COLLOIDAL PHENOMENA

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An Introduction to the Science of Colloids

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Dedicated
to the memory of
those who courageously
pioneered the study of colloidal
phenomena and who thereby laid the foundation
for all further development in
this comparatively new
field of scientific
research.

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Colloid chemistry is the twilight between chemistry and physics—but that is where God has chosen to reveal himself.

MARTIN H. FISCHER

PREFACE

In the introduction to his book "Kolloidik,"[1] A. v. Buzágh remarks that colloids or colloidal phenomena can more aptly be called "the world of dimensions we may no longer neglect" than "the world of neglected dimensions," as Wo. Ostwald titled his pioneer book on colloid chemistry, first published in 1915.[2] Two decades have brought about a development in our understanding of these phenomena unrivaled by any other development of a new branch of natural science. Special cognizance is merited when we realize that this growth was badly handicapped, since it took place during the same period when physicochemistry was prevalent and prejudicial to anything that could not be explained on the basis of its dogmatic teaching.

It required men of courage, convinced by their experimental results, endowed with a keen sense of observation, and capable of sound logical reasoning, to free themselves from conventional viewpoints and establish entirely new lines of thought. Men of this mold were needed to overcome the obstacles resulting from unsuccessful attempts to force the newly discovered facts into the too narrow limits of existing theories.

The study of colloidal phenomena has been and still is largely an experimental science. The great number of variables influencing the properties and behavior of colloidal systems, as compared with other scientific systems, makes it extremely difficult to formulate theories of a general nature. However, it would be suicidal, scientifically, to abandon further attempts to obtain a more profound knowledge of the happenings in this ultramicrocosmos simply because we cannot always describe and predict reactions in rigid mathematical terms as we have been used to doing in other exact sciences. Nor should it be inferred that the science of colloids may not be considered a member of

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[1] Published by T. Steinkopff, Dresden, 1936. English translation, "Colloid Systems," Technical Press Ltd., London, 1937.

[2] "Die Welt der vernachlaessigten Dimensionen," 10th ed., 1927, T. Steinkopff, Dresden. (Translated into English by M. H. Fischer, John Wiley & Sons, Inc., New York, 1922.)

the exact sciences, although such intimations have been frequently made.[1] On the contrary, this proves only that we are not yet sufficiently advanced in the mathematical handling of reactions that are influenced by a large number of independent factors. Likewise, that is the reason why the most important developments in colloidal research are based on purely sound logical deductions and interpretation of experimental facts, and why theories, if formulated at all, never go far beyond the experimentally established facts.

This probing into the unknown, defeating unforeseen obstacles, piecing together individual observations and experimental data to reach a logical new point of view, is what makes the study of colloidal phenomena so fascinating and absorbing.

But it would be carrying coals to Newcastle to write this book as a kind of scientific propaganda of the subject. Those days have passed when the science of colloids was still in need of recognition. Its importance is now fully recognized and established in practically every branch of natural science.

Nor is it the author's intention to offer another textbook on colloidal chemistry, since a sufficient number already exist.[2]

What he has set out to do and hopes to accomplish by this book is to acquaint the reader in as simple a manner as possible with the modern viewpoints in colloidal science and to show where and why they must differ from those so successfully applied in physicochemistry. It is further hoped that such discussions may be helpful in eliminating the belief, still prevalent in some circles, that the science of colloids must be considered either as a development entirely independent of any other branch of known science or that colloidal phenomena must be fully explained in accordance with laws of classical chemistry or physics. If the author is able to achieve this goal, then it should logically follow that colloids as a result of their amazing development can no longer be treated as a negligible side issue and that they consequently not only deserve but demand individual treatment.

The science of colloids or the study of colloidal phenomena is a necessary amendment to physicochemistry, a bridge between

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[1] See, *e.g.*, J. LOEB, "Die Eiweisskoerper," p. 111, Berlin, 1924; "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Company, Inc., New York, 1925.

[2] See references on p. xix.

the study of invisible building units of matter—the actual domain of physicochemical studies—and microscopical dimensions. Therefore, the author has refrained from discussing purely chemical or physicochemical problems in detail in this book, as these can be studied in their appropriate textbooks. As the present book does not pretend to be a complete treatise on colloids but rather more of an introduction or guide to some of our recent viewpoints, the incorporation of the author's personal opinion is necessary to a greater extent than if he were merely to act as a chronologist in writing a formal textbook.

It has been the author's experience that the greatest advantage to the beginner will be derived from considerations of colloidal phenomena without the customary use of complicated mathematical formulas and their derivations. For the benefit of the more advanced student the essential mathematics has been summarized in the appendix, and all necessary references to the original papers have been given.

The book is based on notes written by the author, which have been successfully used as text for regular classes in colloid chemistry and physics at the Massachusetts Institute of Technology. These courses have proved that the average student comprehends a logical presentation of such a subject more readily than a mathematical treatment. Once the principles have been mastered, the student can easily follow the mathematics.

Although being fully aware of the shortcomings of such a method, the author believes that they are more than compensated for by the stimulus gained in any type of research by introducing new trends of thought and reasoning. The author is not a disciple of the Ostwald school. However, the method of presentation in this book is closely related to its views, since with a few essential differences, dictated by practical and teaching experience, the author's approach toward an easy comprehension of the subject matter is very similar to that of Wo. Ostwald. With the permission of Wo. Ostwald and A. v. Buzágh, the author therefore has drawn freely from their publications when he considered this advisable.

In concluding, it may be well to explain the somewhat unconventional title. The customary term "colloid chemistry" has long outlived its justification. In German literature, the term

Kolloidik[1] has been introduced recently as a means of expressing in one word the chemistry and physics of colloids. Since the colloidal state of matter is mainly characterized by specific phenomena and since this book is primarily concerned with their discussion and interpretation, the title as chosen seems most descriptive of the purpose to which this book is dedicated.

The author is indebted to Mr. J. E. Lynn for his help in checking some of the old texts, as well as for his assistance in the reading of the manuscript.

ERNST A. HAUSER.

CAMBRIDGE, MASS.,
December, 1938.

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[1] Coined by K. Spiro.

CONTENTS

APPENDIX

ABBREVIATIONS USED IN LITERATURE REFERENCES

Abh. d. K. Akad. der Wiss. zu Stockholm	*Abhandlungen der Königlichen Akademie der Wissenschaften zu Stockholm*
Agric. Bull. F.M.S.	*Agricultural Bulletin of the Federated Malay States (Kuala Lumpur)*
Am. Inst. Mining, Met. Engrs. Pamphlet	*American Institute of Mining and Metallurgical Engineers Pamphlet*
Am. J. Sci.	*American Journal of Science*
Ann. chim. phys.	*Annales de chimie et de physique*
Ann. Phys. Chem.	*Annalen der Physik und Chemie*
Ann. Phys.	*Annalen der Physik*
Archiv Entwicklungsmech. Organ.	*Archiv für Entwicklungsmechanik der Organismen*
Arch. Sci. phys. nat.	*Archivo Scienza physica naturale*
Arkiv Matem. Astron. Fys.	*Arkiv för Mathematik, Astronomi och Fysik*
Beih. bot. Centralbl.	*Beihefte zum botanischen Centralblatt*
Beibl. Ann. Phys. Chem.	*Beiblatt der Annalen der Physik und Chemie*
Biochem. J.	*Biochemical Journal* (London)
Biochem. Zeit.	*Biochemische Zeitschrift*
Ber.	*Berichte der deutschen chemischen Gesellschaft*
Chem. Ind.	*Journal of the Society of Chemical Industry* (London)
Chem. Met. Eng.	*Chemical and Metallurgical Engineering*
Chem. Rev.	*Chemical Reviews*
Chem. Wbl.	*Chemisches Weekblad*
Chem. Ztg.	*Chemiker Zeitung*
Coll. Symp. Monogr.	*Colloid Symposium Monographs*
Compt. rend.	*Comptes rendus* (Paris Academy of Science)
C. r. Soc. Biol.	*Comptes rendus, Société de Biologie* (Paris)
Drude's Ann. (*Ann. Phys.*)	*Drude's Annalen* (*Annalen der Physik*)
Die chem. Fabr.	*Die chemische Fabrik*

Econ. Geol.	*Economic Geology*
Erg. exakt. Naturwiss.	*Ergebnisse exakter Naturwissenschaften*
Erg. techn. Rönig.	*Ergebnisse der technischen Röntgenologie*
Fortschr. Chem. Phys. u. physikal. Chem.	*Fortschritte der Chemie und Physik und physikalischen Chemie*
Ind. Eng. Chem.	*Industrial and Engineering Chemistry*
J. Am. Ceram. Soc.	*Journal of the American Ceramic Society*
J. Am. Chem. Soc.	*Journal of the American Chemical Society*
J. Biol. Chem.	*Journal of Biological Chemistry*
J. Chem. Educ.	*Journal for Chemical Education*
J. Chem. Phys.	*Journal of Chemical Physics*
J. chim. phys.	*Journal de chimie et physique*
J. Chem. Soc.	*Journal of the Chemical Society* (London)
J. Landw.	*Journal für Landwirtschaft*
J. Gen. Physiol.	*Journal of General Physiology*
J. Math.	*Journal für Mathematik*
J. Oil Color Chem. Ass.	*Journal of the Oil and Color Chemists Association* (London)
J. physique	*Journal de physique*
J. O. S. A.	*Journal of the Optical Society of America*
J. Phys. Chem.	*Journal of Physical Chemistry*
J. Franklin Inst.	*Journal of the Franklin Institute*
J. prakt. Chem.	*Journal für praktische Chemie*
J. Roy. Microsc. Soc.	*Journal of the Royal Microscopic Society*
J. russ. Chem. Ges.	*Journal der russischen Chemischen Gesellschaft*
J. russ. Physiko-chem. Ges.	*Journal der russischen Physikochemischen Gesellschaft*
J. Russ. Phys. Chem. Soc.	*Journal of the Russian Physical and Chemical Society*
Koll. Beih.	*Kolloidchemische Beihefte*
Koll. Zeit.	*Kolloid Zeitschrift*
Liebig's Ann	*Liebig's Annalen*
Mal. Agr. J.	*Malayan Agricultural Journal*
Mem. Soc. Imp. Nat. Moscow	*Mémoires de la Société Impériale des Naturalistes de Moscow*
Naturw.	*Naturwissenschaften*
Nuovi Ann. sci. nat. Bologna	*Nuovi Annalii di scienze naturale di Bologna*
Oesterr. Chem. Ztg.	*Oesterreiche Chemiker Zeitung*
Phil. Mag.	*Philosophical Magazine* (London)

Phil. Trans. Roy. Soc.	*Philosophical Transaction of the Royal Society of London*
Phys. Rev.	*The Physical Review*
Physikal. Zeit.	*Physikalische Zeitschrift*
Physiol. Rev.	*Physiological Reviews*
Pogg. Ann. Phys.	*Poggendorff's Annalen der Physik*
Proc. Natl. Acad. Sci.	*Proceedings of the National Academy of Science*
Proc. Roy. Inst.	*Proceedings of the Royal Institute* (London)
Proc. Roy. Soc.	*Proceedings of the Royal Society* (London)
Proc. Soc. Exp. Biol. Med.	*Proceedings of the Society for Experimental Biology and Medicine*
Rec. trav. chim. Pays-Bas	*Receuil des travaux chimiques des Pays-Bas*
Rev. gen. caout.	*Revue générale du caoutchouc*
Rev. Sci. Instr.	*Review for Scientific Instruments*
Sitzber. Akad. Wiss. Muenchen	*Sitzungsberichte der Akademie der Wissenschaften Muenchen*
Sitzber. Akad. Wiss. Wien	*Sitzungsberichte der Wiener Akademie der Wissenschaften*
Sitzber. Preuss. Akad. Wiss.	*Sitzungsberichte der Preussischen Akademie der Wissenschaften* (Berlin)
Trans. Conn. Acad. Sci.	*Transactions of the Connecticut Academy of Science*
Trans. Faraday Soc.	*Transactions of the Faraday Society* (London)
Verh. deut. physikal. Ges.	*Verhandlungen der deutschen physikalischen Gesellschaft*
Wied. Ann.	*Wiedemann's Annalen der Physik*
Zeit. angew. Chem.	*Zeitschrift für angewandte Chemie*
Zeit. anorg. allg. Chem.	*Zeitschrift für anorganische und allgemeine Chemie*
Zeit. anorg. Chem.	*Zeitschrift für Anorganische Chemie*
Zeit. Elektrochem.	*Zeitschrift für Elektrochemie*
Zeit. Krist.	*Zeitschrift für Kristallographie*
Zeit. mikr.-anat. Forschg.	*Zeitschrift für mikroskopische-anatomische Forschung*
Zeit. Pflanz. Düng.	*Zeitschrift für Pflanzen und Düngemittel*
Zeit. Phys.	*Zeitschrift für Physik*
Zeit. physikal. Chem.	*Zeitschrift für physikalische Chemie*
Zeit. techn. Phys.	*Zeitschrift für technische Physik*
Zeit. wiss. Mikros.	*Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik*

TEXTBOOKS ON COLLOID CHEMISTRY

The following is a list of textbooks on colloid chemistry that have appeared in English (either original or in translation).[1]

(The author does not claim this list to be complete.)

Alexander, Jerome: "Colloid Chemistry," 4th ed., D. Van Nostrand Company, Inc., New York, 1937.

———: "Colloid Chemistry—Theoretical and Applied," 4 vol., Reinhold Publishing Corporation, New York, 1926.

Bancroft, Wilder D.: "Applied Colloid Chemistry," 3d ed., McGraw-Hill Book Company, Inc., New York, 1932.

Bogue, Robert H.: "The Theory and Application of Colloidal Behavior," contributed by the foremost authorities in each division of the subject, McGraw-Hill Book Company, Inc., New York, 1924.

Burton, E. F.: "The Physical Properties of Colloidal Solutions," 3d ed., Longmans, Green & Company, New York, 1938.

Buzágh, A. von: "Colloid Systems," The Technical Press, Ltd., London, 1937.

Fischer, Martin H.: "The Lyophilic Colloids," Charles C. Thomas, Springfield, Ill., 1933.

Freundlich, H.: "Colloid and Capillary Chemistry," Methuen & Company, Ltd., London, 1926.

———: "Elements of Colloidal Chemistry," E. P. Dutton & Company, Inc., New York, 1924.

———: "New Conceptions in Colloidal Chemistry," E. P. Dutton & Company, Inc., New York, 1927.

Gortner, R. A.: "Selected Topics in Colloid Chemistry," Cornell University Press, Ithaca, N. Y., 1937.

Hatschek, E.: "An Introduction to the Physics and Chemistry of Colloids," 5th ed., Churchill, London, 1925.

Hedges, E. S.: "Colloids," Longmans, Green, & Company, New York, 1931.

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[1] Laboratory manuals are not included in this list. References to specialized texts will be found in the appropriate chapters.

Holmes, H. N.: "Introductory Colloid Chemistry," John Wiley & Sons, Inc., New York, 1934.

Kruyt, H. R.: "Colloids," John Wiley & Sons, Inc., New York, 1927; 2d ed., 1930.

Marshall, C. E.: "Colloids in Agriculture," Edward Arnold & Company, London, 1935.

Ostwald, Wo.: "An Introduction to Theoretical and Applied Colloid Chemistry," 2d ed., John Wiley & Sons, Inc., New York, 1922.

———: "Handbook of Colloid Chemistry," 2d ed., P. Blakiston's Son & Company, Inc., Philadelphia, 1919.

———: "Practical Colloid Chemistry," E. P. Dutton & Company, Inc., New York, 1924.

Rideal, E. K.: "An Introduction to Surface Chemistry," 2d ed., Cambridge University Press, England, 1930.

The Svedberg: "Colloid Chemistry," 2d ed., Reinhold Publishing Corporation, New York, 1928.

Thomas, Arthur W.: "Colloid Chemistry," McGraw-Hill Book Company, Inc., New York, 1934.

Ware, ~~T. C.~~ John C.: "The Chemistry of the Colloidal State," John Wiley & Sons, Inc., New York, 1930.

Weiser, H. B.: "The Colloidal Salts," McGraw-Hill Book Company, Inc., New York, 1928.

———: "Inorganic Colloid Chemistry," 3 vols., John Wiley & Sons, Inc., New York, 1933, 1935, 1938.

Zsigmondy, R.: "Colloids and the Ultramicroscope," John Wiley & Sons, Inc., New York, 1909.

———: "Chemistry of Colloids," John Wiley & Sons, Inc., New York, 1917.

COLLOIDAL PHENOMENA

CHAPTER I

THE SCIENCE OF COLLOIDS—HISTORICAL DEVELOPMENT

It was Lémery in his book "Cours de chimie," published in 1765, who was the first to distinguish clearly between inorganic and organic compounds. The fact that the latter compounds were found only in animal and plant life prompted the belief, postulated by Berzelius, that the formation of organic compounds is the result of a special power—*vis vitalis*—which is not at our disposal in the laboratories. In 1828, Woehler disproved this theory by his epoch-making synthesis of urea—a typical product of secretion of animal organisms—from cyanic acid and ammonia.[1] Shortly afterward, the synthesis of acetic acid was accomplished. The scope of synthetic organic chemistry, the development of

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[1] There seems to be some uncertainty in the literature as to the actual procedure that F. Woehler followed in synthesizing urea. In his classical publication "On the Artificial Production of Urea" (translated into English by the author), in *Ann. Phys. Chem.*, **12**, 253 (1828), he states that the best results are obtained by decomposing silver—or preferably lead cyanate—with ammonia water. However, in the introduction to this paper he refers to a previous publication, *Ann. Phys. Chem.*, **3**, 177 (1825), being a reprint of a paper originally published in the *Abh. d. K. Akad. der. Wiss. zu Stockholm, H* 11, 271 (1824), with the title "On Cyano-compounds" (translated into English by the author). In this publication, he already mentions the fact that the introduction of gaseous cyanogen into ammonia water results in the formation of (1) ammonium cyanide; (2) a dark-brown carbonlike substance, which so far has not been studied in very great detail; (3) ammonium oxalate; (4) a peculiar crystallized substance which does not seem to be ammonium cyanate. This substance can be produced in a purer form if lead or silver cyanate is decomposed by ammonia. There can be no doubt, therefore, that Woehler obtained urea for the first time by introducing gaseous cyanogen into ammonia. The other, admittedly more satisfactory, reactions were discovered by him somewhat later.

large-scale manufacture of dyestuffs, etc., on the basis of laboratory discoveries are the direct result of Woehler's work.

There was no need to discover colloids. Long before Thomas Graham published the results of his systematic researches on diffusion and coined the most important terms in the vocabulary of the colloid chemist or physicist, their existence was known, and many of their properties were recognized. Therefore, in contradistinction to the organic chemist, who started out on entirely new ventures, the colloid chemist or physicist's task is to interpret existing phenomena and by correlating the findings in other fields to increase our knowledge of the world, whose dimensions have been overlooked for so long.

We know that the Chinese used gelatin or an equivalent as a protective agent in the manufacture of ink. The Egyptians made use of acacia gum (gum arabic) for the same purpose. Glue as an adhesive for veneer was likewise used by the Egyptians. The dispersive action of straw extract on clay slips was known to Jewish masons prior to their exodus from Egypt. But these are only a few random examples in the literature of the past.

The drinkable gold (*aurum potabile*) and other similar metal solutions produced by the alchemists during the Middle Ages are typical examples of colloidal systems. We know today that the tremendous healing power of these medicaments is a result of the extreme comminution in which the elements are present. Their production by reducing gold chloride solutions in the presence of protecting agents, as, for example, ethereal oils, is quite analogous to the methods used today in making gold sols. Back in 1595, Andreas Libeau described in his "Alchemia" the use of gold solutions in the manufacture of red glass. The interesting fact was that, contrary to other coloring methods then known, the color was homogeneously distributed throughout the glass, comparable to natural rubies. This is presumably the first reference to what is known today as gold-ruby-glass, a distribution of colloidal gold in the glass flux.[1]

These alchemistic preparations are discussed for the first time by the French chemist Macquer in his book "Dictionnaire de chymie," Paris, 1774, wherein he voices the opinion, which, however, he does not prove, that we are dealing here with extremely fine comminuted particles of the actual metal and not with true

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[1] For more detailed references see A. CORNEYO, *Koll. Zeit.*, **12**, 1 (1913).

solutions. The term "drinkable" only gives vivid description to the fluidity of these preparations. Several years after, in 1779, T. Bergmann[1] mentions the fact that precipitates from sodium silicate solutions formed upon the addition of acids can be retained in suspension for practically indefinite periods, provided they are appropriately diluted. Unquestionably, he had produced colloidal silicic acid. The production of colloidal gold *in situ* in the dyeing of silk can be traced back to at least 1794.[2]

Robert Brown, the English botanist, discovered, in 1827, that extremely small particles when suspended in a liquid perform a chaotic, zigzag movement seemingly never ceasing and uninfluenced by any factor outside the system.[3] This movement, which later was termed "Brownian movement" and still later "Brownian molecular motion," has become one of the most important phenomena in the study of "colloidal solutions."

In 1843, the Swedish chemist Berzelius describes arsenium trisulphide solutions of different color shading. From his experiments he deducted that he was not dealing with a true solution but that the arsenium trisulphide must be present in the form of transparent discrete particles. The German chemist Dr. F. M. Ascherson[4] investigated the formation of oil emulsions in water in the presence of traces of albumin. During the year 1838, he discovered by means of a special microscopic technique, which can be considered as a forerunner of the ultramicroscope, that the albumin coats the oil droplets. The protective film thus produced was termed the "haptogen membrane."

Alexandre Baudrimont[5] devotes in his "General Treatise of Chemistry" (1844–1846) for the first time a special chapter to a group of compositions that he terms "particular substances." The substances that he is referring to are today all well-recognized colloids.

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[1] See P. Walden, *Koll. Zeit.*, 6, 233 (1910).

[2] J. Alexander, "Colloid Chemistry," 4th ed., D. Van Nostrand Company, Inc., New York, 1937.

[3] *Phil. Mag.*, 4 (1), 101 (1828); 6, 161 (1829); 8, 41 (1830).

[4] From a reprint of the original paper to be found on p. 13, in "The Foundations of Colloid Chemistry, Selections of Early Papers Bearing on the Subject," edited by Emil Hatschek, Ernest Benn, Ltd., London, 1925.

[5] "Traité de chimie générale et expérimentale," vol. I, p. 82; vol. II, p. 842–850, Paris, 1844–1846. See also P. Baby. "Les origines de la chimie colloidale: A. Baudrimont," Paris, 1928.

At about the same time, the Italian chemist Francesco Selmi, of Bologna, published two papers of exceptional importance. The first[1] dealing with the demulsion of silver chloride refers to colloidal silver chloride sols. The second paper entitled "Pseudosolution of Prussian Blue and of the Influence of Salts in Destroying Them"[2] is of importance in so far as he clearly differentiates in this publication for the first time between "solutions" and "pseudosolutions," the latter, such as Prussian blue, exhibiting particular properties.[3] This is followed by a publication of Ascanio Sobrero and Francesco Selmi on the "Products of Decomposition of Sulphurated Hydrogen and Sulphurous Acid in Aqueous Solution." This paper was read at a meeting of the Academy of Sciences in Turin, on June 11, 1849.[4] Selmi and his collaborators most certainly already had fully recognized the peculiar properties that matter exhibits under certain conditions, as can be gathered from a passage quoted from the paper last mentioned:

> . . . the state in which the sulfur exists can therefore be changed by the presence of substances in the medium in which it deposits. It retains these bodies very firmly, most presumably by simple adhesion; the sulfur may thus form an emulsion or aggregate in such a way that it does not further subdivide itself in water. The emulsifiable sulfur exhibits phenomena similar to those found with many other substances, which have the peculiar property of desintegrating in a liquid, without completely dissolving in it, as for example, soap, starch pastes, prussian blue, etc., about which one of us (F. Selmi) has already reported. These phenomena belong to a group which Mr. Selmi has well characterized and to which he has given the name of "pseudosolutions." It seems that the number of "pseudo-soluble" bodies is fairly large and the organic bodies seem to us to be of exceptional interest from this point of view. . . .

However, Selmi and his school did not probe further into these peculiarities, and as a consequence his contributions were soon forgotten. Other publications which seem to have been overlooked for a long time are the important contributions by Jeremias

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[1] *Nuovi Ann. sci. nat.*, Bologna, 4, (2), 146 (1845).

[2] *Nuovi Ann. sci. nat.*, Bologna, 8, 401 (1847).

[3] See also I. GUARESCHI, "The Pseudosolutions of F. Selmi," *Koll. Zeit.*, 8, 113 (1911).

[4] A. SOBRERO and F. SELMI, *Ann. chim. phys.*, 28, 210 (1850).

Benjamin Richter in regard to "pseudosolutions" of gold and gold purple.[1] So far, the existence of discrete solid particles in such pseudosolutions was an assumption based solely on logical deductions of the experimenter. The actual proof of their existence must be credited to Michael Faraday. In a paper entitled "Experimental Relations of Gold (and Other Metals) to Light,"[2] he discusses the preparation of what we today know to be colloidal gold. He obtained this by adding to a gold chloride solution a few drops of phosphorus dissolved in sulphide of carbon. This results in a reduction to elementary gold, giving the liquid the typical red color. Faraday points out that an excess of sulphide and phosphorus causes a clotting of the gold, which then sinks to the bottom. He then describes in the same publication that the heterogeneity of the seemingly clear liquid can be demonstrated by passing a concentrated beam of light through the solution, the latter preferably placed in a container with plain parallel glass walls. Whereas in the case of pure solutions like water, or the solution of salts, the entire liquid at best is uniformly brightened, the beam becomes clearly visible in the form of a cone in cases where discrete particles are distributed in the liquid (Fig. 1). All of us have experienced this phenomenon again and again when a streak of sunlight passes through a drawn window shade or when the projection machine in a darkened cinema begins to throw the picture on the screen.

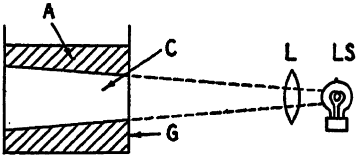

FIG. 1.—Faraday-Tyndall cone. *LS*, light source; *L*, optical lens; *G*, glass container; *A*, colloidal sol; *C*, light cone.

The reason for this phenomenon is explained by the fact that the millions of dust particles suspended in the air or the millions of discrete solid particles suspended in what Selmi termed pseudosolutions scatter and reflect the impinging light. Their extreme smallness, their great number per unit area of space, which is synonymous with exceedingly short distances from one to the other, and the weak intensity of the light reflected by an individual particle make the differentiation of a single particle impos-

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[1] See WILH. OSTWALD, *Koll. Zeit.*, **4**, 5 (1909).

[2] *Phil. Trans. Roy. Soc.*, **147**, 145 (1857); *Phil. Mag.*, **14**, (4) 402 (1857); *Proc. Roy. Inst.*, **2**, 310, 444 (1854–1858). See also R. ZSIGMONDY, "Colloids and the Ultramicroscope," John Wiley & Sons, Inc., New York, 1909.

sible for the naked eye. What we see is the sum of these innumerable reflections. A few years later, another English physicist, Sir John Tyndall,[1] made use of this discovery in a systematic study of liquids, as well as of gases, containing extremely minute particles in suspension. The phenomenon has since been known as the Faraday-Tyndall phenomenon, and the light cone made visible in such systems is generally referred to as the "Tyndall cone."

Although not directly connected with the study of pseudosolutions or the like, reference must here be made from the standpoint of chronology to observations generally attributed to Quincke, because of their bearing on the electric properties of colloids. He found that fine particles suspended in a liquid will migrate in an electric field, a phenomenon today known as "cataphoresis," and that, when a stationary membrane containing many capillaries or pores is placed in a container, the water will migrate from one side to the other in the electric field (electroendosmosis). He also found that, if a liquid is forced through a porous membrane or a capillary, a potential difference is set up between the opposite sides of the membrane.[2] The phenomenon of endosmosis, as well as that of cataphoresis, had previously been reported in research on clay suspensions by F. Reuss in 1809[3] but was seemingly forgotten.

Graham's Work.—Many principles of colloids were known and applied for many centuries, but it was Thomas Graham, F.R.S., who laid the scientific foundation of colloid chemistry. Graham discusses the characteristics of colloids and the colloidal condition of matter and offers at the same time a great part of the nomenclature still in use today. He published two papers,[4] the first of which must be regarded as the actual cornerstone of systematic colloidal research. In those days, Graham was particularly interested in studying the diffusive power of liquids, his purpose being to establish differences comparable to the various degrees

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[1] *Proc. Roy. Soc.*, **17**, 223 (1868). We owe to Tyndall the discovery that the reflected light is plane polarized.

[2] *Ann. Phys. Chem.*, **113**, 513 (1861); *Pogg. Ann. Phys.*, **107**, 1 (1859); **110**, 38 (1860).

[3] *Mem. Soc. Imp. Nat. Moscow*, **2**, 237 (1809).

[4] "Liquid Diffusion Applied to Analysis," *Phil. Trans. Roy. Soc.*, **151**, Part I, 183–224 (1861); "On the Properties of Silicic Acid and Other Analogous Colloidal Substances," *Proc. Roy. Soc.*, **13**, 335 (1864).

of volatility. In his publication, Graham states: "The range also in the degree of diffusive mobility exhibited by different substances appears to be as wide as the scale of vapor tensions." By studying a great number of substances in regard to their diffusivity, he originally drew a distinction between substances that he classified as "volatile" and as "fixed." The respective passage of Graham's paper reads:

> 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 peroxides of the aluminous class, when they exist in the soluble form; with starch, dextrin, and the gums, caramel, tannin, albumen, gelatine, 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 the 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 gelatine appears to be its type, it is proposed to designate substances of the 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 term "colloid" is taken from the Greek expressions *κόλλα* (*kolla*) meaning glue and *ειδος* (*eidos*) meaning like. In the literature following Graham's first publications, one frequently finds statements to the effect that he was of the opinion that certain substances are colloids and others crystalloids. Such assumption seems unjustified in the light of certain passages in his first paper, as for example:

> 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.)

As a method of separation by diffusion, Graham used a parchment membrane and termed the process *dialysis* (taken from the Greek expression for "to dissolve through"). Although, as we shall see, today's definition for colloids had to be amended materially over Graham's original one, at least he certainly had an amazingly clear vision of the formation of matter in the colloidal state. This is demonstrated by another passage from Graham's first publication (page 221). It reads:

> 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 colloidality may not really be this composite character of the molecule. . . .

And it becomes even more evident from the following passages taken from his second paper:

> A dominating quality of colloids is the tendency of their particles to adhere, aggregate, and contract. This idio-attraction is obvious in the gradual thickening of the liquid and when it advances leads to pectization.[1] . . . Bearing in mind, that the colloidal phasis of matter is the result of a peculiar attraction and aggregation of molecules, properties never entirely absent from matter, but greatly more developed in some substances than in others, it is not surprising that colloidal characters spread on both sides into the liquid and solid conditions. . . .

The Pioneer Work of Others.—In the years following Graham's first discussion of colloids and the methods of their preparation, almost all the work reported is concerned with the production of a great number of colloidal preparations. Special reference should be made to the work of men like G. Bredig, A. Coehn, H. Schulze, Spring, Winssinger, Ebell, O. Loew, Muthmann, Lobry de Bruyn, Zsigmondy, Lottermoser, and many others.[2] One of the most comprehensive and important papers of this period is a contribution by M. Carey Lea, "On Allotropic Forms

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[1] *Pectization* is Graham's term for what today is known as gelling.

[2] A detailed and fairly complete reference to these publications can be taken from R. Zsigmondy, "Colloids and the Ultramicroscope," John Wiley & Sons, Inc., New York, 1909.

of Silver."[1] This paper reaches the conclusion already indicated by its title that silver is capable of existing in allotropic forms possessing qualities differing greatly from those of normal silver. Carey Lea makes the following statement:

> These allotropic forms of silver are broadly distinguished from normal silver by color, by properties and by chemical reactions. They not improbably represent a more active condition of silver, of which common or normal silver may be a polimerized form. Something analogous has already been observed with other metals, lead, copper. . . .

In his paper, Carey Lea criticizes the assumption of previous research workers, as, for example, Faraday, Newbury, Muthmann, and others, who consider such silver or other metal-containing liquids as suspensions of solid silver present in extremely fine comminution. Although Carey Lea's work was, as we shall see, considered outstanding in its days, the objective chronologist will undoubtedly credit Wilhelm Muthmann as being the first to discuss properties and preparations of colloidal silver. The respective paper carries the title "The Question of the Silver Suboxide Compounds."[2] In this paper, we find a statement of historical interest to the colloid chemist. Having discussed the effect of charcoal on a highly colored silver suboxide solution and pointed out that adsorption of crystallizing substances by charcoal was known to him, Muthmann says:

> Still, the experiments quoted appear to me to prove that the red color is caused by metallic silver. Nevertheless the phenomenon, which is of great interest in any case, was further investigated by submitting a quantity of the red solution to dialysis.
>
> As was to be expected, no trace of the red substance passed through the membrane, but fairly considerable quantities of normal salt and of ammonia. . . . The remaining red liquid after filtration still showed an intense red color and the same properties as the original solution. . . . All together the solution thus freed from foreign admixtures had become much more stable if the expression is permissible. After standing for four months in a closed vessel in a warm place, it has not deposited any metallic silver.[3] . . . That the color is caused by a body suspended

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[1] *Am. J. Sc.*, **37**, 476 (1889); **38**, 47, 129, 237, 241 (1889); **41**, 179 (1891).

[2] *Ber.*, **20**, 983 (1887).

[3] This is the first known reference to the application of dialysis to a metal sol. (The author.)

and not dissolved in the liquid is proved further by the following experiments. . . .

An attempt to explain adequately these peculiar phenomena would seem premature. W. Stein (*J. prakt. Chem.*, **2**, 6, 172) who considers the so-called gold purple to be finely divided metal, ascribes the differences between these modifications and the so-called *dichroitic gold* to a smaller size of the molecules; and it is not impossible that the various modifications of silver observed by me correspond to various molecular states. . . .

The "Heterogeneous" Theory.—As mentioned, these papers were chiefly concerned with a description and discussion of the production or preparation of colloidal solutions. If considered at all, references to the condition of the compound distributed in the liquid system must be considered as speculations or assumptions based on not too strong experimental evidence or theoretical deductions. The first paper specifically directed toward a final decision as to the actual nature of colloidal solutions was published by Carl Barus and E. A. Schneider, in 1891, with the title "Ueber die Natur der kolloidalen Loesungen" (On the Nature of Colloidal Solutions).[1] This paper, which emphatically disagrees with the assumption that we are dealing with allotropic modifications of the substance in question when discussing colloidal solutions, must be considered as a turning point in the development of colloid chemistry and as the start of one of the most persistent debates in the science of colloids. As the result of very thorough experimental efforts and detailed theoretical argumentations, the authors assume, in comparing the properties of the colloidal silver solutions and those of clay suspensions, as well as on the basis of other experimental facts, that sufficient evidence is now available to prove that the silver is present in a fine state of subdivision. Colloidal solutions can be considered as true suspensions in which sedimentation is governed by the well-established mechanical laws for falling bodies.

The authors conclude their paper with the following statement:

> Summing up all facts we feel entitled to conclude that the assumption that colloidal silver consists of extremely finely comminuted particles of normal silver, which due to the viscosity of the solvent are constantly

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[1] *Zeit. physikal. Chem.*, **8**, 278 (1891).

retained in suspension, is in no way contrary to the properties of colloidal solutions. Since no necessity exists any longer to assume an allotropic molecule, it is simpler to adhere to the normal molecule. The same holds good for colloidal solutions in general. . . .

This paper constitutes the basic contribution for the *heterogeneous theory* of the colloidal state. This attitude was further emphasized in later years by men like G. Bredig,[1] Wernicke,[2] K. Stoeckl, L. Vanino, A. Coehn, and others.

The "Allotropic," or "Solution," Theory.—Those who favored the *allotropic theory* found their platform in a series of papers by Harold Picton and by H. Picton and S. Ernest Linder.[3]

In the summary to the second paper, which discusses the preparation of sulphide solutions of mercury, antimony, and arsenic, all revealing the presence of minute solid particles by Tyndall's experiment, one finds the following important statement:

> Arsenic sulphide is capable of existing in a state of suspension so perfect as to simulate the phenomenon of liquid diffusion, but yet revealing solid particles by Tyndall's experiment, it is easy to conceive of a case in which the process of subdivision has gone still further, and Tyndall's experiment is no longer adequate to discover the suspended particles. Passing on from this, there seems no satisfactory reason for imagining the existence of any sharp boundary between solution and pseudosolution. It is quite possible that the one merges by imperceptible gradations into the other. In this event, the vibratory motion of these minute particles, which so forcibly reminds one of molecular motion,[4] becomes a phenomenon of special interest. . . .

From the third paper, which criticizes the opinion of Wilh. Ostwald,[5] Paternò,[6] and Barus and Schneider[7] that colloidal

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[1] "Anorganische Fermente," Leipzig, 1901.

[2] *Wied. Ann.*, **52**, 515 (1894).

[3] S. E. LINDER and H. PICTON, "Some Metallic Hydrosulphides," *J. Chem. Soc.*, **61** (*Transactions*), 114 (1892). H. PICTON, "The Physical Constitution of Some Sulphide Solutions," *ibid.*, p. 137. See particularly H. PICTON and S. ERNEST LINDER, "Solution and Pseudosolution," *ibid.*, Part I, p. 148.

[4] The historical importance of this statement will become evident when discussing the Brownian molecular movement as first direct experimental proof for the kinetic gas theory. (The author.)

[5] "Lehrbuch der Allgemeinen Chemie," 2d ed., vol. 1, p. 527, Wilh. Engelmann, Leipzig (1891).

[6] *Zeit. physikal. Chem.*, **4**, 457 (1889).

[7] *Zeit. physikal. Chem.*, **8**, 278 (1891).

solutions are probably composed of very finely divided solids in the state of suspension, the following passages are quoted to express the opinion of these authors in the clearest way:

> It seems to us that in the preceding part of this paper we have made out at least a good prima facie case for the belief that between obvious suspension and crystallizable solution there is no break in the series of grades of solution. We have seen that colloidal solution in many ways resembles liquid containing solid particles in suspension. We have seen that we can pass from solution in which these particles are visible under the microscope to those in which they are invisible, but indiffusible, and thence to those invisible and diffusible. . . . Further up the series we find evidence, as in silicic acid, of colloids in a still finer state of subdivision, and giving no positive evidence of the presence of solid particles. . . . The electric evidence is also of great interest from the point of view of the general theory of solution.[1] . . . It may be that the aggregates in these solutions are in an electrified condition, but on this subject it would be rash to dogmatize at present. . . . Throughout the above argument we have necessarily been assuming, what must now be fully stated, that these fine particles revealed by the luminous beam are simply large molecular aggregates, and retain many of their molecular properties. As wholes they can enter into loose combination and as wholes they can attract each other with gradual formation of larger aggregates. . . . Enormous as must in all probability be the number of molecules associated to form a visible aggregate, yet as the transition from them to states of undoubted molecular subdivision seems perfectly continuous, we can scarcely avoid the conclusion that this vibratory motion is one of the molecular properties still retained by them, and that what we are here observing is simply molecular vibration. On the other hand, it might be conceived that these oscillations are due to the impacts of the liquid molecules. . . . Our main conclusion, therefore is that from first to last, from pseudosolution to crystalloidal solution we are concerned with chemical as well as with physical forces and that the progress from the lower to the higher terms of the series is accompanied by increasing fineness of subdivision of the dissolved matter and by increasing definiteness in the action of the chemical forces. . . .

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[1] Seemingly unaware of the work of Quincke and others, the authors describe in their publication electrophoretic experiments. Not being able to detect actual particles and not finding any signs of particle aggregation but simply being able to assume some change in the system by a shift in color from one electrode to the other, they drew a direct analogy to the ionic transfer in acidified water. (The author.)

The *allotropic or solution theory*, as first summed up by Picton and Linder, found further support in men like Schulze, Grimaux,[1] G. Bruni, N. Pappadá, P. D. Zacharias, Calcar, Lobry de Bruyn,[2] Konowalow,[3] R. Zsigmondy,[4] and many others. Although, when looked at from our present-day concept of colloidal phenomena, the argument resulting from these then seemingly incompatible opinions can easily be considered as valueless, it must be pointed out that on its decision depended what we may justifiably term today the basis for the modern concept of colloidal science. Are colloidal solutions heterogeneous or homogeneous in the general sense of these terms? Do colloidal solutions follow the simple mechanics of ordinary suspensions, or are they governed by the fundamental laws of molecular or true solutions? These were the dominant questions at stake.[5]

The Ultramicroscope—Zsigmondy's Work.—Some may think it an ironical fact that the man who was one of the most ardent supporters of the solution theory, R. Zsigmondy, was also he who by pure logical reasoning and strict adherence to the truth of experimental evidence discovered experimental means to solve the problem to a large extent and prove the heterogeneity of colloidal solutions. No one can describe, better than himself, the reasoning that led him, in collaboration with H. Siedentopf, to the construction of the ultramicroscope[6] and to the first observations with the use of this new optical equipment[7]:

> Since these fluids [Zsigmondy is referring to colloidal gold solutions which he had prepared and systematically studied] showed, in general, the mutual properties, and could in practice be differentiated from each other only by their greater or lesser turbidity, I assumed that turbidity

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[1] "Colloides" (Dictionnaire de Wurtz), 2d supplément, vol. 1, p. 1257, 1894.

[2] *Rec. trav. chim. Pays-Bas*, **23**, 218 (1904).

[3] *Zeit. physikal. Chem.*, **33**, 63 (1900); *Drude's Ann.* (*Ann. Phys.*), **10**, 360 (1903); **12**, 1160 (1903).

[4] *Liebig's Ann.*, **301**, 53 (1898); *Zeit. physikal. Chem.*, **33**, 63 (1900); *Zeit. Elektrochem.*, **8**, 684 (1902). A summary of his opinions is published in *Verh. deut. physikal. Ges.*, **5**, 209 (1903); *Koll. Zeit.*, **26**, 1 (1920).

[5] See also Wo. Ostwald, *Koll. Zeit.*, **84**, 258 (1938).

[6] *Drude's Ann.* (*Ann. Phys.*), **10**, 1–39 (1903). H. Siedentopf, *J. Roy. Microsc. Soc.*, 573 (1903).

[7] Zsigmondy, *loc. cit.*

> is not an essential, but an incidental characteristic of colloidal gold solutions, occasioned by the presence of larger particles. . . . The addition of a minute quantity of the very turbid fluid to the perfectly clear one sufficed to endow the latter with the polarized dispersion of the former, as evidenced by means of the light cone; and this made evident how small a quantity of coarse gold particles is necessary to produce in a gold solution assumed to be homogeneous, the diffuse dispersion referred to. . . .
>
> It must be acknowledged, however, that although the facts above referred to were favorable to my view, they gave no evidence of the existence of an optically clear gold solution. I hoped to be able to find out the truth by microscopical examination of the cone of light. . . .

The microscopical experiment actually proved that the difference in turbidity and color of gold sols is due to different sizes of the suspended particles. Zsigmondy says that this result, which contradicts the view earlier advanced by him, is of great significance in judging colloidal solutions in general. Based on the work of Faraday and Tyndall and the observations of Fizeau[1] and Ambronn[2] on the detectability of extremely narrow slits of light, he reasoned as follows:

> It seemed to me probable that the larger particles assumed to be present in gold hydrosols, whose previously mentioned property of dispersing transmitted light was known to me by the above experiments, could be made individually perceptible by a microscopic examination of the light cone; for if the small particles reflected enough sunlight, even if their size was below the limit of microscopic resolvability, they would, just as were the narrow rays of light, be individually perceptible under the microscope and act to a certain extent as fragments of such light slits. The microscopical investigation should also allow me to determine if the space between the coarser individual particles was optically clear or filled with smaller gold particles.

As early as in April, 1900, Zsigmondy was able to perceive the presence of individual particles in solutions of glue, gelatin, tragacanth, gold, silver, etc., by using an apparatus as assembled in Fig. 2. The magnification was extremely small, about 32× linear, and results obtained were not fully satisfactory.[3] Never-

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[1] *Pogg. Ann. Phys.*, **116**, 478 (1862).

[2] *Wied. Ann.*, **48**, 217 (1893).

[3] Side illumination and a magnification of 30 diameters had already been applied by Quincke in the microscopic study of starch grains. *Pogg. Ann., Phys.*, **113**, 568 (1861).

theless, the principle of the new method was established. This primitive instrument was now further improved and put on a sound optical basis in close collaboration with H. Siedentopf, the scientific adviser of the world-famous Carl Zeiss Works in Jena (Germany).[1]

Those who have had occasion to observe a colloidal gold solution under the ultramicroscope will appreciate the vivid description of the phenomenon given by Zsigmondy in one of his lectures shortly after his epoch-making discovery.[2] Having pointed out that large gold particles float quietly in the fluid and slowly sink to the bottom or else show only an unimportant Brownian movement and that, by considering colloidal solutions as suspensions, one would naturally imagine that the gold particles in these, too, would be as quiet as those in the real suspensions, he added:

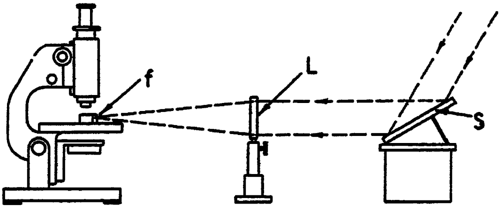

FIG. 2.—Zsigmondy's original ultramicroscope. *S*, reflecting mirror; *L*, collecting lens; *f*, preparation in focal point.

> How entirely erroneous was this idea! The small gold particles no longer float, they move—and that with astonishing rapidity. A swarm of dancing gnats in a sunbeam will give one an idea of the motion of the gold particles in the hydrosol of gold! They hop, dance, jump, dash together, and fly away from each other, so that it is difficult in the whirl to get one's bearings. . . .
>
> This motion gives an indication of the continuous mixing up of the fluid, and it lasts hours, weeks, months, and if the fluid is stable, even years. . . .
>
> Sluggish and slow in comparison is the analogous Brownian movement of the larger gold particles in the fluid, which are the transition forms to ordinary gold that settles. . . .

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[1] SIEDENTOPF and ZSIGMONDY, *loc. cit.* SIEDENTOPF, *Berliner klinische Wochenschrift* 32 (1904); "Druckschriften-Verzeichnis der optischen Werkstaette von C. Zeiss," Sign. M., 164, Jena (1904).

[2] ZSIGMONDY, *op. cit.*, Chap. X.

Not only did the invention of the ultramicroscope increase the range of visibility from about 500 mμ[1] down to dimensions of only a few millimicrons, but it also established the following facts of general importance to natural science:

1. That colloidal solutions must classify as heterogeneous systems in so far as their noncoherent particles, microscopically invisible but detectable in the ultramicroscope, are suspended in a medium. The size of these particles is below 10^{-4} cm. and above 10^{-7} sq. cm.

2. That, since the Brownian motion of the ultramicroscopically visible particles can be considered as a thermal movement following the same laws as deducible from the kinetic-gas theory, ultramicroscopy must be accepted as the first actual experimental proof that the kinetic-gas theory with all its conclusions stands to fact. However, this implies that the molecules may no longer be considered as abstract but that they are actual realities. The particles of a colloidal solution act like noncoherent molecules—they diffuse, they sediment, they create osmotic pressure. Only on the basis of ultramicroscopic observations could these facts be studied and mathematically evaluated by men like Jean Perrin,[3] The Svedberg,[4] M. v. Smoluchowski,[5] A. Einstein,[6] and others.

3. That experimental proof could be offered for the energy-distribution law of Boltzmann-Maxwell.[7]

Zsigmondy's development of the principle of ultramicroscopy is one of the most striking examples of the importance and values to be obtained from systematic and strictly logical reasoning. It demonstrates how one can make for one's own purposes the best

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[1] 1 mμ = 1 millimicron = 1 ten-millionth of a centimeter, or 0.000000039 inch.

[2] 0.00005 to 0.0000001 cm.

[3] *C. r. Soc. Biol.*, **146**, 967 (1908); **147**, 475, 530, 594 (1908); **152**, 1380 (1911). *Ann. chim. phys.*, **18** (8), 5 (1909). *Zeit. physikal. Chem.*, **87**, 366 (1914). "Brownian Movement and Molecular Reality," London, 1910. PERRIN-LOTTERMOSER, "Die Atome," Dresden, 1914.

[4] *Zeit. Elektrochem.*, **12**, 853, 909 (1906). "Die Existenz der Moleküle," Leipzig, 1912.

[5] *Ann. Phys.*, **21** (4), 756 (1906).

[6] *Ann. Phys.*, **17** (4), 549 (1905); **19**, 371 (1906). *Zeit. Elektrochem.*, **13**, 41 (1907); **14**, 235 (1908).

[7] Reference is made to M. v. SMOLUCHOWSKI, *Sitzber. Akad. Wiss., Wien, Math.-Naturwiss.*, Kl. II., **123**, 2381 (1914)· **124**, 263, 339 (1915). *Physikal. Zeit.*, **16**, 321 (1915); **17**, 557 (1916).

use of observations that have originated in entirely different branches of science.

With the invention of the ultramicroscope the study of colloidal phenomena has entered into an entirely new era, and this discovery can be considered as the actual beginning of all modern research in the field of colloidal science.[1]

The foregoing pages have undoubtedly shown the vast amount of information and knowledge already existing on the subject, and due credit must be given to the pioneers in this field for the multitude of collected experimental data, as well as for many assumptions and predictions. The latter seem to be even more characteristic of the strict logical reasoning typical for those days when we realize that these scientists lacked the essential tools necessary to prove their theoretical deductions.

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[1] For a recent discussion of new results and problems in colloidal research see, *e.g.*, P. A. Thiessen, *Zeit. angew. Chem.*, **51**, 318 (1938).

CHAPTER II

THE DISPERSE STATE OF MATTER—THE COLLOIDAL STATE, A GENERALITY

Graham differentiated between colloids and crystalloids according to the diffusivity of their solutions.

Picton and Linder had demonstrated that the same chemical compound (arsenium trisulphide in solution) can exhibit varying degrees of diffusivity, so that Graham's differentiation seemed insufficient. Sabanejew[1] tried to classify the different substances or their solutions by the difference in molecular weight—a very arbitrary proposition even for those days. A. Mueller[2] proposed a division in suspensions of fine particles and solutions of high-molecular compounds. H. Bechhold[3] differentiated between organic and inorganic colloids.

All their theories, as well as those previously referred to in the preceding chapter, culminate in the necessity of differentiating the systems by the size of their particles.

Depending on the point of view taken by the different authors, colloids were considered as belonging either to the group of mechanical suspensions or to molecular solutions.[4] A typical dualistic point of view resulted.

$$\mathrlap{\underbrace{\phantom{\text{Mechanical suspensions}\quad\text{Colloids}}}}\text{Mechanical suspensions}\quad\overbrace{\text{Colloids}\quad\text{Molecular solutions}}$$

When Zsigmondy, one of the strongest supporters of the solution theory, proved with the use of the ultramicroscope that individual gold particles can thereby be made visible, even in what was so far considered as a perfectly clear solution, the heterogeneity of colloidal dispersions seemed definitely established. However, these findings, if viewed in retrospect, have

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[1] *Beibl. Ann. Phys. Chem.*, **15**, 755 (1892).

[2] *Zeit. anorg. Chem.*, **36**, 340 (1903).

[3] *Zeit. physikal. Chem.*, **48**, 385 (1904).

[4] A solution in this connection is considered as a molecular distribution of one substance in another.

demonstrated the existence of a heterogeneous system only by the use of a new research tool. They have undoubtedly assisted in the evaluation of the optical properties of colloidal solutions. But they have not permitted giving a general classification of colloidal solutions in regard to the majority of their properties.

W. B. Hardy[1] differentiated between reversible and irreversible colloids, depending on the results of certain precipitation reactions. A. A. Noyes[2] distinguished between "viscous, gelatinizing colloidal mixtures not easily coagulated by salts" and "non-viscous, non-gelatinizing, but readily coagulable mixtures" which he termed "colloidal suspensions." In a similar way did J. Perrin[3] distinguish "colloides hydrophiles" and "hydrosols stables." We also find in the older literature discriminations as to the dispersion medium, as to the sign of charge, viscosity, etc. However, none of these classifications is capable of general applicability. For example, some of the arsenium trisulphide solutions of Picton and Linder exhibit a very marked rate of diffusion. Since various factors are known to influence particle size, a systematology of colloids in regard to their particle size alone is unsatisfactory. Hardy's classification also is insufficient, because we know of cases where colloids classified by him as irreversible can be redispersed into colloidal solutions.

Most of these classifications are justifiable only if taken to represent a very limited group of properties. The main difficulty in obtaining a complete and universally acceptable nomenclature of colloidal solution. lies in the amazing variety of phenomena characteristic for this field.

The Disperse State of Matter

If we analyzed the entire complex, we should have drawn the conclusion that colloidal solutions at that time could be considered definitely as heterogeneous or multiphase systems.

Wo. Ostwald[4] must receive everlasting credit for having introduced the "heterogeneity of matter" or "the disperse state of matter" as the general point of view, the colloidal state being one step in the series, extending from matter in the coarse state

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[1] *Zeit. physikal. Chem.*, **33**, 326 (1900).

[2] *J. Am. Chem. Soc.*, **27**, 85 (1905).

[3] *J. chim. phys.*, **3**, 50, 84 (1905).

[4] *Koll. Zeit.*, **1**, 291, 331 (1906).

through microscopically detectable solutions to the colloidal state and further down to truly molecular solutions. In his book "An Introduction to Theoretical and Applied Colloid Chemistry,"[1] better known under the descriptive title of the first German edition "The World of Neglected Dimensions," he sums up his point of view with the following statement:

> Modern Colloid Chemistry teaches that there are no sharp differences between mechanical suspensions, colloid solutions and molecular solutions. There is gradual and continuous transition from the first through the second to the third. It is best to regard all three from the same viewpoint and first to emphasize their similarities. After this has been done, their special peculiarities may be taken up.

This conclusion is the result of the following facts proved by colloidal research:

1. That molecules actually exist.
2. That colloidal solutions, as well as mechanical suspensions, contain discrete particles and that therefore both can be considered as disperse systems.
3. That there exists no sharp boundary between mechanical suspensions, colloidal solutions, and true solutions.

Once the fact was established that colloidal solutions must be considered as heterogeneous systems, it seemed of importance to differentiate between two main groups. The general type is characterized by the presence of two or more clearly distinguishable phases whose boundaries are easily detectable. (For example, vapor in contact with a liquid; a sediment at the bottom of the liquid in which the particles originally were suspended.) These systems to which the Gibbs's phase rule specifically applies (for further detail see pages 54*ff.*) are characterized by a larger bulk volume of the phases in comparison to their boundary surface. The special type differs in so far as here the two phases are separated from each other by an exceptionally large surface area. Such a system may be considered as more or less homogeneous, because there is a uniform distribution of the phases in every volume part.

Wo. Ostwald has termed these systems "disperse heterogeneous" systems. Such a terminology naturally called for some limits as to the order of magnitude of the developed surface between the

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[1] See 2d ed., p. 14, John Wiley & Sons, Inc., New York, 1922.

phases in reference to the volume of the dispersed part or phase (specific surface). The principal differences between general and special types of disperse heterogeneous systems are the result of the appearance of special properties as the boundary surfaces are increased. In the case of systems with large specific surfaces they become the outstanding characteristic of such a system. It would seem illogical to postulate any arbitrary limits solely for the purpose of distinguishing between disperse and nondisperse systems. However, if certain properties show a sudden change with variations of specific surface, it then appears justifiable to place an arbitrary limit at this stage. It therefore would seem unreasonable to try to maintain the old idea of sharply differentiating between colloidal and crystalloid solutions by unearthing as many individual differences as possible. Wo. Ostwald was the first to apply a new concept when he set out to describe the existing transitions, between coarse disperse and molecular disperse systems, from a more general point of view.

It is not astonishing that the successful development of the physicochemistry of crystalloid solutions tempted chemists to apply the laws governing them to colloidal solutions, even if considerable discrepancies occasionally had to be considered.

Today it would seem at least equally justifiable to consider the molecular disperse solutions as special cases of disperse systems in general. This all the more since homogeneity of crystalloid solutions is by no means established[1] and the existence of the Faraday-Tyndall phenomenon in highly concentrated crystalloid solutions definitely argues against a perfectly homogeneous system.[2]

However, a simple logical consideration leads to the deduction that molecular disperse systems can also be considered as specific cases of disperse systems in general. In such specific instances, certain properties may have become predominant, and others negligible. Yet it would seem illogical to consider disperse heterogeneous systems generally as special cases of molecular dispersions. Such a deduction, if accepted, must assume that any law that holds for disperse systems in a general way must

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[1] See Lobry de Bruyn, *Rec. trav. chim. Pays-Bas*, **23**, 218 (1904).

[2] See also J. Traube and P. Klein, *Koll. Zeit.*, **29**, 236 (1921). K. Hoffman, *Koll. Zeit.*, **84**, 344 (1938). A. S. C. Lawrence, *J. Roy. Microscop. Soc.*, **58**, 30 (1938). F. C. Frank, *Physikal. Zeit.*, **39**, 530 (1938).

also hold for molecular disperse systems. We need bear in mind only that with increasing degree of dispersion certain properties of the system will preponderate and others will drop to zero significance. This point of view, which, offhand, may still seem rather unconventional to some today, permits a logical explanation, for instance, of why Gibbs's phase rule, van't Hoff's law of solution, etc., do not hold for colloidal dispersions or for normal disperse systems. As will be discussed in detail in one of the following chapters, the former holds good only in such systems where the boundary surface between two phases is negligible in comparison to the volume, and the latter accounts only for extreme dilutions.

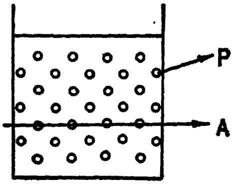

FIG. 3.—Disperse structure. *P*, individual particle in suspension; *A*, imaginary line.

The Disperse Structure.—Wo. Ostwald's aim, based on the arguments just discussed, was to find a general concept for the different systems, to emphasize primarily the properties that they have in common, and to describe on this basis their specific properties, thus eliminating the old argument that had resulted in the dualistic classification once before referred to. *Mechanical suspensions, colloidal solutions, and molecular or true solutions have the disperse state in common.*

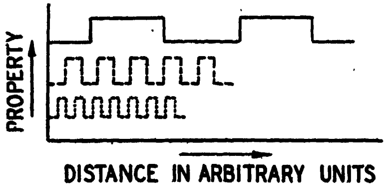

FIG. 3*a*.—Schematic illustration of periodicity in disperse systems. ——— mechanical suspensions; ---- colloidal solutions; . . . molecular or true dispersions.

By disperse structure one understands a system wherein the properties exhibit periodic changes in space along an imaginary straight line drawn through it. Figure 3 is a schematic illustration for this definition. In the three systems under discussion (Fig. 3*a*), the disperse structure is represented by the disperse phase suspended in the form of a varying number of particles in the continuous dispersion medium.

These three systems, all falling according to the given definition under the general heading of disperse systems, differ in their frequency of the periodic changes per unit length along the imaginary line. Mechanical suspensions show a periodic change of a macro- or microscopic order of magnitude. Colloidal solutions have a periodicity of only ultramicroscopically detectable dimensions, whereas the heterogeneity of the true solutions is based on the existence of molecules and atoms. The degree of dispersion increases from mechanical suspensions to true solutions. This shows that colloidal solutions take up an intermediate position.

Dispersed systems

Coarse suspensions — Colloids — Molecular solutions

→ Direction of increasing degree of dispersion

This likewise demonstrates that no definite boundary exists between the different systems and that continuous transitions must exist. If such a systematology is completely analyzed, the results must be that theoretically any substance is capable of existing in this middle degree of dispersion, or, in other words, in the form of a colloidal system.

P. P. v. WEIMARN'S LAW OF PRECIPITATION

Entirely independent of Wo. Ostwald's primarily theoretical deductions, the Russian scientist P. P. von Weimarn conducted, during 1905 to 1907, a series of experiments which offered the necessary experimental proof for Ostwald's statement. Studying the reaction

$$MnSO_4 + Ba(CNS)_2 + aq = Mn(CNS)_2 + BaSO_4 + aq$$

he found that when using sufficiently high concentrations the $BaSO_4$ was precipitated in the form of a jelly,[1] whereas in great dilutions extremely small insoluble crystals were formed in suspension. This observation led to a series of experiments[2] and formed the basis of what today is generally known as the "von Weimarn law of precipitation." A great number (over 200) of precipitates were so produced, it being always possible to obtain extremely fine crystals, coarse flocks, or jellies, depending on the concentration of the reacting substances used.

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[1] *J. russ. Physiko-chem. Ges.*, **37**, 949 (1905).

[2] *Ibid.*, **38**, 263, 466, 624, 933, 938, 1087, 1088, 1089, 1399, 1401 (1906); **39**, 304, 307 (1907).

These results were summarized in von Weimarn's own words:

> This permitted me to ascertain that any clearly crystalline substance can be obtained in the form of a typical jelly as well as in the form of different precipitates, which according to their structure can be considered as intermediate stages of the two extreme cases of forms of precipitates. I have so far found no single exception to these purely experimental results.

As the result of micro- and ultramicroscopic observations, von Weimarn amended the previous statement by saying:

> If we sum up the macroscopic, micro- and ultra-microscopic facts, we are forced to the conclusion that any solid substance (element or compound) can be obtained as well in the form of sols (crystalline suspensions) and jellies, as in the form of different kinds of precipitates that differ from each other only by a different size of the crystalline grain.

In the summary to this first important experimental contribution, we find two basic statements:

> The so-called colloidal, amorphous and crystalloidal states are all together universal (possible) properties of matter. . . . Generally speaking, it follows from these investigations that colloids and crystalloids are by no means two special worlds but that there exist close relations between themselves as well as between them and the gaseous and liquid states of matter.[1]

This basic work was followed up by a sheerly monumental task undertaken with the idea of eventually forming an entirely new concept of the states of matter. The work[2] contains a further abundance of experimental proofs for the statements just mentioned, as well as the first attempts to explain the differences in the precipitates obtained.

The Colloidal State—A General State of Dispersed Matter.—The theoretical deductions of Wo. Ostwald and the experimental results of von Weimarn, Zsigmondy, Picton, and Linder and even

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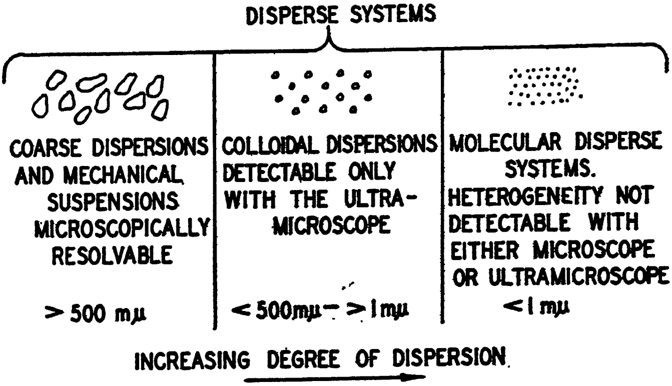
[1] These statements are taken from the first publication of P. P. VON WEIMARN in *Koll. Zeit.*, **2**, 76 (1907); this publication contains a great number of references to previous publications by him as well as other authors.

[2] *Koll. Zeit.*, **2**, 199, 275, 301, 326, I. *Supplementheft* XXVIII; II. *Supplementheft* LII (1907); **3**, 282 (1908); **4**, 27, 123, 198, 252, 315 (1909). See also P. P. VON WEIMARN, "Die Allgemeinheit des Kolloiden Zustandes," Dresden, 1925.

those of Selmi, Berzelius, and others have demonstrated that there exist disperse systems of varying degrees of dispersion and that it is practically impossible to draw a sharp line of demarcation between mechanical suspensions and colloidal solutions or between colloidal solutions and molecular dispersions. This would seem justifiable only if the degree of dispersion, or if a great number of specific properties, were to show a sudden or abrupt change when passing from one type of disperse system into the other. Since no such pronounced change exists, the fixing of any boundaries or lines of demarcation must and should be considered as arbitrary. If such lines have been drawn, it is simply for the purpose of facilitating the grouping of the different systems, but it always should be kept in mind that overlapping cases are not excluded thereby.

The historical development in the science of colloids has resulted in drawing the arbitrary lines of demarcation for the field of colloidal disperse systems by taking as the upper limit the dimension corresponding to the limiting wave length of visible light. This corresponds to the smallest size of a particle that can still be resolved by the ordinary microscope. The dimensions of typical molecules of simple structure were chosen as the lower limit. Therefore today it is the dimensional range between about 500[1] and 1 mμ that is considered as the field of colloidal dimensions.

We can thus picture the entire range of disperse systems as follows:



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[1] 1 mμ = 10^{-7} cm.

CHAPTER III

TERMINOLOGY AND DEFINITIONS[1]

Although the following discussion of the most common terms found in the literature pertaining to colloids and some of its general definitions may detract somewhat from the sequence of the subject matter of this book, nevertheless it seems advisable to make the insertion at this point so that no misinterpretations may arise as to the terms used.

Admittedly a great part of the terminology, even of the most usual words, is rather imperfect, frequently vague, and at times actually misleading. Whenever a new branch of science passes through the early stages of its development, it happens that those engaged in this pioneer research are apt to coin a term for each phenomenon that they consider new. It is only after the development in our knowledge has been sufficiently stabilized that critical analysis can begin to banish unnecessary terms and establish a simpler but nonetheless comprehensive terminology. The science of colloids has been exceptionally prolific in the matter of its terminology, which presumably results from the fact that its scientists originally specialized in different branches of natural science, such as physics, physicochemistry, organic chemistry, biology, and medical chemistry and therefore contributed terms closely related to those with which they were most familiar. Although the development of the science of colloids undoubtedly has come to a point where a simplification of its terminology would be most desirable, very little headway has so far been made in this direction.

We shall mention the most common and important terms found in literature up to the present and at the same time attempt to establish a terminology conforming closer to modern definitions than has hitherto been the case.

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[1] See, *e.g.*, Wo. Ostwald's contribution to A. Kuhn, "Kolloidchemisches Taschenbuch," p. 1, *Akad. Verlagsges.*, *Leipzig*, 1935.

Graham had already differentiated between colloids in liquid form or colloidal solutions by terming them *sols*, and colloids in the solid or gelatinous condition by terming them *gels*. Although these terms are still in use today, our present knowledge calls for a more precise definition. A sol is now considered as the distribution of matter in a liquid medium, its individual particles being of colloidal dimensions. A further characteristic of such a system is that the individual particles are in vivid Brownian motion and that the system will flow under the influence of a differential force. In other words, this means a system that has a zero yield point. We know of cases where such systems will solidify solely owing to a solidification of the dispersion medium, *e.g.*, reduction in temperature, crystallization, etc. In such cases, the Brownian motion of the dispersed phase ceases, owing to the increased viscosity of the dispersion medium, whereby the individual particles are locked into position. In such systems, the disperse phase contributes nothing to the rigidity of the solidified system and therefore has no influence on yield point and the like. The general term for systems answering the definition just given is *solid sols*. As specific examples, one may mention the distribution of colloidal gold in glass, commonly known as ruby-glass. This special type of solid sol is frequently also termed *vitreosol*. The distribution of colloidal gold in molten borax is known as a *pyrosol*. The distribution of a colloidal metal in a crystal, such as colloidal sodium in a sodium chloride crystal, is a *crystallosol*.

Liquid systems in which the solid disperse phase can exist only below its normal freezing point, as, for instance, colloidal ice in chloroform at temperatures around −20°C., are called *kryosols* (from the Greek word κρύος (kruos) for ice cold).

In order more precisely to define a sol as a liquid system, the term *lyosol* has been introduced (derived from the Greek word λύω (lyo), to dissolve). If the dispersion medium is water or a watery solution, the sol is frequently termed a *hydrosol* (derived from the Greek word ὕδωρ (hydor) for water). When the dispersion medium happens to be an organic liquid, the system is usually called an *organosol*. Still more specific terms are *oleosol*, *alcosol*, etc., depending on the liquid used as dispersion medium.

If the colloid to be dispersed swells upon the addition of the dispersion medium or finally even loses its original coherence and goes into a colloidal solution (gelatin in water, or rubber in benzene, etc.), we speak of *lyophilic* sols in general, of *hydrophilic* or *organophilic* sols in particular (the term "philic" is derived from the Greek word φιλος (*philos*), meaning loving). More recently the term *lyo-* (hydro-, organo-)*cratic* has been introduced [the term "cratic" is derived from the Greek κρατέω (*krateo*) meaning to control]. The reason for this new term is the assumption that such sols owe their stability primarily to their affinity toward the dispersion medium.

If, contrary to the foregoing, the disperse phase exhibits no such affinity, does not appreciably swell when brought into contact with the dispersion medium (*e.g.*, colloidal gold in water, graphite in oil), we speak of *lyo-* (hydro-, organo-)*phobic* or *electrocratic* sols.[1] The term "phobic" is derived from the Greek φόβος (*phobos*), meaning fear, whereas the latter is based on the fact that such systems owe their stability primarily to the electric charges of the individual dispersed particles.

Systems consisting of at least two liquids immiscible in each other, in which one is dispersed in the other in the form of droplets of colloidal dimensions, are termed *colloidal emulsions.*[2] Depending on which of the two liquids *A* and *B* is to be considered as the continuous phase or dispersion medium, we have either an *A*-in-*B* or a *B*-in-*A* emulsion (water-in-oil or oil-in-water emulsion). Naturally there are intermediate systems, as, for example, dispersions of waxes or synthetic resins, in water, wherein the correct classification will depend largely on the properties and the actual state of the disperse phase.

Finally, there are systems in which the continuous phase or dispersion medium is a gas, such as smokes, dust, fog, and mist. Such systems are known as *aerosols.*

Today, we understand by *gel* a solid, rigid, and coherent system composed of dispersion medium and disperse part, the latter having particles of colloidal dimensions. In contradistinction to a sol, the particles of the disperse part are at a standstill. Contrary to what has been termed a solid sol, the rigidity of a gel is due primarily to the influence of the disperse part, its particles being held in their position by the interaction of attrac-

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[1] For a recent discussion of hydrophobic colloids see, *e.g.*, H. R. KRUYT, *Chem. Wbl.*, **35**, 44 (1938).

