

Again I want to emphasize the fact that I do not mean that our university men should become industrialists. Let some of them work in these fields that are being applied so successfully. Everything they do will be recognized and used. The most striking thing in applied science to-day is the quickness with which the results of academic research are utilized. Twenty-five years passed before any one made use of Faraday's epoch-making discovery of benzene. It would not be so to-day.

I have had nothing to say of the kind of research that changes the trend of the investigation into the unknown. This is logical because I have been speaking of the type of research that is more or less directed. No one would want the whole world to follow on the paths I have indicated. There are always geniuses who go their own way; unfortunately these are but few. We do not attempt to point the road. They should be provided with every material aid, and that is a part of the plan.

I have outlined in a somewhat discursory way how it appears to me chemistry can be made in the future a more vital factor in America. It all goes back to research. The industries should seek more fully than in the past the cooperation of individual academic investigators in solving their industrial problems. The industries should point out to the chemical world the fundamental unsolved problems underlying their procedures.

Many of our investigators should turn their attention to developing the pure chemistry of the fields upon which our industries are based. The investigator of genius should be encouraged to push his way into the great unknown and should be provided with ample resources for his work.

How can our society help to bring all these things about and how can it in perhaps more efficient ways encourage and support research? I said some of us had been dreaming dreams—daytime dreams. We see the fully developed rose in the tiny bud. The bud is the endowment fund, and it lies next to our hearts. I dream of the day when the society will be supplied with adequate resources to take such a place in aiding research that we shall be the envy of the scientific world. We have just made a start. We must have the cooperation of every one of our members. Each one must feel a personal interest in the success of the effort being made. Each one must see it from an altruistic point of view and at the same time recognize the fact that the development of American chemistry reflects itself on him individually. The dignity of the profession has markedly advanced in the opinion of the man in the street and the employer.

The results up to the present have been encouraging, but much remains to be done. Has each man done what his own conscience dictates? Have you been as generous to your science as to your religion? Think it over.

The large sum of money required to foster research as it should be can not be raised from our own membership. We are not rich, but can afford to do a great deal. But after we have done our best another path lies before us. We must go to the public, especially the men who have amassed wealth as a result of the work of the chemist and tell them the story of their fortunes. We want to say that our society to the last member has done its best. We want to tell the banker, the merchant that his life and happiness have been largely enriched by the chemist.

We can tell the story of chemistry in a way that many will understand, and I am confident of a favorable outcome. We must and we shall win.

As you go to your homes, spend a few minutes in the way I have spent hours. Think what you would do if you had a great sum to devote to the development of chemistry. Draw up a plan, so much for this, so help you if you are not, you will be full of enthusiasm much for that. I guarantee that if you are an optimist, and God help you if you are not, you will be full of enthusiasm and go home determined to wake up your associates to the beauty of the idea underlying our endowment fund.

Don't leave all the delights of achievement to others. Those of us who are steering the ship have an eye fixed on the star. Join the crew and be ready to cheer when we sail into port.

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THE TWILIGHT ZONE OF MATTER¹

WHEN we crush and grind the ordinary coarse matter which we can see and handle, we can break it up into smaller and smaller particles. At first these particles can still be seen by the unaided eye, but as the process of grinding is continued, they become so small that they can be distinguished only with the help of a lens or of a microscope. One can carry the process of subdivision of matter still further, so that the particles become too small to be seen even with the aid of the most powerful microscope, and finally

¹ Address delivered before the seventieth meeting of the American Chemical Society, Los Angeles, August 3, 1925.

reaches the ultimate limit of subdivision, the molecule, beyond which farther subdivision is impossible without destroying the chemical nature of the substance.

Since the smallest particle of matter directly visible under the microscope is perhaps about a thousand times larger than the simplest molecule, a considerable range of subdivision of matter lies between the limits of the microscopically visible and the molecular states; and it is to this intermediate zone that I have ventured to apply the term the "twilight zone of matter."

It is to this range of subdivision of matter that, in more scientific language, the term "colloidal state" of matter is applied.

