pointed out that these physiological variations are the ones most likely to be acted on by natural selection, and that such selection would be expected to bring about changes in the associated somatic characters that are themselves of little or no selective value. This seems to be the most probable cause of the very general occurrence of specific differences that can not be supposed to have any selective value.

One further addition to this idea makes it apply also to orthogenetic variation. If we suppose that variation in a given direction in character A is usually associated with variation in a given direction in character B, then selection of variations in character A will cause character B to change also. An example may make this point clear. If we suppose that the antlers of the Irish elk were dependent for their size largely upon testicular secretions, then selection may have increased the testicular secretions for reproductive or other reasons, and thus have resulted in a purely incidental increase in size of antlers.

In the example given it is assumed that the character not subject to selection is directly dependent for its degree of development upon another character whose variations have selective value. This direct relation is not necessary for the orthogenetic series—all that is required is that there be in general a correlation between the variations in two characters, even in cases where the genetic basis for the variations is not constant. It is, however, likely that diverse genetic changes will not usually produce parallel effects on different characters unless these characters depend on some common developmental process, the primary effect then being on this common process. It is not to be supposed that multiple effects of genes will always show such a correlation—but if such correlated effects do occur where one of the characters concerned is subject to natural selection, orthogenesis is to be expected.

One clear case of the sort of correlation discussed has been reported by Morgan, Bridges and Sturtevant (1921).[2] A large number of small-bristled mutant types occur in *Drosophila melanogaster,* and numerous other effects—roughened eyes, long development period, female sterility, etc.—are more or less regularly associated with the small bristles, though the genetic bases of the different types are quite distinct. It seems likely that natural selection, by operating to eliminate sterile females or slow growing larvae, has kept the bristles of the species large and the eyes smooth.

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[2] Morgan, T. H., C. B. Bridges, and A. H. Sturtevant, 1921. Annual report, in Year Book No. 19, Carnegie Institution of Washington, pp. 329–331.

THE SURFACE EQUILIBRIUM OF COLLOIDAL SOLUTIONS AND THE DIMENSIONS OF SOME COLLOIDAL MOLECULES

THE use of a long discarded method, fallen into disgrace because of its very sensitiveness and inherent difficulties, has made it possible to disclose and study a large number of phenomena connected with the surface tension of solutions, mainly colloidal solutions. The ring method as used by Sondhauss,[1] Timberg,[2] Cantor,[3] Weinberg,[4] and a few others, was difficult to apply and, notwithstanding the soundness of its principle, was never practical. The drop-weight methods with their numerous modifications were considered as ideal, because of the simplicity of the instrument and the excellent results which they yielded in the case of pure liquids. However, when very volatile or viscous liquids were dealt with, they were difficult to handle. They are always time-consuming if any degree of accuracy is required and, above all, absolutely unreliable in the case of colloidal solutions. Surface phenomena are, of course, particularly interesting when substances in solution are adsorbed in the surface layer. As long as it was believed that this adsorption took place almost instantaneously—and this is the general belief even now—there was no fundamental objection to the drop methods, as Gibbs' equilibrium was supposed to have been reached long before the drop would fall. However, such was not the case, as has been shown in an article which appeared in 1922 and other papers.[5] Time must be taken into consideration and more than one hour is required to reach the equilibrium. An interesting fact is that the instantaneous equilibrium of Gibbs, which is function of the concentration,[6] follows the same law as this time-adsorption, and may be expressed by the same equation, $\gamma = \gamma_0 e^{-Kt^{1/2}}$ in which the time *t* is replaced by the concentration *c*, namely: $\gamma = \gamma_0 e^{-Kc^{1/2}}$.

It was only through the ring method that it was possible to observe and study this phenomenon, as it is the only procedure which permits the measurement of the surface tension of the same layer of liquid at very short intervals. For this purpose, an instru-

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[1] Sondhauss, *Pogg. Ann.,* 1878, Ergbd. 8, p. 27.

[2] Timberg, G., *Ann d. Phys. u. Chem.,* 1887, xxx, 545.

[3] Cantor, M., *Ann d. Phys. u. Chem.,* 1892, xlvii, 399.

[4] Weinberg, B., *Zeitschr. f. phys. Chem.,* 1902, x, 34.

[5] du Noüy, P. J., *J. Exp. Med.,* 1922, xxxv, 575, 707; *Compt. rend. Ac. Sc.,* 1922, clxxiv, p. 962; *ibid.,* 1923, lxxxix, 1076.

[6] Lewis, W. C. McC., *Proc. Phys. Soc.,* 1909, xxi, 150; *Phil. Mag.,* 1909, xvii, 466, etc.

ment was devised[7] which made it possible to make measurements in 15 seconds, reliable to 0.1 dyne. Since 1921, a little over 40,000 measurements of surface tension of colloidal solutions have been made in this laboratory, and the purpose of this paper is to summarize the results obtained thus far by this method.

