Anne S. Young, who retained the greater part of the original text and made such changes only as were necessary to bring it down to date. In general the changes were made with discrimination and the text shows an improvement. Astronomy, however, is not a complete science, and changes and improvements are continually being made. This is especially true of the applications of astronomy to practical matters. In some cases there have been marked improvements in the ideas and methods of thirty years ago, and too rigid an adherence to the original text on the part of Miss Young detracts from the general excellence of the revision. In the discussion of the tides, for example, there has apparently been no change, and the old theory of a world tide, originating in the Pacific and Indian Oceans, has been adhered to. No mention is made of the new theory advanced by the Coast and Geodetic Survey that the tides are purely local phenomena; that the tides of each locality originate in and are confined to that ocean basin of which the particular locality is a part; that the tides of the North Atlantic have no connection with those of the Pacific.

The "Lessons" are for beginners, the "Elements" for the more advanced students. Both books are excellent and no better text-books have yet appeared for these classes of students.

CHARLES LANE POOR

SPECIAL ARTICLES

FURTHER STUDIES IN COLLOID CHEMISTRY AND SOAP

THE following summarizes experimental findings and theoretical deductions which continue studies reported in these pages last year.[1]

I

Our previous work had emphasized not only how from pure soaps and water most typical lyophilic colloid systems may be produced but in what way the chemical constitution of the soaps and variations in concentration, temperature, presence of electrolytes and non-electrolytes, etc., changes the physical properties of these colloid systems. Practically all attempts to explain such changes are to-day electrical in nature. Without denying that electrical phenomena sometimes play a rôle, our newer experiments show that it may be very small or need not function at all.

Typical lyophilic colloid systems may be made of pure soaps in the practical or complete absence of all water. The pure soaps yield such colloid systems with the various absolute alcohols, benzene, toluene, chloroform, carbon tetrachloride and ethyl ether. We feel that our future definitions of lyophilic colloid systems and the understanding of their processes of swelling, gelation, syneresis, reversibility of sol and gel states, hysteresis, etc., must be expressed in the broader terms of mutual solubility. As the hope of getting all phenomena of "solution" reduced to electrical terms seems remote, the hope of getting these fundamental colloid chemical findings reduced to a similar level seems equally remote.

Of the list of effective "solvents," the alcohols have received most study. The solvation capacity of the different soaps (as measured by the maximum amount of alchohol that will be taken up to yield a "dry" or non-syneretic gel at ordinary temperatures) varies in the case of absolute ethyl alcohol for molar equivalents of the sodium soaps of the acetic series of fatty acids from practically zero in the lowermost member to over 27 liters per gram molecule in the case of sodium arachidate. When the solvation capacity of unit weights of any one soap for different alcohols is compared, it is found that this is different not only as mon-, di- or triatomic alcohols are used but different, also, for the different alcohols in any one of the series. For the monatomic alcohols, for example, the solvation capacity increases progressively and smoothly as the position of the alcohol rises in the series. A gram of sodium stearate will just form a gel at room temperature, for example, with 50 c.c. of methyl alcohol, but the same amount of the same soap will form a gel with over 132 c.c. of amyl alcohol. When sodium oleate is the soap employed all the absolute

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[1] Martin H. Fischer and Marian O. Hooker, "Ternary Systems and the Behavior of Protoplasm," SCIENCE, 48, 143, 1918.

absorption capacities for the different alcohols lie lower, but their order remains the same

II

If we attempt to say why we obtain these typical colloid systems from such a variety of materials we may begin with the fundamental and now generally accepted conclusion that colloid systems result whenever one material is divided into a second with the degree of subdivision coarser than molecular. A suspension colloid results whenever the colloidally dispersed phase is *not* a solvent for the "dispersing medium"; a hydrophilic or lyophilic colloid whenever the dispersing medium *is* such a solvent (and independently of the fact that the subdivided phase is solid, liquid or gaseous at the temperature employed). When soap is dissolved in acetone and the temperature is lowered the soap falls out as a colloidally dispersed suspension colloid because the acetone is not soluble in the soap; but the same soap dissolved in an alcohol, toluene or carbon tetrachloride, comes out as a lyophilic colloid because these solvents *are* soluble in the precipitating soap.