Not only does matter in the twilight zone of subdivision present many problems of peculiar fascination to the seeker after a fuller knowledge of natural phenomena, but the important rôle which colloidal matter plays in almost all the diverse fields of human activity appeals also to the man of more practical instincts. In agriculture and in the tanning of leather, in the working of clay for the manufacture of the common brick or for the production of the finest porcelain, in the production of artificial silk and of smokeless ammunition, in the dyeing of textile fibers and in the production of the blue of the sky or the blue of the eye, the colloidal state of matter plays a part.

When, further, we recall that nature has selected matter in the colloidal state to be the vehicle of life and as the medium in which all life processes take place, the importance and interest of a study of the twilight zone of matter become obvious.

It was the Scottish chemist, Graham, who first discovered a useful method of distinguishing between the molecular state of subdivision and the state of subdivision known as colloidal.

Certain substances in solution were found to diffuse through parchment paper or animal membrane, whereas other substances could not do so; and since the substances which did not diffuse through parchment paper were thought to be non-crystallizable and of the nature of gelatin, glue and similar materials, Graham called them colloids, from the Greek word for glue.

Substances that diffused through parchment paper and existed in solution in the molecular state of subdivision—sugar and salt, for example—were called crystalloids. Although we recognize the imperfections of Graham's classification, his distinction is of considerable practical importance, for the process of dialysis, discovered by him, gave a means of distinguishing between molecularly dispersed matter and matter in the so-called colloidal state.

Since the peculiar and characteristic properties of

the twilight zone of matter do not depend on the physical state of the finely subdivided matter or of the medium in which the matter is dispersed, we shall find the colloidal properties exhibited not only by colloidal suspensions or emulsions, where we have solid particles or liquid droplets dispersed in a liquid medium, but by smokes (solid particles in a gaseous medium), mists (liquid droplets in a gaseous medium), forms (gas bubbles in a liquid) and so on.

Whereas it could be inferred from the experiments of Graham that the colloidal systems, although apparently homogeneous like a solution of sugar, are nevertheless heterogeneous and contain particles which have a magnitude greater than molecular, the actual existence of such particles has been rendered evident by the scattering of light by these particles and the so-called Tyndall effect—and the introduction of the ultra-microscope by Siendentopff and Zsigmondy has enabled the eye to detect the presence of particles of a magnitude of about six millionths of a millimeter, which is about sixty times the dimensions of a hydrogen molecule. By the use of ultra-violet light and a photographic plate instead of the eye, particles of still smaller dimensions can be detected. This fact has proved of great value in biochemistry in the examination of filterable viruses, as in the case of the virus of cancer, according to recent announcements from London.

In the scattering of light by finely divided particles, it is mainly the light of shorter wave length that is scattered and the light reaching the eye is therefore blue. The very fine smoke rising from a wood fire, for example, when illuminated from the side and viewed against a dark background appears blue, but when viewed against a background of white cloud, that is, by the transmitted light, the smoke appears reddish brown in color.

In the same way, as Leonardo da Vinci suggested long ago, one may explain the blueness of the sky by the scattering of the sunlight by finely dispersed particles in the atmosphere (or, as is now thought, by the molecules of the atmospheric gases themselves), the background being the blackness of infinite space.

The blue color of the eye and the blue colors of feathers are similarly to be explained, as Bancroft has so fully shown, by the scattering of light by finely dispersed matter.

Matter in the colloidal state is therefore matter in a very fine state of subdivision, so that the extent of surface exposed is very large compared with the total volume of the matter.

Surface forces, therefore, play a predominant part and bring about changes in the distribution or concentration of matter at the surface of the particles.

This change of concentration at a surface, brought about by surface forces, is spoken of as adsorption. We see the effect of adsorption, for example, in the removal of coloring matter from solution by charcoal. By reason of its high adsorbing power, charcoal was employed, during the great war, in the construction of gas masks for the adsorption of so-called poison gases—many of which were not gases at all, but finely subdivided solids—colloidal smokes—similarly, the recently introduced, highly porous silica gel is used for the recovery of volatile solvents, for the removal by preferential adsorption of gasoline from natural gas and for freeing crude petroleum from deleterious sulphur compounds.

