

COLLOID CHEMISTRY

AN INTRODUCTION, WITH SOME
PRACTICAL APPLICATIONS

BY

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ILLUSTRATED

• SECOND EDITION, REVISED AND ENLARGED



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PREFACE TO SECOND EDITION

The favorable reception accorded the first edition of this little book has led the author to enlarge and extend greatly this second edition, both in the theoretical and the technical sections, so that it may be used as an adjunct in teaching colloid chemistry, if not indeed as a text book. A large number of new practical applications have been introduced, and the effort has been made to develop the subject in a simple, coherent, and interesting manner, using, as far as possible, non-technical language and homely illustrations, so as to enable the reader's interest to aid memory.

The growing realization of the importance of colloid chemistry is evidenced by the fact, that, whereas the Decennial Index of Chemical Abstracts covering the years 1907-1916 contains only twelve columns of titles under Colloids, the 1922 Index alone contains five columns, and the 1923 Index contains four columns. These figures do not include many germane papers which are indexed under such headings as Adsorption, Diffusion, Coagulation, Gelatin, Gel, Sol, and a wide variety of physical, biological, and technical topics; but they do show that the colloidal zone is no longer "the world of neglected dimensions" as Wo. Ostwald once called it.

Matter in the colloidal state has unique properties which necessitate a revision of some of our preconceived notions; and this fact cannot be avoided by attempting to alter definitions and the established

meaning of language, or nullified by a Procrustean effort to fit all experimental data to existing theories.

To use a good old-fashioned term, we need *natural philosophers*, men whose view of the various fields of science is sufficiently broad and keen to enable them to see, understand, and correlate correctly apparently scattered facts in physics, chemistry, biology, technology, and related branches.

Science is not a sporting event. The true scientist's slogan is not "May the best man win," but rather "May the truth prevail."

Colloid chemistry comes not to destroy, but to fulfill. It does not destroy or even replace the known facts of chemistry, physics, and other sciences, but draws attention to certain aspects of Nature which have often been overlooked.

JEROME ALEXANDER

50 EAST 41ST ST.,
N. Y. CITY,
July 1, 1924

PREFACE TO FIRST EDITION

This little book is the result of an attempt to compress within a very limited space the most important general properties of colloids, and some of the practical applications of colloid chemistry. Its object will be accomplished if it is helpful in extending the sphere of interest in this fascinating twilight zone between physics and chemistry.

J. A.

NEW YORK,
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COLLOID CHEMISTRY

CHAPTER 1

INTRODUCTION

Although many facts and principles concerning colloids have from time immemorial been known and utilized empirically, the scientific foundation of modern colloid chemistry was laid by an Englishman, Thomas Graham, F.R.S., Master of the Mint. In two basic papers on this subject, the first entitled "Liquid Diffusion Applied to Analysis," read before the Royal Society of London, June 13, 1861, the second entitled "On the Properties of Colloidal Silicic Acid and other Analogous Colloidal Substances," published in the *Proceedings of the Royal Society*, June 16, 1864, Graham pointed out the essential facts regarding colloids and the colloidal condition, and established much of the nomenclature in use at the present day. In the first of these papers Graham says: "The property of volatility, possessed in various degrees by so many substances, affords invaluable means of separation, as is seen in the ever-recurring processes of evaporation and distillation. So similar in character to volatility is the diffusive power possessed by all liquid substances, that we may fairly reckon upon a class of analogous analytical resources to arise from it. The range also in the degree of diffusive mobility exhibited by different substances appears to be as wide as the scale of vapor tensions. Thus hydrate of potash may be said to pos-

sess double the velocity of diffusion of sulphate of potash, and sulphate of potash again double the velocity of sugar, alcohol and sulphate of magnesia. But the substances named belong all, as regards diffusion, to the more "volatile" class. The comparatively "fixed" class, as regards diffusion, is represented by a different order of chemical substances, marked out by the absence of the power to crystallize, which are slow in the extreme. Among the latter are hydrated silicic acid, hydrated alumina and other metallic peroxids of the aluminous class, when they exist in the soluble form; with starch, dextrin and the gums, caramel, tannin, albumen, gelatin, vegetable and animal extractive matters. Low diffusibility is not the only property which the bodies last enumerated possess in common. They are distinguished by the gelatinous character of their hydrates. Although often largely soluble in water, they are held in solution by a most feeble force. They appear singularly inert in the capacity of acids and bases, and in all the ordinary chemical relations. But, on the other hand, their peculiar physical aggregation with the chemical indifference referred to appears to be required in substances that can intervene in the organic processes of life. The plastic elements of the animal body are found in this class. As gelatin appears to be its type, it is proposed to designate substances of this class as colloids, and to speak of their peculiar form of aggregation as the colloidal condition of matter. Opposed to the colloidal is the crystalline condition. Substances affecting the latter form will be classed as crystalloids. The distinction is no doubt one of intimate molecular constitution.

