der allgemeinen Physik und theoretischen Chemie," 1906, p. 187.

For a series of organic substances the relation has been shown by Pavlov, *Z. physik. Chem.*, 69, 316 (1909).

[3] *Z. physik. Chem.*, 65, 1 (1908); 74, 562 (1910).

[4] *Ibid.*, 34, 495 (1900).

[5] *Ibid.*, 37, 385 (1901); 47, 357 (1904).

Systems with Negative Surface Tension.—Dispersed systems with negative surface tension are not so familiar as those with positive surface tension. It is evident from a thermodynamic point of view, however, that the surface tension must be negative in systems which are undergoing spontaneous subdivision, since only then will there be a decrease in free energy accompanying the increased surface produced by the dispersion. Examples of systems which do undergo spontaneous dispersion are the lyophyllic colloids, such as gelatin, lecithin,[1] etc., which go spontaneously into colloidal solution, and the lyophobic colloidal precipitates, such as ferric hydroxide, arsenic sulfide, and zinc sulfide, whose degree of dispersion is known to increase under suitable conditions.

The most important fact to be noticed is that systems with negative surface tension are characterized by spontaneous dispersion, and are not stable.

Systems with Zero Surface Tension.—Since the equilibrium in dispersed systems having either positive or negative surface tension can never be better than metastable, we may establish the presence of zero surface tension between the phases as a criterion of permanent stability, and shall regard such dispersed systems with particular interest.

Critical Mixtures.—Very simple dispersed systems, with a surface tension whose value is at least nearly zero, may be formed from a liquid and its vapor in the neighborhood of the critical point, where the surface tension has at least become very small. Under these conditions the free energy of the divided phase will be nearly independent of the size of the regions and we should expect such systems to show considerable permanence, and as a matter of fact they are stable enough so that their opalescent appearance similar to that of colloidal solutions is well known.

Similar to the above are the very important dispersed systems, with a colloidal-like opalescent appearance, which are formed from two liquids just below the temperature where they become mutually soluble in all proportions. These dispersed systems may be regarded as a simple kind of colloidal solution, having an existence over a narrow range of temperature. Within this range such dispersed systems show *permanent stability*, and their properties, in particular opalescence and viscosity, are a definit function of the temperature.[2]

The measurements of opalescence in these systems obviously show that there is a definit degree of dispersion corresponding to permanent stability, and we may conclude that the surface tension between the phases which is small for these systems when there is no dispersion

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[1] The spontaneous increase in surface accompanying the colloidal solution of lecithin can be very nicely watched under the microscope.

[2] Friedländer, *Z. physik. Chem.*, 38, 385 (1901).

becomes exactly zero for dispersed particles of the size that have permanent existence. These systems form a natural approach to the subject of colloids.

The Colloids.—The most important and interesting of all dispersed systems are formed by the colloids, and when they have reached that degree of dispersion which they permanently maintain, we shall conclude in general from our thermodynamic considerations that the surface tension between the phases is zero. (For the present we are neglecting colloidal solutions which seem to be permanent but may not be in true thermodynamic equilibrium.) We shall further conclude for colloidal solutions that the surface tension is negative if the dispersion is automatically increasing, and positive if the dispersion is decreasing.

The possibility of explaining automatic "colloidal solution" and the permanent colloidal state by assuming a negative surface tension between the phases which becomes zero at a definit degree of dispersion was first outlined by Donnan,[1] on the basis of a suggestion of van't Hoff, and it is evident that our thermodynamic considerations give definit support to the view. From a molecular standpoint, Donnan has considered the factors which might produce a negative surface tension which would become numerically less as the size of the dispersoid particle decreases, while Reynold and Rücker[2] have shown by experiment that the surface tension in soap films *is* dependent on dimensions. For our immediate considerations it is important to notice that we shall expect permanent stability only at the one definit degree of dispersion which corresponds to zero surface tension.