In the production and characterization of colloidal systems, adsorption plays a very important part. By the adsorption of ions from the dispersion medium or from electrolytes present in the solution, the colloid particles acquire an electric charge; and adsorption of the dispersion medium as a whole may also take place to a greater or less extent whereby variation in the general behavior of colloids may be produced. In the case of the so-called suspensoid colloids or hydrophobe colloids, such as colloidal solutions of gold, or arsenous sulphide, the dispersed particles may adsorb none or practically none of the dispersion medium and they exist therefore in suspension as non-hydrated particles, the stability of which is due to their electric charge and to their Brownian movement. In the case of the so-called emulsoid or hydrophile colloids, such as solutions of gelatin or starch, the dispersion medium itself is adsorbed and the stability and properties of such a colloidal solution are due to the adsorbed water as well as to the electric charge on the particles; the greater the adsorption of the dispersion medium, the more will the stability and properties of the colloidal solution be dependent on this adsorbed medium and the less will they depend on the electric charge.

If the electric charge on a suspended colloid is neutralized, agglomeration of the particles followed by precipitation takes place, and this neutralization can readily be effected by the addition of electrolyte.

Negatively charged colloid particles will preferentially adsorb the positive ions of the added electrolyte, and positively charged colloids the negative ions, thus neutralizing the charge on the colloid. Although multivalent ions are in general, according to Hardy's rule, more effective in producing precipitation than univalent ions, recent investigation shows that there is no exact relationship between valency and precipitating power, and that the adsorbability of the ion may exercise an important influence. In the precipita-

tion of colloidal sulphur, for example, caesium ion is a hundred times more effective than the lithium ion and has a greater precipitating power than the bivalent ions of zinc, cadmium or nickel.

The precipitation of fine particles by electrolytes is well illustrated in nature, where the finely divided clay carried by many rivers is deposited when the river water mingles with the sea, thus silting up river mouths and forming deltas.

The electrical charge on a colloid particle may be neutralized not only by the ion of an electrolyte, but also by another colloid carrying an electric charge of opposite sign. Colloids of opposite sign may mutually precipitate each other and produce adsorption complexes, as Bancroft has called them, which simulate chemical compounds.

Purple of cassius, for example, is an adsorption complex of stannic oxide and colloidal gold.

Although mutual precipitation may take place essentially as a result of adsorption, chemical reaction may later occur. As Bayliss has shown, when alumina adsorbs free congo red acid, which is blue in color, a blue precipitate is formed, but when this precipitate is suspended in water, the blue color changes to red, which is the color of the salts of Congo red.

Adsorption plays an important part in the dyeing of textiles and the staining of animal tissues. Here the negatively charged color ion of the acid dyes is predominantly adsorbed by a positively charged fiber, and a positively charged dye (basic dye) by a negatively charged fiber.

In an acid both the positive charge on the fibers is increased by adsorption of hydrogen ions and adsorption of a negative or acid dye by the fiber is increased. On the other hand, in alkaline solution, the negative charge on the fiber is increased, and adsorption of a positive or basic dye by the fiber is facilitated.

Similarly, addition of a salt giving a readily adsorbed ion, *e.g.*, sulphate ion, will both increase the adsorption of a basic dye and diminish that of an acid dye.

In the case of substantive dyes, the dye itself is in colloidal solution and addition of electrolyte, in small amount, increases the dye adsorption by diminishing the stability of the colloid.

Where mordants are used, adsorption takes place, the mordant, a colloid, adsorbing the dye from the dye bath and fixing it on the fiber. It is really the mordant that is dyed, not the fiber.

After the dye has been adsorbed, secondary changes may take place, leading to the formation of a more stable adsorption complex.

In the face of colloidal solutions of the gelatin type, the stability of the colloid is due mainly to adsorbed water or adsorbed dispersion medium, and consequently such solutions are not so sensitive to added electrolytes. Although the addition of small amounts of an electrolyte may produce changes in the amount of water adsorbed by the colloid, actual precipitation does not take place until the concentration of added electrolyte is relatively large.