But the physical characteristics of the ultimately resulting system are not yet explained when we have thus taken into account the mutual solubility characteristics of their phases. In any given case, as with a given soap and its "solvent," four possible results and consequently four main types of ultimate system may be foreseen. At the top exists a non-colloid, "molecular" or "ionized" "solution" of soap (soaped-solvent). For example may be cited a fairly concentrated solution of soap at a higher temperature. At the bottom is found another "solution" but of the solvent in the soap (solvated-soap). Between these extremes exist two main types of mixed systems, namely, one below the top which is a dispersion of solvated-soap in soaped-solvent, and another, above the bottom, which is a dispersion of soaped-solvent in solvated-soap. These are respectively the sols and gels about which we talk. A concentrated solution of soap in any solvent, it will at once be apparent, passes successively, on lowering of the temperature and when not too much solvent is used, from the top of this series through the two middle zones to the bottom.

All the systems below the true solution at the top and above the true solution at the bottom are "colloid." Gel formation is characteristic of the middle zones. Such gels are "dry" anywhere below the point where enough solvated-soap falls out on lowering the temperature to yield a continuous *external* phase enclosing the soaped-solvent. Just above this point they sweat, the amount of such "syneresis" obviously increasing progressively as the amount of solvated-soap becomes inadequate to form a continuous external phase. If the "syneresis" is very great we no longer apply the term, for the syneretic liquid (soaped-solvent) now forms the continuous external phase. The colloid system is said to have remained or to have passed into the "sol" state.

Since change or rate of change in temperature (as well as other factors) affects the solubilities of the two phases in each other unequally it is obvious that the sum total of changes in any system need not be identical *at any given moment and at any given temperature* when the temperature is being approached from a higher level with the sum total of these same changes when the same temperature is being reached from a lower level. The attainment of equilibrium takes time and so the systems hold over the characteristics of the systems from which they came. This is the "hysteresis" of lyophilic colloid systems.

III

The effects of adding different hydroxides and different neutral salts in increasing concentration to standard soap "solutions" has received further study. In order to understand the effects observed and their explanation it is well to divide the experimental findings into three groups while keeping in mind the solubility characteristics of the pure soaps themselves *in* water and *for* water.[2]

1. *Soaps are formed more soluble in the dispersion medium.* The viscosity of the soap mixture regularly *falls.* This happens when

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[2] See our previous paper, Martin H. Fischer and Marian O. Hooker, SCIENCE, 48, 143, 1918.

ammonium hydroxide is added in any amount whatsoever to a potassium or sodium soap.

2. *Soaps are formed less soluble in the dispersion medium.* This is observed when magnesium, calcium, iron or copper salts are added to a solution of sodium or potassium oleate. The systems as a whole again become more liquid though not in this instance because the soaps are better "dissolved" in the solvent but because they fall out and allow the viscosity of the pure solvent (essentially salt water) to come to the front.

3. *The change in kind of soap is negligible or absent.* This happens, for example, when a neutral potassium salt or potassium hydroxide is added to a potassium soap. Under these circumstances the most interesting of all series of changes are to be noted with increasing concentration of the added material. There is, first, an increase in viscosity which, if the amount of solvent is not too great, results in gelation, followed by a secondary liquefaction and then a progressively increasing separation of soap from the dispersion medium until it finally floats as a dry mass upon the underlying solution of salt or alkali.

If, in explanation, we do not wish to make too many violent assumptions the following seems a reasonable way out. *The fixed alkalies and the various neutral salts are hydrated in water.* As more and more salt is added the number of such hydrated particles (or their size) increases. The effect is two-fold. Through deprivation of solvent the concentration of the soap is increased while the particles of hydrated salt remain emulsified in the hydrated soap.[3] *This emulsification* (with the increase in the concentration of the soap itself) *accounts for the initial increase in viscosity.* As more salt is added the hydrated salt phase attains a value which makes the particles begin to touch. The hydrated soap now becomes the internal phase and the hydrated salt the external one. This change in type of emulsion explains the secondary liquefaction of the gel, a characteristic of these systems not previously noted so far as we are aware. More salt increases further the hydrated salt phase which now begins to separate off at the bottom while the still hydrated soap floats to the top. By adding enough salt all the water is taken from the soap which then floats as a dry layer upon the concentrated salt solution.

IV

Various incidental observations upon the reaction of soap-water systems toward indicators of various kinds have proved of importance not only for the theory of these systems but for the understanding of various biological problems, for living matter, too, as so often emphasized, is essentially nothing but a hydrophilic colloid system. The findings show how dangerous it is to assume that physico-chemical methods and opinions (such as hydrogen ion determinations) as derived from the study of the dilute solutions may, without reserve, be applied to living protoplasm.