We may now apply to colloidal systems our equilibrium rule

$$f = c - p + v.$$

The simplest colloidal systems contain two components, such as gelatin and water, ferric hydroxide and water, etc., so that c equals 2. If the system consists of the dispersoid, the dispersing medium and a vapor phase, p equals 3. Besides the variables, pressure and temperature, the only other variable will be the concentration of dispersoid, C_D, since we have just seen that the degree of dispersion is determined by the re-

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[1] *Z. physik. Chem.*, **37**, 735 (1901); **46**, 197 (1903). It is possible that Donnan has abandoned his original surface-tension theory as a satisfactory explanation of the colloidal state. See Ellis, *Z. physik. Chem.*, 80, 611 (1912). See also Perrin, *J. chim. phys.*, **3**, 92 (1904). "Il me semble donc que l'existence meme d'un hydrosol force à regarder la tension superficielle comme étant un fonction du diamétre du granule, fonction qui, nulle pour un certain diamétre, est positive pour un diamétre inferieur, et negative pour un diamétre supérieur." In a later paragraph (*Loc. cit.*, p. 94) Perrin somewhat modifies the point of view that the surface tension is exactly zero at the degree of dispersion which is stable.

[2] Reynold and Rücker. *Trans. Roy. Soc. London*, [2] **177**, 627 (1886).

quirement of zero surface tension.[1] Applying our equilibrium rule we shall expect $f = 2 - 3 + 3 = 2$ degrees of freedom. In other words, at a given temperature the pressure of the system (*i. e.*, the vapor pressure) will be definitly determined by the concentration of the dispersoid. The importance of this result must be emphasized, since we thus find for colloidal solutions the same number of degrees of freedom and the same kind of variables as for true solutions, the vapor pressure of a colloidal solution depending on the concentration of dispersoid in the same way that the vapor pressure of a true solution depends on the concentration of solute. This fact substantiates the view which has long been held that there is no dividing line between true and colloidal solutions.

Colloids with Non-Identical Regions.—We may now consider very important and interesting colloidal systems in which one of the phases is not only divided into a large number of particles but is also present in an undivided region. A typical example of such systems is furnished by the sol and gel of a mixture of gelatin and water. In the sol, water is the dispersing medium and gelatin the dispersoid, and in the gel, water is the dispersoid and gelatin the dispersing medium. To find the number of degrees of freedom of such a system we may apply the equilibrium rule

$$f = c - r + v$$

where r is the number of non-duplicated regions. In the sol all the gelatin particles will be identical since they have to be of that size which corresponds to zero surface tension, and in the gel all the water regions will be identical for the same reason. Hence we shall have in all four non-duplicated regions, $r = 4$. If we are interested in the state of affairs under constant (*i. e.*, at atmospheric pressure) we shall have three variables, the temperature, the concentration in the sol of the dispersed gelatin, and the concentration in the gel of the dispersed water. We may expect $f = 2 - 4 + 3 = 1$ degree of freedom. In other words, at a given temperature, the concentration of the dispersed gelatin in the water and of the dispersed water in the gelatin will be determined. The system shows, indeed, complete analogy to the case of two substances partially soluble in each other, where, as is well known, the solubility of each in the other is determined by the temperature. This is, of course, further substantiation of the view that there is no dividing line between true and colloidal solutions.

Part II. The Thermodynamic Theory of Colloids

In our treatment of colloids we have seen that the hypothesis of a negative surface tension between dispersoid and dispersing medium which

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[1] Any other theory which necessitates a definit degree of dispersion for stability would give to colloidal solutions the correct number of degrees of freedom. The theory proposed necessitates a definit degree of dispersion, since it requires for stability the degree of dispersion which gives zero surface tension between the phases.

becomes zero at a definit degree of dispersion, successfully accounts for automatic colloidal solution and for the stable colloidal state, and gives to colloidal systems the number of degrees of freedom which we should expect from their analogy with true solutions. We may now consider a number of specific phenomena for *lyophobic* and *lyophyllic* colloids[1] which also find explanation with the help of this theory.

The Lyophobic Colloids.—The lyophobic colloidal solutions are particularly characterized by the definit electrical charge which the dispersoid always assumes, by their easy coagulation by electrolytes, by their comparative rarity in nature, and by the general necessity of first producing a certain degree of artificial subdivision by mechanical, electrical, or chemical means before they can be formed.

The electrical charge which lyophobic dispersoids always assume in colloidal solution is presumably produced in accordance with the views of Freundlich,[2] in large part by the selective adsorption of electrolytic ions present in the dispersing medium with the formation of a "double electrical layer." For example, negative colloids, such as the noble metals, gold, platinum, silver, mercury, etc., would have a greater adsorption capacity for hydroxide ion than for hydrogen ion, while positive colloids, such as the hydroxides of iron, aluminum, and other metals presumably adsorb hydrogen ion the more readily.