The comparatively great insensitiveness to electrolytes, shown by hydrophilic colloids of the gelatin type, may be transferred to hydrophobic or suspensoid colloids of the colloidal gold type.

When gelatin, for example, is added to a colloidal gold solution, the gold is adsorbed by the gelatin and a much greater concentration of electrolyte is required in order to precipitate the gold that is necessary in the absence of the gelatin. The gelatin is said to protect the gold. This so-called protective action, which varies greatly in different hydrophilic colloids, is of much importance in many directions.

In the Mississippi and Nile rivers the water is always turbid and muddy, owing to the presence of a large amount of colloidal organic matter which stabilizes the fine suspension of clay and soil; and it is only when the rivers reach the salt water of the sea, with its high concentration of salts, that the finely dispersed mud is precipitated, forming deltas.

The water of the Ohio River, on the other hand, is at all times clear, owing to the absence of protective colloids and the presence of lime and other salts which act as precipitating agents.

By the use of protective colloids, sparingly soluble substances produced by chemical reaction can be kept in a colloidal state and so prevented from undergoing flocculation and sedimentation. In the production of the photographic plate, the silver bromide is prevented from forming a precipitate of coarse particles unsuitable for photographic purposes and is kept by the protective action of gelatin in a finely divided form.

In many physiological processes the protective action of hydrophilic colloids may also play an important part. In normal bile, the bile salts, albuminoids, etc., act as protective colloids which keep the sparingly soluble substances, such as cholesterol and the calcium salt of bilirubin, in the colloidal state and so prevent their deposition, but when the amount of protective colloids is reduced by pathological conditions, deposition of the sparingly soluble substances, as gall stones, takes place.

The nature of the curd that separates from milk and the readiness with which it is formed are greatly affected by the presence of protective colloids. Cow's

milk contains a large amount of casein and a small amount of the protective colloid, lactalbumin. It, therefore, curdles readily. In human milk there is a smaller proportion of casein and a larger proportion of lactalbumin, so that the casein is more effectively protected and curdling takes place less readily. In asses' milk the relative proportion of protective colloid is highest of all, and curdling takes place with greatest difficulty. The digestibility of asses' milk is consequently greatest. By increasing the amount of protective colloid in cow's milk, by addition of gelatin or white of egg or even of barley water (starch) curdling occurs less readily and the digestibility of the milk is increased.

The smoothness of a good ice cream also is due to protective colloids, such as gelatin or white of egg, which prevent the coagulation of the casein and keep the crystals of ice extremely small.

Many colloids of the hydrophilic type, *e.g.*, gelatin, fibrin, etc., when cooled, pass into a jelly, owing to a coalescence of the hydrated colloid particles. This jelly may be dried and is then obtained as a more or less hornlike material, such as ordinary dry gelatin. These jellies have the important property of taking up or imbibing water, even against very great pressures. This imbibing power is of great biological and agricultural importance. The amount of water imbibed is greatly affected by the presence of electrolytes, being increased by acids and alkalies up to a certain concentration, but the increased swelling produced by dilute acids is diminished by the addition of salts.

The protoplasm of the cells, as has been demonstrated by Gaidukov and by Price, consists of a mixture of colloids. In the cell we have a complex emulsion which under the changing conditions of life may vary in consistency from that of a colloidal solution to that of colloidal gel or jelly. In this system there occur processes of adsorption, changes in dispersity and alterations of the distribution of water between the colloidal particles and the dispersion medium. The living protoplasm, indeed, is a complex system of colloids between which the mutual relations are in a constant state of flux under the action of electrolytes and of stimuli of different kinds; and in which the mass law relationships are altered, now in this direction, now in that, enabling the processes of decomposition and of synthesis to take place. Only in such a colloid system is it possible to have the flexibility and adaptability to the varying requirements of what we call life and growth; just as gelatin, fibrin and other colloids can imbibe and hold large quantities of water, so it is possible for the living organism, aided no doubt by osmotic forces and the

presence of membranes of a semi-permeable character, to hold the 80 per cent. of water present in the body tissues and to preserve the turgor necessary for healthy life. Moreover, the many diverse chemical reactions involved in the breaking down of complex foodstuffs into simple substances and the building up again of these simple compounds into the complex proteins of the protoplasm are accomplished in the living body under the catalytic activity of the enzymes, and these are themselves colloids.

