

PREFACE

THIS introductory text was written in response to a general demand for a short, clear, yet moderately comprehensive statement of the fundamentals of colloid chemistry. Most learners advance the more rapidly in a new subject if they begin with a brief general survey.

Although the larger texts and reference books are invaluable to workers in this field many chemists wish to have on the desk a "handy volume" to which they can turn for quick reference. Others having only a limited time for a survey of colloid chemistry find such a text suited to their needs.

Those desiring to extend the range of their reading will find a great many helpful suggestions and the most important references.

The time when colloidal gold and the ultramicroscope occupied the center of the stage has passed. In an effort to achieve a proper present-day balance of topics the author has stressed adsorption (the heart of the subject, as Bancroft puts it), emulsions, and that important group of subjects including surface and interfacial tensions, films, froths, and wetting. Of course the gels and proteins and soaps are not neglected, nor is catalysis.

The third edition of the author's "Laboratory Manual of Colloid Chemistry" appears with this volume.

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INTRODUCTORY COLLOID CHEMISTRY

CHAPTER I

PARTICLE SIZE

About 1861 Graham founded the science of colloid chemistry by comparing the rates of diffusion of a considerable number of substances through membranes such as parchment paper and bladder. Observing that crystalline material dissolved in water diffused readily through these membranes, while glues, gums, and other non-crystalline substances failed to pass through, he decided to divide all materials into crystalloids or rapid diffusers and colloids or slow diffusers.

These membranes he termed "dialyzers," and the process of identifying colloidal matter by their use, dialysis. By dialysis he also found it possible to remove the crystalloid material from any mixture with colloids. To this day we have found no more convenient means of recognizing and purifying colloidal dispersions than Graham's dialysis.

It may seem ungrateful to observe that Graham was wrong in believing colloids to be definite substances, but the fact is that common soap is colloiddally dispersed in water and truly dissolved in alcohol. Sodium chloride was classed by Graham as a crystalloid, yet it has since been colloiddally dispersed in benzene. Theoretically, any substance may be prepared in the "colloidal state of matter" by using the proper methods of preparation. Nevertheless it is convenient to use the term "colloids," and we shall continue to do so.

In recent years the X-ray photographic method has shown that many substances supposed to be amorphous are really crystalline in their sub-microscopic units. However, gelatin refused to reveal any crystalline structure. Such revelations forced us to a revised definition of the colloid state of material.

Colloid material is merely a dispersion of one phase (matter enclosed by well-defined surface) in another as, in Bancroft's words, "grains, drops, bubbles, filaments, and films," provided that in at least one dimension¹ the dispersed material is approximately from $5\text{ m}\mu$ to $200\text{ m}\mu$. We are falling back upon size of dispersed particles as the determining factor. If tomorrow you discover a molecule of greater diameter than $5\text{ m}\mu$ but not above $200\text{ m}\mu$, we shall term it a colloidal particle. As a matter of fact, molecules so far known are smaller than $1\text{ m}\mu$.

Evidently colloidal dispersions are coarser than true solutions (molecular dispersions) with particles usually built up from many molecules or ions. The selection of $5\text{ m}\mu$ and $200\text{ m}\mu$ as limits for the colloidal particle was not wholly arbitrary, for the resolving power of the ordinary microscope does not extend below $200\text{ m}\mu$ nor does the largest molecule yet known have any dimension as great as $5\text{ m}\mu$. The ultramicroscope reveals the presence of colloidal particles as so many points of light, but not when these particles are smaller than about $5\text{ m}\mu$. Material so subdivided shows remarkable properties meriting special study with a specialized technique. Since there is no abrupt change in properties as material is brought into this range from either direction it is best to consider the limits as approximate.

Colloidal dispersions, as was intimated before, are two-phase systems, the very small particles (from $5\text{ m}\mu$ to $200\text{ m}\mu$) being called the **dispersed phase**, and the liquid,

¹ The symbol $1\text{ m}\mu$ stands for 1 millimicron or one-millionth of a millimeter = 10^{-7} cm . This is the colloid unit of measure. Many writers have made the mistake of expressing this as $1\text{ }\mu\mu$ (a unit only 0.001 as large.) See International Critical Tables, 2, Vol. I.

solid, or gas separating such small particles the **dispersion medium**. Other terms used with the same meaning as above are internal and external phases, inner and outer phases.

A large lump, 100 g. for example, of a homogeneous and amorphous material cannot be colloidal for it contains no 5-m μ to 200-m μ particles separated by other material. The entire 100-g. particle is too large a unit. Yet a heterogeneous lump of that size is truly a colloidal mass if the particles of one phase conform to the standard size of the colloidal unit.

