completion and will be ready for occupancy about December 1, when Dr. Arthur A. Noyes will go to Pasadena, where from now on he will spend half of each year. James H. Ellis, Ph.D. (Mass. Inst.) has been appointed research associate in physical chemistry in the college.

THE appointments of Drs. Edward H. Nichols and Charles A. Porter as clinical professors in the Harvard Medical School have been confirmed by the university's board of overseers. Both men formerly held positions as associate professors.

HAROLD VEATCH BOZELL has been appointed assistant professor of electrical engineering in the Sheffield Scientific School of Yale University for the college year 1916–17, for which period he has secured leave of absence from the University of Oklahoma, where he is dean of the school of electrical engineering and professor of electrical engineering.

PROFESSOR C. N. HASKINS, of Dartmouth College, has been promoted to a full professorship of mathematics. Drs. R. D. Beetle and F. M. Morgan have been promoted to assistant professorships of mathematics.

ROY G. HOSKINS, associate professor of physiology in the Northwestern University Medical School, has been promoted to be full professor and head of the department. Virgil Ernest Dudman, M.D., interne in Cook County Hospital, Chicago, has been elected assistant professor of hygiene and director of student health.

H. H. BUNZELL, Bureau of Plant Industry, has been appointed assistant professor of biochemistry at the University of Cincinnati Medical School.

DR. A. A. BENNETT, of Princeton University, has been appointed adjunct professor of mathematics at the University of Texas.

O. F. BURGER has been appointed instructor in plant pathology in the Graduate School of Tropical Agriculture of the University of California at Riverside, and Alfred Free Swain, formerly of Montana State College and of Stanford University, assistant in entomology there.

DISCUSSION AND CORRESPONDENCE

COLLOIDS AND NEGATIVE SURFACE TENSION

IN a review of Professor Fischer's translation of Wo. Ostwald's " Handbook of Colloidal Chemistry " which recently appeared in this journal,[1] Professor W. A. Patrick states that the existence of negative surface tension which is assumed by Ostwald is contrary both to experimental evidence and to the fundamental ideas of surface tension. Although the present writer does not agree with all of Ostwald's energetic considerations, he wishes to point out that the existence of negative surface tension under certain circumstances is not only supported by a vast body of experimental evidence but is necessitated by the thermodynamic theory of the stability of colloidal solutions.

Surface tension may be defined in the usual way as the work which has to be done in order to increase the surface in question by one square centimeter, this increase in surface being carried out of course reversibly and isothermally. This work, however, and hence also the surface tension, may be either positive or negative.

If for a given two-phase system the surface tension at the boundary between phases is positive, then a positive quantity of work will have to be done in order to increase this surface, and such an increase in surface will be accompanied by an increase in the free energy of the system. Since all spontaneous changes in a system must be in the direction of decrease of free energy, these systems with positive surface tension if left to themselves will automatically decrease the surface between phases. Thus, for example, in the case of finely divided crystals of copper sulfate in contact with a saturated solution, we have a system in which there is positive surface tension at the boundary between the phases, and if this system is left to itself there will be a spontaneous decrease in surface, the smaller crystals going into solution and precipitating on the larger until finally we have all the solid copper sulfate in one large crystal, this being the condition of smallest possible surface.

If, on the other hand, we have a two-phase

[1] SCIENCE, 43, 747, 1916.

system with negative surface tension at the boundary between phases, instead of it requiring work to increase the surface, the system could actually be made to do external work on its surroundings when an increase in surface takes place. In such systems there will obviously be a *decrease* in free energy accompanying increase in surface and if left to themselves these systems will spontaneously increase their surface either by an increase in the convolutions of the boundary or by dispersion into smaller particles. Since spontaneous changes can only take place when accompanied by decrease in free energy it is evident then that *we have negative surface in the case of all systems which are undergoing a spontaneous increase in surface.*

There are of course, as a matter of fact, an enormous number of systems which undergo spontaneous increase in surface, and hence possess negative surface tension. All of the hydrophyllic colloidal substances, such as gelatine, agar-agar, lecithin, etc., will spontaneously disperse when placed in contact with water and hence have negative surface tension. (When lecithin is placed in contact with water the formation of protuberances and consequent increase in surface can be observed under the microscope.) Also in the case of hydrophobic colloidal systems it is well known that under proper conditions an increase in the degree of dispersion will take place; thus colloidal solutions of ferric hydroxide increase their dispersion when hydrogen ion is added to the solution, flocculent gold can be dispersed with ammonia,[2] ferric hydroxide which has been precipitated with sodium chloride is redispersed when the chloride is washed out,[3] and, as shown by Mr. R. J. McKay working in the writer's laboratory, the size of the particles in a colloidal solution of carbon (Higgin's drawing ink) depends on the concentration of added sodium chloride, and particles whose size has been increased by addition of sodium chloride grow gradually smaller again on dialysis with pure water. Hence in all these

cases we have experimental evidence of negative surface tension.