(1) As mentioned above, the surface tension decreases in function of the time, according to an exponential formula: the drop is rapid at first (1 to 4 dynes in the first minute, according to the substance and the concentration). At the end of one hour, the rate of decrease becomes very slow, and the curve expressing the phenomenon, asymptotic to the axis of abscissae.

(2) Stirring even slightly, or shaking the solution after the lower value has been attained, causes an immediate rise in the surface tension which, however, does not generally reach its original value. Then it decreases again, and rises once more if stirred. The law of decrease is the same, only the coefficient K is changed, and its value becomes smaller every time.[5]

(3) When higher dilutions of the substances are used, the decrease of the surface tension becomes more rapid and the drop in function of the time greater, until a certain optimum dilution is reached. Then it decreases progressively. The value of this "maximum drop," even for fat-free substances, may be as high as 15 dynes (albumin) at a concentration of 1/80,000. Serum diluted 10,000 times shows a drop of 10 to 20 dynes in 2 hours; sodium oleate, glychocholate, etc., a drop of about 30 dynes at 1/100,000 in 2 hours. In these cases, the initial value of the surface tension is that of pure water.

(4) A close investigation showed the existence of sharp minima in the curve representing the values of surface tension of a certain number of colloidal solutions, plotted in function of the concentration. In the case of serum albumin and globulins, three main minima were found; in the case of sodium oleate, three were also found. In order to explain these minima, the hypothesis was brought forward that they correspond to polarized monolayers; (the writer proposes the term "monolayers" instead of the clumsy "monomolecular layer"). As the surface tension of water is high, and since only the substances which are capable of lowering its surface tension can be adsorbed in the superficial layer, it is clear that, if the molecules of these substances, instead of being piled up in disorder, are organized geometrically and symmetrically, their action on the surface tension of the solvent will be increased—hence the minimum in the curve. As soon as the dilution is increased, the number of molecules present decreases. They can no longer cover the surface with a continuous pavement and the surface tension rises. The other minima can be explained by the formation of a monolayer of *horizontal* molecules. Experiments showed that the colloid was adsorbed on the glass of the vessel, as well as on the free surface.[8] Knowing exactly the area of these two surfaces and the specific gravity of the substance, it was then possible to compute the thickness of these layers. For sodium oleate, the minima occurred at 1/750,000, 1/1,220,000, and at 1/1,390,000. The first minimum corresponded to a thickness of 12.30×10^{-8} cm; the second, to a thickness of 7.56×10^{-8} cm; the third, to a thickness of 6.64×10^{-8} cm. The length of the molecule of sodium oleate has never been measured, nor has that of the molecule of any colloid; but the length of oleic acid, a fat, has been measured by Langmuir,[9] and found to be equal to 11.2×10^{-8} cm. The difference between the two figures is only 1.1×10^{-8}, which is due to the additional sodium atom. This quantity does not express the length of the atom, but the projection of its actual distance from the oxygen atom to which it is linked, on the vertical axis of the molecule. The figure is well in accord with that which could be expected, and the hypothesis of the monolayer of vertically polarized molecules, based on the minimum of surface tension as a criterion, is probably well founded. The second minimum gives a thickness of 7.56×10^{-8}, which would then correspond to one of the dimensions of the base of the parallelopiped, and the third minimum gives a thickness of 6.64×10^{-8}, which is the second dimension of the base. Langmuir, in order to obtain the dimensions of the base of the molecule of oleic acid, assumed that it was square, and took the square root of the surface experimentally found by him, *i.e.*, 46×10^{-16} sq. cm. This gave him 6.8×10^{-8} cm. which is intermediate between our two values.[10]

Serum albumin from rabbits shows minima around 1/100,000, 1/140,000, and 1/190,000. These correspond to thicknesses of about 55, 45 and 32×10^{-8} cm. It is probable that the monolayer whose thickness is 45.0×10^{-8} cm. represents vertical molecules, while that of 32.0×10^{-8} cm would correspond to horizontal molecules. Under these assumptions, the specific gravity being 1.265, the molecular weight would be comprised between 35,000 and 36,000. A similar figure is obtained for the globulins.[11]

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[7] du Noüy, P. L., *J. Gen. Physiol.*, 1919, i, 521; *La Nature*, 1920, No. 2391, p. 63; H. N. Holmes (Laboratory Manual of Colloid Chemistry, 1922; Sir W. M. Bayliss, The Colloidal State, Oxford Med. Publications.

[8] du Noüy, P. L., *Jour. of Exp. Med.*, in press.

[9] Langmuir, I., *J. Am. Chem. Soc.*, 1917, xxxix, 1848.