Now, apart from the effect which the adsorption of any substance may have upon surface tension, it is evident, as pointed out by Bredig,[3] that the mutual electrical repulsion following this adsorption of charged ions will decrease the surface tension. Hence the zero value of surface tension which determins the stable colloidal state is undoubtedly dependent on the presence of the electrical charge which the lyophobic colloids apparently have to assume. If the charge is neutralized a coagulation is to be expected, since the surface tension would then be positive. Now, as a matter of fact, if electrolytes are added whose adsorption neutralizes the electrical charge, we observe such coagulation. Furthermore, the point of maximum instability corresponds with that of zero potential difference

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[1] The division into lyophobic and lyophyllic colloids is that advocated by Freundlich and Neumann, *Z. Chem. Ind. Kolloide*, 3, 80 (1908), in agreement with Perrin, *J. chim. phys.*, 3, 84 (1904). The two classes correspond in experimental properties with the colloidal suspensions and colloidal solutions of Noyes, THIS JOURNAL, 27, 85 (1905). In most cases the classification would correspond with the suspension and emulsion colloids of W. Ostwald, see p. 329 of this article.

[2] As suggested by Noyes, THIS JOURNAL, 27, 85 (1905), the charge on the particles would also be dependent on the ionization of the dispersoid substance. Thus the positive charge of a colloidal particle of ferric hydroxide might be partly due to dissociation into a number of ordinary hydroxyl ions and a positively charged residue. For an excellent description of the way in which the potential differences between colloidal particles and the medium presumably arise, see Freundlich, *Loc. cit.*, p. 243, *et seq.*

[3] Bredig, "Anorganische Fermente," Leipzig, 1901, p. 15.

between dispersoid and dispersing medium.[1] With decreasing magnitude of potential difference between dispersoid and dispersing medium, the equilibrium size assumed by the dispersoid particles increases.[2] Positive colloids are stabilized by the presence of hydrogen ion, negative colloids by the presence of hydroxide ion.[3] Ions of opposit sign to that of the charge on the dispersoid are effective in producing coagulation in the same order as they are adsorbed.[4] The polyvalent ions are more effective in producing coagulation than univalent ions.[5] Indeed, in general the facts seem at least not to contradict the theory.[6]

The fact that lyophobic colloidal solutions are but seldom found in nature, and that a certain degree of artificial subdivision in general has to be produced by mechanical, electrical or chemical means before such systems form, is further evidence of their naturally positive surface tension which, at a certain degree of subdivision, can be neutralized by the forces of electrical repulsion.

On the quantitative side attempts have already been made to calculate the decrease in surface tension which would actually be produced by the electrical charge,[7] but the theory of the calculation has not yet been completely developed, and even after such calculations have been made we are still at a loss for data as to the magnitude of the total surface tension at the boundary of such small dispersoid particles as are actually present in a colloidal solution. Experimentally, Merritt and Barnett[8] have shown that the surface tension of water *is* decreased about 4% by a charge of surface density 1.74 electrostatic units and that of mercury is decreased about 1% by a charge of surface density 2.33.

The Lyophyllic Colloids.—In contradistinction to the lyophobic colloidal solutions, the lyophyllic solutions are characterized by the *lack* of *definit* electrical charge on the dispersoid, by a wide range of stability in the presence of electrolytes, by the frequency of their occurrence in nature, and by the facility with which the dispersoid goes spontaneously into colloidal solution. All the facts seem to indicate a naturally strong negative surface tension between dispersoid and dispersing medium which only becomes zero when a high degree of dispersion has been reached. In the case of these colloids there is no necessity for an electrical charge to

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[1] See Burton, *Phil. Mag.*, 12, 476 (1906); Ellis, *Z. physik. Chem.*, 80, 608 (1912).

[2] Linder and Picton, *J. Chem. Soc.*, 87, 1906 (1905).

[3] Hardy, *Proc. Roy. Soc. London*, 66, 118 (1900).

[4] Freundlich, *Loc. cit.*, p. 353.