Suspensions of solids in liquids such as the red colloidal gold made by Faraday and, earlier, by the alchemists have been studied so intensively that we are in danger of overlooking other important dispersions. The possibilities are listed below.

| | |
|---|-----------------------------|
| Solid in liquid | Suspensions (gold in water) |
| Solid in gas | Smokes |
| Solid in solid | Some alloys |
| Liquid in liquid | Emulsions |
| Liquid in gas | Mists |
| Liquid in solid | Solid emulsions (butter) |
| Gas in liquid | Foams |
| Gas in solid | Solid foams (volcanic ash) |
| (A gas-in-gas system is a molecular mixture or solution.) | |

Colloid suspensions may slowly change to a distinctly crystalline condition, as was once shown with an apparently amorphous precipitate of arsenic trisulfide which was kept just below 100°, under water, for a month or two. It became distinctly crystalline to the eye and would no longer dissolve in hot concentrated potassium hydroxide solution.

Every chemist knows that barium sulfate precipitated in the cold will run through filter paper whereas the same precipitate digested in hot water for an hour is retained by the filter. The solubility of small particles, slight though it may be, is greater than that of larger particles (greater surface). This solubility is increased by rise in

temperature so the smaller particles dissolve and the dissolved salt deposits on the larger particles which are in contact with their own saturated solution.

VARIATION OF PROPERTIES WITH CHANGE IN SIZE OF PARTICLE SURFACE

Surface. Surface increases enormously with subdivision, and all surface phenomena become greatly magnified. A cube, 1 cm. on edge, when subdivided into cubes $10\text{ }\mu$ on edge would possess a total surface of 6,000,000 sq. cm., and the number of particles would be 10^{18} . The surface has been multiplied one million times. If the subdivision is carried to the lower limit of $5\text{ }\mu$ the free surface becomes almost one acre in extent. Consequently the importance of surface energy and of all surface properties becomes overwhelming. Colloid chemistry might well be called **surface chemistry**.

Osmotic Pressure. Osmotic pressure depends upon the number of dispersed or dissolved particles per unit of volume, so it is relatively very small for colloidal suspensions. There are many difficulties and inaccuracies in its measurement with colloidal systems. Read the Duclaux chapter in Alexander's "Colloid Chemistry," 1, 515 (1926). Temperature effects may be much greater than with true solutions, and the number of ions tenaciously held by dispersed particles may actually be greater than the number of colloidal particles present. Other errors due to the membrane complicate matters.

Brownian Movement. Suspended particles below $3\text{ }\mu$ (not $3\text{ }m\mu$) in diameter are observed to be in incessant, rapid, oscillating motion if viewed through a microscope with magnification of about 500 diameters and with a dark ground illumination equipment. This Brownian movement was named for Robert Brown, the botanist who first observed it with pollen grains (1827).

Einstein explained the phenomenon by the assumption that the molecules of the solvent and the much larger suspended particles all have the same kinetic energy.

The larger particles must certainly show less violent motion and a shorter free path than the smaller particles. Experiment supports the theory. An oscillating or zigzag motion must become apparent when in a given brief interval of time the impacts of solvent molecules on opposite sides of a suspended particle are unequal. There is certainly a greater probability of this with the smaller colloidal particles.

Under the ultramicroscope, Brownian movement is startling.

Rate of Sedimentation. A dozen methods of determining particle size are listed in *Kolloid-Z.*, **37**, 365 (1925). Among these the sedimentation method gives information as to size and distribution of particles of mixed sizes.

Audibert states that dust particles 4μ in diameter settle in still air at a rate of less than 1 cm. per sec. Of course this is an approximate measure since the density of the particle is a vital factor. In liquids, settling or sedimentation is much slower than in gases, the best gold settling 1 cm. in 7 years. Stokes gave us a formula for settling that brings in various factors:

$$V = \frac{2r^2(s - s')g}{9n}$$

V = rate of settling.

r = radius of a spherical particle.

s = density of particle.

s' = density of fluid.

g = 981 (gravity constant).

n = viscosity of fluid.

It has been pointed out that the density of the suspension rather than the density of the pure liquid (water, etc.) must be used, and also that it is the viscosity of the liquid mixture that must be used.

Of course lighter particles, as oil drops in water, rise, but Stokes' law applies just as well. Sedimentation may be greatly hastened by use of the centrifuge, a device of great value in the dairy industry.

The Sharples turbine-driven laboratory centrifuge exerts

40,000 times the force of gravity, but Svedberg's super-centrifuge shows 100,000 times this force. By its use Svedberg was able to show that the hemocyanin from the blood of *Octopus* has a molecular weight of 2,000,000 and that from the blood of *Helix* a value of 5,000,000.