[2] For a recent discussion of emulsions see, *e.g.*, J. L. VAN DER MINNE, *Chem. Wbl.*, **35**, 122, 125 (1938).

tive and repulsive forces. Gels are systems that will exhibit flow only upon the influence of a finite force necessary to overcome the forces holding the particles in place. Therefore, gels are systems with a measurable yield point. Here, again, we can differentiate between *hydro-* and *organogels*, *lyophilic* and *lyocratic gels*, etc.

A *coagel* is a macroscopic, fully dehydrated (desolvated) precipitate of a sol or a gel.

Special types of gels and intermediate systems leading to true coagels will be dealt with separately in the appropriate chapters (see page 162).

Monodisperse systems are those in which the individual particles of the disperse part are practically of uniform dimensions. *Polydisperse* systems are those in which the disperse part consists of particles of different dimensions. *Concentration-variable dispersoids* are systems in which the degree of dispersion decreases with increasing concentration (*e.g.*, soaps, certain dyestuffs). *Temperature-variable dispersoids* are systems where the degree of dispersion changes with variation in temperature (for example, soaps show an increase in their degree of dispersion with increasing temperature).

One frequently finds the expression *highly solvated dispersoids*, which is synonymous for lyophilic; and *poorly solvatized dispersoids*, synonymous for lyophobic. *Heterodispersoids* are systems in which the disperse part and the dispersion medium are chemically different (as in the case of gold sols). *Iso-* (*allo-*) *dispersoids* are systems in which the disperse part and the dispersion medium are polymers, isomers, or allotropic forms of the same basic substance.

Eudispersoids or *eucolloids* are systems in which the colloidal dimensions are obtained by chemical summation of atoms by accumulation of primary or chemical main valencies. Valencies can act either in one direction of space, forming *thread molecules* or *thread micellae*, *e.g.*, in cellulose or rubber; or in two directions, forming *lamellar molecules*, as in the case of graphitic acid.

Further terms and definitions which are less common will be discussed when the occasion arises.

CHAPTER IV

DIFFORM SYSTEMS

In Chap. II, we developed the idea of considering the disperse state of matter under the same general point of view as we have been accustomed to do with the more familiar states, such as the liquid or gaseous, the amorphous or crystalline. The fact has been established that colloidal disperse systems are those in which the ultramicroscopically resolvable discrete particles of one substance are for all practical purposes uniformly distributed in a dispersion medium. So far, our entire discussion and definition of colloidal systems have centered around dispersions characterized by a periodicity, or, in other words, by the size of the corpuscular particles, being of colloidal dimensions. However, it would be a mistake to limit the study of colloidal phenomena exclusively to such disperse systems and to develop separate lines of thought for other systems exhibiting phenomena very similar to those observed with colloidal dispersions, just because they do not fit into the definition of a disperse system. What we again need here is a general point of view which will offer a better understanding of similar phenomena, even if they are observed in systems of entirely different configuration. Again, we owe the basis for this point of view to Wo. *Ostwald*,[1] although empirical recognition of Ostwald's theoretical deductions is all but new.[2]

Ostwald introduced into the discussion the terms of "continuity" and "discontinuity" which have already proved their value often in the philosophical evaluation of natural science.

If we consider space and time as absolute continua, we shall find that whatever is in, or with, them exhibits discontinuities as

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[1] *Koll. Zeit.*, **55**, 257 (1931). See also A. von Buzágh, "Kolloidik," p. 6, T. Steinkopf, Dresden, 1936.

[2] See, *e.g.*, M. Frankenheim, "Die Lehre von der Kohäsion," p. 63, Breslau, 1835. Carl Ludwig, "Lehrbuch der Physiologie," 2d ed., vol. 2, p. 221, Leipzig, 1861. Wilh. Ostwald, "Grundriss der allgemeinen Chemie," 5th ed., p. 518, Leipzig, 1909.

well as continuities. We are dealing with a discontinuity when the parameter or graphical illustration of a functional relationship of physical or chemical data exhibits sudden changes in direction or an abrupt end. It must naturally be kept in mind that such changes, which in graphical illustration will show up as definite kinks in the curves, are relative and depend largely on the accuracy of measurement applied to any observation. Therefore, the term "continuity" or "discontinuity" must also be taken relatively. We frequently observe phenomena which, when macroscopically studied, show abrupt changes over a comparatively small interval of space but when adequately magnified show an absolute continuous change. As an example of this, take the change in density at the interface, liquid-gas. Such relativity is illustrated in Fig. 4. On the other hand, we can conceive of cases where a functional relationship may be considered to be a continuous one, as long as inadequate methods of observation are applied; but when more sensitive instruments are used, the system reveals the presence of a great number of discontinuities. The resolvability of colloidal solutions with the ultramicroscope is a typical example for such a case and is schematically illustrated in Fig. 5.

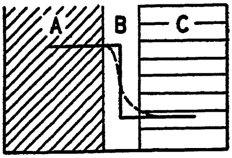

Fig. 4.—The change of density at a liquid/gas interface. *A*, liquid phase; *B*, interface; *C*, gas phase; ——result of macroscopic investigation; ---- result of microscopic investigation.

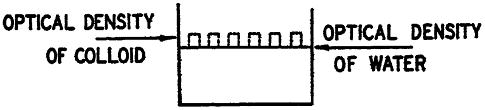

Fig. 5.—Ultramicroscopic resolvability. ——macroscopic and microscopic discontinuities; ---- ultramicroscopic discontinuities.

We know of discontinuities of space, time, and energy. Those of space can be subdivided into two main groups: the discrete or analytical discontinuity of matter and the coarse or obvious discontinuity of matter. Corresponding to these groupings, we can consider the field of the atomistic or molecular doctrine as physics and chemistry of the former; and the study of interfaces, *e.g.*, interfacial tension or potential or adsorption, as the physicochemistry of coarse discontinuities. In the days before the study of colloidal phenomena had revealed the existence of very specific properties, it seemed only logical to assume that a thorough knowledge of the peculiarities of the discrete discontinuities of matter would suffice to explain the properties of coarse discontinuities. However, it was found necessary to differentiate clearly between the structural elements responsible for discrete and coarse discontinuities and the building units of medium discontinuities as represented by the colloidal range of dimensions. Although the colloidal dimensions are arbitrary, colloidal discontinuities are most frequently characterized by very pronounced maxima and minima for different properties.[1]

The following example may illustrate somewhat better the importance of the foregoing deduction. We know that colloidal particles are built with atoms, electrons, etc. In the final analysis, a house or a living organism is also composed of atoms and the like, and in many cases the ultimate building element may be the same in the two. Nevertheless, such a purely atomistic analysis is insufficient as a satisfactory description of matter and its properties, and the introduction of larger units, such as bricks and cells, is therefore necessary. Just as the introduction of the cell as the building unit of the organism resulted in the amazing development of biology, so any further development in the physicochemistry of matter depends on the acceptance of the specific properties exhibited by such intermediate discontinuities.

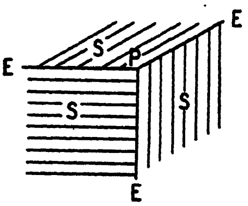

FIG. 6.—Stereometrically distinguished parts of a cube. *S*, boundary surfaces; *E*, edges; *P*, points.

As previously pointed out, we have devoted our attention so far exclusively to *corpuscular discontinuities.* These are systems with fully closed discontinuity surfaces, such as spheres and individual particles. These corpuscular systems must be considered only as *one* possible type of stereometric discontinuity; films and threads are other possibilities.

For example, if we consider a system of coarse discontinuity, let us say a cube, we find that it possesses parts which, in comparison to the undifferentiated interior, are stereometrically distinguished. These are the *boundary surfaces, edges,* and *points* (Fig. 6). These boundary fields are distinguished parts also from a physicochemical point of view. They always have a

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[1] WO. OSTWALD, *Koll. Beih.*, **32**, 1 (1930). VON BUZÁGH, *op. cit.*, pp. 29*ff.*

certain depth, in most cases of colloidal dimensions, and therefore can be considered to be of tridimensional construction, becoming monodimensional only in theoretical mathematics. Located in them we find specific physicochemical forces and properties. This makes it evident that these properties must become the more pronounced the more the boundaries of this system are increased in comparison to its constant volume or mass. The total energy E of a given body can be divided into the inner energy ei and into the boundary energies eb:

$$E = ei + eb$$

The inner energy must be proportional to the volume or mass of the body v, whereas the boundary energies must be proportional to the discontinuities w.

If we term the energy of a volume unit in the interior i, and the intensity factor of the discontinuity energies f, then the total energy of the body can also be written

$$E = vi + wf$$

and the total energy per unit volume would become

$$E' = i + \frac{w}{v} \cdot f$$

If we increase the value of w/v, *i.e.*, increase the discontinuities of a system in regard to its volume, the boundary energies will preponderate accordingly. Theoretically, there is no limit for w; however, practically, owing to the inadequacy of our methods of observation, we reach the point where the total energy of a system is once more entirely made out of the inner energy, *i.e.*, when the term "boundary surface" loses its practical sense. For all purposes, this is the case when dealing with true solutions or analytical dispersions.

Referring once more to the example of the cube, Wo. Ostwald distinguishes between planar, linear, and point discontinuities. Therefore, a cube of 1 cc. volume will have a specific planar discontinuity of 6 sq. cm. (discontinuity planes in square centimeters per volume in cubic centimeters), a linear one of 12 cm., and a specific point discontinuity of 8.

Laminar, Fibrillar, Corpuscular Dispersion.—By taking a cube of 1 cc. volume and dividing it into slices of 1 mμ in thickness, we have produced a *laminar dispersed* system. If we now continue to subdivide this lamella into rods 1 mμ thick, we have produced a *fibrillar* system; and, finally, if we subdivide this into individual cubes of 1 mμ edge length, we have produced a *corpuscular disperse system* (Fig. 7). Whereas the total volume has thereby undergone no change, the surface has increased from 6 sq. cm. to 6.000 sq. m. Such a method of increasing the surface of a given system is by no means the only possible one. For example, if we take a piece of gold and hammer it out until it reaches the thickness of a gold leaf, we shall have increased the surface, starting with a cube of 6 sq. cm. total surface, to about 2 sq. m. If we take 1 cc. of viscose and spin a thread of 1 μ diameter, the thread would be about 800 miles long. Such extreme cases of deformation have been termed "difformation," and the systems obtained are known as *difform systems.*

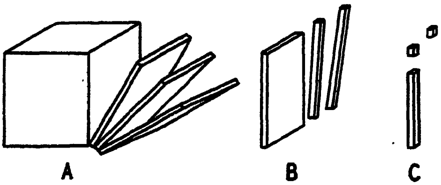

FIG. 7.—Dispersed systems. *A*, laminar; *B*, fibrillar; *C*, corpuscular.

As a logical consequence of the systematology of disperse systems, we can now equally well distinguish between coarse difform systems, if the thickness of the lamella or film is thicker than 500 mμ; or, in the case of fibrillar systems, if width, thickness, or diameter oversteps this figure. Systems where one or two of the dimensions lie in the colloidal range are called *colloidal difform systems;* and those with dimensions smaller than 1 mμ, *analytical difform systems.*

It is evident that depending on the type of difformation, *i.e.*, if it is carried out to increase one dimension or two, we shall obtain filmlike or threadlike systems. The main differentiation between difformation and dispersion is that in the former case the increase in the discontinuities concerned is absolutely continuous, the body retaining thereby its coherent character; whereas in the latter case its original coherence is disrupted, and individual particles in dispersion are formed.

On the basis of the previous discussion, Wo. Ostwald amended as follows his own and von Weimarn's statement as to the generality of the colloid disperse state of matter: "*Films and threads are equally general possible states of matter as dispersions. Just as well as dispersions of every conceivable degree of dispersion exist, there also exist films and threads of all possible degrees of difformation.*"

The Scope of Science Dealing with Colloids.—This statement naturally must result in an amendment of the scope of the science dealing with colloidal phenomena. It is no longer limited to the study of disperse systems, the disperse part being of colloidal dimensions, but it logically must now also include the study of the phenomena of difform systems as long as at least one of the systems' dimensions falls within the limits arbitrarily selected as colloidal.

Table I.[1]—Disperse Systems

Dispersion medium	Disperse part	Type of disperse systems		
		Coarse disperse	Colloid disperse	Highly disperse
Gaseous	Gaseous	....	....	Mixture of gases
	Liquid	Rain, fogs	Mist (aerosol)	
	Solid	Dust, smoke	Aerosol	
Liquid	Gaseous	Foams and gas bubbles	Foams and gas bubbles;	Adsorbed gases
	Liquid	Coarse emulsions	Lyogels, colloidal solutions (hydrosols, organosols);	Solutions, mixture of liquids
	Solid	Mechanical suspensions	Lyosols, colloidal solutions (hydrosols, organosols, pyrosols)	Solutions
Solid	Gaseous	Solid foams, minerals with gas	Solid foams	Adsorbed gases
	Liquid	Minerals with liquid inclusions	Solid foams	Water of crystallization
	Solid	Dry mixtures, conglomerates	Solid sols, *e.g.*, gold-ruby-glass	Solid solutions, mixed crystals

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[1] This table, with the exception of a few changes, has been taken from A. v. Buzágh's book "Kolloidik," p. 20, T. Steinkopff, Dresden, 1936.

TABLE II.[1]—DIFFORM SYSTEMS

	Laminar	Fibrillar	Corpuscular
I. Solid films, threads, and corpuscules:			
1. Solid-solid-solid..	Mica, graphite, clay (individual lamellae)	Asbestos (individual fibers)	Crystal powder particles
2. Solid-solid-liquid	Electrolytic deposit on electrode in bath	....	Particles adhering to container walls in presence of nonwetting liquids
3. Solid-solid-gaseous.	Thin coatings on solid base in air	....	Particles adhering to walls in air
4. Liquid-solid-liquid.	Dialyzing membrane in use	Textile fiber in dye bath	Suspended particles, *e.g.*, in a sol
5. Liquid-solid-gaseous.	Colloidion membrane on water	....	Carbon-black particles floating on water
6. Gaseous-solid-gaseous.	A thin sheet of cellophane in air	A fine thread in air	Smoke
II. Liquid films, threads, and corpuscules:			
7. Liquid-liquid-liquid.	Ternary equilibrium between benzene, acetic acid-water[2]	Mixture of certain liquids (intertraction threads)[3]	Drops of an emulsion
8. Liquid-liquid-gaseous.	Oil film on water	....	Oil drops on water surface
9. Solid-liquid-solid.	Film of lubricant between solid surfaces	Mercury column in thermometer capillary	Liquid inclusions in rocks
10. Solid-liquid-liquid.	Oil film spread on glass and covered with water	....	Drops of oil in water adhering to container wall
11. Solid-liquid-gaseous.	Condensated water film on solid surface	....	Drops adhering to windowpane
12. Gaseous-liquid-gaseous.	Soap lamella	Liquid threads[4]	Liquid drops in air
III. Gaseous films, threads, and corpuscules:			
13. Solid-gaseous-solid.	Air film between adhesion plates	Air-filled capillary	Gas inclusions in minerals and rocks
14. Solid-gaseous-liquid.	Leidenfrost phenomenon		
15. Liquid-gaseous-liquid.	Leidenfrost phenomenon on liquid surfaces		
16. Liquid-gaseous-gaseous.	Two-dimensional gas layers		
17. Solid-gaseous-gaseous.	Adsorption film		

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[1] With the exception of a few minor changes, this table is taken from v. BUZÁGH's book, "Kolloidik," p. 21, T. Steinkopff, Dresden, 1936.

[2] F. A. H. SCHREINEMAKERS, *Zeit. physikal. Chem.*, **25**, 552 (1898). J. FRIEDLAENDER, *ibid.*, **38**, 480 (1901).

[3] A. E. WRIGHT, *Proc. Roy. Soc.*, *B* **92**, 118 (1921); *A* **112**, 212 (1926); **114**, 576 (1927); **115**, 587 (1928); *Koll. Zeit.*, **51**, 366 (1930); **54**, 93 (1931).

[4] See J. JOCHIMS, *Protoplasma (Berlin)*, **9**, 298 (1930).

To avoid any misconception in our future discussions, it might be worth while to emphasize at this point that the terms "disperse" and "difform" systems, as used in the colloidal range, may not be confused with the homogeneous and heterogeneous systems of Gibbs's phase rule. Coarse dispersions and coarse difform systems are heterogeneous, whereas highly disperse systems would be considered homogeneous in the sense of the phase rule. We know that in between these extremes lie the colloid disperse and colloid difform systems. The colloid systems, as has been pointed out, are characterized by an extreme development of surface. They cannot be discussed on the basis of the phase rule, because, although their optical heterogeneity has been established, Gibbs's phase rule is specifically applicable only to such systems, which in the state of equilibrium possess a negligible phase boundary energy in comparison to the inner energy. That means that Gibbs's rule[1] applies only to phases that make contact with each other along comparatively short boundary surfaces.

By the introduction of the terms "colloid disperse" and "colloid difform" state, a very material advance has been achieved in the general trend of thoughts.

Besides subdividing the disperse state of matter into three main groups, according to the degree of dispersion, a further subdivision into the type of dispersion medium present has proved advantageous. Table I offers typical examples for the nine theoretically possible types of systems.

In the case of difform systems, the possibilities are still more numerous. Table II gives us a general idea of the possibilities existing in difform systems.

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[1] J. Willard Gibbs, *Trans. Conn. Acad. Sci.*, 3, 228 (1876).

CHAPTER V

FORM AND SHAPE OF MATTER

In our previous discussions of disperse and difform systems, reference has been made to the importance of what we termed "specific discontinuities." This means that we consider the form or shape of the disperse or difform system, or at least the form or shape of its disperse or difform part, of significance in regard to its properties. These depend, according to our previous deductions, to a large extent on such specific discontinuities. The logical result of such a statement is that in the study of colloidal systems and colloidal phenomena, considerations of form or shape may not be entirely overlooked.

The science of the relation between form or shape of matter and its properties and functions (morphology) dates back to Goethe, Cuvier, v. Baer, Roux, and others. Whereas sciences, as, for example, geology, crystallography, anatomy, botany, etc., and to some extent biology, have materially benefited in their development by the introduction of such considerations, other branches of natural science, as mathematics, classical physics, basic chemistry, and classical physicochemistry, have so far made but very little use of morphological considerations.

This might be explained by the fact that the gas laws and the laws of liquids and solutions of low concentration, the actual domain of physicochemistry, had no need to introduce stereometric (shape) factors, since the laws can all be derived by the use of thermodynamic and molecular kinetic reasoning, where the form or shape is of no importance.

Basic chemistry has been interested largely in stoichiometric equations for the reacting compounds but up to quite recently has disregarded possible stereometric factors. More recent discoveries, such as stereoisomeric compounds and A. Werner's complex salt theory,[1] have necessitated the introduction of

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[1] "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 4th ed., F. R. Vieweg, Braunschweig, 1920.

morphological considerations in classical physicochemistry. These have demonstrated that a fully satisfactory description of types of matter depends not only on the chemical nature and number of building units but also on their arrangements in space. However, such considerations have been more or less limited to substances that are available in the form of well-definable crystals.

Importance of Shape in Colloidal Systems.—In contradistinction thereto, the scientist working with colloidal systems has long been fully aware that morphological considerations are indispensable for their complete description. For example, we know that an excess of sulphur milled into crude rubber at elevated temperature will reappear, upon cooling, not in the form of regular crystals but as fernlike configurations;[1] when evaporating iron oxide sols we obtain characteristic concentric curved filamentlike deposits[2]; the practically concentric layers in agate or chalcedony and the formation of silicate trees are further typical demonstrations for the relation between chemical constitution and form or shape, since the latter is always reproducible under constant conditions. This means that their formation can certainly not be considered as a chance effect but must be governed in a way comparable to the growth of regular crystals.

Such stereometric considerations are by no means limited to matter in the solid state, but gelatinous substances or gels must also be considered from a morphological standpoint. Soap gels, for example, owe their rigidity and elastic properties to a threadlike alignment of their individual particles. Lying parallel in the form of bundles, the so-called liquid crystals are seemingly the result of orientation of the building units in one preferential direction. The cell protoplasm and the living cell itself exhibit a persistence in form, although they are of easily deformable shape.[3]

Naturally, it is extremely difficult to evaluate the importance of stereometric form in regard to properties in every detail. Modern physics of the structure of matter has been able to obtain during the past years with the aid of x rays, electron diffraction, etc., a very deep insight into the structure of finest matter. Many of its findings have proved of extreme value in the study of

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[1] See, *e.g.*, E. A. Hauser *et al.*, *Coll. Symp. Monogr.*, **6**, 207 (1928).

[2] P. Bary, "Les Colloides," p. 183, Dunod, Paris, 1933.

[3] See, *e.g.*, W. Seifriz, *Science*, **88**, 21 (1938).

colloidal phenomena, permitting us to draw very close and valuable analogies simply by substituting a colloidal particle for an atom. For example, the most recent theories in regard to gelation or coagulation of colloidal systems find their perfect analogues in the attraction/repulsion relationship of two atoms[1] (see page 219).

Wo. Ostwald was the first to sum up the importance of such morphological considerations in the study of colloidal phenomena and to offer the first morphological systematology of disperse and difform colloidal systems.[2] A. v. Buzágh[3] devotes an extensive chapter in his book to the morphology of disperse and difform systems.

The former based his systematology on the controlled increase of discontinuities. This can be achieved by deformation or difformation as well as by dispersion. Naturally we could achieve the same result by assuming a systematic construction of the shaped matter from its ultimate building elements (atoms, molecules). In this case, aggregates of different size, form, and internal structure result. However, a dissimilarity is involved in following Ostwald's trend of thought: the difform system must be considered as the primary shape, whereas by the aggregation theory the form of a singular body would be a secondary shape based on its structural configuration.

Let us once more refer to the fact that the characteristic cross section of a *difform* system is a curve exhibiting two fields of discontinuities, linked together with one of constant properties (Fig. 3). Threads will show this effect in two dimensions and tridimensional difform systems, or singular corpuscles in three. If such coupled discontinuities repeat themselves periodically, we are dealing with a *disperse* system. Of course, a great number of transitory systems or mixtures exist between difform and disperse systems.

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[1] See, *e.g.*, ABRAM F. JOFFÉ, "The Physics of Crystals," McGraw-Hill Book Company, Inc., New York, 1928. R. HOUWINK, "Plasticity, Elasticity and Structure of Matter," Cambridge University Press (England), 1937.

[2] *Koll. Zeit.*, **55**, 257 (1931); *Koll. Beih.*, **32**, 1 (1930).

[3] "Kolloidik," pp. 59*ff.*, T. Steinkopff, Dresden, 1936; "Colloid Systems," pp. 56*ff.*, English translation of "Kolloidik," The Technical Press, Ltd., London, 1937.

Definitions.—For example, in cases where the individual particle of the dispersed part is not a compact structure but in itself represents a disperse system, we are dealing with a *disperse structure of secondary order*. We may consider a suspension of clay in its totality as a laminar-difform system; the individual clay particle possesses a laminar-disperse structure of second order, because it is built up from sheets of silica and aluminum, bonded together by oxygen. Cellulose fibers suspended in a dispersion medium represent a fibrillar-disperse system, with a disperse structure of second order, since the individual fiber in itself is composed of a great number of building units of fibrillar configuration. Finally, in the case of corpuscular-disperse systems, such as that of a gold sol, we know that we can distinguish between primary particles (sols of faint pinkish color) and sols in which several primary particles have joined to form larger but still colloidal units[1] (sols of violet color).

Distribution and Its Bearing on Colloidal Properties.—It is decidedly more difficult to reach a satisfactory systematology for the types of distribution,[2] because a far greater possibility for variations due to shape and size of the disperse part, packing, etc., comes into play. Concentration of the system must also be considered, because at high concentrations of the disperse part, or during sedimentation, the particles are forced closer together so that we then have to deal with disperse systems, the properties of which depend not only on the disperse part but also on the changes in the dispersion medium. Whereas, for example, the properties of a given clay suspension will depend largely on the degree of dispersion of the disperse part, the properties of its sediment will also depend, at least to some extent, on the properties of the now lamellar-difform dispersion medium, it being interlocked in lamellar shape between the sedimented and closely packed platelike particles. (For further details, see the chapters on the structure of pastes and gels.) Fibrillar difformation of the

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[1] W. Mecklenburg, *Zeit. anorg. allg. Chem.*, **74**, 262 (1912), differentiates between single- and multiparticles. R. Zsigmondy, *Zeit. angew. Chem.*, **35**, 449 (1922); *Zeit. physikal. Chem.*, **98**, 14 (1921), differentiates between protons or monons and polyons.

[2] See, *e.g.*, P. Niggli, "Geometrische Kristallographie des Discontinuums," "Handbuch der Experimental Physik," Leipzig, 1928. K. Weissenberg, *Zeit. Krist.*, **62**, 13, 52 (1925); *Zeit. Phys.* **34**, 406, (1925).

dispersion medium will result in systems sedimenting or packing in such a way that a system with typical pores results.

In systems of high concentration, the degree of difformation, as well as the final stereometric configuration of the dispersion medium, will depend exclusively on the shape of the disperse part and its type of packing, particle size and particle-size distribution being of secondary importance. Particles of any size or configuration can pack more or less densely, so that interstices of macro- or microscopic, colloidal or amicroscopic dimensions can result. However, if the dimensions fall into the colloidal range, then such systems—according to the definition of the colloidal state—must exhibit colloidal properties in regard to these interstices, independent of the size of the individual particles of matter representing the solid part, or skeleton, of the system. For example, the adsorptive properties of paper, textiles, sand beds, etc., are not necessarily the result of a property specific to the skeleton-forming substance but are due to the colloidal properties of the interstitial dimensions of the formed system.

CHAPTER VI

THE PECULIARITY OF THE COLLOIDAL STATE

Based on the work of Wo. Ostwald and P. P. v. Weimarn, we have previously concluded that the colloidal state of matter refers to systems intermediate between coarse dispersions and analytical dispersions or true solutions. We have established the fact that no abrupt changes have so far been detected which would permit drawing sharp lines of demarcation between colloid disperse systems and those which exhibit some other degree of dispersion. Finally, we have accepted the most commonly used dimensional limits of the colloidal range as arbitrary, based mainly on the historical development of this field of science and, specifically, as a result of the discovery of the ultramicroscope.

Keeping these statements well in mind, it is only logical to ask for what good reason phenomena exhibited by most varied substances have, if present in a middle degree of dispersion, resulted in a new and today practically independent branch of science. Wo. Ostwald[1] argues this point even more precisely when he asks if it is not really surprising to base the fundamental definition of a science on a stereometric dimension, *e.g.*, the degree of dispersion, especially when one must admit that the dimensions under consideration have arbitrary limits. Unless variations in degree and type of dispersion cause characteristic changes other than simply stereometric ones, it would seem as illogical to base thereon a new branch of science as it would be to develop a special science for an arbitrarily selected range of pressures, temperatures, or the like. As we have previously determined, matter can be classified into disperse and difform systems. Therefore, a close study of the relation between physical and chemical properties and the degree of dispersion or difformation should prove of special value in determining the existence of properties specifically or materially pronounced in a limited range of dimensions. If such dispersion or difformation functions exhibit a pronounced

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[1] *Koll. Beih.*, **32**, 13*ff*. (1930).

change in the colloidal range, then the development of a special branch of science seems justified.[1]

DISPERSION AND DIFFORMATION FUNCTIONS

Neither of these two functions is linear. If we plot curves representing changes in certain properties, as, for instance, light absorption, electric conductivity, color strength, electric resistance, and rate of diffusion, against the degree of dispersion or difformation, we find that in most cases they exhibit characteristic maxima or minima or are of hyperbolic nature. If we sum up in a few examples in the following pages the three possibilities demonstrated, we find that the maxima or minima, or the apex of the hyperbola, is generally located either in the range of colloidal dimensions or at their upper or lower limits (Fig. 8).

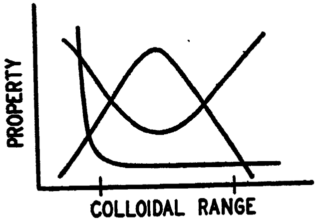

FIG. 8.—Dispersion and difformation functions.

Physical Functions of Degree of Dispersion.—Thomas Graham based his differentiation between colloidal and crystalloidal matter (see Chap. I) chiefly on the rate of diffusion. It is known that this rate increases with decreasing molecular size. The mathematical evaluation of this function, which, assuming particles of spherical shape, has been experimentally proved to be correct, was worked out by A. Einstein and M. v. Smoluchowski in their classical contributions to the theory of the Brownian motion (see page 227). We obtain the following relation:

$$D = \frac{RT}{N \cdot 3d \cdot \pi \cdot \eta}$$

where D = coefficient of diffusion.
d = diameter of particle.
η = viscosity of dispersion medium.
N = Avogadro's figure = $6.06 \cdot 10^{23}$.
R = gas constant = $8.319 \cdot 10^{7}$.
T = absolute temperature.

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[1] See WO. OSTWALD, *Koll. Beih.*, **42**, 109 (1935).

The following table (III) shows the relation between particle diameter and coefficient of diffusion as calculated in accordance with the Einstein-Smoluchowski equation.

Table III[1]

ϕ mμ	$D \cdot 10^5$	ϕ mμ	$D \cdot 10^5$	ϕ mμ	$D \cdot 10^5$
0.1	4.25	1	0.425	10	0.0425
0.2	2.13	2	0.213	20	0.0213
0.3	1.42	3	0.142	30	0.0142
0.4	1.06	4	0.106	40	0.0106
0.5	0.85	5	0.085	50	0.0085
0.6	0.71	6	0.071	60	0.0071
0.7	0.61	7	0.061	70	0.0061
0.8	0.58	8	0.058	80	0.0058
0.9	0.47	9	0.047	90	0.0047
1.0	0.425	10	0.0425	100	0.00425

[1] The calculations are based on a temperature of 20°C.

If we plot this function (Fig. 9), we obtain a hyperbolic curve with its apex at a particle diameter of about 0.5 to 1 mμ. Here we have a case where a pronounced change in one property of the system takes place at the lower limit of the colloidal range. Since it has been shown by referring to Graham's own words in his paper on silicic acid that the terms "colloids" and "crystalloids" were intended mainly to differentiate between dialyzable and nondialyzable systems and were not intended to exclude crystals of colloidal dimensions, the foregoing data prove that Graham's differentiation was amazingly correct.[1]

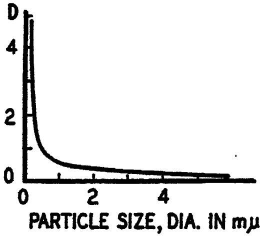

Fig. 9.—Particle size versus coefficient of diffusion.

The relation between Brownian motion and particle size and the sedimentation equilibrium of disperse particles also shows a similar trend in their curves (see page 228). As we shall see later, coagulation is one of the most characteristic phenomena of colloidal systems. The reason why this phenomenon is so pronounced in the range of middle discontinuities can be explained

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[1] See R. Auerbach, *Koll. Zeit.*, **35**, 202 (1924).

as the sum of several dispersion functions.[1] Disperse particles are influenced by thermal agitation, gravity, and molecular cohesion forces (van der Waals' forces). The thermal movement of disperse particles decreases with increasing particle size, and gravity increases; the van der Waals' forces do likewise. With extremely small particles the thermal movement will overbalance the tendency of the particles to cohere. Gravity is of negligible influence in systems of extreme degree of dispersion. When dealing with a suspension of comparatively large particles (microscopic dimensions), the influence of the thermal movement decreases more and more, so that the cohesion forces become more and more predominant. However, in these latter systems gravity can no longer be neglected. The particles are pulled down by gravity and taken thereby out of the danger zone before collisions can result in permanent coherence.

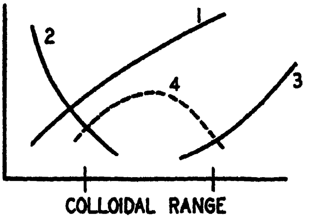

Fig. 10.—Factors influencing the stability of dispersion. 1, van der Waals' forces; 2, thermal motion; 3, gravity; 4, resultant force.

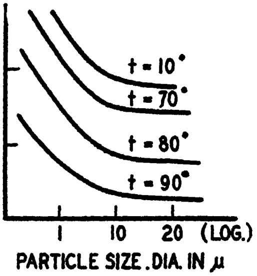

Fig. 11.—Solubility of gypsum versus particle size.

In the middle range of discontinuities, the resultant of these three effects shows a pronounced maximum (Fig. 10), which fully explains stability of colloidal dispersions in general and coagulation in particular. (The importance of these deductions will be more fully appreciated after detailed consideration is given to the chapters dealing with molecular- and electrokinetics of colloidal systems.)

Another hyperbolic function having its apex at the upper limit of the colloidal range is, for example, the relation between solubility and particle size. Figure 11 demonstrates the sudden

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[1] A. v. Buzágh, "Kolloidik," p. 39, T. Steinkopff, Dresden, 1936. ("Colloid Systems," p. 37, The Technical Press Ltd., London, 1937.)

increase in the solubility of gypsum, as determined by Jones and Portington, as soon as the particles are of colloidal dimensions.

By taking a piece of gold and rolling and hammering it down to sheets of extreme thinness, we find that it loses its strong ability to reflect light rays, which is synonymous for opacity. At a thickness of about 200 mμ, gold has lost its yellow shine and becomes translucent with a green color. Similar results are obtained with silver and other metals. If we continue such difformation or dispersion, we ultimately obtain perfectly transparent systems of brilliant colors. For instance, colloidal gold dispersed in glass will produce with decreasing particle size color variations ranging from brilliant blue through violet to deep red. Similar changes can also be observed in dispersions of sulphur and other nonconducting elements. Figure 12 shows the changes in absorption of light of different wave lengths by sulphur particles of varying size, according to N. Pihlblad.

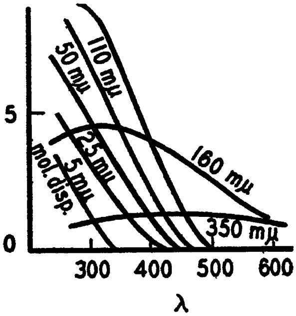

FIG. 12.—Light absorption and particle size. λ, wave length.

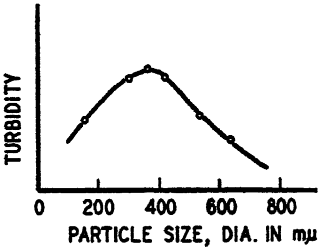

FIG. 13.—Turbidity and particle size.

Sulphur sols show pronounced changes in their color with decreasing particle size in the colloidal range. The variations pass from orange through violet to blue and finally to gray.[1]

We also know of substances that materially change their optical properties with degree of dispersion, even if they do not absorb light in the visible spectrum. Barium sulphate shows a pronounced maximum of turbidity in the colloidal range.[2] The change is schematically shown in Fig. 13.

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[1] R. AUERBACH, *Koll. Zeit.*, **27**, 223 (1920).

[2] H. BECHHOLD and F. HEBLER, *Koll. Zeit.*, **31**, 70 (1922). F. HEBLER, *ibid.*, **41**, 365 (1927).

If we consider the reciprocal function, for instance, *i.e.*, the transparency of a suspension of zinc oxide in oil, in relation to particle size, we obtain a typical minimum curve in the colloidal range, as shown in Fig. 14.[1]

One of the most interesting dispersion functions is the hardness of carbon. Figure 15 shows the results obtained by Else Koch-Holm.[2]

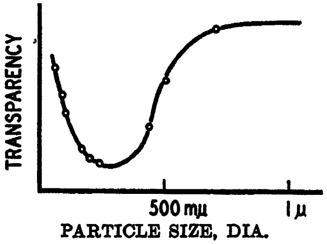

Fig. 14.—Transparency and particle size.

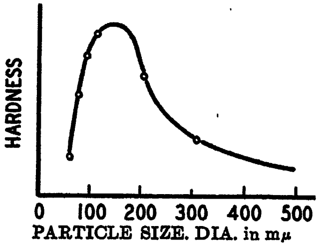

Fig. 15.—Hardness and particle size.

W. Fraenkl found that the hardness of silver-copper alloys shows a maximum at medium annealing temperature, which results in different grain sizes. Frequently, also, we find statements asserting that the electric breakdown of insulators is a function of their thickness and that a multitude of thin sheets laminated together will resist higher current densities than a compact piece of the same dimensions. However, recent researches have thrown some doubt on the correctness of such statements.

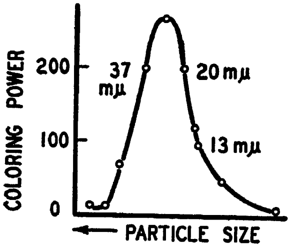

Fig. 16.—Color strength and particle size.

Equally important and interesting is the coloring and covering power of dispersions and pigments. The Svedberg has proved that gold sols show their strongest color at about 30 mμ (Fig. 16). Most pigments will show a noticeable increase in covering power in the colloidal range.

A great number of further examples could be enumerated to demonstrate pronounced changes in the properties of disperse or

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[1] G. F. A. Stuetz and A. H. Pfund, *Ind. Eng. Chem.*, **19**, 51 (1927).

[2] *Veroeffentlichungen des Siemens-Konzerns*, (Berlin) **6**, 188 (1927).

difform systems in relation to their degree of dispersion or difformation. The technical development of the radio industry has offered a great number of such functions. For example, it has been ascertained that the emission capacity of electrons from the cathode in photocells, rectifiers, etc., depends to a large extent on the grain size of the oxide or metal particles in the layers. It has been found that the thickness of properly functioning Cu_2O rectifiers varies between 0.3 and 30 mμ.[1] The emission of barium cathodes shows a typical maximum if the barium particles are present in the colloidal range (Fig. 17).[2]

The photoelectric effect of gold layers increases up to a thickness of 30 mμ.[3] With platinum and silver layers[4] a maximum photoelectric effect exists when the layers are of typical colloidal dimensions. The same has been found to be the case with the oxide layers of the alkali photoelectric cells.[5] In this instance, it has been ascertained that the efficiency is not the result of the continuous layer but of its submicroscopic, colloidal structure.

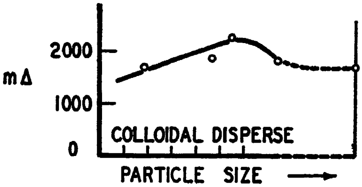

FIG. 17.—Electron emission capacity and particle size.

Another field of extreme importance in modern industrial work is the so-called "heterogeneous catalysis." As detailed research has shown, the efficiency of a catalyst depends largely on its degree of dispersion; and here, again, a maximum is found in the colloidal dimensions.[6]

A recent survey of this entire field has been published by A. v. Buzágh,[7] wherein he discusses further numerous examples.

Chemical Functions of Degree of Dispersion.—So far we have dealt with physical and physicochemical functions of dispersion

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[1] W. SCHOTTKY and DEUTSCHMANN, *Physikal. Zeit.*, **30**, 839 (1929).

[2] E. PATAI and Z. TOMASCHEK, *Koll. Zeit.*, **74**, 253 (1936); **75**, 80 (1936).

[3] See PH. LENARD and A. BECKER, "Handbuch der Experimentalphysik," vol. 13, p. 2, Leipzig, 1928.

[4] *Ibid.*

[5] R. POHL and P. PRINGSHEIM, *Verh. deut. Physikal. Ges.*, **15**, 625 (1913). B. LANGE, *Physikal. Zeit.*, **31**, 139 (1930). M. WILDERMANN, *Zeit. physikal. Chem.*, **60**, 70 (1907).

[6] ST. RUSZNYAK, *Zeit. physikal. Chem.*, **85**, 681 (1913); O. SCHMIDT, *ibid.*, **118**, 222 (1925).

[7] *Koll. Zeit.*, **77**, 172 (1936).

and difformation. Do we also know of any purely chemical functions in which the degree of dispersion or difformation is a variable and where special properties result in dealing with systems in the colloidal range of discontinuities?

STOICHIOMETRY AND COLLOIDS

To what extent does stoichiometry apply to colloids? Do colloids follow the constant-valency law? In this connection, Wo. Ostwald and A. v. Buzágh[1] discuss the chemical composition of a simple crystal of cubical shape.

Since the introduction of x-ray diffraction analysis as a new tool in structural research, it has been possible to evaluate what is generally known as the "elementary cell," *i.e.*, that space grouping of the smallest number of atoms which build up the crystallized substance, which, by repeating itself in the three dimensions of space, results in the formation of the crystal.[2]

To those more familiar with the evaluation of x-ray diffraction patterns of crystals, it is a well-known fact that the composition of the unit crystal generally does not correspond to what should be assumed on the basis of simple chemical analysis. Figure 18 shows the elementary cell of sodium chloride and fluorspar, respectively, as computed from x-ray diffractions. We find that in the former the proportion of chloride to sodium ions is 14:13 and that in the latter case the proportion of calcium to fluorine ions is 14:8. By chemical analysis, or stoichiometrically, the proportion should be 1:1 or 14:14 for sodium chloride and two fluorine ions to every calcium ion for calcium fluoride, instead of $C_{14}F_8$ of the unit crystal. The reason for this discrepancy has been discussed by F. Rinne,[3] who remarked that since the elementary cell repeats itself in all three directions of space, the structural units belong to a number of adjacent cells as well. Therefore, with an increasing number of elementary cells, the discrepancy between stereometric and stoichiometric composition decreases. This means that with increasing size of the crystal

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[1] *Ibid.*, **47**, 314 (1929).

[2] For details concerning x-ray analysis of crystals and methods applied, see Appendix, p. 244.

[3] "Die Kristalle als Vorbilder des feinbaulichen Wesens der Materie," Berlin, 1921.

the microstructure must approach the composition of the crystal as found by chemical analysis.

In Table IV, the first column gives the number of elementary cells placed along one edge of the cubical crystal under consideration; the second and third column contain the number of respective ions of such crystal; the fourth shows us the ionic ratio; and the last column contains the length of one cubical edge in millimicrons.

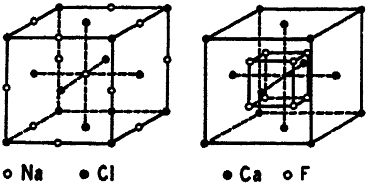

FIG. 18.—Unit cells of crystals. $NaCl = 13:14$; $CaF_2 = 14:8$.

A graphical presentation of these data gives a curve of hyperbolic type with its apex in the colloidal range of dimensions. This means that the transition from purely stereometrical to stoichiometric composition takes place in the colloidal range. A. v. Buzágh calculated the minimum size necessary to obtain

TABLE IV.—THE MICROSTRUCTURAL COMPOSITION OF NaCl AND CaF_2 CRYSTALS[1]

Common Salt

n	N_{Cl}	N_{Na}	N_{Cl}/N_{Na}	Length of edge in millimicrons
1	14	13	1.076	0.563
5	666	665	1.0014	2.815
10	4,631	4,630	1.0002	5.63
20	34,461	34,460	1.0000	11.26
00	00	00	1	

Fluorite

n	N_{Ca}	N_F	N_{Ca}/N_F	Length of edge in millimicrons
1	14	8	1.749	0.62
2	63	64	0.984	1.24
5	663	1,000	0.666	3.10
10	4,631	8,000	0.578	6.20
100	4,060,301	8,000,000	0.507	62.00
500	501,501,501	1,000,000,000	0.501	310.00
1,000	4,006,003,001	8,000,000,000	0.5007	620.00

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[1] Wo. OSTWALD and A. v. BUZÁGH, *Koll. Zeit.*, **47**, 314 (1929).

different crystal types of stoichiometric composition and thus materially strengthened this seemingly paradoxical but nevertheless exceedingly important fact. His results are contained in Table V.

TABLE V[1]

Lattice type	Number of elementary cells = n^3	Length of edge in millimicrons
Rock-salt type	$1.2 \cdot 10^3$	8 to 14
Fluorite type	$4.5 \cdot 10^4$	300
Caesium chloride type	$1 \cdot 10^5$	400
Cuprite type	$1 \cdot 10^5$	400
Rutile type	$0.5\text{–}1 \cdot 10^5$	300

[1] A. v. Buzágh, "Colloid Systems," p. 47, The Technical Press, Ltd., London, 1937.

These considerations show that the ionic composition of a crystal can vary noticeably with changes in particle size and that this effect is most pronounced in the colloidal range. Since x-ray analysis of crystals of colloidal dimensions has so far never revealed any noticeable distortion of the lattice, it seems fully justifiable to discard the theoretically possible assumption that elementary units are always present in such numbers that stoichiometric demands are fulfilled. The assumption that crystals of colloidal dimensions differ from larger sized crystals by having a composition at variance with the stoichiometric one seems to be more satisfactory. Although this fact is rarely considered in classical chemistry, its logical interpretation leads us to the further assumption that the surface of *colloidal* crystals must consist to a large extent of chemically unsaturated or unevenly combined building elements. These must exhibit a high potential of unsaturation, and this is satisfied by *adsorption* of compensating ions from the environment. This deduction offers a simple explanation as to the extreme efficiency of matter in the colloidal state as adsorbents. If compensating ions are not available, or if the colloidal matter is present in high concentration, rearrangement of the building units will take place in time, until stoichiometric equilibrium is reached and a system of a minimum free energy is obtained. So, for example, is the aging of disperse systems frequently accompanied by a noticeable change in the analytical or stereometric composition until a state of stability has been reached.

This concept has received valuable support in A. Smekal's[1] mosaic-structure theory of crystals, postulating the existence of a secondary, disperse structure; by the observation of J. Traube and P. Klein[2] and others, that crystals do not dissolve uniformly but first split up into crystal fragments of ultramicroscopic size; by the work of D. Balarew[3] on the chemical composition of very fine precipitates and their purification, where attention is drawn to the importance of foreign ions present in the system (these have so far too frequently been considered as indifferent); by the numerous contributions to the relation of base exchange of clay minerals to particle size;[4] etc.

However, there is another field in which the deductions just discussed are of primary importance. It is the chemistry of natural and certain synthetic colloids. Such colloids, for instance, are the proteins, polysaccharides, cellulose, rubber, and the majority of natural and synthetic resins. By organochemical analysis the chemical composition of most of these natural substances has been ascertained long ago. But a synthesis of the ultimate building unit has failed to produce a substance corresponding in properties to the natural product. For example, we know that the ultimate building unit for rubber is isoprene (C_5H_8), a liquid. Only when these building units aggregate, condense, or polymerize to form particles of colloidal dimensions do we approach substances with properties similar to the natural product. This infers that, upon destruction of the colloidal condition, the essential characteristics are simultaneously destroyed. It furthermore demonstrates that to synthesize such substances or substances of similar properties a purely molecular-chemical consideration is insufficient. If one wants to reach the goal successfully colloidal considerations can no longer be omitted.

EQUILIBRIUM AND NONEQUILIBRIUM SYSTEMS

As remarked previously, classical physicochemistry is based on the existence of molecules that are uniformly but haphazardly

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[1] *Ann. Phys.*, **83**, 1204 (1927).

[2] *Koll. Zeit.*, **29**, 236 (1921).

[3] *Koll. Beih.*, **30**, 249 (1930); **32**, 205, 304 (1931); **33**, 279 (1932); **34**, 441 (1932); **37**, 180, 324 (1933); *Koll. Zeit.*, **68**, 265 (1934).

[4] See, *e.g.*, E. A. HAUSER and C. E. REED, *J. Phys. Chem.*, **41**, 911 (1937).

distributed in space. The gas laws and the laws of dilute solutions postulated by van't Hoff are applicable to these physicochemical molecules. In this connection, the molecule must be considered as the smallest structure of matter that still exhibits all the properties characteristic for the compound. The further rigorous evaluation of this basic concept does not need to consider stereometric dimensions as being of primary importance. Temperature, pressure, concentration, and chemical composition of the molecule are the four variables essential for a complete definition of such a system. It is clear that such a definition can hold only if the system is in perfect equilibrium. However, if no equilibrium has been established, *i.e.*, if some of the properties of two systems differ, although the previously mentioned variables are constant in both systems, classical chemistry logically must assume a different structure of the molecule. But it is just this nonequilibrium condition that very often causes specific properties, especially in colloidal systems.

In the foreword to the English translation of A. v. Buzágh's book,[1] Wo. Ostwald gives the following excellent examples for this point of view. If a piece of bread reaches equilibrium in a physicochemical sense, we consider it as stale. A piece of steel in physicochemical equilibrium is described by the specialist as "fatigued." An emulsion, according to the classical definition of heterogeneous systems by J. W. Gibbs, would be considered to be in a true state of equilibrium when it has broken, *i.e.*, when the value of the energy and entropy contained in the interfaces is negligible compared with their values in the two bulk phases. However, then the system is technically valueless and scientifically only of questionable interest.

CLASSICAL LAWS OF PHYSICOCHEMISTRY AND COLLOID SYSTEMS

The reasons have previously been discussed why the phenomenon of coagulation is a specific characteristic of colloidal systems. With increasing particle size of suspensions or emulsions, the probability that the particles will cohere to each other as long as they are suspended or emulsified in the system is diminished, owing to the effect of gravity or creaming. Coagulation of very coarse falling particles (termed *orthokinetic coagulation* by G.

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[1] *Op. cit.*

Wiegner) is increasingly prevented by the influence of gravity as coarseness increases. The validity of van't Hoff's laws, therefore, becomes more and more questionable as the particle size increases through the entire colloidal range. The same happens when applying other classical physicochemical laws to colloidal systems. Another example is the electrochemical behavior of colloidal solutions in which the particles possess an electric charge. Since, in electrophoresis, quantities of electricity are transported by the migrating particles just as in electrolysis, the colloidal particle has frequently been termed a colloidal ion. However, Faraday's law is not valid in colloidal solutions—a point discussed exceptionally well by Wo. Ostwald.[1] For example, equal parts of the disperse part by no means carry equal parts of electricity. The quantities that they carry differ depending on particle size and on the nature and concentration of foreign ions present in the system.

The application of the concepts of homogeneity and heterogeneity, so fundamental in the classical phase rule, does not hold in the case of colloidal systems. This is clearly evident by a careful perusal of J. Willard Gibbs's[2] own words:

> We started, indeed, with the assumption that we might neglect the part of the energy, etc., depending on the surfaces separating heterogeneous masses. Now, in many cases, and for many purposes, as, in general, when the masses are large, such an assumption is quite legitimate, but in the case of these masses which are formed within or among substances of different nature or state, and which at their first formation must be infinitely small, the same assumption is evidently entirely inadmissible as the surfaces must be regarded as infinitely large in proportion to the masses. . . .

Colloids are systems exhibiting as one of their most outstanding characteristics surfaces extremely large in comparison to their mass. Therefore it seems valueless to try to apply to colloidal systems the phase rule in its classical form.

Another case where fundamental physicochemical laws fail to apply to colloidal systems occurs in the laws of Gay-Lussac—in particular, the second law, which states that true solubility is

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[1] *Koll. Zeit.*, **7**, 132 (1910); **32**, 1 (1923).

[2] *Trans. Conn. Acad. Sci.*, **3**, 108, 228, 343 (1874–1884). See also W. P. A. YONKER, *Koll. Zeit.*, **8**, 15 (1911); **10**, 126 (1912). E. H. BÜCHNER, *ibid.*, **14**, 2 (1914).

independent of the amount of solute present. This law, which is valid for the formation of true solutions, has been replaced in colloid chemical systems by the "rule of dispersed amount" (*Bodenkoerperregel*) postulated by Wo. Ostwald and A. v. Buzágh.[1] (For further details in regard to this rule, see page 157.)

The foregoing examples have been taken at random and by no means can be considered as forming a complete picture of the discrepancies from classical scientific laws displayed by colloids. Innumerable further examples, chosen either from purely scientific research or from applied colloid chemistry, could be offered to substantiate further the undeniable fact that many, and generally the most, characteristic properties of colloidal systems can be neither explained nor deduced on the basis of classical physicochemical reasoning. This is by no means astonishing to those who are sufficiently objective in their deductions to admit that these physicochemical laws have been based on systems in which there is no functional relationship between the properties of the entire system and the degree of dispersion or difformation of one part thereof.

After its epoch-making development, being linked forever with names like J. W. Gibbs, van't Hoff, Svante Arrhenius, Wilh. Ostwald, W. Nernst, and many others, physicochemistry has become more and more a typical representative of what is generally termed exact science. Mathematical interpretation and deduction have become of increasing importance to physicochemistry, and all efforts of the past decades have centered around systems which, being in equilibrium, permit the application of such methods. In contrast, the colloid chemist and physicist is dealing with systems that at present in the majority of cases do not permit rigid mathematical interpretation. It is a deplorable fact that many physicochemists still take the attitude that colloid chemistry should be disregarded because it is a waste of time to work with systems that, according to their training, can rarely be mastered by mathematical equations. It is likewise deplorable that specialists in the colloidal field assume that physicochemistry can be fully neglected in the science of colloids. These attitudes unquestionably have created a tension between these two extreme lines of thought

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[1] *Koll. Zeit.*, **41**, 163, 169 (1927); **43**, 215, 220 (1927); **48**, 33 (1929).

which must be overcome if further development is not to be seriously hampered.

Innumerable facts prove that colloidal systems have an array of specific properties to their credit which clearly distinguish them from both the physics of visible matter and molecular chemistry. Hence an autonomous treatment becomes justifiable and essential, at least as long as we are not in possession of general laws applicable to matter present in any degree of dispersion or difformation. If we ever desire to be able to interpret the phenomena involved in complex colloidal systems on a mathematical basis, further refinements in our mathematical technique are necessary. It would be inexcusable to fold one's hands and await such improvements or to wait until the laws of neighboring regions of dimensions are definitely established and then try to extrapolate them to cover the colloidal field. Is it not more logical to assist in the erection of the complete building by supplying as many bricks of information as can be produced?

The colloid chemist or physicist has assigned himself the task of furnishing all information in regard to the special properties and laws of colloidal systems. Lacking for the time being any better or more exact methods, his work must be primarily inductive. His second step will be to determine if, and how closely, the results obtained can be correlated with the laws governing all other noncolloidal systems.

As with every new development, it is only natural that time must be expended in organizing the field and working systematically toward the goal. The modern colloid chemist has fully realized this responsibility, and during the past years we have had ample evidence to prove that systematic research is now on its way. The major difficulty to be overcome in the first stage of systematic research is to obtain colloidal systems that are homogeneous in regard to the degree of dispersion, *i.e.*, systems in which the particles of the disperse part are uniform in size and shape (monodisperse systems). If we once establish the various functions pertaining to systems of that type, we shall be in a position to approach more intelligently the so-called polydisperse systems. Transition into neighboring fields will then follow automatically. Such development cannot be accomplished in a day; nor is everyone who is earnestly interested in colloidal phenomena adapted to such work. Therefore we shall always have two types of research problems to consider, just as has been the case in any scientific development: the systematic probing into the innermost details of comparatively simple systems, and the devotion chiefly to the qualitative discovery of new reactions and phenomena.[1] Both serve the main purpose in their way, and both are equally needed in furthering this new branch of science, which, as has been outlined herein, is entitled to autonomous treatment by reason of its own merits.

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[1] In this connection see, *e.g.*, P. P. v. WEIMARN, "On the Numerical Data of Dispersoidology," *J. Chem. Educ.*, **3**, 373 (1926). R. KRUYT, *Nature*, June, 1923, p. 827. A. W. THOMAS, *J. Chem. Educ.*, **2**, 323 (1925). J. W. McBAIN, *Coll. Symp. Monogr.*, **4**, 7 (1926); *Koll. Zeit.*, **40**, 1 (1926).

CHAPTER VII

THE PRODUCTION OF COLLOIDAL SYSTEMS

Disperse Systems

In Chap. II, it was pointed out that the colloidal state of matter, being a general possibility, takes up a position intermediate between the coarse, or microscopic, and the molecular, or analytical, disperse systems. Therefore, there must be at least two ways to produce colloid disperse systems, *viz.*, (1) by comminution of systems existing in the state of coarse dispersion, such methods being termed *dispersion methods*; (2) by aggregating or condensing ions, atoms, or molecules until the dimensions of such dispersed aggregates have reached the colloidal range, such processes being known as *condensation methods.* We still know of methods that can be considered as a combination of the two aforementioned possibilities. The most important of these are the *electrical methods.*

Whatever way is taken, it is essential that the formed dispersions are of sufficient stability to remain in the state in which they have been brought. Since the factors governing stability will be discussed in detail in the chapters pertaining to molecular kinetics and to electrokinetic properties, a further discussion of their importance seems unnecessary at this point (see pages 89*ff.*).

Dispersion Methods

Dispersion methods will first receive our attention. In general, we must distinguish in dispersion processes among several classes, depending on the order in which the two basic steps of dispersion, *viz.*, disintegration and distribution, follow each other. Under the first heading, we can write the subdivision of an originally compact mass without distributing the particles so obtained over a larger volume. Such is the case in all dry disintegration processes, milling, etc., of a solid substance. The second possibility would be the distribution of existing individual particles in a dispersion medium. Such is the case when producing dispersions from powders or the like. Finally, we have instances in which the subdivision of a substance and its distribution in a dispersion medium is carried out simultaneously. If we grind a nonsubdivided system or a system already present in the disperse state into a finer degree in the presence of a dispersion medium, *i.e.*, if we perform a wet-grinding operation, subdivision is the primary process. On the other hand, if we increase the degree of dispersion of an already disperse system by further subdivision of the suspended particles or by simple dilution, distribution is unquestionably of primary importance.

The process of subdivision can be considered as the transformation of some kind of energy into surface energy, or one may also consider subdivision as work that must be done in order to separate the structural units of the substance to be dispersed. We can therefore differentiate among various types of dispersions depending on the energy involved, as, for example, mechanical, thermal, electrical, radiant, chemical. The distribution of individual particles in the dispersion medium is a purely kinetic process. It is obtained either by mechanical means, such as stirring, shaking, and rolling, or by thermal agitation, electric repulsion, etc. Besides the term dispersion, we frequently find in the literature the term *peptization*. By this term, its originator Thomas Graham defined the solution of a solid substance in a liquid which finally resulted in a colloidal solution, aided by the addition of a third substance, the so-called "peptizing agent." The younger generation of colloid chemists[1] has amended this concept. In its present meaning, peptization covers all dispersion processes which, starting from coarse suspensions or emulsions, lead to the formation of *stable* lyosols. Therefore, in contrast to the definition of dispersion, peptization covers the production of a *stable* colloidal solution or lyosol from substances that originally may be present in massive form in which the colloidal particles are not preformed, as well as such systems where these particles already preexist in the substance to be dispersed.[2] In this case, the latter substance is a coherent colloidal aggregate, which needs only to be brought in contact

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[1] See, *e.g.*, A. v. Buzágh, "Colloid Systems," p. 244, The Technical Press, Ltd., London, 1937.

[2] In the modern definition of the term peptization, stress is laid on the *stability* of the produced disperse system.

with an appropriate dispersion medium to go into colloidal solution. In this class we may list most of the so-called high-molecular organic compounds, *e.g.*, gelatin, rubber, and cellulose, which if brought into contact with an appropriate solvent will readily go into colloidal solution, because their building units (molecules) are in themselves of colloidal dimensions.

Mechanical Processes.—Theoretically, there is no reason why dispersions whose disperse part is of colloidal dimensions should not be producible by mechanical means. However, mechanical methods produce systems containing particles of varying sizes, the colloidal size being present usually as only a small percentage. The amount of matter of colloidal size that can be recovered will depend to a large extent on the physical properties of the substance to be comminuted.[1] Substances such as silicon, graphite, arsenium, or antimony can be ground comparatively easily to yield appreciable quantities of colloidal suspensions. Substances that resist grinding because of their softness have frequently been processed satisfactorily after they had been made more brittle by extreme cooling. P. P. v. Weimarn[2] obtained very interesting results by rubbing down the substance to be dispersed with an indifferent solid, which has the added property of becoming highly dispersed upon being dissolved. If this procedure is repeated several times, very satisfactory results can be achieved. N. Pihlblad applied this method for the production of aniline blue BB.[3] Later, the same author produced sulphur sols by this method and determined the average particle size to be 120 mμ.[4] A. L. Stein,[5] assistant to v. Weimarn, was the first to produce a large number of colloidal solutions by this method. A very comprehensive publication on this subject was made by S. Utzino.[6]

Often we find that the so-called ball, or pebble, mills are used to disperse solid matter in liquids and at the same time to decrease the size of the particles. This method, however, does not permit

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[1] See, *e.g.*, G. Wegelin, *Koll. Zeit.*, **14**, 65 (1914).

[2] "Grundzuege der Dispersoidchemie," p. 82, T. Steinkopff, Dresden, 1911.

[3] *Zeit. physikal. Chem.*, **81**, 417 (1912).

[4] "Dissertation on Light Adsorption and Particle Size in Disperse Systems," p. 47, (Thesis), Upsala, 1918.

[5] *Koll. Zeit.*, **11**, 315 (1912).

[6] *Ibid.*, **32**; 149 (1923).

the securing of large amounts of colloidalized matter as long as the pebbles are allowed to drop in free fall on the matter to be dispersed. If the speed of rotation is sufficiently reduced, to prevent free fall, the efficiency of the mill is materially increased.[1] This can be explained as a result of the shearing force exerted by the gliding pebbles.[2]

Colloid Mills.—The fact that a possibility of producing colloidal systems by mechanical means would be of extreme importance, from a technical point of view, accounts for the unceasing efforts to construct adequate apparatus. This resulted in a series of machines known as *colloid mills.* Subdivision in colloid mills is generally carried out in the presence of a dispersion medium. The first instrument of this type, known as the *Plauson mill,* was originally constructed and described by H. Plauson[3] and later materially improved in collaboration with B. Block.[4] The principal feature of this machine consists of a cylindrical container in which a drum carrying several protruding arms is eccentrically located. These throw the liquid which cannot elastically escape against appropriate baffles, thus performing an appreciable amount of comminution work.[5] Plauson noticed that extremely high revolutions per minute were necessary to obtain dispersions of truly colloidal dimensions. The amount of power and the great wear and tear hampered further introduction of such devices. Whereas the Plauson mill was based on the principle of actually disintegrating the particles by strong impact, another type of mill is based more on a shearing and tearing effect on the system to be dispersed. The shearing occurs as a result of the movement of members of the apparatus rotating at high speed, leaving a minute free space between their surfaces through which the system is forced to travel.

One of the earliest constructions is the china, or disk, mill.[6] The system to be dispersed, suspended in a dispersion medium,

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[1] See German Patent No. 541.468 to K. Bergl and J. Reitstoetter.

[2] WILLIAM H. WITTINGTON, *Ind. Eng. Chem.*, **30**, 897 (1938). E. M. UNDERWOOD, *ibid.*, **30**, 905 (1938). W. A. KOHN, *ibid.*, **30**, 909 (1938).

[3] *Chem. Ztg.*, **44**, 553, 565 (1920).

[4] *Zeit. angew. Chem.*, **34**, 25 (1921).

[5] See German patents Nos. 427.076, 429.015, and 429.016 for construction details.

[6] W. A. LEAN. *Chem. Met. Eng.*, **30**, 675 (1924); *Ind. Eng. Chem.*, **16**, 494 (1924).

is introduced into the machine through a hollow shaft *A* (Fig. 19) and is projected against a disk *B*, rotating at high speed. The shaft itself carries a similar disk *C*, which rotates at the same speed but in a direction opposite to *B*. The suspension must pass between these two rotating members, with the result that its middle layer is subjected to considerable shearing force, and the suspended particles are torn apart[1] (Fig. 20). A large number of different constructions, all of which are based on the principle just outlined, have become known. They differ only in technical details, as, for example, in the shape of the rotating members, the use of one stationary (stator) and one rotary member (rotor), etc. The most widely known representatives are the Summar, Kek, Oderberg, Passburg, Block, and Cyclone mills of European construction and the Premier (Fig. 21*a*, *b*, *c*), Hurrell, and Manton-Gaulin (Fig. 22) mills in the United States.

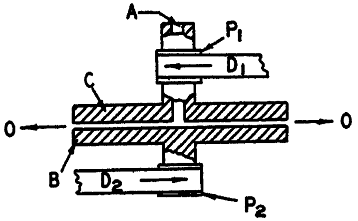

FIG. 19.—Disk mill. *A*, hollow driving shaft through which dispersion enters; P_1P_2, pulleys; D_1D_2, driving belts; *C*,*B*, rotating disks; *O*, discharge.

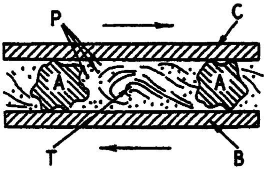

FIG. 20.—Mechanism of disintegration. *B*,*C*, rotating disks; *A*, aggregates; *P*, dispersed particles; *T*, turbulence of liquid.

Since it is evident that such constructions will always produce polydisperse systems, and since only a small percentage of the total solid matter present will be obtained in truly colloidal dimensions, the term "colloid mill" is somewhat misleading and should be replaced by "dispersion mill" or the like. O. Chwala, to whom we owe comprehensive treatises on the subject, has

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[1] That hydraulic shear is of primary importance is very nicely demonstrated by an experiment communicated to the author by H. L. Bullock of the Premier Mill Corporation. In running a mixture of heavy oils and waxes dispersed in water through the mill at room temperature, a very viscous paste of a high degree of dispersion was obtained. At elevated temperature, the outflow was thin, and the dispersion poor.

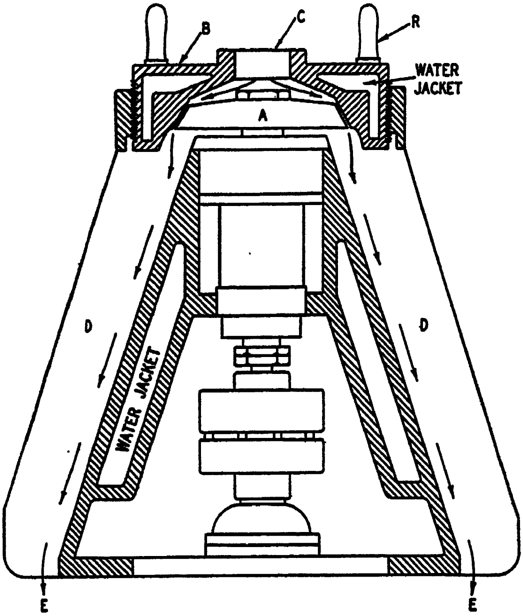

FIG 21*a*.—Premier mill (schematic). *A*, rotor; *B*, stator; *C*, inlet; *R*, gauge regulator; *D*,*E*, outlet.

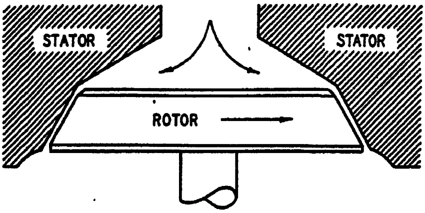

FIG. 21*b*.

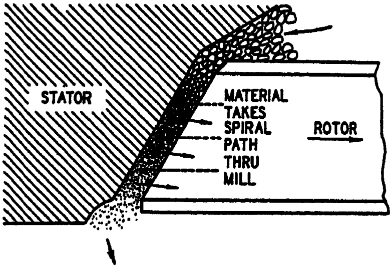

FIG. 21*c*.

termed such systems, which must be considered as transitions between microscopic dispersions and colloid dispersions, *cloudy systems*, or *mechanical turbidities.*[1]

Homogenizers.—Emulsification must also be considered as a special type of dispersion process, as it is the subdivision and distribution of one liquid in another. The production of stable systems will depend on the degree of comminution and on the presence of appropriate emulsifying and stabilizing agents, generally known as emulsifiers or emulgators. The fundamental reasons for their emulsifying action will be discussed in the chapter on surface phenomena. The machines used in the production of stable emulsions are known as *homogenizers.* In principle, the liquids to be emulsified are simultaneously forced under high pressure through nozzles, the orifice of which is so constructed (Fig. 23) that the

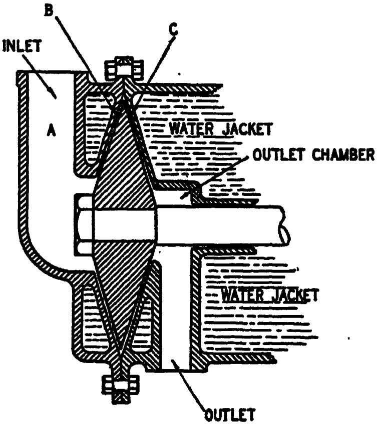

FIG. 22.—Manton-Gaulin mill (schematic). *B*, first-stage gap; *C*, second stage, or back face.

The material to be treated is introduced at *A* and is impelled through the first-stage gap *B* by impellers located on the front rotor face. These impellers also act as cutters and shredders, breaking down and thoroughly disintegrating the material as it passes through. In this gap the material receives a treatment that is in most cases equivalent to the entire treatment given by other mills. The impelling action of the rotor then forces material across the top edge of the rotor and down the second stage, or back face *C*, where it receives another and finishing treatment. The second stage *C* is adjustable by means of an adjusting dial which is calibrated in thousandths of an inch. All adjustments can be made while the mill is running.

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[1] *Koll. Beih.*, **31**, 222 (1930); *Koll. Zeit.*, **52**, 366 (1930); **53**, 137, 266 (1930); **54**, 117, 243, 358 (1931); **55**, 122, 251, 371 (1931); **56**, 117 (1931). Chapter "Colloid Mills and Comminution Chemistry," in J. ALEXANDER, "Colloid Chemistry," vol. 3, p. 179, D. Van Nostrand Company, Inc., New York, 1931.

For more technical summaries on the subject, see J. REITSTÖTTER, "Herstellung kolloider Loesungen anorganischer Stoffe," T. Steinkopff, Dresden, 1931; his chapter "Herstellung kolloider Loesungen" in LIESEGANG, "Kolloidchemische Technologie," 2d ed., p. 9, T. Steinkopff, Dresden, 1932; his contribution in KUHN, "Kolloidchemisches Taschenbuch," p. 11, Leipzig, Akad. Verlags-Ges., 1935. P. M. TRAVIS, "Mechano-chemistry and the Colloid Mill," Reinhold Publishing Corporation, New York, 1928. A. H. M. ANDREASEN, S. BERG, and E. KJAER, *Koll. Zeit.*, **82**, 37 (1938). G. WEGELIN, *Koll. Zeit.*, **14**, 65 (1914).

liquids are broken up while being forced through. Another construction applies a principle similar to the colloid mill by forcing the liquids in the form of very fine jets against disks rotating at high speed, thus causing their complete disintegration.