[5] Schulze, *J. prakt. Chem.*, 25, 431 (1882); Hardy, *Loc. cit.*, p. 125; Freundlich, *Z. physik. Chem.*, 44, 129 (1903).

[6] See Perrin, *Loc. cit.*, p. 85.

[7] See Perrin, *Loc. cit.*, p. 92; Ellis, *Loc. cit.*, p. 610.

[8] *Phys. Rev.*, 10, 65 (1900). In the language of these authors the change in surface tension is called apparent but is of the nature which we have in mind.

produce the zero value of surface tension required for stability, and, as a matter of fact, we find it impossible to distinguish between positive and negative colloids as could be done in the case of the lyophobic colloids —the charge when present apparently being determined by the accidental traces of electrolyte which are adsorbed. In fact, Pauli[1] has shown that an absolutely pure egg albumen solution, free from electrolytes, shows no cataphoresis at all, while a very slight addition of alkali produces a strong negative charge, and of acid a strong positive charge. Since an electrical charge is not necessary for zero surface tension, these colloids show wide stability in the presence of electrolytes.

The other characteristics of lyophyllic colloids which were mentioned, the frequency of the occurrence of lyophyllic solutions in nature, and the facility with which lyophyllic dispersoids (gelatin, lecithin, etc.) spontaneously go into colloidal solution also substantiate the view of a negative surface tension between dispersing medium and *undispersed* dispersoid.

Although in the case of lyophyllic colloids the presence of an electrical charge is unnecessary for zero surface tension, it is nevertheless evident that the degree of dispersion at which it does become zero will be dependent on the charge. Since in the presence of a small concentration of acid lyophyllic colloids are found to have a large positive charge, and in the presence of alkali have a negative charge, we shall expect the degree of dispersion corresponding to stable colloidal solution to be increased by the presence of either acid or alkali. In fact, it has been shown that the osmotic pressure exerted by gelatin solutions is enormously increased by a slight trace of either acid or alkali.[2] So far as we know, this important phenomenon has hitherto received no explanation.

In this connection we may also consider some apparently related phenomena which are of great importance. It has been shown by the experiments of Spiro,[3] W. Ostwald,[4] and, in particular, by the researches of M. H. Fischer[5] that the addition of small amounts of either acid or alkali causes a swelling and imbibition of water on the part of the common hydrophyllic colloids which are present in the animal body, and, further, that such imbibition can be reduced by the addition of neutral salts, the ions following a definit order of effectiveness, the polyvalent ions being in general the more efficient. If we make the reasonable assumption that the water held by these hydrophyllic colloids is water of adsorption, or, at least, that the capacity for imbibition is dependent on the surface of the colloid, the explanation of these phenomena on the basis of our theory is obvious. Addition of either acid or base is accompanied by the selective

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[1] Pauli, *Beitr. chem. Physiol.*, 7, 531 (1906).

[2] Freundlich, "Kapillarchemie," 1909, p. 422.

[3] Spiro, *Beitr. chem. Physiol.*, 5, 276 (1904).

[4] W. Ostwald, *Pflüger's Archiv.*, 108, 563 (1905).

[5] M. H. Fischer, New York, 1910, "Oedema;" Dresden, 1910, "Das Oedem."

adsorption of hydrogen or hydroxide ion, which produces an electrical charge on the surface of the dispersoid; this charge causes a negative surface tension and further dispersion results before the attainment of the zero value of surface tension which corresponds to the equilibrium state. The increase in surface, accompanying the further dispersion, increases, of course, the capacity for the imbibition of water. The decrease in imbibition on addition of neutral salts is also obviously accounted for. It would be very interesting if such a theory could explain these phenomena, since their important applications, both clinically and to the theory of water metabolism, have been so masterfully established by Professor Fischer.[1]

Further phenomena of lyophyllic colloids find explanation in agreement with our theory.[2]

It should be noticed that the general division into lyophobic and lyophyllic colloids drawn on the above lines is not identical with a division into suspension colloids (having a solid dispersoid) and emulsion colloids (having a liquid dispersoid). In fact, although, perhaps, most liquid dispersoids do act as lyophyllic colloids, it is well known, for example, that fine emulsions of oil[3] in water have the properties ordinarily associated with lyophobic colloids. Attention must also be called to the fact that there are, of course, all gradations between the marked lyophyllic colloids formed from a dispersoid having high negative surface tension and the lyophobic colloids in which zero surface tension can be attained only with the help of an electrical charge and at a high degree of dispersion.[4]

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[1] M. H. Fischer, New York, 1912, "Nephritis;" Dresden, 1912, "Die Nephritis."