[10] du Noüy, P. L., *C. R. Ac. Sc.*, T. 178, p. 1102, 1924, and *Jour. of Exp. Med.*, in press.

[11] du Noüy, P. L., *Philosophical Magazine*, in press.

From the dimensions found for the sodium oleate molecule, the volume is readily calculated—$V = 12.3 \times 7.56 \times 6.64$ cc. $\times 10^{-24}$. By multiplying by the specific weight (0.821), the weight of each individual molecule is obtained—507×10^{-24} grams. Hence a new method is found to calculate the number N of Avogadro, since the molecular weight is well known and equal to 304.35. In this manner we obtain for the number N the value, 6.003×10^{23}, while Millikan's last figure is 6.062×10^{23}. The probable error in our figure is 0.15 per cent., or

$$N = 6.003 \pm 0.08.$$

This method is probably the more direct, and is based only on Avogadro's definition of the number N. The details of this work, and a discussion of it, will appear shortly in the *Philosophical Magazine*.

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Division of Organic Chemistry

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Introductory remarks: Gilbert N. Lewis.

The mechanism of ester formation: James F. Norris and Francis B. Stewart. The velocity constants for the esterification of ethyl, normal butyl, secondary butyl and tertiary butyl alcohols with acetic and trichloroacetic acids with and without a catalyst were determined. The results show that the ratio between the constants in the uncatalyzed and catalyzed reactions for a given acid are about the same, whichever alcohol is used. On the other hand, in the case of any alcohol this ratio varies widely as the acid is changed. The results furnish experimental evidence for the conclusion that the catalyst functions through its action on the acid and not the alcohol. With the weak acid the influence of the catalyst is very great compared with its influence on the strong acid in increasing the rate of the reaction. The ratio of the velocity constants of the catalyzed reactions between a given acid and different alcohols is approximately the same as the ratio between the reactivities of the hydrogen atoms in the hydroxyl groups in these alcohols, and varies widely from the ratio between the reactivities of the hydroxyl groups. These facts show that in ester formation the hydroxyl group is furnished by the acid and the hydrogen atom by the alcohol.

Reactivity in acetal formation: Homer Adkins and E. W. Adams. The problem of the relationship between structure, reactivity (Michael) and rate of reaction has been studied by determining the equilibrium point and the rate with which it is reached, in the formation of about forty acetals. It has been established that there is no relationship between reactivity and rate of reaction. The reactivity and effect on rate of reaction of a number of groupings has been determined (eleven of the lower alkyls, phenyl in various positions, olefinic linkage, etc.). The significance of these facts in interpreting the mechanism of the reaction has been considered.

The mechanism of reduction in homogeneous solution: J. B. Conant and H. B. Cutter. The following types of reductions can be accomplished by such reducing agents as titanous chloride, vanadous chloride and chromous chloride; (1) reversible monomolecular reduction; (2) irreversible monomolecular reduction with or without cleavage; (3) reversible dimolecular reduction (formation of free radicals); (4) irreversible dimolecular reduction (pinacone formation). All these processes are conditioned by the reduction potential of the reducing agent, the hydrogen ion activity of the medium and the nature of the organic substance which in (1) and (3) can be measured as a potential. The irreversible processes probably proceed through a reversible phase which also has a characteristic reduction potential. Examples of (4) are the dimolecular reduction of benzaldehyde, and alpha, beta unsaturated ketones by vanadous salts.

Mechanism of vapor phase oxidation: R. T. Haslam. This paper reviews the various theories offered for the mechanism of combustion of hydrocarbons. These theories are discussed in view of the existing experimental data on the subject and the theory that hydrocarbons burn by means of successive hydroxylations together with the importance of this concept is treated at some length. It is conclusively shown that the vapor phase oxidation of organic compounds other than straight chain hydrocarbons, although little studied, is different from the oxidation of the same compounds with liquid oxidizing agents. Some conclusions are drawn about the influence of substitution and of the relative position of groups in a molecule on their oxidability. As a practical application of the knowledge of the subject, it is shown how the burning of hydrocarbons can be improved by favoring the hydroxylation process, thus eliminating the formation of soot.

The mechanism of oxidation of organic compounds with potassium permanganate: William Lloyd Evans. This paper deals with mechanism of the oxidation of organic compounds in aqueous solutions by means of potassium permanganate alone, and also in the presence of added potassium hydroxide. The purposes of these oxidations have been to ascertain the several molecular stages through which certain organic compounds pass when they undergo this type of chemical change. These oxidations have been studied under chosen conditions of temperature and initial alkalinity with a view of ascertaining the effect of these variable factors on the course of the oxidation. The experimental results thus obtained have been used to deduce an appropriate mechanism which will best explain the observed oxidation phenomena. The following compounds have been made the object of