In recent years, a new mechanical dispersing method has been introduced. In this case, dispersion or emulsification is obtained by the use of ultrasonic waves. In principle, a piezoelectric quartz plate, placed in an oil bath, is caused to vibrate by applying a high-frequency alternating current. The frequency of the current must correspond to the natural period of vibration of the plate. The energy of the vibration is transferred to the surrounding oil, which rises above the plate in the form of a fountain. If the container holding the dispersion medium and the substance to be dispersed is held in this fountain, dispersion takes place. Undoubtedly such a method, which permits excellent dispersion of a variety of substances, would have the advantage that the preparation is not contaminated with any foreign matter and is not exposed to any deleterious secondary effects. However, so far, the difficulty in procuring satisfactory plates of appreciable size and other technical difficulties have hampered the application on a larger scale. Nevertheless, a closer understanding of the phenomena involved promises an interesting development in the near future.[1]

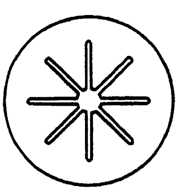

FIG. 23.—Homogenizer nozzle (schematic).

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[1] The following literature references pertain exclusively to the application of ultrasonic waves in the production of dispersed systems (other applications are not considered): Langevin, British Patent No. 145691, 1921. Wood and Loomis, *Phil. Mag.*, **4** (7), 417 (1927); *Physiol. Rev.*, **29** (2), 373 (1927). Schmitt, Johnson, and Olson, *J. Am. Chem. Soc.*, **51**, 370 (1929). Garden, Freundlich, and Soellner, *Zeit. physikal. Chem.* (*A*), **160**, 469 (1932). H. B. Bull and K. Soellner, *Koll. Zeit.*, **60**, 263 (1932). C. Bondy and K. Soellner, *Trans. Faraday Soc.*, **31**, 835, 843 (1935). A complete summary on the subject matter has been published by H. A. Wannow, *Koll. Zeit.*, **81**, 105 (1937). Detailed technical data on the production of ultrasonic waves can be found in a paper by H. Freundlich, F. Rogowski, and K. Soellner, *Koll. Beih.*, **37**, 223 (1933); and especially in E. Grossmann's book "Ultraakustik," Leipzig, 1934. H. Freundlich, *Trans. Inst. Chem. Eng.* (London), **15**, 223 (1937). K. Söllner, *J. Phys. Chem.*, **42**, 107 (1938). J. J. Hermans, *Phil. Mag.*, **25**, 426 (1938). Naoyasu Sata, *Koll. Zeit.*, **81**, 182 (1938). H. Freundlich and D. W. Gillings, *Trans. Faraday Soc.*, **34**, 649 (1938).

Another field of mechanical dispersion is the production of *aerodispersoids*. The liquids to be dispersed are atomized and thrown against disks revolving at high speed. Highly viscous liquids or solid substances can be dispersed in this way if they are first dissolved in an appropriate solvent. Particle size of the resulting fog is controlled by the concentration of the solution and the circumferential velocity of the revolving disk. If one intends to produce monodisperse systems by this method, one can obtain good results by applying a device originally introduced by Regener. The fog or smoke is blown at high velocity through a narrowly wound spiral, which causes the larger particles to be deposited on the walls as a result of the centrifugal forces.[1]

Chemical Dispersion Methods.—In many cases, coarse precipitates can be dispersed into a sol by washing out the electrolytes until complete peptization occurs.[2] A practical application is the process devised by Kuzel,[3] by which such metals as zirconium, thorium, tungsten, vanadium, and platinum were converted into their hydrosols. The metals were alternately treated with acidic and alkaline liquids, a thorough washing step being interposed between two treatments. This treatment formed surface salts, which, upon washing, opened up the surface to further attack, by the liquid. The dispersion of graphite by thorough oxidation, as devised by H. Karplus,[4] is based on the same principle.

Comparatively little is known in regard to the application of other types of energy—with the exception of electricity—in dispersion processes. None of them has so far attained any importance. German Patent No. 387.207 mentions the possibility of dispersing metal by raising its temperature until it glows while placed in a dispersion medium. A. Scala and M. Traube-Mengarim[5] state that certain metals such as iron, zinc, copper, and nickel can be dispersed simply by prolonged boiling in dis-

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[1] See, *e.g.*, V. Kohlschütter, *Koll. Zeit.*, **42**, 209 (1927). A. Stäger, *ibid.*, **42**, 223 (1927). W. L. H. Moll, *ibid.*, **81**, 225 (1937).

[2] The occurrence of turbid filtrates of CuS, due to excessive washing of the precipitate, is an example of this phenomenon.

[3] German Patent No. 197.379.

[4] German Patent No. 292.729.

[5] *Ibid.*, **6**, 65, 240 (1910); **10**, 113 (1912).

tilled water. The Svedberg[1] mentions the dispersion of metals by radiant energy, as, for instance, ultraviolet light or x rays. H. Nordenson[2] expresses the opinion that the reason for these phenomena is primarily a surface oxidation. A method that can also be termed thermal is described by I. Nordlund,[3] in which mercury vapor is condensed on a water surface. Bogdandy, Boehm, and Polany[4] obtained satisfactory sols by condensing molecular rays obtained by cathodic atomization in an appropriate solvent. N. Semenoff, A. Schalnikoff, and F. Roginsky[5] evaporate two substances in high vacuum and condense them simultaneously on a surface cooled with liquid air.

Condensation Processes.—If we have a supersaturated solution or vapor and reduce the solubility by excessive cooling, introduction of foreign matter, electrical discharge, dilution, or the like, the excess of the dissolved phase will show up as a third part in the system. In accordance with the continuity of the disperse state of matter, previously discussed, this new "phase" must pass through the colloidal range of dimensions prior to becoming a microscopical or visible precipitate. Depending on the nature of the system and on the specific conditions causing the destruction of the supersaturation, we can not only produce but can also maintain the newly formed part in the colloidal range. For instance, if we have a resin dissolved in alcohol and add water to this system, the solvent power of the alcohol will be reduced. The excess of resin will form a new part, which, when using the right proportions, will be obtainable in colloidal dimensions. By the same method, P. P. v. Weimarn produced sulphur sols from alcoholic solutions, whereas Wo. Ostwald and I. Egger[6] obtained sulphur sols by dissolving sulphur in hydrazine hydrate and diluting the solution with water. The production of aerosols by condensation of supersaturated vapor or by the formation of a disperse part, as a result of a chemical reaction in the gas phase, also falls into the same group.

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[1] *Ibid.*, **6**, 129 (1910).

[2] *Koll. Beih.*, **7**, 91, 110 (1915).

[3] *Koll. Zeit.*, **26**, 121 (1920).

[4] *Zeit. Phys.*, **40**, 211 (1926).

[5] *Ibid.*, **38**, 738 (1926); *Koll. Zeit.*, **43**, 67 (1927); **63**, 263 (1933).

[6] *Koll. Zeit.*, **43**, 353 (1927).

As previously mentioned, an interesting device for the production of fogs has been constructed by Regener[1] (Fig. 24). Hot air enters through pipe *A* and passes around the container *B*, until it reaches the surface of the liquid contained therein; taking up the vapor, it leaves through pipe *C*, where a series of electrical discharges cause condensation of the supersaturated vapor.

Fogs and smokes are also frequently produced in chemical reactions, *e.g.*, during the manufacture of sulphuric acid. The reaction between ammonia and gaseous hydrochloric acid results in the formation of an aerosol of ammonium chloride.[2] Aerosols of metallic oxides can be obtained by evaporating the corresponding metal in an electric arc.[3]

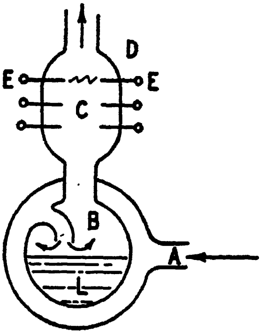

FIG. 24.—Production of aerodispersoids. *A*, hot-air inlet; *B*, container; *L*, liquid; *C*, discharge container; *E*, electric connections; *D*, fog discharge.

Reduction Methods.—The most commonly used condensation processes are based on reduction methods. Theoretically, all reducing agents can be used. Most generally known are formaldehyde, hydrazine hydrochloride—sulphate or hydrate—in the production of gold or platinum sols from salts of the respective elements. Pure hydrogen has been applied for the reduction of silver. Excellent reversible sulphur sols have been produced by decomposing sodium thiosulphate with sulphuric acid.[4] In the preparation of gold sols, gold chloride is also reduced by pure hydrogen peroxide. It has also been possible to produce very stable gold sols by reducing the salt at elevated temperature in sodium silicate.[5]

Oxidation Processes.—If an insoluble body is formed by an oxidation process, colloid disperse systems can be produced. For

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[1] See H. FREUNDLICH, "Kapillarchemie," vol. II, p. 786, Akad. Verlags-Ges., Leipzig, 1932.

[2] V. KOHLSCHÜTTER, *Koll. Zeit.*, **42**, 209 (1927).

[3] G. JANDER and A. WINKEL, *ibid.*, **63**, 5 (1933); **65**, 290 (1933).

[4] M. RAFFO, *Koll. Zeit.*, **2**, 358 (1907–1908). THE SVEDBERG, *Koll. Zeit.*, **4**, 49 (1909).

[5] C. FRONDELL, *Econ. Geol.*, **33**, 1 (1938).

example, if hydrogen sulphide and sulphur dioxide are allowed to react upon each other at temperatures around 0°C., colloidal sulphur of extremely fine particle size is produced.[1] Iron oxide sols can be obtained by oxidizing iron carbonyl with hydrogen peroxide.[2]

Hydrolysis.—Many oxide and hydroxide sols can be produced by hydrolysis. The latter can be induced by a temperature rise, extreme dilution, dialysis, or a combination of these possibilities.

Double Reactions.—So-called double reactions frequently also lead to colloidal systems; *e.g.*, colloidal lead sulphide is obtained by having hydrogen sulphide react with colloidal lead hydroxide. According to Freundlich and Nathansohn,[3] colloidal silver sulphide is obtained by the interaction of silver and sulphur sols. If arsenic acid is dissolved in glycerin, and hydrogen sulphide is introduced, a highly concentrated arsenium trisulphide sol is obtained.[4]

All the sols discussed so far must be considered as polydisperse. Iso-(mono-) disperse sols of gold have been produced by R. Zsigmondy.[5] By reducing gold salt with etherial phosphor solution, an amicronic nucleus solution was produced, and this added to the gold solution to be reduced. The reduction was carried out in such a way that the rate of nuclei formation was low. Since further reduction takes place on the preexisting nuclei, an isodisperse system is obtained. Similar results with silver have been reported by Vogt and Heumann.[6]

Electrical Processes.—When a metal is used for the electrodes, and an arc is formed between two pieces of the same metal submerged in a liquid, the metal disperses and forms a sol. However, a spectrographic study of this process, originally described by G. Bredig, reveals that the metal is first vaporized, and the vapor then condensed. It has been found that the best results are obtained by applying a direct current of 5 to 12 amp. and a potential of 20 to 100 volts. The addition of traces of a

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[1] German Patent No. 427.585. This reaction is also made use of in the vulcanization of thin-walled rubber goods by the "Peachey" process, British Patent No. 129826/1918.

[2] H. Freundlich and H. P. Zeh, *Zeit. physikal. Chem.*, **114**, 65 (1925).

[3] *Koll. Zeit.*, **29**, 16 (1921).

[4] Faust, German Patent No. 424.141.

[5] *Zeit. physik. Chem.*, **56**, 65, 77 (1906).

[6] *Zeit. anorg. allg. Chem.*, **152**, 163 (1926); **173**, 34 (1929).

peptizing agent or an electrolyte, with a di- or trivalent anion, improves the result. If very stable sols must be obtained, the addition of a protective colloid (see page 148) is advisable. If easily oxidizable metals are to be dispersed, the addition of a reducing agent, such as sodium sulphite, is advantageous. The Svedberg has obtained a steadier arc by enclosing it in a quartz tube which is immersed in the dispersion medium. The Svedberg and E. O. Kraemer applied alternating current of high frequency (10^5 to 10^7 cycles).[1] A. N. Fraser and J. Gibbard discuss a similar method.[2]

F. Haber, M. Le Blanc, and E. Mueller have transformed a series of metals and metalloids into sols by simple electrolysis in the presence of an electrolyte in the dispersion medium.[3]

The fact that reactions between dilute solutions and those of medium concentration most frequently result in the formation of crystalline particles (see page 73) has resulted in a number of attempts to discuss condensation processes from a molecular kinetic point of view, similar to the way De Coppet[4] and later Tammann[5] discussed crystallization. Both distinguish between the formation of seed crystals and their growth. When a melt is cooled, the freely moving molecules or ions will unite, if their kinetic energy is sufficiently small, and form centers of crystallization or nuclei. Since the kinetic energy depends on the temperature of the melt, it becomes evident that crystallization will be greater at temperatures well below the melting point, when the kinetic energy is sufficiently reduced. The viscosity of the melt increases with decreasing temperatures, and an

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[1] *J. Am. Chem. Soc.*, **46**, 198 (1924). See also G. Börjeson and The Svedberg, *Koll. Zeit.*, **25**, 154 (1919). W. Naumoff, *ibid.*, **32**, 95 (1923). S. Miyamoto, *ibid.*, **67**, 284 (1934); **69**, 179 (1934); **71**, 297 (1935); **74**, 32 (1936).

[2] *Canad. J. Research*, 133 (1932).

[3] There are excellent summaries to be had on the production of colloidal disperse systems. Besides those mentioned in footnote 1, p. 65, the following may be added: Wo. Ostwald, "Praktikum der Kolloidchemie," T. Steinkopff, Dresden, 1930. The Svedberg, "Methoden zur Herstellung kolloider Loesungen," T. Steinkopff, Dresden, 1922. F. V. von Hahn, "Herstellung und Stabilität kolloider Loesungen anorganischer Stoffe," Stuttgart, 1922. H. B. Weiser, "Inorganic Colloid Chemistry," John Wiley & Sons, Inc., New York, 1933–1937.

[4] *Ann. Chim. Phys.*, **6** (5), 275 (1875); **10** (8), 475 (1907).

[5] "Kristallisieren und Schmelzen," L. Voss, Leipzig, 1903.

increased viscosity counteracts the free movement of molecules to a certain extent. Therefore, we must reach a maximum condition for nuclei formation at an intermediate temperature, as described by Bakhuis Roozebohm.[1] The number of seed crystals formed in unit time per unit weight of the supercooled liquid is termed *rate of nuclei formation.* The *rate of crystallization, i.e.,* the growth of a formed nucleus to a well-oriented crystal, refers to the second step of the process and also passes through a maximum with decreasing temperatures.

In the case of supersaturated solutions, the conditions are somewhat more involved, since besides temperature the concentration of the solute must be considered. From the foregoing, it is evident that the degree of dispersion of a system obtained by condensation depends on the rate of nuclei formation and rate of crystallization. The greater the rate of nuclei formation and the smaller that of crystallization the higher will be the degree of dispersion of the system. Since these rates, in the case of solutions, depend on temperature and concentration, the degree of dispersion of a system obtained by condensation must also be a function thereof.

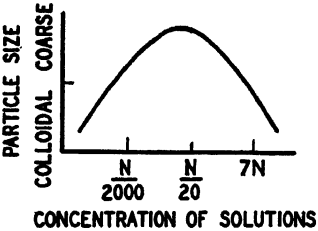

Fig. 25.—P. P. von Weimarn's law.

If we refer again to v. Weimarn's law of precipitation (see page 23) which controls condensation processes, we find that *colloidal* disperse systems are obtainable by the interaction of very dilute or of extremely concentrated analytical disperse systems.

If we prepare solutions of manganese sulphate and barium thiocyanate of $N/2000$ concentration and mix these slowly together, a barium sulphate sol will result. If we raise the concentration to about $N/20$ and pour the solutions, preferably heated, together, a coarse precipitate will settle out rapidly. If we increase the concentration further to about $7\ N$, a thick paste of jellylike consistency results. If traces of this paste are mixed with a large quantity of water, a sol, corresponding in its outer appearance to the one obtained with solutions of low con-

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[1] "Die Gleichgewichte," F. R. Vieweg, Braunschweig, 1901.

centration, will be formed. This proves that the individual particles of the gel must also be of colloidal dimensions. The v. Weimarn rule is schematically pictured in Fig. 25.

X-ray analysis of the three types of precipitates revealed that those of the dilute and medium concentrations are of crystalline nature, whereas the reaction product of the highly concentrated solutions is amorphous. This fact is inexplicable by the De Coppet-Tammann theory without some amendment. F. Haber[1] introduced for this purpose the terms *rate of aggregation* and *rate of orientation.* On their relation depends whether a newly formed body will be crystalline or amorphous. The rate of aggregation indicates the tendency of the dissolved substance (solute) to form a new phase, whereas the rate of orientation measures the tendency to form systems with the least possible free energy. The former is a function of temperature, concentration, etc.; the latter, a specific property of the solute (dissolved substance).

With highly concentrated solutions the rate of aggregation (nuclei formation) is predominant, thus causing at first the formation of amorphous precipitates. Because of the dense packing of the great number of suddenly formed nuclei, the free movement of the aggregates and still available individual ions is mechanically restricted. This results in an extremely slow rate of orientation. However, in time, a coarse crystalline structure will finally result out of the originally random aggregation of molecules. If the originally amorphous aggregation is immediately diluted, the chances for secondary orientation will be proportionally diminished, because the chances of molecules hitting each other in a way that will result in oriented growth are extremely small. A dilute, but stable, amorphous colloidal suspension will result. If concentrated, stable, amorphous colloidal precipitates are desired, it is necessary to coat the formed amorphous nuclei with a protective colloid, *e.g.*, gelatin or fatty acids. Such a coat will prevent orientation and crystal growth during prolonged storage. In the case of dilute systems and slow reaction, the rate of orientation will be predominant. The relatively few available molecules can move freely and orient themselves. Growth of the crystals beyond colloidal dimensions is impossible owing to lack of more dissolved, crys-

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[1] *Ber.,* **55,** 1717 (1922).

tallizable matter.. In medium concentrations, the rate of orientation is further accentuated; and if elevated temperatures are applied during the reaction, this will increase the probability that molecules meet in the right position to each other in order to link up in crystal-lattice orientation. Therefore a coarse crystalline precipitate must result.

CHAPTER VIII

KINETICS OF COLLOIDAL PARTICLES

THERMAL MOVEMENT OF MOLECULES

When a substance upon being dissolved forms a highly disperse system—a true solution—then the classical molecular theory postulates that the solid substance has been dispersed into its individual molecules, which are able to move freely between the molecules of the dispersion medium. We can picture a colloidal solution in a very similar way, simply by substituting a colloidal particle for the individual molecule of the solute, the former, as we know, being built up out of many individual molecules of the substance. (We speak of a colloidal particle when so many individual molecules have aggregated that the dimensions of the newly formed unit fall into the colloidal range.) If we take this point of view, then an individual particle of a gold sol would correspond to one molecule in a true solution. The difference between true and colloidal solutions, therefore, can be considered to exist mainly in the degree to which the dissolved substance is dispersed between the molecules of the dispersion medium. Thus, the colloidal particle has frequently been termed "physical molecule" in contradistinction to the ultimate units generally known as "chemical molecules." Such definition and deduction are in full accord with the points of view that we have taken, *viz.*, that there is no sharp line of demarcation between the coarser suspensions and true solutions. The colloidal dispersions have to be considered as systems characterized by intermediate discontinuities.

The classical theory ascribes thermal movement to all molecules, their speed depending on their size. The velocity of a colloidal particle should therefore also be intermediate between the movement of a coarse or microscopically visible particle, just small enough to overcome too rapid sedimentation, and individual molecules that cannot be discerned even with the most refined optical equipment. Their existence, at least from an experimental point of view, is hypothetical. According to the classical theory, the molecules move about in an absolutely irregular manner, and their arrangement at any time differential is that of "ideal disorder." If it is possible to make the colloidal particles in a colloidal solution visible or at least prove their individual existence and observe the movement that they perform, then we actually ought to be able to test experimentally the theory of molecular kinetics.

THE IMPORTANCE OF THE BROWNIAN MOTION

The Brownian molecular movement permitted such studies. Discovered in 1827, it received but little attention at first, presumably because the assumption prevailed that the reason for this phenomenon was due to external influences, such as vibrations or thermal currents. Not until C. Wiener[1] pointed out that it was impossible to alter the movement by the elimination of any external influence and expressed the opinion that the reason for this phenomenon depended, according to thermokinetics, on the irregular bombardment of the suspended particles by the surrounding molecules of the dispersion medium did Brown's discovery find the interest and recognition that it deserved. G. Gouy[2] and Cantoni[3] strengthened Wiener's point of view by very carefully conducted experiments.

The possibility that the reason for the movement might be due to a different rate of dissolution at different points of the particles (comparable to the movement of camphor particles on the surface of a liquid) was definitely discarded by W. N. Hartley,[4] who could demonstrate that very small gas bubbles in liquid enclosures of minerals also exhibit Brownian motion.[5]

ELECTROKINETIC INFLUENCE

Another more serious objection to the kinetic theory was that the addition of electrolytes can materially influence Brownian movement. The theory itself offers no reason why the addition

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[1] *Pogg. Ann. Phys.*, **118**, 79 (1863).

[2] *J. physique*, **7** (2), 561 (1888); *C. r. Soc. Biol.*, **109**, 102 (1889).

[3] *Nuovo Cimento* (Bologna), **27**, 156 (1867).

[4] *Proc. Roy. Soc.*, **26**, 150 (1877).

[5] See also THE SVEDBERG, *Koll. Zeit.*, **7**, 1 (1910). R. FÜRTH, *ibid.*, **42**, 197 (1927).

of further ions could influence the impacts of the molecules of the dispersion medium on the dispersed particle. The Svedberg[1] proved that the reason for the influence which electrolytes exercise upon Brownian motion is not connected with molecular kinetics but is an electrokinetic phenomenon (see page 106). This causes the suspended particles to adhere to each other when they collide, thus forming larger particles with reduced velocity until finally the particles grow to such an extent by aggregation that their rate of sedimentation becomes appreciable. The Svedberg demonstrated that in suspensions that had been sufficiently diluted so that comparatively few collisions between particles occurred, no change in the Brownian motion of the individual particles took place, even upon the addition of electrolyte, which otherwise would cause aggregation.

THE CAUSE FOR BROWNIAN MOVEMENT

Carbonelle and Thirion[2] substantiated this assumption with a series of model experiments. If we take a colloid particle in water, the "giant molecule" will be surrounded by a great number of comparatively small water molecules which bombard the particle as a result of their absolutely irregular thermal motion. The impacts will not be uniformly distributed at different time differentials, so that the particle will be submitted to a constant change of intensity and direction of the resultant force. (Fig. 26). C. Nägeli[3] opposed this point of view; according to his opinion, a single molecular impact is far too weak to cause a discernible movement of the particle. The molecular impacts are not additive; they occur irregularly from all sides and therefore must compensate each other. M. v. Smoluchowski,[4] in his classical contribution to the mathematical evaluation

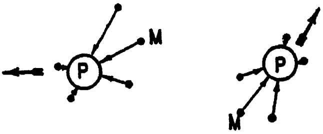

FIG. 26.—Brownian motion of colloidal particles. *P*, colloidal particle; *M*, molecules of dispersion medium.

The arrows indicate the direction of the impacts; their length illustrates the strength of the impacts.

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[1] *Nova Acta Regiae Societatis Scientiarum Upsaliensis*, Upsala, **2** (4), 146–155.

[2] *Revue des questions scientifiques, Bruxelles*, **7**, 44, 53 (1888).

[3] *Sitzber. Akad. Wiss. Muenchen*, **9**, 389 (1879).

[4] *Ann. Phys.*, **21** (4), 762 (1906).

of the Brownian motion, pointed out that such compensation will become evident only if the time during which the particle is observed is appreciable. He developed the theory of the Brownian motion from a molecular-kinetic point of view. The middle kinetic energy of a particle, which is moved about by the impact of the surrounding molecules of the liquid, must in stationary condition be equal to the kinetic energy of these molecules. *Therefore, the particle must behave as if it were a molecule of a dissolved substance.* A. Einstein[1] came to a very similar deduction by assuming that discernible particles in Brownian motion will exert the same osmotic pressure on an impermeable membrane as an identical number of molecules.

DIFFUSION

For the purpose of simplifying the understanding of these fundamental theories, it seems appropriate to consider the diffusivity of colloids.[2] We must assume the colloidal particles to be individual molecules being bounced around by the molecules of the liquid in exactly the same way, for instance, as sugar molecules in a sugar solution. *Diffusivity is the property of a substance dissolved in a certain part of the medium to distribute itself throughout until its concentration is uniform in the entire system.* The same phenomenon occurs when a concentrated solution migrates into a diluted solution until the concentration is the same in both. Theoretically, the colloidal particles must also exhibit some diffusivity, which, however, will be negligible owing to their low molecular velocity.

The speed at which a uniform concentration between liquid layers of different concentrations is established differs in one case to another. Its mathematical expression is the *coefficient of diffusion.* Since the rate of diffusion of colloidal particles decreases with their increase in size, it is advisable to use highly disperse colloidal systems when studying the question if *Fick's law of diffusion* also holds for colloidal systems. This law states that the amount of matter passing in a time unit through a cylindrical tube in the direction of the concentration gradient

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[1] *Ann. Phys.*, **17** (4), 549 (1905); **19**, 371 (1906). *Zeit. Elektrochem.*, **13**, 41 (1907); **14**, 235 (1908).

[2] M. v. SMOLUCHOWSKI *Koll. Zeit.*, **18**, 48 (1916). R. AUERBACH, *ibid.*, **37**. 379 (1925).

is proportional to the cross section and to the concentration gradient at this point. The concentration gradient is the difference in concentration at two cross sections of the cylinder, separated from each other by a small distance. For example, if the distance is 1 cm. and the concentration at one end is found to be 2 grams per liter and at the other end 3 grams per liter, there is a concentration gradient of 1. The diffusion coefficient, therefore, determines the amount of matter passing in a unit of time, *e.g.*, 1 hour, through a cross section of 1 and a concentration gradient of 1. A careful evaluation of this factor from the point of view of molecular kinetics will materially assist in the study of diffusion and of Brownian motion. Offhand, it might seem difficult to understand how the one-sided movement of diffusion (migration from layers of high to those of low concentration) can be caused by such irregular motion as the Brownian movement.

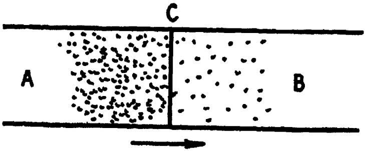

FIG. 27.—Diffusion. *A*, *B*, identical phases but of different concentration of dispersed part; *C*, imaginary cross section.

If we consider Fig. 27, assume a decreasing concentration from *A* to *B*, and study the phenomenon of diffusion at the imaginary cross section *C*, we must admit that the concentration to the left of *C* will be somewhat higher than to its right. Therefore, there will be more particles in the close nieghborhood of the cross section on its left than on its right side. For the sake of simplification we shall consider only those particles which move parallel to the horizontal axes of the cylinder. As a result of the law of ideal disorder (probability calculus), half of the particles present at the left and right of *C* will be pushed, in any time differential, to the left and to the right. Therefore, in every time differential, the Brownian movement will force one-half of the particles present on each side of the cross section through the plane *C*. Since we postulated a large number of particles to have been originally present on the left side, there must be a larger migration to the right. As soon as the number of particles on both sides becomes the same, a dynamic equilibrium has been established, and diffusion comes to a standstill. (For a rigorous mathematical evaluation, see Appendix, p. 227.)

R. E. Liesegang, in 1896, recorded a peculiar rhythmically banded structure obtained when a silver nitrate crystal was placed on a sheet of gelatin, which had been impregnated with potassium dichromate. The banded structure very closely resembles that found in nature in agates, chalcedony, and other silicates. The formation of these minerals most presumably took place by diffusion of salts while the silicates were still present in gel condition.

A voluminous literature on such banded structures (Liesegang rings) resulting from reactions in gels has been accumulated. Although a great number of theories as to their formation have been offered, none as yet can be considered as really satisfactory.[1]

OSMOTIC PRESSURE

If we continue to discuss analytical disperse and colloid disperse solutions from the same general point of view as before, it is essential also to consider the osmotic pressure. (For a detailed discussion of osmotic pressure and its mathematical evaluation, the reader is referred to the standard textbooks of physics and physicochemistry.)

It is a well-recognized fact that the osmotic pressure of a solution is proportional to the number of molecules dissolved in a unit volume. It is independent of the nature or chemical composition of the dissolved substance. This means that an equal number of molecules of different substances, if dissolved in the same volume and if measured at the same temperature, will result in solutions exhibiting the same osmotic pressure. Since col-

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[1] Some of the most important papers are listed below:
E. Hatschek, *Koll. Zeit.*, **10**, 124 (1912); **14**, 115 (1914).
E. Küster, *ibid.*, **13**, 192 (1913); **14**, 306 (1914); **18**, 107 (1916).
W. P. Draeper, *ibid.*, **14**, 163 (1914) in liquids.
F. Köhler, *ibid.*, **19**, 65 (1916).
W. Moeller, *ibid.*, **20**, 242 (1917); **22**, 155 (1918); **23**, 11 (1918).
Martin H. Fischer and G. D. McLaughlin, *ibid.*, **30**, 13 (1922).
H. Kägi, *ibid.*, **33**, 284 (1923).
C. A. Schleussner, *ibid.*, **34**, 338 (1924).
J. Traube and K. Takehara, *ibid.*, **35**, 245 (1924).
Wo. Ostwald, *ibid. Erg. Bd.*, **36**, 380 (1925); **40**, 144 (1926).
E. B. Hughes, *ibid.*, **72**, 212 (1935).
H. Knöll, *ibid.*, **82**, 76 (1938).
V. Gore, *ibid.*, **82**, 79, 203 (1938).
K. Neumann and V. Costeanu, *ibid.*, **84**, 130 (1938).

loidal particles, if considered as physical molecules, are decidedly larger and of greater volume than a true (chemical) molecule, their number in a solution of a given weight concentration will be materially smaller than the number of molecules in a true solution. Therefore, it is logical that the osmotic pressure, as defined, will be negligible if compared with a molecular solution of the same concentration. This explains, furthermore, the difficulty of accurately determining osmotic pressures of colloidal dispersions.[1] In addition, one may not overlook the fact that most stable colloidal dispersions contain electrolytes. Owing to the concentration of their molecules, these electrolytes by themselves may very well cause a decidedly larger osmotic pressure than the colloid part of the system. (There are other complications that must be considered, such as Donnan equilibrium; see page 110.)

Reduction in freezing point and increase in boiling point, which are closely connected with osmotic pressure, are, to all intents and purposes, immeasurable in colloidal systems.

Osmotic pressure can also be understood as the driving force of diffusion. If we substitute in Fig. 27 a semipermeable membrane for the imaginary cross section *C* and construct it so that it can be moved free of friction and does not permit diffusion of the dissolved molecules, then the impact of the particles from both sides must give a resultant force strong enough to push the membrane in the direction of *B*. The osmotic pressure tends toward the same direction as the diffusion. The latter has been expressed by the coefficient of diffusion, which can be obtained if the temperature, the viscosity of the dispersion medium, the diameter of the dispersed particles, and Avogadro's figure are known. This important deduction, originated by W. Nernst and A. Einstein, has been proved by experimentally determining the coefficient of diffusion of a given system and recalculating therefrom Avogadro's figure ($60.6 \pm 0.1 \cdot 10^{22}$). Attempts have also been made to determine the molecular weight of colloids by measuring their coefficient of diffusion. However, it must be borne in mind that such results can be considered only as first approximations. (For mathematical evaluation of osmotic pressure in colloidal systems, see Appendix, page 228.)

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[1] R. S. Lillie, *Proc. Soc. Exp. Biol. Med.*, **4**, 111 (1907); *J. Gen. Physiol.*, **20**, 127 (1907).

INFLUENCE OF GRAVITY

So far we have purposely omitted from our discussion of diffusion and Brownian motion the possibility that external forces might further complicate matters. Most important of these is gravity, *i.e.*, where the thermal movement of the particles is influenced or complicated by gravitational fall or sedimentation. Every movement of a particle that happens to be directed earthward will be somewhat increased by gravity, whereas any upward movement will be proportionally decreased. Depending on the mass of the molecule (particle), we finally reach an equilibrium between gravity and thermal motion. Since gravitational *acceleration* is independent of the molecular weight, the molecular movement decreases only with the square root of the molecular weight. However, the force of gravity is not independent of weight; therefore it will become predominant with heavy particles. Particles where thermal movement cannot overcome gravitational movement will not be able to stay in suspension. In the atmosphere of the earth, we have to reach an elevation of about 3.12 miles to strike a layer where the number of molecules per unit volume or where the density of the air is just about one-half of its value on the surface of our globe. Yet, if we determine the height of the layer having half the concentration of the bottom layer in a colloidal dispersion, we find that we need move only a few microns upward to reach it.

Jean Perrin was the first to study systematically such sedimentation equilibriums. For his classical experiments he used emulsions of mastic and of gum-gutta in water.[1] (The mastic emulsions are produced by introducing an alcoholic mastic solution into an excess of water, whereas one can produce the gum-gutta emulsion by simply grinding the resin in water.) He could demonstrate that the number of particles (Fig. 28) decreases logarithmically with the height and that an equilibrium is set up. (For mathematical evaluation, see Appendix, page 228.) In honor of the discoverer of this fundamental analogy between

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[1] *Compt. rend.*, **146**, 967 (1908); **147**, 530, 594 (1908); **152**, 1380 (1911). *Ann. chim. phys.*, **18** (8), 5 (1909). PERRIN-LOTTERMOSER, "Die Atome," Dresden, 1914. See also B. ILJIN, *Zeit. physikal. Chem.*, **87**, 366 (1914). H. FREUNDLICH "Kapillarchemie," vol. I, pp. 488*ff*., Akad. Verlags-Ges., Leipzig, 1930. C. BARUS, *Koll. Zeit.*, **9**, 14 (1911).

gases and colloidal systems, such sedimentation equilibriums have been termed "Perrin atmospheres."

If the dispersion medium is of higher density than the dispersed particles (for example, as is the case in cream), we obtain a "reversed Perrin atmosphere," the equilibrium condition resulting from the interaction of buoyancy and thermal motion.

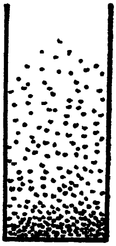

Fig. 28.—Perrin's atmosphere.

The mathematical evaluation of the sedimentation equilibrium can be carried out by applying a formula analogous to Halley's hypsometric or barometer formula (see Appendix, page 229.) On the basis of the amended equation, J. Perrin was able to determine Avogadro's number, after having determined the number of particles in two layers of the system, the size of the particles, their density, and the density of the dispersion medium. Perrin obtained for (N) (Avogadro's figure) a value of $68.2 \cdot 10^{22}$.[1] Westgren[2] improved the optical equipment and obtained for (N) a value of $60.5 \cdot 10^{22}$, which is extremely close to *Millikan's* value of $60.6 \cdot 10^{22}$, the latter being considered today as the most accurate. Nordlund,[3] using mercury droplets suspended in water, found for (N) a value of $59.1 \cdot 10^{22}$. Similar values were obtained in highly viscous systems. These experiments proved beyond doubt that the particles of dilute emulsions behave similarly to the molecules of a gas or of a dissolved substance. The *Brownian* motion, therefore, corresponds to what the theory of molecular kinetics postulates. The particles will obey in dilute systems van't Hoff's law. The emulsified particles may be considered as large molecules. Since the mathematical evaluation assumes a system in perfect equilibrium, it is essential that particle-distribution measurements should be carried out in comparatively shallow containers, as otherwise the time necessary to attain equilibrium is extremely long. According to calculations by Mason and Weaver,[4] Weaver,[5] and R. Fuerth,[6] the time to attain equilibrium in a column of 100 cm. height

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[1] J. Perrin and J. Bjerrum, *Compt. rend.*, **152**, 1569 (1911).

[2] *Zeit. anorg. Chem.*, **93**, 231 (1915).

[3] *Zeit. physikal. Chem.*, **87**, 40 (1914).

[4] *Phys. Rev.*, **23** (2), 412 (1924).

[5] *Ibid.*, **27**, 499 (1926); *Zeit. Phys.*, **43**, 296 (1927); **49**, 311 (1928).

[6] *Zeit. Phys.*, **40**, 351 (1926).

would be 1½ years, approximately, in a watery system containing particles of 200 mμ diameter and a difference in the specific density of the particles and the water of 1.

SEDIMENTATION EQUILIBRIUM AND VELOCITY

On the basis of the foregoing, it becomes evident that the attainment of a sedimentation equilibrium will be the more difficult the smaller the dispersed particles are. However, one can obtain sedimentation values if one replaces gravity by centrifugal acceleration, which, depending on the number of rotations and the type of apparatus used, can exert a pull several hundred thousand times stronger than plain gravity.

The Svedberg and his collaborators in Sweden as well as in the United States (H. Rinde, J. B. Nichols, R. Fåhraeus, A. Lysholm, E. O. Kraemer, W. D. Lansing, O. Lamur, K. O. Pedersen, A. Tiselius, J. W. Williams, etc.) must be credited with the outstanding contributions in this field. By the construction and use of a special type of centrifuge, generally known as "ultracentrifuge," they have studied sedimentation rates and equilibriums as well as particle-size distribution down to sizes of only a few millimicrons. The determination of molecular weights of proteins and other organic high-molecular compounds by ultracentrifugal measurements is becoming of increasing importance.[1] Recently a somewhat simpler instrument has been constructed by J. W. Beams and E. G. Pickels.[2] The fact that centrifugal methods are the most accurate for the purpose of determining particle size as well as particle-size distribution and the fact that they offer simple means of producing monodisperse fractions make it understandable why considerable time and efforts have been devoted to the construction of such apparatus in recent years and also to the mathematical evaluation of particle-size determination by their use.[3]

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[1] For further details, see, *e.g.*, LEE H. CLARK, *Coll. Symp. Monogr.*, **2**, 174 (1925). J. B. NICHOLS and H. C. LIEBE, *ibid.*, **3**, 268 (1925). J. B. NICHOLS, *ibid.*, **6**, 287 (1928). For a recent detailed discussion of the development of the ultracentrifuge, its working and use, as well as for a complete list of literature references, see THE SVEDBERG, "The Ultracentrifuge and Its Field of Research," *Ind. Eng. Chem.* (*Anal. Ed.*), **30**, 113 (1938).

[2] *Rev. Sci. Instr.* **6**, 299 (1935).

[3] For a detailed discussion and literature references, see, *e.g.*, E. A. HAUSER and C. E. REED, *J. Phys. Chem.*, **40**, 1169 (1936). C. E. MARSHALL, *Proc.*

Quite recently J. W. McBain[1] described a very simple type of closed (opaque) ultracentrifuge, specifically constructed for laboratory work.

Instead of determining sedimentation equilibriums, the measurement of sedimentation velocity is frequently applied for determination of particle sizes. This is accomplished by the use of *Stokes'* formula (see Appendix, page 243). Sedimentation experiments, furthermore, permit determining the percentage of particles of different size present in one system (polydisperse system), or, in other words, ascertaining the particle-size distribution—a function of increasing importance in the systematic analysis of colloidal dispersions.

THE KINETICS OF THE BROWNIAN MOTION

We can now revert again to a more detailed discussion of the fundamental laws of the Brownian motion. When observing a sufficiently small particle in the ultramicroscope, we notice an irregular vibrationlike movement of the particle and simultaneously a rather apparent transition from one point to the other. If we consider that the movement is not restricted to one plane, it becomes clear that the projection of this movement into the focal plane of the microscope is only a very rough approximation of what actually happens. W. Exner[2] hoped to be able to determine the speed of the movement by measuring the time that a particle needed to move a predetermined distance. However, his calculations resulted in much lower velocity than that obtained by calculating it on the basis of the kinetic theory.

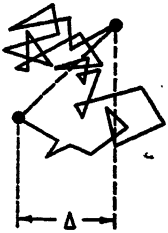

Fig. 29.—Brownian motion. Δ, mean displacement.

A. Einstein and M. v. Smoluchowski applied for their evaluation the displacement of a given particle in a unit of time. As middle displacement we simply take the projection of the horizontal displacement on to one axis of a coordinate system (Fig.

Roy. Soc., *A* **126**, 427 (1930); *Chem. Ind.*, **50**, 444, 457 (1931). See also H. Gessner, contribution in Kuhn's "Kolloidchemisches Taschenbuch," p. 358, Akad. Verlags-Ges., Leipzig, 1935.

[1] *J. Phys. Chem.*, **42**, 1063 (1938).

[2] *Ann. Phys.*, **2** (4), 843 (1900).

29). Perrin determined a great number of displacements in a given gum-gutta emulsion. He found that the result obtained is in full accord with Maxwell's law of velocity distribution of gas molecules. If we determine the average of a great number of displacements, we can evaluate the distribution law of particle displacements by probability calculus. J. Perrin and Langevin demonstrated their results graphically (Fig. 30). They recorded the various displacements in a system of concentric rings, its center being taken as the starting point, and size and direction being registered as the distance from the end point to the center. The space between each circle corresponds to one-fourth of the average displacement value.

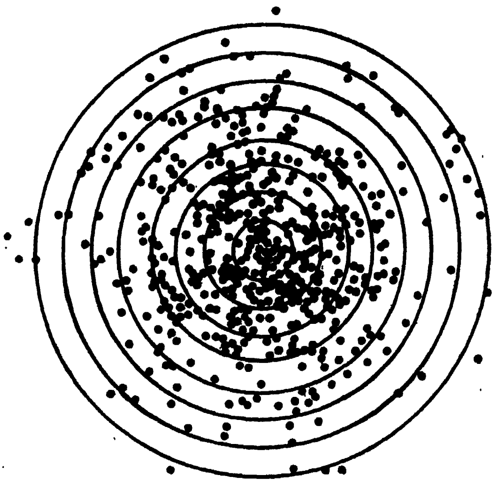

Fig. 30.—Displacement of gum-gutta particles.

Probability of Displacement.—The probability with which the displacement will vary can be well demonstrated by using the so-called "Galton board" (Fig. 31). The bottom of a pan is placed at a slight angle to the horizontal plane. In compartment *C*, several rows of nails have been placed. Above, there is a storage compartment *A*, in which little steel balls may be permitted to run out through opening *B*. Below section *C*, zone *D* has been subdivided into several compartments. If a sufficient number of balls are allowed to run through the rows of nails, we find, in full accordance with the probability laws, that medium displacements will prevail and that, taking the middle axis as the criterion, extreme positive or negative values are rare.

As has already been pointed out, there exists a simple relation between average displacement, coefficient of diffusion, and the selected time of observation. According to A. Einstein's evaluation,[1] we find that the average displacement increases with the square root of the time interval between two observations, or the square of the average displacement is proportional to this time interval (see Appendix, page 229). The amazing correlation between theory and experiment can be seen from the determinations made by The Svedberg on gold sols, with particles 54 mμ in diameter shown in the table below.

A. Einstein postulated that the Brownian motion is composed not only of a translatory component but also of a rotary one. He came to the conclusion that a third of the square of the angle of rotation is proportional to the time of observation (see Appendix, page 231). Again, J. Perrin[2] was able to prove that this theoretical deduction can be substantiated by experimental facts.

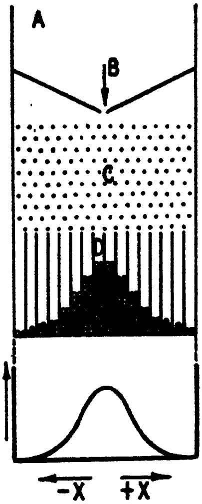

FIG. 31.—Galton board. *A*, storage compartment; *B*, opening for balls; *C*, rows of nails; *D*, receiving compartments. At the bottom is Gauss' error curve.

Finally, it seems of importance to refer to the so-called fluctuation phenomena. When talking about the concentration of a colloidal solution, we must realize that we are discussing only

Time interval, seconds	Average displacement, millimicrons	
	Observed	Calculated
1.48	3.1	3.1
2 · 1.48	4.5	4.4
3 · 1.48	5.3	5.4
4 · 1.48	6.4	6.2

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[1] *Zeit. Electrochem.*, **14**, 235 (1908).

[2] *Compt. rend.*, **149**, 549 (1909).

statistical average values; the true concentration in the smallest element of space will constantly fluctuate around the defined middle value. The Svedberg[1] determined the changes of concentration photographically in intervals of $\frac{1}{39}$ minutes, using a gold sol. The following figures are extracted from over 500 observations recorded, giving the number of particles observed in consecutive exposures in the microscopic field used:

1 2 0 0 0 2 0 0 1 3 2 4 1 2 3 1
1 0 2 1 1 1 1 3 1 1 2 5 1 1 1 0
2 3 3 1 3 3 3 2 2 1 1 1 2 2 4 2
2 1 2 2 6 1 2 2 1 4 2 3 4 5 2 4
. . . .

In the mathematical evaluation, we must differentiate between "fluctuation number" and "fluctuation velocity." The former defines the relative occurrence of the same number of particles in the microscopic field; the latter, the average time elapsed between the appearance of the same number of particles. It has been found that in the foregoing experiments the complete absence of particles will repeat itself every 9½ minutes, one particle will be present every 4.8 seconds, two particles every 6.2 seconds, four particles every 28.6 seconds, etc. The presence of 17 particles would give one probability for every 15,000 years. These data, which do not fully satisfy van't Hoff's laws, were later corrected by *Westgren*,[2] who applied a more satisfactory optical equipment. His results permitted perfect correlation with the theory. He obtained for (N) an average value of $60.9 \cdot 10^{22}$.

Summing up, we can now state that the systematic study of the Brownian motion of colloidal systems has contributed only indirectly to the practical colloid chemist. However, the fundamental importance of these studies to theoretical physics and physicochemistry seems to justify their incorporation in a book devoted primarily to demonstrating the importance of a systematic study of colloidal phenomena and of the benefit to natural science in general.

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[1] THE SVEDBERG and K. INOUYE, *Zeit. physikal. Chem.*, **77**, 145 (1911); *Arkiv för Kemi, Mineralogi och Geologi*, **4**, No. 19 (1911). The value for (N) averaged $62 \cdot 10^{22}$.

[2] *Arkiv Matem., Astron. Fys.*, **11**, No. 8 (1916).

CHAPTER IX

ELECTRICAL PROPERTIES OF COLLOIDAL SYSTEMS

In the historical introduction it was mentioned that Quincke, in 1850, discovered that a great number of substances when suspended in water in the form of very small particles tend to migrate to one specific pole if an electric field is applied to the system from the outside. This phenomenon is known as *cataphoresis*. Since then, a great number of other phenomena have been observed which have found their explanation in the electric properties of colloidal dispersions and discontinuities. All phenomena that involve the change in charges and that are associated with capillary effects, as, for example, adsorption, surface and interfacial tension, are generally known as *capillary electric phenomena*. What we are mainly interested in are the electrokinetic phenomena which make themselves specifically noticeable at boundary surfaces in systems where at least one of the existing phases is a liquid. Therefore, we have three possibilities to consider, *viz.*, liquid/liquid, gas/liquid, and solid/liquid systems.

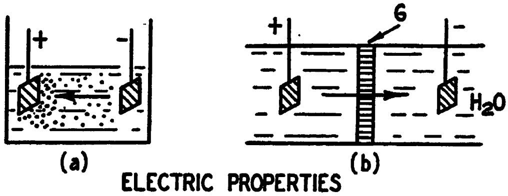

FIG. 32.—Electrophoresis and electroosmosis. The colloidal particles in *a* are negatively charged and therefore migrate to the positive pole (anode). *G*, capillary membrane.

Besides the aforementioned phenomenon of cataphoresis, in which an externally applied potential difference causes the suspended particles to migrate in the direction of that pole which carries a charge of opposite sign to that of the particles, three further possibilities present themselves (Fig. 32*a*).

If we place a capillary tube or a membrane, which can be considered as being built up of numerous capillary tubes, in a container filled with liquid and again apply a potential difference from the outside, the liquid will be caused to move. This phenomenon is known as *electroosmosis* (Fig. 32*b*).

If we force suspended particles to migrate through a dispersion medium without externally applying a potential difference, then an electric potential difference will be set up in the system by the movement of the particles. This phenomenon is known as *fall potential.*

If we move a liquid against another phase, *e.g.*, flowing liquid through a tube, an electric potential will result. This is known as *streaming*, or *flow*, *potential.*

As examples for these four types of electrokinetic phenomena, the following may serve as illustrations. The particles of rubber hydrocarbon that make up the disperse part in the natural milk sap, or "latex," of the rubber tree are negatively charged. If a potential difference is externally applied, these particles will migrate to the positive pole, or "anode," where they are deposited. (This plating out of rubber from its natural dispersion is the basis for different patented processes, for the coagulation of latex and the manufacture of a variety of rubber goods direct from latex.)[1]

Peat or kaolin pastes have the property of firmly retaining a comparatively large quantity of water. To eliminate this tightly held water, the system is placed in an electric field. The solid peat or the solid kaolin particles act as the stationary membrane, thus causing the water contained in the capillaries of the structure to migrate toward the cathode, or negative pole.[2]

Extremely fine solid particles if allowed to move rapidly through air or the like will become noticeably charged. This is the basic reason for most dust explosions.

Water being sprayed through air will also exhibit fall potential. P. Lenard[3] demonstrated that the potential difference between

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[1] T. Cockerill, British Patent No. 21441/1908, 5854, and 5855/1909. Clingett, *Rubber Receuil*, p. 377 (1914). S. E. Sheppard and W. Eberlin, U.S. Patent No. 1,476,374, 1922. P. Klein, U.S. Patent No. 1,548,689.

[2] Electro-Osmose, A. G., German Patent No. 179.086/1903, 181.841/1906, 252.370/1911, 263.454/1912, 272.383/1913, etc. For a detailed discussion of the process, see, *e.g.*, the contribution of E. W. Mayer in Liesegang, "Kolloidchemische Technology," 2d ed., p. 834, T. Steinkopff, Dresden, 1932.

[3] *Ann. Phys.*, **46**, 584 (1892).

the top and the bottom of an alpine waterfall can reach several thousands of volts.

THE DEVELOPMENT OF THE DOUBLE-LAYER THEORY

These four different types of electrokinetic phenomena prove beyond doubt that the boundary layers or the interfaces between phases possess an electric charge, or, in other words, that an electric potential must exist at the interface. Primarily, we are naturally interested in finding out why and how such an interfacial potential originates and what factors influence the electrical properties of interfaces and particularly those of dispersed particles.

As a result of the intermediate location of the colloidal state between macro- or microscopic dispersions and analytically disperse systems, we again find two schools of thought in the pioneer days of the study of colloidal phenomena. C. Barus and E. A. Schneider, G. Bredig, etc., who considered colloids as suspensions of extremely comminuted matter, tried to explain colloidal phenomena by simply transferring the physical properties of coarse suspensions to colloids. On the other hand, the exponents of the chemical theory, *e.g.*, J. Duclaux and Wo. Pauli, applied the laws of analytically dispersed electrolytes to colloidal systems. They consider the colloidal particle to be able either to dissociate and act like a true electrolyte or not to dissociate.

The intermediate position of colloidal solutions between coarse and analytical dispersions, if looked at from Wo. Ostwald's general viewpoint, necessitates an overlapping of the outstanding peculiarities of the two previously mentioned states in the colloidal range. However, this immediately offers an explanation why a satisfactory understanding of the electrokinetics of colloidal systems is possible only by a suitable combination of the two concepts.

The Helmholtz Double Layer.—The purely physical interpretation is based on the theory of the electrical double layer, originally formulated by H. von Helmholtz.[1] In simple cases, this double layer can be regarded as an electric condenser, the potential of which is generally termed electrokinetic, or ζ (zeta), potential. It is assumed that the layer consists of two parts, one located at a

[1] *Wied. Ann.*, 7, 337 (1879).

monomolecular distance in the liquid surrounding the particle, the other being firmly attached to the wall or surface of the solid phase. The former part located in the liquid is considered movable. (For mathematical evaluation and connection with cataphoretic rate of migration, see Appendix, page 231.) The general concept of the Helmholtz electrical double layer of a colloidal particle or a surface in contact with a liquid is schematically shown in Fig. 33.

This concept of a compensating charge located in the liquid immediately in contact with the particle explains why a colloidal sol as a whole is not an electrically charged system and why the individual particle cannot be considered as being statically charged. Cataphoresis must be explained by a stripping off of the movable part of the double layer. Thereby the particle loses its electric neutrality and starts to migrate to one of the poles. As has been shown, the electrical double layer is made up out of ions so that we are entitled to consider that cataphoresis and ionic migration are in principle similar phenomena.

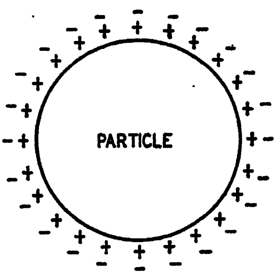

FIG. 33.—Schematic drawing of a Helmholtz double layer.

The deductions above result in the setting up of opposing electromotive forces. Owing to the fact that the dispersion medium (water) can be considered as a conductor, we have a compensating effect, and the particle moves toward the electrode. In the Helmholtz theory, the potential gradient at the interface is sudden and necessitates the assumption that the layers carrying opposite charges are separated only by a *monomolecular distance.*

But even without any really scientific basis for doubt, the Helmholtz theory becomes questionable if applied to colloidal dispersions. The migration as described would call for the movement of a perfectly dry particle through the surrounding liquid. This seems to stand in direct opposition to any observation that one can make by moving any piece of matter through a liquid. If withdrawn, this piece will always appear to be coated with a layer of the liquid, the thickness of the layer depending on the circumstances of the experiment.

Gouy's Diffuse Double-layer Theory.—Therefore, it must be considered as a substantial step forward when G. Gouy[1] formulated an amended theory. He assumes that the potential gradient is not abrupt but diffuses over a short distance. Hence this theory is known as the one of the diffuse double layer. H. Freundlich,[2] who must be credited with the most important experimental contributions to this theory, gives a detailed account of the concept. The principal assumption is as follows:

The charge on the surface of a solid body is distributed in the plane of the surface or can be considered as embedded therein. The countercharges are located in the surrounding liquid in such a manner that the double layer extends considerably over monomolecular dimensions into the liquid. The part of the double layer that is located in the liquid consists of two constituent layers: the first one lies in the liquid, which is firmly attached to the wall or to the surface of the dispersed particle; whereas the second is located in the freely movable liquid and extends into the solution up to the point where the mean electric charge reaches a zero value. In electrokinetic phenomena, the firmly attached layer remains motionless, *i.e.*, acts as if it would be an integral part of the solid wall or dispersed particle. This being the case, the liquid does not move against the solid interface but against the liquid layer firmly adhering to the interface. Figure 34 offers a schematic interpretation of the diffuse double-layer theory. This theory still explains why the particles of a colloidal sol cannot be considered as statically charged, and at the same

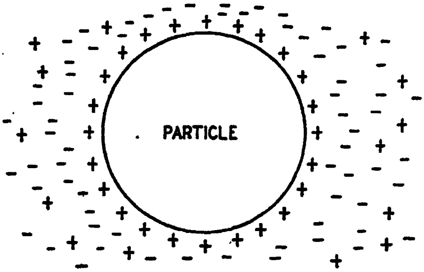

FIG. 34.—Schematic interpretation of a diffuse double layer according to Gouy-Freundlich.

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[1] *Le Journal de physique et le radium*, 9 (4), 457 (1910). See also J. BILLITZER, *Zeit. physikal. Chem.*, 45, 307 (1903).

[2] "Kapillarchemie," vol. I., 4th ed., pp. 356*ff.*, Akad. Verlags-Ges., Leipzig, 1930.

time it satisfies the objections that were raised against the Helmholtz double layer, Fig. 35*a*. Figure 35*b* shows that the thickness of the double layer is abstract and depends on the charge present and the concentration of ions in the surrounding liquid.

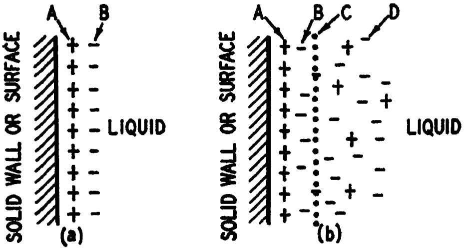

FIG. 35.—Double layers. *a*, Helmholtz; *b*, Gouy-Freundlich; *A*, charges firmly attached to particle; *Ba*, charges of liquid layer; *Bb*, ions in liquid layer attached to particle; *C*, thickness of attached layer depending on mean offstand distance of ions from solid wall; *D*, diffuse ions in movable part of liquid. The particle plus the complete diffuse double layer is called a colloidal micelle.

(See Appendix, page 231, for mathematical correlation with the Helmholtz theory.)

THERMODYNAMIC AND ELECTROKINETIC POTENTIAL

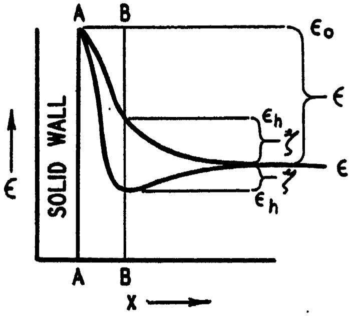

FIG. 36.—ϵ and ζ potential. *A-A*, boundary solid/liquid; *B-B*, boundary of attached liquid against free-moving liquid.

Since it has previously been pointed out that the study of colloidal phenomena is specifically a study of surface phenomena and reactions, and since it has been shown that one part of the double layer found in the liquid is firmly attached to the solid interface, it becomes evident that it is the solid particle plus its motionless liquid layer that is of primary interest to the colloid chemist and physicist. If such theoretical deductions are correct, then the ζ potential, according to the Gouy-Freundlich theory, must differ from the thermodynamic potential[1] as measured in galvanic circuits. Figure 36 offers a schematic

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[1] Also known as galvanic, or Nernst, potential. For a precise definition, see, *e.g.*, W. NERNST, "Theoretische Chemie," 10th ed., p. 749, Ferdinand Enke, Stuttgart, 1921.

explanation. It is assumed that the surface of the solid wall is represented by the vertical line *AA* and that in electrokinetic processes the double layer breaks off at the vertical line *BB*. If we describe the potential of the solid surface as ϵ_0 and that of the interior of the liquid as ϵ_l, then the thermodynamic potential $E = \epsilon_0 - \epsilon_l$. If we designate the potential on the line *BB* as ϵ_h, the ζ potential will be represented by $\zeta = \epsilon_h - \epsilon_l$. The drawing furthermore shows that the electrokinetic potential can have a different sign from the galvanic one if the potential curve runs through a minimum.

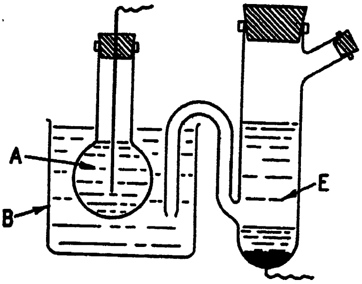

FIG. 37.—Determination of ϵ potential of glass. *A*, thin-walled glass bulb; *B*, beaker containing electrolyte solution; *E*, normal (calomel) electrode.

H. Freundlich, E. Ettisch, and P. Rona[1] proved that the electrokinetic potential of glass is different from the galvanic potential. A thin glass bulb *A* (Fig. 37), according to the method of Haber and Klemensiewicz,[2] is immersed in a beaker *B* containing an electrolyte solution whose H^+ and OH^- ion contents can be varied. The glass bulb contained a constant electrolyte solution. Into the glass bulb an electrode connected to an electrometer was inserted. A normal (calomel) electrode *E* was inserted into the beaker, the electrode being earthed. Such an arrangement permits the determination of the galvanic potential. Figure 38 shows the changes of the thermodynamic potential with different concentrations of different electrolytes. The ζ potential was then

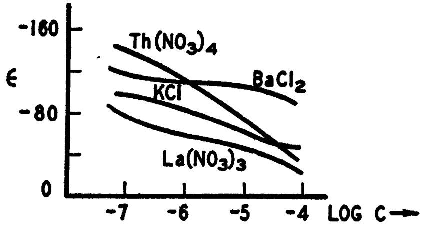

FIG. 38.—ϵ potential of glass with different concentrations of electrolytes.

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[1] *Sitzber. Preuss. Akad. Wiss.*, **20**, 397 (1920); *Zeit. physikal. Chem.*, **116**, 401 (1925).

[2] *Zeit. physikal. Chem.*, **67**, 385 (1909).

determined for the same type of glass by measuring flow potentials in capillaries and evaluating the ζ potential by the use of the Helmholtz formula (see Appendix, page 231). The results corresponding to the electrolyte concentrations used in Fig. 38 are given in Fig. 39, which immediately demonstrates the noticeable difference in results. The outstanding findings can be summarized as follows:

1. The $\zeta - c$ and the $\epsilon - c$ curves have an entirely different form.

2. The ζ potential is less than 0.1 volt; the ϵ potential, mostly 1 volt.

3. A ζ potential can be detected at interfaces where no ϵ potential exists.

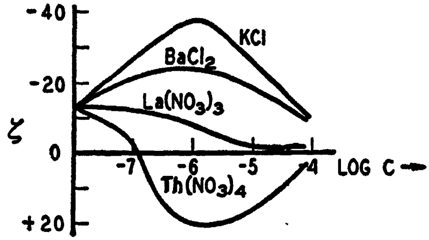

FIG. 39.—ζ potential of glass with different concentrations of electrolytes.

4. In solutions of electrolytes, the ϵ potential depends on the activity and valency of *one* ion, which is the determining factor. In contrast thereto, the ζ potential depends on *all* ions present.

5. The ϵ potential is altered only to a small extent by a small quantity of added electrolyte, whereas the ζ potential is thereby strongly influenced and can even change its sign.

The effect of electrolytes is controlled by the following rules:

The anions influence a positive ζ potential in preference to cations; they decrease the potential. A negative ζ potential is primarily influenced by cations. The over-all effect increases with the valency of the active ion. The so-called "Hofmeister ionic series" (see page 132) is applicable.

As will be seen in the following chapter, these rules are in close analogy to those governing ionic adsorption, which justifies the assumption that ion adsorption is a vital factor in explaining the influence of electrolytes on the ζ potential.

Three possible trends for the ζ-c curves have been found and are illustrated in Fig. 40. In a curve of type 1, the ζ potential passes at first with increasing concentration of added electrolyte through a maximum, then decreases and approaches the condition of electroneutrality. Curve 2 defines a system in which the absolute value of the ζ potential decreases continuously with increasing concentration of electrolyte. In curve 3, the absolute value decreases sharply at first until the isoelectric point I is reached. Then the value begins to rise again, but with reversed sign of charge, until it attains a maximum, from which time on it again decreases. Offhand, there is no reason why a curve of type 3 cannot be realized with any type of electrolyte; however, with electrolytes of low valency the isoelectric point is theoretically reached only at such high concentrations that the dilution of the system brought about simultaneously makes a charge reversal difficult to realize. Therefore, the probability of achieving such reversals is increased with increasing valencies of the active ion. The stability of the colloidal system decreases as we approach the isoelectric point. To prevent coagulation before charge reversal is accomplished, it is advisable to approach the isoelectric point carefully by adding mono- or divalent ions and then to overstep it by the addition of a trivalent salt. The presence of protective colloids facilitates such procedure.

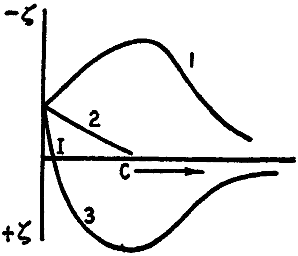

FIG. 40.—Possible shapes of ζ potential-electrolyte concentration curves. I, isoelectric point; curve 1, for weak (monovalent) electrolytes; curve 2, for medium (divalent) electrolytes; curve 3, for strong (multivalent) electrolytes.

Curves of type 1 seem to be responsible for the formation of highly dilute thixotropic gels (see page 216). Curve 2 is the one most commonly found and responsible for normal coagulation (see pages 167*ff.*). Curve 3 describes a phenomenon that has been known up to recently as the *irregular series.* Such cases have been reported by B. H. Buxton and O. Teague[1] for suspensions of certain types of bacteria; by G. St. Whitby,[2] W. H. C. Bel-

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[1] *Zeit. physikal. Chem.*, **57**, 64, 76 (1907). See also B. H. BUXTON and PH. SHAFFER, *ibid.*, p. 47.

[2] *Koll. Zeit.*, **12**, 147 (1913); *Agric. Bull. F.M.S.*, **6**, 374 (1918).

grave,[1] and H. Freundlich and E. A. Hauser[2] for latex of *Hevea brasiliensis.*

THE FORMATION OF THE DIFFUSE DOUBLE LAYER

How can one assume the formation of such a diffuse double layer at the interface of a solid wall and an electrolyte solution? To illustrate this we may consider as an example the precipitation of silver bromide from solutions of potassium bromide and silver nitrate. If these are mixed in exactly chemically equivalent proportions of medium concentration, a coarse precipitate will form which rapidly settles to the bottom. Yet if the reaction is carried out with low concentrations and in the presence of an excess of either one of the reagents, then a large proportion of the formed silver halide remains in suspension as a sol. If the reaction has taken place in the presence of an excess of silver nitrate, we find that the particles of this sol will migrate toward the cathode, if placed in an electric field, which means that they must carry a net positive charge. On the other hand, if potassium bromide is in excess, we obtain a sol, the particles of which are negatively charged. The individual particles, therefore, although being identical, chemically speaking, are definitely different from a colloidal point of view. The reason for this difference finds its explanation in the existence of active and inactive areas in the surface of a neutral particle. This thought, developed on the basis of the atomic structure of a crystal as revealed by x rays, was first postulated by I. Langmuir.[3] In Fig. 41*a*, we have schematically pictured a vertical lattice plane of a neutral silver bromide particle, showing the component atoms spaced in definite arrangement to each other and held together by secondary valence attractive forces.

Upon considering the silver atom 1 or 2 or any other silver ion located in the center, we readily see that it is surrounded by six equidistant bromide ions (four in the plane of the paper, one in front, and one behind). However, a silver atom lying in the surface, as, for instance, No. 3 or No. 4, lacks one bromide ion to saturate its affinity (there are three bromide atoms in the plane, one in front, and one behind, totaling five in all). The

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[1] *Mal. Agr. J.* vol. XI, December, 1923.

[2] *Koll. Zeit., Erg. Bd.*, **36** (*Zsigmondy Festschrift*), 15 (1925).

[3] *J. Am. Chem. Soc.*, **38**, 2221 (1916); **40**, 1361 (1918).

silver atoms on corners, such as Nos. 5 and 6, lack two bromide ions for saturation. If the pictured plane happens to be a surface plane, then the corner atoms would lack three ions for saturation.

As previously explained, a neutral particle is unstable and will cause the formation of a precipitate. But if the reaction takes place in the presence of an excess of potassium bromide, then the active spots of the lattice will satisfy their unsaturated secondary valencies by accumulating negative bromine ions at the location of the positive silver ions in the particle surface. One may naturally argue that the bromine ions, being equally

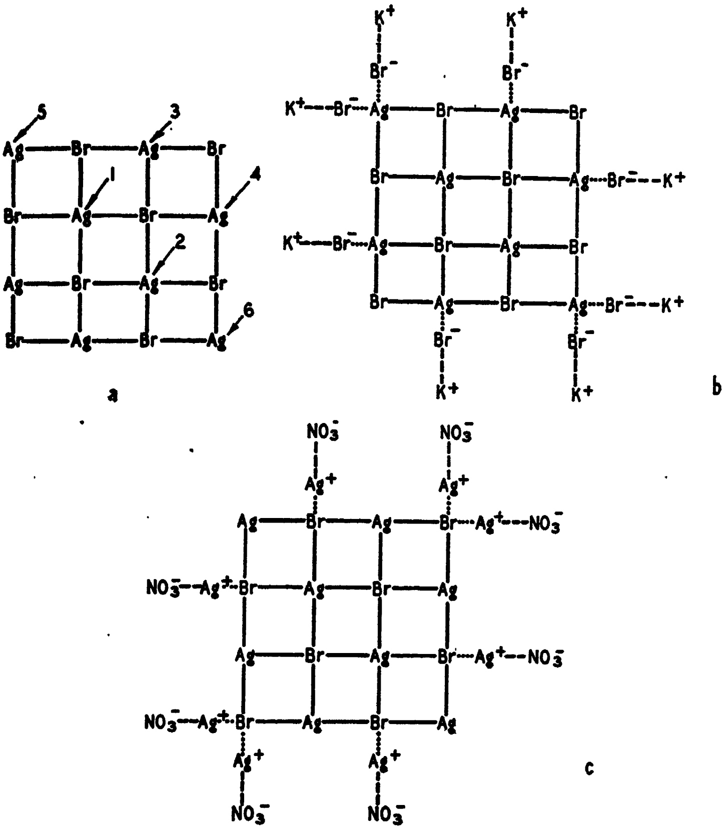

FIG. 41.—The formation of a diffuse double layer. *a*, neutral silver bromide particle; *b*, negatively charged silver bromide particle; *c*, positively charged silver bromide particle.

unsaturated, could attract positive potassium ions. That this is not the case is explained by the Fayans-Hahn law, which postulates that such ions are preferentially attracted that can be incorporated into the lattice structure, or, in other words, ions of the same kind. Furthermore, there always will be a trend to form least soluble matter, and thus the formation of potassium bromide is less probable than the formation of highly insoluble silver halide. This reaction, pictured in Fig. 41*b*, produces a negatively charged particle, which attracts the positively charged potassium ions repelling a further excess of anions in the solution. In the light of the Gouy-Freundlich diffuse double-layer theory, one can visualize the arrangement of ions as shown in Fig. 42*a*. The firmly attached bromide ions form the rigid part; the potassium ions, the mobile stratum. We see that the distribution of ions in the rigid stratum is controlled by electrostatic energy and by adsorption and also by thermal movement. The mobile layer is the result of electrostatic and thermal action. This alignment results in the formation of a double layer carrying, in the case here considered, a net negative surface charge.