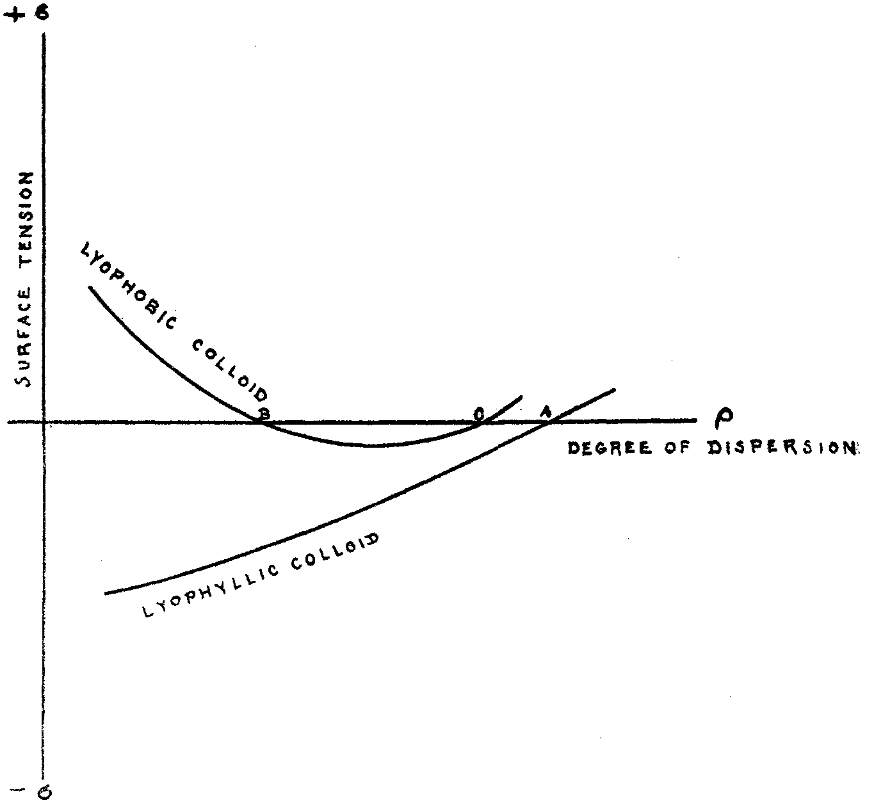
[2] Since a lyophyllic dispersoid would presumably exhibit zero surface tension both when divided into fine droplets and when divided into thin films, many of the anomalous *viscosity* phenomena of lyophyllic solutions could find explanation in terms of our theory.

[3] Ellis, *Loc. cit.*

[4] The accompanying diagram shows possible relations between surface tension (plotted as ordinates) and degree of dispersion (plotted as abscissae) which could account for the properties of lyophobic and lyophyllic colloids. The *undispersed* lyophyllic colloid shows a large negative surface tension which passes through zero at a definit degree of dispersion A. Particles corresponding to this degree of dispersion will be stable, smaller particles will tend to increase in size, and larger particles, even the completely undivided material, will undergo automatic dispersion.

The *undispersed* lyophobic colloidal material shows positive surface tension, and there is no tendency for automatic dispersion. Nevertheless, after a certain degree of dispersion B has been produced by artificial means, the surface tension becomes negative, because of the mutual repulsion of the electrical charges on the surface of the small dispersoid particle. Automatic dispersion now takes place until zero surface tension is reached at *C* and permanent equilibrium attained. Particles of dispersion B also have zero surface tension but are obviously in metastable equilibrium, since particles slightly larger than B have positive surface tension and those slightly smaller than B negative surface tension. The positions of the points A, B and C will