The living organism, therefore, is a vast colloidal community, the diverse members of which are held together in common service by surface forces and by the mutual actions and reactions of electrical changes, and in this community the colloidal workers are engaged in carrying out the multifarious and complex chemical operations on which the life and the health of the community depend.

Martin Fischer has emphasized, perhaps over-emphasized, the analogy between the inhibition of water by gelatin and the water absorbing and retaining power of the colloids of the living organism as affected by variations in the concentration of electrolytes and especially of acids. That work is of great interest and importance, but I wish here to refer more especially to the work of Bancroft and of Clowes on emulsions as affording a suggestive explanation of the action of the plasmatic membrane of cells.

One of the most interesting phenomena in connection with the action of electrolytes on living cells is the so-called antagonistic action of ions. The beat of a heart, for example, continuously perfused with a solution of sodium chloride, isotonic with the blood, soon ceases, but the "toxic" action of the sodium ions can be counteracted by the addition of a small amount of a calcium salt. Similarly, as Loeb showed, the marine organism *Fundulus* dies when placed in a solution of sodium chloride of the same osmotic pressure as sea water, and it dies also in a solution of calcium chloride. In a mixed solution of these two salts, however, containing the salts in the ratio of about fifty molecules of sodium chloride to one molecule of calcium chloride, the organism continues to live. Since, as Straub has shown, the effect of electrolytes is an effect on the cell membrane, it is to the latter effect that we may turn our attention.

The protoplasm of the living cell is surrounded by a membrane or surface layer which allows the passage of certain dissolved substances but prevents the passage of others. Although in some respects this plasmatic membrane is similar to the artificial semi-permeable membrane, like copper ferrocyanide, experiment shows that very important differences exist. The membrane of the living cell, as Nägeli has shown, is self-forming, and it differs also from the inorganic

semi-permeable membranes in that its permeability may vary and that it is adaptable to the varying requirements of an everchanging life process. While the cell is resting, for example, the plasmatic membrane is impermeable to glucose and the amino-acids, but when the cell passes into a state of functional activity, these substances can pass through the membrane.

The permeability of the plasmatic membrane is also variously affected by different ions. Frog's muscle, for example, placed in an isotonic solution of potassium chloride, is permeable to potassium ions. When, however, sodium and calcium salts, which are normally present in blood plasma, are added, the normal impermeability of the muscle cells to potassium is regained. Although the resting muscle cell is impermeable to potassium salts, the active muscle cell is permeable.

The plasmatic or cell membrane is a surface film or layer comparable with the layer of increased concentration which forms at the boundary surface of a solution when the surface tension of the solvent is lowered by the solute (*e.g.*, solutions of peptone). The materials forming the plasmatic membrane must be drawn therefore from the constituents of the cell, more especially lipoids. Various views have been put forward to explain the selective permeability of the cell membrane, in view of the variability of the cell membrane under different conditions, and more especially of the antagonistic action of ions on the permeability, much interest attaches to the work and suggestions of Bancroft and of Clowes.

When water and olive oil, for example, are shaken vigorously together, the oil is broken up into drops. These drops are comparatively large and no permanent emulsion is formed. In order that the droplets of oil may become sufficiently finely divided and a permanent colloidal emulsion obtained, an emulsifying agent must be added to break up the drops and prevent them from coalescing.

Bancroft has shown that a water solution of a sodium soap has a lower surface tension than when the soap is dissolved in oil, and that when a mixture of oil and aqueous soap solution is shaken, an emulsion of oil in water is formed. On the other hand, the surface tension of a solution of a calcium soap in water is greater than in oil, and therefore an emulsion of water in oil is formed. In the first case the water is the continuous phase, while in the second the oil is the continuous phase.