To be sure of strictly reproducible ground materials we have always prepared our soaps by adding to each other the necessary gram equivalents of fatty acid and alkali. *Any soap as thus formed is either acid, neutral or alkaline to such an indicator as phenolphthalein depending upon the concentration of the water in the system.* Phenolphthalein added to a concentrated sodium oleate solution remains colorless, but this oleate with its contained indicator turns pink or strongly red as more and more water is added to the system. It does not suffice to say that a hydrolysis of the soap is suppressed in the concentrated solution to come to the fore in the dilute solution. It is more reasonable to say that when the water is dissolved in the soap the system is something different from that resulting when the soap is dissolved in the water. If a gel of sodium stearate is used, direct application of phenolphthalein to its fresh section shows the framework of the gel (the water-in-soap portion of the system) to remain uncolored while the soap-in-water portion of the system turns bright red.

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[3] Regarding the making and breaking of emulsions, see Martin H. Fischer and Marian O. Hooker, SCIENCE, 43, 468, 1916; "Fats and Fatty Degeneration," 29, New York, 1917.

A future communication will show how these colloid chemical facts may be used in the erection of secretory models which, like the salivary gland or kidney, yield "secretions" either more alkaline or more acid than the allegedly neutral (or even acid or alkaline) tissues.

It has proved impossible to find an editor with space available for the details of the experiments outlined above and previously reported upon. They must in consequence be brought out in a book. But since the making of such takes time, it has seemed of interest to make a preliminary report upon work which has at various times been lectured upon to different scientific audiences.

Martin H. Fischer
Eichberg Laboratory of Physiology,
University of Cincinnati,
May 5, 1919

THE BUFFALO MEETING OF THE AMERICAN CHEMICAL SOCIETY. III

Testing the mildew resistance of fabrics: F. P. Veitch and S. S. Levine. A method has been devised for testing the mildew resistance of fabrics treated by so-called mildew-proofing processes. The method takes into consideration the important determining mold growth and is conducted in the laboratory under conditions which are highly favorable to the development of mildew and which are carefully controlled. It is briefly described as follows: Six discs about 3.5 inches in diameter are cut from the sample to be tested and soaked in running tap water for two or three days in order to wash out easily removable fungicides and fermentable matter. The damp discs are placed in petri plates containing ten to fifteen cubic centimeters of agar jelly from nutrient matter. The plates are then incubated for seven to ten days in a dark chamber at from 20° C. to 25° C. The condition of the fabric as to the color, extent and character of the growth are observed and recorded. Following this pre-inoculation period the discs are inoculated with pure cultures of several species of molds and reincubated for three weeks to a month and examined each week for mold growth. The observed conditions are rated on a scale of ten. At the conclusion of the tests the discs are washed and preserved as records. The test is a severe one which is borne perfectly for the full period only by canvas treated by the cupra-ammonium process. Its utility has been demonstrated, however, by the fact that canvas which gives a rating of 6 or better has not mildewed on exposure to the weather at Washington, D. C., during the summer and fall months.

Testing materials for increasing the water resistance of sole leather: H. P. Holman and F. P. Veitch. To determine waterproofing value, several pieces of sole leather which are always of the same tannage and from the same section of the hide but which differ in texture are impregnated by immersing in the treating material for ten minutes at 60° C., followed by warming in an oven at 60° for fifteen minutes. Water absorption is determined by soaking in water for twenty-four hours, with periodical flexing, and weighing the wet leather after removing all excess from the surface. The leather is also weighed before treating, after treating, and in the air dry condition after testing. From these weights the quantity of treating material taken up by the leather, the actual water absorption, and the loss in weight on testing are calculated in percentages. The actual water absorption is calculated on the basis of the final dry weight. All dry weights should be made after exposing the leather to the same atmospheric humidity. Eighty samples, including practically all the commercial materials used in waterproofing sole leather, were tested by this method. Only twenty were found to waterproof sole leather sufficiently to prevent its absorbing an average of more than 35 per cent. of water under the conditions of the test. This percentage was arbitrarily adopted as a limit for satisfactory materials for increasing the water resistance of sole leathers.

Method for determining the water resistance of fabrics: F. P. Veitch and T. D. Jarrell. In developing more effective methods of making canvas water- and mildew-resistant, and for testing for the War Department deliveries of canvas and clothing for water resistance, it was necessary to employ methods of testing that are both expeditious and indicative of the effectiveness and durability of the treatment. Modifications of the old bag or funnel and of the spray test have been devised which have proved very satisfactory in that all canvas given high ratings by these methods have been found to be water resistant during six months of outdoor exposure throughout the summer and fall. Of the two, the spray test yields possibly the most information. Neither the de-