From the foregoing considerations we see that there is positive surface tension in the case of all colloidal solutions in which the size of the dispersoid particles is automatically increasing, and negative surface tension in case the size of the particles is decreasing, and that for stable colloidal solutions the surface tension at the boundary between dispersing medium and dispersoid will be zero. Furthermore, since in cases where automatic dispersion is taking place, this continues only until a definite size of particle is reached, we are led to the conclusion that surface tension is in general a function of the size of the particles. A stable colloidal solution is thus one in which the particles have that particular size which has zero surface tension.

Such ideas as to positive, negative and zero surface tension, and as to the relation between surface tension and size have already appeared in the literature. The possibility of explaining automatic colloidal solution and the permanent colloidal state by assuming a negative surface tension between phases which becomes zero at a definite degree of dispersion was first outlined by Donnan,[4] on the basis of a suggestion of Van'T Hoff; has also been expressed by Perrin,[5] and has been definitely adopted by the present writer on thermodynamic grounds in a presentation of a somewhat complete thermodynamic theory of equilibria of dispersed systems in general and of colloids in particular.[6]

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[2] Whitney and Blake, *J. Amer. Chem. Soc.*, 26, 1,341, 1904.

[3] Linder and Picton, *J. Chem. Soc.*, 87, 1,924, 1905.

[4] Donnan, *Z. physik. Chem.*, 37, 735, 1901; 46, 197, 1903. It is possible that Donnan has since abandoned this theory as a satisfactory explanation of the colloidal state. See Ellis, *Z. physik. Chem.*, 80, 611, 1912.

[5] Perrin, *J. chim. phys.*, 3, 92, 1904. ''Il me semble donc que l'existence même 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 inférieur, et negative pour un diamétre supérieur.'' In a later paragraph (*loc. cit.*, p. 94) Perrin somewhat modifies this point of view that the surface tension is exactly zero at the degree of dispersion which is stable.

[6] *J. Am. Chem. Soc.*, 35, 317, 1913.

It has there been shown that such ideas can be successfully employed for the general treatment of the phenomena of lyophobic and lyophyllic colloids. In the case of lyophyllic colloids it is pointed out that in general the surface tension for undispersed dispersoid is negative and hence automatic dispersion takes place until the size of particles is reached which have zero surface tension. While for lyophobic colloids large particles have positive surface tension, and this only becomes zero for very small particles. This necessitates a preliminary dispersion by electrical, mechanical or chemical means for the artificial preparation of lyophobic colloidal solutions which unlike lyophyllic colloidal solutions are of infrequent occurrence in nature. The writer has also discussed there the rôle of the electrical charge always present on lyophobic colloidal particles in producing the state of zero surface tension necessary for permanent stability.[7]

Freundlich[8] is perhaps the principal exponent of a theory of colloidal solution which does not take zero surface tension as the necessary accompaniment of the stable colloidal state. According to this theory the surface tension at the boundary of the dispersoid particles is always positive and hence there is always a 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. Although the writer would not deny that there may be some colloidal solutions which may be in a relatively permanent state without having really reached a condition of minimum of free energy, he believes, however, that the Freundlich theory is entirely inade-

quate for a general treatment of colloidal phenomena. Not only does the absolutely permanent stability of colloidal solutions point to true thermodynamic equilibrium, but the actual growth of particles to a new equilibrium size on small additions of electrolytes to colloidal solutions and their redispersion to the old size on washing out the electrolyte could only be the case if we have a real thermodynamic equilibrium. Furthermore, Freundlich's assumption that an actual collision and union of particles is necessary for a decrease in degree of dispersion seems to be entirely unjustified since with positive surface tension, as is well known, the material in the smaller particles would have a higher solubility than that in the larger particles, and the latter would grow at the expense of the former. Indeed, the *continuous* growth of particles from one equilibrium size to another is evidence that some other process than that of simple union is taking place. Finally, the existence of a *definite equilibrium size* of particle contradicts his theory since if the stability were due merely to an electrical repulsion that kept particles apart this would work equally well with particles of all sizes, while microscopic examination shows that in typical lyophobic colloidal solutions all the particles have the same size except for a few very large ones which are floating around with the others and are apparently so large that they lie in the region of positive surface tension which, as we have already seen, characterizes *undispersed* lyophobic dispersoid.[9]

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[7] If we wish to extend our considerations to the case of particles so small that they contain only a few ultimate molecules, it may seem somewhat misleading to speak of a definite value of the surface tension, and in that case it may seem more desirable to relate the free energy of the dispersoid directly to the degree of dispersion, without intermediate considerations as to surface tension. This, however, involves no change in principle in our method of attack.

[8] Freundlich, "Kapillarchemie," 1909.

[9] There are of course in all probability some lyophobic dispersoids in which the surface tension is nearly zero for particles having a considerable range of size, and in such cases even in a stable solution there will be considerable variation around the equilibrium size of particle. Indeed, in colloidal solutions in equilibrium, we shall expect in general a distribution in the size of the particles according to the laws of probability around that size which has exactly zero surface tension, and the more rapid the change of surface tension with dimensions the more nearly will all the particles be of the same size.