Objections to the Theory of Colloids.—We have shown that a somewhat successful theory of colloids can be based on the principle that the value of the surface tension between dispersoid and dispersing medium must be zero for a permanently stable colloidal solution. The chief evidence in favor of such a principle is of a thermodynamic nature, since the free energy of the material in the regions containing dispersoid can, in general, be a minimum only when the surface tension does become equal to zero. Apparent objections to our theory, however, can be raised from a very interesting point of view, since it may well be questioned whether we have any right to speak of the free energy of the material inside a region so small as a particle of dispersoid. The free energy of a substance is obviously a statistical property depending on the "average behavior" of its molecules, and we must certainly use caution in applying such a conception to the material inside a particle which is so small that it partakes



obviously depend on the concentration of electrolytes in the dispersing medium. In a lyophobic colloidal solution, particles larger than corresponds to dispersion C will not tend to disperse. This could account for the familiar presence in the field of the microscope of large particles of indefinit sizes among the small particles of equilibrium size.

in the thermal motion characteristic of molecules themselves, and indeed may itself contain only a few ultimate molecules.

In this connection, however, we may point out that our considerations might certainly be approximately correct in the case of the more coarsely dispersed systems in which the Brownian motion is small and the number of molecules in a particle large, and also call attention to the fact that in a great part of the experimental work upon dispersed systems, the dispersoid particles have certainly been great enough to contain a large number of molecules. In this connection the following table[1] is of interest:

Substance.	Diameter.
Mastix suspension of Perrin	500–1000 $\mu\mu$
Limit of microscopic vision	100
Particles of dispersed gold	6–130
Limit of ultramicroscopic vision	6
Starch molecule	5
Chloroform molecule	0.8
Water molecule	0.1

We may further call attention once more to the fact that our considerations have given to dispersed systems the same number of degrees of freedom as we should expect from their analogy with true solutions, and hence point out that a proper interpretation of the phrases, surface tension at the boundary of a dispersoid particle, and free energy of material inside a dispersoid particle might indeed permit us to extend the same considerations to systems of any degree of dispersion.[2]

Our thermodynamic theory of the colloidal state is also open to objection from another point of view. It is well known that many systems, such as supercooled liquids, can show very permanent configuration even when thermodynamic equilibrium has not been attained, owing to the slowness with which changes in the direction of decrease of free energy occur, and it might be argued that the majority of permanent colloidal solutions can persist without being in true thermodynamic equilibrium. This can hardly be the case in most colloidal systems, however, since we find them existing in an apparently stable and unchanged state over long periods of time, while the facility and rapidity with which a change in conditions is followed by a change in degree of dispersion is well known. Doubtless, however, there are some apparently permanent dispersed systems which are not in true equilibrium.[3]

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[1] See Wo. Ostwald, *Loc. cit.*, p. 32.

[2] In order to speak of the free energy of a component when only a few of its molecules are present, or the surface tension at the boundary of such a particle, we should have to carry out our "averages" over a period of time.

[3] One of the common theories (for example, see Freundlich, *Loc. cit.*), which denies a true thermodynamic equilibrium in permanent colloidal systems and appears to the writer entirely inadequate for a general theory of colloids, is as follows: The surface tension at the boundary of the dispersoid particles is positive and hence there is a

Summary.

In the foregoing article the conditions for thermodynamic equilibrium in dispersed systems, including the colloids, have been considered.

After considering the different variables upon which the free energy of dispersoid and dispersing medium depend, it was shown that for equilibrium all the particles of dispersoid must be of the same size, and that with either a positive or negative value of surface tension between the phases the equilibrium is metastable.

A number of dispersed systems with positive or negative surface tension were discussed, and the equilibrium rule for divided systems, derived by the author in a previous paper, was applied.

The necessity of a zero value of surface tension between the phases was then proposed as a requirement for the permanent stability of dispersed systems, and hence for the permanent colloidal state. On this

tendency for the particles to unite with decrease of surface. The electrical charges on the particles, however, by mutual repulsion prevent such a union and keep the system in a permanent, although thermodynamically unstable, state. On addition of electrolytes and consequent neutralization of the charges, coagulation does take place.