The reversal of an oil-in-water emulsion to a water-in-oil emulsion can be effected by different salts. Alkali salts, for example, favor the formation of oil-in-water emulsions, while calcium salts favor the formation of water-in-oil emulsions. Here again we have

the same antagonistic action of ions as in the case of heart muscle. Similarly, blood plasma may be regarded as an emulsion of fibrinogen and other colloids in an aqueous medium, and the blood clot an emulsion of water in fibrin. The production of the latter system is favored by calcium salts, but is retarded by sodium salts.

Clowes has shown that there is a very close resemblance between the effects produced in emulsions of oil and water and those produced in biological systems, and he has made the valuable suggestion that the cell membrane is a system, a colloidal emulsion, of two phases; a watery solution of protein and a lipoid phase. In the resting state of the cell the membrane consists of an emulsion of protein solution in lipoid, the latter being the continuous phase. In this state, therefore, the membrane will be permeable only to the substances that are lipoid-soluble. In the active state of the cell, there is a reversal of the emulsion, and the aqueous phase becomes the continuous one. In this case, substances soluble in water will now be able to pass through. In each instance, however, regarding the emulsion-membrane as a sieve, the membrane will be permeable only to those substances the particles or molecules of which are small enough to pass through the "pores" between the droplets of the dispersed phase.

We can thus regard not only the protoplasmic cell contents but also the surface layer or cell membrane as a colloid system, and by adopting the view, probably not complete in itself, that the cell membrane is a complex emulsion of colloids, the two phases of which are capable of undergoing reversal, we can explain many of the phenomena associated with the action of the cell membrane.

Although we must recognize the essential importance of colloidal matter in connection with the phenomena of life, and matter in the colloidal state is the vehicle of life; although, further, we may interpret much of the behavior of living matter in terms of physics and chemistry, I am of the opinion that we can not explain life itself in terms of physical science. There seems to be no continuity between inanimate colloidal matter and living matter, but there is a distinct and sharp break in the curve of relations. In other words, life is a new factor, a new set of potentialities, introduced into inanimate matter. Life is a new creation.

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WALTER SCOTT HENDRIXSON

On July 1, Professor Walter Scott Hendrixson was found dead in his summer cottage at Portage Point, near Manistee, Michigan, where he had been tempo-

rarily alone. Death had occurred suddenly from hemorrhage in the brain.

Professor Hendrixson was born in Ohio in 1859; was graduated from Union Central College, Meron, Indiana, in 1881; was instructor and later professor of physics and chemistry at Antioch College, 1882-8; assistant and graduate student in chemistry at Harvard 1888-90, receiving the degrees of A.M. in 1889 and Ph.D. in 1903. He came to Grinnell College as professor of chemistry on the Dodge foundation in 1890, and at the time of his death was the senior member of the Grinnell College faculty, yet a most active and aggressive member and a valued adviser in affairs of the college.

During leaves of absence from Grinnell he had spent one year as graduate student at Goettingen and Berlin; one semester as lecturer in chemistry at the University of Illinois; a year as research fellow at Johns Hopkins University. He was a frequent contributor to the *Journal of the American Chemical Society*; was a member of learned societies; had served as president of the Iowa Academy of Sciences.

As a teacher, Professor Hendrixson was an inspiration to his students, sending many of them on to graduate and professional work in chemistry. As a chemist, the work of his earlier years was with water analyses and in the investigations of artesian waters underlying Iowa, by the United States Geological Survey. In his later years he has been a regular contributor in the development and applications of electrometric methods in chemistry, his last publication bearing date of May 5, 1925.

As a fitting and permanent memorial of a long and distinguished service, Professor H. W. Norris, a colleague of more than thirty years, has proposed the establishment of the Walter Scott Hendrixson Memorial Fund, for the promotion of research in pure science by members of the faculty of Grinnell College; a fund, the income of which is to be used for the promotion of research by paying the actual expenses involved in original investigations. The aptness of this suggestion was immediately recognized and measures promptly taken looking toward securing an endowment of not less than \$10,000 for such a memorial.

FRANK F. ALMY

SCIENTIFIC EVENTS

RESEARCH AND INDUSTRY IN GREAT BRITAIN

THE British Science Guild have published a report, by the Research and Inventions Committee of the Guild, on the present position with regard to the supply of trained scientific research workers, and their utilization in industry.