"Although chemically inert in the ordinary sense,

colloids possess a compensating activity of their own, arising out of their physical properties. While the rigidity of the crystalline structure shuts out external impressions, the softness of the gelatinous colloid partakes of fluidity, and enables the colloid to become a medium for liquid diffusion, like water itself. The same penetrability appears to take the form of cementation in such colloids as can exist at high temperature. Hence a wide sensibility on the part of colloids to external agents. Another and eminently characteristic quality of colloids is their mutability. Their existence is a continued metastasis. A colloid may be compared in this respect to water, while existing liquid at a temperature under its usual freezing-point, or to a supersaturated saline solution. Fluid colloids appear to have always a pectous modification; and they often pass under the slightest influences from the first to the second condition. The solution of hydrated silicic acid, for instance, is easily obtained in a state of purity, but it cannot be preserved. It may remain fluid for days or weeks in a sealed tube, but is sure to gelatinize and become insoluble at last. Nor does the change of this colloid appear to stop at that point. For the mineral forms of silicic acid deposited from water, such as flint, are often found to have passed, during the geological ages of their existence, from the vitreous or colloidal into the crystalline condition. (H. Rose.) The colloidal is, in fact, a dynamical state of matter, the crystalloidal being the statical condition. The colloid possesses *Energia*. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place

(for they always demand time as an element) may the characteristic protraction of chemico-organic changes also be referred. . . .

"It may perhaps be allowed to me to apply the convenient term dialysis to the method of separation by diffusion through a septum of gelatinous matter. The most suitable of all substances for the dialytic septum appears to be the commercial material known as vegetable parchment, or parchment-paper. . . ."

At the beginning of the second paper above referred to, Graham states: "The prevalent notions respecting solubility have been derived chiefly from observations on crystalline salts, and are very imperfectly applicable to the class of colloidal solutions." From this it may be seen that Graham appreciated the fact that all the laws of crystalloidal solutions could not be applied to colloidal solutions. In the case of crystalloidal solutions the dissolved substance is present in a state of molecular subdivision, and, according to the ionization theory, is in many cases dissociated into ions. With colloidal solutions, on the other hand, we have a lesser degree of subdivision, and the particles in solution are larger and more cumbersome. As Graham remarked, "The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the basis of colloidity may not really be this composite character of the molecule." This is to-day the idea generally accepted.

Colloid Chemistry Defined

Colloid chemistry deals with the behavior and properties of matter in the colloidal condition, which,

as we now know, means a certain very fine state of subdivision. While there are no sharp limitations to the size of particles in colloidal dispersions, it may in a general way be stated that their sphere begins with dimensions somewhat smaller than a wave length of light, and extends downward well into dimensions which theory ascribes to the molecules of crystalloids. (See Table II, p. 27.)

Suspension vs. Solution

With the aid of the ultramicroscope, which renders visible particles approaching in minuteness molecular dimensions, Zsigmondy has shown that there is no sharp line of demarcation between suspensions and colloidal solutions, but that with increasing fineness in the subdivision of the dissolved substance, there is a progressive change in the properties of the resulting fluids, the influence of gravity gradually yielding to that of the electric charge of particles, of surface tension and of other forms of energy. Thus in the case of metallic gold, subdivisions whose particles are $1\ \mu$ and over act as real suspensions and deposit their gold, whereas much finer subdivisions ($60\ \mu\mu$ and under) exhibit all the properties of metal hydrosols or colloidal solutions. In the ultramicroscope the coarser subdivisions show the well-known Brownian movement, which greatly increases as the particles become smaller, until at the present limit of ultramicroscopic visibility (about $5\ \mu\mu$) it becomes enormous both in speed and amplitude.

On the other hand, there is no sharp distinction between colloidal and crystalloidal solutions, but as the particles in solution become smaller and smaller, the

optical heterogeneity decreases correspondingly, finally vanishing as molecular dimensions are approached.* That even crystalloid solutions are not in a strict sense homogeneous, is indicated by an experiment of van Calcar and Lobry de Bruyn (*Rec. Trav. chim. Pays-Bas*, 1904, 23, 218), who caused the crystallization of a considerable part of saturated crystalloid solutions at the periphery of a rapidly rotating centrifuge.

* In an article entitled "Pedetic Motion in Relation to Colloidal Solutions" published in *Chemical News*, 1892, Vol. 65, p. 90, William Ramsay, Ph.D., F.R.S. (afterward Sir William Ramsay), clearly expressed this view in the following words: "I am disposed to conclude that solution is nothing but subdivision and admixture, owing to attractions between solvent and dissolved substance accompanied by pedetic motion; that the true osmotic pressure has, probably, never been measured; and that a continuous passage can be traced between visible particles in suspension and matter in solution; that, in the words of the old adage, *Natura nihil fit per saltum*."

CHAPTER 2

MATERIAL UNITS AND THE FORCES DOMINATING THEM

Next to accurate observation and due allowance for all influential factors involved, perhaps nothing is more important in scientific matters than the mental separation of seasoned facts from the theories designed to systematize and explain them. For facts are hard, stubborn things that survive the theories whose downfall they may cause.