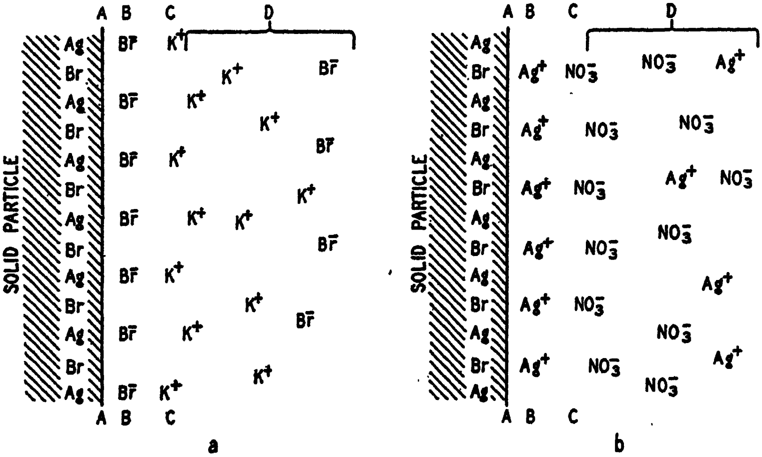

FIG. 42.—Schematic arrangement of the diffuse double layer surrounding a silver bromide particle. *a*, negatively charged particle; *b*, positively charged particle; *A*, surface of particle; *B*, attached rigid ionic layer; *C*, imaginary boundary between attached and movable liquid layer; *D*, diffuse ionic atmosphere in movable part of liquid.

Should the reaction be carried out in the presence of an excess of silver nitrate, then we find the reverse case, *i.e.*, the preferential attachment of positive silver ions on the active surface areas in which unsaturated bromide ions are located. The ionic distribution resulting is shown in Fig. 41*c*; and the arrangement of the diffuse double layer, in Fig. 42*b*.

If we start with a system having a given ζ potential and add electrolyte to the solution, we thereby reduce the ζ potential, because more ions of opposite electric charge are crowded into the liquid zone firmly attached to the particle. This results in increased neutralization of the net particle charge. The higher the valency of the added ions the stronger will be the influence that they exercise (Hardy-Schulze valency rule). The thickness of the complete diffuse electric double layer decreases; and if the decrease reaches the point where the entire potential drop takes place in the liquid zone firmly attached to the particle, the ζ potential reaches a zero value; we have produced an unstable system from a colloidal point of view, although the ϵ potential still exhibits a finite value (Fig. 43).

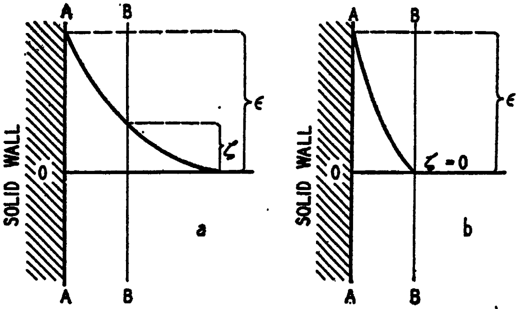

FIG. 43.—Changes of the ζ potential. *a*, ζ potential prior to the addition of electrolyte; *b*, ζ potential after the addition of electrolyte.

For example, in bringing a pure (electrolyte-free) silver halide suspension in contact with an electrolyte solution of increasing concentration, such as potassium chloride, a double layer is immediately formed. We shall find chloride ions in the inner layer, whereas in the outer layer the potassium ions will prevail. The preferential adsorption of Cl^- ions is again explainable on the basis of the Fajans-Hahn law. Cl^- fits better into the AgCl lattice than K^+. Besides, the reaction product of Cl^- with Ag^+ is less soluble than that of K^+ and Cl^-. The ζ potential and also the charge will increase until such a concentration of potassium chloride has been reached corresponding to a maximum of surface saturation with chloride ions (Fig. 44*a*). Upon further increasing the concentration of potassium chloride, increasing numbers of potassium ions are forced into the inner layer, thus decreasing the charge; at the same time the diffused ions are concentrated into a smaller space, thereby decreasing the thickness of the layer. The ζ potential drops (Fig. 44*b*). Finally, the potassium ions become electrostatically bonded with the chloride ions, forming a monomolecular electrically neutral layer.

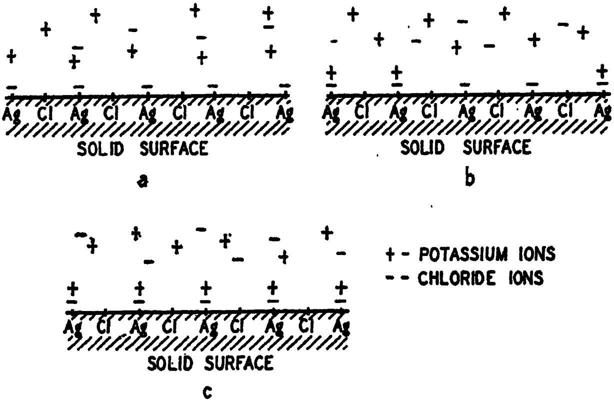

FIG. 44.—Changes of electric charge of particle. *a*, charging of particle (maximum); *b*, discharge—drop of ζ potential; *c*, complete neutralization = isoelectric point.

The isoelectric point has been reached; the system flocculates, *i.e.*, forms flocks[1] (Fig. 44*c*).

As previously explained, the changes of the ζ potential do not necessarily come to an end at the isoelectric point when we apply polyvalent electrolytes, *e.g.*, aluminum salts. In this case, a new diffuse layer is formed in which positive aluminum ions form the inner stratum, and the negative chloride ions the outer. The charge naturally has been reversed (Fig. 45*a*). With further increase of electrolyte the analogy is to one already described, finally ending in a second zone of discharge or coagulation, when we again have caused neutralization of the net surface charge (Fig. 45*b*).

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[1] Flocks are micro- or macroscopically visible aggregates of colloidal particles.

Influence of Hydration.—So far we have entirely disregarded the possibility of hydration of the surfaces and of the ions present. We have learned to differentiate between hydrophilic and hydrophobic sols. One characteristic difference is the fact that hydrophilic colloids have no tendency to flocculate at the isoelectric point, although they admittedly exhibit a minimum of stability at this point. The reason for this phenomenon seems to be that the stability of a hydrophilic colloid is primarily due to its hydration, its electrical charge being of secondary importance.

The flocculation of hydrophilic colloids with alcohol, salts, or other dehydrating agents can be explained by the assumption that these reagents strongly attract water molecules, depriving the colloidal particles therefrom. In the case of hydrophobic colloids, we may consider the stability of a sol as mainly a result of the electrical charge.

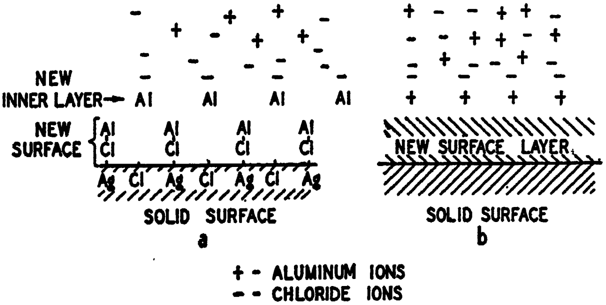

Fig. 45.—Charge reversal. *a*, charging with + sign; *b*, discharge-second zone of coagulation.

It has been pointed out that the neutral particle is charged in the presence of minute quantities of electrolyte which form the double layer. Since the ions of this electrolyte are themselves hydrated, the particle is not only surrounded by an ionic atmosphere but also carries a water hull or layer with it. Therefore, the electric double layer can be considered as a diffuse hydrated or solvated (hydration refers only to systems in which water is the dispersion medium) shell of definite thickness, made up of the bound dipoles[1] of the dispersion medium and the ions

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[1] P. Debye, "Polar Molecules," Reinhold Publishing Corporation, New York, 1929; "The Dipole Moment and Chemical Structure," Blackie & Son, Ltd., London, 1931. See also C. P. Smyth, "Dielectric Constant and

of the dissolved substance. The individual particle in a disperse system consisting of a charged nucleus, surrounded by a diffuse ionic atmosphere, is generally termed a *colloidal micelle*, according to a suggestion made by J. Duclaux.[1]

Electric charge or the electrokinetic potential and solvation are the predominant factors governing the stability of colloidal systems. Depending on which of the two is predominant, we so far differentiate between hydrophobic colloids in the former case and hydrophilic in the latter. That we cannot draw an absolutely clear distinction between the two has been demonstrated by H. R. Kruyt and his collaborators with the particles of an agar-agar sol. Particles of this sol are negatively charged. If they are discharged by the addition of small quantities of electrolyte, the stability of the sol will be retained owing to the presence of the solvated hulls. If a dehydrating agent such as alcohol is now added, flocculation occurs. If the sol is first dehydrated carefully, we obtain a sol of still noticeable stability. However, this sol will exhibit typical hydrophobic properties,

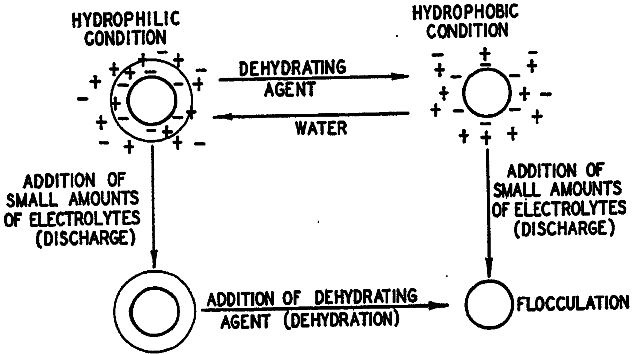

Fig. 46.—Electric neutralization and dehydration of colloidal particles.

Molecular Structure," Reinhold Publishing Corporation, New York, 1931. N. V. Sidgsick, "Some Physical Properties of the Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933. Eirich, Mark, and Huber, *Papier Fabrikant*, **35**, No. 27 (*Fest-Auslandsheft*) *Techn. Teil* 251 (1937). A. V. Dumanskii, *Bulletin de l'académie des sciences de l'Union des Républiques Sovietiques Socialistes*, p. 1165 (1937). B. V. Deryagin and M. Kusakov, *ibid.*, p. 1119 (1937). T. P. Tyazhelova, *Colloid Journal of the U. S. S. R.*, **3**, 631 (1937). S. M. Lypatov and P. M. Lapin, *ibid.*, **3**, 721, 729 (1937).

[1] *C. r. Soc. Biol.*, **140**, 1468, 1544 (1905); *Koll. Zeit.*, **3**, 126 (1908).

being easily flocculated upon the addition of minute quantities of electrolyte (Fig. 46).

Dipoles.—The cause for the bonding of the water molecules on the colloidal particle is presumably closely connected with their asymmetric structure. The water molecule is of polar nature, frequently also termed "dipole," according to P. Debye. This means that the molecule is of angular shape, the center of gravity for its positive charges not coinciding with the one for the negative charges (Fig. 47).[1] Such dipoles will preferentially adsorb on such atom groups that are also polar in character.[2] Therefore, similar principles can also be applied to sols in organic dispersion media. Metal sols will be more stable in liquids with polar molecules than in those made of apolar ones.

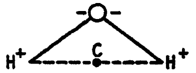

Fig. 47.—Dipolar water molecule. *C*, center of gravity of plus charges.

The Inner Layer.—Frequently we still encounter the assumption that the inner, or rigid, layer must be considered as a more or less perfect coat or "monoionic layer." On this assumption O. Stern[3] bases his theory of the dependence of charge distribution and of the ζ potential on the concentration of the electrolyte. However, later work seems to prove that a uniform distribution of charges exists only in specific cases and that, in general, the rigid layer must also be considered as diffuse. In measuring the flow potential through capillaries at different rates of flow (pressure), G. Ettisch and A. Zwanzig[4] proved that the ζ potential varies with the rate at which the liquid is forced through the capillary. The ζ potential increases with increasing pressure, tending toward a limiting value. The double layer will break the closer to the liquid/solid interface the stronger the mechanical influence. This finding has been correlated by A. v. Buzágh,[5] who could prove that the solvated hull, and thereby the diffuse electric double layer, can be noticeably distorted by the application of mechanical forces.

Possibly deviations in the rate of particle migration between experimental findings and calculations based on the Helmholtz-

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[1] Only the centers of the atoms and ions are given.

[2] For a simple discussion, see, *e.g.*, S. J. French, *J. Chem. Educ.*, March, 1936, p. 122.

[3] *Zeit. Elektrochem.*, **30**, 508 (1924).

[4] *Zeit. physikal. Chem.*, **147**, 151 (1930).

[5] *Koll. Zeit.*, **52**, 46 (1930).

Smoluchowski formula can be accounted for by a distortion of the electric double layer when applying very steep potential gradients.

THE STABILITY OF COLLOIDAL DISPERSIONS

We have pointed out that the stability of a colloidal dispersion is connected with the ζ potentials of the dispersed particles. What changes occur in the electric double layer when the ζ potential is altered, for example, by the addition of electrolytes? According to the Helmholtz equation (see Appendix, page 231), the change can be brought about by a change either in the charge or in the thickness or in both. So far we can determine experimentally only the change of the potential but not the change attributable to one or the other of the two variables. Gouy expresses the idea that a decrease in the ζ potential is proportional to a decrease in the thickness of the ionic layer. This could explain the drop in the ζ-c curves (Fig. 40), as no change in charge necessarily would need to be considered. However, the rising part of curve 1 and the charge reversal in curve 3 would find no satisfactory explanation. H. Freundlich[1] assumes that with small concentrations of added electrolyte the ζ potential increases in accordance with an adsorption isotherm (see page 124). At the maximum, the increased charge and the decreased thickness of the double layer will just be compensated, whereas with increasing concentration the decreasing thickness will predominate.

A. Gyemant[2] offered a mathematical evaluation of this theory. Shortly after, O. Stern[3] published his previously mentioned theory. According to him, not only the actual coating of the solid wall but also the unmovable part of the liquid layer is adsorbed. He explains any change in the ζ potential as caused exclusively by an alteration in charge due to adsorption. More recently, H. Müller[4] criticized the Stern theory on grounds that the ζ potential owes its existence to the diffuse double layer. He points out that conditions inside the inner layer affect the ζ poten-

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[1] *Op. cit.*, p. 360.

[2] *Zeit. Phys.*, **17**, 190 (1923).

[3] *Loc. cit.*

[4] *Koll. Beih.*, **26**, 257 (1928). See also FREUNDLICH and ZEH, *Zeit. physikal. Chem.*, **114**, 65 (1925).

tial only in so far as they can alter the total charge of the diffuse double layer. If no specific effects take place resulting in a change of charge of the inner layer, then the ζ-c curve can be explained in full accordance with Gouy's postulations. In this connection, we refer to the work of A. v. Buzágh[1] (for further details see page 208), who on the basis of his studies of adhesion of microscopic particles to solid walls could prove that a change in the ζ potential is always connected with a change in charge as well as a change in the thickness of the double layer. However, the changes of these variables need not be in the same direction. Furthermore, the thickness of the double layer depends not only on the concentration of the ions present in the system but equally on their degree of hydration. This means that, all other conditions being equal, the layer will be the thinner the less hydrated the ions therein are.[2]

THE PREEXISTING DOUBLE LAYER—ION EXCHANGE

The theoretical basis for the diffuse electric double layer has been discussed and also the simple case of its formation when bringing a neutral surface or a disperse particle in contact with an electrolyte solution. However, in nature as well as in practice we shall more frequently come across systems in which the dispersed particles that are already coated with an electric double layer come in contact with another electrolyte in increasing concentrations. In such instance, the double layer will undergo a drastic change. The final result is an ion exchange or an extreme case of polar or ion adsorption.[3] In the simplest cases, the outermost ions are gradually replaced by new ions. The so-called base exchanges of zeolite, permutites, and certain clay minerals are such reactions;[4] in more complicated cases, new ions may

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[1] *Koll. Zeit.*, **52**, 46 (1930).

[2] See also B. V. DERYAGIN, *Bulletin de l'académie des sciences de l'Union des Républiques Sovietiques Socialistes*, p. 1153 (1937). E. J. W. VERWEY, *Chem. Wbl.*, **35**, 70 (1938). J. KASPAR, *Helvetica Chimica acta.*, **21**, 650 (1938).

[3] See, *e.g.*, E. J. W. VERWEY, "Ionenadsorption und Austausch," *Koll. Zeit.*, **72**, 187 (1935). H. J. C. TENDELOO, *Chem. Wbl.*, **35**, 79 (1938).

[4] For detailed literature on this subject see, *e.g.*, G. WIEGNER, *Chem. Ind.*, **50**, *Transactions*, 1931. C. E. MARSHALL, "Colloids in Agriculture," pp. 69*ff*., Edward Arnold & Company, London, 1935. G. WIEGNER, *Koll. Zeit.*, **77**, 10 (1936).

also occur in the rigid layer either by adsorption or by ion exchange. The double layer will at low concentrations of added electrolyte consist of various positive and negative ions. In such a mixed double layer, the aforementioned possibility exists that charge and thickness of the layer change in different directions. With increasing concentration of added electrolyte, the double layer becomes more and more uniform until it is finally composed exclusively of ions of the added electrolyte (see Donnan equilibrium, page 110).

Surface Dissociation.—We can also visualize the charging of a particle or the building up of a double layer as a result of "chemosorption" (see page 119). The simplest example would be the separation of a surface ion of a solid in contact with a liquid. If a solid substance is dispersed in a liquid, and ions are split off from the surface of the particles, the particles will surround themselves with diffuse double layers. For example, in dispersing sodium stearate in water, we find that the sodium ions in the surface go into solution, thus forming the "outer" ions in the diffuse electric double layer, whereas the stearate ions make up the nucleus of the micelle (Fig. 48). Such a phenomenon is generally termed *surface dissociation*, because of its similarity to the dissociation of electrolytes. It is difficult to explain why in most of the cases studied it is the sodium or corresponding ion that splits off and not the stearate ion. Here it seems that the Hardy-Harkins rule of least abrupt change in a system holds (see page 122). The high affinity of the sodium ion for water results in a more gradual transition from the hydrophobic stearate to the water than if the stearate ion were to dissociate out of the surface. We know, furthermore, that generally the simple ions dissociate, leaving the more complex ones to form the inner layer. This finding, as can be readily realized, is of outstanding importance in all such cases where

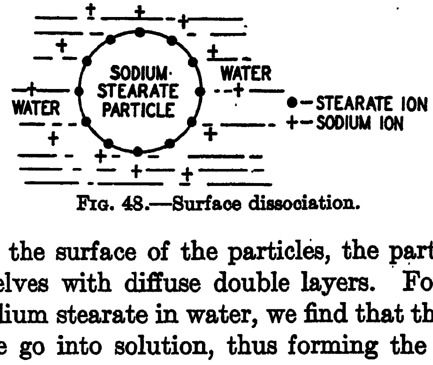

FIG. 48.—Surface dissociation.

complex matter, adsorbed on to solid surfaces, is brought into contact with a liquid.

However, if the dispersed solid reacts with the electrolyte or an ideal chemosorption takes place, then the phenomenon is decidedly more complex. We produce a complex or normal salt on the surface which is totally or partially adsorbed. If iron (ferric) oxide is dispersed in one case in hydrochloric acid and in the other case in a ferric chloride solution of suitable concentration, we find that in both cases a double layer is produced around the particles, the inner layer (rigid) being made up out of ferric ions; the outer, of chloride ions. If sulphuric acid is substituted for the hydrochloric acid, we shall very materially change the ζ potential of the dispersion. Sulphuric acid will form iron sulphate on the surface, which is less soluble and less dissociatable than iron chloride, so that the particles will be less charged and therefore less stable.[1]

The Dominating Ion.—Which will be the charging ion in cases where chemical reaction takes place? The purely physical concept of the electric double layer as developed by Gouy can give no satisfactory answer to this question. *Here, the combination with our chemical knowledge is essential, if we wish to obtain a picture that is equally satisfactory in explaining the physical and chemical properties of a system.* There can be no doubt that this is permissible, since the double-layer theory has no restrictions as to how the charging is effected, *i.e.*, by simple adsorption or as the result of a chemical reaction. If we give due consideration to both points of view, then we should be able to predict and evaluate certain properties of colloidal systems much better than if we adhere rigidly only to one type of interpretation. We need only refer to what we discussed in regard to precipitation in order to see that the pure chemical assumption of the formation of an insoluble compound lacks the detail for a really satisfactory understanding, which the combination with the physical point of view can fully offer.

CHEMICAL VERSUS PHYSICAL VIEWPOINT

Whereas, in a large number of inorganic systems, *e.g.*, clays, the physical theory has been most favored, we find that in the

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[1] See, *e.g.*, A. v. BUZÁGH, "Colloid Systems," p. 226, The Technical Press, Ltd., London, 1937.

chemistry of proteins it is the chemical theory that has predominated. Since proteins generally are considered as systems on the border line between highly disperse systems and colloids, it is understandable why in former days so many attempts were made to interpret colloidal properties on a purely chemical basis (S. P. L. Sørensen,[1] J. Loeb,[2] Wo. Pauli,[3] T. B. Robertson,[4] etc.). Nevertheless, a critical survey of the experimental facts pertaining to the interaction between proteins and various electrolytes has proved more and more that they cannot be satisfactorily explained on the basis of purely chemical deductions[5] and that colloidal principles must be introduced.

THE DONNAN EQUILIBRIUM

There is one more electrokinetic phenomenon of colloidal systems which is equally important from a physicochemical and a biological standpoint and which may not be overlooked in the discussion of electrokinetic phenomena. When we dialyze a "colloidal electrolyte," *e.g.*, the sodium salt of a dye acid (Congo red) against pure water, then the sodium ion will penetrate the membrane, whereas the colloidal-dimensioned dyestuff anion cannot penetrate. However, it is not possible for a large amount of sodium ions to separate from the dyestuff anion, since this would result in an excess of positive ions in the outer compartment and an excess of negative charges in the inner compartment. This would be against the rules of electrochemistry. To retain the electric equilibrium, water molecules must split to the amount of the sodium ions that pass through the membrane. The OH^- ions will migrate with the Na^+ ions, the equivalent number of H^+ ions associating with the dye anion. The result is a dye acid in the inner compartment, and sodium hydroxide in the outer. This phenomenon is known as *membrane hydrolysis* and is a special case of the *Donnan membrane equilibrium.*[6]

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[1] "Proteins," Fleischmann Laboratories, New York, 1925.

[2] "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Company, Inc., New York, 1925.

[3] "Kolloidchemie der Eiweisskoerper," T. Steinkopff, Dresden, 1920.

[4] "Die Physikalische Chemie der Proteine," T. Steinkopff, Dresden, 1912.

[5] For a detailed discussion, see, *e.g.*, v. BUZÁGH, *op. cit.*, pp. 229*ff.* SØRENSEN, *Koll. Zeit.*, **53**, 102 (1930). ETTISCH, *Zeit. physikal. Chem.*, *A* **174**, 199 (1935). W. T. ASTBURY, *Koll. Zeit.*, **83**, 130 (1938).

[6] T. R. BOLAM, "The Donnan Equilibria," George Bell & Sons, Ltd., Lon-

Upon dialyzing a colloidal chloride against a dilute sodium chloride solution, we shall find in accordance with the foregoing deduction that the sodium chloride will not distribute itself uniformly between the two compartments. It will be larger in the outer compartment. If we consider the following to represent equilibrium condition:

$$\begin{array}{l|l} \mathrm{Na^+} & \mathrm{Na^+} \\ \mathrm{Cl^-} & \mathrm{Cl^-} \\ \mathrm{A^-} & \\ (1) & (2) \end{array}$$

the sodium chloride must diffuse with equal velocity in both directions. An ion can pass through a membrane only if either an ion of the same electric sign passes the membrane simultaneously from the other side or an ion of different sign passes through the membrane from the same side. The number of impacts of sodium and chloride ions on the membrane must be the same for both sides of the membrane if equilibrium is to be maintained. This number N must be proportional to the ion concentrations.

$$N_1 = k[\mathrm{Na^+}]_1[\mathrm{Cl^-}]_1$$

and

$$N_2 = k[\mathrm{Na^+}]_2[\mathrm{Cl^-}]_2{}^*$$

Since in equilibrium $N_1 = N_2$, we obtain

$$[\mathrm{Na^+}]_1[\mathrm{Cl^-}]_1 = [\mathrm{Na^+}]_2[\mathrm{Cl^-}]_2$$

to satisfy electric neutrality we must have

$$[\mathrm{Na^+}]_2 = [\mathrm{Cl^-}]_2 \qquad \text{and} \qquad [\mathrm{Na^+}]_1 = [\mathrm{Cl^-}]_1 + [\mathrm{A^-}]$$

From the first of these two equations it follows that

$$[\mathrm{Na^+}]_2[\mathrm{Cl^-}]_2 = [\mathrm{Cl^-}]_2^2$$

and from the second:

$$[\mathrm{Na^+}]_1 > [\mathrm{Cl^-}]_1$$

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don, 1932; German translation, "Die Donnan-Gleichgewichte," T. Steinkopff, Dresden, 1934.

* The brackets refer to molar concentrations.

This results in

$$[Cl^-]_2 > [Cl^-]_1$$

This means that the concentration of sodium chloride must be larger on the side of the membrane where no NaA is present.

This phenomenon can be easily demonstrated by using plain numbers instead of the chemical symbols.

If we write:

$$\begin{aligned} Na_2 &= Cl_2 = x \\ Cl_1 &= y \\ A^- &= z \end{aligned}$$

and

$$Na_1 = y + z$$

then we have, at equilibrium,

$$(y + z)y = x^2$$

or, in figures, $(2 + 6)2 = 4^2$; *i.e.*, $8 > 4$ and $4 > 2$.

The importance of these deductions will be realized in all cases where adsorption; the swelling of gels; equilibriums in systems separated by semipermeable membranes, such as living tissues and cell walls; and their technical significance, *e.g.*, in dyeing and tanning, have to be considered.

In the foregoing chapter, we have discussed the most important electrical phenomena pertaining to colloidal systems. The significance of the concept of the diffuse electric double layer, the ζ potential and its changes, surface dissociation, ion-exchange reaction, and membrane equilibriums in regard to the stability and reactivity of colloidal systems cannot be overemphasized. Since it is impossible to go into great detail in such an introductory and general treatise, the specialized texts should be consulted for a more comprehensive discussion of these fascinating and vitally important phenomena.

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CHAPTER X

SURFACE PHENOMENA

SURFACE DEVELOPMENT AND SURFACE ENERGIES

It has been frequently pointed out that colloidal systems are mainly characterized by their extreme development of surfaces and surface boundaries. It has also been mentioned that in such boundaries there are energies typical thereto which are generally designated as *boundary energies.* Whereas classical chemistry defines the properties of a system by the properties of its mass, we find that properties of colloidal systems are primarily governed by those of the developed surface. The colloidal state differs in respect to the surface development of its systems from matter in the coarse state, or "heterogeneous systems," by reason that in the latter case the boundary surfaces are small and therefore negligible compared to the mass, whereas in colloidal systems it is just the reverse. In highly disperse systems, or "homogeneous systems," boundary energies are transformed into inner energies; *i.e.*, these systems are void of boundaries. However, it should be borne in mind that such a distinction is naturally arbitrary, depending on our present inability to differentiate between actual mass and surface in systems of a higher degree of dispersion than the colloidal range. However, there is a trend, at least in the theoretical field, to carry the fruitful conclusions of research of colloidal systems into the field of highly disperse systems, thus retaining the continuity of the general point of view of the disperse state of matter. Increasing evidence of a structural orientation of the molecules in liquids may be presented as an example of such endeavors.

The boundary-surface energies manifest their presence in various ways, generally known as *capillary phenomena.* The study of these special properties of boundary-surface layers or of extremely thin layers of matter is the subject of *capillary physics and chemistry.* The most important capillary phenomena can be classified into three groups, *viz.*, surface and interfacial tension, adsorption, and capillary electric phenomena.

SURFACE TENSION[1]

The simplest instance is the phenomenon observed at the boundary between a liquid and a gas, or at the liquid-gas interface. A liquid always tends to reduce its surface to a possible minimum, *i.e.*, it takes up a shape with the least free surface energy. A drop of water on a plate will try to retain its shape and resist spreading. The molecules of water in the drop will be attracted to each other by cohesion forces. Those that happen to be or move into the surface will mainly be pulled in one direction, toward the interior of the liquid, because the pull exerted by the gas (surrounding air) molecules is negligible in comparison to that of the interior liquid molecules (Fig. 49). Therefore, the liquid will try to assume the smallest surface possible. The determination of this basic phenomenon of capillary physics is known as the measurement of *surface tensions*. For instance, if a wire *A* (Fig. 50), which is mounted and movable by means of two loops *B* on a wire frame *D*, with another wire *C* in fixed position, is immersed in a liquid and then withdrawn, a film of liquid is built up between the wires *ADC*.

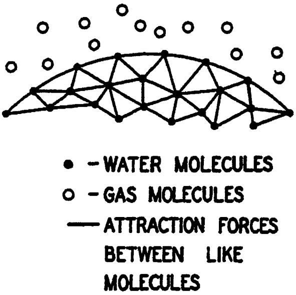

FIG. 49.—Molecular attraction (surface tension).

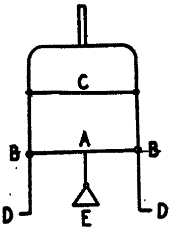

FIG. 50.—Surface-tension determination. *A*, movable wire; *B*, wire loops; *C*, fixed wire; *D*, wire frame; *E*, balance.

As a result of what has just been discussed, it is evident that the liquid will tend to decrease its exposed surface. Since the wires *C* and *D* are fixed, this tendency must result in an upward pull on wire *A*. If a small balance *E* is attached to the wire *A*, the upward pull can be counteracted or compensated by placing weights on the balance. These weights act on the distance *BB* of the film, which can be measured in centimeters. As

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[1] P. LECOMTE DU NOÜY, *Coll. Symp. Monogr.*, **3**, 25 (1925); "Surface Equilibria of Biological and Organic Colloids," Reinhold Publishing Corporation, New York, 1926.

soon as the added weights compensate the tendency of the liquid to contract and reach a minimum free surface energy, we can determine the surface tension σ of the liquid, since σ = energy:surface or force:length. (For a detailed discussion of the most common methods of determining surface tension and their limitations, see Appendix, page 231.) This means that a liquid will always tend to reduce its free surface energy, and surface tension can thus be defined as either that amount of work necessary in a system to increase its surface by 1 sq. cm. or that tension with which a surface of 1 cm. length tries to contract.

A further consequence of this simple deduction is that in order to increase the surface of a liquid we must put more work into the system than what is just needed to compensate its surface tension. For example, to froth a liquid we must *over*compensate its free surface energy. Since low surface tension corresponds to systems of small free surface energy, less work will be necessary to increase their surfaces as compared to a system exhibiting high surface tension. One knows that certain soluble substances, if added to a liquid, materially alter the surface tension of the system, thereby automatically also influencing its free surface energy. Substances (*capillary active* or *capillary positive*) such as higher alcohols, fatty acids, amines, and aldehydes are known to reduce surface tension. Some inorganic salts (*capillary inactive* or *capillary negative*) slightly increase surface tension. In the case of alcohols and fatty acids, it has been found that reduction in surface tension or capillary activity increases in the homologous series with increasing length of the carbon chain, within definite limits. This phenomenon is known as *Traube's rule.*[1]

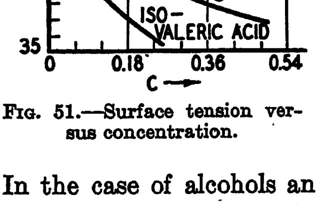

FIG. 51.—Surface tension versus concentration.

As already stated, the addition of certain substances causes a reduction of the surface tension; in most cases, the reduction will be more pronounced as the concentration of the added substance

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[1] See, *e.g.*, M. VOLMER and S. BOAS-TRAUBE, *Zeit. physikal. Chem.*, **178**, 323 (1937).

is increased (Fig. 51).[1] Surface tension and, keeping the surface area constant, also the free surface energy will be the smaller the higher the concentration of the *capillary active substance* in the surface layer. This deduction infers that a substance that decreases surface tension must concentrate in the surface layer, the reason being that the water molecules will have less attractive force for the unwetted ends of the added molecules than for water molecules. This must result in an increased lowering of surface tension with increased surface concentration. Such an increase in concentration of a dissolved substance in a surface, or, generally speaking, boundary, has been termed *adsorption*, or *sorption*. Its theoretical basis was given by J. W. Gibbs and J. J. Thomson, who state that a substance which reduces the free surface energy by reducing the surface tension of a system must be concentrated within the surface and therefore diffuse from the interior of the system into the surface layer[2] (see Appendix, page 237).

SURFACE CONCENTRATION

The theoretical deduction that substances which reduce surface tension of a liquid must concentrate in the interface has been experimentally proved by F. G. Donnan and his collaborators,

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[1] However, we know of certain exceptions to this rule. Certain soaps, rubber latex, etc., show a distinct minimum in surface tension with increasing concentration. For example, see J. W. McBAIN, T. F. FORD, D. A. WILSON, *Koll. Zeit.*, **78**, 1 (1937). E. A. HAUSER and P. SCHOLZ, *Kautschuk*, **3**, 332 (1927). H. E. EDGERTON, E. A. HAUSER, W. B. TUCKER, *J. Phys. Chem.*, **41**, 1017 (1937). McBain, Ford, and Wilson consider three possible trends for the surface-tension/concentration function. In the first case, the surface tension drops continuously with increasing concentration of solute. The drop is first rapid, slowing down later. This is in full accord with Gibb's theory. In the second case, we find a noticeable increase of the surface tension at the start, giving figures higher than those of water (negative adsoprtion). In the third case, the surface tension first drops rapidly, goes through a minimum, and then rises again (never reaching the water value). The authors explain this phenomenon by assuming an electric double layer below the soap-coated surface due to the high degree of dissociation of the soap in great dilution. (Double layers reduce the surface tension.)

[2] *Trans. Conn. Acad. Sci.*, **3**, 391 (1876). J. W. GIBBS, "Collected Works," Longmans, Green, & Company, New York, 1928.

McBain, Harkins, Lewis, and others.[1] After capillary active substances, such as fatty acids, had been added, the liquid was thoroughly agitated, and a strong foam produced. This was then skimmed off, and the difference in concentration of the added substance determined in the foam and in the residual liquid. It was found that the concentration in the foam was decidedly higher. It might be argued that the mechanical agitation in producing the foam contributes toward bringing the added substances into the vastly increased surface. However, another method was described by McBain and Humphreys[2] which avoids such criticism. The apparatus used is known as the "surface microtome." A microtome blade is placed on rails running along a trough so that it may be dipped into the liquid to any desired depth. After the solution has been poured into the trough and the surface allowed to rest a desired time, the blade is moved at high speed over the surface, thereby skimming off the top layer into another trough where its composition as well as that of the liquid remaining in the first trough can be analytically determined.

Substances that increase the free surface energy of a system will diffuse out of the surface layer into the interior.

ADSORPTION TERMINOLOGY

Since the change in concentration in the boundary layers is the only constant factor of a multitude of phenomena caused by the action of different types of energy, Wo. Ostwald has defined *adsorption* simply as a change in concentration of a component between the boundary layer and the interior of the adjacent phases. Therefore, cases where a reduction in surface tension occurs are known as *positive adsorption*, an increase corresponding to a *negative adsorption*. Adsorption phenomena resulting from changes in surface tension are frequently also simply

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[1] F. G. DONNAN and I. T. BARKER, *Proc. Roy. Soc.*, *A* **85**, 557 (1911). J. BAUCELIN, *J. chim. phys.*, **22**, 538 (1925). DONNAN and BENSON, *J. Phys. Chem.*, **7**, 532 (1905). MCBAIN and DAVIES, *J. Am. Chem. Soc.*, **49**, 2230 (1927). MCBAIN and DUBOIS, *ibid.*, **51**, 3534 (1929). E. A. GUGGENHEIM and N. K. ADAM, *Proc. Roy. Soc.*, *A* **139**, 218 (1933). HARKINS and WAMPLER, *J. Am. Chem. Soc.*, **53**, 850 (1931). W. C. LEWIS, *Phil. Mag.*, **15**, 499 (1908); **17**, 466 (1909); *Science Progress*, **11**, 198 (1916).

[2] *J. Phys. Chem.*, **36**, 300 (1932). See also MCBAIN and R. E. SWAIN, *Proc. Roy. Soc.*, *A* **154**, 608 (1936).

referred to as *mechanical adsorption.* However, there can exist in the boundary layer between two phases different energy potentials which can be reduced by a change in the concentration of the dispersed substance in the boundary layer. Such potentials can be of chemical, electrical, thermal, or other nature. Wo. Ostwald, therefore, amended the definition for adsorption with the following statement: "*If there exists in a boundary surface an energy potential, which can be diminished by a change in concentration of the adjacent dispersoid, then such a change, i.e., adsorption will take place.*"[1]

If a chemical reaction takes place at the interface, and the reaction product remains in it, we speak of *chemical adsorption*, or *chemosorption,* since a chemical potential exists between the adsorbed substance and the adsorbent (solid particle), and chemical energy brought about a concentration of the disperse constituent.

In the preceding chapter, a great number of cases were discussed wherein the solid substance possessed an electric charge of opposite sign to the charge of some of the ions contained in the surrounding liquid. By concentrating these ions at the interface, a reduction in the electric charge was effected. Since such a phenomenon, on the basis of Ostwald's definition, must also be classified as adsorption, it is known as *electrical adsorption.*

There are still other types of energy that may cause adsorption, and it is also possible that two types either reinforce or oppose each other. Thus, it is imperative to analyze every case very carefully and individually in order to obtain a perfect insight into the reaction.

FACTORS INFLUENCING ADSORPTION

The many factors involved in adsorption phenomena have made it so far impossible to obtain a quantitative conception and mathematical formulation satisfying all possibilities. However, we have a number of qualitative data that show the following factors to be of predominant influence:

1. The physical state of the adsorbent and the adsorbed substance: solid (amorphous, crystalline), liquid, gaseous.

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[1] "An Introduction to Theoretical and Applied Colloid Chemistry," 2d ed., p. 130, John Wiley & Sons, Inc., New York, 1922.

2. The size of the adsorbing interface (specific surface area of the adsorbent).
3. The structure of the adsorbing interface.
4. The radius of curvature of the adsorbing interface (geometrical form of the adsorbent).
5. Physical structure of the adsorbent (external and internal interfaces).
6. The degree of dispersion of the adsorbed substance.
7. The relative quantity of adsorbent (ratio of the quantity of adsorbent to adsorbed substance).
8. Concentration of the adsorbed substance.
9. The nature of the medium (solvent containing adsorbed substance).
10. The temperature.
11. The pressure.
12. The chemical affinity between the adsorbent and adsorbed substance. (Chemical nature of adsorbent and adsorbed substance.)[1]

Having defined adsorption as a change in concentration of dispersed matter in the interface of a system consisting of at least two immiscible phases, we can visualize the following general possibilities for adsorption at an interface, between a

1. Liquid disperse system–gaseous disperse system.
2. Liquid disperse system–liquid disperse system.
3. Solid body–gaseous disperse system.
4. Solid body–liquid disperse system.

LIQUID-GAS SYSTEMS: FOAMS

It has been stated that substances which reduce the surface tension of a liquid will concentrate in the interface, in accordance with the Gibbs-Thomson theorem. Such systems can be frothed more easily than those with high surface tension, since, according to definition, less work has to be put into the system to overcome the existing free surface energy. However, this does not yet imply that the produced foam is stable. To obtain a stable foam, a simple reduction of surface tension is insufficient. What is needed is the formation of a tenacious film at the inter-

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[1] This list has been compiled by A. VON BUZÁGH, "Colloid Systems," p. 172, The Technical Press, Ltd., London, 1937.

face. This can be accomplished by changing the condition of the dispersed substance concentrated in the interface, *e.g.*, by oxidation or coagulation. Certain proteins will coagulate, for instance, if subjected to the influence of air in thin layers. A solid skeleton-like framework of finely comminuted coagulated protein results (beer foam, milk foam, the scum of rubber latex, etc.). Another way of producing stable foams consists of the use of such capillary active substances that will concentrate and simultaneously orient themselves in the interface. This phenomenon, which also plays an important part in emulsification, is generally known as *oriented adsorption.*

In some cases, it is also possible to concentrate finely comminuted solid matter in the interface between a liquid and a gas. By the use of certain reagents added to the liquid, it is possible to induce the solid matter either to adsorb into the liquid-gas interface or to remain in the residual liquid, depending on the surface condition of the solid matter. This effect is the basis for the process known as ore flotation, in which the mineral particle is separated from the gangue.[1]

LIQUID-LIQUID SYSTEMS

Similar conditions as discussed above exist at the interface of two immiscible liquid systems. For example, in considering a system containing a pure oil and water, we are dealing with a very simple case of adsorption between the aqueous phase and the oil phase. However, if either or both of the two phases contain a dissolved substance that is insoluble in the other liquid, an asymmetric adsorption layer will form at the interface (Fig. 52). In this instance, one side of the layer will contain a large part of

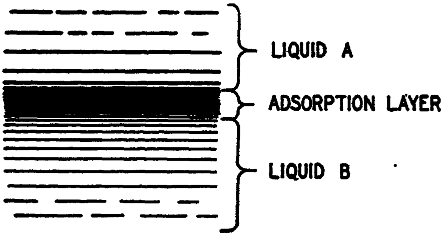

FIG. 52.—Schematic interpretation of interfacial adsorption layer.

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[1] See, *e.g.*, A. F. TAGGART, *Coll. Symp. Monogr.*, 9, 130 (1931). F. E. BARTELL and G. B. HATCH, *ibid.*, 11, 11 (1935).

the substance dissolved in the one liquid, and the other will be saturated with the other liquid. In dealing with systems—the most frequent cases—where one phase contains a substance partially soluble in it and partially soluble in the other phase, an interface is again formed which is characterized by oriented adsorption of that substance. For example, soap molecules are considered as little rods of about 0.4 to 0.5 $m\mu$ in thickness and dependent on their carbon chain of 2 to 3 $m\mu$ in length. At one end they carry the carboxyl group (COOH) in which the hydrogen is normally replaced by sodium or potassium, whereas at the other end they carry the hydrocarbon. In the interface, these molecules are more or less closely packed (Fig. 53) in such a way that the hydrophilic groups (such as COOH, COOM, CHO, OH, NH_2, double bonds) are located in the direction of the water phase; the organic radical, in the direction of the gas (liquid-gas system) or in the direction of the organic liquid phase (liquid-liquid system) (Fig. 54).

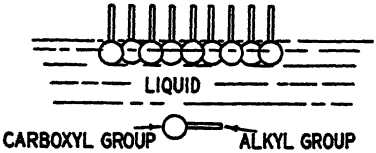

Fig. 53.—Orientation of soap molecules in a liquid/gas interface.

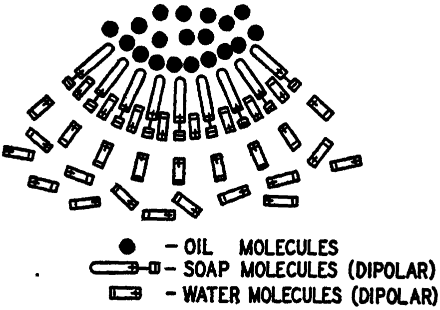

Fig. 54.—Dipolar orientation of soap molecules at an oil-water interface (emulsification).

According to the Hardy-Harkins theorem,[1] the molecular arrangement in the interface will always be such that the transition to the neighboring phase is the least abrupt possible.[2] Similar results are obtainable with other substances possessing

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[1] *Proc. Roy. Soc.*, *A* **86**, 634 (1912); **88**, 303 (1913).

[2] W. D. Harkins, *Coll. Symp. Monogr.*, **2**, 141 (1925).

molecules which, like the soaps and higher fatty acids, have "partial" solubility; *i.e.*, their hydrocarbon end is soluble in organic liquids but insoluble in water; their carboxyl or equivalent group, easily soluble in water but more or less insoluble in organic liquids. Other such substances are saponines; the mono- and, to some extent, divalent salts of humic and sulphonic acids; certain proteins; etc. Quite recently, true monosulphonates of petroleum fractions have been added to this group.

SOLID-GAS SYSTEMS

The adsorption at the interface between a solid body and a gaseous disperse system is considerably more involved than the cases discussed so far. The reason for this is that with decreasing dimensions of the solid phase a point is finally reached where adsorbent and adsorbendum are of the same dimensions. In this condition, adsorption is no longer possible by definition, and a chemical reaction—coagulation or the like—results. Therefore, the concentration of an inert gas at the surface of a solid adsorbent is the only system that can be considered as a gaseous adsorption in the correct sense of the word. A further limitation one must naturally impose is that adsorption takes place above the critical temperature. Since inertness of the gas has been postulated, the phenomenon must be reversible. This means that the equilibrium condition must be attainable from both sides; *i.e.*, at a given temperature, a standardized quantity of the adsorbent must adsorb a given amount of the gas. The amount will depend exclusively on the pressure of the gas.

Although such ideal cases, such as the adsorption of argon by pure carbon, have proved of considerable value for the purpose of forming a basis for theoretical treatment, most adsorption processes are decidedly more complex and therefore do not follow this simple law. In a truly ideal case, the adsorption equilibrium is reached very rapidly (contrary to chemosorption); the adsorption equilibrium depends for given substances on temperature and pressure. The pressure and density isotherms (Fig. 55) curve toward the abscissa; the adsorbed amount depends on the pressure or density of the gas, in accordance with Boedeker's formula (see Appendix, page 238); the quantity of adsorbed substance decreases with increasing temperature at constant pressure; the adsorption of a gas is accompanied by evolution of heat.

Where adsorption takes place below the critical temperature, we must distinguish between cases where the solid substance is wetted by the liquefied vapor and those where no, or partial, wetting takes place. In the latter, adsorption occurs in the same manner as discussed; *i.e.*, it follows the ordinary adsorption isotherm (Fig. 56). In the case where we are dealing with porous, wettable adsorbing mediums—these are the most general industrial ones—such as activated carbon, charcoal, and silica gel, we find a difference in the appearance of the adsorption isotherm.[1] The curve shows a second rise as the vapor approaches its saturation pressure (Fig. 57). Zsigmondy[2] explains this behavior with the assumption that capillary forces cause a condensation of the vapor in the pores of the adsorbent. Therefore *capillary condensation* depends mainly on the wettability and the porosity of the adsorbent.[3]

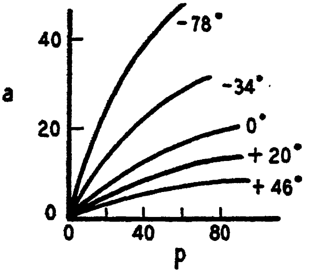

FIG. 55.

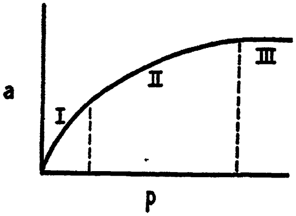

FIG. 56.

FIG. 55.—Adsorption isotherms of carbon monoxide on carbon for different temperatures. *a*, adsorbed matter per gram adsorbent; *p*, pressure at equilibrium.
FIG. 56.—General adsorption isotherm.

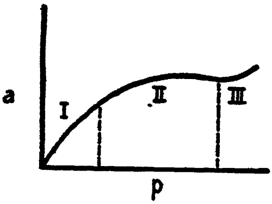

FIG. 57.—Adsorption isotherm and capillary condensation for porous adsorbents.

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[1] See, *e.g.*, E. HÜCKEL, "Adsorption und Kapillarkondensation," Akad. Verlags-Ges., Leipzig, 1928. A. A. SCHUCHOWITZKI, *Koll. Zeit.*, **66**, 139 (1934). G. E. CUNNINGHAM, *Coll. Symp. Monogr.*, **11**, 69 (1935).

[2] *Zeit. anorg. allg. Chem.*, **71**, 356 (1911).

[3] See, *e.g.*, GURWITSCH, *J. Russ. Phys. Chem. Soc.*, **47**, 805 (1915). POLANYI and GOLDMANN, *Zeit. physikal. Chem.*, **132**, 321 (1928).

The adsorption of gases or vapors on solid bodies is becoming of increasing industrial importance in the field of solvent recovery.[1] The principle of these processes is the use of materials of high adsorptive capacity, *e.g.*, activated carbon or silica gel.[2] The air, which is laden with the vapor of the solvent used in intermediate steps of various industrial processes, such as in the rubberizing of fabrics with organic rubber solutions or the manufacture of sheets or films from substances dissolved in organic solvents, is passed from the enclosed apparatus through filters containing the adsorbent. As soon as the adsorbent has been fully saturated, the solvent can be recovered by heating the adsorbent, preferably by passing steam through the filter. This becomes logical when it is remembered that adsorption is decreased with increasing temperature. A schematic drawing of such a regenerating device is shown in Fig. 58. Figure 59 shows the amount of solvent that activated carbon is capable of *ad*sorbing, depending on the amount of solvent present in the air, in comparison with an *ab*sorption process in paraffin oil. There

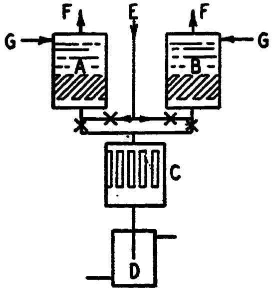

FIG. 58.—Solvent-recovery plant. *A*, *B*, activated carbon filters; *C*, cooling system; *D*, condensor; *E*, air inlet; *F*, air outlet; *G*, steam inlet.

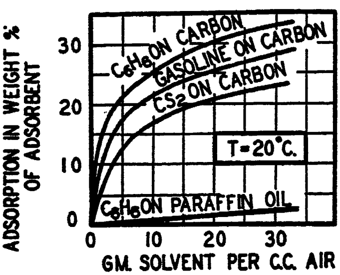

FIG. 59.—Adsorption of different solvents on activated carbon and paraffin oil.

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[1] For detailed literature in regard to solvent recovery, refer to the following summaries: The contribution of A. Engelhardt in HAUSER, "Handbuch der gesamten Kautschuktechnology," vol. I, p. 805, Union Deutsche Verlags-Ges., Berlin, 1935. Contribution of W. MECKLENBURG in LIESEGANG, "Kolloidchemische Technologie," 2d ed., p. 38, T. Steinkopff, Dresden, 1932.

[2] For a brief summary of manufacture and application of active substances see, F. KREZIL, *Koll. Zeit.*, **84**, 122 (1938).

are different methods in use for activating carbon. We find products that are simply activated by treating the charred raw material, such as wood, with water vapor at temperatures between 800 to 1000°C. Other processes apply a treatment with phosphoric acid, potassium carbonate, or zinc chloride. The latter treatment, which is second in importance to the water-vapor process, permits activation at temperatures slightly above 300°C.

SOLID-LIQUID SYSTEMS

Undoubtedly the most important of all adsorption phenomena are those taking place in a solid-liquid interface. However, at the same time they must be considered as extremely complex. The phenomenon that a pure and true solution, being brought in contact with an insoluble solid substance, is tenaciously retained on the surface of the solid is generally known as *lyosorption*.[1] The wetting of a solid body is the simplest example of this phenomenon.

According to Wo. Ostwald,[2] the adsorption layer thus formed is termed *lyosphere*. The lyospheres are to be considered as diffuse, so that a continuous transition exists between them and the interior of the surrounding liquid. Experiments on sedimentation volumes of comparatively coarse suspensions in different liquids, as carried out by Wo. Ostwald and W. Haller,[2] A. v. Buzágh,[3] H. Freundlich,[4] Freundlich and H. L. Röder,[5] and E. A. Hauser,[6] seem to prove that the thickness of the lyospheres is, contrary to previous assumptions, far in excess of normal molecular dimensions. The thickness of the lyosphere seems to depend on the type of adsorbing surface and on the liquid present. It has been ascertained that lyosorption is exceptionally pronounced with such substances as can be considered as

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[1] See A. FODOR, "Die Grundlagen der Dispersoidchemie," T. Steinkopff, Dresden, 1925.

[2] *Koll. Beih.*, **29**, 354 (1929).

[3] *Ibid.*, **32**, 114 (1930).

[4] *Trans. Faraday Soc.*, **34**, 308 (1938).

[5] "Thixotropy," No. 267 of "Actualités scientifiques et industrielles," Hermann & Cie., Paris, 1935.

[6] DENTON and ROBINSON, unpublished M. Sc. thesis, Massachusetts Institute of Technology, 1937.

extremely heteropolar, *e.g.*, most of the silicates. This leads to the assumption that the development of a lyosphere depends to a large extent on the residual electrostatic valencies of the adsorbent. This results in the important conclusion that lyosorption can be very materially influenced by changes in the charge of the adsorbing surface. With increasing charge, lyosorption must also increase. Wo. Ostwald and W. Haller have found that there is a connection with the dielectric constant of the liquid. In general, liquids of high dielectric constant will show lyosorption to a smaller degree than those of a low dielectric constant.

It is of no noticeable importance in which state of comminution the absorbents happen to be present. It is a simple matter of terminology if lyosorption in the case of colloidal systems is more generally known as *solvation* or *hydration.*

The problem becomes decidedly more difficult in the case where the solution contains dissolved matter, such as electrolytes or a colloidal dispersion. Then the case may occur where dissolved matter, as well as solvent, is simultaneously adsorbed, and it becomes extremely hard to differentiate between true adsorption of an individual component and an adsorption resulting from an intimate linkage of one of the components to the other one that has been actually adsorbed.

ION ADSORPTION–BASE EXCHANGE ADSORPTION

We have previously mentioned polar adsorption when discussing liquid-liquid systems. The same naturally holds good for solid-liquid systems. Here we find, for instance, in the case of electrolytes or their ions, that only one constituent is really adsorbed, whereas the other remains in solution. Since the electric neutrality of the system as a whole must be maintained, another ion must be substituted. This ion can either be given off by the adsorbent in exchange for one taken on, or it must be obtained by a secondary reaction in the dispersion medium. This phenomenon is generally known as *exchange adsorption*, or *ion-exchange reaction.* Presumably the most typical instance is the so-called *base exchange* of zeolites or permutites as used with increasing success for water-softening purposes. The zeolites correspond generally in their chemical constitution to the clays.

They are very open-textured aluminum hydrosilicates.[1] The oxygen atoms present in the surfaces or at the edges or corners of the crystal lattice possess residual electrostatic fields. These are satisfied by available cations, such as sodium (Fig. 60). If such a zeolite is brought into contact with water containing calcium salts, the calcium ions will be adsorbed, and the sodium ions given off. This can be explained, on the basis of a Donnan equilibrium, besides the fact that the lower degree of hydration of the calcium ion will give an added incentive to the exchange.

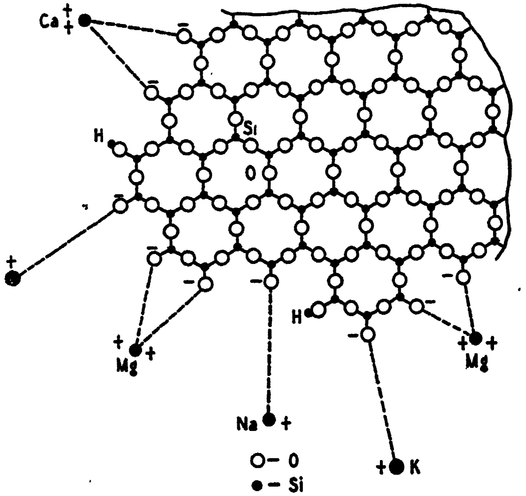

FIG. 60.—Schematic interpretation of a silica plane in a clay crystal. [*From U. Hofmann & W. Bilke, Koll. Zeit.*, 77, 238 (1936).]

The dotted lines give an approximate idea of the offstand distance and the degree of bond of the adsorbed cations.

When all the sodium has been replaced by calcium we can regenerate the zeolite by backwashing it with a highly concentrated brine solution. A large amount of sodium ions will eventually replace the calcium. For example, if a sodium clay is submitted to dialysis or electrodialysis, no ions are available in the solution for replacement of those that are being removed. To retain the electric equilibrium of the system, it is therefore necessary that the water split and release the needed amount of

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[1] See H. B. WEISER, "Inorganic Colloids," John Wiley & Sons, Inc., New York, 1933–1938.

hydrogen ions to replace the removed metallic cations.[1] The result is so-called hydrogen-clay, or acid clay.

In the case of apolar adsorption, we are dealing mainly with a random aggregation of molecules in the interface or adsorption layer, which, being made up out of dissolved substance and dispersion medium, is a typical example of a solvated hull. In general, apolar adsorptions are reversible. The amount of adsorbed substance per unit quantity of adsorbing matter depends only on the relative quantity of adsorbent, the concentration of the substance to be adsorbed, and the temperature. An equilibrium is quickly reached unless secondary phenomena, *e.g.*, chemosorption or *ab*sorption, are involved. In Fig. 61, taken from a paper published by Wo. Ostwald and Izaguirre,[2] the most common functions of equilibrium concentration per unit volume of the adsorbed substance and the quantity adsorbed are given.

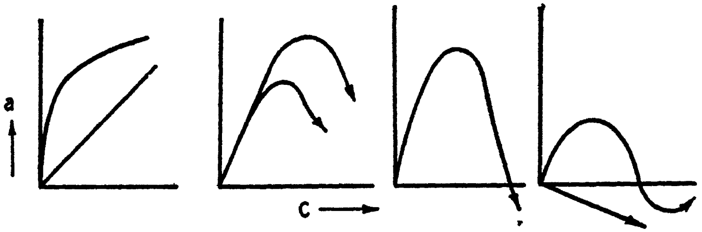

FIG. 61.—Different adsorption curves.

CLASSIFICATION OF ADSORBING SURFACES

When considering adsorption phenomena, one should not overlook the type of adsorbing surface available, since adsorption

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[1] A more detailed discussion of ion-exchange reactions can be found, *e.g.*, in the following literature: G. WIEGNER and K. W. MUELLER, *Zeit. Pflanz. Düng.*, *A*-**14**, 321 (1929). G. WIEGNER, *J. Landw.*, **60**, 111, 197 (1912); *Koll. Zeit.*, *Erg. Bd.*, **36**, 341 (1925); *J. Soc., Chem. Ind.*, **65** *T*, February, 1931; *ibid.*, **103** *T*, March, 1931. KELLEY, JENNY, and BROWN, *Soil Science*, **41**, 259 (1936). U. HOFMAN, K. ENDELL, and D. WILM, *Zeit., Krist.*, **86**, 238, 340 (1933). U. HOFMAN and W. BILKE, *Koll. Zeit.*, **77**, 246 (1936). C. E. MARSHALL, "Colloids in Agriculture," pp. 79*ff.*, Edward Arnold & Company, London, 1935.

[2] *Koll. Zeit.*, **30**, 279 (1922); **32**, 57 (1923). See also GUSTAVER, *ibid.*, **31**, 358 (1922). OSTWALD and SCHULZE, *ibid.*, **36**, 289 (1925). HEYMAN and BOYE, *ibid.*, **63**, 154 (1933). BARTELL *et al.*, *J. Am. Chem. Soc.*, **51**, 1637 (1929); **53**, 2501 (1931).

can vary between cases where external or internal surfaces are concerned. For this reason, one has differentiated between the following types of surfaces:

1. Surfaces of the first order: The external surface and the surface of internal pores are of coarse dimensions.
2. Surfaces of the second order: The surface of the pores is of submicroscopic dimension.
3. Surfaces of the third order: The surfaces of the pores and the capillaries are of amicroscopic dimensions.

Such a differentiation materially assists in an evaluation or explanation of adsorption phenomena. It becomes evident that at surfaces of first order the adsorption can freely develop, whereas at those of third order only layers of amicroscopic thickness are conceivable. The degree of comminution of the adsorbent will also materially influence adsorption, depending on the type of surface available. An adsorbent having surfaces of first order will show but little change upon further subdivision. However, one containing a large percentage of surfaces of second and third order upon comminution shows a noticeable increase in its adsorptive capacity, owing to the transformation of these surfaces into those of first order (Fig. 62).

FIG. 62.—Types of surface. *a*, surface of second order prior to disintegration; *b*, after disintegration.

From this discussion it is clear that spacial arrangement of the adsorbent can be of importance. For example, if particles of an adsorbent characterized by surfaces of first order are sedimented and caused to pack closely, an adsorbent with surfaces of second or even third order may result, so that the adsorptive capacity per unit mass of adsorbent may materially decrease.

Naturally, the geometric form or shape of the adsorbent also has a decided influence on the adsorption capacity. It has been pointed out that surface or interfacial energies depend not only on the actual size of the interface but also to a large extent on the number of available preferential areas (edges, corners, etc.). This explains why the roughness of an adsorbing surface is also of importance. Since subdivision increases the over-all surface per given volume unit as well as the number of edges, corners, etc., it is logical that comminution of an adsorbent in many cases helps to increase its adsorptive capacity.

As to the chemical nature of the adsorbent, no general rule has been found so far. However, the chemical properties of the adsorbed substance have a very considerable influence on its adsorbability. The greater the capillary activity of a substance the higher will be its adsorbability, in general. This is in full accord with Traube's law (page 116). In the case of electrolytes, we find that free bases and free acids are generally more strongly adsorbed than their corresponding salts.

POLAR ADSORPTION

One frequently finds the statement that the surface tension of the dispersion medium has some influence on adsorption. The greater the surface tension the greater is the adsorption of a substance dispersed therein. In connection with what has been said when discussing the theory of surface tension, this appears logical, because high surface tension is the result of a strong field of force between like molecules of the dispersion medium, so that the attraction toward foreign molecules distributed therein is easily compensated for by the forces causing adsorption. This means that a substance dissolved or dispersed in a liquid of high surface tension, *e.g.*, water, is more readily adsorbed than if it were dissolved in a liquid of low surface tension, *e.g.*, an organic solvent. However, there is no question that the influence of the dispersion medium on adsorption has not yet received sufficient attention, and considerable further work is needed before this factor can be fully evaluated.

Reference has briefly been made to the so-called ion- or base-exchange reactions. In working with activated carbon, for example, one frequently finds, when adsorbing anions or cations from neutral salt solutions, that an end point is reached at which the solution takes on a definitely alkaline or acid reaction. This phenomenon, known as *adsorption hydrolysis*, is caused by the fact that the carbon gives off an OH^- or an H^+ ion for every cation or anion that it adsorbs. But such cases must be considered as limiting ones, because most often both types of ions are simultaneously adsorbed to some extent. Therefore, polar and apolar adsorption can take place simultaneously, just as polar adsorption and chemosorption frequently merge into each other. Since this is the case, we might consider polar adsorption as a phenomenon intermediate between apolar adsorption and chemosorption (Fig. 63). It explains why the adsorption isotherm for polar adsorption is, in principle, similar to those typical for apolar adsorption. The main difference is that the former is more curved, terminating in a way similar to those typical of heterogeneous chemical equilibriums. The previously mentioned fact that in the case of polar adsorptions an equilibrium condition is reached only after a comparatively long time strengthens the classification for polar adsorption given above. Considerable experimental evidence is now available for this. For instance, L. Imre[1] could show that the adsorption of ions on to crystals takes place in three steps: (1) They are drawn into the outer sphere of the adsorption layer; (2) they penetrate this layer with measurable velocity; (3) they snap into the crystal lattice. Also, chemosorption mostly takes place in steps, as can be demonstrated by the color change of a blue Congo-red sol when brought into contact with aluminum hydroxide.

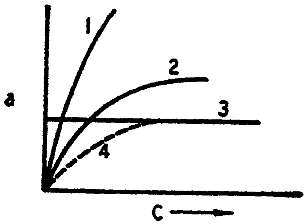

FIG. 63.—Adsorption isotherms for different types of adsorption. 1, apolar adsorption; 2, polar adsorption; 3, 4, heterogeneous reactions.

In the case of polar adsorption, we generally distinguish between basic and acid adsorbents. The former, such as metal hydroxides, will preferentially adsorb anions; whereas the latter, *e.g.*, silicates, will adsorb cations. Since this phenomenon is largely of electrical nature, it is, as has been mentioned, generally known as *electric adsorption.*

It has been found that the adsorbability of various ions follows the so-called Hofmeister, or lyotropic, series:[2]

$$SO_4 < F < NO_3 < Cl < Br < I < CNS < \ldots OH$$
$$Li < Na; \quad K < Mg < Ca < Sr < Ba < Al < \ldots H$$

K. Fayans and Beer[3] and O. Hahn[4] found that there is some connection between adsorbability and solubility in the adsorption

[1] *Zeit. physikal. Chem.*, **144**, 161 (1929); **146**, 41 (1930).

[2] A. VOER, *Chem. Wbl.*, **35**, 113 (1938).

[3] *Ber.*, **46**, 3486 (1913); **48**, 700 (1915).

[4] *Ibid.*, **59**, 2014 (1926).

of radioactive elements. Also, taking into account the fact that a radioactive element is precipitated only if it can be incorporated in the crystal lattice of an isomorphous sparingly soluble precipitate (R. Marc's law[1]), Hahn made the following statement:

> . . . an inactive adsorbent will adsorb a radio-active element only if it acquires by adsorption of foreign ions a charge opposite to that of the radio-active ions, and if the radio-active element is capable of forming a compound of low solubility or dissociation with the adsorbed foreign ion.

A generalization of this empirical rule is known as the *Fayans-Hahn law* and has already been referred to when discussing the preferential adsorption of one ion on a precipitate in the formation of the electric double layer (see page 100).

As to the part that the internal structure plays in polar-adsorption phenomena, it is evident that in the case of extremely disperse or difform systems it becomes more and more difficult to distinguish between ionic adsorption and chemical combination. Frequently, one has found that the adsorbed ions react through the entire adsorbent, resulting in a complete ion exchange but without altering the structure of the adsorbents. Such an adsorption, according to V. Kohlschuetter,[2] is termed "topochemical reaction," or "transformation." A typical example is H. Kautsky's[3] Siloxen ($Si_6O_3H_6$). Its microstructure coincides with that of calcium silicide, yet it is not changed when transformed into trihalogen siloxide or by the adsorption of various compounds.

The close external resemblance of topochemical transformations and chemical reactions has resulted in an argument as to whether such extreme cases of ionic substitution may be classified as adsorption processes or should be considered as simple heterogeneous reactions. Whereas, for example, R. Gans considers base exchange as a formation of sparingly soluble salts, V. Rothmund and G. Kornfeld[4] consider permutites as solid solutions. H. Freundlich,[5] G. Wiegner,[6] and E. A. Hauser and

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[1] *Zeit., physikal. Chem.*, **75**, 710 (1911); **81**, 641 (1913).

[2] *Koll. Zeit.*, **42**, 254 (1927).

[3] *Zeit. physikal. Chem.*, **139**, 135 (1925).

[4] *Zeit. anorg. allg. Chem.*, **103**, 129 (1918); **108**, 215 (1919); **111**, 76 (1920).

[5] "Kapillarchemie," 4th ed., pp. 309*ff*., Akad. Verlags-Ges., Leipzig, 1930.

[6] *Koll. Zeit., Erg. Bd.*, **36**, 341 (1925).

C. E. Reed[1] disagree with this purely chemical concept. They base their arguments on the experimental proof that base-exchange reactions give adsorption curves typical for polar adsorption and that the Hofmeister ion series hold good in these processes. The latter investigators have furthermore proved that also, in cases of base-exchange reactions other than permutites, a reaction throughout the mass takes place if the particle size of the adsorbent is sufficiently small. Therewith, the only remaining difference between the concept of polar adsorption and topochemical reaction has been eliminated. Naturally, the adsorbed ions are bound to the adsorbent by chemical linkages, so that this ionic substitution can be termed a chemical reaction, but one must also consider the simultaneous adsorption of foreign ions. This adsorption deserves far more recognition than it has so far received, since, as has been demonstrated, analytical results will vary in accordance with the anions present in the solution.

ADSORPTION OF COLLOIDS

The intermediate position of colloidal systems between coarse and fine dispersions results in the fact that true adsorption and the adhesion of coarse particles to solid bodies will overlap in the colloidal range. Since colloidal systems always contain some matter in a high degree of dispersion (*e.g.*, the electrolyte responsible for stability), adsorption becomes complicated. We have to differentiate between the adsorption of the colloid and that of the highly disperse matter on the adsorbent and also consider the adsorption of the latter on the colloid itself. The adsorption of lyophobic colloidal particles corresponds in principle to the adhesion of microscopic particles on walls (see page 208). The governing factors are primarily the electric charge and the thickness of the lyospheres. That electric charge plays an important part in the adsorption of colloids is demonstrated by the fact that colloid particles of positive sign are preferentially adsorbed by negative adsorbents; and negatively charged ones, by positive ones.

The adsorption of lyophilic colloids follows, in general, the adsorption of highly disperse substances. That the adsorption of lyophilic colloids is frequently an irreversible process can be

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[1] *J. Phys. Chem.*, **41**, 911 (1937).

explained by the fact that chemical reactions or alterations in the adsorption layer occur, *e.g.*, the denaturation of proteins.

STRUCTURE IN IONIC ADSORPTION LAYERS

So far, all the assumptions in regard to the arrangement of the ions or molecules in an adsorption layer have been entirely hypothetical. Naturally, it would be extremely valuable if one could obtain a real insight into such a microstructure. The great development in structural physics (M. v. Laue's fundamental work on the space lattice of a well-defined crystal by the use of x rays and P. Debye and P. Scherrer's application of x-ray analysis to fine powders, the discovery of fibrous structure in cellulose, stretched rubber, etc.) resulted in the application of this method to a study of possible molecular orientation in adsorption layers. J. J. Trillat[1] applied to a study of fatty acid films on surfaces extremely soft x rays known to penetrate only to a small depth. Although Trillat's results definitely proved that the molecules are oriented at the surface or in an interface, the information obtained was not yet sufficient to draw further conclusions in regard to the true structure of the surface.

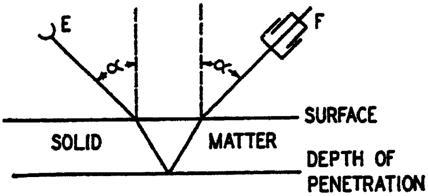

FIG. 64.—Electron diffraction. *E*, source of electrons; *F*, Faraday cage; α, angle of impact and reflection.

More recently, Davisson and Gerner,[2] Rupp,[3] Trillat and Mark,[4] Hengstenberg and Wolf,[5] and Harkins and his collaborators[6] have investigated surfaces by a most ingenious method based on the reflection of electron rays. Rupp allowed an

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[1] *Metallwirtschaft*, 7, 101 (1920); "Les applications des rayons X," pp. 263*ff*., Les Presses Universitaires de France, Paris, 1930.

[2] *Physiol. Rev.*, 30, 705 (1927).

[3] *Ann. Phys.*, 85, 981 (1918); *Zeit. Phys.*, 52, 8 (1928).

[4] *Erg. techn. Röntg.*, 4, 69 (1934).