Larger particles settle more rapidly than smaller ones so there is a certain distribution of sizes of particles, changing with the lapse of time. A particle of $5.5 \text{ m}\mu$ diameter has 17,000 times the mass of another of the same shape and material but $0.212 \text{ m}\mu$ diameter. To determine the proportion of small, medium, and large particles in a soil

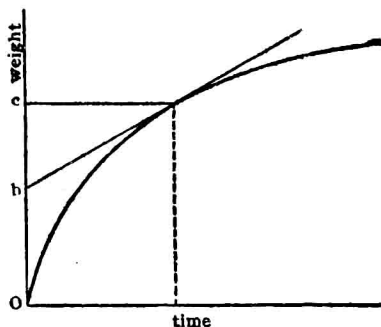


FIG. 1.—Sedimentation curve.

or a paint pigment, etc., may be important. Recourse is had to sedimentation analysis.

Odén devised a method for use in soil analysis. A quotation from Keen in "The Physicist in Agriculture" explains the use of Odén's sedimentation curve:

A flat pan, attached to one arm of a delicate balance, is immersed in the soil suspension, and the increasing weight, P , of particles settling on the plate is measured from time to time. The curve obtained by plotting these results is called the accumulation curve (Fig. 1), and from it the distribution curve can be derived graphically or arithmetically.

The average particle size of fine pigments, and more especially the percentage of the different particle sizes that go to make up a given pigment, has always been important in the study of the physical properties of paints. Calbeck and Harner² describe in detail the technique of sedimentation analysis of a paint pigment and show clearly how to plot and read the curves.

Odén³ exhaustively discusses "Sedimentation Analysis

¹ Ind. Eng. Chem., 19, 58 (1927).

² Alexander's "Colloid Chemistry," 1, 860 (1926); Proc. Roy. Soc., 36, 219 (1926).

and Its Application to the Physical Chemistry of Clays and Precipitates." In Holmes' "Laboratory Manual of Colloid Chemistry" there may also be found many references to methods used in this field. An automatic recorder for determining particle size by the sedimentation method has been described by Sumner.⁴

Perrin's microscopic study of the atmospheric distribution of gamboge particles in suspension within 0.12 mm. of the surface of the liquid led him to announce that dispersed particles arrange themselves under the influence of gravity in the same way as the molecules of the earth's atmosphere: a greater number of particles in lower layers and fewer in upper layers. At this rate the concentration 1 cm. below the surface would be thousands of times that at the surface, an obvious absurdity. Brownian movement and other influences maintain for varying lengths of time a uniform concentration throughout colloidal suspensions. It is only in the layers within 0.12 mm. of the surface that Perrin's atmospheric distribution holds.

Nephelometry. The Kober nephelometer⁵ (or turbidimeter) is used in determining the amount of suspended material by optical methods. A very simple turbidimeter consists of a small electric lamp placed below a column of suspension to be viewed from above. By varying the height of the column a point is found at which the glowing filament just disappears. The reciprocal of this height in millimeters may be taken as a measure of turbidity. Comparison with a standard solution containing a known weight of suspended material of the same color makes possible a quantitative estimation.

The whole subject of nephelometry may be studied in the excellent book by Yoe and Kleinmann.⁶

Nephelometric methods of great delicacy have been developed for the determination of sulfur in blood, acetone in blood, lipase, and many other substances.

⁴ Trans. Faraday Soc., 28, Pt. I, 20 (1932).

⁵ Ind. Eng. Chem., 7, 843 (1915).

⁶ "Nephelometry and Colorimetry," John Wiley & Sons (1929).

Color. Red gold suspensions contain smaller particles than those in blue gold suspensions. Colloidal silver has also been obtained in a variety of colors—red, yellow, brown, depending upon size. Some variation of color with size has also been observed with colloidal sulfur. When Fehling's solution is treated with a reducing substance it is generally expected that a bright-red precipitate will be obtained. Frequently, however, an orange or yellow precipitate is obtained, and in certain instances nothing but a yellowish green discoloration results.

These color changes are coincident with differences in size of particles of the cuprous oxide formed. The smallest particles are yellowish green; as they grow in size they become yellow, then orange, and when very coarse they are red. When the bright blue Fehling's solution is mixed with a little dextrose solution, or some diabetic urine, and the mixture is not boiled as ordinarily, but is allowed to stand several hours at room temperature, this series of color changes, beginning with bluish green and ending with red, is observed. Drops of these suspensions examined under the microscope show the corresponding growth in size of particle.

The Tyndall Effect. The path of a powerful beam of light through a colloidal suspension (or even a coarser suspension) appears strongly luminous when viewed at right angles. When viewed from the side through a Nicol prism the luminosity seems to change with rotation of the prism—an indication that the light is polarized by reflection from the surfaces of the suspended particles. There is no such change when the luminosity is due to mere fluorescence.

The Ultramicroscope. The ultramicroscope differs from the ordinary microscope in that the light does not reach the eye directly but only by the diffraction phenomenon. It is not an image but a diffraction ring representing the colloid particle that the eye observes. As Kruyt puts it, this is observation, in a way, of the Tyndall effect.