A theory must interminably run the gauntlet of the whole far-flung tribe of scientists, and may be stricken down after long years of apparent safety. Einstein's Theory of Relativity has been checked by astronomers and physicists in such diverse fields as the deflection of alpha particles shot out from radium, the deviation of starlight by the sun, and the precession of the axis of the orbit of the planet Mercury. How convenient it would be if a scientist, when confronted with facts that run counter to the very theories he has been taught to revere, could only say, as Ko-Ko remarked to Pooh-Bah:—"Come over here where the Lord High Treasurer can't hear us!"

Divisibility of So-called Elements

Among the disconcerting discoveries of recent times may be mentioned those connected with radio-activity, which eventually led to the demonstration that electricity consists of discrete particles, and that our supposedly infrangible elements are complexes of positive and negative electrons, and that some of these

complexes are breaking up spontaneously and uncontrollably, while others may be shattered by the terrific impact of alpha particles moving at the rate of 10,000 miles or more per second.*

Then the basic assumption of Dalton's atomic theory fell, when T. W. Richards, J. J. Thompson, Aston, Dempster, Harkins and others showed that with many of the elements, the atoms are not all alike, but have different atomic weights.

It is startling to learn, for example, that lithium consists of a mixture of atoms having atomic weights of 6 and 7, chlorine of atoms having atomic weights of 35 and 37, and that krypton has six *isotopes*, as they are called. In an address before the Chemical Society (London) Aston remarked:—"Though as a chemist I view with some dismay the possibility of eighteen different mercuric chlorides, as a physicist it is a great relief to find that nature employs at least approximately standard bricks in her operations of element building." And, to the endless disgust of small boys, Harkins has pointed out the possibility of 63 different kinds of calomel.

Some of our other new discoveries cast doubt upon what were heretofore accepted as facts. Thus the recognition of vitamins and certain salts as food essen-

* To give an idea of the minuteness of an electron, Prof. R. A. Millikan states that if the entire population of Chicago, estimated at 2,500,000 people, were to begin to count the number of negative electrons passing as an electric current through an ordinary incandescent lamp in one second, and were to count continuously day and night at the rate of two per second, it would take them about 20,000 years to finish the count. In the highest vacuum we can produce, the number of residual molecules is so great that in each cubic inch there is a molecule for every inhabitant of the earth.

tials has necessitated the revision of conclusions drawn from some previous experiments on food values, which in some cases showed simply the minimum quantities of food needed to supply the necessary amount of vitamins or salts. The incompleteness of mere calorie-fat-protein-carbohydrate specifications is now well recognized.

Chemical vs. Physical Forces

We make free use of the expressions "physical mixture" and "chemical compound" with the full confidence that we know exactly what we are talking about. But when we attempt to define these terms exactly, we appreciate the truth of Aristotle's remark that to frame an exact definition requires complete knowledge.

The difference between chemical and physical attraction is explained in many elementary text books by taking the example of iron filings and flowers of sulphur. From their physical mixture the iron may be separated magnetically or the sulphur dissolved out by carbon bisulphide; and the two ingredients may be separately identified in the microscope. If they are heated, however, the non-magnetic chemical compound FeS is formed, from which CS_2 extracts no S. Furthermore, while Fe and S may be physically mixed in any desired proportions, in the chemical compound FeS they combine in the definite proportions of 56 parts by weight of Fe to 32 parts by weight of S, and any excess of S may be dissolved out by CS_2 .

This fixes homogeneity and closeness of union in definite proportions by weight, as criteria of chemical combination.

But the transition between chemical and physical forces is not so sharp as our definitions demand; and it is in the transition zone that there appear the phenomena encountered in that extremely fine state of subdivision or dispersion known as the colloidal condition, where combination depends *not* upon the *total mass* involved, but upon the *total free or active surface*.

The Sub-microscopic Structure of Matter

A whole series of complexities underlie even the smallest particle of matter visible in the most powerful microscope. Negative electrons, and protons or positive electrons are the only material units not at present *known* to be complex. While the number of steps in this series may vary in individual cases, in many instances the following degrees of aggregation may be definitely traced.

Material Unit	Order of Size*	Order of Complexity	Mode of Examination
Protons	$10^{-9} \mu\mu$	0?	Positive ray and particles from radium
Electrons.....	$2 \times 10^{-6} \mu\mu$	0?	Electric field, while floating on ultramicroscopic particles
Atoms.....	$0.1-2.0 \mu\mu$	1	X-ray spectrometer
Molecules.....	$0.5-5.0 \mu\mu$	2	X-ray spectrometer
Molecular Groups.....	$1-10 \mu\mu$	3	Diffusion and Ultramicroscope
Primary Colloidal Particles.....	$2-20 \mu\mu$	4	Diffusion and Ultramicroscope
Secondary Colloidal Particles.....	$5-100 \mu\mu$	5	Diffusion and Ultramicroscope
Microscopically Resolvable Particles.....	over $250 \mu\mu$	6	Microscope
Visible Particles.....	about 10μ	7	Eye

* Diameter.