[5] "Elektronenstrahlen und ihre Wechselwirkung mit Materie," Akad. Verlags-Ges., Leipzig, 1935.

[6] *J. Phys. Chem.*, 40, 941 (1936).

electron ray E to impinge on a solid surface at a constant angle α. The intensity of reflection is determined at the same angle by the use of a Faraday cage F (Fig. 64). If the surface structure of the solid has once been established, this method permits a closer study of the structure of adsorbed layers. These studies have already demonstrated that the hypothesis of active centers or areas is borne out by the fact that the arrangement of adsorbed gas ions is not even but is grouped at symmetrically distributed active centers. An application of a similar method to the study of the thickness of an interfacial layer of a liquid in contact with its own vapor has resulted in the astonishing discovery that the thickness is far beyond molecular dimensions.[1] Yet so far these results have given us only an indication as to boundary structures of pure substances. We are particularly interested in the thickness of typical adsorption layers and the range of forces therein.

THICKNESS OF ADSORBED LAYERS

v. Buzágh[2] discusses two methods for determining the range of adsorption forces. By covering the surface of a well-known substance A (Fig. 65) with another substance B in layers of increasing thickness, we shall find a layer thickness D_1 at which the properties of A no longer appear. At the thickness D_2, the properties typical for substance B will show up. It has been found that the thickness of the two layers is generally of collodial dimensions and that a great number of specific properties are changed when the thickness of the interfacial layer has reached this dimensional range.[3]

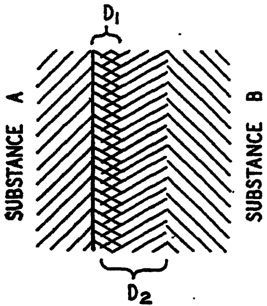

FIG. 65.—Critical adsorption layer.

The second method consists in determining the thickness of the maximum quantity of a substance which is adsorbed on a well-defined surface of an adsorbent. It has been found by I. Langmuir that the adsorption layer is generally not a coherent film but that, as mentioned, adsorption mostly takes place in

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[1] See, *e.g.*, G. BAKKER, *Zeit. physikal. Chem.*, **93**, 154 (1919); "Kapillarität und Oberflächenspannung," Akad. Verlags-Ges., Leipzig, 1928.

[2] "Colloid Systems," p. 200.

[3] For further references, see, *e.g.*, v. BUZÁGH, *loc. cit.*

patches. This infers that adsorption very rarely consists of a monomolecular layer. Here attention should be drawn to the work of O. Bartsch,[1] Wo. Ostwald and W. Haller,[2] and A. v. Buzágh[3] which also demonstrates that adsorption layers exist *which greatly exceed* molecular dimensions.

SURFACE ORIENTATION

As has been pointed out, the structure of the adsorption layer follows the Hardy-Harkins rule of least abrupt change. This must result in a definite orientation of the molecules at the interface. For example, in a water-air interface, molecules of fatty acid orient themselves as previously indicated in such a fashion that their COOH groups are turned toward the water; their alkyl groups, toward the air. Such orientation becomes particularly marked when the molecules are densely packed.[4] The same holds true not only for liquid-gas but also for liquid-liquid or liquid-solid interfaces.

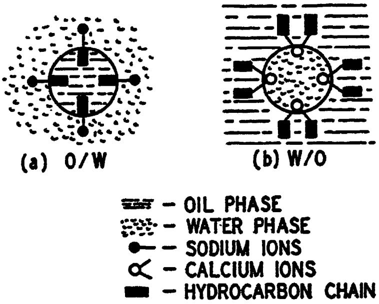

FIG. 66.—Emulsification.

The problem of emulsification is closely related with interfacial adsorption in liquid-liquid systems. If the adsorbable substance, such as sodium oleate, is more readily wetted, for instance, by water than by oil, we shall obtain an oil-in-water emulsion (Fig. 66*a*). However, if the emulsifying agent, such as calcium oleate, is more readily wetted (adsorbed) by the oil phase, a water-in-oil emulsion will result (Fig. 66*b*).[5] Ore flotation processes, to which reference has already been made, are examples of adsorption phenomena on solid-liquid and solid-air interfaces.[6]

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[1] *Koll. Zeit.*, **38**, 321 (1926).

[2] *Koll. Beih.*, **29**, 354 (1929).

[3] *Ibid.*, **32**, 114 (1930).

[4] R. E. WILSON and E. D. RIES, *Coll. Symp. Monogr.*, **1**, 145 (1923).

[5] For a detailed discussion of emulsions, see, *e.g.*, W. CLAYTON, "The Theory of Emulsions and Their Technical Treatment," 3d ed., P. Blakiston's Son & Company, Philadelphia, 1935. F. G. DONNAN, "The Technical Aspects of Emulsions," A. Harvey, London, 1935.

[6] For detailed discussion, see, *e.g.*, W. PETERSEN, "Schwimmaufbereitung," T. Steinkopff, Dresden, 1936. This book contains a discussion of the

SURFACE FILMS

The kinetics of such adsorption layers, or films, worked out by Langmuir, Harkins, and Volmer must be considered today as the outstanding contributions to colloidal physics in the last decade. The molecules adsorbed in the interface are in free thermal motion, resulting in a lowering of the surface tension of the liquid and a spreading of the film over the surface. These layers behave in two dimensions exactly as macroscopic bodies of the solid, liquid, or gaseous state behave in three dimensions. If the adsorbed amount is small, and the temperature high, we speak of an *ideal two-dimensional gas,* because the molecules adsorbed in the surface layer are free to move in the plane (two dimensions), just as gas molecules move freely in the three dimensions of space. On further concentration and lowering of temperature, we obtain two-dimensional liquids and finally two-dimensional solids. If such a film acts like a gas, its molecules must have the tendency to spread unhindered, as do the molecules of a gas. The only difference is that in the case of a gas the spreading tendency can be compensated by a *space*-limiting *plane,* whereas in that of a film the spreading tendency must be compensated by a limiting *line.* The *spreading pressure* of a gas is measured in *dynes per square centimeter;* that of a film, in *dynes per centimeter.*

On the basis of the pioneer work of A. Pockels, I. Langmuir[1] devised an instrument to measure directly the expansion of surface films. This method was further developed by N. K. Adam,[2] and the instrument is today known as a "lyophil balance." The instrument consists, in principle, of a rectangular metallic well-paraffined trough *B* (Fig. 67). The trough is filled with water, and a trace of the substance to be investigated placed

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theories as well as of the most common practical applications. It also gives an up-to-date, complete list of literature and patent references. See also the purely scientific discussion of "Wetting in Flotation," by H. FREUNDLICH, in "Wetting and Detergency," A. Harvey, London, 1937.

[1] "Surface Chemistry," *J. Am. Chem. Soc.*, **38**, 2246 (1916).

[2] "The Physics and Chemistry of Surfaces," 2d ed., Oxford, Clarendon Press, New York, 1938; *Chem. Rev.*, **13**, 147 (1933). See also I. Langmuir's contribution in J. ALEXANDER, "Colloid Chemistry" (Theoretical and Applied) vol. I, p. 525, D. Van Nostrand Company, Inc., New York, 1926; *Coll. Symp. Monogr.*, **3**, 48 (1925).

on the surface of the water, where it spreads out. Two barriers *A* and *C* permit us to increase or decrease the surface available for the film. The barrier *C* is free movable between the edges of the trough and connected with a torsion balance *D* which permits measuring the spreading pressure. It has been found that with dilute films the product of spreading pressure and available film surface is constant. This is in accord with the gas law of Boyle-Mariotte, which states that the product of pressure and volume of a gas is constant at a given temperature. If we now decrease the available surface by carefully pushing the barrier *A* closer to *C*, the spreading pressure increases (part 1 of Fig. 68). The pressure rises to a certain point, after which a further decrease in surface causes no change (part 2 of Fig. 68). This corresponds to the known fact that a highly compressed gas is transformed at constant pressure into a liquid. In such condensed films, the molecules are considered to be in dense packing, so that attraction forces begin to act between them. In trying to decrease the surface still further, the spreading pressure rises very markedly (part 3 of Fig. 68), just as liquids show an extremely small compressibility.

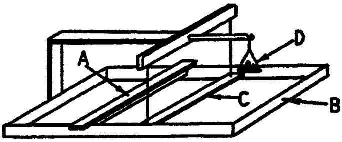

FIG. 67.—Lyophil balance. *A*, pushing barrier; *B*, trough; *C*, free-moving barrier connected with *D*; *D*, balance (in the newer models this is built as a torsion balance).

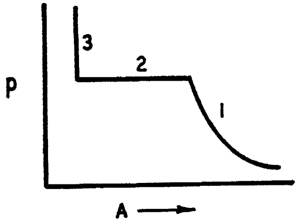

FIG. 68.—Spreading pressure diagram. *A*, area covered by film; *p*, spreading pressure.

By dividing the minimum surface of the film by the number of molecules (to be evaluated from the amount of substance used), it is possible to calculate the area in the surface occupied by one molecule. The most striking result obtained thereby is that the area occupied per molecule of all the higher fatty acids in the condensed films is more or less identical, amounting to approximately 0.21 $m\mu^2$. Since these molecules are considered to be of rodlike shape, their length varying only with the length of their carbon chains, it seems logical that in a condensed film they must be oriented in such a way that their carbon chains take up a position more or less at right angles to the interface.

The same point of view as outlined by Langmuir, in connection with the properties of monomolecular adsorption layers, has been taken by M. Volmer and G. Adhikari[1] to apply to the adsorption on solid adsorbents. Here the adsorbed molecules are freely movable on a solid adsorbent parallel to the interface. The investigators cemented a benzophenone crystal to a glass plate and permitted a stream of mercury to flow by the crystal but without touching it. It was found that the crystal diminishes in weight. Since benzophenone has a low volatility and is also insoluble in mercury, the only explanation left is to assume that benzophenone crystal units are pulled out of the lattice and spread along the glass to the mercury surface. J. Estermann[2] shows that the results of subliming silver on glass surfaces can be explained only by the assumption that the silver atoms move toward preferential spots when hitting the glass surface, where they grow to form minute crystals.

It may be well to refer here again to the Hardy-Harkins rule to see if and to what extent it is applicable to the adsorption of electrolytes out of their solution, a phenomenon discussed in the preceding chapter. If a crystal surface is in contact with a saturated solution of the crystal, then, according to A. v. Buzágh,[3] the water dipoles of the solution will be attracted by the electric fields of the ions at the surface of the crystal. This means nothing else than the formation of a lyosphere. The ions at the surface are not hydrated to the same extent as the free ions in the solution, because they are only partially provided with a water hull. We can compare the ions in the solution with islands completely surrounded by water, whereas the adsorbed ions in the surface would correspond to peninsulas. However, some of the other ions also present in the solution are likewise attracted by the ions of the crystalline surface. Hence a layer consisting of water dipoles and ions is formed in the vicinity of the solid crystalline surface, which guarantees a continuous transition between the crystal surface and the solution.

CAUSES OF ADSORPTION

The importance of adsorption in many technical processes and the great variety of possibilities that this phenomenon

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[1] *Zeit. physikal. Chem.*, **119**, 46 (1926); *Zeit. Phys.*, **35**, 170, 722 (1926).

[2] *Zeit. physikal. Chem.*, **106**, 403 (1923). An excellent survey on the subject has been given by E. HEYMANN, *Koll. Zeit.*, **57**, 81 (1931).

[3] "Colloid Systems," p. 204.

embraces have naturally resulted in a considerable amount of speculation as to the fundamental causes. Here, again, we find the dualism of opinion so often encountered. Some favor a purely physical explanation; others support a purely chemical point of view.

The Potential Theory.—A. Eucken,[1] M. Polanyi,[2] A. M. Williams,[3] etc., assume that as a result of some kind of attraction forces, an "adsorption potential" exists at a certain point in space in the close vicinity of the adsorbent. The potential then would be defined by the work that would have to be done to remove a molecule from that point to an infinite distance from the surface of the adsorbent. These theories, generally known as "potential theories," must assume that the adsorption layer can be several molecules deep or, in other words, that the adsorbing forces are evident at supermolecular distances. This supposition has been strongly opposed by physicists who consider the range of molecular forces, such as the van der Waals' forces, to be of the order of molecular dimensions only. However, the theoretical deductions of F. London,[4] H. Kallmann, M. Willstaetter, C. Hamaker, I. Langmuir, Wo. Ostwald, E. A. Hauser, and D. S. le Beau (for a detailed discussion, see page 219) seem to demonstrate that the range at which these forces can act is, at least in colloidal systems, of decidedly supermolecular dimensions.

Residual Valence Theory.—In discussing the formation of the diffuse electric double layer (see page 98), we have already drawn attention to the differences in saturation between atoms located in the interior and those on the surface of the particle. An analogous concept in respect to adsorption was postulated by F. Haber,[5] who assumed that the atoms at the surface of an adsorbent, being saturated only toward the interior, must possess unsaturated or residual valencies toward the outside (see Fig. 41). If molecules of the substances to be adsorbed touch these unsaturated points, they will adhere. Since in such a case only one molecule, atom, or ion can be adsorbed for every residual

[1] *Verh. deut. physikal. Ges.*, **16**, 345 (1914).

[2] *Ibid.*, **18**, 1012 (1915); *Zeit. Elektrochem.*, **26**, 370 (1920).

[3] *Proc. Roy. Soc.*, **38**, 23 (1918); **39**, 48 (1919); *A* **96**, 287 (1919)

[4] *Trans. Faraday Soc.*, **33**, 8 (1937).

[5] *Zeit. Elektrochem.*, **20**, 521 (1914).

valency, maximum adsorption will correspond to maximum saturation of these residual valencies. H. Freundlich[1] expresses the opinion that such saturation is the result of a much looser binding than is the case in a true chemical combination. I. Langmuir[2] is to be credited for having materially elaborated this concept. Its limitations lie in the fact that saturation of the adsorbent can at best result in a monomolecular adsorption layer and that only homogeneous surfaces are considered. However, if the surface of the adsorbent is not homogeneous or well-defined, *e.g.*, in systems of a high degree of dispersion, where active corners or edges can no longer be neglected, the results called for by the theory become questionable. (For mathematical evaluation, see Appendix, page 240.)

Chemical Theory.—From the purely chemical point of view, adsorption is a chemical reaction taking place on the surface of the adsorbent. The resulting compound is considered as that reaction product which under given conditions has the least solubility of all products obtainable by chemical combination of the adsorbent and the adsorbed substance. In instances where the resulting compound has an electric charge, that molecule, atom, or ion with which the adsorbent gives the least soluble and dissociable compound will be most strongly adsorbed. (For mathematical discussion of the chemical point of view, see Appendix, page 240.)

Electric Theory.—The most recent approach to an explanation of adsorption phenomena can be presented under the general heading of "electric theories." The founder of modern physicochemistry, Svante Arrhenius, even assumed that adsorption forces might be identical with van der Waals' forces. This work, pioneered by Keesom and P. Debye,[3] was elaborated by R. Lorenz and A. Landé,[4] E. Jaquet,[5] E. Hückel,[6] and others. They regard the solid as continuous and conducting. A dipole approaching such a conducting surface will be attracted to it, just as if the

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[1] "Kapillarchemie," vol. 1, 4th ed., pp. 190*ff.*, Akad. Verlags-Ges., Leipzig, 1930.

[2] *J. Am. Chem. Soc.*, **40**, 1361 (1918).

[3] *Physica*, **1**, 362 (1921).

[4] *Zeit. anorg. allg. Chem.*, **125**, 47 (1922).

[5] *Fortschr. Chem. Phys. u. physikal. Chem.*, **18**, 1 (1925).

[6] "Adsorption und Kapillarkondensation," pp. 152*ff.*, Akad. Verlags-Ges., Leipzig, 1928.

surface were a mathematical plane midway between the dipole and its mirror image with the poles reversed (Fig. 69). The results of these considerations can be summarized as follows: From an electrostatic point of view, adsorption energy decreases rapidly with distance. The adsorption of molecules on crystalline surfaces depends on the size, shape, and distance between the molecules. The adsorption potential is not independent of temperatures.

Here, again, we must consider the more recent developments referring to the sphere of influence of the attractive forces. As already pointed out, F. London[1] and H. Kallmann have been able to show that we not only need to consider the comparatively short-range electrostatic forces in the attraction of molecules but that we must also take into account the forces resulting from mutual short-period disturbances of the internal movement of the electrons. Since it has been shown that these forces can act over more than molecular distances, the formation of multimolecular adsorption layers does not seem improbable. This assumption has been confirmed, meanwhile, by L. Imre,[2] H. Cassel,[3] and recent and still unpublished works of the author in connection with studies on the ionic adsorption of hydrous aluminum silicates.

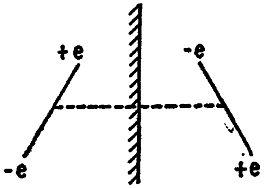

FIG. 69.—Dipole attraction by a conducting surface.

If one bears in mind the fact that the electric theories are of comparatively recent date and that the amendments as to the possible distance at which attraction forces can exert their influence are even still more recent, it seems rather premature to express any definite opinion as to the final value of these theories. However, if one may take as a barometer the few experimental proofs so far available, there would seem to be great possibilities that a careful combination of these theories will eventually lead to a more acceptable concept of adsorption phenomena in general.

In trying to summarize the most plausible present concepts of adsorption, we can distinguish between those theories that in one

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[1] *Zeit. physikal. Chem., Abt. B*, **2**, 207 (1929); *Zeit. Phys.*, **60**, 417 (1930); *Trans. Faraday Soc.*, **33**, 8 (1937).

[2] *Zeit. physikal. Chem.*, 171, 239 (1934).

[3] *Zeit. Elektrochem.*, **37**, 642 (1931).

way or another follow the idea of active centers first introduced by F. Haber[1] and later amended by G. Gurvich,[2] I. Langmuir,[3] H. S. Taylor,[4] H. G. Tanner,[5] and others and the assumption that the molecules of the adsorbed substance are free to move in the interface as postulated primarily by A. Magnus.[6] In cases where no specific chemical relationship exists between adsorbent and the substance to be adsorbed, one may assume that the molecules are really free to move in the interface. This might be termed *ideal*, or *physical, adsorption.* If a chemical interaction occurs between adsorbent and substance to be adsorbed, then a stronger localized bond on active centers seems more probable. Quite frequently we find that physical adsorption is predominant at low temperatures, such as in the adsorption of oxygen on metal surfaces; whereas, at elevated temperatures, an *activated adsorption* or chemical localization takes place. This difference finds its simple explanation in the fact that chemical reactions proceed extremely slowly at low temperatures.

A great number of adsorption phenomena must be thought of as combinations of both types. The change which a blue Congo acid sol undergoes when adsorbed on aluminum oxide is a typical example. Upon adsorption of the sol, the aluminum oxide first takes on the blue color, which, however, is changed to red upon storage or slight elevation of temperature. This is caused by the gradual formation of the red-colored aluminum salt of the Congo acid in the interface. Many dyeing processes appear to be closely related to this phenomenon, *e.g.*, the dyeing of wool, wherein first adsorption and then a salt formation is to be assumed. In the case of dyeing artificial silk, it is more probable that a change in particle size of the adsorbed colloidal dye is responsible for the change in color. The colloidal dye particles are first adsorbed individually. In adsorbed condition, the formation of larger aggregates is facilitated.

The formation of so-called lyospheres may be considered a special case of adsorption.

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[1] *Zeit. Elektrochem.*, **20**, 521 (1914).

[2] *J. Russ. Phys. Chem. Soc.*, **48**, 837 (1916).

[3] *J. Am. Chem. Soc.*, **40**, 1361 (1918).

[4] *Ibid.*, **28**, 939 (1924).

[5] *Ibid.*, **34**, 2171 (1932).

[6] *Zeit. physikal. Chem.*, **142**, 401 (1929).

HETEROGENEOUS CATALYSIS

Undoubtedly, the most interesting and industrially most important adsorption reaction is heterogeneous catalysis. I. Langmuir's[1] discussion of the catalytic formation of carbon dioxide and water on platinum may well be considered a turning point in our entire concept of this phenomenon. He assumes that every oxygen molecule striking a clean platinum surface will tie up with a single platinum atom. This bond is so strong that no appreciable evaporation takes place even at high temperatures.

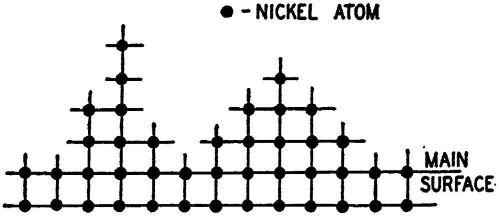

FIG. 70.—Surface configuration of a catalyst (schematic).

The oxygen atoms so bonded are extremely reactive toward carbon monoxide. Every monoxide molecule that collides with an oxygen atom reacts therewith. The oxygen atom, its valencies now fully saturated, is easily removed from the surface (because of the resulting loosening of the oxygen-platinum bond), leaving a vacant space. This space can now again be filled by either an oxygen or a carbon monoxide molecule. If a carbon monoxide molecule collides with the clean platinum, it is the carbon atom that will tie up with the platinum. The oriented adsorbed film so formed is inactive to a colliding oxygen atom, because it is the oxygen atom of the carbon monoxide that is directed to the outside. The carbon monoxide film is not held so firmly as the previously discussed oxygen film, and appreciable evaporation takes place at a fairly low temperature. This explains the advantages of working at elevated temperatures, because a carbon monoxide film if once formed acts as a "poison" for further catalytic reactions. Similar deductions can be drawn in the case of hydrogen instead of carbon monoxide.

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[1] *Trans. Faraday Soc.*, 17, 621 (1921); see also *ibid.*, p. 609.

H. S. Taylor,[1] working mainly with nickel as a catalyst, discusses the discrepancy that exists between the amount of a "catalyst poison" in a given system and the corresponding reduction in adsorptive capacity at the surface of the catalyst. To overcome this serious drawback in the "active-center theory," he conceived for the surface of the catalyst a configuration schematically shown in Fig. 70. He postulates that the "poison" is preferentially adsorbed on the protruding points of the catalyst, thereby rendering its surface less active. This concept also offers a simple explanation for the experimentally often proved fact that rough surfaces are better adapted for catalytic reactions than smooth ones. Furthermore, Taylor's idea of active peaks offers a simple explanation for more complicated catalytic processes, *e.g.*, the hydrogenation of oils. The highly unsaturated nickel atoms can simultaneously adsorb hydrogen and unsaturated oil, chemical combination due to close vicinity of the adsorbed atoms being the second step. If the bond between the nickel atom and the adsorbed atom is sufficiently strong, the nickel can even be torn out from the surface. Such an assumption would explain, according to E. F. Armstrong and T. P. Hilditch,[2] the frequently determined presence of minute quantities of nickel in the reaction product and especially the frequently observed pitmarks or roughness of originally smooth surfaces of catalysts.

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[2] *Chem. Ind.*, **44**, 701 (1925).

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CHAPTER XI

PROTECTION AND SENSITIZATION OF COLLOIDAL SYSTEMS

STABILITY OF COLLOIDS

When the difference between lyophobic and lyophilic colloids was being discussed, it was pointed out that the former are extremely sensitive to the influence of electrolytes. Owing to the lack of an easily hydratable surface, they cannot, after having once been desiccated, be brought back into their original degree of dispersion without drastic physical or chemical means. In contrast thereto, desiccated lyophilic colloids can be redispersed without difficulty.

It has been found that upon adding an appropriate quantity of a lyophilic colloid to a lyophobic one, the latter is not only noticeably stabilized against influence of electrolytes but can now easily be redispersed, even after it has been more or less completely dried out. Colloids that exert such a protective action on other colloids have been termed, after a suggestion made by A. Lottermoser,[1] *protective colloids.*

PROTECTIVE COLLOIDS[2]

Mechanism of Protection.—According to R. Zsigmondy[3] and E. Joël, *protective colloids are colloids that by themselves are highly stable toward the influence of electrolytes (lyocratic sols) and capable of imparting this property to electrocratic sols if added thereto.* Zsigmondy supposed two possibilities of protection to exist. The lyophilic particles may be adsorbed on the surface of the lyophobic particle to be protected, thus forming a more or less thick layer (Fig. 71*a*). This layer furnishes the protected particle with the specific properties of the protective colloid. The electrocratic

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[1] *J. prakt. Chem.*, **56**, 272 (1897); *Zeit. physikal. Chem.*, **62**, 284 (1908).

[2] See the contributions by A. GUTBIER in *Koll. Zeit.*, vols. **18**, **19**, **20**, **25**, **28**, **29**, **30**, **31**, **32**, **33**, and **34**.

[3] *Zeit. physikal. Chem.*, **113**, 299 (1924).

particles are no longer sensitive to the influence of small quantities of electrolytes; they can be reversibly desiccated and will even migrate in an electric field at a rate typical for the migration of the respective protective colloid used. This has been demonstrated by H. Freundlich and H. A. Abramson,[1] in determining the rate of migration of quartz particles coated with varying amounts of gelatin. When the particles of the protective colloid are large compared to the colloid to be protected, then Zsigmondy assumes that the lyophobic particles are adsorbed by the lyophilic ones. In this case (Fig. 71*b*), the electrocratic particles also would be immobilized and acquire the properties of the protective agent. This possibility has been demonstrated by the addition of gelatin to a concentrated gold sol. The sol was materially increased in stability but showed a very noticeable change in color from red to blue. This color change indicates an increase in effective particle size as a result of the agglomeration of the particles adsorbed on the surface of the gelatin particles acting as a protective colloid.

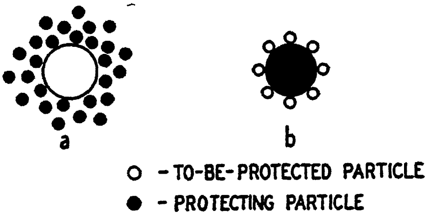

FIG. 71.—Colloidal protection.

There are numerous experimental proofs for the theory advocating a protective coating. J. Loeb[2] and Limburg[3] could prove that hydrophobic collodion or paraffin particles, if coated with gelatin, react as if they were gelatin particles. W. Reinders and W. M. Bendien[4] demonstrated that a gold sol sufficiently protected with a protein can exhibit positive or negative signs of

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[1] *Zeit. physical. Chem.*, **133**, 51 (1928). H. A. Abramson, *J. Am. Chem. Soc.*, **50**, 390 (1928). G. Lindau and F. Rhodius, *Zeit. physikal. Chem.*, *A* **172**, 321 (1935). C. Bondy and H. Freundlich, *Compt. rend. du Laboratoire Carlsberg*, **22**, 89 (1937).

[2] *J. Gen. Physiol.*, **5**, 395, 479, 505 (1923).

[3] *Rec. Trav. Chim. Pays-Bas*, **45**, 875 (1926).

[4] *Ibid.*, **47**, 977 (1928).

charge, depending on the pH values of the solution. Besides the formation of a protective coating, the possibility exists that the molecules of the protective colloid are oriented in the interface. In such cases, protection is generally increased.

Since the days when A. Lottermoser and E. v. Meyer[1] showed that silver sols can be protected against coagulation by the addition of a protein, similar effects have been observed with many other protective colloids, especially organic hydrophilic colloids. For example, the lysalbinic and protalbinic acids and their alkali salts, first described by C. Paal,[2] are outstanding in their protective action. Both are decomposition products of proteins. As inorganic protective colloids, the sols of stannic and silicic acid and thorium hydroxide should be mentioned. The stannic acid sol offers good protection for metal sols; the silicic acid sol has been applied by A. Fodor and A. Reifenberg[3] in the protection of Fe_2O_3 and Cr_2O_3. C. Frondel and E. A. Hauser[4] have demonstrated that colloidal silica is an excellent protective colloid for colloidal gold. Surface active substances, such as soaps and saponin, have proved to be satisfactory protective colloids in only a few cases, *e.g.*, with sulphur and Prussian blue. Several protective colloids such as tannin or Paal's acids can simultaneously also act as reducing agents in the case of noble metals, *e.g.*, the production of gold sols in the presence of tannin.

Up to now we have discussed only the protective action that typically hydrophilic colloids exert on hydrophobic systems. In most investigated cases, inorganic matter has been protected by organic matter. However, there are also cases in which organic substances, possessing a small amount of hydrophilic organic protective colloid, have been materially improved in regard to their stability by the addition of an appropriate amount of a highly efficient organic hydrophilic colloid. A typical example of such a procedure is the fundamental idea of the so-called "Revertex" process[5] for rubber latex concentration by evaporation. Rubber latex as such is a dispersion of the hydrophobic

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[1] *J. prakt. Chem.*, **56** (2), 242 (1897).

[2] *Ber.*, **35**, 2195 (1902).

[3] *Koll. Zeit.*, **42**, 18 (1927); **45**, 22 (1928).

[4] *Econ. Geol.*, **33**, 1 (1938).

[5] See, *e.g.*, E. A. HAUSER, "Latex," p. 114, Reinhold Publishing Corporation, New York, 1930.

rubber hydrocarbon in a watery medium. The proteins present in this medium are adsorbed on the individual rubber particles, thus giving the system the stability that it needs to carry out its functions in the plant. However, the protection is insufficient to stabilize the latex, if brought outside the plant, against the influence of coagulating electrolytes or of evaporation. If a suitable protective colloid is added to such latex, it can be reversibly evaporated down to the consistency of a thick paste or even to a dry powder.

THE GOLD AND RUBY FIGURES

For the purpose of obtaining some comparable figures in regard to the protective efficiency of different substances, R. Zsigmondy devised the so-called "gold figure." This can be defined as *that concentration of a protective colloid, expressed in milligrams per* 10 *cc. of the solution, sufficient to prevent a change in color of a bright-red gold sol to violet upon the addition of* 1 *cc. of a* 10 *per cent sodium chloride solution.* The difficulty in standardizing gold sols has resulted in substituting, at Wo. Ostwald's[1] suggestion, a Congo ruby sol for the gold sol and determining the "ruby figure," which is *that amount of protective colloid calculated on* 100 *grams of Congo ruby sol of a final concentration of* 0.01 *per cent which will just permit the observation of the color change* 10 *minutes after* 160 *millimoles of KCl have been added.*

Gold figure as well as ruby figure may not be considered as very exact from the point of view of a general classification of protective efficiency of different colloids. A number of cases are known where colloids with extremely low gold and ruby figures have completely failed in their protective efficiency on other colloidal dispersions. This is not astonishing if one realizes that the natural stability of colloidal dispersions depends on a great number of factors, *e.g.*, the entire prehistory of production, charge, size and shape of the particles, concentration, and type of ions in the dispersion medium. Here the old Roman proverb "*Quot licet iovi, non licet bovi*" can be applied. What protects a gold sol need not be effective for another type of colloidal system.[2]

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[1] *Koll. Beih.*, **10**, 179 (1919); **11**, 74 (1919); **12**, 92 (1920).

[2] See H. M. CASSEL, *J. Phys. Chem.*, **42**, 955 (1938).

Sensitization

In the case of many sols, it has been found that their stability under the influence of electrolytes is decreased even below their natural stability if protective colloids have been added in amounts lower than called for by the gold or ruby figure.

No final and completely satisfactory explanation of this phenomenon, known as "sensitization" (sensibilization), can yet be offered. So far, the assumption postulated by N. Peskoff[1] and elaborated by H. Freundlich and collaborators[2] seemed the most probable. Particles of lyophilic sols like those of lyophobic sols can unite with particles of another sol if they carry opposite charges. If we assume the case where a positively charged hydrophobic sol should be protected by a negatively charged hydrophilic sol, we shall form secondary particles. These consist of two different types of primary particles and because of partial neutralization of charge must be less stable than the individual systems were. A small amount of lyophilic particles can thus cause destabilization, and only with increasing quantities will the stabilizing effect of the lyophilic sol become predominant. However J. T. G. Overbeck[3] has recently pointed out that sensitization and protection are not dependent on the charges of the two colloids (a negatively charged protective colloid can be adsorbed on a

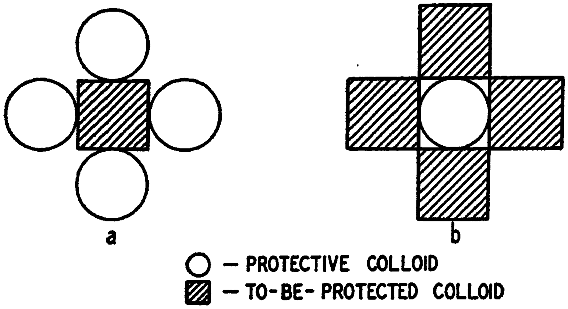

Fig. 72.—Colloidal protection and sensitization (schematic).

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[1] *J. Russ. Chem. Ges.*, **49**, 1 (1916).

[2] H. Freundlich and G. Lindau, *Biochem. Zeit.*, **208**, 91 (1929); **219**, 385 (1930). H. Freundlich and A. Brossa, *Zeit. physikal. Chem.*, **89**, 306 (1915). H. Freundlich and E. Loening, *Koll. Beih.*, **16**, 1 (1922).

[3] Symposium on hydrophobic colloids, Utrecht, 1937, p. 121; *Chem. Wbl.*, **35**, 117 (1938).

negative electrocratic particle) but that primarily the concentration of protecting colloids and those to be protected decides between protection and sensitization.

With extremely low concentrations of lyophilic colloid, the electrocratic particles coat the former, so that it is in no position to exercise its protective action upon the influence of electrolytes from the outside. Once the hydrophobic particles are discharged, they will readily unite with other particles coming in contact with them (Fig. 72).

CHAPTER XII

DISPERSION (PEPTIZATION)

Terminology and Definition.—Wo. Ostwald[1] has enumerated as the three most characteristic properties of dispersion or peptization the *solution intensity*, *solution capacity*, and *solution dispersivity*. It therefore seems appropriate to define and discuss these properties separately. *Solution intensity* is synonymous with the stability of the sol obtained by peptization and its resistance to coagulating influences. In Chap. VII, it was pointed out that one must differentiate between spontaneous colloidal dissolution of highly lyophilic colloids and the peptization of lyophobic coagula. The first phenomenon is primarily the result of a very pronounced solvation of the particles, whereby constitutive relationship between solvent and substance to be dissolved also must be taken into consideration. Since the hydration (solvation in a watery medium) of particles depends, as shown in Chap. IX, on the type and arrangement of the ions present in the double layer, the electric charges and therefore electrical processes may also not be neglected. For instance, in the case of the peptization of distinctly lyophobic coagula, the electrical effects are mainly to be considered. The individual particles are already preformed in the coagulum; they adsorb the added peptizing agent, causing the formation of an electrical double layer. As soon as such a double layer has been established, the particles repel each other. Since repulsion will be the greater the more strongly the particles are charged and the thicker the diffuse double layer is, one is led to the conclusion that those compounds which have strong charging properties will be the most effective dispersing or peptizing agents. Compounds that easily form soluble and dissociable reaction products with the particle or result in oriented adsorption are especially suited. Solvation is also of importance, since the adsorbed ions or complexes, which sometimes are formed by the peptizing agent and surface dissociated ions of the particle, will bind a certain amount of water.

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[1] *Koll. Zeit.*, **43**, 249 (1927).

Ionic adsorption of appropriate substances on suspended particles aids in increasing their electric charge, thus resulting in improved dispersion of the material.[1]

The term *solution capacity* refers to the maximum concentration obtainable in the resulting system. The term, therefore, is synonymous with solubility in its usual sense. As simple as the determination of solubility is in the case of perfect solutions, so complicated does the determination of solution capacity become in the case of colloidal systems. The reason for this is that systems containing a colloidal constituent are in the majority of cases polydisperse systems. A correct answer for solution capacity, then, can be given only by determining the complete particle-size distribution curve[2] for the entire system.

This is admittedly a tedious undertaking, and therefore one is generally satisfied in isolating a fraction characterized by a certain maximum particle size. This can be accomplished by simple sedimentation, centrifuging, or filtration. The "dissolved quantity" in a definite volume of the sol is then determined and generally called *peptized quantity*. There are a number of factors affecting the amount of peptized matter, *e.g.*, type and concentration of the peptizing agent; amount of the substance to be peptized; its structure; temperature; time; and the method applied in performing peptization. The results are generally given in the form of simple peptization curves (functional relationship between peptized quantity and the governing variable) or, as suggested by A. Dumanski,[3] in the form of triangular diagrams.

CONCENTRATION OF PEPTIZING AGENT[4]

As a logical consequence of the foregoing discussion, we can also infer that in the case of peptization by adsorption of electrolytes, there must exist a similar relationship in regard to the

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[1] See, *e.g.*, J. WAGNER, M. Sc. thesis, Chemical Engineering Department, Massachusetts Institute of Technology, 1938.

[2] For a detailed description of methods, see, *e.g.*, the contribution by Sven Odén in J. ALEXANDER, "Colloid Chemistry (Theoretical and Applied)," vol. I., pp. 861–909, Reinhold Publishing Corporation, New York, 1926; *Koll. Zeit.*, **18**, 33 (1916).

[3] *Koll. Beih.*, **31**, 418 (1930); *Koll. Zeit.*, **60**, 39 (1932).

[4] A. v. BUZÁGH, "Colloid Systems," p. 251, The Technical Press, Ltd., London, 1937.

concentration of electrolyte, as has already been discussed in the case of the ζ potential. Peptization reaches a maximum at a given concentration of electrolyte which depends on the amount of gel available. On both sides of the maximum, the possibility of sol formation decreases. In contrast thereto, we find in the case of peptization by dissolution that the amount of peptized matter increases with increasing concentration of peptizing agent, assuming that a constant amount of gel is present. The reason for this is the fact that more and more gel particles will go into solution.

The optimum of peptizability corresponds to a given adsorbed amount of the peptizing agent. In most chemical reactions where gels are formed, we deal with systems containing an excess of electrolyte. If such a system is placed in water, no noticeable changes take place, because the adsorbed electrolyte retains its influence on the gel particles. However, if such a gel is submitted to repeated washings, the coagulating electrolyte will be gradually removed, and the gel will show signs of peptization as soon as it has reached a certain degree of purity. (Such is the case when sulphides, for example, are washed excessively on a filter.) In a further purification of the gel, peptization will cease as soon as the ζ potential of the system has again dropped below its critical value.

The relationship between peptization, ζ potential, and electrolyte concentration, or, in other words, the correct relationship between repulsive and attractive forces of colloidal systems and their stability (see also page 219*ff*), can be demonstrated by the following experiment: A sol stabilized by the addition of electrolyte just beyond its critical potential is submitted to rapid ultrafiltration.[1] If the filter residue is taken up with electrolyte free water, an unstable suspension results. However, if the residue is redispersed in its filtrate, original stability will be restored immediately.[2]

THE INFLUENCE OF THE DISPERSED PART

In highly disperse systems, solubility is independent of the quantity of both components, *i.e.*, of the quantity of the bulk

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[1] For a recent discussion of ultrafiltration see, *e.g.*, M. AMAT and J. DUCLAUX, *J. chim. phys.*, **35**, 147 (1938).

[2] These experimental results substantiate a theoretical deduction by C. Hamaker, communicated to the author.

phases. This fundamental fact is generally known as the *law of Gay-Lussac.* In the case of colloidal dispersions, such an independence of "dissolved" amount of the disperse part does not exist. In quantitatively studying colloidal dispersion processes, Wo. Ostwald[1] and A. v. Buzágh[2] established a new rule known as the *disperse-part rule* (*Bodenkoerperregel*), which postulates the direct opposite of Gay-Lussac's law. *Colloidal peptizability* (*solubility*) *is not independent of the quantity of the disperse part originally present; we find either that it increases continuously with increasing amounts of disperse part present or that it exhibits a maximum at medium amounts of dispersed matter.* The rule of Gay-Lussac can hold only for systems whose "active mass" can be considered as constant. This is not the case of colloidal aggregates, as has been previously discussed. Furthermore, we must bear in mind that colloidal peptization can be influenced by several factors. They may be of kinetic nature or connected with interfacial phenomena, adsorption, spacial arrangements, etc., all of which can be fully neglected in the case of truly molecular solutions.

If, according to Wo. Ostwald and A. v. Buzágh, varying quantities m of an insoluble substance are dispersed in an equal amount of a liquid that is inert toward the powder, and one determines after a given time t the amount of nonsedimented matter in a given column of liquid x_t, different $x_t - m$ curves will be obtained, depending on how the distribution of particle sizes varies with the total quantity of suspended matter. If the distribution of particle sizes were independent of the total suspended amount, the function $x = f(m)$ would be represented by a straight line. Such a case can be realized only in extreme dilutions and systems where no forces act between the particles and where no particle interference occurs during sedimentation. In instances where attracting forces act between the sedimenting particles, a coagulating effect results which, according to a suggestion by G. Wiegner,[3] has been termed *orthokinetic coagula-*

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[1] *Koll. Zeit.*, **41**, 169 (1927); **43**, 225, 227 (1927); **50**, 65 (1930). See also v. Buzágh, *op. cit.*, pp. 251*ff.*

[2] *Koll. Zeit.*, **41**, 165 (1927); **43**, 215, 220 (1927); **48**, 33 (1929). See also K. C. Sen and N. R. Dhar, *ibid.*, **33**, 193 (1923); **43**, 17 (1927). J. Traube, **47**, 45 (1929).

[3] See P. Tuorila, *Koll. Beih.*, **24**, 1, 27 (1927). H. Gessner, "Die Schlemmanalyse," Akad. Verlags-Ges., Leipzig, 1931.

tion (see page 54). This will become the more pronounced the more concentrated the suspension. In such a case, the non-sedimented quantity can be expressed by the equation

$$x_t = m - m_s$$

where m_s represents the quantity settled out in time t. m_s can be any function of the total suspended matter. This is no longer a linear function. The amount of sediment, owing to a continuous decrease in degree of dispersion, increases with the suspended quantity. The function $x_t = m - m_s$ must pass through a maximum. The most concentrated suspension is obtained with a medium amount of disperse part. This is schematically shown in Fig. 73, taken from A. v. Buzágh. Moreover, it must be kept in mind that the amount that settles out in the time t depends not only on the added quantity but also on the original degree of dispersion, because larger particles will settle more rapidly and because the attractive forces between particles also increase with size. In the case where particles are dispersed in an electrolyte solution, the phenomenon becomes even more involved, since in this case one may assume that their ζ potential, as well as the forces acting between them, may undergo various changes. In this respect, the quantity of adsorbed electrolyte is of importance.

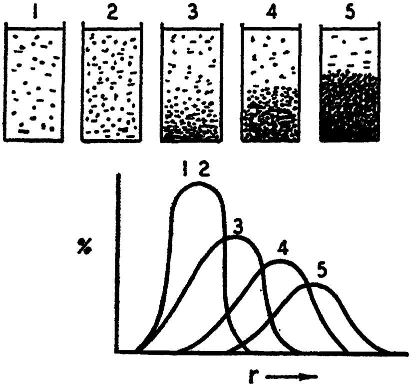

FIG. 73.—Sedimentation of suspensions and change in degree of dispersion for various concentrations of suspended matter. r, particle size.

PEPTIZATION BY ELECTROLYTE ADSORPTION

According to Kroeker's relationship (see Appendix, page 239), the quantity of electrolyte adsorbed per unit quantity of the suspended matter decreases when the added amount is increased. With small quantities of dispersed matter present, the peptizing agent (electrolyte) will be too strongly adsorbed, causing flocculation (neutralization of charge). With too large a quantity of suspended matter, the amount of peptizing agent that can be adsorbed on one particle is insufficient to charge the particles up to the critical potential. Consequently, the maximum of peptization must correspond to a maximum of charge per particle.[1] This deduction is schematically shown in Fig. 74, taken from Wo. Ostwald's cited publication. m is the amount of dispersed matter present; x, the adsorbed amount. x/m therefore represents the *specific adsorption*, *i.e.*, the amount adsorbed per unit weight of adsorbent. To obtain peptization, the value of x/m must lie between the mean values (x/m) and $(x/m)_2$ which correspond to a medium amount of disperse part.

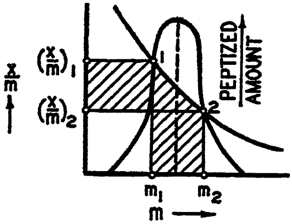

FIG. 74.—Specific adsorption and peptization in relation to the quantity of dispersed matter.

SOLUTION DISPERSIVITY

The distribution curve of the particle sizes of the dispersed constituent is the main criterion for the solution dispersivity. Since most natural colloidal dispersions are of a polydisperse nature, a clear definition of the solution dispersivity of such a system calls for a complete particle-size-distribution analysis. But even when dealing with originally monodisperse systems, changes due to aggregation of particles in time may not be overlooked. The solution dispersivity can also change when dealing with temperature- or concentration-variable systems, *e.g.*, soap solutions.

Rate of Peptization.—The rate of peptization is generally measurable. According to Wo. Ostwald and H. Schmidt[2] and

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[1] See WO. OSTWALD, *Koll. Zeit.*, **43**, 249 (1927); **49**, 188 (1929). A. v. BUZÁGH, *ibid.*, **46**, 178 (1928); **49**, 185 (1929). E. HEYMANN, *ibid.*, **48**, 195 (1929).

[2] *Ibid.*, **43**, 276 (1927).

A. von Buzágh,[1] the peptization velocity curve of lyophilic systems is generally S shaped. The peptization of lyophilic coagula can be expressed by the equation for monomolecular reactions, as can also that of most lyophobic gels. The peptization of lyophobic, nonswelling coagula, if carried out under vigorous mechanical agitation in the neighborhood of the critical ζ potential, follows a maximum curve (Fig. 75). The decrease is the result of mechanical coagulation.

The influence of temperature on peptization is not yet sufficiently explained to warrant any final conclusions.

SWELLING

When a solid substance absorbs liquid with which it is brought in contact and thus increases its own volume, we call this phenomenon *swelling*. In such an instance, if the liquid penetrates into the interstices between the particles of the aggregated structure and pushes them apart, we can speak of a dispersion process, since the degree of dispersion of the solid constituent is increased. However, if the liquid penetrates into the interior of the ultimate structural units and causes these units to swell themselves, they increase in size, and we therefore decrease the actual degree of dispersion.

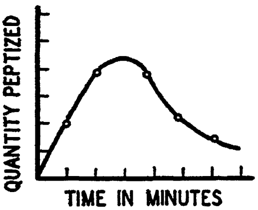

Fig. 75.—Mechanical coagulation.

Limited and Unlimited Swelling.—We can distinguish, too, between limited and unlimited swelling. In the first, the amount of liquid absorbed reaches a maximum; the product obtained is known as a *lyogel*. In the second, that of unlimited swelling, the amount of liquid does not reach a maximum, but the substance continues to swell after once having reached the state of a lyogel, the distance between its structural units increasing until they finally break apart and are dispersed. As examples of limited swelling, one may take gelatin or agar in pure water at temperatures below 30°C. or crude, unmilled or soft vulcanized rubber in organic solvents. Unlimited swelling phenomena can be represented by gelatin or agar in water above 30°C. or gum arabic or soluble starches at any temperature or crude but well-

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[1] *Koll. Zeit.*, **44**, 156 (1928).

milled rubber in organic solvents.[1] Naturally there will be transition cases between these two types of swelling, since in the final analysis they are not fundamentally different from each other.

MONO- AND MULTIPHASE SYSTEMS

May one consider the swelling of a gel as a solid solution? Or is it the result of the adsorption of the liquid on the solid substance? The question can also be put as follows: In physicochemical terms, may one consider the swollen matter as a monophase system, or should it be classified as a multiphase one? In trying to answer this question, it must be borne in mind that systems of any degree of dispersion or difformation can absorb liquid and thus increase their volumes. Such systems if stable show a more or less uniform mixture of the liquid and of the solid constituent. Whether we obtain a paste, a lyogel, a true gel, or what is known as a hydrate will depend on how the liquid has been distributed in the solid. In the case of highly disperse systems, a solid solution may be produced as one extreme; and if we are dealing with coarse dispersed matter at the other extreme, a paste will be the result. In between these two limiting cases, a great number of further possibilities can be imagined, so that here, again, the colloidal range of dimensions, being intermediate between the foregoing limits, is bound to demonstrate the great difference in properties that have become so characteristic to matter in this condition.

In the case of solid solutions or hydrates, we must assume such a uniform intermixture of components, so that their distribution corresponds to those of discrete or molecular discontinuities. Hence such systems may well be termed "single-phase systems." With coarse dispersions we would have to speak of "multiphase systems." We are now in the same quandary as when we tried to find a more general point of view for the systematics of the colloidal range. Again, we must look for one outstanding factor common to all swelling phenomena. This factor is the liquid entering into the solid substance. It attaches itself in one way or another to the solid without disrupting, at least at the start, the cohesion that exists between the individual particles of the solid. In highly disperse systems, the swelling liquid will be

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[1] E. BRODA, *Nature*, **142**, 116 (1938).

attached to the most discrete building elements by chemical valencies or solvation, resulting in the formation of typical hydrates. Nevertheless, the liquid may also enter into the preexisting interstices and hollows by capillary action. That such is the case has been clearly demonstrated by J. Traube and P. Klein[1] and by J. E. Lynn,[2] who showed that the dissolution of crystals is not a continuous process but that the crystal is first broken down into submicrons. This means that the solvent will take the path of least resistance by first entering the intermicronic channels and only afterward penetrating into the intermolecular or interionic insterstices. In the case of pastes, consisting of coarse powders, which do not swell by themselves, we are dealing with pure adsorption of the liquid penetrating into the powder heap by capillary action. With felt, sponges, and the like the apparent increase in volume is mainly due to the adsorption of the liquid on the solid matter and the formation of lyospheres, whereas the penetration into the actual interstices of the fiber is of secondary importance only.

XEROGEL
a

LYOGEL
b

Fig. 76.—Gels.

Xerogel; Lyogel

We have called attention to the fact that the basic difference between a sol and a gel is that the former has its colloidal micelles sterically and dynamically separated from each other, whereas in the gel state they are held in position by an equilibrium between attractive and repulsive forces or by actual contact and formation of a rigid skeleton. Differentiation can now be made between so-called *xerogels*, where the micelles are in direct contact with each other or connected by some cementing substance (Fig. 76*a*), and *lyogels*, where they are sterically but not dynamically separated by layers of liquid (Fig. 76*b*). If the liquid is *ab*sorbed in such a way that it is actually only *ad*sorbed on the surface of the

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[1] *Koll. Zeit.*, **29**, 236 (1921).

[2] B.S. thesis, Massachusetts Institute of Technology, 1937, unpublished.

micelles, thereby forming lyospheres, the micelles will retain both structure and arrangement.

INTER- AND INTRAMICELLAR SWELLING

According to J. R. Katz,[1] this type of swelling has been termed *intermicellar swelling*. In such cases, the x-ray diagram (but only if the micelles are crystallites) will show no change in the position and intensity of the interference spots or lines. When liquid enters into the interior of the micelles, it is called *intramicellar swelling*. The x-ray diagram fades out. In certain instances, both types of swelling phenomena take place simultaneously, *e.g.*, in bentonite gels, where an oriented intramicellar swelling of the single clay particle and an intermicellar swelling of the clay micelles must be considered.

SWELLING PRESSURE

When a substance swells, it exerts a certain amount of pressure on its surroundings. This is known as the *swelling pressure*. The concept that the formation of lyospheres is responsible for such pressure has often been disputed. However, since the total of the volume of the swelling substance plus that of the adsorbed liquid decreases in the swollen gel, and because of the connection between the contraction of the gel and the heat evolved during swelling, there seems to be sufficient proof for the formation of such lyospheres. The contraction in volume might be explained by a rearrangement of the micelles as well as by a condensation of the liquid in the adsorption layers.

v. Buzágh[2] expresses the opinion that the mechanical tension of the lyospheres is opposed by the elastic attracting force between the particles and the surface tension of the liquid. At a certain degree of swelling, an equilibrium is reached. A similar view was expressed by C. v. Terzaghi,[3] who assumes that the force responsible for swelling is an elastic force between the micelles preventing their approach. The surface tension of the liquid tends to lower its vapor pressure by decreasing the surface area in the interstices, thereby opposing expansion. Terzaghi's

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[1] *Physikal. Zeit.*, **25**, 321, 659 (1924).

[2] "Colloid Systems," p. 264.

[3] *Coll. Symp. Monogr.*, **4**, 58 (1926).

view takes into consideration the ratio of volume of liquid to volume of gel structure.

However, it seems insufficient to consider only purely mechanical factors to be of importance; electrical charges of the micelles, solvation, and possibly osmosis[1] (Donnan equilibrium, see page 110) are factors that may not be overlooked. Wo. Pauli[2] and also A. Küntzel[3] demonstrated that electric charges can play an important role. The swelling increases with increasing charge and exhibits a minimum at the isoelectric point.

Frequently an attempt has also been made to correlate swelling with osmotic pressure. Although it cannot be denied that osmosis plays some part in certain swelling phenomena, it is hardly justifiable to consider this possibility of primary significance. At present, we must admit that all available information indicates that swelling phenomena are the result of various causes and that they are governed by different ones in different steps of the process. The complexity of the phenomenon as such and the fact that most of the colloid systems so far investigated are polydisperse and therefore complex in themselves have made the finding of a fundamental answer highly improbable from the very start. In recent years, more attention has been paid to studying various colloidal phenomena with well-defined and reproducible monodisperse fractions. On the basis of results so far available, the prediction seems justified that the fundamentals governing swelling phenomena will be forthcoming in the near future.

RECENT CONSIDERATIONS

Probably a new approach offers itself as an amendment to the purely theoretical deductions of H. Freundlich and J. Rubin[4] and especially C. Hamaker,[5] based on the work of F. London[6] and

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[1] Wo. Ostwald and K. Mündler, *Koll. Zeit.*, **24**, 7 (1919). E. L. Lederer, *ibid.*, **55**, 41 (1931).

[2] "Elektrochemie der Kolloide," Julius Springer, Vienna, 1919.

[3] *Biochem. Zeit.*, **209**, 326 (1929).

[4] "Thixotropy," No. 267 of "Actualités Scientifiques et Industrielles," p. 13, Hermann & Cie, Paris, 1935.

[5] *Rec. trav. chim. Pays-Bas*, **55**, 1015 (1936); **56**, 3, 727 (1937); **57**, 61 (1938); *Physica*, **4**, 1058 (1937).

[6] *Zeit. physikal. Chem., Abt. B*, **2**, 207 (1929).

H. Kallmann and of H. Kallmann and M. Willstaetter.[1] (For further details, see discussion on page 198.) If it is assumed that repulsion of particles can be brought about either by increasing the charge on their surface, *i.e.*, by the formation of an electric double layer, or by increasing solvation and thereby increasing the active thickness of the so-called lyosphere, and, assuming attraction to remain constant for a given system, depending on cohesive forces proportional to the mass of the particle, it seems possible to offer a simple explanation without having to resort to complicated structural assumptions. With the latter we are referring to the web- or honeycomblike structures or to the assumption of network formed by an interlinking of long chainlike molecule- or filamentlike aggregations of colloidal micelles (see also page 214). The only assumption that has to be made is that the particles present in gel form retain the ability to solvatize or to form electric double layers upon being brought in contact with the swelling liquid.

As soon as the repulsive forces make themselves evident, they will tend to push the particles apart. The result must be a swelling of the mass and exertion of pressure on the surrounding walls of the container. Since increase of charge as well as solvation depends on a variety of factors attributable to the characteristics of the solid constituent and also of the swelling liquid, it appears logical that differences in type of swelling can occur. In gelatin, for instance, we have stated that up to a temperature of 30°C. there is limited swelling; and at higher temperatures, unlimited swelling. In both cases, the amount of water is the same. It may be safely assumed that the degree of solvation is the same but that the kinetic energy of the particles at low temperature is insufficient to take them out of the sphere of influence of the attraction forces. This is also in complete accord with the fact that hydration generally decreases with increasing temperature. In the case of unmilled rubber, solvation alone cannot overcome the undestroyed molecular attraction of the long main-valency chain molecules; whereas in milled rubber, the size and configuration of the molecule is no longer capable of exercising a compensating attraction force. Another example is the colloidal clay bentonite, which swells upon the addition of water as a result of intramicellar expansion; and the formation of

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[1] *Naturw.*, **20**, 952 (1932).

double layers as a result of surface dissociation. As long as the built-up repulsive forces and the concentration of such a system are so matched that the distance between two particles still falls in the range where attractive forces can exert their influence, we shall retain a gel. However, if concentration is decreased by dilution, the particles will be forced out of the zones of mutual attraction, and a sol will result.

CHAPTER XIII

COAGULATION AND DISSOLUTION

THE DESTRUCTION OF COLLOIDAL SYSTEMS

The colloidal range has been defined as being intermediate between the coarse and the analytical state of dispersed matter. Just as it is possible to produce colloidal systems either by comminuting (dispersing) coarse matter or by condensing highly disperse systems, so there must logically be two ways of destroying colloidal systems. We can either decrease the degree of dispersion, thus forming coarser suspensions or large coherent solid bodies, or we can increase the degree of dispersion and produce analytical or highly disperse systems. The former procedure is generally known as *coagulation*, whereas the latter is called *dissolution*.

Recrystallization is an example of a continuous decrease in the degree of dispersion of a system. It is an established fact that the solubility of crystals increases with decreasing particle size. If we deal, as is mostly the case, with polydisperse systems, then the smaller particles will dissolve and cause the larger ones to grow proportionally. Hence such a system can never be in true equilibrium, which makes a physicochemical interpretation mathematically impossible. Besides size, it seems that the shape of the particles is also of importance, according to J. J. P. Valeton,[1] so long as their size is of micro- or submicroscopic dimension. If substances, *e.g.*, protective colloids, are added to the dispersion, they are adsorbed on the particles and will materially retard dissolution or even possibly prevent it entirely and at the same time will retard the rate of orientation, *i.e.*, the growth of the larger crystals. This explains the importance of adding such substances when the purpose is to produce systems of given particle sizes that remain stable over a prolonged period of time.

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[1] *Physikal. Zeit.*, **21**, 606 (1920).

COAGULATION

A more common and important case is the discontinuous decrease of the degree of dispersion, which occurs when the single particles of a sol agglomerate to form secondary particles, coagula, and finally a coarsely disperse part. This phenomenon, generally known as coagulation, is presumably the best known colloidal one and therefore the most studied. In discussing the various possibilities of producing colloidal systems, it was demonstrated that this could be achieved by various energies. Does it not seem logical, therefore, to assume that different energies again can cause a destruction of colloidal systems? Bearing in mind that in most cases a combination or coordination of such possibilities needs to be considered, we can distinguish the following:

1. Coagulation by the addition of electrolytes.
2. Mechanical coagulation.
3. Electrical coagulation.
4. Thermal coagulation.
5. Coagulation by radiant energy.

In the chapter dealing with electrokinetic phenomena, we have discussed the importance of electrical influence in the case of lyophobic sols. This is demonstrated not only by the fact that positively charged sols are preferentially coagulated by anions, whereas in the case of negatively charged particles the cations are mostly responsible for coagulation, but also by what is known as the *Hardy-Schulze valency rule*. The coagulating power of the dominating ion increases with its valency roughly in the proportion of 1:100:1000, for mono-, di-, and trivalent ions.

The Influence of the Solvated Hull.[1]—Recently, the contributions by A. v. Buzágh[2] on the adhesiveness of microscopic particles on walls (for further discussion, see page 208) have materially contributed to a better understanding of the entire phenomenon. It has been demonstrated that all electrolytes which coagulate negatively charged sols also increase the adhesion. Before these

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[1] References to solvated hulls: E. HATSCHEK, *Koll. Zeit.*, **11**, 280, 284 (1912). R. FRICKE, *ibid.*, **35**, 264 (1924). A. KUHN, *ibid.*, **35**, 274 (1924). W. HALLER, *ibid.*, **56**, 257 (1931). N. S. SCHEINKER, *ibid.*, **72**, 192 (1935).

[2] *Ibid.*, **47**, 370 (1929); **51**, 105, 230 (1930); **52**, 46 (1930). *Koll. Beih.*, **32**, 114 (1930).

experiments, it had been frequently taken for granted that the stability of a hydrophobic (electrocratic) sol depends entirely on the electric charge of the particles, measurable by their ζ potential. Wo. Ostwald,[1] however, pointed out that coagulation by electrolytes finds no satisfactory explanation when considering only this. Several authors[2] have shown that certain suspensions can be coagulated even if the ζ potential rises. v. Buzágh demonstrated that the stability of disperse systems depends not only on the net electric charge but also on the thickness of the solvated hulls. If the electric charge of a lyophilic sol decreases without change in thickness of the solvated hull, a certain stability will be retained even at the isoelectric point (*isostable disperse systems*, according to Wo. Ostwald). A. March[3] has made it evident that for purely theoretical reasons the electrostatic repulsion of a typical lyophobic sol alone is insufficient to account for its stability. In the case of lyophilic colloids, H. R. Kruyt[4] has similarly demonstrated (see page 104) that dissolvation is an insufficient explanation for coagulation of such systems. More recently, Wo. Ostwald[5] has expressed the opinion that the coagulation of lyophobic sols is influenced by the properties of the dispersion medium and not only by the properties of the micelles. He introduced G. V. Lewis's concept of electrolyte activity for the explanation of coagulation of colloidal sols.

A colloidal sol can be considered a statistical mixed crystal. The ions of the electrolyte in the dispersion medium are held together by interionic forces and carry the disperse colloidal particles in the statistical lattice. If the concentration of electrolyte is increased, the interionic forces also increase. The ions holding more strongly together will push the dispersed particles closer together and finally eliminate them from the ionic lattice (coagulation).

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[1] *Koll. Zeit.*, **26**, 28, 69 (1919); **32**, 1 (1923); **40**, 201 (1926).

[2] See, *e.g.*, H. R. Kruyt and P. C. van der Willigen, *Zeit. physikal Chem.*, **130**, 170 (1927). P. Tuorila, *Koll. Beih.*, **27**, 44 (1928). H. Freundlich and H. P. Zeh, *Zeit. physikal. Chem.*, **114**, 65 (1925).

[3] *Koll. Zeit.*, **45**, 97 (1928).

[4] *Ibid.*, **31**, 338 (1922); *Koll. Beih.*, **28**, 1 (1928); **29**, 396 (1929); *Zeit. physikal. Chem.*, **100**, 250 (1932).

[5] *Koll. Zeit.*, **73**, 301 (1935); **75**, 39 (1936); **80**, 304; **81**, 48 (1937); **85**, 34, (1938). A summary of all contributions is given in *J. Phys. Chem.*, **42**, 981, (1938).

Whereas coagulation, if looked at from a purely chemical point of view, is a chemical reaction between the dispersed particle and the coagulating agent, resulting in a highly insoluble undissociated compound, the colloid chemist must also consider the influence of the opposite (*Gegen-*) ion of the electrolyte. For example, in the case of precipitation caused by sulphate ions, it has been shown that the cations are also of importance and that here, too, the lyotropic series (see page 132) should be considered.

Electrodecantation.—If lyophilic sols are coagulated under certain suitable conditions, a solid coagulum is not produced as is the case in rapid coagulation, but two distinct liquid phases, one of them very rich in the amount of colloidal matter, the other extremely poor, are formed. Similar phenomena are undoubtedly the cause for the so-called electrodecantation, described by Wo. Pauli and collaborators.[1] Upon very careful electrodialysis[2] of hydrophilic colloids, two distinct strata are present, one having a high concentration of the colloidal matter, the other an extremely low one. This method has been applied for the purpose of purifying or concentrating hydrophilic colloids.[3]

Coacervation.—The difference in the general aspect of this demixing[4] and the formation of an actual coagulum is so striking that H. G. Bungenberg de Jong and H. R. Kruyt[5] coined the special term of *coacervation*. They are of the opinion that coacervation is caused by a discharge of the particles without complete dehydration. They picture the colloidal particle in the sol condition as being hydrated as well as electrically charged.

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[1] *Naturw.*, **30**, 555 (1932). See also M. Blank and E. Valkó, *Biochem. Zeit.*, **195**, 220 (1928). M. Samec and Haerdtl, *Koll. Beih.*, **12**, 281 (1920). M. Adolf and W. Pauli, *Biochem. Zeit.*, **152**, 362 (1924). F. Modern and Wo. Pauli, *ibid.*, **156**, 484 (1925). A. Kuhn, "Wörterbuch der Kolloidchemie," T. Steinkopff, Dresden, 1932. E. J. W. Verwey and H. R. Kruyt, *Zeit. physikal. Chem.*, *A* **167**, 149 (1933). Moyer, *J. Biol. Chem.*, **121**, 331 (1937). A. Tiselius, *Biochem. J.*, **31**, 1464 (1937).

[2] A recent discussion of electrodialysis see, *e.g.*, H. de Bruyn and S. A. Troelstra, *Koll. Zeit.*, **84**, 192 (1938).

[3] See, *e.g.*, Wo. Pauli and P. Stamberger, Canadian Patent No. 370,858, Dec. 28, 1937.

[4] By demixing is meant segregation of a mix. (The author.)

[5] *Koll. Zeit.*, **50**, 39 (1930); Verhandelingen der koninklijke Akademie v. Wetenschappen te Amsterdam, **32**, 849 (1929). See also the summarizing review on this subject by Bungenberg de Jong, *Koll. Zeit.*, **80**, 221, 350 (1937).

During coacervation the particles are discharged but not fully dehydrated. This gives the particles the possibility of coming closer together, whereby a part of the solvated hulls may be lost. However, the remaining solvated hulls are still sufficient to retain the characteristics of a "liquid" phase.

Electrical Coagulation.—Similar effects can also be obtained by the interaction of hydrophilic colloids of opposite electric sign.[1] Such phenomena seem to be closely related to complex coacervation as described by H. G. Bungenberg de Jong (see footnote 5, page 170). Typical coacervation also occurs in certain base-exchange reactions. In submitting a sodium bentonite sol, for example, to careful electrodialysis, thereby producing hydrogen bentonite, we obtain coacervation as a result of the fact that the electric charge as well as the degree of hydration of the clay micelles is materially reduced. The hydrogen bentonite represents a liquid gel which is redispersible as long as it remains hydrated to a sufficient degree, *i.e.*, as long as the particles are kept apart by their residual hydration.[2]

In cases where no base exchange takes place, the process of dialysis or electrodialysis, or even simple washing of filtered precipitates, removes the electrolyte which acts as a stabilizer. The result is that the ζ potential of the particles is constantly decreased. If the critical value of the ζ potential is passed, then coagulation occurs. (In this connection, see the discussion of the most recent theories on the stability of colloidal systems and the formation of gels, pages 213*ff.*). If we are dealing with lyophobic colloids, a loose sediment forms; in the case of lyophilic sols, we obtain a gel, and only isostable colloids exhibit no readily discernible change.

In the electrophoresis of lyophobic sols, a coagulation in the interior of the sol can sometimes be seen, besides the discharge of the particles on the appropriate electrode. This is one of the few examples of pure electrical coagulation.

Mechanical Coagulation.—Frequently coagulation occurs when shaking or stirring a sol. This phenomenon is known as "mechanical coagulation." Offhand one might assume that the reason for this type of coagulation could be explained kinetically. The particles are simply driven together by the mechanical

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[1] See E. A. HAUSER and C. E. REED, *J. Phys. Chem.*, **41**, 911 (1937).

[2] E. A. HAUSER and D. S. LE BEAU, *ibid.*, **42**, 1031 (1938).

agitation, and the probability of their collision thus increased. H. Freundlich and S. K. Basu,[1] H. Kroch,[2] S. Loebmann,[3] and R. v. Recklinghausen[4] express the view that mechanical coagulation is the result of a surface effect, since an increased concentration of the disperse part always exists in an interface. It seems natural that coagulation will occur more easily in such a concentrated layer, especially if the ζ potential of the system is low. If a sol is mechanically agitated, the interface is constantly being renewed, thus causing more and more particles to coagulate. Such a concept can unquestionably account for various coagulation phenomena, particularly in cases where an oxidation or denaturation of colloids takes place in the interface. The coagulation of milk protein during buttering and the formation of a stable beer foam, due to surface coagulation of the proteins, are typical examples. However, other cases of mechanical coagulation are known where such surface effects fail to offer a satisfactory explanation and where a purely kinetic reasoning seems to give the best answer. For instance, we know that when producing dispersions of different substances in a ball mill, there is a maximum comminution obtainable for every given set of conditions, such as volume of charge, amount and size of pebbles, number of revolutions per minute. If milling is carried beyond this maximum, a reagglomeration of the previously comminuted particles occurs. The same phenomenon has been observed in the milling of carbon black into rubber. First we obtain increased dispersion throughout the mass, but afterward reagglomeration sets in.[5]

Thermal Coagulation.—A great number of sols are materially influenced in their stability by radical changes in temperature. Many lyophobic sols will coagulate when being frozen. On the other hand, certain lyophilic colloids coagulate upon being heated. In most cases, this is due to a chemical change in the micelles, *e.g.*, denaturation.

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[1] *Zeit. physikal. Chem.*, **115**, 203 (1925).

[2] *Ibid.*, **124**, 155 (1926).

[3] *Ibid.*, **139**, 368 (1928); *Koll. Beih.*, **28**, 391 (1929).

[4] *Zeit. physikal. Chem.*, Abt. *A*, **157**, 325 (1931).

[5] See, *e.g.*, E. A. GRENQUIST, *Kautschuk*, **6**, 230 (1930). Also E. A. HAUSER, "The Colloid Chemistry of the Rubber Industry," p. 38, Oxford University Press, London, 1928.

Coagulation by Radiant Energy.—A phenomenon still awaiting satisfactory explanation is that stability of colloidal systems can be materially influenced (decreased) by radiant energy, *e.g.*, by radioactive substances, x rays, and especially ultraviolet radiation. More recently it has been found that short wireless waves can be detrimental to the stability of colloidal systems.[1] In some cases, ultrasonic waves, which have been mentioned as possible means for making dispersions, have been found to exercise a coagulating effect.[2]

(A discussion of the rate of coagulation will be found in the Appendix, page 241.)

DISSOLUTION

As mentioned in the introduction to this chapter, colloidal systems can also be destroyed by dissolution, *i.e.*, by transforming the colloidal disperse system into a highly disperse system. In many cases (temperature-variable sols), *e.g.*, soaps, a mere increase in temperature results in complete dissolution. If a liquid in which the dispersed particles are soluble is added to the sol, the colloidal dispersion will be transformed into a truly molecular solution. This, for instance, is true when adding alcohol to a sulphur sol. If a substance that will react with the particles to form compounds of molecular solubility is added to a sol, as in treating a silver sol with nitric acid or a gold sol with aqua regia, we have again carried out a dissolution process. In the latter instance, naturally, the sol is first coagulated by rapidly changing its double layer, chemical reaction taking place as a secondary step.