In contradiction to this theory we may call attention to the following considerations: Actual collision of the particles is not necessary for the decrease in dispersion, which tends to take place with positive surface tension, since material in the smaller particles has a higher solubility than the same material in the larger particles. Indeed, the *gradual* growth of dispersoid particles to a definit size, when less than the precipitating amount of electrolyte is added, shows that the decrease in dispersion has not been produced by mere collision and union. Furthermore, if an electrical charge is all that is necessary to keep the particles from uniting, why should practically all the particles in a colloidal solution ($Fe(OH)_3$ for example) assume exactly the same size, and a definit size corresponding to the composition? Finally, with a positive value of surface tension, how can we account for the familiar increases in dispersion which take place automatically? For example, ferric hydroxide precipitated with sodium chloride is redispersed on washing (Linder and Picton, *J. Chem. Soc.*, **87**, 1924 (1905); see also Mayer, Schaeffer and Terroine, *Compt. rend.*, **145**, 918 (1907)), flocculent copper sulfide and arsenic trisulfide are dispersed by treatment with hydrogen sulfide (Linder and Picton, *J. Chem. Soc.*, **61**, 114 (1892)) and gold can be dispersed by treatment with ammonia (Whitney and Blake, THIS JOURNAL, **26**, 1341 (1904)). In fact, Freundlich states (*Loc. cit.*, p. 346) that particles of diameter less than 6 $\mu\mu$ are apparently completely reversible with respect to their growth and subsequent redispersion. Working in the writer's laboratory, Mr. R. J. McKay has shown by microscopic examination that the size of the particles in a colloidal solution of carbon (Higgin's drawing ink) depends on the concentration of added sodium chloride, and further, that particles whose size has been increased by addition of sodium chloride grow gradually smaller again on dialysis with pure water. On continued dialysis this increase in dispersion was quite interestingly followed by a coagulation which is apparently due to removal of an original stabilizer (caustic?).

Permanent dispersed systems in which the size of the dispersoid particles is not a function of the composition might indeed belong to a class which are not in true thermodynamic equilibrium. (In many of these, however, it may be true that particles of a considerable range of size have zero surface tension.) For systems of this class, the theory outlined in the first paragraph of the foot-note might apply.

basis it was shown that colloidal solutions have the same number of degrees of freedom as "true" solutions.

It was found possible to explain a large number of the properties of lyophobic and lyophyllic colloids on the assumption that the surface tension between a lyophobic dispersoid and its dispersing medium is positive unless the dispersoid particles are electrically charged, and that for lyophyllic colloids the surface tension between *undispersed* dispersoid and dispersing medium is negative.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 215.]

AQUA REGIA, II. THE EFFECT OF CHLORIDE ION ON THE POTENTIAL OF THE NITRIC ACID ELECTRODE.

BY WILLIAM C. MOORE.

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In a previous contribution[1] the author has shown that the chloride ion decreases the efficiency of dilute nitric acid when the latter is used to oxidize ferrous ions to the ferric condition. In seeking an explanation of this fact it was decided to ascertain what effect the presence of chloride ions might have on the oxidation potential of nitric acid.

It seems that no accurate measurements of the oxidation potential of nitric acid have heretofore been made. Bancroft,[2] it is true, publishes a value for this quantity, but his work was carried out with irreversible electrodes. Abegg and Pick[3, 4] studied the electromotive force of the cell silver | normal silver ion | normal nitrate ion | normal nitrite ion | platinum:—the nitrate-nitrite platinum electrode being saturated with nitric oxide at 760 mm. pressure. However, not a single detail of their experimental work is given except that the potential was 0.34 volt, the silver electrode being positive; and even this value is uncertain, for in the second article cited above[4] the value of the potential is given at 0.27 volt, instead of the *calculated* value, 0.34 volt.

It was at first thought that the purpose of this research could be accomplished by setting up two nitric acid electrodes, using acid of the same concentration in each, and measuring the difference of potential existing between them while both were saturated with nitric oxide under the same conditions; nitric acid of the same concentration but containing a definit concentration of chloride ion was then to be substituted for one electrode, the potential measured again, and the difference between these sets of measurements taken as a measure of the effect of the chloride ion on the

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[1] THIS JOURNAL, 33, 1091 (1911).

[2] *Z. physik. Chem.*, 10, 387 (1892). The results of Ihle, *Z. physik. Chem.*, 19, 577 (1896), were likewise obtained under irreversible conditions.

[3] Abegg and Pick, *Z. anorg. Chem.*, 51, 1 (1906).

[4] *Z. Elektrochem.*, 12, 592 (1906).