INNER CHANGES

Besides these drastic changes there are also in colloidal systems changes that do not result in complete destruction of the colloidal system but only in a change of the degree of dispersion in the limits of the colloidal range. Generally these can be classified as limited cases of the ones just discussed. Among others to be counted under this heading are sedimentation or creaming, the

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[1] See, *e.g.*, E. WILKE and R. MUELLER, *Koll. Zeit.*, **65**, 257 (1933).

[2] Recent summaries on the application of ultrasonic waves in colloid systems have been given by H. FREUNDLICH, *Trans. Inst. Chem. Eng.*, (London) **15**, 223 (1937); and K. SOELLNER, *J. Phys. Chem.*, **42**, 1071 (1938).

aging of colloidal systems, sedimentation by centrifuging, changes in degree of dispersion by mechanical agitation, temperature, etc.[1]

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———: *Koll. Zeit.*, **31**, 338 (1922).
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R. Ellis: *Zeit. physikal. Chem.*, **78**, 321 (1912).
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———: *Koll. Zeit.*, **73**, 301 (1935).
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Coagulation by Particles of Reversed Charge

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H. Müller: *Koll. Zeit.*, **38**, 1 (1926).
G. Wiegner: *Koll. Zeit.*, **38**, 3 (1926).

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H. G. Bungenberg De Jong and W. A. L. Dekker: *Koll. Beih.*, **43**, 213 (1936).

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[1] For detailed references, see, *e.g.*, A. v. Buzágh, "Colloid Systems," pp. 286*ff.*, The Technical Press, Ltd., London, 1937.

——— and H. R. Kruyt: *Koll. Zeit.*, **50**, 38 (1930).
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CHAPTER XIV

THE INFLUENCE OF PARTICLE SHAPE—THE OPTICS OF COLLOIDAL SYSTEMS

In previous chapters, it was explained that in the case of colloidal disperse systems the shape of the particles is a factor of extreme importance. The shape, or stereometric form, is that variable which governs and controls the specific surface and simultaneously the boundary energies of the system. If we change the particle shape of a sol, we automatically change the conditions in regard to adsorption. Often this will entail a change in the electric double layer, and this, again, will noticeably influence the forces and their zone of action between the dispersed particles. We shall revert to a more detailed discussion of these phenomena in chapters treating the most important types of aggregates and the structure of gels. However, a number of properties exist which are not directly controlled by the boundary energies and which should be discussed at this point. The two most important of these are the mechanical and the optical properties.

Mechanical Properties

Under mechanical properties, we find that the frictional resistance between the dispersed particles and the dispersion medium is largely dependent on the shape of the colloidal particle. This can be expressed by Stokes' law (see Appendix, page 243). From the mathematical equation of this law we can calculate the size of the particle if its rate of sedimentation or its sedimentation equilibrium is known. We can also calculate it from the velocity of the Brownian motion. Stokes' law refers only to spherical and rigid particles. This being the case, the determination of particle sizes either by sedimentation or by centrifugation will, when basing the calculation on Stokes' law, give us only the dimensions of spherical particles, or the so-called "apparent particle size," in cases where a deviation from the spherical shape seems to exist. Only for very simple cases have formulas been devised to permit the calculation of frictional resistance of nonspherical particles.[1]

VISCOSITY

Viscosity is also materially influenced by the shape of the dispersed particle. A. Einstein and E. Hatschek have devised an equation (see Appendix, page 243) that permits the evaluation of the viscosity of a disperse system under the following assumptions:

1. The particles must be spherical and not deformable.
2. The dimensions of the particles must be large in comparison to the molecular dimensions of the dispersion medium.
3. The particles must be small in comparison to the measuring instrument, *e.g.*, diameter of the capillary of the viscosimeter or the dimensions of a falling ball.
4. The movement of the dispersion medium in the direct vicinity of a particle may not be influenced by the presence of other particles.

If these factors are fulfilled, then the Einstein-Hatschek equation calls for a proportionality between viscosity and concentration. Generally, it is assumed that in highly disperse systems, this equation is fulfilled, even within a fairly wide range of concentrations. But in the case of typical colloidal dispersions, fulfillment is rare and seems to be limited to extreme dilutions and systems whose lyophilic properties are not too pronounced. For example, H. Fikentscher and H. Mark[2] report such correlation in very dilute nitrocellulose sols. At higher concentrations, increasing divergence occurs. Similar results have been reported with inorganic colloids, such as colloidal clays. Although many attempts have been made to interpret mathematically the rapid increase of viscosities at higher concentrations, no really satisfactory answer has been found. This is not so astonishing considering the numerous factors that may be involved, *viz.*, solvation, electric charge, aggregation of particles, shape of molecules, etc.

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[1] See, *e.g.*, R. GANS and J. OBERBECK, *J. Math.*, **81**, 62 (1876); *Sitzber. Akad. Wiss. Muenchen*, p. 191 (1911).

[2] *Koll. Zeit.*, **49**, 135 (1929); **53**, 32 (1930).

Most lyophilic sols and those which can be considered as exhibiting lyophobic as well as lyophilic properties ordinarily exhibit a pronounced difference from normal liquids as to their viscosity. In normal liquids the volume of liquid flowing through a capillary is proportional to the pressure applied. The discrepancy in the viscous flow of colloidal dispersions becomes more pronounced as the degree of solvation increases and as the shape of the particles becomes more and more anisometric. Wo. Ostwald[1] considers these discrepancies to be caused by structural changes and therefore calls the phenomenon *structural viscosity*. H. Freundlich and E. Schalek[2] have connected these anomalies with the "elasticity of flow" of the sols. M. v. Smoluchowski[3] added another factor to the Einstein equation for the purpose of accounting for the influence of the electric charge of the particle. The electric double layer surrounding the particles exerts a resistance to the flow of the dispersion medium, thereby increasing the viscosity. This phenomenon is known as the *electroviscous* effect, which is the more pronounced the smaller the particles and their conductivity and the larger their potential.

The extreme high viscosity of certain suspensions and lyophilic colloids has frequently been explained by the assumption that some of the dispersion medium is held and immobilized on the surface of the particles by adsorption forces. However, the solvation theory is confronted with several facts that are inexplicable. It has been found that in the case of suspensions the viscosity increases the poorer the wetting between particles and dispersion medium. With lyophilic colloids it has been found that the viscosity increases with increasing particle size. This stands in direct contradiction to what should be assumed in accordance with the theory of solvation, since solvation should show an over-all increase with decreasing particle size. Another explanation that has been offered is the aggregation of particles.[4] In the case of suspensions, the particles tend to aggregate more easily the less their affinity is for the dispersion medium and the less solvated they are. Such aggregates are frequently very voluminous and loosely connected, resulting in a material

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[1] *Zeit. physikal. Chem.*, **111**, 62 (1924).

[2] *Ibid.*, **108**, 153 (1924).

[3] *Koll. Zeit.*, **18**, 190 (1916).

[4] G. Broughton and C. S. Windebank, *Ind. Eng. Chem.*, **30**, 407 (1938).

increase in the apparent volume of the disperse part. This theory furthermore assumes that the particles at rest will arrange themselves into a loose, voluminous, but coherent structure, and, resisting small tangential pressure, the system would show a yield point. With increased pressure or other mechanical agitation (depending on the type of instrument used for determination of viscosity), the structure would break down, the aggregates redisperse, and the viscosity finally reach a stationary value.

Likewise, in the case of lyophilic colloids, has aggregation been frequently considered as a possible cause for the abnormally high viscosities found. In this instance, however, one had to admit that high viscosities are also encountered where aggregation is out of the question. More recently, H. Staudinger[1] considered the chainlike structure of the molecules to be responsible for the high viscosity of most lyophilic colloids. He assumes that such threadlike molecules, which take up considerable space, will immobilize the dispersion medium by their interlacing structure and thus increase viscosity. R. Eisenschitz[2] came to similar conclusions from a purely theoretical angle in evaluating the viscosity of dispersions containing elongated particles. (For the mathematical evaluation, see Appendix, p. 244.) Staudinger's concept has recently been seriously criticized. According to his assumption, the threadlike molecules should be considered as rigid rods which in the case of a sol are freely movable around their center. This infers that their space in the sol must correspond to a sphere whose diameter equals the length of the particle. It seems more than questionable that such long rod-shaped particles can exist in rigid form in solution. Hence, the more recent assumption of the molecules being bent or skeined is quite plausible.

None of the known hypotheses pertaining to the viscosity of high-molecular compounds differentiates sufficiently between swelling of fiber bundles and ultimate rupture of cross linkages (increase in number of long individual fibers), and therefore *increase* in viscosity,[3] or rupture of fiber length (depolymerization), and *reduction* in viscosity. The concentration of the sols

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[1] *Koll. Zeit.*, **51**, 71 (1930).

[2] *Zeit. physikal. Chem.*, *A* **163**, 133 (1933.)

[3] See P. Koets and H. R. Kruyt, *Koll. Zeit.*, **82**, 315 (1938).

naturally remains unchanged, as it is independent of the fiber length or degree of aggregation.

There are numerous and even more recent contributions to this highly important problem, such as those by H. L. Bredée and L. A. van Bergen,[1] H. Fickentscher and H. Mark,[2] R. Houwink and K. H. Klaassens,[3] W. Haller,[4] E. Guth and R. Simha,[5] F. Eirich[6] and H. Mark, F. Eirich, M. Bunzl, and H. Margaretha,[7] H. L. Bredée and J. de Booys,[8] R. Houwink,[9] W. Kuhn,[10] M. L. Huggins[11] and others,[12] none as yet fully satisfactory. For such a general evaluation it would seem necessary that a correlation be established among solvation, particle attraction and repulsion, and the exact influence of the particle shape. The assumption that the formation of aggregates or chainlike arrangement of micelles is the main factor causing viscosity increases has become extremely doubtful on the basis of very accurate viscosity determinations coupled with determinations of changes in specific gravity, optical density, and ultramicroscopic observations on colloidal clay sols by E. A. Hauser and D. S. le Beau.[13] These experiments show that marked changes in viscosity and even pronounced yield values are found in systems where no sign of agglomeration or alignment can be detected. However, systems exhibiting a measurable yield point are characterized by a very noticeable change in the Brownian motion of the particles. In most cases, the latter has been reduced to an oscillatory motion; in extreme cases approaching gelation, it has come to a perfect standstill. It would seem that increase in viscosity in such

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[1] *Chem. Wbl.*, **30**, 223 (1933).

[2] *Koll. Zeit.*, **49**, 135 (1929); **53**, 32 (1930).

[3] *Ibid.*, **79**, 138 (1937).

[4] *Ibid.*, **56**, 265 (1931).

[5] *Ibid.*, **74**, 147, 266 (1936); **75**, 15 (1936).

[6] *Erg. exakt. Naturwiss.*, **15**, 1 (1936); *Koll. Zeit.*, **81**, 7 (1937).

[7] *Koll. Zeit.*, **74**, 276 (1936).

[8] *Ibid.*, **79**, 31, 43 (1937).

[9] *Oesterr. Chem. Ztg.*, No. 21 (1937).

[10] *Zeit. physikal. Chem.*, *A* **161**, 1, 427 (1932); *Koll. Zeit.*, **62**, 269 (1933); **68**, 2 (1934); **76**, 258 (1936).

[11] *J. Phys. Chem.*, **42**, 911 (1938).

[12] See E. Hatscheks original contributions, *Koll. Zeit.*, **7**, 301 (1910); **8**, 34 (1911); **12**, 238 (1913); **40**, 53 (1926). Wo. Ostwald, *ibid*, **43**, 190 (1927).

[13] *J. Phys. Chem.*, **42**, 1031 (1938).

systems finds its simplest explanation in the interaction of repulsive and attractive forces acting between the particles. Such a concept would be free of any necessary assumption as to aggregation or alignment and furthermore would not necessitate assuming the immobilization of an excessive amount of dispersion medium on the surface of the particles, although it has been ascertained that considerable amounts of dispersion medium are compressed on to the surface of the particles. That such anomalous viscosities are most frequently found in systems containing anisometric particles of rod or plate shape, for instance, is logical only on the basis of what has been previously discussed regarding their reactivity.[1]

ROPINESS

A phenomenon also frequently but, contrary to previous assumptions, not generally found in colloidal systems exhibiting anomalous viscosities is the so-called "stream-double refraction," or "ropiness" (see page 188). When rotating a bottle containing, for example, a soap solution or a vanadium pentoxide sol or the coarser fractions of colloidal clay suspensions, we can see the appearance of silvery streaks parallel to the horizontal plane of motion. This phenomenon is caused by a parallel orientation of anisometric particles to each other. Its appearance seems to depend on the presence of particles or chainlike aggregates of not less than about 100 mμ in length.

PLASTICITY

Plasticity in mechanically stable bodies, which to some extent can be considered closely related to the property of viscosity of liquids, will be discussed in the chapter dealing with gels (see pages 213*ff*.).

Today there are various methods at our disposal for determining viscosity. The choice of the right type of instruments, *i.e.*, capillary viscosimeter with or without the application of pressure, rotation viscosimeters, and viscosity determinations by the falling-ball method, will depend to a large extent on the nature and properties of the system under investigation. So long as one deals with dilute systems with no structural viscosity, the capillary viscosimeters, and especially F. Hoeppler's refined

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[1] E. A. HAUSER and D. S. LE BEAU, *Koll. Zeit.* (in press).

construction of the falling-ball type,[1] are very satisfactory. Where systems exhibiting distinct structural viscosity are to be studied, the use of a rotation viscosimeter seems to be more applicable.

For more detailed discussion of different methods and their theoretical background, a series of specialized textbooks are available.[2]

THE OPTICS OF COLLOIDS

Optics unquestionably plays a more important role in the study and evaluation of colloidal systems and colloidal phenomena than is played by any other branch of science. Optics, if properly applied, can thus be considered as the outstanding tool in colloidal research, and it is a deplorable fact that more emphasis has not been placed on this branch of science in the general routine of colloid chemical research and education.

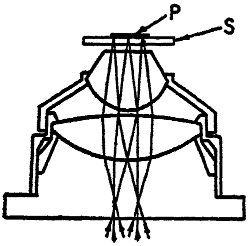

FIG. 77.—Light-field condenser for transmitted light. *S*, glass slide; *P*, preparation.

Dark-field Illumination.—The introductory chapter pointed out that the final answer to the question whether colloidal solutions should be classified as heterogeneous or homogeneous systems is to be found in the application of optics (Faraday-Tyndall phenomenon; Zsigmondy-Siedentopf slit ultramicroscope). Since then, the so-called *dark-field illumination*, or *ultramicroscopy*, has been further developed and applied to the normal type of microscope construction. Instead of using what is known as a light-field condenser in the substage of the microscope to concentrate the light to be transmitted *through* the

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[1] *Zeit. techn. Phys.*, **14**, 165 (1933); *Chem. Ztg.*, **57**, 62 (1933).

[2] See, *e.g.*, E. HATSCHEK, "The Viscosity of Liquids," D. Van Nostrand Company, Inc., New York, 1928. E. C. BINGHAM, "Fluidity and Plasticity," McGraw-Hill Book Company, Inc., New York, 1922. G. BARR, "A Monograph of Viscosimetry," Oxford University Press, London, 1931; R. HOUWINK, "Physikalische Eigenschaften und Feinbau von Natur-u. Kunstharzen," Akad. Verlags-Ges., Leipzig, 1934; *Verhand. d. Kon. Nederl. Akad. Wetensch. Afd. Natuurk.* (1 Sectie) D 1., **16**, 4, pp. 185–240 (1938); "Elasticity, Plasticity, and Structure of Matter," Cambridge University Press, England, 1937. W. HALLER, in A. KUHN, "Kolloidchemisches Taschenbuch," Akad. Verlags-Ges., p. 271, Leipzig, 1935.

preparation (Fig. 77), so-called dark-field condensers were built. In these, the light is capable of entering the condenser only through a circular opening in the bottom lens; the center is silver-plated, thereby forming a mirror from which light is reflected backward and prevented from entering the lens system (Fig. 78). As the result of a further arrangement of the lens combinations in the condenser, no light can actually be transmitted through the preparation but can only impinge in an over-all circular fashion. This results in the development of reflection disks wherever these circular arranged beams of light strike a colloidal particle. It must be emphasized again that the ultramicroscope does not reveal the individual colloidal particle or its actual configuration or shape but solely its presence, due to the development of a reflection disk.

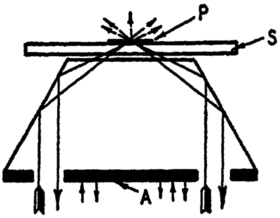

FIG. 78.—Dark-field condenser. *A*, silver-plated reflecting mirror; *S*, slide; *P*, preparation.

The Slit Ultramicroscope.[1]—Let us now consider a colloidal dispersion containing only *spherical* particles, which we have placed in a slit ultramicroscope. We should obtain reflection disks of unchanged intensity wherever an individual particle moves in the field of vision and at whatever speed it rotates around any of its possible axes, as long as the particle remains in one horizontal plane, *i.e.*, the focusing distance of the optical system used. The reason for this is evident, since with a stationary source of parallel light beams the angle of reflection from the surface of a *spherical* particle must remain unchanged as long as these conditions set forth above are fulfilled. Truly spherical disperse parts are very rarely found in nature, the only real exception being colloidal emulsions, the emulsified liquid being present in droplets of colloidal dimensions. In most natural colloidal systems, the disperse part consists of *nonspherical* particles, such as rods, threads, plates, or disks.

If such a system is placed in the slit ultramicroscope, the picture that we see is different from the one discussed before. As an example, we may assume the presence of rod-shaped particles or plates whose width and thickness are of amicronic dimensions (smaller than half the wave length of the light

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[1] H. SIEDENTOPF, *Koll. Zeit.*, 1, 173, 271 (1906–1907).

applied), their length being of definitely ultramicroscopic or medium colloidal dimensions. If we now make our observation at the moment when particle *a* (Fig. 79*A*) happens to lie with its long dimension parallel to the illuminating light beam and the particle *b* at an angle of approximately 45 deg. to the light beam, the observing eye will in that instant register the presence of particle *b* only. Because of the Brownian molecular motion, the particles of a sol are kept in constant translatory and rotary motion so that in the next instant the two particles may lie in regard to the direction of the incoming light beams as shown in Fig. 79*B*. Therefore, particle *a* will disclose its presence by the development of a reflection disk, whereas particle *b* will apparently have vanished. Needless to say, all conceivable intermediate conditions are possible, so that a preparation containing nonspherical or anisometric particles in suspension will show a constant change in the intensity of the light reflected by one and the same particle. The sum of all the changes occurring during the period of observation gives the impression of a constant twinkling or flickering of light. The more the dispersed particles of the sol under investigation deviate from spherical shape, *i.e.*, the more anisometric or anisotropic they are, the more pronounced is this twinkling phenomenon. This phenomenon is considered as the most refined method of determining deviations from the spherical shape on the border of molecular dimensions.

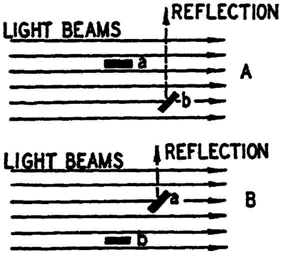

FIG. 79.—Reflection of anisometric particles (parallel one-sided illumination).

The Dark-field Condenser.[1]—Since, in the case of a dark-field condenser, light of uniform intensity impinges from every side (circular) on every solid particle of the preparation, all particles must reflect light with unchanged intensity, whatever their shape and orientation may be at any time during observation. Therefore, a dark-field condenser (if properly centered) is incapable of demonstrating the twinkling phenomenon and is thus unsuitable for this qualitative but none the less extremely sensitive method of determining the presence of isometric or anisometric particles of truly colloidal dimensions.

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[1] H. SIEDENTOPF, *Koll. Zeit.*, *Erg. Bd.*, **36**, 1 (1925); **37**, 327 (1925).

We know many cases in which anisometric colloidal micelles tend to align or orient themselves as soon as the Brownian motion is stopped for one reason or another, *i.e.*, when the originally liquid system (sol) solidifies to a more rigid state (lyogel or xerogel; coagels are generally disoriented, since aggregation is too rapid to permit preferential orientation). Such oriented alignment has been observed in soap jellies, in vanadium pentoxide gels,[1] etc. In soaps, the individual micelles tend to line up in the form of threads,[2] and several of these threads then line up parallel to each other to form bundles. If we again imagine such a bundle to lie with its long axes parallel to the entering beam of light in a slit ultramicroscope, the best we shall be able to observe is a blur of light caused by reflections from the over-all thickness of the bundle, but quite possibly the field of vision will be optically void. Since bundles in such a system are rarely oriented in the same direction (Fig. 80), the observer will register only those that permit satisfactory reflection. In the case of a properly centered dark-field condenser, every bundle will reflect the light with uniform intensity. Although in this case none of the disperse part will escape detection, it is evident that this method cannot reveal the existence of any localized preferential orientation.

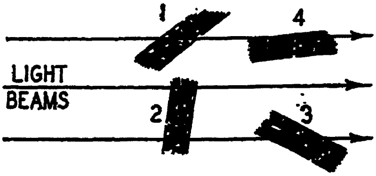

FIG. 80.—Limitations of the slit ultramicroscope. 1, 3, partial reflection; 2, total reflection; 4, no reflection.

The Azimuth Error.—The twinkling phenomenon which was first pointed out by H. Siedentopf[3] can, as previously mentioned, be considered as the most sensitive reaction at the limits of the amicronic range. If we are investigating a sol containing anisometric particles in the slit ultramicroscope, the twinkling phenomenon will be very pronounced, as previously mentioned, because in such an instrument the light can enter the preparation in only one direction, or from one azimuth. (Azimuth refers to the angle formed between the illuminating beam of light and a plane drawn through the optical axes of the microscope.)

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[1] H. FREUNDLICH, *Coll. Symp. Monogr.*, **2**, 46 (1925).

[2] R. ZSIGMONDY and W. BACHMANN, *Koll. Zeit.*, **11**, 145 (1912); **23**, 85 (1918). W. SEIFRITZ, *Coll. Symp. Monogr.*, **3**, 285 (1925).

[3] *Zeit. wiss. Mikros.*, **29**, 1 (1912).

Contrary to such one-sided illumination, the so-called dark-field condensers permit illumination of particles from all possible azimuths. If we now use a dark-field condenser without having carefully checked the centering of the illumination, the particles will receive more light from one direction than from the other, causing a very disagreeable and disturbing distortion of the reflection disks. Siedentopf has termed this effect *azimuth error*.

The Azimuth Stop.—A. Szegvari[1] has made controlled use of this effect in the construction of his *azimuth stop*, which consists

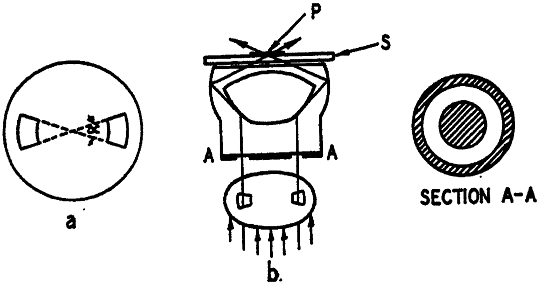

Fig. 81.—The azimuth stop.

of a slit stop so designed that the size of the slits, forming segments of a circle, can be changed at will. Owing to the construction of the instrument, the slits are located at 180 deg. from each other (Fig. 81*a*). The stop is mounted beneath the condenser in a manner to permit the parallel beams of light to pass through the available openings of the slit before they can enter the condenser (Fig. 81*b*). If the stop has been carefully centered, and the slits have been formed by closing the stop, we can produce a type of illumination in a dark-field condenser that closely resembles that of a slit ultramicroscope, because the light can now enter the preparation only by two azimuths located at 180 deg. from each other.

It is logical that the twinkling phenomenon of a given sol will become the more pronounced the more the stop is closed, since the closing of the segmentary slits reduces the possible azimuths of illumination. This, in turn, will increase the probability of particles moving out or appearing in the preferred direction of reflection. Furthermore, the azimuth stop is so constructed

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[1] *Physikal. Zeit.*, **24**, 91 (1923); *Zeit. Phys.*, **21**, 348 (1924); *Zeit. physikal. Chem.*, **112**, 277, 295 (1924).

that it may be rotated under the condenser, permitting change in direction from which the light impinges on the preparation. This makes it possible to study preferential orientations in colloidal systems, as they have been found in soaps, vanadium pentoxide gels, etc., with great accuracy and ease. The instrument has also been applied advantageously in studying structural alignments in films under tension.[1] The construction of the azimuth stop applies the azimuth error as the basis of an ingenious optical experiment and has, in a way, transformed this rather discouraging phenomenon into the so-called *azimuth effect*, which must be considered as one of the most accurate methods of ultramicroscopic structural analysis of colloidal systems.

Intensity of Faraday-Tyndall Cone.—Another optical phenomenon primarily dependent on the shape of the dispersed particles of a sol is the intensity of the light reflection of a Faraday-Tyndall cone. In the case of isodimensional particles, the intensity of this reflected light remains unchanged and independent of the condition of the sol, *i.e.*, if it is at rest or in movement. However, in dealing with anisometric particles, one will observe a pronounced change between stationary and flowing condition.[2] The reason for this phenomenon is that anisodimensional particles will orient longitudinally in the direction of flow. This phenomenon can, as previously pointed out, be macroscopically observed by the appearance of a silky streakiness parallel to the direction of movement (see page 181).

Polarization of Faraday-Tyndall Light.—An optical effect associated with particle shape is the type of polarization of the Faraday-Tyndall cone. That the Tyndall light is polarized is an established fact. If we are dealing with a sol containing spherical particles, we obtain a pure polarized light, because the direction of the vibrations of the polarized Faraday-Tyndall cone is perpendicular to a plane drawn through the direction of illumination and observation. With particles of increasing anisodimensional shapes, the light becomes more and more depolarized. A quantitative determination of the degree of

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[1] See, *e.g.*, E. A. HAUSER, *Koll. Zeit.*, **53**, 78, (1930).

[2] See, *e.g.*, H. DIESSELHORST, H. FREUNDLICH, and A. LEONHARDT, "Elster-Geitel-Festschrift," p. 453, 1915. H. FREUNDLICH, *Zeit. Elektrochem.*, **22**, 27 (1916). H. DIESSELHORST and H. FREUNDLICH, *Physikal. Zeit.*, **17**, 117 (1916). F. G. DONNAN and K. KRISHNAMURTI, *Coll. Symp. Monogr.*, **7**, 1 (1930).

depolarization permits an approximate measurement of particle size and shape as well as of changes that a colloidal particle undergoes.[1]

STREAM-DOUBLE REFRACTION

Stream-double refraction is another phenomenon for which anisometric shapes of disperse particles are mainly responsible. If we observe a sol containing crystalline particles of rod or plate shape, we shall obtain no double refraction between crossed Nicol prisms, even if the individual crystals are of the double-refracting type. The cause for this is the constant Brownian motion of the particles dispersed in the sol, which prevents them from taking on an oriented position. If such a liquid is caused to flow or rotate, the sol will then exhibit double refraction.[2] O. Wiener[3] has demonstrated that the dispersed particles themselves need not be double refracting to exhibit stream-double refraction so long as the particles are anisometric and oriented with their longitudinal axes parallel to each other and so long as their thickness and distance from each other are commensurable with the wave length of the light applied.

J. Björnstahl,[4] J. Böhm[5] and S. Berkmann, and H. Zocher[6] have demonstrated that mercury-sulphosalicylate and even gold sols are mostly double refractive, which seems to prove that they contain at least a certain amount of definitely anisometric particles. Recently E. A. Hauser,[7] and D. S. le Beau in studying the double refraction of monodisperse fractions of bentonite sols, have been able to prove that the stream-double refraction decreases with decreasing particle size of the fractions; in systems containing particles of an average apparent spherical diameter of 15 mμ, the effect becomes practically negligible.

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[1] See, *e.g.*, R. GANS, *Ann. Phys.*, **65**, 97 (1921). B. LANGE, *Zeit. physikal. Chem.*, **132**, 1 (1928). Especially H. ZOCHER, *Koll. Zeit.*, **37**, 336 (1925). H. FREUNDLICH, "Kapillarchemie," vol. 2, pp. 5–57, Akad. Verlags-Ges., Leipzig, 1932. K. HOFFMAN and H. A. WANNOW, *Koll. Zeit.*, **83**, 258 (1938).

[2] See, *e.g.*, H. ZOCHER, *Zeit. physikal. Chem.*, **98**, 293 (1921).

[3] Ambronn-Festschrift (*Koll. Beih.*), **23**, 189 (1926).

[4] "Die Akzidentelle Doppelbrechung in Kolloiden," Dissertation, Upsala, 1924.

[5] *Koll. Zeit.*, **42**, 276 (1927).

[6] *Zeit. physikal. Chem.*, **124**, 83 (1926); *Koll. Zeit.*, **42**, 309 (1927).

[7] *J. Phys. Chem.*, **42**, 1031 (1938); see also W. HELLER, *Compt. rend.*, **205**, 971, (1937).

X-RAY DIFFRACTION PATTERNS

Another method that offers certain indications as to the shape of the individual particles of colloidal aggregates is the x-ray diagram. The assumption here to be made is that the individual particles are of crystalline nature; *e.g.*, J. Böhm[1] ascertained that certain lines in the x-ray spectrum will be either sharp or diffuse, depending on the shape of the particle. (For a discussion of other optical methods used in colloid chemical research and for a brief explanation of the fundamentals of x-ray diffraction methods, see Appendix, pages 244*ff*.)[2]

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[1] *Zeit. Krist.*, **68**, 567 (1928).

[2] An excellent summary of the optics of disperse systems is given in H. ZOCHER, "Optik disperser Systeme," in A. KUHN, "Kolloidchemisches Taschenbuch," Akad. Verlags-Ges., Leipzig, 1935, pp. 84*ff*. In the same book, pp. 184*ff*., G. v. Susich offers a valuable summary on interferences caused by x rays.

CHAPTER XV

AGGREGATES BOUNDED BY PRIMARY FORCES

Definition.—Although it has been demonstrated in previous chapters that colloidal systems can be obtained either by disintegrating coarse matter or by condensing highly disperse systems, it is evident that in a final analysis all matter independent of its degree of dispersion must have originally been built up by an aggregation of the ultimate building units of matter. The modern concept of the structure of an atom, as visualized by men like N. Bohr, E. Rutherford, A. Sommerfeld, P. Debye, and others, has entirely changed the old classical atomistic viewpoint. With the concept of the existence of protons and electrons and the great variability of their possible configuration, the formation of isotopes, for example, finds a simple explanation, impossible on the basis of the classical theory of atoms.

It is of primary importance to find a definition for the term "aggregate" as it will be henceforth used. It is a structure made up of building units, complete in themselves and dynamically interlinked. Certain forces act between these units so that the whole structure coheres and can, if viewed from outside, be considered as a unity.

In discussing the importance of the colloidal state of matter, it was pointed out that the colloidal particle is understood to be made up out of still higher dispersed aggregates but that it plays its own part as a new building unit in further organized constructions. Therefore, we can distinguish between aggregates of different degrees of dispersion. Yet the binding forces holding the individual elements of the aggregates together are equally important. One is used to differentiating between primary and secondary aggregates, depending on the prevailing combining force. v. Buzágh[1] devotes considerable space to this entire topic and compares this classification to the classical concept of chemical and physical binding forces. The chemical

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[1] "Colloid Systems," pp. 88*ff*., The Technical Press, Ltd., London, 1937.

concept of valencies explains the combination between atoms in a chemical compound. In the classical theory, these forces can be saturated, whereas physical forces, such as van der Waals' cohesion forces, cannot be saturated. However, further developments in the field of theoretical physics have made it somewhat doubtful if such differentiations can still be maintained. In this connection, W. Kossel's[1] theory, according to which chemical bonds can also be considered as electrostatic phenomena between opposite charges, deserves special attention.

PRIMARY AGGREGATES

In agreement with the basic law of the least free energy, atomic aggregations always tend toward maximum stability. If such is achieved by a rearrangement of electrons, primary bonding forces must be taken into account, and the resulting corpuscle represents a *primary aggregate.* The possibility of other types of forces acting simultaneously and the general complexity of the problem make a clear differentiation as yet impossible.

Under primary aggregates are understood to be such systems as in accordance with the definition given above are the result of a rearrangement of electrons or are due to primary bonding forces. Starting with an atom, we can visualize ions, molecules, and the atomic and ionic crystal lattices to represent such cases. Although a detailed discussion of these examples of typical primary aggregates is not only fascinating and of increasing importance for our modern concepts of the structure of matter in general, it lies, nevertheless, too far outside the actual scope of this introductory treatise.[2] The discussion therefore will be

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[1] *Ann. Phys.*, **49**, 229 (1926); *J. Am. Chem. Soc.*, **38**, 762 (1916).

[2] For detailed discussions of primary aggregates and primary bonding forces, see, *e.g.*, W. KOSSEL, "Valenzkräfte und Röntgenspektren," Julius Springer, Berlin, 1921. G. N. LEWIS, "Valence and the Structure of Atoms and Molecules," Reinhold Publishing Corporation, New York, 1923, German ed., "Die Valenz und der Bau der Atome und Molekule," F. R. Vieweg, Braunschweig, 1927. C. A. KNORR, *Zeit. anorg. Chem.*, **129**, 110 (1923). N. R. CAMPBELL, *Nature*, **111**, 569 (1923). A. SOMMERFELD, "Atombau und Spektrallinien," F. R. Vieweg, Braunschweig, 1923. A. HAAS, "Materiewellen und Quantenmechanik," Akad. Verlags-Ges., Leipzig, 1929. K. FAYANS, *Science* **62**, 107 (1930). A. E. VAN ARKEL and J. H. DE BOER, "Chemische Bindung als Elektrostatische Erscheinung," S. Hirzel, Leipzig, 1931. For further literature references see, *e.g.*, v. BUZÁGH, *op. cit.*

kept in a very general manner with the sole purpose of pointing out those deductions which are of specific significance in regard to modern concepts of colloïdal phenomena.

According to our present knowledge, the formation of an ion is due to the removal or addition of so-called valency electrons from atoms. This results in the loss of the atoms' electrical neutrality and gives rise to a definite electrical charge. If the centers of the positive and the negative charge fall into the center of the ion, we speak of an "ideal case." Oppositely charged ions can be compared with electrically charged rigid spheres which attract each other in accordance with Coulomb's law. These attraction forces are evident only at comparatively large distances, since at short distances repulsion will be predominant. This is completely in accord with the results of wave mechanics, according to which the density of atomic or ionic electron clouds decreases at first rapidly and then less rapidly as we move to the outside. If two ions come close together, the electron clouds interpenetrate each other, setting up elastic repulsion forces.

Formation of Molecules.—From our present concept, molecules are formed from atoms, by either ionic or atomic linkage. The assumption that ions forming a molecule are held together by electrostatic attraction forces explains the formation of such substances as are composed of oppositely charged radicals, *e.g.*, sodium chloride, magnesium oxide, almost all sulphides. In such molecules, it is assumed that all the outer electrons are displaced nearer to one of the atomic residues present. Such compounds will exhibit a large dipole moment and are known as polar or heteropolar substances. However, it seems impossible to explain the formation of molecules of hydrogen, chloride, and many organic compounds on the same basis, since we are dealing here with a combination of atoms of the same type. G. N. Lewis[1] and C. A. Knorr[2] postulate an atomic linkage for such compounds. It is supposed that the atomic linkage is the result of the fact that a certain number of outer electrons belong simultaneously to several atomic residues. In such a case, several centers of attraction will exist for the outer electrons, and this, in turn, must result in an extreme difformation of the electron hull. If the distribution of outer electrons in regard to atomic residues is a uniform one, it is then a question of an *apolar*

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[1] See footnote 1, p. 193.

[2] See footnote 1, p. 193.

or a *homopolar* compound, which exhibits no dipole moment. But if the mean center of gravity of the outer electrons does not coincide with the electrical center of gravity of the atomic residues, then the molecule must behave like an electric dipole. Such polar compounds as water, for instance, take up an intermediate position between ionic and apolar atomic linkage, as demonstrated schematically by K. Fayans[1] (see Fig. 82). This concept of linkages and induction of dipoles by distortion of the electron shells is becoming increasingly important in the interpretation of a variety of colloidal phenomena, such as gelation and stability of colloidal dispersions.

Molecular Models.—Another recent development that has proved to be very valuable in the study and interpretation of various colloidal phenomena is the study of the form or shape of molecules, finally resulting in the construction of so-called molecular models. We know today that we must distinguish between *isodimensional* and *anisodimensional* molecules. The latter can be further subdivided into *laminar* and *fibrillar* ones. We have learned that fiber-type molecules can exist in different forms and that long-chain molecules can exist in a kinked or spiral form. One of the outstanding deductions based on a specific form of certain organic molecules and at the same time an ingenious proof for the correctness of such assumptions are the experiments in regard to molecular orientation of fatty acid films on the surface of water, as carried out by men like W. D. Harkins,[2] I. Langmuir,[3] N. K. Adam,[4] J. J. Trillat.[5] The

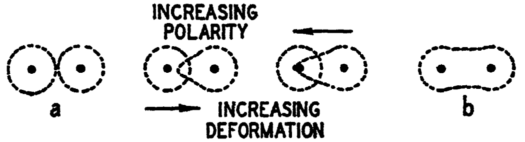

Fig. 82.—Continuous change from ionic to atomic linkage. *a*, ideal ionic linkage; *b*, ideal atomic linkage (nonpolar).

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[1] See footnote 1, p. 192. See also Sidney J. French, *J. Chem. Educ.*, March, 1936, p. 122.

[2] *J. Am. Chem. Soc.*, **39**, 354, 541 (1917).

[3] *Ibid.*, **39**, 1848 (1917).

[4] *Proc. Roy. Soc.*, *A* **99**, 336 (1921); **101**, 452, 516 (1922); **103**, 676 687 (1923). *J. Phys. Chem.*, **29**, 87 (1925). See also "The Physics and Chemistry of Surfaces," 2d ed., Oxford, Clarendon Press, New York, 1938; *Koll. Zeit.*, **61**, 168 (1932).

[5] *C. r. Soc. Biol.*, **180**, 1329 (1925).

experiments proved beyond doubt that the actual shape of a fatty acid molecule stands in excellent agreement with the generally assumed hydrocarbon-chain structure. By measuring the surface area taken up by them in such compressed surface films, Langmuir was able to calculate the cross section of the head. Since these measurements remained unchanged in a homologous series, it was proved that the carbon chain must be directed in approximately vertical position out of the surface (see Fig. 53 and page 139).

Eucolloids.—As previously mentioned, the lower dimensional limit for the colloidal range has been arbitrarily fixed at one-millionth of a millimeter. This has been found to be about the maximum dimension of a typical simple molecule. However, we know that a large number of substances of colloidal degree of dispersion which exist are the result of primary valency linkage between a large number of atoms. Typical examples of such compounds are proteins, rubber, cellulose, and a great number of synthetic organic compounds like polystyrene, chloroprene, and polyethylene tetrasulphide ("thiokol"). These substances or macromolecular compounds have been termed by Wo. Ostwald[1] *eucolloids*, whereas H. Staudinger[2] has named them *molecular colloids*. He considers as eucolloids only such compounds as have an excessively *high* molecular weight and has used the term *hemicolloids* for those under a molecular weight of 10,000.

Macromolecular Compounds.—In the opinion of the author, the latter differentiation is questionable in value, since no definite limits can be drawn between these groups. Besides this, the term "molecule" loses all its significance when given such a wide interpretation.

It is important to point out that such macromolecules need not attain colloidal dimensions in all three directions of space and actually very seldom do. According to the definition of the colloidal state of matter, it is sufficient if the colloidal dimensions exist in just one direction. Since most of the high-molecular compounds are of organic nature and can be obtained by poly-

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[1] *Koll. Beih.*, **32**, 1 (1931).

[2] *Koll. Zeit.*, **53**, 19 (1930). See also "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932. Kurt H. Meyer and H. Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akad. Verlags-Ges., Leipzig, 1930.

merization or by condensation with splitting off of water from low-molecular compounds, it is only natural that this specific field of colloidal research is strongly linked with the development of classical organic chemistry. Moreover, besides the study of primary valency-chain linkages, we must also consider the possibility of forming network structures due to two- or three-dimensional primary valency linkages or bridge linkages. Typical examples of such macromolecular compounds are a great number of synthetic resins, *e.g.*, bakelite, the condensation product of phenol and formaldehyde. According to recent assumptions, the vulcanization of rubber may well be considered as a transformation from a primary valency-chain system to a tridimensional bridge linkage.

It would lie far beyond the scope of this book to discuss in more detail the development of this very modern branch of colloidal science, even if one has to admit that it is extremely fascinating. The reader is referred to the excellent highly specialized textbooks available.[1] However, further attention will be drawn to these developments and the deductions that are based thereon, wherever it seems essential for a clear understanding.

Instead of atoms and ions combining in such a way that they form molecules, they can also combine, influenced by primary bonding forces, to form ionic or atomic lattices.[2] Sodium chloride and quartz crystals are typical examples of such ionic lattices. The building units can also be linked together by chemical main valencies. The diamond is a typical example. A lattice layer of atomic linkage is represented by graphite.

The colloid chemist and physicist is interested primarily in an answer to the question as to what lattice structures and shapes the colloid particles possess and secondarily as to what connection

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[1] R. Houwink, "Plasticity, Elasticity, and Structure of Matter," Cambridge University Press, England, 1937. K. H. Meyer and H. Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akad. Verlags-Ges., Leipzig, 1930. H. Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932. W. J. S. Naunton, "Synthetic Rubber," Macmillan & Company, Ltd., London, 1937. See also Per K. Frolich, "Chemical Trends in the Petroleum Industry," *Ind. Eng. Chem.*, **30**, 916 (1938).

[2] For further details and literature references, see, *e.g.*, v. Buzágh, *op. cit.* pp. 111*ff*.

exists between the stoichiometric and stereometric composition of the colloidal particle.

Long before x rays were applied to the determination of crystal structures, P. P. von Weimarn demonstrated beyond any reasonable doubt that colloidal particles can also have a lattice structure and that this is not confined to perfectly grown crystals or to any dimensional limitation. With the advent of x-ray diffraction analysis and especially as a result of the work of P. Debye and P. Scherrer (see Appendix, pages 249*ff.*), it could be proved that even the smallest colloidal dimensions give an x-ray pattern if the particles possess a lattice structure. Scherrer was able to obtain a distinct x-ray pattern from a gold sol (after coagulation) which contained particles of about 6 mμ in size. E. Wiegel[1] has obtained perfect diagrams using silver sols containing particles of not over 10 mμ in size. In both cases, the diagrams obtained were absolutely identical with those obtained from large pieces of the same metal. As R. Brill[2] has shown, the interference bands become broader and less distinct the more highly the system is dispersed. As a matter of interest, it may be noted that Scherrer applied this method for the purpose of obtaining a qualitative figure for the particle size. J. Boehm[3] is of the opinion that clear x-ray diagrams become noticeable as soon as the particle enters the lower range of colloidal dimensions, or, to put it in another way, that a clear diffraction pattern disappears as soon as the degree of dispersion reaches so-called molecular dimensions.

The second question (connection between stoichiometric and stereometric composition of the colloidal particle) has already been discussed in a previous chapter.

[1] *Koll. Zeit.*, **53**, 96 (1930).

[2] *Ibid.*, **69**, 301 (1934).

[3] *Ibid.*, **42**, 276 (1927).

CHAPTER XVI

AGGREGATES BONDED BY SECONDARY FORCES

There is no doubt that, from the point of view of the colloid chemist or physicist, secondary aggregates are by far the more interesting. Such aggregates as have been pointed out are formed from molecules, ionic lattices, main valency chains, etc., or, generally speaking, primary aggregates by linkages resulting from secondary bonding forces. A secondary aggregate, therefore, consists of individual building units bound to each other by interionic and interatomic forces which, in turn, are bound together by secondary forces. That this is the general construction can be easily proved by the difference of energy required to decompose or destroy the two types of linkages. A linkage resulting from secondary combining forces is much weaker and therefore needs less energy to be destroyed than a primary force linkage.

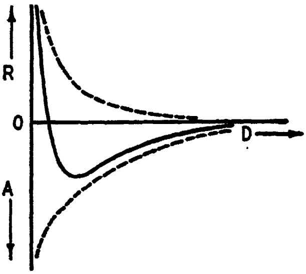

Fig. 83.—Intermolecular forces. *A*, attraction; *R*, repulsion; *D*, distance between particles of coherent systems.

ATTRACTION AND REPULSION FORCES

It is generally assumed that attraction and repulsion forces act between molecules. The cohesion between the individual particles forming a liquid or a solid would be inconceivable without the assumption of a force of attraction. But since the compression of matter requires energy, one must also count on the existence of a repelling force. According to the theories of Laplace and Gauss, the repelling force decreases more rapidly than the attracting force. At a certain distance, the forces must compensate each other. This is schematically demonstrated by Fig. 83, where the dotted lines represent the individual forces the drawn line being the resulting force.

The idea of studying molecular forces and especially the potential of the molecular attraction force was originated by van der Waals and has since been materially developed by men like W. H. Keesom and P. Debye,[1] who introduced the theory that interionic, interatomic, and molecular forces are all electrical forces. Later, F. London and H. Kallman,[2] H. Kallman and M. Willstätter,[3] and recently C. Hamaker[4] further extended the theory of energy potentials. (For further details, see pages 219*ff*.)

DIPOLES

According to Debye's theory, it is the distribution of the electric charges that determines the intermolecular forces. If the charges are not symmetrically distributed, we obtain molecules of typically polar nature. Depending on the number of poles, we can distinguish between so-called permanent dipoles, quadrupoles, etc. If two ideal dipoles approach each other, they will tend to orient themselves in such a way that the free energy of the resulting system is at a minimum. This will be true when the positive pole of one dipole contacts the negative pole of the other (Fig. 84). On the basis of such an assumption, the aggregation of polar molecules finds a logical explanation. P. Debye[5] has been able to show that the aggregation of molecules can also be explained in such cases where the dipoles contain movable charges, since on approaching each other polarization must result. If we have two dipoles approaching each other, *e.g.*, owing

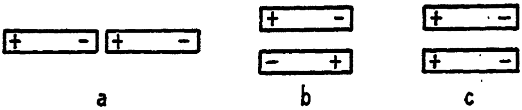

FIG. 84.—Orientation of dipoles. *a*, unstable (intermediate) condition; *b*, stable condition (low-potential energy); *c*, unstable (high-potential energy).

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[1] *Physikal. Zeit.*, **21**, 178 (1920); **22**, 129, 302 (1921).

[2] *Zeit. Phys.*, **63**, 245 (1930); *Zeit. physikal. Chem., Abt. B*, **2**, 207 (1929).

[3] *Naturw.*, **20**, 952 (1932).

[4] *Rec. trav. chim. Pays-Bas*, **55**, 1015 (1936); **56**, 3,727 (1937); **57**, 61 (1938). *Physica*, **4**, 1058 (1937). Symposium on the dynamics of hydrophobic suspensions and emulsions, p. 16, Utrecht, 1937. *Chem. Wbl.*, **35**, 47 (1938). See also contributions by W. KAST and W. MAIER, A. MICHELS, J. DE BOER, and A. BIJL, J. H. DE BOER and J. F. H. CUSTERS, DE BOER and G. HALLER and A. J. STAVERMAN, in the special issue of *Physica*, **4**, November, 1937.

[5] "Polar Molecules," Reinhold Publishing Corporation, New York, 1929.

to their thermal movement as shown in Fig. 85*a*, they will repel each other, since the poles of the same sign are closest together. However, at the same time the charges, too, will be displaced, as shown in Fig. 85*b*, and the dipole moment will diminish. This will cause a reduction in the repelling force, and a system with reduced free energy results.

If poles of opposite sign get close together (Fig. 85*c*), attraction will result, causing an increase of the dipole moment and an increased force. Since the changes in forces caused by a reciprocal polarization of movable dipoles depend only on the internal structure of the molecule, it must be considered as that important and so far neglected part of the van der Waals attraction forces which is independent of temperature. London and Kallman have amended Debye's concept, which cannot satisfactorily explain the attraction forces in apolar gases, by assuming that the electrons in the atoms are displaced if the molecules come sufficiently close to each other. Such reciprocal displacements should lead to attraction forces even between originally nonpolar molecules. London states that:

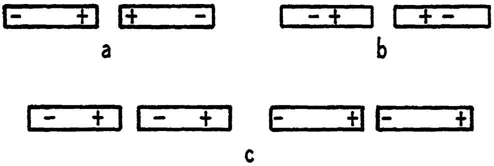

FIG. 85.—Polarization of dipole.

1. These attracting forces are effective over multimolecular dimensions, which is not the case with electrostatic forces.

2. That they are independent of the temperature and the position of the molecule.

3. That the dipolar properties are of only secondary importance and that these forces are superimposable, which means that the force acting between two molecules is not disturbed by the presence of a third one.

The additive character is the factor that makes this theory valuable in the discussion of a variety of colloidal phenomena. It is the first theoretical attempt to interpret experimentally observed supermolecular distances between particles in stationary systems.

ASSOCIATION AGGREGATES

A direct result of dipole arrangement in molecular disperse systems is their preference to aggregate in the form of swarms. If the molecular forces are strong, *i.e.*, if the molecules have a high dipole moment or are easily polarized, so that they can overcome temperature effects and the like, molecular aggregates will be formed by association. The degree of association will depend not only on the actual dipole moment, as we can now readily understand, but also on the location of the dipoles in the molecule and on the shape and size of the molecule itself. If we are dealing with typically anisodimensional molecules of fibrillar or lamellar type, the system exhibits a minimum of free energy when the molecules line up with their longitudinal axes parallel to each other (Fig. 86*a*).

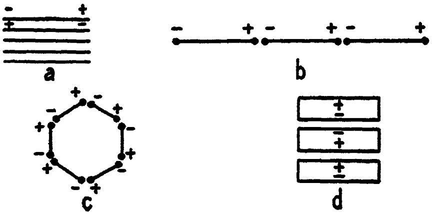

FIG. 86.—Dipole aggregates.

A somewhat less stable configuration is visualized when the molecules link together and form a chain (Fig. 86*b*). This must ultimately result in an increased dipole moment of the associated molecules. However, the length of such a chain must be limited, because the opposite charges at the end of the chain finally become so large that they lead to a collapse of the chain, *e.g.*, a ring formation (Fig. 86*c*). If the dipolar axes happen to lie perpendicular to the axes of the molecules, it is probable that more stable chains of different type of molecular arrangement could be formed (Fig. 86*d*). In the case of spherical molecules, the probability of a strong association seems decidedly less, because of the dipoles lying in a more central position.

ASSOCIATION COLLOIDS

If normal molecules associate until the newly formed aggregate is of colloidal dimension, we speak of *association colloids*. We have already stated that association depends on the dipolar character of the molecules; it also depends on the dielectric properties of the medium, on the concentration of dissolved substance, and on the temperature. Therefore, association colloids must also be influenced by these factors. Soaps, *i.e.*, salts of higher fatty acids, are typical association colloids. The individual soap molecule is amicroscopic, but it is highly anisodimensional and has a high dipole moment. With increasing concentration,[1] the degree of association increases. Increasing temperature will decrease the degree of association (Fig. 87).

In considering again what has been said about the factors governing association, we can now readily understand why systems containing molecules of an increasing number of carbon atoms exhibit an increased tendency to associate. The dipole moment and the anisometric shape increase. Besides soaps, a great number of other compounds, *e.g.*, many dyestuffs, tend to form association colloids. This discussion of association colloids also explains why and how their degree of dispersion can, under varying conditions, undergo continuous changes, whereas, for example, eucolloids or macromolecular compounds never give highly disperse systems unless chemically decomposed.

FIG. 87.—Association colloids. *a*, associated soap molecules at low temperature; *b*, disrupted dipole chain at high temperature.

Just as ionic and atomic lattices exist, we also know of compounds in which the absolutely independent molecules can arrange themselves into a crystal lattice without losing their independence. In such systems, the cohesion of the atoms or ions in the building unit of the crystal is naturally much larger than the linkages between the units themselves. The latter are held together by in*ter*molecular forces, which are, as has been previously discussed, decidedly weaker than the in*tra*molecular forces. This difference is also evidenced by the fact that intermolecular distances are generally greater than intramolecular ones.

Such molecular lattices and the forces holding them together are of extreme interest to the colloid chemist and physicist,

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[1] See *e.g.* P. EKWALL, *Koll. Zeit.*, 77, 320 (1936); 85, 16 (1938).

because a great number of chemical compounds (especially organic) of colloidal dimensions belong to this group. It would exceed the scope of this book to consider molecular lattices and their importance to colloid chemistry in more detail. It must suffice to have drawn attention to such structures, but the reader is referred to the specialized textbooks and publications.[1]

Main Valency Chains.—The tendency of high-molecular compounds such as cellulose, rubber, and natural silk is to form highly difform primary building units or main valency chains. Here, again, x-ray analysis has permitted an excellent insight into the structure of these products. It has been shown that the fiber structure is the result of an orientation of the minute crystallites in the direction of the fiber axes, without, however, being specifically oriented perpendicular to these axes. Except for a general discussion of the theoretical basis for x-ray spectrography, to be found in the Appendix, the reader is referred to special textbooks. This field has undergone such an amazing development that it is a hopeless task even to attempt a satisfactory discussion in the available space.[2]

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[1] The parallel arrangement of lattice molecules in naphthalene, anthracene etc., is discussed, for example, in P. P. Ewald, "Kristalle und Röentgenstrahlen," Julius Springer, Berlin, 1923. The crystalline character of paraffin and higher fatty acids has been demonstrated by M. de Broglie and G. Friedel, *Compt. rend.*, **176**, 738 (1921); A. Mueller and E. Shearer, *J. Chem. Soc.*, **123**, 2043, 3152, 3156 (1923). Especially J. J. Trillat, *Compt. rend.*, **180**, 280, 1329, 1485 (1925). See also F. Halle, *Koll. Zeit.*, **56**, 77 (1931). Laminar structures formed by double molecules have been studied in lauric acid by K. H. Meyer and R. Brill, *Zeit. Krist.*, **67**, 590 (1927). See also I. E. Langmuir, *J. Am. Chem. Soc.*, **39**, 1848 (1917). More general discussions on the subject and methods of evaluation can be found in the many textbooks dealing with x-ray spectrography, *e.g.*, W. L. and W. H. Bragg, "X-rays and Crystal Structure," George Bell & Sons, Ltd., London, 1925. G. L. Clark, "Applied X-rays," McGraw-Hill Book Company, Inc., New York, 1927. H. Mark, "Die Verwendung der Röntgenstrahlen in Chemie und Technik," J. A. Barth, Leipzig, 1926. J. J. Trillat, "Les Applications des Rayons-X," Les Presses Universitaires de France, Paris, 1930. von Buzágh, *op. cit.*; etc.

[2] For a detailed discussion of the structure of high-molecular compounds, the following books may be consulted: G. L. Clark, "Applied X-rays," McGraw-Hill Book Company, Inc., New York, 1927. R. O. Herzog, H. Hoffmann, and O. Kratky, "Fortschritte auf dem Gebiet der hochmolekularen Verbindungen" ("Handbuch der Biochemie des Menschen und der Tiere"), Gustav Fischer, Jena, 1930. K. Hess, "Chemie der Cellulose"

MESOPHASE SYSTEMS

In the case of systems containing anisodimensional dispersed particles, it can happen that some of the movements are periodic, whereas others are statistically uniform. This results in the fact that such *mesophases*, or the *mesomorphic state*, will exhibit an orientation only in certain preferred directions of space. According to this definition given by Wo. Ostwald, we are dealing with a condition intermediate between truly amorphous and crystalline. It therefore is possible to talk of mesophases of a coarse degree of dispersion just as well as of colloidally disperse mesophases. Such a differentiation seems to be more in accord with the general systematization followed throughout this book than other definitions found in the literature.

Two basic forms of the mesomorphic state are usually distinguished: one, the so-called *nematic;* and the other, the *smectic state*.

The Nematic State.—In the nematic condition, the longitudinal axes of the anisodimensional particles lie parallel to each other, but the directions of the two remaining perpendicular axes and the distances between the individual particles vary from one particle to the other (Fig. 88*a*). Furthermore, we can distinguish between a nematic state with a linear fibrous structure and one with a plane fibrous structure. To picture a linear fibrous structure we might look at a bundle of pencils held together in parallel position, whereas a plane fibrous structure would result if these pencils were spread at random on a flat surface. If such nematic bodies take on a helical shape, *e.g.*, by rotation of their elements, they are known as *cholesteric forms*, the phenomenon being very pronounced in cholesterol derivatives.

(contribution by J. R. Katz), Akad. Verlags-Ges., Leipzig, 1928. K. H. MEYER and H. MARK, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akad. Verlags-Ges., Leipzig, 1930. H. STAUDINGER, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932. A. KUHN, "Kolloidchemisches Taschenbuch" (contribution by G. VON SUSICH), Akad Verlags-Ges., Leipzig. 1935. R. HOUWINK, "Elasticity, Plasticity, and Structure of Matter," Cambridge University Press, England, 1937. VON BUZÁGH, *op. cit.* See also O. KRATKY, *Koll. Zeit.*, 84, 149 (1938).

The Smectic State.—In the smectic state, the intervals between the individual particles are also uniform in the preferred direction so that the individual particles form layers evenly distanced from each other (Fig. 88*b*). Another possibility, *i.e.*, a system in which the particles are oriented with their longitudinal axes parallel to each other and equidistant, also seems possible. The regular x-ray fiber diagram can be taken as an example of such a configuration. If perfect symmetry is present, then we speak of a crystal-lattice type of arrangement (Figs. 88*c* and *d*).

A careful search reveals that these conditions are far more common than generally assumed. For example, it has been ascertained that the so-called liquid crystals are typical mesomorphic systems.[1]

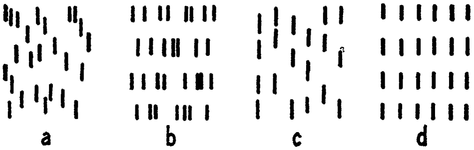

FIG. 88.—Mesomorphic systems. *a*, nematic arrangement of molecules (viewed at right angle to fixed molecular axes); *b*, smectic arrangement; *c*, unknown as mesomorphic substance (corresponds to oriented fiber arrangement); *d*, unknown as mesomorphic substance (corresponds to crystal lattice).

It is quite evident that mesophases will form the more easily the more anisodimensional the building units of the system are. It is logical that soaps or vanadium pentoxide sols, with typical fibrillar or lamellar particles are predestined to form mesophases. The forces that orient these building units are very similar to those which we have discussed in connection with the formation of association molecules. All the deductions in this former discussion can be fully applied to systems containing mesophases. Since mesomorphic systems are most pronounced if present in a colloidal degree of dispersion, it is natural that the colloid chemist

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[1] See, *e.g.*, D. VORLÄNDER, *Zeit. physikal. Chem.*, **93**, 516 (1918); O. LEHMANN, "Flüssige Kristalle," I. F. Bergmann, Wiesbaden, 1911; *Koll. Zeit.*, **15**, 64 (1915). G. FRIEDEL, "Les états mesomorphes de la matière," Paris, 1922; *Ann. phys.*, **18**, 273 (1922). H. HERMANNS, *Rec. trav. chim. Pays-Bas*, **45**, 6 (1926). J. PERRIN, *Koll. Zeit.*, **51**, 2 (1930). H. FREUNDLICH, R. STERN, and H. ZOCHER, *Biochem. Zeit.*, **138**, 307 (1923). Especially H. ZOCHER and V. BIRSTEIN, *Zeit. physikal. Chem.*, *A* **141**, 413 (1929); **142**, 113, 126, 177, 186 (1929); and H. ZOCHER's contributions in A. KUHN, "Kolloidchemisches Taschenbuch," pp. 129*ff.*, Akad. Verlags-Ges., Leipzig, 1935. Also *Trans. Faraday Soc.*, **29**, 881 (1933).

and physicist is especially interested in this phenomenon. Most important of all problems connected with this phenomenon is the question as to what forces besides the attraction forces act to cause the formation of mesomorphic systems in the colloidal range. Although no absolutely final answer can yet be offered, it seems more than probable that interfacial effects play a predominant part. This idea, originated by Wo. Ostwald,[1] has since found so many experimental proofs that its correctness can no longer be questioned.

The results obtained in the study of mesomorphic systems and the constant improvements in x-ray spectrography have demonstrated that a great number of substances previously considered as amorphous are definitely crystalline or at least mesomorphic. These findings have made us assume that only true liquids may really be considered amorphous. However, very recent observations seem to show that even in such liquids some specific groupings of molecules exist.[2]

CYBOTACTIC CONDITION

Some assume that in a liquid there are molecules which at every time differential are surrounded by other molecules in definite arrangement, similar to the structure of crystals. Others assume that the liquid is always filled with a great number of regions, each of which exhibits a regularity of its own (*cybotactic condition*). Since the molecules constantly shift from one group to the other, a continuous transition between the cybotactic groups must be assumed.

Although it seems too early to discuss any possible further development of such theories and their influence on different colloidal phenomena, they may no longer be overlooked, since the dimensions of such cybotactic orientation may easily extend into the colloidal range. The discovery of submicroscopic emulsions in what so far have been considered as true solutions seems materially to strengthen the theory of cybotactic regions. Similar considerations have recently been postulated in regard to the formation of glasses, which so far have not given any sign of crystallization by x-ray analysis.[3]

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[1] "Die Welt der vernachlässigten Dimensionen," 10th ed., pp. 146*ff*., T. Steinkopff, Dresden, 1927.

[2] See especially G. W. STEWARD, *Koll. Zeit.*, **67**, 130 (1934).

[3] B. E. WARREN and J. BISKOE, *J. Am. Ceram. Soc.*, **21**, 49 (1938).

CHAPTER XVII

COLLOIDAL AGGREGATES

Definitions.—In the two preceding chapters, those aggregates of elementary building elements, *i.e.*, atoms or ions, were first discussed which are held together by primary binding forces (chemical main valencies). These were termed primary aggregates. Then aggregates were examined that are formed from such primary aggregates by binding several of these together by intermolecular or secondary binding forces. These were called secondary aggregates. One of the outstanding characteristics of these aggregates is that they are themselves highly disperse systems. If their degree of dispersion falls into the colloidal range, they are termed *primary colloidal particles*, according to the nomenclature of R. Zsigmondy[1] and W. Mecklenburg.[2] Primary colloidal particles may be defined as submicroscopic particles exhibiting only discrete discontinuities. It can also be said that they consist only of highly difform building elements. If such primary colloidal particles associate without losing their individuality, *colloidal aggregates* are formed. As long as the size of such aggregates is still of colloidal dimension, we speak of *colloidal secondary particles*. However, if the size of the aggregates surpasses the colloidal range, we refer to them, depending on their physical properties and morphological characteristics, as gels (lyogels, xerogels, coagels), or jellies. Such aggregates either can be formed by coagulation of highly disperse or colloidally disperse systems (true solutions or sols), as has been discussed, or they may be already preformed in nature. The group of the macromolecules or eucolloids represent such natural coarse colloidal aggregates. An explanation of the internal structure of these aggregates and of the forces acting between the primary colloidal particles are today the two factors that must be considered as the most important problems of modern colloid science.

[1] *Zeit. physikal. Chem.*, **98**, 14 (1921).

[2] *Zeit. anorg. allg. Chem.*, **74**, 262 (1912).

THE STRUCTURE OF THE COLLOIDAL AGGREGATE

The structure of the colloidal aggregate is mainly determined by:

1. The degree of dispersion or size of the primary particle.
2. Its shape, or geometric form.
3. The spatial distribution of the primary particles.

The last can also be expressed in terms of packing and density. The size of the primary colloidal particles or the particle-size distribution in the system is important in so far as it permits a differentiation between monodisperse and polydisperse aggregates.[1] The size of the particles determines the specific surface of the system and, in connection with the shape, also the magnitude of the inner voids of the system, or the "intermicellar space."

The geometric form is of importance, as it controls largely the physical and physicochemical properties of the system.

It seems advisable to discuss first the different postulated theories in regard to the spatial arrangement of the primary colloidal particles in the colloidal aggregates, *i.e.*, the prevailing theories of gel structure and our present assumption of the forces acting between the colloidal particles, before attempting to sketch the most probable further development in this field.

In the case of a sol, we are dealing with a system in which sterically as well as dynamically independent particles are dispersed throughout a fluid. Upon the addition of a coagulator (used in the broadest sense), these particles lose their dynamic independence and adhere to each other. This phenomenon can be explained either by the fact that the addition of such a coagulator or corresponding change of the original system produces an attraction between the particles, which originally was not there, or by the fact that originally existing repelling forces have been reduced or, finally, by the fact that an increased concentration of electrolyte in the dispersion medium has so strengthened the ionic bonds in the liquid that the dispersed particles are pushed together and eliminated (see page 169). Such an assumption naturally involves the possibility that originally both types of

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[1] Monodisperse aggregates are made up out of primary particles of uniform size, whereas polydisperse aggregates are built from primary particles of varying sizes.

forces existed, the repelling forces overbalancing the existing attraction between the individual particles. On the basis of what has been discussed in the chapter dealing with the electrokinetic properties of colloidal systems, it becomes evident not only that such forces depend on the composition of the disperse part but that the composition of the dispersion medium as well as its affinity for the disperse part is equally important. Whereas molecular cohesion forces are governed exclusively by the constitution, size, and shape of the disperse part and therefore are independent of the type of the dispersion medium, the repulsion forces can be caused by different factors. They can be ionic (electrical nature) in the case of watery dispersions, primarily as a result of the formation of diffuse double layers. In cases where the dispersion medium is of typical apolar character, repulsion can be the result of particle solvation, etc.

INFLUENCE OF PARTICLE SHAPE

Besides shape and size of the individual particles, the intermicellar forces seem to play an important part in gel structure which makes it advisable to subdivide the problem into three groups, depending on the form of the colloidal particles (corpuscular, laminar, and fibrillar). In the case of corpuscular particles, one may assume that those with the most symmetrical field of force, *i.e.*, spherical particles, will yield the most dense aggregates. They also should yield isodimensional macroscopic forms. This should be independent of the questions whether the aggregated particles actually touch each other, as is true in xerogels (see page 162), or are still separated from each other by films of the dispersion medium (lyogels, see page 162).

Polyhedral particles generally give loose structures. The structure of gels made up out of polyhedral-shaped particles will be loose in proportion to the strength of adhesion between the particles. This apparent paradox calls for more detailed explanation.

ADHESION NUMBER AND ADHESION ANGLE

A. von Buzágh[1] carried out highly interesting research, which has considerably clarified this point, by studying the adhesion of

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[1] *Koll. Zeit.*, **47**, 370 (1929); **51**, 105, 230 (1930); **52**, 46 (1930); **76**, 2 (1936); **83**, 279 (1938); **84**, 16 (1938). *Koll. Beih.*, **32**, 114 (1930).

microscopic particles to walls consisting of the same material. He applied two methods for his studies. They are today generally known as the *adhesion-number* and the *adhesion-angle* methods. In the first method, the particles of a *polydisperse* suspension are allowed to settle out on the base plate of an appropriate container, the plate being of the same substance as the disperse phase of the system. The concentration of the dispersion is so selected that the number of particles which sediment on the base plate can be easily counted; *i.e.*, the sediment forms a single layer. The vessel is now turned upside down, and the particles that then still adhere to the former base plate are counted. The adhesion number is simply the percentage of the particles adhering to the base plate after the container has been overturned. The result of a great number of such experiments proved that, all other conditions being equal, the medium-sized particles of a polydisperse system will adhere to the base plate, the largest and smallest ones dropping off. The reason for this can be explained by assuming that the influence of gravity overcompensates adhesion forces in the case of the large particles and that in the case of the smallest particles it is the increasing influence of the thermal motion that takes them out of the zone of influence of the adhesion forces of the base plate.

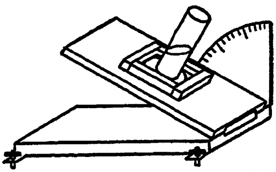

FIG. 89.—A. von Buzágh's apparatus for determining the angle of adhesion.

Where the method of measuring the adhesion angle is applied, the polished base plate of the vessel containing the suspension is placed on a platform that can be tilted to any desired angle (see Fig. 89). At an angle characteristic for the system under observation, known as the *angle of adhesion*, the particles begin to slide down.

On the basis of a large number of experimental data, v. Buzágh was able to calculate approximately the adhesion forces (see Appendix, page 244). His calculations indicate that the particles do not actually touch the wall but are separated from it by a film of the dispersion medium. It has also been observed that small particles seemingly adhering to the plate are nevertheless in vivid Brownian motion. They perform a two-dimensional movement, *i.e.*, are not able to move out of the plane into which they originally sedimented. A film of liquid of appreciable thickness (many molecular dimensions) prevents direct contact with the base plate. The attraction force that the base plate exercises on the individual particles prevents them from increasing their distance from it, unless a molecular impact of sufficient kinetic energy strikes them and pushes them out.

TACTOSOLS AND TACTOIDS

These facts prove undoubtedly that far-reaching forces which exceed molecular attraction forces must be present between particles and wall. Such far-reaching forces also explain H. Zocher[1] and K. Jacobsohn's investigations on the so-called tacto sols and tactoids, as well as Wo. Ostwald and W. Haller's[2] and A. v. Buzágh's[3] studies on the sedimentation volumes of coarse dispersions. H. Zocher observed an extremely regular layer-like orientation of the anisodimensional sol particles in aged samples of ferric hydroxide,[4] tungstic oxide, and vanadium pentoxide sols. He termed such sols *tactosols;* and the patches made up out of the parallel-oriented colloidal particles, *tactoids*. The interesting fact is that the distance between such layers is absolutely regular, so that interference colors are produced by the reflected light (iridescent layers). Distances of 200 to 400 mμ have been observed. Zocher and his coworkers were furthermore able to prove that the distance between these layers can be varied by the addition of electrolytes. If an electrolyte is added which will cause a reduction of the repelling forces, then the layers will move closer together. So far there seems to be no other satisfactory explanation than the assumption of far-reaching attraction forces and varying repulsion between the particles.[5]

SEDIMENTATION VOLUME

Similar conclusions can be drawn from the foregoing studies in regard to sedimentation volume. v. Buzágh demonstrated, for

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[1] *Koll. Zeit.*, **41**, 220 (1927); *Koll. Beih.* **28**, 167 (1929).

[2] *Koll. Beih.*, **29**, 354 (1929).

[3] *Ibid.*, **32**, 114 (1930); *Koll. Zeit.*, **79**, 156 (1937).

[4] See also K. COPER and H. FREUNDLICH, *Trans. Faraday Soc.*, **33**, 348 (1937).

[5] See also the recent contribution by M. A. LAUFFER on the optical properties of solutions of tobacco mosaic virus protein, *J. Phys. Chem.*, **42**, 935 (1938).

example, that very thin glass disks will sediment from a sufficiently dilute aqueous suspension in such a way that a film of about 300 mμ in thickness will separate the particles from each other in the sediment. The presence of water films of appreciable thickness separating the particles in stable clay pastes has been pointed out by F. H. Norton.[1] In the condition of best workability, F. H. Norton and F. B. Hodgdon[2] found water-film thicknesses varying with different types of clay from 2.1 to $3.3 \cdot 10^3$ Å. H. Freundlich[3] calculates the distance between particles in a solid sodium-bentonite suspension to be 120 mμ. That such liquid layers are not necessarily limited to systems with a watery dispersion medium has been shown in the case of kaolin suspended in carbon tetrachloride. A calculation of the sedimentation volume has demonstrated that the particles are separated by liquid layers of appreciable thickness.

As was previously pointed out, we may assume that the cohesion of the particles cannot be accounted for by a single cause. One of them, the attraction, is the direct mass action of neighboring particles and originates in the liquid layer covering the surface of the wall, or surrounding the particle. This layer consists of molecules of the dispersing medium as well as ions of the solute. As we have mentioned, the adsorption layer built up from molecules of the pure dispersion medium is known as the lyosphere. In the case of a solute's being present, its adsorbed ions are held in this lyosphere and form an electrical double layer. Lyosphere plus electrical double layer makes what is known as the solvated layer. This must be considered of diffuse nature, since there is a continuous transition between the particle surrounded by the solvated layer and the free dispersion medium. The solvated layer prevents adhesion of particles, partly owing to its internal friction, partly to the production of Coulomb repulsion forces. The first resistance is more of a mechanical nature; the second, more electrical.

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[1] *J. Am. Ceram. Soc.*, **16**, 86 (1933).

[2] *Ibid.*, **15**, 191 (1932).

[3] *Koll. Zeit.*, **46**, 295 (1928). For detailed discussions and further references, see, *e.g.*, R. Houwink, "Elasticity, Plasticity and Structure of Matter," pp. 333*ff.*, Cambridge University Press, England, 1937. K. Endell, W. Loos, M. Meischeider, and V. Berg, *Degebo Veröffentlichung*, Heft 5 (1938). E. A. Hauser and C. E. Reed, *J. Phys. Chem.*, **41**, 911 (1937). E. A. Hauser and D. S. le Beau, *ibid.*, **42**, 961 (1938).

LYOSPHERES

On the basis of such an assumption, two particles of a stable dispersion are prevented from getting into close contact, since stability calls for a thick solvated layer or at least an appreciable lyosphere. If particles possess a high kinetic energy, because of either sufficient size or high velocity, the solvated layers or lyospheres will be difformed. This will result in coalescence of the solvated layers, and a new arrangement is formed with less free energy. Such deduction offers a simple explanation for the reason why the specific adhesion is the greater the larger the particles. The heavier particle will difform the solvated layer to a large extent and therefore come in closer contact with the wall. Furthermore, this theory offers an explanation as to why the adhesion of anisodimensional particles is, as a rule, stronger than that of spherical particles. The surfaces facing each other are larger in the former case.

If particles lose their electric charge or are deprived of their lyosphere, they may come into actual contact with each other. In such an instance, the binding forces will become predominant.

FACTORS INFLUENCING SEDIMENTATION VOLUMES

These deductions also permit a simple explanation for the differences in sedimentation volumes obtained by different methods of precipitation and throw some light on the changes that a colloidal system undergoes when transformed from a sol to a gel.

If we allow particles of an anisodimensional suspension to settle out of their own accord, they will tend to pack themselves in such a way that a sediment of minimum free energy results. This means that they line up with their large surfaces lying opposite to each other. The unchanged solvated layers or lyospheres will thereby act like a lubricant, permitting the particles to slide over each other until they have found their proper location. If, with increasing sedimentation, the solvated layers of the first settled particles are distorted, because of pressure exerted upon them, this can end only in making the packing somewhat denser. However, if the particles (by addition of an appropriate substance) are suddenly deprived of their repelling "coat," they will coalesce or cohere to each other in a random arrangement. This must result in a comparatively loose packing or a large volume of sedimentation (Fig. 90).

However, these differences will not only show up in variations of sedimentation volume and retention of dispersion medium, but they will also materially influence the mechanical properties of the formed aggregates. Although it may seem somewhat paradoxical, it follows none the less from the foregoing discussion that the formed aggregates will be the looser the stronger the spontaneous adhesion between the particles at the moment of their formation. This explains why such aggregates as dried coagula of metallic sols show little mechanical strength and exhibit brittleness and friability.

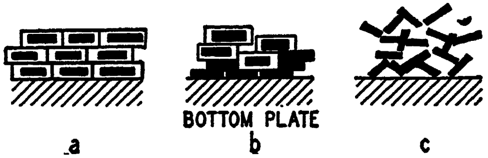

Fig. 90.—Sedimentation volumes. *a*, free (unhindered) sedimentation; *b*, distortion of lyosphere due to pressure (close packing); *c*, loose packing due to coagulation prior to sedimentation.

If we accept the undeniable fact that nature is the most economical chemist and engineer in that it always tends to form systems with a minimum of free energy, the reason for structures like cellulose, silk, and cotton wool becomes readily understandable. In all these cases, the highly anisodimensional building units (mostly formed by primary valency linkage) will be oriented and deposited with their long axes parallel to each other (see discussion on fiber structures, pages 253*ff*). However, in the case of a sol-gel transformation and especially when this transition is very rapid (rapid discharge or dehydration), rod-shaped or laminar particles may adhere only to each other at random points and thus form an open-textured loose network.

GELATION AND GEL STRUCTURES

It has been an accepted theory for a long time that gels formed by the addition of a coagulant are the result of the particle's approaching each other to such an extent that the lyospheres intersect each other. Instead of obtaining this result by introducing a coagulant or the like, an increase in concentration of the disperse part must result in a similar effect. The dispersion medium in such instances remains an integral part of the aggregate.[1] It is assumed that the liquid constituent in such structures, which are known as lyogels, is chiefly retained by lyosorption. Instead of forming densely packed aggregates, which after losing the liquid constituent are known as xerogels (see Fig. 76), the sol particles may combine in a more open structure, as we have already mentioned. This structure can consist either of thin walls or of threads (spongoid or reticular structure). Thus we can form so-called capillary gels (Fig. 91). The liquid in such gels is retained, according to the theory, by lyosorption, capillary action, or simple mechanical occlusion. Such systems exhibit feeble liquid retention. Instead of single particles' being responsible for the formation of the gel skeleton, one may also consider the possibility of a honeycomb or network structure produced by an association of the particles in fibrillar or laminar formation (see Fig. 92). If we are dealing with extremely long primary aggregates or if, upon drying of such a gel, the individual particles are combined by primary linkages, we have a honeycomb gel whose walls are of massive construction. We can compare these xerogels with solid foams, or *spumoid* systems.


FIG. 91.—Capillary gel.

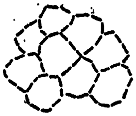
FIG. 92.—Network gel structure.

O. Bütschli[2] postulated that gels are composed essentially of two liquids, one mobile and the other tenacious. These liquids are evenly intermixed in the sol condition but separate upon gelation to form a honeycomb structure. The idea found some support in the studies of W. B. Hardy,[3] who discovered that the gelation of the system, gelatin—alcohol—water, is preceded by

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[1] See I. D. JONES and R. A. GORTNER, *Coll. Symp. Monogr.*, **9**, 387 (1931), for a differentiation between free and bound water. E. HATSCHEK, *Proc. Roy. Soc.*, **A163**, 327, 330 (1937).

[2] "Untersuchungen über die Mikrostruktur künstlicher und natürlicher Kieselsäuregallerten," Engelmann, Heidelberg, 1900.

[3] *Zeit. physikal. Chem.*, **33**, 326 (1900).

the formation of a two-phase liquid system. However, this theory cannot offer an explanation for gels of liquid-solid systems.

The theory that has obtained the greatest amount of attention is unquestionably the micellar one, which assumes the formation of a network structure by the interlacing of threadlike aggregates. However, such a theory makes it difficult to explain cases of gelation in systems where the ultimate particles themselves are not definitely anisodimensional. For example, we know that the individual particles of rubber latex, although egg-shaped rather than spherical, cannot be considered as laminar or fibrillar systems but that if coagulated by the addition of small quantities of electrolyte they will line up in pearl-string formation. This finally results in a threadlike network.[1] Francis L. Usher[2] offered an explanation for this phenomenon based on microscopic observations of the coagulation of microscopically visible particles. According to his point of view, a particle coming in contact with a doublet, *i.e.*, two particles surrounded by a coalesced solvated layer, will attach itself only to one, thus forming a pearl-string arrangement. The reason for this, according to theory, is that the approaching particle has to overcome the residual force of only one particle instead of two, which it would have to if it tried to attach itself in a middle position (Fig. 93). This author assumes that all gels are formed by such a mechanism. Cases where microscopic or even ultramicroscopic observations were unable to demonstrate the existence of such strings are explained by the assumption that the gel-forming structure is made up of particles too small to become detectable even with the best microscopic equipment.

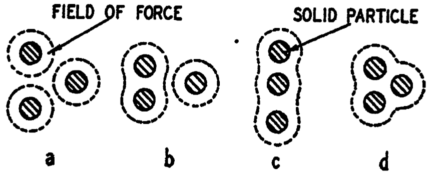

FIG. 93.—Formation of pearl-string aggregates. *a*, separate particles; *b*, joining of two particles and coalescence of their lyospheres; *c*, probable chain formation; *d*, improbable arrangement.

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[1] See, *e.g.*, V. HENRI, *Compt. rend.*, **144**, 432 (1907); his contribution (illustrated) in L. MORISSE, "Le Latex," Augustin Challamel, Paris, 1908.

[2] *Proc. Roy. Soc.*, *A* **125**, 143 (1929).

Most gelation theories were ably summarized by Wo. Ostwald,[1] who offered the following general definition: *Gels are systems of various composition (liquid + liquid, solid + liquid, liquid + solid) containing a large amount of liquid and of varying, mostly colloidal, degree of dispersion. Their structural elements subdivide the entire system by mechanical linkage (intermicellar forces), coalescence, or uniformly arranged distribution in such a way that the greater part of the liquid is subdivided into lyospheres.*

Thixotropy.—In 1923, A. Szegvari and E. Schalek[2] noticed that an iron oxide sol of high concentration will set to a gel upon the addition of an electrolyte. This gel can be reconverted into a sol simply by shaking, and the procedure repeated indefinitely.

This phenomenon was termed *thixotropy,* according to a suggestion made by T. Peterfi,[3] who had previously observed the same phenomenon in cell protoplasma. H. Freundlich and H. A. Abramson[4] assume that thixotropy is also evident in gelatin, since the viscosity of a gelatin solution increases after standing and upon agitation of such a solution decreases again until it reaches a minimum value. Similar effects have also been observed in oil paints, which are known to thicken upon standing. As pointed out by Pryce-Jones,[5] it seems questionable whether such phenomena as observed in paints are actually the result of thixotropic behavior or caused by other changes in the system. To differentiate from true thixotropy, Pryce-Jones calls such cases "false body systems." It is the opinion of the author that the changes in viscosity of the gelatin solutions are also due to other factors, *e.g.*, reduction of the thickness of the lyospheres due to shear. H. Freundlich,[6] R. K. Schofield and B. A. Keen,[7] and A. v. Buzágh[8] have reported that pronounced thixotropy can be found even in such coarse disperse systems as clay and bentonite

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[1] *Koll. Zeit.*, **46**, 248 (1928).

[2] *Ibid.*, **32**, 318 (1923); **33**, 326 (1923).

[3] *Archiv Entwicklungsmech. Organ.*, **112**, 660 (1927). The term is derived from the Greek words θίξις (*thixis*) meaning the touch, and τρέπω (*trepo*), meaning to change.

[4] *Zeit. physikal Chem.*, **128**, 25 (1927); **131**, 278 (1927); **133**, 51 (1928).

[5] *J. Oil Color Chem. Ass.*, **19**, 295 (1936).

[6] *Koll. Zeit.*, **46**, 290 (1928).

[7] *Nature*, **123**, 492 (1929).

[8] *Koll. Zeit.*, **47**, 223 (1929).

suspensions.[1] It has been ascertained that thixotropy occurs only upon the addition of electrolyte in a limited range of concentrations and that the addition of excessive amounts results in the formation of an irreversible coagulum, or of flocks that can no longer be redispersed. Very careful ultramicroscopic observations[2] of dilute thixotropic systems have demonstrated that at first the translatory component of the Brownian molecular motion comes to a standstill and that upon complete solidification of the system the rotary component also ceases.

As long as one dealt with polydisperse systems, it was difficult to make any accurate statement on the existence or nonexistence of a definite particle arrangement upon gelation. The production of thixotropic systems, which to all intents and purposes could be considered as monodisperse, must be judged as a great step forward toward better understanding of this phenomenon.[3] A systematic study of such monodisperse fractions of varying particle size not only revealed that no definite alignment is observable in the ultramicroscope but that, contrary to former belief, the strength of thixotropic gels increases with decreasing particle size. This has permitted, at least in the case of bentonite dispersions, the production of highly thixotropic gels at concentrations well below 1 per cent.[4]

It has now been definitely ascertained that in truly thixotropic systems of highly disperse bentonite fractions, no definite geometrical alignment of particles is detectable. The particles that have ceased to move seem to be clearly separated from each other. Since the dispersions have been obtained by careful multiple fractionation, the argument cannot now be upheld that invisible particles form the actual gel structure. The acceptance of far-reaching attraction forces, coupled with appropriate

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[1] Bentonite (montmorillonite) in pure form does not contain particles larger than approximately 200 mμ. The larger particles present are impurities like quartz and feldspar and do not contribute at all to the thixotropic effect of such a system. True thixotropy seems definitely to be limited to systems containing a sufficient amount of truly colloidal particles.

[2] See, *e.g.*, E. A. Hauser, *Koll. Zeit.*, **48**, 57 (1929). E. A. Hauser and C. E. Reed, *J. Phys. Chem.*, **40**, 1169 (1936). E. A. Hauser and D. S. le Beau, *ibid.*, **42**, 961 (1938).

[3] See E. A. Hauser and C. E. Reed, *J. Phys. Chem.*, **40**, 1169 (1936).

[4] *Ibid.*, **41**, 911 (1937).

repulsion forces or the existence of strong bonds between the ions of the electrolyte in the dispersion medium, seems at present the only basis for a theoretical interpretation of this extremely important case of isothermal sol-gel transformation. H. Freundlich,[1] in collaboration with J. Rubin, has attempted to calculate the potential energy of the repulsion and attraction forces between two colloidal particles, in a system containing various concentrations of electrolyte, as a function of the distance separating them (Fig. 94). The dotted lines are the result of adding the values of the potential energies (repulsion plus attraction). We see that in curves 1 and 2, stable sols must prevail, since the curves demonstrate increasing repulsion with decreasing distance. However, curve 3 shows a definite minimum, and curve 4 demonstrates the predominance of the attraction forces over the entire range.[2]

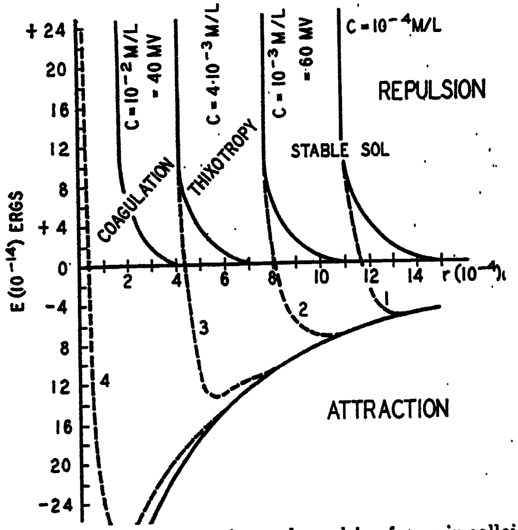

FIG. 94.—Potential energies of attraction and repulsion forces in colloidal systems.

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[1] "Thixotropy," No. 267 of "Actualités scientifiques et industrielles," Hermann, & Cie, Paris, 1935. This booklet, written in English, is the most up-to-date *summary* in regard to our knowledge of the phenomenon of thixotropy. See also W. HELLER and G. QUIMPE, *Compt. rend.*, **205**, 857 (1937). H. FREUNDLICH and D. W. GILLINGS, *J. Chem. Soc.*, 546 (1938). W. HELLER and E. VASSY, *Compt. rend.*, **207**, 157 (1938).

[2] The calculations are based on particles of 4 μ in diameter.

In the first case, the characteristic minimum represents an equilibrium condition at a given distance of the particles from each other. This corresponds to the formation of a thixotropic gel. Curve 4 denotes an entirely unstable, or coagulated, system. According to this point of view, thixotropy must be considered as an intermediate, highly labile system on its way from perfect stability to coagulation. Yet this point of view cannot completely satisfy more recent results obtained in the study of well-defined thixotropic systems.

The Application of Potential Curves.—A more detailed study of the van der Waals-London theory and its applicability to various colloidal phenomena, such as stability, differentiation between lyophilic and lyophobic colloids from one general point of view, gelation, thixotropy, and coagulation, has recently been reported by C. Hamaker.[1] He also applies potential curves representing the energy of two particles plus their surrounding fluid as a function of the distance between such particles. In Fig. 95*a*, we see such a set of potential curves. *R* represents the repulsive energy which rises when the particles approach each other. *A* represents the energy of attraction which decreases with the distance separating the particles. (The reason for the steep rise of the curve to the left of the vertical axis is that the strong elastic forces prevent the particles from actually penetrating each other).

If attraction and repulsion act simultaneously, as is usually the case, then a sum of the curves *A* and *R* would give us a picture of the total-energy variation in the system, and it is the *total* energy that governs the system's mechanics. The curves *R* and *A*, as shown, therefore, can also be taken to represent extreme cases of *total* potential curves. The curve *R* would then represent a system wherein repulsion is predominant; the curve *A*, a case where attraction is outstandingly important.

If the sol undergoes some change by which the total potential curve is displaced from *R* to *R′* or from *A* to *A′*, this change will not show up in any alteration of particle arrangement, since these sols would be either stable or flocculated continually. To realize the possibilities lying in between these extremes, we need only

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[1] *Rec. trav. chim. Pay-Bas*, **55**, 1015 (1936); **56**, 3, 727 (1937); **57**, 61 (1938). *Physica*, **4**, 1058 (1937). "Symposium on Hydrophobic Colloids," p. 16, Utrecht, 1937. See also R. Houwink, *op. cit.*, pp. 340*ff.*

study systems where a curve of type *R* is gradually transferred into one of type *A*. Figure 95*b* gives us such a set of possibilities. The intermediate curves refer to systems where the attractive forces are predominant at large distances, the repulsion becoming more pronounced when the particles are close together.

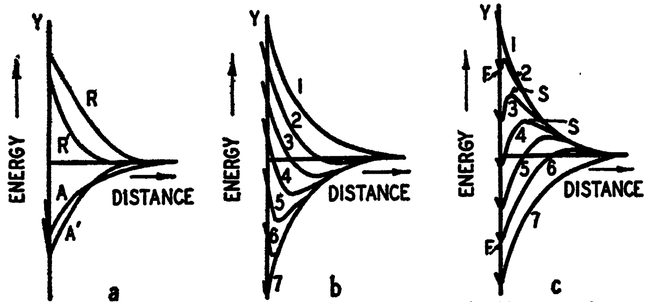

FIG. 95.—Different types of energy-potential curves. *A*, *A'*, attractive energy; *R*, *R'*, repulsive energy; *F*, energy-potential minima.

Therefore, Fig. 95*b* explains a transition in which attraction gains more and more and repulsion loses in influence. Figure 95*c* shows the exact reverse and should be equally possible.

A further logical deduction which can be drawn now is that the systems defined in Figs. 95*b* and 95*c* are not absolutely separate but that cases must exist that connect the potential curves of these two figures. To simplify, we can now construct the different curves in Figs. 95*b* and 95*c* by adding the partial energies due to a repulsion and attraction. In Figures 96*a* and 96*b*, curve *R* represents again the repulsive energy; and curve *A*, the attractive one—however, this time with positive sign. The total energy *T*, in which we are mainly interested, can now be obtained by subtracting curve *A* from *R*. We see that the

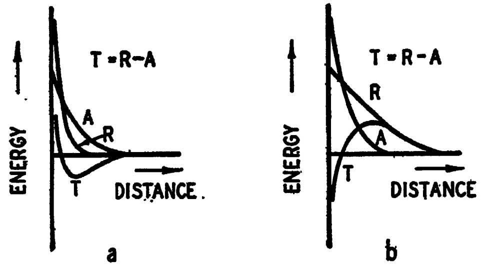

FIG. 96.—The computation of total-energy-potential curves.

curve T, in Figs. 96*a* and 96*b*, corresponds to the shape of the intermediate curves in Figs. 95*a* and 95*b*, respectively. Now, if we again gradually transform Fig. 96*a* into Fig. 96*b*, we must pass a stage at which the respective curves R and A intersect twice. This is shown in Fig. 97, and we find there that the total-potential curve now shows a new minimum at a large distance, combined with a pronounced maximum at a shorter distance, or a maximum at a large distance combined with a minimum at a comparatively short distance. Figures 98*a* and 98*b* give us another series of curves based on these deductions and lying intermediate between Figs. 95*b* and 95*c*.

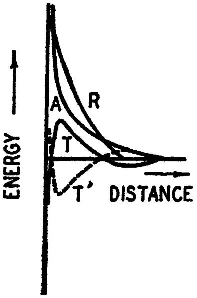

FIG. 97.—Special cases of potential-energy curves. T, T', total energy.

This set of curves shows that a colloidal system will behave differently, depending on the type of total-potential curves by which it is represented. For example, if we consider a sol, which is represented by Fig. 95*c*, and reduce the influence of the repulsive force, either by the addition of electrolyte or by decreasing hydration, we shall decrease the stability of this sol. The system will show itself in a curve of a higher number. As long as the maximum in the potential curve is sufficiently pronounced, the sol will remain stable. If this maximum is reduced to an extent comparable to the kinetic energy of the Brownian motion, then colliding particles will have sufficient energy to surpass the residual maximum and drop right into the minimum when they can no longer separate. This scheme brings out a point that so far has been insufficiently considered, *viz.*, the existence of a

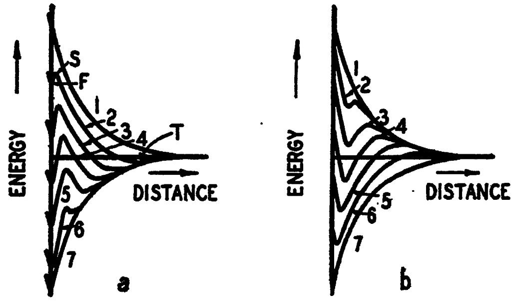

FIG. 98.—Intermediate potential-energy curves.

sharp limit at which flocculation must become observable. If this point has once been reached, further addition of electrolyte, etc., must result in a rapid increase in the rate of coagulation.

Now, when we consider Fig. 95*b* and again move from the lower numbers of the curves to the higher ones, we can immediately see that the answer is tied up with the concentration of the sol. If the average distance between the particles in the final concentration is not more than their distance at minimum energy, the mass will solidify into a true gel. It must be remarked here that the state of minimum energy is actually reached only when the available fluid is homogeneously distributed throughout the whole mass. Even if we are dealing with a system where the average distance between particles is slightly higher than the minimum called for, we can still conceive of gel formation, *since it is the shortest distance between neighboring particles, which is fixed* by the minimum in the potential curve. In such circumstances, a gel will not be stable but will reorient itself on storage to produce a system of minimum total energy. This can be done only by forming a higher particle density and expelling the corresponding amount of fluid. This phenomenon is known as "synaeresis."

If the distance of the particles in comparison to the minimum energy is large, we might assume the preferential formation of individual flocks (coacervation).

The phenomenon of the isothermal sol-gel transformation (thixotropy) finds no completely satisfactory answer if systems corresponding to curves 95*b* and 95*c* are taken into consideration, because neither of these curves explains the ease of such transformation. However, Fig. 98*a* is in full accord with the experimental findings. In this set of curves, two minima F and T develop simultaneously, being separated by an energy maximum. As long as this maximum is high enough, as already mentioned, the minimum F is of no significance. Such a system will exhibit normal gel formation and thixotropy, due to the minimum T. But if we reduce S too far, then the gel will change at a clearly definable point into a coagulated system.

As already pointed out, this newly advanced theory must be taken as a further development of the van der Waals-London-Kalmann theory. It therefore considers the attraction between particles as of predominant importance and offers new concepts which permit the assumption that these forces are far reaching.

However, it does not consider the influence of the electrolyte in the dispersion medium and the electrolyte activity.[1]

This results in the fact that the calculated possible distances between the particles in a gel are still decidedly smaller than those actually found although admittedly beyond molecular distances.[2] If, however, one considers the influence of the dispersion medium and its electrolyte concentration, one obtains figures that are at least of the same order of magnitude as those found experimentally.

According to the latest theoretical concepts,[3] which check with the authors' experimental data, one may assume that gelation occurs when the kinetic energy kT of neighboring particles is of the same order of magnitude as the electrostatic potential energy of particles at an average distance. If, for example, a particle is negatively charged, it is surrounded by a large number of positive ions. Their potential energy is large compared to kT. These ions are bound ions, which reduce the effective charge of the particle. However, we must also consider those ions of equal sign which are sufficiently far from the particle so that their energies are not large compared to kT. Their distribution is given by the Debye-Hückel theory, and the forces of repulsion between the negatively charged particles, if calculated on this assumption, result in distances in accord with the experimental evidence. Whatever the final conclusion, it cannot be denied that the introduction of energy-potential curves must be considered a very important step forward in the final attempt to offer a comprehensive explanation of the phenomenon of gelation.

If we bear in mind the fact that repulsion not only can be caused by electric double layers formed through the interaction of disperse phase and the solute present in the dispersion medium but also can be due to electric repulsion caused by the interpenetration of the diffuse ionic atmosphere and to the presence of lyospheres, this newly advanced concept seems to explain satisfactorily all the data so far experimentally obtained. If such an interpretation is accepted, the necessity of assuming the

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[1] For a summary of our present point of view, see Wo. OSTWALD, contribution in *J. Phys. Chem.*, **42**, 981 (1938).

[2] C. HAMAKER, *Rec. trav. chim. Pays-Bas*, **57**, 61 (1938).

[3] R. HOUWINK, "Second Report on Viscosity and Plasticity," Chap. 4, pp. 233–237, Nordermann Publishing Co., New York, 1938; I. LANGMUIR, *J. Chem. Phys.*, **6**, 873 (1938).

presence of thread or pearl-stringlike arrangements becomes of secondary importance. In a recent contribution by E. A. Hauser[1] and D. S. le Beau it is shown that, upon careful evaporation of bentonite dispersions containing extremely fine particles, gelation occurs at a certain concentration without any specific geometrical alignment of the particles. However, on further concentration, resulting in the formation of coherent self-supporting solid films, one observes the formation of distinct filaments as a result of the particles lining up in this preferential form.

This phenomenon demonstrates that the presence of threadlike aggregates or filamentous structures is not essential for gelation.[2] Although such a structure might facilitate gelation, it has so far never been actually proved. The existence of interlacing molecular threads in gelatin, rubber, etc., is only an assumption.[3] However, the observable fact that the individual clay particles present in random orientation but in a high degree of regularity of spacing in the gel state align upon further dessication, seems to point to a basic law in coherent film structure. Coherent self-supporting films can be produced only if the film-forming substances possess long chain molecules or are capable of polymerization or condensation in chainlike fashion or if the individual micelles will preferentially align to form filaments if brought sufficiently close to each other.

In concluding, a phenomenon recently discovered by H. Freundlich and F. Juliusburger[4] may be briefly discussed. An aged concentrated vanadium pentoxide sol was made thixotropic so that it set to a gel in about 60 minutes. However, if the container was rolled between the palms of the hands or gently tapped, it solidified in about 15 seconds. Since then, this phenomenon has been observed by Freundlich and his collaborators in several other concentrated sols of highly anisometric particles. E. A. Hauser and C. E. Reed[5] were able to produce the same phenome-

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[1] *J. Phys. Chem.*, **42**, 961 (1938).

[2] A similar conclusion had already been arrived at by W. B. Hardy, *Koll. Zeit.*, **46**, 268 (1928).

[3] See, *e.g.*, S. E. Sheppard and J. L. McNally, *Coll. Symp. Monogr.*, **7**, 17 (1930). S. E. Sheppard and R. E. Houk, *ibid.*, **10**, 37 (1932). F. W. Busse, *ibid.*, **10**, 14 (1932).

[4] *Trans. Faraday Soc.*, **31**, 920 (1935). F. Juliusburger and A. Pirquet, *ibid.*, **32**, 445 (1936).

[5] *J. Am. Chem. Soc.*, **58**, 1822 (1936).

non in very dilute bentonite dispersions of extremely fine particle size. This permitted an ultramicroscopic study of the phenomenon, which, according to a suggestion made by Freundlich, has been termed *rheopexy*.[1] Since this phenomenon seemingly occurs only in an extremely narrow range of electrolyte concentration, and since a distinct layer arrangement of the particles is observable, it seems probable that it is caused by a combination of thixotropy and the formation of tactoids.

Finally, attention is drawn to a phenomenon that erroneously is often mentioned as being thixotropy, although it is the direct opposite thereto. For instance, if starch granules are brought into paste form by adding just so much water as to make a barely fluid mixture, we can stir the mixture as long as we do it slowly. Increasing speed results in increasing resistance until a seemingly dry mass is obtained. This phenomenon seems to be identical with observations first made by Osborne Reynolds[2] on moist sand. He termed it *dilatancy*. It can easily be observed on an ocean beach during ebbtide. If the moist sand is trod upon, it becomes dry and hard and even develops cracks but upon release of the pressure will regain its moist appearance.

The most recent explanation is offered by H. Freundlich.[3] According to him, the system at rest must contain particles independent of each other, thus permitting them to form closely packed sediments with a low volume of sedimentation. The external force causes unequal distribution of the particles; they pile up locally, thus forming cavities in other places, which fill up with the liquid. If the external force is removed, the particles will again repel each other and take up their original place. So far, dilatancy has been reported only in systems containing more or less spherical particles. According to the hypothesis just discussed, systems with anisometric particles must also be able to exhibit this phenomenon if the proper conditions are present. The most important of these are:

1. Particles of sufficient size to permit sedimentation.
2. The particles must be absolutely independent of each other and free to move.

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[1] Derived from the Greek words *ῥέω* (reo), meaning to flow, and *πηκτός* (pectos), meaning solidified, curdled.

[2] *Phil. Mag.*, **20** (5), 469 (1885); *Nature*, **33**, 429 (1886).

[3] *Trans. Faraday Soc.*, **34**, 308 (1938).

3. The correct relation of solid to liquid must be maintained. H. Whittaker[1] has actually been able to produce such systems with monodisperse fractions of kaolin (plates) of 1 to 5μ particle diameter. If particle size is not one of the predominant factors controlling thixotropy and dilatancy, then it should be possible to control the characteristics of the disperse part (electrokinetic potential, solvation) in such a way that either one or the other effect appears. So far no experimental evidence is available to substantiate the latter assumption.

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[1] D. Sc. thesis, Massachusetts Institute of Technology, 1937.

APPENDIX

DISPLACEMENT AND DIFFUSION

The displacement ξ is closely connected with the diffusion of the disperse particles.

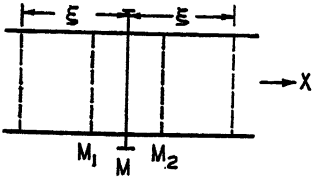

FIG. 99.—Diffusion. M, M_1, M_2, selected planes; x, direction of diffusion; ξ, displacement.

In a horizontal tube with a cross section of 1, we have diffusion in the direction of x (Fig. 99). In the time t, only those particles can pass the plane M whose distance from M is smaller than the average displacement ξ. If the concentration in the plane M_1 is c_1, then $\frac{1}{2} \cdot \xi \cdot c_1$ particles can pass M. From the other side, $\frac{1}{2} \cdot \xi \cdot c_2$ particles can pass M if their concentration in the plane M_2 is c_2. In the direction of diffusion x, therefore, $\frac{1}{2} \cdot \xi \cdot (c_1 - c_2)$ particles will pass M in the time t. If ξ is so small that we may write

$$\frac{c_2 - c_1}{\xi} = \frac{dc}{dx}$$

then the number of particles passing through M is

$$\frac{1}{2}\xi \cdot (c_1 - c_2) = -\frac{1}{2}\xi^2\frac{dc}{dx}$$

and in the time unit we have

$$-\frac{1}{2} \cdot \frac{\xi^2}{t} \cdot \frac{dc}{dx}$$

The number of particles passing through the cross section 1 per time unit is the *diffusion coefficient* D, if the concentration gradient $dc/dx = 1$.

$$D = \frac{1}{2} \cdot \frac{\xi^2}{t}$$

Since D is constant at constant temperature, we have

$$\frac{\xi^2}{t} = \text{const.}$$

The square of the average displacement is proportional to the time of observation.

COEFFICIENT OF DIFFUSION AND PARTICLE SIZE

According to A. Einstein, the coefficient of diffusion D of a molecule is inversely proportional to the frictional resistance E.

$$D = \frac{RT}{N} \cdot \frac{1}{E} \qquad (1)$$

In the case of a sphere that is moved through a liquid, we have, according to the laws of hydrodynamics:

$$E = 6\pi\eta r \qquad (2)$$

From (1) and (2) we obtain for the diffusion of a spherical particle (large in comparison to the molecules of the dispersion medium):

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r}$$

R = gas constant $8.31 \cdot 10^7$.
T = absolute temperature.
N = Avogadro's figure $60.6 \pm 0.1 \cdot 10^{22}$.
η = coefficient of viscosity of dispersion medium.
r = radius of spherical particle.

OSMOTIC PRESSURE

The osmotic pressure for true solutions can be expressed by the equation

$$p = RTc$$

R, T represent the gas constant and absolute temperature; and c, the number of molecules per liter.

In the case of colloidal dispersions, or sols, we must replace c with the expression u/N, where u represents the number of particles per unit volume; and N, Avogadro's figure.

Therefore we have as expression for the osmotic pressure in colloidal systems

$$p = \frac{RT}{N}u$$

However, this refers only to nonsolvated colloids. If the colloid splits off ions, then the osmotic pressure must be considered from the standpoint of the Donnan membrane equilibrium.

We must also consider the swelling pressure in solvated colloids. The latter can be expressed, according to H. Freundlich and Posnjak,[1] by the equation

$$P = P_0 \cdot c_g^K$$

P_0 and K are constants; c_g is the concentration of the colloid in the gel (grams dry gel in 1000 cc. gel + liquid). The constant K has been found to vary between 2 to 5.

SEDIMENTATION EQUILIBRIUM

Sedimentation is counteracted by the Brownian motion of the particles. After sufficient time has elapsed, an equilibrium of particle distribution is

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[1] H. Freundlich "Kapillarchemie," 4th ed. vol. 2, pp. 570*ff*., Akad. Verlags-Ges., Leipzig, 1932.

attained. The number of particles decreases logarithmically with height. We can apply here the same law as for changes in air pressure with height.

$$h = \frac{RT}{gM} \cdot \ln \frac{p_0}{p}$$

h = height.
R = gas constant.
T = absolute temperature.
g = gravitational acceleration.
M = molecular weight.
p_0 = pressure at zero height.
p = pressure at height h.

For our purpose we must replace M with the mass of the individual particle and substitute for the pressures the respective concentrations of particles. For spherical particles,[1] the formula can now be written:

$$h = \frac{RT}{g \cdot N \cdot \tfrac{4}{3}r^3(s - s^1)} \cdot \ln \frac{n_0}{n}$$

s = specific density of particle.
s^1 = specific density of liquid.
N = Avogadro's figure.
n_0 = concentration at zero height.
n = concentration at height h.

RATE OF SEDIMENTATION

In 1852, Stokes demonstrated that a particle settles after a short time through a liquid with constant velocity. This velocity finds its mathematical expression in the following formula:

$$v = \frac{2r^2(s - s^1)g}{9\eta}$$

r = radius of particle.
s = density of particle.
s^1 = density of liquid.
η = viscosity of liquid.
g = gravitational acceleration.

This formula does not take into account any wall effects, *i.e.*, it applies only to sedimentation without appreciable particle interference.

Particle size can be determined (assuming spheres) if s, s^1, and η are known, and v is measured experimentally.

PROBABILITY OF DISPLACEMENT

If the kinetic theory holds, then we must assume that the probability of displacement of a particle from its starting point to the left or right in a horizontal plane will be equal. Small displacements are more probable than large ones. This is expressed in Gauss's *error curve* (Fig. 100). The

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[1] The formula assumes monodisperse systems. It is also known as the "hypsometric," or "Halley's barometer," formula.

horizontal displacements are plotted as abscissas, the probability P, that a displacement between x and $(x + dx)$ is obtained, as ordinates. The probability P is expressed by the following equation:

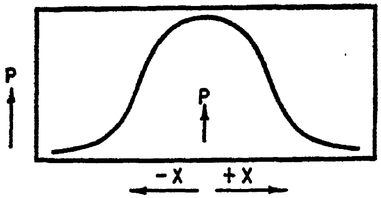

FIG. 100.—Gauss's error curve (probability of displacement). P, probability of displacement; $-x$, $+x$, actual displacements.

$$P = \frac{1}{\sqrt{2\pi\xi^2}} \cdot e^{\frac{-x^2}{2\xi^2 dx}}$$

ξ^2 represents the average of the squares of the medium horizontal displacement.

If one has observed N displacements and wants to find ΔN, which corresponds to the displacements larger than x_1 and smaller than x_2, we must multiply x with the probability and integrate between the limits of the considered displacements.

$$\Delta N = N\int_{x_1}^{x_2} \frac{1}{\sqrt{2\pi\xi^2}} \cdot e^{\frac{-x^2}{2\xi^2 dx}} *$$

Perrin and Chaudesaigues[1] proved the equation experimentally, as is shown by the following table.

Horizontal displacement x, microns, between	x (observed)	x (calculated)
0 to 1.7	48	44
1.7 to 3.4	38	40
3.4 to 5.1	36	35
5.1 to 6.8	29	28
6.8 to 8.5	16	21
8.5 to 10.2	15	15
10.2 to 11.9	8	10
11.9 to 13.6	7	5
13.6 to 15.3	4	4
15.3 to 17.0	4	2

ROTARY COMPONENT OF BROWNIAN MOTION

A. Einstein was the first who connected the displacement of a particle in Brownian motion, particle size, viscosity of dispersion medium, and time of observation in the following equation:

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* For detailed evaluation, see, *e.g.*, DE HAAS-LORENTZ, "Die Brownsche Bewegung," F. R. Vieweg, Braunschweig, 1913. R. FUERTH, "Schwankungserscheinungen in der Physik," F. R. Vieweg, Braunschweig, 1920. FREUNDLICH, *op. cit.*, vol. 1, p. 493.

[1] PERRIN-LOTTERMOSER, "Die Atome," p. 109, T. Steinkopff, Dresden, 1923.

$$\frac{\xi^2}{t} = \frac{RT}{3\pi N\eta r}\ ^{*}$$

He evaluated a similar equation for the rotary component of the Brownian motion:

$$\frac{A^2}{t} = \frac{RT}{4\pi N\eta r^3}$$

A^2 is one-third of the square of the average angle of rotation in the time t. This equation has also been experimentally proved by J. Perrin.[†]

THE HELMHOLTZ THEORY

The electric double layer can be considered in its simplest form as an electric condenser. Its potential can be expressed

$$\zeta = \frac{4\pi ed}{D}\ ^{\ddagger}$$

e = electric charge.
d = thickness of double layer.
D = dielectric constant of medium.

M. von Smoluchowski connected the electrokinetic potential with the cataphoretic rate of migration:

$$\zeta = \frac{4\pi \cdot \eta \cdot u}{H \cdot D}$$

u = rate of cataphoretic migration.
η = viscosity of dispersion medium.
H = potential gradient of electromotive force.

This formula shows no connection between migration and shape and size of particle. P. Debye and E. Hückel[§] have amended this formula by introducing a shape factor. They wrote the following expression:

$$u = C\frac{HD}{\eta}\zeta$$

For spheres, $C = \frac{1}{6}\pi$; for cylindrical particles, $C = \frac{1}{4}\pi$.

SURFACE-TENSION MEASUREMENTS[||]

The literature of surface-tension measurement contains numerous references to methods that are all more or less workable but of which few possess the desired qualities of simplicity, reliability, speed, accuracy, and pre-

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[*] For detailed evaluation see, *e.g.*, FREUNDLICH, *op. cit.*, p. 497.

[†] *Compt. rend.*, **149**, 549 (1909).

[‡] The same formula applies to Gouy's diffuse double-layer theory. d represents the fictitious thickness of the firmly attached ionic layer.

[§] *Physikal. Zeit.*, **25**, 49, 204 (1924).

[||] This section is based on the Sc. D. thesis of J. M. Andreas and W. B. Tucker, Massachusetts Institute of Technology, 1938. See also J. M. ANDREAS, E. A. HAUSER, and W. B. TUCKER, *J. phys. Chem.*, **42**, 1001 (1938).

cision. An excellent general survey made by N. E. Dorsey,[1] in 1936, lists no less than seventeen methods and points out that of these only three or four are in common use. A full discussion of each of these methods can be found in the original papers or in the more extended texts on surface chemistry. As a key to the literature it is well to read Harkins and Brown[2] on the drop-weight method, Jones and Ray[3] on capillary rise,[4] and Macy[5] on the ring method.

The analysis of the forces acting on a static pendant drop offers the most versatile method of surface-tension determination. It is very rapid, uses a sample of minimum size, gives high precision, is equally well adapted to making interfacial tension measurements, and permits the determination of surface tension at any instant after a static drop is formed, without disturbing the surface being examined. The method is therefore particularly well adapted to the study of viscous or surface-active solutions or to the study of changes in the structure of a fluid surface as that surface ages. The method is independent of the angle of contact that the liquid surface makes with the drop-forming tip.

The mathematical treatment of pendant drops is based upon two fundamental relationships: The first connects the pressure difference between the two sides of a liquid surface with its surface tension and mean curvature. The second states that when the drop is in equilibrium, the vertical forces acting across any horizontal plane are balanced.

$$p = \gamma\left(\frac{1}{R} + \frac{1}{R'}\right) \tag{1}$$

$$2\pi\, x\, \gamma \sin\phi = V\sigma g + \pi x^2 p \tag{2}$$

where p = pressure due to curvature of surface.
γ = surface tension.
R and R' = two principal radii of curvature.
x = horizontal distance from axis of rotation.
ϕ = angle between normal and axis of rotation.
V = volume of fluid hanging from plane.
σ = difference in density between two fluids.
g = acceleration of gravity.

Given an accurate profile of a drop, it is possible to calculate the surface tension of the liquid in many different ways by selecting various combinations of planes and by employing either equation (1), equation (2), or both. Experience shows that two of these methods are superior to all the others

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[1] *U. S. Bureau of Standards, Sci. Papers*, **21**, 563 (1936).

[2] *J. Am. Chem. Soc.*, **41**, 499 (1919).

[3] *Ibid.*, **59**, 187 (1937).

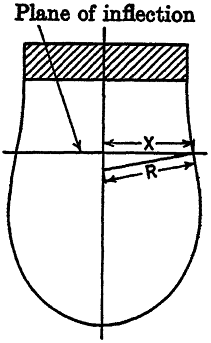
[4] The capillary-rise method is not only the most accurate but also the oldest of all known surface-tension determinations. According to C. Wolf, *Pogg. Ann. Phys.*, *Ser.* iv, **2**, 550 (1857), Libri discusses in his "Histoire des sciences mathematiques en *Italie*," vol. 3, pp. 54, Leonardo da Vinci's capillary-rise experiments.

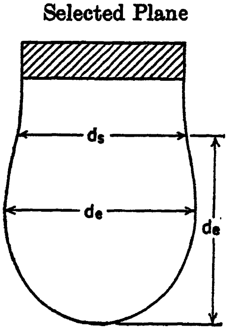
[5] *J. Chem. Educ.*, **12**, 573–576 (1935).

that have been tested. The method of the plane of inflection is described because it is straightforward and permits the calculation of surface tension from drop shape by simple theory. The method of the selected plane is given because it is the most precise and permits the routine calculation of surface tension with the least labor.

The Method of the Plane of Inflection.—A combination of equations (1) and (2) leads to the expression

$$\gamma = \frac{V\sigma g}{2\pi x \sin \phi - \pi x^2\left(\frac{1}{R} + \frac{1}{R'}\right)} \tag{3}$$





At the plane where the profile curve of the drop passes through a point of inflection, R' is infinite, and $1/R'$ is zero. Accordingly, since R is always equal to $\frac{x}{\sin \phi}$, equation (3) can be reduced to

$$\gamma = \left(\frac{g}{\pi}\right)\left(\frac{V\sigma R}{x^2}\right) \tag{4}$$

The usefulness of this method is limited by the difficulty of determining the precise location of the plane of inflection. Note that if the location of the plane is estimated too high, V will be too large, R/x will be approximately unchanged, and x will be too small. The computed value of the surface tension will therefore be too large because of an error in both V and x. These two errors will act in the same direction and will augment each other. With good apparatus and careful technique, the results obtained by this method will have a probable error of less than ±2 per cent. The measurement of a picture and the subsequent calculations should require about 15 minutes.

The Method of a Selected Plane.—The profile curves of all possible pendant drops form a two-parameter family and differ from each other in "size" and in "shape."

The size of a drop is most conveniently and precisely gauged by measuring its diameter at the equator, and the shape can be described by giving the ratio of the diameters measured at two different arbitrary planes.

If one plane is the plane of the equator, and the other is a plane whose distance from the end of the drop is equal to the equatorial diameter, the shape can be described by the ratio

$$S = \frac{d_s}{d_e} \tag{5}$$

where d_e is the diameter at the equator, and d_s is the diameter at the selected plane.

Bashforth and Adams have shown that the shape is also described by the dimensionless group

$$\beta = \frac{gb^2}{\gamma} \tag{6}$$

where b is the radius of curvature of the drop at the point where its surface cuts the axis of rotation.

Since both β and (d_e/b) are functions of the drop shape, the product

$$H = \beta\left(\frac{d_e}{b}\right)^2 \tag{7}$$

can be expressed as a function of S [see table (S vs. $1/H$)].

Equation (6) can now be solved for γ and used in conjunction with the table for determining the value of the surface tension from a photograph of a pendant drop.

$$\gamma = \frac{g\sigma b^2}{\beta} = \frac{g\sigma(d_e)^2}{\beta(d_e/b)^2} = \frac{g\sigma(d_e)^2}{H} \tag{8}$$

Equation (8) is exact and convenient to use. Its precision depends upon the accuracy with which the linear measurements are made and upon the labor expended in determining the value of H as a function of S. The method is a primary standard if H is computed from the differential equation of the surface; it is a secondary standard if H is determined by calibrating the method against drops of a pure liquid of known surface tension.

Sample Calculation

Surface Tension of a Pendant Drop by the Method of the Selected Plane

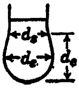
(Carbon tetrachloride in air at 25.0°C.; surface 15 seconds old)

Density of CCl_4..........	1.585 grams per cubic centimeter
Density of air............	0.001 grams per cubic centimeter
Effective density, σ........	1.584 grams per cubic centimeter
Diameter of drop at equator d_e..................	0.228 cm.
Diameter of drop at selected plane d_s................	0.224 cm.

$S = d_s/d_e = 0.224/0.228 = 0.982$

ARITHMETIC TABULATION OF *H*-*S* FUNCTION FOR PENDANT DROPS

S vs. $\frac{1}{H}$



$S=\frac{d_s}{d_e}$

$$\gamma = \frac{(\rho_1 - \rho_2)gd_e^2}{H}$$

Interpolation is unwarranted

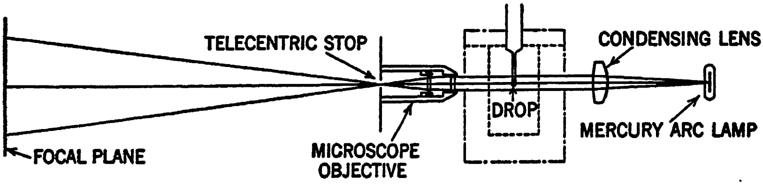
S	0	1	2	3	4	5	6	7	8	9
0.70	0.797	0.795	0.792	0.790	0.787	0.785	0.782	0.780	0.777	0.775
0.71	0.772	0.770	0.767	0.765	0.762	0.759	0.757	0.754	0.752	0.749
0.72	0.747	0.744	0.742	0.739	0.737	0.735	0.732	0.730	0.727	0.725
0.73	0.722	0.720	0.718	0.715	0.713	0.711	0.709	0.706	0.704	0.702
0.74	0.699	0.697	0.695	0.692	0.690	0.688	0.685	0.683	0.681	0.679
0.75	0.676	0.674	0.672	0.670	0.668	0.665	0.663	0.661	0.659	0.657
0.76	0.655	0.652	0.650	0.648	0.646	0.644	0.642	0.640	0.637	0.635
0.77	0.633	0.631	0.629	0.627	0.625	0.623	0.621	0.619	0.617	0.615
0.78	0.613	0.611	0.609	0.607	0.605	0.603	0.601	0.599	0.597	0.595
0.79	0.593	0.591	0.589	0.587	0.585	0.583	0.581	0.579	0.577	0.575
0.80	0.573	0.571	0.570	0.568	0.566	0.564	0.562	0.561	0.559	0.557
0.81	0.555	0.553	0.551	0.550	0.548	0.546	0.544	0.542	0.540	0.539
0.82	0.537	0.535	0.533	0.532	0.530	0.528	0.526	0.524	0.523	0.521
0.83	0.519	0.518	0.516	0.515	0.513	0.511	0.509	0.507	0.506	0.504
0.84	0.502	0.501	0.499	0.498	0.496	0.494	0.493	0.491	0.490	0.488
0.85	0.486	0.485	0.483	0.482	0.480	0.479	0.477	0.476	0.474	0.473
0.86	0.471	0.470	0.468	0.467	0.465	0.464	0.462	0.461	0.459	0.458
0.87	0.457	0.455	0.454	0.452	0.451	0.450	0.448	0.447	0.446	0.444
0.88	0.443	0.441	0.440	0.439	0.437	0.436	0.434	0.433	0.431	0.430
0.89	0.429	0.428	0.426	0.425	0.423	0.422	0.420	0.419	0.418	0.417
0.90	0.415	0.414	0.413	0.411	0.410	0.409	0.408	0.406	0.405	0.404
0.91	0.403	0.401	0.400	0.399	0.398	0.396	0.395	0.394	0.393	0.391
0.92	0.390	0.389	0.388	0.386	0.385	0.384	0.383	0.382	0.381	0.379
0.93	0.378	0.377	0.376	0.375	0.373	0.372	0.371	0.370	0.369	0.368
0.94	0.366	0.365	0.364	0.363	0.362	0.361	0.359	0.358	0.357	0.356
0.95	0.355	0.354	0.353	0.352	0.351	0.350	0.349	0.348	0.346	0.345
0.96	0.344	0.343	0.342	0.341	0.340	0.339	0.338	0.337	0.335	0.334
0.97	0.333	0.332	0.331	0.330	0.329	0.328	0.327	0.326	0.325	0.324
0.98	0.323	0.322	0.321	0.320	0.319	0.318	0.317	0.316	0.315	0.314
0.99	0.313	0.312	0.311	0.310	0.309	0.308	0.307	0.306	0.305	0.304
1.00	0.303									

From the table I, $1/H = 0.321$

$$\gamma = \frac{g\sigma(d_e)^2}{H} = (0.321)(980.4)(1.584)(0.228)^2$$
$$= 26.0 \text{ dynes per centimeter}^*$$

Experience shows that if the linear dimensions of a drop can be measured with a probable error of not more than ±0.1 per cent, this method will give values for the surface tension that have an uncertainty of about ±0.5 per cent. Measurement and calculation require about 5 minutes per picture.

Experimental Equipment.—The method of pendant drops is recommended as a general method of high precision for the measurement of either surface tension or interfacial tension. Since the method is new, and success is to a large extent dependent upon overcoming a number of experimental problems, it seems worth while to point out certain features that are essential if the apparatus is to give optimum results.



The principal parts of the optical system are a light source, condensing lens, thermostat chamber, microscope lens, telecentric stop, shutter, and photographic plate. An excellent monochromatic light source can be obtained by using a G.E., type H3, 85-watt, high-pressure, mercury-arc lamp in combination with a Wratten 77A filter. The thermostat chamber should be totally enclosed to prevent the loss of liquid by evaporation and should be capable of maintaining any desired temperature within ±0.05°C., since both solubility and surface tension change with temperature. A standard microscope objective of 48 mm. effective focal length is quite satisfactory, provided that it is fitted with a 1- or 2-mm. telecentric stop. This stop is quite necessary, since an error in perspective is introduced unless the drop is viewed by light traveling parallel to the optical axis. Glass plates are required if difficulties due to paper shrinkage are to be avoided, and their size depends upon the method by which the measurements are to be made. Plates as large as 5 by 7 inches may be required if measurements are to be made by comparison with an ordinary scale; they may be as small as 2 by 2 inches if some sort of traveling microscope can be used.

Drop-forming tips can be conveniently made by welding short lengths of 2-mm. pyrex tubing on standard 1½-cc. hypodermic syringes. Inter-

* The International Critical Tables, vol. IV, p. 447, give for the surface tension of carbon tetrachloride 26.77 ± 0.1 at 20°C. and 25.53 ± 0.1 at 30°C.

facial-tension measurements require a set of tips of different diameters if the drops are to have a convenient shape. Diameters ranging from 20 to 0.2 mm. may be required in exceptional cases, and the correct size is readily found by calculation or by trial. Rectangular cuvettes built of optically flat glass are available in a variety of shapes and sizes through the Research and Development Company of New York City.

Results.—A series of pictures which were made during the aging of a drop of soap solution is reproduced as an illustration of the sort of results that are obtainable with this method. Note that as the drop ages and its surface tension decreases, the drop becomes less spherical, and the shape parameter S increases. The density and volume of the drop remained constant throughout the period during which the pictures were made.

CHANGE OF DROP SHAPE AND SURFACE TENSION WITH AGE

0.025% SODIUM STEARATE IN WATER AT 25° C.

AGED 10 SECONDS $S=0.787$ $\gamma=71.9$ | AGED 60 SECONDS $S=0.818$ $\gamma=58.2$ | AGED 120 SECONDS $S=0.828$ $\gamma=54.4$ | AGED 1800 SECONDS $S=0.849$ $\gamma=39.2$

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THE GIBBS FORMULA

J. Willard Gibbs[1] was the first to deduce from thermodynamic principles the relationship between the effect of a dissolved substance on the surface tension of a liquid and the change in concentration in the boundary layer. He derived the following expression:

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[1] *Trans. Conn. Acad. Sci.*, **3**, 228, 391 (1876).

$$U = -\frac{c}{RT}\cdot\frac{d\sigma}{dc}$$

U = excess of substance in surface layer.
c = concentration of substance in bulk of liquid.
σ = surface tension.
R = gas constant.
T = absolute temperature.

This equation shows that a substance which reduces surface tension must concentrate in the surface and that one which increases it will migrate from the surface into the bulk of the liquid. It also explains why reduction can be appreciable; increase, however, not.

BOEDECKER'S ADSORPTION FORMULA

Gibbs and J. J. Thomson have evaluated the following principle of adsorption:

$$a = -f(T, c \cdot \cdot \cdot)\left(\frac{d\sigma}{dc}\right)\Omega$$

We have positive adsorption if the surface tension decreases with increasing concentration.

If we now combine Gibbs's equation $\left(a = -\frac{c}{RT}\cdot\frac{d\sigma}{dc}\right)$ with Freundlich's empirical formula for surface tension

$$\frac{\sigma_M - \sigma_L}{\sigma_M} = S \cdot c^{\frac{1}{n}*}$$

σM = surface tension of solvent.
σL = surface tension of solution.
S = constant.
$1/n$ = constant (approximate 0.7).

and differentiate the latter, we obtain

$$a = \alpha c^{\frac{1}{n}} = \alpha' p^{\frac{1}{n}}$$

known as the Boedecker, Wilh. Ostwald, and Freundlich empirical adsorption isotherm.

If we differentiate Szyszkowszki's[1] equation

$$\frac{\sigma_M - \sigma_L}{\sigma_M} = \beta_i \ln\left(\frac{c}{i} + 1\right)$$

(β and i are constants and, introduced into Gibbs's equation, give us

$$a = \frac{\beta c}{c + i}$$

which corresponds to Langmuir's equation.

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* For a detailed evaluation, see Freundlich, *op. cit.* pp. 82*ff.*

[1] Freundlich, *op. cit.* p. 76; see also *Zeit. physikal. Chem.*, **64**, 385 (1908).

THE ADSORPTION EQUATIONS OF WO. OSTWALD AND R. DE IZAGUIRRE

So far, all theories have entirely neglected the fact that it is not only the solute but also the solvent that is adsorbed. Wo. Ostwald and R. de Izaguirre,[1] basing their work on Boedecker's equation, have given this deficiency theoretical consideration and have derived the following equations:

1. The solvent is directly adsorbed:

$$\frac{N}{m}(c_0 - c) = kc^n(100 - c) - l(100 - c)^\alpha \cdot c$$

2. The solvent is adsorbed owing to solvation of the solute:

$$\frac{N}{m}(c_0 - c) = kc^n[100 - c(1 + s(100 - c)^\beta)]$$

3. Adsorption of the solvent is a result of both of the foregoing reactions:

$$\frac{N}{m}(c_0 - c) = kc^n[100 - c(1 + s(100 - c)^\beta)] - l(100 - c)^\alpha \cdot c$$

N = amount of solution at start in grams.
m = amount of adsorbent in grams.
c_0 = concentration of solution prior to adsorption.
c = concentration of solution after adsorption in weight per cent.
$k, l, s, n, \alpha, \beta$ = constants.

KROEKER'S EQUATION[2]

The relation between adsorbed amount and amount of adsorbent m, assuming a constant initial concentration of the substance A to be adsorbed and constant volume of solution v, is expressed in Kroeker's differential equation

$$\frac{dx}{dm} = k(A - x)$$

If it is integrated, we obtain

$$\frac{x}{m} = a = \frac{A}{m}(1 - e^{-km})$$

This has been amended by Freundlich[3] to read

$$\frac{v}{m}\ln\frac{A}{x} = \alpha\left(\frac{A}{v}\right)^{-\frac{1}{n}}$$

---

[1] *Koll. Zeit.*, **30**, 279 (1922); **32**, 57 (1923). See also A. v. Buzágh, contribution in A. Kuhn "Kolloidchemisches Taschenbuch," pp. 216*ff.*, Akad. Verlags-Ges., Leipzig, 1935.

[2] See Wo. Ostwald, *Koll. Zeit.*, **43**, 249, 268 (1927).

[3] *Op. cit.*, pp. 249*ff.*

v = volume of solution.
x = amount adsorbed by m.
$\alpha, 1/n$ = constants.

RESIDUAL VALENCY THEORIES

F. Haber[1] must be credited as the first to assume adsorption to be the result of an unsaturation of valencies of surface atoms. H. Freundlich[2] deduced that the force of adsorption must be very weak and much weaker than the influences between molecular compounds.

This concept was further elaborated by I. Langmuir.[3] He derived the following adsorption isotherm:

$$\alpha = \frac{N_0}{N} \cdot \frac{\beta\mu}{1 + \beta\mu}$$

N_0 = total number of residual valency points per square centimeter.
N = number of saturated residual valencies per square centimeter.
μ = number of mols per second of adsorbable substance that impinge on 1 sq. cm. of adsorbent.
β = constant.

Since μ must be proportional to p, we can rewrite the equation

$$\alpha = \frac{x\beta' p}{1 + \beta' p}$$

p = pressure at equilibrium.
x = a constant depending on the adsorbents.

This equation demands full saturation of the adsorbents.

GYEMANT'S CHEMICAL INTERPRETATION OF ADSORPTION

$$K = \frac{C \cdot \left(\frac{N_0}{N} - \alpha\right)}{\alpha}$$

N_0/N = molar surface density of residual valencies.
C = concentration of substance to be adsorbed in solution.
α = adsorbed amount.
$(N_0/N - \alpha)$ = molar density of area of still unsaturated residual valencies.
K = equilibrium constant.

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[1] *Zeit. Elektrochem.*, **20**, 521 (1914).

[2] *Op. cit.*, pp. 190*ff*.

[3] *J. Am. Chem. Soc.*, **40**, 1361 (1918). See also GYEMANT, "Grundzüge der Kolloidphysik," F. R. Vieweg, Braunschweig, 1925. PAULI-VALKO, "Elektrochemie der Kolloide," Julius Springer, Berlin, 1929. E. HÜCKEL, "Adsorption und Kapillarkondensation," Akad. Verlags-Ges., Leipzig, 1928. A. KUHN, "Kolloidchemisches Taschenbuch." Akad. Verlags-Ges., Leipzig, 1935.

If solved for α, this equation reads

$$\alpha = \frac{C \cdot \frac{N_0}{N}}{K + C}$$

If we now substitute x for N_0/N, β for $1/K$, and p for C, we again have

$$\alpha = \frac{x\beta p}{1 + \beta p}$$

or Langmuir's equation.

This is not surprising, since Gyemant applied the simple mass-action law to his derivation, and Langmuir's isotherm represents nothing else but the mass-action law of the surface reactions.

RATE OF COAGULATION

According to M. v. Smoluchowski,[1] the rate of coagulation is defined as the decrease in number of kinetically uniform particles present in a unit volume of sol per unit of time.

On the basis of probability calculus, he evaluated the following equation:

$$\sum v = v_1 + v_2 + v_3 + \cdots = \frac{v_0}{1 + \beta t}$$

where Σv = total amount of kinetically independent particles in a unit of volume at time t after coagulation has set in.

v_0 = number of originally present free-moving primary particles.

$v_1, v_2, v_3 \ldots$ = amount of primary, secondary, or tertiary particles present at time t.

$$\beta = 4\pi D r v_0$$

where D = coefficient of diffusion.

r = radius of the sphere of attraction.

v. Smoluchowski termed the time necessary to coagulate one-half of the original amount of particles "coagulation time" T.

$$\frac{v_0}{2} = \frac{v_0}{1 + \beta T}$$

$$T = \frac{1}{\beta} = \frac{1}{4\pi D r v_0}$$

This means that the coagulation time depends only on original concentration, coefficient of diffusion, and sphere of attraction, *i.e.*, particle size. However, such an assumption seems justifiable only if one assumes that every collision between two particles results in permanent cohesion. This will be the case only in rapid coagulation. Furthermore, the equation

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[1] *Physikal. Zeit.*, **17**, 557, 585 (1916); *Zeit. physikal. Chem.*, **92**, 129 (1917).

accounts only for coagulation of monodisperse systems. The particles must be entirely discharged. However, we know that, particularly in the case of lyophobic sols, coagulation is noticeable before the system has reached the isoelectric point, *i.e.*, before the particles are fully discharged and are still surrounded with a solvated layer. Permanent cohesion of particles will depend on their kinetic velocity and their ability to break through the still existing solvated shell and sphere of repulsion. This phenomenon is known as *slow* coagulation.[1] In the v. Smoluchowski equation, this can be expressed by inserting a correction factor ϵ, which represents the proportion of collisions leading to cohesion.

$$T = \frac{1}{\epsilon\beta} = \frac{1}{\epsilon 4\pi D r v_0}$$

With increasing electric charge and/or solvation, ϵ must decrease.

The coagulation of polydisperse systems has been evaluated by H. Müller:[2]

$$Nt + nt = \frac{N_0}{1 + \frac{t}{T_{N_0}}}\left(1 + \frac{\lambda}{(\lambda V_n + 1)\left(1 + \frac{t}{T_{N_0}}\right)^{\lambda} - 1}\right)$$

N_0 = original number of large particles.
Nt = total number of large particles at time t.
nt = total number of small particles at time t.
T_{N_0} = coagulation time of large particles.
R = radius of large particles.
r = radius of small particles.
V_n = N_0/n_0; n_0 = original number of small particles.

$$\lambda = \frac{V_r^2 + 1}{2V_r}; \qquad V_r = \frac{R}{r}$$

This theory assumes that the large particles act as center of coagulation for the smaller ones. However, it has been proved that the small particles can detach themselves again, owing to their thermal movement. This is the basis for fractional coagulation,[3] *i.e.*, the phenomenon that upon addition of small quantities of electrolyte to polydisperse systems we first coagulate only the coarse particles. One of the few known industrial applications of this phenomenon is the production of pure white crepe rubber (bridal veil, corset crepe) from rubber latex. The yellowish color of crepe rubber is caused by some oxidation of one of the components of

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[1] See H. FREUNDLICH and N. TSHIZAKA, *Koll. Zeit.*, **12**, 230 (1913) and Freundlich's book "Colloid and Capillary Chemistry," Methuen & Co., Ltd., London, 1926.

[2] *Koll. Zeit.*, **38**, 1 (1926); *Koll. Beih.*, **27**, 223 (1928).

[3] See, *e.g.*, SVEN ODÉN, "Der kolloide Schwefel," Akademische Buchdruckerei, Upsala, 1908. A. v. BUZÁGH, *Koll. Zeit.*, **51**, 105 (1930).

natural latex, which remains in the serum or attaches itself to the smaller particles if coagulation is carried out very carefully.

STOKES' LAW

$$W = 6\pi\eta r$$

W = resistance to shear.
η = viscosity coefficient.
r = radius of a spherical particle.

VISCOSITY EQUATIONS OF A. EINSTEIN AND E. HÁTSCHEK

For concentrated emulsions, Hatschek[1] devised the following equation:

$$\frac{\eta}{\eta_0} = \frac{1}{(1 - \sqrt[3]{\varphi})}$$

where φ is the proportion of disperse part to the entire volume, and η_0, the viscosity of the continuous phase.

Einstein[2] derived the following equation:

$$\frac{\eta}{\eta_0} = 1 + k\varphi$$

where k is a constant depending on the shape of the particles. For spherical rigid particles, $k = 2.5$.

v. Smoluchowski[3] amended this equation for systems in which the particles still carry an electric charge (electroviscous effect):

$$\frac{\eta}{\eta_0} = 1 + 2.5\varphi\left(1 + \frac{1}{\lambda\eta_0}\left(\frac{D\zeta}{2\pi r}\right)^2\right)$$

D = dielectric constant.
λ = conductivity.
ζ = potential of double layer (electrokinetic potential).

The electroviscous effect will be the more pronounced the smaller the particle and the conductivity and the larger the potential.

STAUDINGER'S VISCOSITY EQUATION

According to H. Staudinger,[4] there exists a correlation between molecular weight and viscosity of solutions of threadlike macromolecules.

$$\frac{\eta}{\eta_0} = 1 + cMK$$

c = concentration.
M = molecular weight.
K = factor depending on substance and solvation.

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[1] *Koll. Zeit.*, **8**, 34 (1911).

[2] *Ann. Phys.*, **19**, 289 (1906).

[3] *Koll. Zeit.*, **18**, 194 (1916).

[4] *Ibid.*, **51**, 71 (1930).

EISENSCHITZ'S VISCOSITY EQUATION

R. Eisenschitz[1] calculated the viscosity of very long particles:

$$\frac{\eta}{\eta_0} = 1 + \varphi \frac{f^2}{15(\ln 2f - \frac{3}{2})}$$

f = proportion of axes of the ellipsoidic particle.

Both these equations account for an increase in viscosity with increase in length of particle.

VON BUZÁGH'S DERIVATION OF ADHESION FORCES

If we can determine the size of the particles that just barely adhere to the base plate, we can evaluate the adhesion force.

If p is the attraction force acting on a unit area (specific adhesion), then the effective force for the projection of a spherical particle must be

$$\pi r^2 p$$

With particles that are just about to fall, this must be equal to the weight of the particle, or

$$\pi r^2 p = \frac{4}{3} r^3 \pi (C_1 - C) g$$

where C_1 = density of the particle.
C = density of dispersion medium.
g = gravity.

The attraction force can be similarly calculated from the adhesion angle x:

$$\pi r^2 p = \frac{4}{3} r^3 \pi (C_1 - C) g \sin x$$

(The specific adhesion for quartz suspended in pure water was found to be a few tenths of a dyne per square centimeter.)

THE THEORY OF X-RAY DIFFRACTION[2]

What are x rays? They are electromagnetic waves. So far, we have no real concept of an electromagnetic wave. However, there is one type of wave with which all of us are familiar, one that all of us have seen produced and followed, *viz.*, waves on a water surface. If we throw a stone into a smooth surface of water, we know that it will cause a ripple or wave on the smooth surface, the ripple moving outward in the form of a ring. We notice that a series of ripples follows the first one, which is due to the vibration of the water caused by the impact of the stone that was thrown on the smooth surface. As these vibrations fade out, the ripple movement

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[1] *Zeit. physikal. Chem.* (*A*), **163**, 133 (1933).

[2] A large part of this section and the illustrations are based on R. Brill's masterly contribution "Erforschung der Kolloide mit Röntgenstrahlen," in H. Bechhold "Einführung in die Lehre von den Kolloiden," T. Steinkopff, Dresden, 1934.

becomes weaker; and if a cross section were made through that surface, we should obtain a picture somewhat like that schematically shown in Fig. 101*a*, where we see that the first wave or ripple is strong, the following ones fading out as the vibrations cease. This is generally known as a dampened wave. A wave length in this case would be the distance from one peak to the next. The wave length is usually designated by the Greek letter λ.

Those wave lengths, however, are not uniform; as the vibration changes, the wave length will also change constantly. If we now tie a string to the stone, drop it into the water, and pull it up again and repeat this movement at equal time intervals, we shall produce a wave where no dampening takes place, because we always produce a new impact. We obtain an undampened wave where the wave length is uniform, depending only on the time intervals at which the stone is dropped in and pulled out (Fig. 101*b*). The wave length can be changed at will; the faster the movement is performed the shorter the time interval between two impacts, and therefore the shorter the wave length. If the time interval is increased between two of those impacts, then the wave length will become larger. If a uniformity is maintained in this impact motion, then the wave lengths should also be uniform.

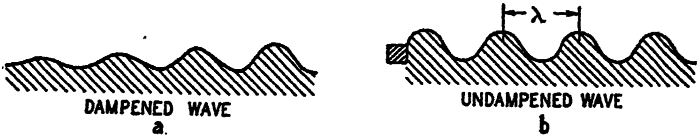

Fig. 101.—Water waves.

This explanation is about the simplest to demonstrate an ordinary wave. We have every right to assume that the light waves behave very similarly. The cause for the light wave is the disturbance of the surrounding medium due to the vibration of material particles. We know that temperature or heat causes increased vibration of molecules, which can be considered as those particles, and that this increased vibration will cause a disturbance of the electromagnetic field surrounding them. The main difference here as compared with the water picture is that in the latter we were dealing with a plane surface, a maximum of two dimensions coming into the picture, whereas in the case of the disturbance set up by the vibration of those material particles in the electromagnetic field this will take on a tridimensional aspect. In other words, the waves that we have seen move along on water two dimensionally will move out into space in three dimensions, and instead of obtaining circles we shall obtain in the latter case waves of spherical shape.

Therefore, we can postulate at this point that the electromagnetic wave is a wave motion of spherical extension into space. Depending on the length of those waves caused by different disturbances, we can distinguish between different types of wave mechanisms. If we are dealing with extremely long waves, they are not directly visible to our eyes. However, these long waves become noticeable to us as heat waves, the feeling of warmth being given off by the subject emitting such waves. Thus, long before we can see a glow caused by increased temperature of, let us say, a piece of metal, we can feel that it is becoming hot. Here, waves of fairly long wave length are being emitted. If we come into somewhat shorter ranges, we shall produce light and actually see the effect. If we carry on and decrease the wave length further, our eyes will again fail to register, because we have then entered the range of ultraviolet radiation where wave lengths are so short that our eyes cannot perceive them or feel them directly. Going still further down and reaching wave lengths of only a few Ångström units (1 Ångström unit = 1 Å = 0.00000001 cm. = 10^{-8} cm.), we have then reached the range of what today is known as the x-ray range of the spectrum. Such waves are so short that one cannot assume them to be originated by an increase in temperature. If one were to calculate the temperature needed to produce waves of such shortness, the temperature would be so excessive that, first of all, one could not produce the temperature, nor could anything exist in such temperatures. Therefore, such short waves are produced by an entirely different mechanism. They are caused by the impact of extremely fast-moving electrons on to a solid surface. This is the principle of the x-ray tube, where electrons are shot out from a piece of metal (the cathode) on to what is known as the anticathode, x rays being emitted from there.

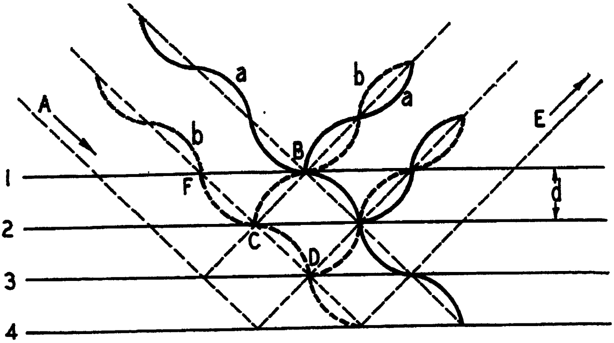

FIG. 102*a*.

FIG. 102.—X-ray diffraction. 1, 2, 3, 4, crystal lattice planes; *a*, *b*, x-ray

If we look at a highly polished metal surface or at a very smooth paint coating in ordinary light, we shall say that this surface, or coat, reflects the light to a greater or less extent. If, instead of this highly polished or glazed and smooth surface, we use the surface of paper, we are obliged to admit that the actual reflection of light is no longer so strong as it was on the polished steel. On an ordinary sheet of writing paper, we note that the light reflection is very small indeed and that the surface has a somewhat dull appearance. Looking at a polished metal surface under the microscope and then doing the same with the paper surface, we discover immediately that there is a considerable difference in texture. Whereas the highly polished metal will even under comparatively high microscopic magnification show a more or less smooth surface, the paper will show up a noticeable degree of roughness. If the irregularities of that surface are measured, we find that they are well over 1μ. At the moment when the range of roughness and uneveness is less than about 0.5μ, we shall obtain highly glossy, reflecting surfaces, because the average wave length of normal light is somewhere around 0.5μ. Therefore, any unevenness that is smaller in dimensions than that wave length will reflect the light.

We have said that x rays have extremely short wave lengths, so it is natural for an x ray not to be reflected by this material. It will also not be reflected by a perfectly smooth glazed surface, unless the unevenness or the discontinuities of the surface are again such that they are small in comparison to the wave length of that type of radiation. To obtain a reflection of an x ray, it becomes evident and logical that some material is needed that exhibits discontinuites in about the same range of Ångstrom units as the wave lengths of the x rays. Here nature has given us a perfect tool to work with—the crystals. We are dealing here with a piece of matter made up of individual atoms of the elements forming that type of compound, so spaced that the discontinuities between them lie roughly somewhat below the range of applied x rays, *i.e.*, around 0.3 to 0.1 mμ, or from 3 to 1 Å units.

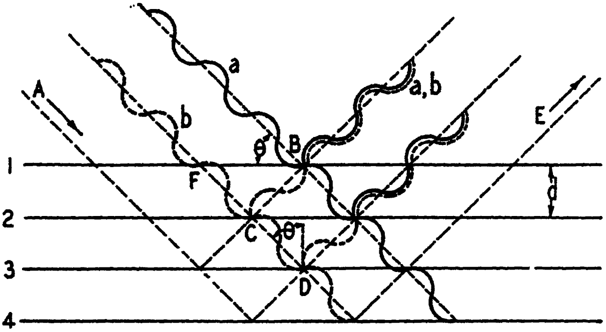

FIG. 102*b*.
beams; *B*, *C*, *D*, *F*, lattice points; *d*, lattice-plane distance; *θ*, reflection angle.

There is another very noticeable difference in the behavior of ordinary visible light and x ray. Visible light, if it is not reflected, will not penetrate the surface very deeply but will be absorbed, whereas x rays have the property of penetrating through matter to fairly considerable depths. This is important, because if we look at a crystal, for example, it may have a rough and uneven surface and still give a fairly satisfactory x-ray pattern, since the x ray will penetrate through the surface into the interior structure, as we shall see later.

In Fig. 102*a*, we have drawn schematically a series of lattice planes.[1] Thus, lines 1, 2, 3, and 4 correspond to what we today call *lattice planes*. We assume that a parallel beam of x rays enters in the direction of the arrow

[1] A crystal is considered to be made up of a series of planes in which the different atoms are located and held together by cohesion forces.

A, the location of the individual rays being marked by the dotted lines a, b. To show the wave characteristic of that x ray, a wave line is drawn to give an idea as to the wave length of the particular x ray used. The x ray strikes the first lattice plane at B and is partially reflected on the drawn line a in the direction of E. The rest of the beam passes through the first plane and reaches the lattice plane 2, is reflected again in the drawn line a in parallel direction to the reflection of the first plane, and so on. But we also consider the ray b coming in parallel to a and striking the lattice plane at F. This ray would reflect here, but it has been purposely omitted in the picture to avoid complication.

That part of the x-ray beam which has not been reflected will hit plane 2 at C. Here, again, we obtain a reflection, and that is shown in the wave form by the dotted line b. Continuing to plane 3, we meet at D and here, again, receive a reflection. Looking at this picture carefully, we see that the reflection of the b beam meets the reflected a beam in B, for instance, but in a reverse wave direction, with the result that those two waves will compensate each other and, optically speaking, will extinguish each other. Therefore, in the case shown, we shall obtain no reflection of x rays worth mentioning. This phenomenon is known as *compensation by interference.*

Let us continue to the next picture (Fig. 102*b*), which is drawn to the same scale as the first. We have planes 1, 2, 3, and 4 and likewise the x-ray beams coming in from A and being diffracted in the direction of E. The only difference between this picture and the former is that here an x ray has been chosen which has only half the wave length of the one in the first picture. Furthermore, here one lattice distance corresponds to one full wave. In this case, beam b reaching C is so reflected that now, because of the shortening of the wave, it will not compensate but coincide with the reflection of a, with the result that both reflections synchronize and reinforce each other. This phenomenon is known as *reinforcement by interference.*

On looking at the picture[1] again, we see that a reinforcement is possible only if the distance CB corresponds to one wave length of the x-ray beam or to a straight multiple of it. Therefore, BC corresponds to n wave lengths, or $n \cdot \lambda$. We can simplify and generalize by replacing the distance BC with the reflection angle θ and the distance d between two of those lattice planes. In the rectangular triangle BCD, $BC/BD = \sin \theta$. Since $BC = n \cdot \lambda$, n being an integer, BD must equal $2d$. From these data we can write the fundamental law of reflection

$$n = 2d \sin \theta$$

For example, if a beam of monochromatic x rays (x rays of one uniform wave length) enters a slit and impinges on a crystal, a photographic plate or fluorescent screen having been placed in the proper location beforehand, a reflection is made on the screen from that crystal. With ordinary light the crystal can be turned around axis A, and a picture obtained of the slit on the photographic plate or screen (Fig. 103); only the location of the slit on the screen will move as the crystal is turned, producing different angles of reflection. If the equation resulting from these simple schematic draw-

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[1] The picture as drawn is a special case $\theta = 45$ deg.

ings holds good, we should not be able to obtain a constant picture of the slit as the crystal is rotated about axis A when using x rays, because only certain angles of reflection will fulfill the equation. In carrying out such an experiment, we find that we get a line where $n = 0, 1, 2, 3$, etc. (Fig. 104), but no picture at all where n is 0.5, 0.6, etc. Knowing the wave length of the monochromatic beam and the angle θ, which can easily be determined, we can find the orientation or location of atoms in a crystal by using the law of reflection. By knowing the wave length of the x ray and by knowing θ, we can easily determine d, which would be $d = n\lambda/2 \sin \theta$.

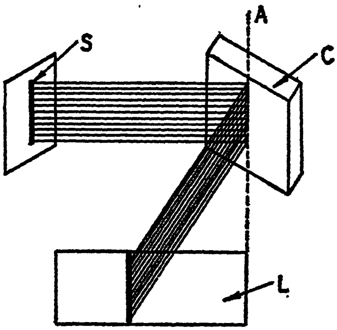

FIG. 103.—Light reflection by crystals. S, slit; C, crystal; A, axes of rotation; L, screen.

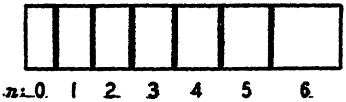

FIG. 104.—X-ray diffractions on screen.

A schematic drawing of a cross section through a sodium chloride crystal is given in Fig. 105. The white circles denote sodium; and the black, chloride atoms. It will be seen that there are different D's, depending on how we look at the crystal. The more complicated the crystal becomes the more probability there will be for D's. By carrying out a complete x-ray analysis of a crystal, a number of measurements will be obtained that will give the different D's present in such a crystal; this suffices to permit an evaluation of the orientation or the alignment of the various atoms present in such a structure.

It is unnecessary to carry such an analysis very far, because it will be found that certain units repeat each other in crystals. When a diffraction is taken from several angles, a full story is presented of the ultimate unit. To define the crystal, only that unit is needed which will repeat itself over and over again, *e.g.*, *ABCDEFGH* in Fig. 106.

With the aid of what has been demonstrated so far, we should be able to calculate fully the location of the atoms making up such a unit cell. It is then easy to calculate the number of unit cells making up one small or large crystal. Moreover, we are today in a position to determine the type of atom actually present in one location or another by the intensity of reflections in the different planes. This method has opened an entirely new field of research, and the results of crystal-structure research of today are based on this discovery.

However, this method, theoretically developed by M. v. Laue and proved experimentally by his collaborators Friedrich and Knipping, necessitated well-grown and well-defined crystals to work with. Therefore, v. Laue's method was of no direct value to the colloid physicist. But soon after v. Laue's discovery, P. Debye and P. Scherrer developed a method that did permit structural studies, even with the substance available only in the form of a fine powder. They reasoned as follows: If a crystal is ground to an extremely fine powder, it can be assumed that the powder has the crystal particles present in absolutely random arrangement. If the powder is subjected to a parallel monochromatic x-ray beam, it can be assumed that the many lattice planes present will lie in all the angles called for by the equation. If in one cubic millimeter we can place 1000 million crystals of cubical shape of 1 μ edge length, which is not beyond colloidal dimensions, there exists great probability that all angles which will give us an x-ray diffraction will be represented. Apparently by the general rule of disorientation it is highly improbable that any possible angle will not be fully represented and the equation fully satisfied.

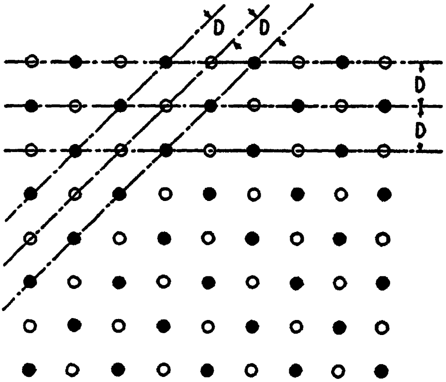

Fig. 105.—Schematic cross section through sodium chloride crystal.

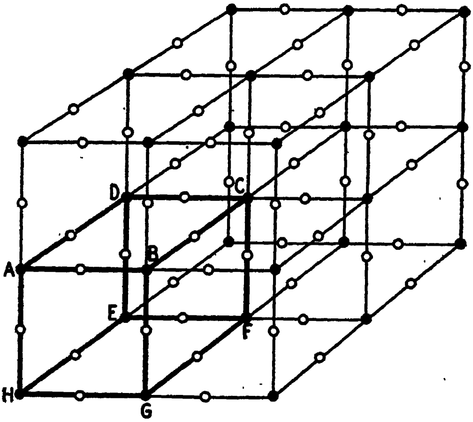

Fig. 106.—Crystal structure. *A-B-C-D-E-F-G-H*, unit or elementary crystal.

All rays reflected from a given lattice into different directions must have the same angle with the x ray. Therefore, Debye and Scherrer decided on the following scheme (Fig. 107): An absolutely parallel x-ray beam *R* was stopped with a slit *S*, so that only an extremely thin pencil of parallel x-ray radiation entered the cylindrical chamber *C*. In the middle of the chamber the powder *P* was placed, either in the form of a compressed little stick cemented with glue or in a tiny, very thin parchment-paper sack or an exceptionally fine glass capillary. According to the conclusion and the demands of the equation, the reflections from here on must lie on a cone (shown by dotted lines). In Fig. 108, we receive a somewhat clearer picture. A certain number of crystals will reflect to cause a reflection at *A*, whereas others will lie so as to permit a reflection at *B*, etc. In a random orientation of crystal planes, a perfect and well-defined circle should result. Figure 109*a* shows a drawing of this effect. The cylindrical chamber with the substance to be x-rayed is shown, the latter in the exact center, and a photographic film placed around the chamber (*F*, Fig. 107). Where the x-ray beam passes clear through the center, called the equator, there is a black spot. Each of the rings corresponds to one angle of diffraction. If this film were cut open and laid flat, it would present a picture similar to Fig. 109*b*.

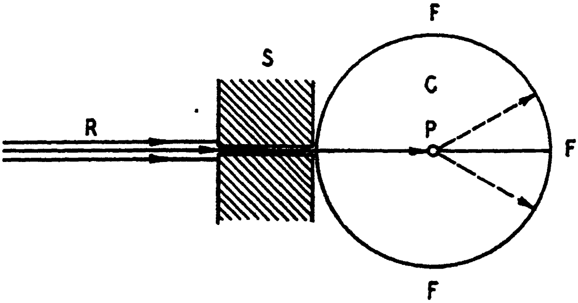

FIG. 107.—Debye-Scherrer x-ray diffraction method. *R*, x-ray beams; *S*, stop; *C*, camera; *P*, preparation; *F*, photographic film.

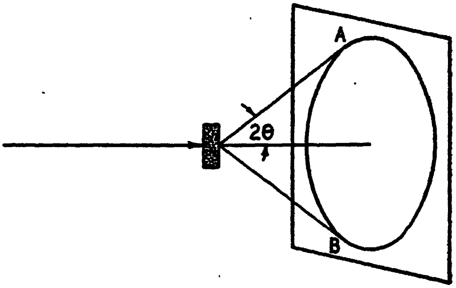

FIG. 108.—X-ray diffraction of crystal powder specimen. *θ*, angle of reflection; *A*, *B*, points of reflection on film.

Some time later, an improvement was made by Hull in rotating the crystal for the purpose of increasing the probability that all planes would be present in the right angle of reflection as demanded by the equation.

The Debye-Scherrer method has revealed other interesting facts. If we investigate matter with a preferential orientation in one direction or the other, we note that the plain concentric rings will be broken and show typical increases of intensity at certain points. This denotes the presence of preferential orientation, because only a certain angle is available for reflection. Since such a type of pattern was originally found in cellulosic and other fibrous matter, such a pattern is generally known as fiber diagram. The type of orientation can be determined by the location of those intensity spots, because every point on a circle corresponds to a location of the plane in the actual crystal. But the Debye-Scherrer work has shown something of still greater importance. If we take a Debye-Scherrer pattern of a substance of known lattice structure powdered to microscopic size, we shall obtain a very precise ring picture of the x-ray interferences. If the substance is futher comminuted, thus permitting no change in the substance to take place, and an x-ray picture is again made, the interference bands or rings will be found located in practically the same spot, but their sharpness will have noticeably diminished. If disintegration is continued, the sharpness will be less and less. An explanation is easy: To obtain a perfectly sharp picture, a maximum reinforcement is needed; and for that maximum, there must be a sufficiently large number of planes, one lying behind the other. If matter is broken up or disintegrated, such particles will split up, and the number of planes per unit particle will diminish accordingly. Whereas the coarse matter perhaps had 10 planes, lined one behind another, and the reflection received an enormous amount of reinforcement, in the medium range it was broken down to only 5 planes, and the intensity of the reinforcement was less; and consequently the sharpness of the interference bands also, but the location was the same for the given angle. If only two planes remain to give reinforced interference, then the sharpness will be very materially reduced.

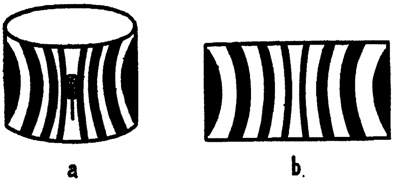

FIG. 109.—Debye-Scherrer diffraction patterns. *a*, film in camera; *b*, film unfolded.

This procedure offers an inaccurate, but nevertheless not-to-be-neglected, method of determining particle size of dry materials in a range where the microscope completely fails and where the ultramicroscope, although making the particles visible, is incapable of permitting an actual determination of particle size. Best results have been obtained in measurements between 1 and 100 $m\mu$. This is one case in which the colloid chemist can be very materially interested. The only difficulty is that we must have the material in a fairly concentrated form, and in dealing with a very dilute sol this method is naturally inadequate.

There is still another factor, *viz.*, the width of the interference bands, to be considered. It has been found that the width changes with the geometrical configuration of the particle. It is otherwise with a platey particle, a cubical particle, a spherical one, etc., so that a knowledge of these details permits an investigator today to make at least a fairly good assumption on the most probable geometrical configuration of the colloidal particle that he is investigating.

Fiber Diagrams.—With cellulose a so-called fiber pattern is obtained immediately, which denotes that the crystallites are oriented in preferential line-up, the axis of fiber growth. Since then, many substances have been found that exhibit similar fiber patterns. One of these is rubber *when stretched*. If unstretched, rubber does not show such patterns; rather a typical amorphous ring diagram is obtained (Fig. 110*a*). This means that there is no specific orientation whatsoever to be found in the specimen—in other words, no crystalline matter or any definite orientation. If the same piece of rubber is brought into cool environment, say from 5 to 6°C. plus, and stored for several days or weeks, it will become opaque where originally transparent and will become hard and boardlike, losing its elasticity. The trade refers to such rubber as "frozen." If an x-ray diffraction picture is taken of the rubber, several very distinct sharp rings will be seen instead of a simple amorphous ring (Fig. 110*c*). (Each ring corresponds to one plane at a different angle of reflection.) These rings denote the presence of well-oriented matter, or, generally speaking, crystals. From these rings one can determine with some accuracy the configuration, or make-up, of such a crystal.

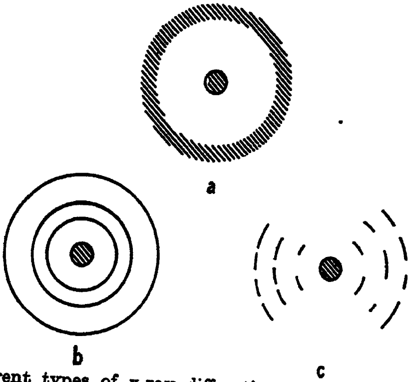

FIG. 110.—Different types of x-ray diffraction patterns. *a*, amorphous ring; *b*, Debye-Scherrer crystal pattern; *c*, Debye-Scherrer fiber diagram.

Therefore, during cold storage we produce some crystallization of the hydrocarbon. Not enough work has been done so far to study this peculiar phenomenon. It should reveal much in respect to structure research. If the amorphous, typically elastic piece of rubber is stretched to several hundred per cent, and an x-ray pattern taken thereof, we find in place of the amorphous ring present in the unstretched condition specific intensity maxima on the different circles (Fig. 110*c*). This is a typical fiber diagram showing that matter has been oriented in a preferential direction. By certain calculations we can find that this orientation is in the axis or in the direction of stretch. A pattern is now obtained that in its general make-up corresponds to the patterns received from cellulose without any treatment of the cellulose fiber. The cellulose is in a preformed oriented condition, whereas the rubber needs the stretch to show orientation.

Before the first x-ray work on rubber became known (J. R. Katz and K. Bing,[1] E. A. Hauser and H. Mark),[2] L. Hock[3] had already shown in a much simpler way that rubber if stretched changes into a fibrous structure in comparison to its unstretched condition and predicted the x-ray fiber diagram for stretched rubber. He took a piece of smooth crude rubber, immersed it in liquid air, and, after the piece was thoroughly frozen, shattered it with a hammer. It broke into irregular pieces, with sharp and clear-cut edges. Then he stretched another piece several hundred per cent and immersed it in stretched condition in the liquid air. Upon being shattered, this piece broke in a fibrous, feather-edged fashion, proving that some orientation of the building units had occurred during stretch. On looking at the pattern of cellulose, we find that it denotes the presence of some crystalline matter in the fiber and, furthermore, that this crystalline matter must be present in a very definite arrangement; otherwise only concentric rings would be obtained and not a pronounced fibrous diagram characterized by the intensity maxima distributed over the ring peripheries. This does not mean that all the crystals forming the cellulose must be absolutely equally distributed. A comparison might be the same as when holding a few dozen pencils together in a bundle, some having their points up, some down; the names of the firms of some will show to the right, whereas others will show on the other side, etc.; they will all be parallel to each other, but their rotation around the main axis can be quite different. The x-ray pattern offhand denotes only a parallel orientation. We must make use of other points of the pattern to describe the exact way in which they are located.

The structure obtained with cellulose is known as a simple fiber structure, or diagram. If the diagram is evaluated in detail, further information can be gained as to the size of the elementary body or cell, which always repeats itself. Once this is calculated and the specific weight of the cellulose known, we have a good basis for further calculations. The weight of the atoms forming cellulose is known, since the chemical analysis for cellulose was established many years ago. Therefore, if the weight of the elementary unit is known, to be figured from the weight of the atoms, we can calculate x in the formula.

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[1] *Zeit. angew. Chem.*, **38**, 439 (1925); *Gummi-Ztg.*, **39**, 1554 (1925); *Koll. Zeit.*, **36**, 300; **37**, 19 (1925); *Naturw.*, **30**, 410 (1925).

[2] *Koll. Beih.*, **22**, 63 (1926); **23**, 64 (1926). *Zeit. Elektrochem.*, **32**, 463 (1926).

[3] *Gummi Ztg.*, **39**, 1740 (1925).

The accepted formula for cellulose is $(C_6H_{10}O_5)x$. x was found by x-ray analysis to be equal to 4, which means that the elementary cell of the cellulose contains four glucose anhydride groups.

A similar result was obtained in rubber, the basic formula of which is $(C_5H_8)x$. When first published, this result created considerable argument among the cellulose and organic chemists, because such a low figure for x was not correlatable in any way with the behavior and properties of cellulose as found by ordinary chemical methods and analysis. Exactly the same happened when the unit crystal for rubber was determined to be $(C_5H_8)_4$, the elementary body containing only four isoprene molecules.

The fact revealed by the x ray, that only about four glucoseanhydride rests build up one cellulose unit cell, or four isoprenes the unit cell in rubber, and the discrepancy with the properties and the results found in ordinary organochemical work, brought about what must be considered one of the most outstanding developments in furthering and deepening our insight into the actual building methods of nature. The final result of this reasoning and thinking showed that the single glucose residue ties up with the next glucose and finally forms long-chained molecules out of equal fragments contained in the elementary body and composing the crystal. Here is the big difference from the mineralogical point of view. In the case of such organic matter, the crystal is not something to be taken out of matter and put in another place. It is an imaginary thing. In organic compounds like cellulose and rubber, we have such long molecular chains of glucose residue or isoprene, which tie up, one to the other. Several of these chains lie parallel to each other and form the unit elementary bodies or unit cells which always repeat themselves. To make up that unit cell we must use several fragments of such long molecular chains.

For example, if a piece is chipped off a lump of rock salt, we again have rock salt and shall continue to obtain the same going down the line of dispersion until we obtain the atomic unit. But if we disintegrate the cellulose, the properties are lost because they lack the units of the elementary body, or the structure that is necessary to the properties referred to.

Today we have gone a step further and from the study of simple organic compounds have learned to determine the size of the oxygen or carbon atom of certain organic radical groups. We have also learned more about the arrangement and distances of such atoms in various compounds. On the basis of that knowledge, we are in a position today to calculate actual dimensions of glucose or isoprene molecules or groups, and, in doing it, it has been possible to prove that the results check perfectly with the dimensions obtained in studying x-ray patterns. If we take cellulose in the old way of writing, we obtain roughly a formula represented in Fig. 111*a*, which is $C_6H_{12}O_5$. If one water is subtracted therefrom, we obtain a glucose residue $C_6H_{10}O_5$. Corresponding to more modern organic methods of describing not only the condition but also the arrangement of the different atoms and their grouping, cellulose can be drawn as shown in Fig. 111*b*. The top line and the line at the bottom each denote a free valence, and hence we can assume that the next glucose rest will presumably tie to these points. A modern way of drawing molecular designs is shown in Fig. 111*c*. The dark circles correspond to the carbon atoms; the white, to the oxygen. The hydrogens, which would be small in comparison, have been left out so that the picture does not become too complicated. If definite dimensions are taken for carbon and oxygen, and the spacing between them is measured in accordance with our present-day knowledge, we can draw up a crystal or a particle model in proportional measurements or dimensions.

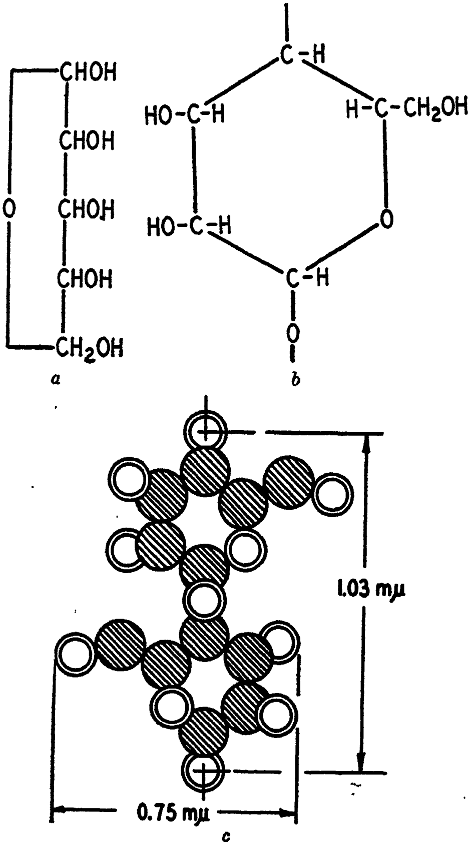

Fig. 111.—Different methods of picturing a cellulose molecule.

Measuring the distance from left to right, we find that it is roughly 0.75 mμ, whereas the distance from top to bottom, *i.e.*, for two glucose residues, will be 1.03 mμ. The x-ray diffraction patterns, if evaluated mathematically, give exactly those figures, thus making a perfect check. Figure 112 shows such a unit cell. The rest of the molecules on the right front edge have been purposely omitted. The dimensions are *a* = 0.835, the *c* axis being 0.79, and the *b* axis, 1.03.

Figure 113 shows a fiber in cross section. If an actual fiber is considerably magnified, we may receive a simple picture such as shown in Fig. 114.

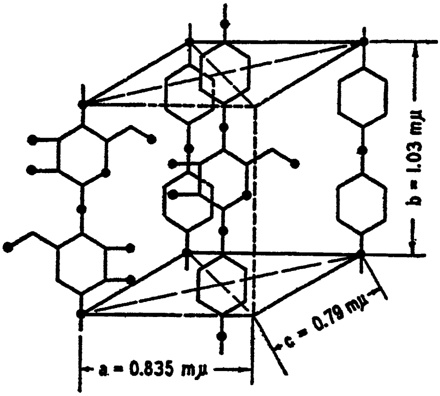

FIG. 112.—Schematic drawing of a unit cell of cellulose. (*According to K. H. Meyer and H. Mark.*)

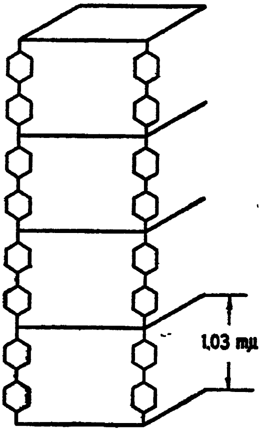

FIG. 113.—Schematic cross section through a cellulose fiber.

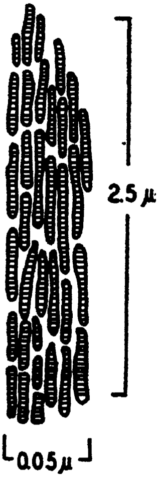

FIG. 114.—Schematic interpretation of the arrangement of molecular chains in a fiber.

Let us take artificial silk for comparison. What is our purpose in making artificial silk? It is to transfer the natural short fiber, such as wood-pulp cellulose, into a long-stem fiber. We are interested in producing a synthetic fibrous structure, and to do this we must produce cellulose in a highly oriented condition. The interesting part of the artificial-silk industry is that long before this work and line of reasoning were known, the manufacturers managed to produce entirely satisfactory products. By stretching or using a stretching operation during the actual manufacturing process of the artificial silk during spinning, they produced artificial fibers having a diagram practically identical with the diagram of the natural cellulose material.[1] An x-ray diagram of viscose, for example, is absolutely comparable to the x-ray diagram of natural cellulose fibers.

Has the crystallization of this matter already taken place in the solution or only during the spinning operation? In the manufacture of the viscose, the natural crystalline structure of the cellulose has undoubtedly been destroyed to some extent, and this has been rebuilt or reproduced during the spinning operation.[2]

Another highly interesting substance is gelatin. If this is dried, and an x-ray pattern taken of the dried gelatin, an admittedly poor but nevertheless existing Debye-Scherrer concentric-ring diagram is obtained. This means that in the dried gelatin there must be some crystalline "matter" in preformed condition, because the x-ray patterns show the preformation of aggregates. If the gelatin is swollen in water, the aggregates will loosen, and the diagram will lose in sharpness until finally when the gelatin goes into perfect solution they will disappear, and only an amorphous ring will remain. If the gelatin is allowed to swell slightly, is then stretched, and is dried in stretched condition, an x-ray pattern shows a perfect fiber diagram. By the stretching operation a preferential orientation of the preformed aggregates has been produced. The gelatin is midway between rubber and cellulose in general line-up of crystalline matter. In the cellulose, it is preferentially oriented; in rubber, it is not present in the unstretched condition, and it must first be oriented; in the gelatin, crystallized matter exists but in random arrangement.

If an x-ray pattern is taken of a tendon, which is one of the substances from which gelatin can be obtained, a fiber diagram results which practically coincides with the gelatin pattern. This is interesting, because in order to make gelatin we must go through a considerable number of steps. These one would assume would completely change or decompose the matter, but still this is not the case, as during the production of gelatin from the tendon the fiber structure is decomposed but not the individual unit-building elements. Therefore, by stretching, orientation can be reproduced such as was had originally, the only exception being that the tensile strength is not so high, since a number of skeleton-forming ingredients are missing.

All these findings demonstrate that nature does not resort to the individual atom as a building element when building matter of high rigidity or elasticity but rather to a more advanced unit, just as the contractor uses

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[1] Similar analogies have been found with wool and artificial wool produced from dehydrated and stretched casein.

[2] W. K. Farr and her collaborators have seriously contested this point of view. They believe that the cellulose is reduced to building units of only about 1 μ in length, which reorient again during the spinning process.

bricks to build a house and does not begin with more elementary units of matter, such as clay, analogous in our case, to molecules or atoms.

Literature.—From a large selection of specialized textbooks, the following may be mentioned:

W. H. Bragg and W. L. Bragg, "X-rays and Crystal Structure," George Bell & Sons, Ltd., London, 1925.

George L. Clark, "Applied X-rays," McGraw-Hill Book Company, Inc., New York, 1927.

H. Mark, "Die Verwendung der Röntgenstrahlen in Chemie und Technik," J. A. Barth, Leipzig, 1926.

J. J. Trillat, "Les applications des rayon X," Les Presses Universitaires de France, Paris, 1930.

Separate interesting contributions with special reference to colloidal systems are found in *Koll. Zeit.*, 69, 266, 301, 312, 369, 378 (1934). See also G. L. Clark, *Coll. Symp. Monogr.*, 4, 145 (1926).

OPTICS IN COLLOID CHEMISTRY AND PHYSICS

It is only natural that a science treating matter of such fine degree of subdivision that its dimensions are far smaller than the recording power of the human eye must depend greatly on the use of microscopic and other optical equipment. As was mentioned in the brief discussion of the ultramicroscope (see page 183), a colloid chemist or physicist of today must be familiar with at least the principles of optics and the various instruments that have found successful application in the experimental studies of colloidal systems and colloidal phenomena.

One could easily write a book exclusively on the application of optical instruments in colloid chemical or colloid physical research. Many detailed discussions of the different instruments and their applicability are available in scientific literature as well as in special pamphlets obtainable from the manufacturers of such instruments. The following lines are therefore limited to a very brief enumeration and discussion of the most important instruments, their specific field of application, and such points as, based on many years of experience, deserve special attention when working with these instruments.

Slit Ultramicroscope.—The theoretical basis for the development of this research tool and its value, as well as limitations, in the study of colloid-disperse systems have been previously discussed. The slit ultramicroscope offers, besides the simple detection of colloid-disperse matter, one of the methods for determining the size of such particles. For this purpose it is necessary, as in any microscopic work, to have the instrument perfectly centered in regard to the light source. Slight deviations can cause misleading light effects and decrease the sharpness of the picture. If the opening of the slit and the magnification of the system are known, then the illuminated volume, corresponding to a standard grating in the eyepiece, can be easily calculated. To obtain satisfactory measurements, it is essential that the number of particles visible in one square of the grating do not exceed a maximum of 0.6 particles per square. This average figure has proved satisfactory in the case of extremely small particles. The larger the particles are the greater should be their dilution. Only those particles should be counted which are perfectly in focus at the moment of counting. Diffraction disks and blurred particles should not be considered. The counts should be carried out by varying the procedure frequently; *e.g.*, start with the square in the left top row, continuing to the right, starting the second row now again at the left. The second count should begin with the square to the right of the bottom row and proceed horizontally to the left. The next should make use of a vertical sequence. Special precautions should be taken to make the counts in uniform time intervals. About half to 1 second has proved satisfactory. To obtain reliable averages, at least 1000 but, if possible, 2000 individual counts should be made and then averaged.

It is advisable to check the result by diluting the sol to exactly half its original concentration and repeating the count. At the end of the experiment one may add an effective electrolyte to see whether amicrons were present, which show up only after complete coagulation.

It is furthermore advisable to place heat-absorbing filters between light source and specimen to prevent the formation of convection currents.

The diameter of a particle in centimeters can be calculated as follows:

$$d = \sqrt[3]{\frac{G}{m \cdot s}}$$

where G = grams of disperse part in the optically limited volume.
m = average number of particles counted in volume.
s = specific weight of disperse part.

The preceding equation assumes that the particles are of cubical shape. If they are considered to be spheres, then the following equation should be applied:

$$d = 2\sqrt[3]{\frac{3G}{4\pi m s}} = 1.2407\sqrt[3]{\frac{G}{m \cdot s}}$$

In the older literature, the specific weight was taken as that determined from the same substance in its coarse form. Correctly, one should use the "apparent specific weight" of the substance in dispersion. The differences will be especially pronounced in the case of lyophilic colloids.

Dark-field Condensers.—In regard to the use of ultracondensers with uniform illumination from all sides, necessary details as to construction and methods of use, the literature referred to above, and the descriptive material of the various manufacturers should be consulted.

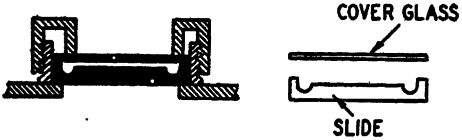

FIG. 115.—Special cell for use with dark-field condensers.

The construction of these condensers also necessitates very accurate focusing of the light source and the use of objective slides of great precision in regard to thickness. Since too thick a layer of the preparation will result in a blurred effect, special precautions should be taken to insure an even thickness of the specimen. It is advisable to use special cells which guarantee an even thickness of the preparation (see Fig. 115) and are obtainable from the different manufacturers of ultramicroscopical equipment.

Literature.

O. HEIMSTÄDT, "Apparate und Arbeitsmethoden der Ultramikroskopie und Dunkelfeldbeleuchtung," Frank'sche Verlagshandlung, Stuttgart, 1915. Wo. OSTWALD, "Licht und Farbe in Kolloiden," T. Steinkopff, Dresden, 1924. E. A. HAUSER, "Optik der Kolloide," in BECHHOLD, *op. cit.* G. WIEGNER, "Ultramikroskopie," in A. KUHN, "Kolloidchemisches Taschenbuch." (This summary contains further literature references.) For limitations of the method and the most frequently occurring errors, see, *e.g.*, J. REISSIG, *Koll. Zeit.*, **5**, 265 (1909). G. WIEGNER, *Koll. Beih.*, **2**, 213 (1911). Especially G. WIEGNER and E. W. RUSSELL, *Koll. Zeit.*, **52**, 1, 189 (1930). MAX POSER, "Ultramicroscopy," in J. ALEXANDER, "Colloid Chemistry," vol. 1, D. Van Nostrand Company, Inc., New York, 1926. R. ZSIGMONDY, "The Immersion Ultramicroscope," in J. ALEXANDER, "Colloid Chemistry," vol. 1. COTTON and MOUTON, "Les ultramicroscopes et les objects ultramicroscopiques," Masson et Cie, Paris, 1906. E. M. CHAMOT and C. W. MASON, "Handbook of Chemical Microscopy," 2d. ed., John Wiley & Sons, Inc., New York, 1938.

FLUORESCENT LIGHT MICROSCOPY AND ITS APPLICABILITY TO COLLOID CHEMICAL RESEARCH

The ultraviolet spectrum was discovered in 1801 by J. W. Ritter. The fact that certain substances glow in the visible range of the spectrum when irradiated with ultraviolet light was first noticed by David Brewster, in 1833. In 1852, G. G. Stokes termed this phenomenon "fluorescence." However, it took over 50 years from then before the ultraviolet light was introduced into microscopy. This was in 1904, when A. Koehler[1] described for the first time a microscope using quartz optics, thereby permitting microphotography with the use of ultraviolet light. Though Koehler's paper was principally directed to a detailed study of microscopy in the ultraviolet, he did point out that under certain conditions direct observations should be possible if the preparation would emanate visible light, *i.e.*, fluoresce, when radiated with ultraviolet light. He also pointed out that in cases where the substances under investigation do not fluoresce themselves, other substances might possibly be added which exhibit pronounced fluorescing properties. Such substances he termed "colorless dyes." Quite recently, M. Haitinger and L. Linsbauer described the use of a variety of water-soluble substances exhibiting specific fluorescence as additions to nonfluorescing preparations. These substances, now known under the term "fluorochromes,"[2] are selectively adsorbed on surfaces and have found

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[1] *Zeit. wiss. Micros.*, **21**, 129, 273 (1904).

[2] *Beih. Bot. Centralbl.*, **50**, *Abt.* 1, *Heft* 2, 432 (1933); **53** (*A*), 378, 387, (1935).

much application in the colorless dyeing of plant or biological tissues. The concentration needed is extremely low, so that no changes in a system due to chemical reaction have to be considered.

Since the publication of Koehler's work, several more or less successful attempts have been made toward the construction of microscopes permitting direct observation of the specimen by its actual fluorescence. They can generally be divided into two groups: The first makes use of the ordinary types of mercury-arc lamp as light sources for observation in incident or transmitted light; the second uses as light source an arc created between specially impregnated carbons or metal electrodes. Detailed literature references to the earlier work in this field have been summarized, for instance, by J. A. Radley and J. Grant,[1] E. M. Chamot and E. W. Mason,[2] and M. Haitinger.[3]

Up to very recently, electric arcs using impregnated carbons or special metal electrodes[4] have found wider application than the mercury arc. The reason lies in the fact that the surface luminosity of the former (light intensity per unit area of specimen) is much superior. However, in the last years, entirely new light sources, so-called capillary mercury-vapor lamps, have been developed[5] which must be considered as ideal for the purpose.

The light emitted from the light source is usually collected through an ultraviolet-transmitting optical-lens system and then passed through a filter or cuvette containing a 10 to 20 per cent copper sulphate solution to eliminate all red (heat) rays of the spectrum. Then the light passes through a filter which will transmit only ultraviolet radiation, *e.g.*, from 3100 to 3900 Å in wave length. It is reflected from the microscope mirror into the ultraviolet transmitting condenser and after passing the ultraviolet transmitting slide reaches the preparation. To reduce loss in ultraviolet radiation it is advisable to use aluminum mirrors or glass mirrors on which aluminum has been deposited by vapor condensation. If incident light must be used, it is necessary to apply microscopes that permit vertical illumination. In such cases, it is naturally essential that the optics transmit the ultraviolet light to the preparation. The objective and the eyepiece of the instrument should be made of ordinary optical glass, since fluorescent colors lie in the visible spectrum, and stray ultraviolet rays will be absorbed and made unharmful to the observer's eye. To be quite sure, it is advisable to use a safety filter on top of the eyepiece, which eliminates exactly that spectral band transmitted by the other filter. When using oil-immersion systems, a nonfluorescing oil is essential. The same applies to the glass used for slides and cover glasses.

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[1] "Fluorescent Analysis in Ultra-violet Light," Chapman & Hall, London, 1933.

[2] *Op. cit.*

[3] *Mikrochemie*, **9**, 430 (1931); "Die Anwendung der Fluoreszenzanalyse in der Mikrochemie," Heim & Co., Vienna, 1937; *Zeit. mikr.-anat. Forschg.*, **33**, 193 (1933). See also R. W. Wood, *J. Physique* (1919).

[4] See M. Haitinger, *Mikrochemie*, **9**, 220, (1931); "Fluorescenzmikroskopie," Akad. Verlags-Ges., Leipzig, 1938.

[5] See S. Dushman, *J. O. S. A.*, **27**, 17 (1937).

Fluorescent-light microscopy has found many applications in botany and biology. Its application to colloidal phenomena and their study is of very recent date.[1] Nevertheless, the results so far recorded have already proved that fluorescent-light microscopy has offered a new research tool in the study of emulsification; surface and interfacial reactions; ore flotation; the concentration and orientation of surface-active substances in interfacial layers; changes of accelerators during the vulcanization of rubber; and impregnation of fibers, leather, etc. The possibility of obtaining quantitative and comparable data as to the actual fluorescing color and its intensity by appropriate recording instruments (photometer eyepiece, microspectrographs, etc.) that are now available[2] has very materially enlarged the applicability of this new branch of microscopy to colloidal research. (The availability of color plates or films permits the permanent recording of fluorescent effects.) Since, in a majority of cases, exposures of several seconds are necessary to obtain the correct color reproduction, it is advisable to ascertain in advance whether or not the ultraviolet radiation influences the fluorescent color with time.

INFRARED SPECTROSCOPY

The application of infrared spectroscopy in the study of molecular structures of inorganic and organic compounds is constantly increasing. The method apparently will develop very rapidly into a new tool in the field of structural chemistry. Problems pertaining to the type of linkages present in organic compounds, the mechanism of polymerization, isomerization, tautomerism; the detection of hydrogen bonds, —OH groups; and the study of the state in which water is present in different compounds and gels are at present the most prominent ones. If one bears in mind that all synthetic polymers, such as modern plastics and artificial rubbers, and certainly all reactions leading to gelation and gels as such must be classified as typical colloidal systems, it becomes self-evident that the modern colloid chemist and physicist must familiarize himself with this new tool. He must consider its possibilities not only from a scientific angle but also from the point of view of its industrial importance. Although the results are so far still highly qualitative, they have offered extremely interesting and promising results in domains where other methods have come to a deadlock.

R. Bowling Barnes[3] has offered an excellent summary in regard to the importance of infrared spectroscopy in organic chemistry. Dudley Williams[4] has applied this new tool to rubber chemistry. Although the work so far

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[1] See, *e.g.*, E. A. Hauser, *Rev. gén. caout.*, **11**, No. 106, 3 (1934); E. A. Hauser and C. J. Frosch, *Ind. Eng. Chem.* (*Anal. Ed.*), **8**, 423 (1936); *J. O. S. A.*, **27**, 110 (1937).

[2] See, *e.g.*, E. Hatschek and M. Haitinger, "Farbmessungen," Heim & Co., Vienna, 1936.

[3] *Rev. Sci. Instr.*, **7**, 265 (1936). See also "Proceedings Fifth Summer Conference in Spectroscopy," p. 71, John Wiley & Sons, Inc., New York, 1938. F. Daniels, *ibid.*, p. 76.

[4] *J. Chem. Phys.*, **4**, 460 (1936); *Physics*, **7**, 399 (1936).

published is more of an informative character, it demonstrates that valuable information can be expected in the evaluation of the mechanism of vulcanization and additional data on structural changes during the stretching of rubber.

The use of the infrared spectrograph for studying the state of water in different compounds was originated by W. W. Coblentz.[1] He also noted definite absorption bands in gelatin containing some moisture. This work was continued on a theoretical basis by W. M. Latimer and W. H. Rodebush,[2] who expounded the idea of hydrogen bonds as explanation of the valency in certain compounds. A. M. Buswell[3] applied this theory to gelation of various colloids (gelatin, silica, starch, clays, etc.), assuming that the free electron pairs of their oxygen or nitrogen atoms could share one hydrogen with water. A. M. Buswell, K. Krebs, and W. H. Rodebush[4] have published data on β-amylose, agar, gelatin, and montmorillonite that substantiate the above assumption and throw light on the bonding of water by these substances.

THE DETERMINATION OF PARTICLE SIZE AND PARTICLE-SIZE DISTRIBUTION BY THE USE OF SCATTERING IN THE NEAR INFRARED

The determination of particle size of pigments can be accomplished by direct microscopic (ordinary or ultraviolet light) measurement. The pigment is dispersed in a mounting medium and then spread out between cover glass and microscopic slide. The size of the particles can be determined by direct measurement on an enlargement of the microphotograph or by direct projection.

Ultramicroscopic counts can be carried out either in liquid dispersion or after dispersing the pigment in rubber or the like. They give figures only for apparent particle diameter but no indication as to the condition or configuration of the surface. Turbidometric methods are used extensively in the paint, cement, and ceramic industries. They, as well as hydrometer methods, permit a study of particle-size distribution curves to be obtained. Ultracentrifugal or supercentrifugal sedimentation methods are undoubtedly excellent in determining particle sizes and size distribution in suspensions of very fine particles. The latest addition to the methods available for particle-size determination is the adaptation of infrared scattering.[5]

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[1] *J. Franklin Inst.*, **172**, 309 (1911); *Nat. Bur. Stand. Res. Paper* 830, September, 1935.

[2] *J. Am. Chem. Soc.*, **42**, 1419 (1920).

[3] *Am. Chem. Soc. Monograph* 38, 53, 60, (1929).

[4] *J. Am. Chem. Soc.*, **59**, 2603 (1937). For the instrument used see, *e.g.*, A. M. Buswell, Victor Dietz, and W. H. Rodebush, *J. Chem. Phys.*, **5**, 84, 501 (1937).

[5] See, *e.g.*, Gehman and Morris, *Ind. Eng. Chem.* (*Anal. Ed.*), **4**, 157 (1932). For a good résumé see P. V. Wells, *Chem. Rev.*, **3**, 331 (1926). Also A. Casagrande (not published). The Svedberg and Rinde, *J. Am. Chem. Soc.*, **45**, 943 (1923). E. A. Hauser and C. E. Reed, *J. Phys. Chem.*, **40**, 1169 (1936). Pfund, *J. O. S. A.*, **24**, 143 (1934). Especially D. L. Gamble and C. E.

The amount of light transmitted through a suspension of particles dispersed in a transparent medium is determined by the refractive indexes of the particles and the medium, the size of the particles, and the applied wave length. The transparency at various wave lengths and its variations offer information as to average size and distribution. Rayleigh has calculated the shape of the wave-length transmission curve for cases when the particles are small in comparison with the short wave-length limits of the light source applied. This is expressed by the formula

$$I = I_0 \exp. - \left[\frac{8\pi^3}{3}\left(\frac{n^2 - n_0^2}{n_0^2}\right)\left(\frac{3n_0^2}{n^2 + 2n_0^2}\right)\frac{NV^2}{\lambda 4}\right]$$

I = intensity of transmitted radiation.
I_0 = intensity of incident radiation.
n = refractive index of particle.
n_0 = refractive index of medium.
N = number of particles per cubic centimeter.
V = volume of each particle.
λ = wave length.

If we assume the refractive indexes as constant, and since the mass per unit volume (concentration) c is equal to $N \cdot V \cdot p$ (p = specific gravity of particles), we can substitute $N \cdot V = \frac{c}{p}$. In the simplified exponent, $\frac{NV^2}{\lambda^4}K$, we obtain: $\frac{cV}{\lambda^4}K$.

At constant concentration of one pigment, and assuming the volume V to be proportional to d^3 (d = diameter of equivalent spherical particle), we can write the equation

$$I = I_0 \exp. - \frac{Kd^3}{\lambda^4}$$

The intensity of the transmitted radiation varies inversely as the fourth power of the wave length and directly as the third power of the particle diameter. If particle size approaches the wave length of the radiation, transmission becomes less dependent upon wave length and loses in selectivity in its transmission characteristics. Raleigh's conditions are no longer fulfilled. If we measure the spectral transmission of a pigment suspended in oil or rubber, from the visible blue to a wave length of about 4 μ in the infrared, the shape of the transmission curve should give us a good indication as to relative average size and size distribution (Fig. 116).

Barnett, *Ind. Eng. Chem.* (*Anal. Ed.*), **9,** 310 (1937), from which this discussion as well as the illustration has largely been taken. See also W. J. Kelly, *Coll. Symp. Monogr.*, **2,** 29 (1925). A. J. Stamm, *Coll. Symp. Monogr.*, **2,** 70 (1925). A. Kuhn, *Koll. Zeit.*, **37,** 365 (1925). A. Dumanski, E. Zabotinski, and M. Ewsejew, *ibid.*, **12,** 6 (1913); **13,** 222 (1913). V. Henry, *ibid.*, **12,** 246 (1913). W. Mecklenburg, *ibid.*, **16,** 97 (1915); **15,** 149 (1914); **14,** 172 (1914). H. J. C. Tendeloo, *ibid.*, **41,** 290 (1927). P. Tuorila, *ibid.*, **44,** 11 (1928).

Low transmission in the short wave length indicates small particles. Increasing selectivity (slope of curve toward longer wave length) combined with low initial transmission indicates increasing fineness. The average particle size is indicated by the point at which selectivity is first observed on the curve. Curve A indicates a *uniform* material of very fine particles. (Average equivalent spherical diameter about 0.5 μ.) Curve B represents a pigment of fairly small average size but containing a large portion of coarse matter. Curve C represents a fairly uniform coarse material (about 2 μ).

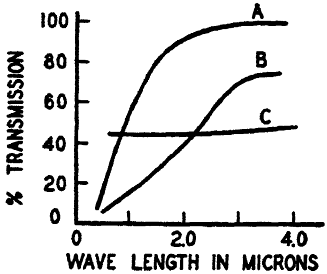

FIG. 116.—Light-transmission curves in the near infrared for different particle sizes.

MICROMANIPULATION

A number of instruments have been constructed which, if combined with a microscope, permit a number of operations to be performed with microscopically small objects. The so-called "micromanipulators" have long been an established research tool in biology, entomology, and special studies of cell life, etc. However, their application to colloid chemical problems is of much more recent date, and even today only few very specialized publications have become known. The author is of the opinion that it is not lack of possibilities for very successful application but rather hesitation on the part of the research worker and insufficient knowledge of the possibilities offered by these instruments which have delayed their more extensive use.

In principle, the micromanipulator is a microscope accessory which permits carefully controlled and accurate movement of microinstruments, such as needles and pipettes to any desired place of the preparation. With its help, microscopic objects can be dissected, liquids introduced or removed, etc. In the hands of a skilled colloid chemist with thorough training in general microscopy, these instruments can be used to study the structure of semicolloidal particles. E. A. Hauser[1] applied micromanipulation in his studies on the structure of individual rubber latex particles. A study of the elasticity of gels is reported by H. Freundlich and W. Seifritz.[2]

A tiny nickel particle (diameter about 18 μ) is introduced with a micro-glass needle into a gel. Then an electromagnet, one pole having needle shape, is brought close to the preparation. The extent of pull exerted by the magnet and the degree to which the particle returns to its original position permit a measurement of elasticity. The construction of special dark-field or ultracondensers[3] has further increased the applicability of the instrument. Thus it has been possible to perform microtensile tests on various substances and at the same time demonstrate orientation or alignment of the molecular aggregates.[4]

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[1] *Zeit. wiss. Mikros.*, **41**, 465 (1924).

[2] *Zeit. physikal. Chem.*, **104**, 233 (1923).

[3] See E. A. HAUSER, *Koll. Zeit.*, **53**, 78 (1930).

[4] See E. A. HAUSER, *ibid.*, **38**, 76 (1926).

The use of micropipettes has permitted a closer study of the influence of electrolytes on colloidal dispersions; the injection of solvents enables a microscopic study of swelling and peptization. The use of microelectrodes permits study of cataphoretic and galvanoplastic phenomena on a micro scale. A microstudy of thixotropy should yield valuable information on the mechanism of gelation.

VERTICAL ILLUMINATIONS

Ordinary microscopy by transmitted light (in special cases, ultraviolet light and fluorescence) and dark-field illumination are today an accepted tool in the study of many colloidal phenomena. Microscopy with incident light or so-called "vertical illumination" is comparatively new in this field of science.

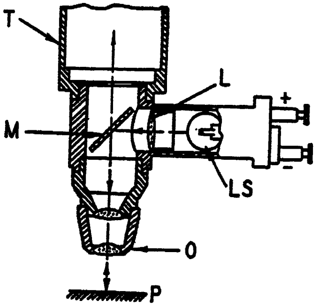

FIG. 117.—Totally reflecting optic (incident light). *LS*, light source; *L*, lens; *M*, reflecting mirror; *O*, microscope objective; *T*, microscope tube; *P*, surface of specimen.

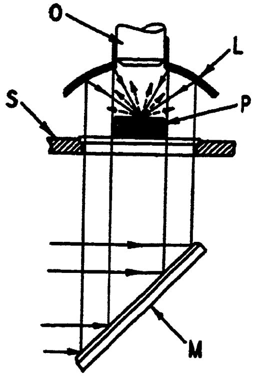

FIG. 118.—Lieberkühn mirror. *O*, microscope objective; *L*, Lieberkühn mirror; *P*, preparation mounted on glass slide; *S*, microscope stage; *M*, regular microscope mirror.

The use of totally reflecting optics (Fig. 117), as primarily applied in metallography and petrography, is of very limited value when studying colloidal systems, *e.g.*, pastes or slips (portland cement, clays, etc.), to determine particle arrangement or deposition of dyes on fibers, etc., because they demand perfectly smooth and polished surfaces. Total reflection is comparable to transmitted light in its optical effect.

Vertical illumination by Lieberkühn's mirror is more comparable to dark-field illumination, since the light reaches the preparation circularly, *i.e.*, from all sides (Fig. 118). The disadvantages are limitations as to size of specimen and inability to use high magnifications, *i.e.*, lenses with a short focal distance. A big step forward in this direction was the vertical dark-field condenser invented by F. Hauser[1] (Fig. 119), which permitted the use of oil

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[1] E. A. HAUSER, *Die Chem. Fabr.*, **4**, 277 (1931).

immersions, *i.e.*, maximum magnifications. The size of the specimen was still limited. However, these constructions also call for fairly smooth surfaces, because otherwise the picture is easily blurred, thereby making perfect resolution impossible.

A construction that may be mentioned here for sake of completeness is the so-called "Spierer condenser" (Fig. 120),[1] a combination of a condenser for transmitted light, a cardioid condenser, and total reflection. Although some research workers[2] have attributed to this instrument the possibility of resolving ultra structures, the author has previously expressed the opinion, shared by a great number of optical experts, that this accessory is to be regarded with suspicion. Its construction actually forces interference bands on to any surface observed under the microscope.

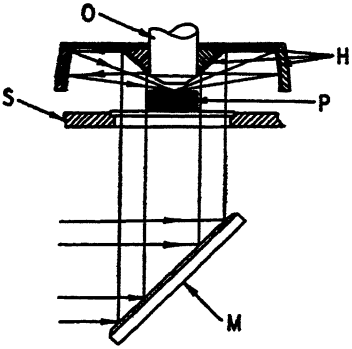

FIG. 119.—F. Hauser's dark-field condenser. *O*, microscope objective; *H*, mirror planes; *P*, preparation; *S*, microscope stage; *M*, microscope mirror.

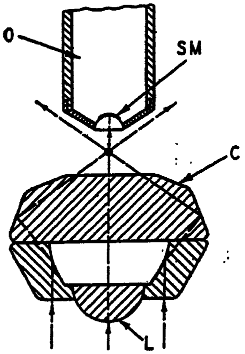

FIG. 120.—Spierer condenser. *O*, microscope objective; *SM*, silver backing of front lens; *C*, ultracondenser; *L*, central lens.

Lately several of the manufacturers of optical equipment have solved the problem by constructing objectives that permit the light to reach the preparation through a circular lens system, surrounding the objective. These instruments make any limitations as to size of specimen unnecessary and allow the use of any desired magnification. In some constructions, the illuminating lens ring can be focused independently from the focus of the objective. This permits individual selection of the illumination for the surface under observation (Fig. 121). These instruments have already proved their great value in many a study of colloidal systems.

Literature.—Special literature is obtainable from all manufacturers of microscopes with vertical illumination. See also F. HAUSER, "Grundlinien der Beleuchtung mit auffallendem Licht," *Zeiss Nachrichten*, **1**, 12 (1932);

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[1] C. SPIERER, *Arch. Sci. phys. nat.*, **8**, 21 (1926); *Koll. Zeit.*, **51**, 162 (1930); **53**, 88 (1930); **54**, 17 (1931); **55**, 36 (1931).

[2] See, *e.g.*, W. SEIFRITZ, *J. Phys. Chem.*, **35**, 118 (1931); *Ind. Eng. Chem.*, **28**, 136 (1936). S. WOODRUFF, *Ind. Eng. Chem.*, **30**, 1409 (1938).

E. A. Hauser, *Die Chem. Fabrik* 4, 277, (1931); *Mittlg. d. Leitz-Werke* 47 and 49; H. Heine, *Zeit. wiss. Mikros.*, **48**, H4 (1932).

ELECTRON DIFFRACTION

Count Louis de Broglie's theories, already classical, have shown that every part of matter exhibits wavelike properties. He proved that the wave length decreases with increasing mass.

It therefore seemed of special interest to make use of accelerated electrons in testing these theories. J. C. Davison and L. H. Germer[1] and G. P. Thomson[2] deserve credit for the first experimental proof. They could demonstrate that electrons are diffracted by crystal lattices. Since then, the use of electron diffractions for the study of ultimate structures has been greatly developed.

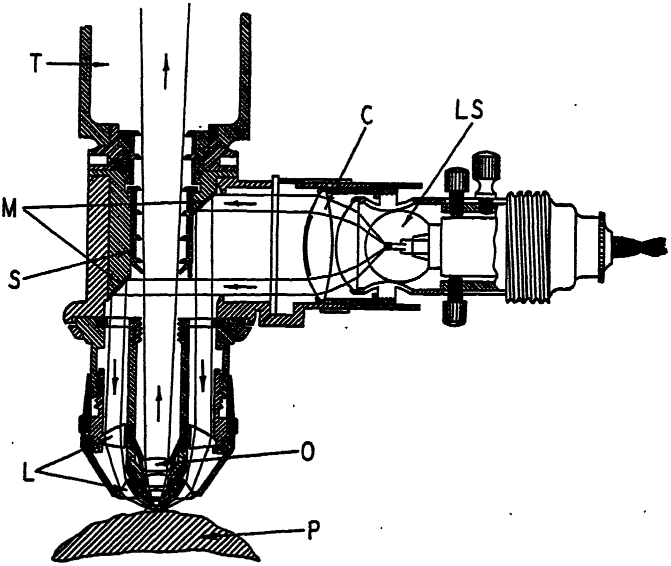

Fig. 121.—Vertical illumination with Ultropak (Leitz). *LS*, light source; *C*, collecting lens; *M*, reflecting mirror; *S*, stops; *T*, microscope tube; *O*, microscope objective; *L*, light-focusing lens rings; *P*, preparation.

By changing the volt velocity of an electron beam, keeping the reflection angle constant, we obtain diffraction maxima. Their location is expressed by an equation derived by E. Rupp:[3]

$$V(1 - \sin^2 \alpha) = \frac{150^2}{4d^2} - E_0$$

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[1] *Phys. Rev.*, **30**, 705 (1927); *Proc. Natl. Acad. Sci.*, **14**, 317 (1928).

[2] *Proc. Roy. Soc.*, (A), **117**, 600 (1928).

[3] *Zeit. Phys.*, **52**, 8 (1928).

where V = volt velocity of electrons.
E_0 = inner lattice potential of applied metal.
d = lattice-plane distance of crystal surface.
n = an integer.

If the structure of a pure metal has once been determined, those of adsorbed layers can be evaluated. However, electron-diffraction analysis is not limited to the study of metals but is increasingly used in the structural analysis of colloidal systems.

Excellent reviews have been published by E. Schiebold (contains complete literature reference), R. Brill, R. Fricke, F. Halle, E. Rupp, J. J. Trillat,[1] and G. L. Clark and E. Wolthuis.[2]

THE USE OF POLARIZED LIGHT

Polarizing microscopes have also found considerable application in the study of colloidal systems and thus permitted a better understanding of the structure of so-called liquid crystals, the orientation of tactoids, etc.

Since their use is absolutely identical with their regular application in mineralogy, appropriate textbooks or literature published by the manufacturers of such instruments should be consulted.

MICROPHOTOGRAPHIC EQUIPMENT

It lies far beyond the scope of this book to give a detailed discussion of the available microphotographic equipment and its applicability. Here, again, the literature published by the various manufacturers of optical equipment should be consulted. For almost all purposes the author has found that miniature cameras, which can be directly attached to the tube of the microscope, are not only very satisfactory and economical in use but give pictures of perfect definition. (It is naturally understood that fine-grain films and fine-grain developers are used.) In comparison with more refined and unquestionably more accurate equipment, they have the advantage of great ease in handling and fast work. The latter is frequently essential when it is desired to take a series of pictures of rapidly changing systems, such as the setting of cement pastes or the drying of rubber latex films.

Reference has already been made in the main text to the leading books on microscopy and microphotography. However, the author is of the opinion that neither of these techniques can be acquired exclusively from the study of textbooks, as only by prolonged and careful training can successful results be achieved.

ULTRAVIOLET MICROSCOPY

The ordinary microscope using regular white light has a resolving power for dimensions not smaller than the average wave length of such light,

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[1] These papers appeared in *Koll. Zeit.*, **69**, 266, 301, 312, 324, 369, 378 (1934).

[2] *J. Chem. Educ.*, **15**, 64 (1938); this paper contains a very complete bibliography on the subject.

according to Ernst Abbe's theory. The lower limit for the resolution of an ordinary microscope therefore lies at about 1 μ. As a further result of Abbe's theory, it should be possible to obtain increased resolution if light of shorter wave length is applied. The two main obstacles are the invisibility of such radiation to the human eye and the fact that regular optical glass will absorb such radiation to a large degree.

In 1904, A. Koehler[1] described, for the first time, a microscope, constructed according to his ideas by Zeiss, which uses pure ultraviolet radiation as a light source. The entire lens systems were made of quartz, which has a high transmission coefficient for ultraviolet light. Instead of direct observation, a microphotographic equipment using highly sensitive ultraviolet plates or films was attached. Preliminary focusing was done with regular light, and the focus then corrected for final exposure in the ultraviolet. Although ultraviolet microscopy has a technique of its own and calls for a very skilled microscopist, excellent results have been obtained in the study of such systems exhibiting discontinuities just slightly below the resolving power of the ordinary microscope. For instance, the study of the shape and actual size of fine pigments like zinc oxide, the study of the efficiency of dispersing agents and the study of rubber latex and its vulcanization, etc., have been published. Moreover, it is known that a great number of research and industrial laboratories constantly apply this instrument as part of their routine (Fig. 122).

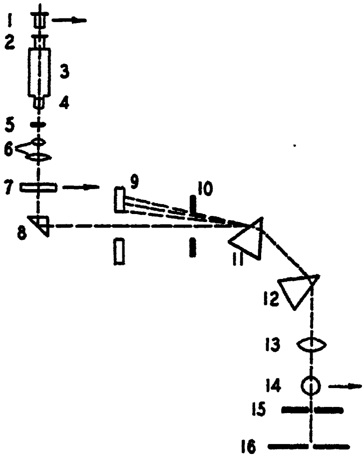

FIG. 122.—Schematic diagram for ultraviolet microscopy. 1, removable searcher eye-piece for visible light; 2, quartz eye-piece; 3, microscope tube; 4, quartz objective; 5, specimen; 6, quartz substage condenser; 7, removable glass filter for visible light; 8, quartz prism; 9, window in microscope base; 10, iris diaphragm; 11, 12, quartz prisms; 13, collimator; 14, spherical condenser for filter solution; 15, quartz slit; 16, cadmium electrodes.

Detailed descriptions in regard to the technique are obtainable from the manufacturers of ultraviolet microscopes. See also H. GREEN, *Ind. Eng. Chem.*, **17**, 802 (1925). F. F. LUCAS, *Am. Inst. Mining, Met. Engrs.*, *Pamphlet* 1576-*E* (1926); *Proc. Natl. Acad. Sci.*, **16**, September, 1930; *J. Franklin Inst.*, **217**, June, 1934; *Ind. Eng. Chem.*, **30**, 146 (1938). The latter publication contains an excellent short description of the instrument and a series of very well-defined photomicrographs. (The colloid chemical conclusions contained in this paper, with which the author cannot agree, are immaterial as far as the technique goes.)

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[1] *Zeit. wiss. Mikros.*, **21**, 129, 273 (1904).

TURBIDITY MEASUREMENT

The determination of the existence or nonexistence of colloidal dispersion in liquids, a study of condensation reactions of aggregation and incipient flocculation of colloidal systems, and the detection of particle orientation are all phenomena that deserve more attention from the viewpoint of the modern colloid physicist than they have so far received. A series of possibilities for such determinations are available. Regular photometers can be adapted for such purpose if the instrument is first calibrated with a substance of standardized turbidity (Fig. 123). Differences and changes in turbidity can be expressed in percentage transmission for the entire visible spectrum when the light is passed through a standardized thickness of liquid. This principle has been developed to a remarkable degree in the Hardy color analyzer.[1] Finally, the recording can be obtained by the use of sensitive photocells, *e.g.*, those used in the colorimeter of Lange in the Photolometer of the Central Scientific Company, the instrument of Hilgert (London), and others.

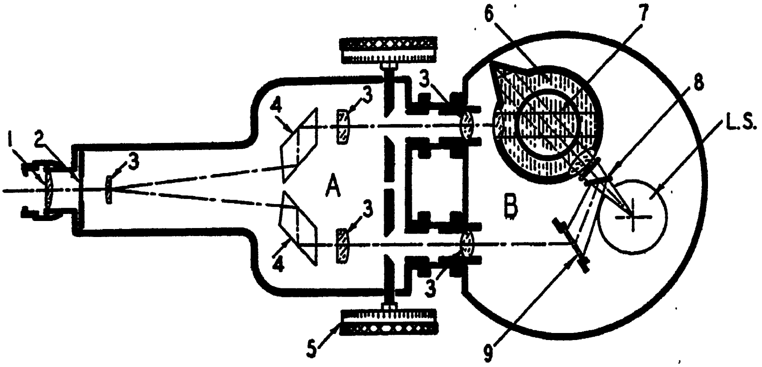

FIG. 123.—Photometer with attached turbidimeter (construction by Zeiss). *A*, photometer; 1, eyepiece; 2, slit and color filters; 3, collecting lens; 4, prisms; 5, measuring drums; *B*, turbidimeter; 6, container with distilled water; 7, beaker with suspension; 8, reflecting mirror; 9, comparator for light intensity; *LS*, standard light source.

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[1] A. C. HARDY, *J. O. S. A.*, **25**, 305 (1935).

INDEX OF NAMES

SUBJECT INDEX